

# 七壽

The 77<sup>th</sup> Birthday

## Activity Report

Hiroshi MASUHARA

National Yang Ming Chiao Tung University, Taiwan

July 7, 2021



**Increasing International Visibility of  
National Yang Ming Chiao Tung University**



## Contents

1. Preface
2. Biography
3. List: Professors and Doctors from Masuhara Laboratory and Group
4. From a Book “The 40<sup>th</sup> Anniversary Book of College of Science, National Chiao Tung University”
5. Essay: Thirteen Years Life in Taiwan and COVID-19
6. Essay: From Nanosecond Photochemistry to Optical Force Chemistry: My Journey
7. Review: Optical Force-Induced Chemistry at Solution Surfaces
8. Account: Nanoparticle Assembling Dynamics Induced by Pulsed Optical Force







## Preface

I was born on March 29, 1944 and turned 77 years old this year. In Japan, 77 years old is called the age of longevity and is a memorable age to celebrate. In the first half of my elementary school life, I was weak due to childhood tuberculosis. I did not attend elementary school for two years. I am amazed that I have been able to live and continue my research until 77.

I have been wanting to write my scientific journey to mark milestone anniversaries and to introduce recent activity at the National Yang Ming Chiao Tung University in Taiwan (which name was changed from National Chiao Tung University in February 2021). Fortunately I was invited to submit Essay and Personal Accounts in *The Chemical Record* and Review in *Annual Review of Physical Chemistry*. I have summarized them as included in this issue. In addition, I wrote my essay “Thirteen Years Life in Taiwan and COVID-19” and copied the report by Professor Yuan-Pern Lee, former Dean of the College of Science, National Chiao Tung University, in the 40th-anniversary issue of the College of Science.

I have been very happy throughout my research life, particularly, I have published more than 100 papers of *The Journal Physical Chemistry* among 600 publications and graduated more than 100 professors and doctors from my group. I would like to express my sincere thanks to National Yang Ming Chiao Tung University for offering me a chance to perform experimental research since 2008. Thanks are also due to my colleagues, researchers, graduate students, secretaries and family for their kind understanding and strong support so far.

July 7, 2021

A handwritten signature in black ink, appearing to read 'H. Masuhara', with a long horizontal flourish extending to the right.

Hiroshi Masuhara

# BIOGRAPHY

Chair Professor, National Yang Ming Chiao Tung University

Professor Emeritus, Osaka University

Foreign Fellow, National Academy of Sciences, India (2010-present)

Doctor Honoris Causa de Ecole Normale Supérieure de Cachan, France (2006-2013)

Foreign Member, Royal Flemish Academy of Belgium for Science and the Arts (1998-present)

---

**Dr. Hiroshi Masuhara** graduated from Tohoku University (1966) in Sendai and obtained Ph.D. degree from Osaka University (1971). He is a physical chemist working in multidisciplinary areas in departments of chemistry (Tohoku University), synthetic chemistry (Osaka University), polymer science and engineering (Kyoto Institute of Technology), applied physics (Osaka University), frontier bioscience (Osaka University), life science (Hamano Foundation), and materials science (Nara Institute of Science and Technology). In 2008 he joined Department of Applied Chemistry of National Yang Ming Chiao Tung University as Chair Professor. In Laser Bio/Nano Science Laboratory he extended seminal researches on (1) laser trapping dynamics of nanoparticles, (2) laser trapping crystallization of molecules and proteins, and (3) application of femtosecond laser for fabricating individual cell-based devices.

---

## Links

Masuhara Lab in NYCU

<https://masuhara.nctu.edu.tw/>

Hiroshi Masuhara website

<http://www.masuhara.jp/>

---

## Publications

About 600 papers in English, 120 Japanese mini-reviews, and 20 writing and editing books.

## Research Articles (2016-2021)

### Optically Evolved Assembling of Polystyrene Particle at Solution Interface

*J. Chin. Chem. Soc.*, Accepted (2021)

*J. Phys. Chem. C*, 124, 27107-27117 (2020)

*J. Phys. Chem. Lett.*, 11, 6057-6062 (2020)



*Langmuir*, 36, 14234-14242 (2020)

*J. Phys. Chem. C*, 120, 15578-15585 (2016)

*Langmuir*, 32, 12488-12496 (2016)

*Nano Lett.*, 16, 3058-3062 (2016)

### Optically Evolved Swarming of Au Nanoparticle at Solution Interface

*J. Phys. Chem. C*, Accepted (2021)

*J. Phys. Chem. C*, 124, 16604-16615 (2020)

*Opt. Express*, 28, 27727-27735 (2020)

*Nano Lett.*, 18, 5846-5853 (2018)

*J. Photochem. Photobiol. A: Chem.*, 346, 177-186 (2017)

### Optically Evolved Assembling of Molecules and proteins

*J. Phys. Chem. C*, Accepted (2021)

*J. Mater. Chem. C*, 9, 7545-7554 (2021)

*Angew. Chem. Int. Ed.*, 59, 7063-7068 (2020)

*Appl. Phys. Express*, 12, 112008 (2019)

*Appl. Phys. Express*, 11, 85502 (2018)

*Cryst. Growth Des.*, 18, 7079-7087 (2018)

*Phys. Chem. Chem. Phys.*, 20, 6034-6039 (2018)

*Angew. Chem. Int. Ed.*, 56, 6739-6743 (2017)

*Langmuir*, 33, 755-763 (2017)

*Langmuir*, 33, 8311-8318 (2017)

*Cryst. Growth Des.*, 16, 1953-960 (2016)

*J. Mater. Chem. C*, 4, 5231-5240 (2016)

### Femtosecond Trapping and Optical Resonance Effect

*ACS Photonics*, 8, 1832-1839 (2021)

*Opt. Express*, 28, 28656-28671 (2020)

*J. Phys. Chem. C*, 123, 27823-27833 (2019)

*J. Phys. Chem. C*, 122, 13233-13242 (2018)

*Opt. Express*, 25, 655-4664 (2017)

*RSC Adv.*, 7, 42606-42613 (2017)

*J. Phys. Chem. C*, 120, 392-2399 (2016)

*J. Phys. Chem. C*, 120, 251-5256 (2016)

### Review, Accounts, and Feature Articles

*Annu. Rev. Phys. Chem.*, 72, 565-589 (2021)  
*Chem. Rec.*, 21, 1473-1488 (2021)  
*Chem. Rec.*, 21, 1261-1269 (2021)  
*J. Photochem. Photobiol. C*, 28, 1-28 (2016)  
*Opt. Rev.*, 22, 143-148 (2015)  
*Chem. Soc. Rev.*, 43, 2147-2158 (2014)  
*Bull. Chem. Soc. Jpn.*, 86, 755-783 (2013)  
*Acc. Chem. Res.*, 45, 1946-1954 (2012)  
*Pure Appl. Chem.*, 83, 869-883 (2011)  
*Chem. Asian J.*, 6, 2878-2889 (2011)  
*Acc. Chem. Res.*, 41, 1790-1798 (2008)  
*Pure Appl. Chem.*, 78, 2205-2226 (2006)  
*J. Phys. Chem. B*, 106, 3049-3060 (2002)  
*J. Photochem. Photobiol. C*, 1, 57-78 (2000)  
*Pure and Appl. Chem.*, 64, 1279-1284 (1992)  
*Accounts Chem. Res.*, 14, 312-318 (1981)

### Awards

2017 The Order of the Sacred Treasure, Gold Rays with Neck Ribbon (瑞宝中綬章)  
2010 Asian Photochemistry Association Award  
2010 Mukai Prize (Tokyo Ohka Foundation)  
2008 Medal with Purple Ribbon (紫綬褒章)  
2006 The Spectroscopic Society of Japan Award  
2006 Porter Medal (European, American & Asian Photochemistry Associations)  
2006 The Chemical Society of Japan Award  
2005 Kenjiro Sakurai Memorial Prize (Optoelectronic Industry and Technology Development Association, Japan)  
1994 Osaka Science Prize  
1994 Divisional Award of Chemical Society of Japan  
1993 Moët Hennessy Louis Vuitton International Prize "Science for Art" Da Vinci of Excellence (France)  
1989 Japanese Photochemical Association

### The List of Professors and Doctors from Masuhara Laboratory and Group

23 Underlined members studied and/or worked in National Yang Ming Chiao Tung University, Taiwan

#### 《Outside Japan》

Wei-Yi Chiang, Rice University, USA

Victor Volkov, Nottingham Trent University, UK

Johan Hofkens, Katholieke Universiteit Leuven (KU Leuven), Belgium

Hiroshi Ujii, KU Leuven, Belgium/Hokkaido University, Japan

Roger Bresoli-Obach, KU Leuven, Belgium

Ursula Pfeifer-Fukumura, RheinMain University, Germany

Rachel Méallet-Renault, Université Paris-Sud Paris-Saclay, France

Michel Sliwa, Université de Lille, France

Takuji Adachi, University of Geneva, Switzerland

Jino George, Indian Institute of Science Education and Research, Mohali, India

Anwar Usman, Universiti Brunei Darussalam, Brunei

Trevor Smith, University of Melbourne, Australia

Yuqiang Jiang, Chinese Academy of Science, China

Koji Hatanaka, Academia Sinica, Taiwan

Teruki Sugiyama, National Yang Ming Chiao Tung University, Taiwan

Shuichi Toyouchi, National Yang Ming Chiao Tung University, Taiwan

Shun-Fa Wang, National Yang Ming Chiao Tung University, Taiwan

Jaihyung Won, Tokyo Electron Korea Ltd., Korea  
Jing-Ru Tu, Taiwan Semiconductor Manufacturing Company Limited, Taiwan  
Chi-Shiun Wu, Standard Foods Corporation, Taiwan  
Pawel Borowicz (UK)  
Christopher F. Porter (UK)  
Klaus Kemnitz (Germany)  
Guillame Louit (France)  
Kalman Pasztor (Hungary)  
Marc Hauer (Switzerland)

**《In Japan》**

Noboru Kitamura, Hokkaido University  
Yasutaka Matsuo, Hokkaido University  
Hiroaki Misawa, Hokkaido University  
Keiji Sasaki, Hokkaido University  
An-Chie Cheng, Hokkaido University  
Atsushi Miura, Hokkaido University  
Hideki Fujiwara, Hokkai-Gakuen University  
Sanyo Hamai, Akita University  
Jun'ichi Hotta, Yamagata University  
Hiroshi Fukumura, Tohoku University  
Muneaki Hase, University of Tsukuba  
Kiyoharu Nakatani, University of Tsukuba  
Shuichi Hashimoto, National Institute of Technology, Gunma College  
Sho Fujii, National Institute of Technology, Kisarazu College  
Norihiko Hayazawa, RIKEN  
Atsushi Sekiguchi, Kogakuin University  
Mototsugu Suzuki, Metropolitan Police Department  
Yoshito Tanaka, The University of Tokyo  
Yuriko Matsumura, Tokyo Helthcare University  
Tatsuya Uchida, Tokyo University of Pharmacy and Life Sciences  
Takayuki Uwada, Josai University  
Musubu Ichikawa, Shinshu University  
Tetsuhiro Kudo, Toyota Technological Institute  
Nobuyuki Ichinose, Kyoto Institute of Technology  
Noriaki Ikeda, Kyoto Institute of Technology  
Akira Itaya, Kyoto Institute of Technology  
Hiroyuki Sugimura, Kyoto University  
Kazuya Watanabe, Kyoto University  
Hiroshi Furutani, Osaka University

Syoji Ito, Osaka University  
Masayasu Muramatsu, Osaka University  
Hiroshi Y. Yoshikawa, Osaka University  
Chie Hosokawa, Osaka City University  
Yasuyuki Tsuboi, Osaka City University  
Ken-ichi Yuyama, Osaka City University  
Tamitake Itoh, National Institute of Advanced Industrial Science and Technology  
Kenji Kamada, National Institute of Advanced Industrial Science and Technology  
Mitsuru Tsukima, Osaka Electro-Communication University  
Yoichiroh Hosokawa, Nara Institute of Science and Technology  
Ryohei Yasukuni, Nara Institute of Science and Technology  
Kazunori Okano, Nara Institute of Science and Technology  
Takahiro Kaji, National Institute of Information and Communications Technology  
Sadahiro Masuo, Kwansei Gakuin University  
Naoto Tamai, Kwansei Gakuin University  
Tsung-Han Liu, Kwansei Gakuin University  
Morihiko Hamada, Kobe City College of Technology  
Hisashi Fujiwara, Hiroshima City University  
Hiroyuki Yoshikawa, Hiroshima Institute of Technology  
Akihiro Furube, Tokushima University  
Tsuyoshi Asahi, Ehime University  
Hyeon Gu Jeon, Ehime University  
Hideki Matsune, University of Miyazaki  
Yu Nabetani, University of Miyazaki  
Yoshiaki Tamaki, University of the Ryukyus

Norimasa Fukazawa, DIC Corporation  
Seiji Funakura, DIC Corporation  
Tetsuyuki Kurata, Mitsubishi Electric Corporation  
Naonori Kurokawa, The University of Tokyo Edge Capital Partners Co., Ltd.  
Kazuhiko Nakamura, Toyo Seikan Co.,Ltd.  
Takayuki Negishi, Tokuyama Corporation  
Nobuo Shimo, Idemitsu Kosan Co.,Ltd.  
Minoru Toriumi, Hitachi, Ltd.  
Masatoshi Yanagimachi, Mitsui Chemicals, Inc.  
Yugo Hayashi, Sartorius Japan  
Shino Sasaki, 3M Japan  
Issei Aibara, NuFlare Technology Inc.  
Takuji Tada, Fujifilm Corporation  
Hisamasa Sakai, Kyocera Corporation



Yasuyo Maezawa, Sumitomo Dainippon Parma Co., Ltd.

Chie Matsubara, Saraya Co., Ltd.

Isamu Oh, ABsize

Takanori Iino, Sysmex Corporation

Tomoaki Hinoue

Hayato Inoue

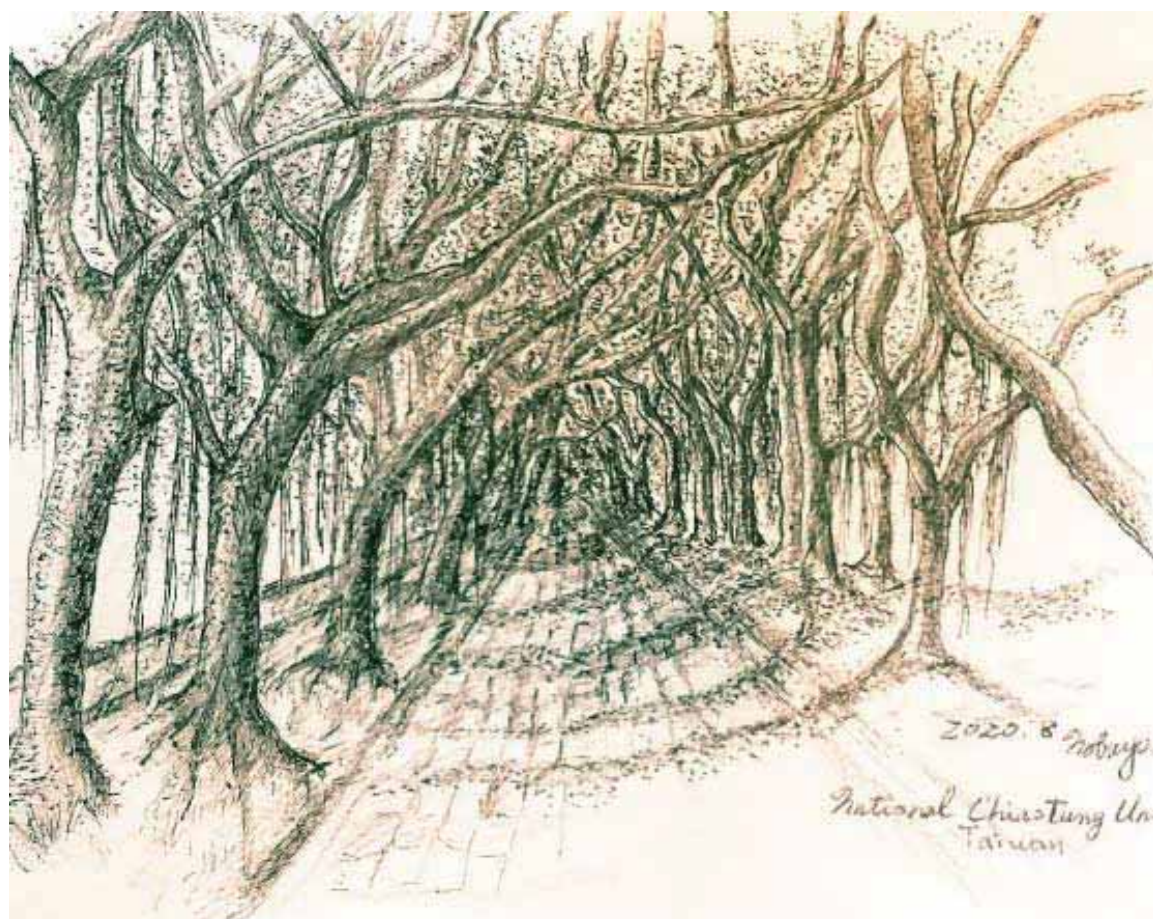
Ryo Kihara

Takashi Mito

Tsuyoshi Ohmoto

Atsushi Yamaguchi

Kenji Suzuki (Passed away)





2019 年秋

國立交通大學理學院

四十周年專刊（2019 年秋發刊）の

肆 啟山林者（歷代理學院長に聞く）

「獨飛，領飛，放手飛」 李 遠鵬

# 肆拾，拾事

40

國立交通大學  
理學院  
四十週年專刊

## 目錄

附錄 p.1  
謝詞與致謝 p.2

# 肆

## 一

### 啟山林者

——歷任院長專訪

郭南宏 p.74

鄭國順 p.83

郭滄海 p.93

林松山 p.102

李遠鵬 p.111

盧鴻興 p.123

陳永富 p.133

黃為德 p.80

郭義雄 p.88

褚德三 p.97

張豐志 p.108

莊振益 p.118

李耀坤 p.127

歷任院長餐敘 p.140

啟山林者

"Fly solo, Lead, and Let it go"

獨飛，領飛，放手飛 李遠鵬

採訪 / 吳盈真、范瑋真  
撰文 / 范瑋真

學而優則仕，這條路徑不只是古代讀書人的「指定賽道」，在今日台灣亦為學界鉅子拓展事業第二春的熱門選項。但也有一群「學術狂人」，若擔任行政顯要是「江山」，研究與教學是「美人」，他們肯定直奔美人懷抱。交大理學院的箇中代



## **“GOING INTERNATIONAL” by placing full time leading experts from Japan**

Among all in-depth international exchange promoted by both Applied Chemistry department and Electrophysics department, the collaborations with Japan were bonded the most.

With the lead of Professor Hiroshi Masuhara and Professor Hiro-o Hamaguchi, both honored with Medal of Purple Ribbon, many other Japanese professors have joined the faculty of the Applied Chemistry. The Department of Electrophysics, too, have the world famous, Takayoshi Kobayashi, who is the expert of ultrafast laser in the early stage, worked in SPROUT, NCTU for over ten years. And Kimitoshi Kono, the low-temperature physics expert has also joined us last year.

Professor Lee found it difficult to invite prominent Japanese professors to NCTU full-time without any prior interaction. So he planned first to invite professors' students to deepen exchanges with NCTU students having them build up an academic bridge and then invite professors. However, NCTU has prepared ample research funds. NCTU thought that by inviting the entire group, including associate professors and assistant professors, NCTU could attract prominent Japanese professors to NCTU. And then, professors would accept the invitation from NCTU.

Until the past few years, the reputation of accepting Japanese professors has spread out, a lot of Japanese professors are willing to come to NCTU with their equipment to continue on their research career. “Professor Kimitoshi Kono joined NCTU last year. He brought not only his existing equipment, but also with JPY¥10 million/per year for research use.”

## **Amazing Professor Hiroshi Masuhara – Promoting academic exchange between Taiwan and Japan**

Among all these Japanese Professors in NCTU, Prof. Masuhara has the greatest contribution to Taiwan. Speaking of his contribution, Prof. YP Lee knows better than anyone. Who would have known that a small talk between Prof. Masuhara and him would turn out to today's Taiwan-Japan academic exchange, not even Prof. Lee himself. At that time, while Prof. Masuhara was invited to NCTU ten years ago, the original plan was going to hire his student to NCTU for the collaboration. But around the same time, Prof. Masuhara's private foundation in Japan was going to closed for

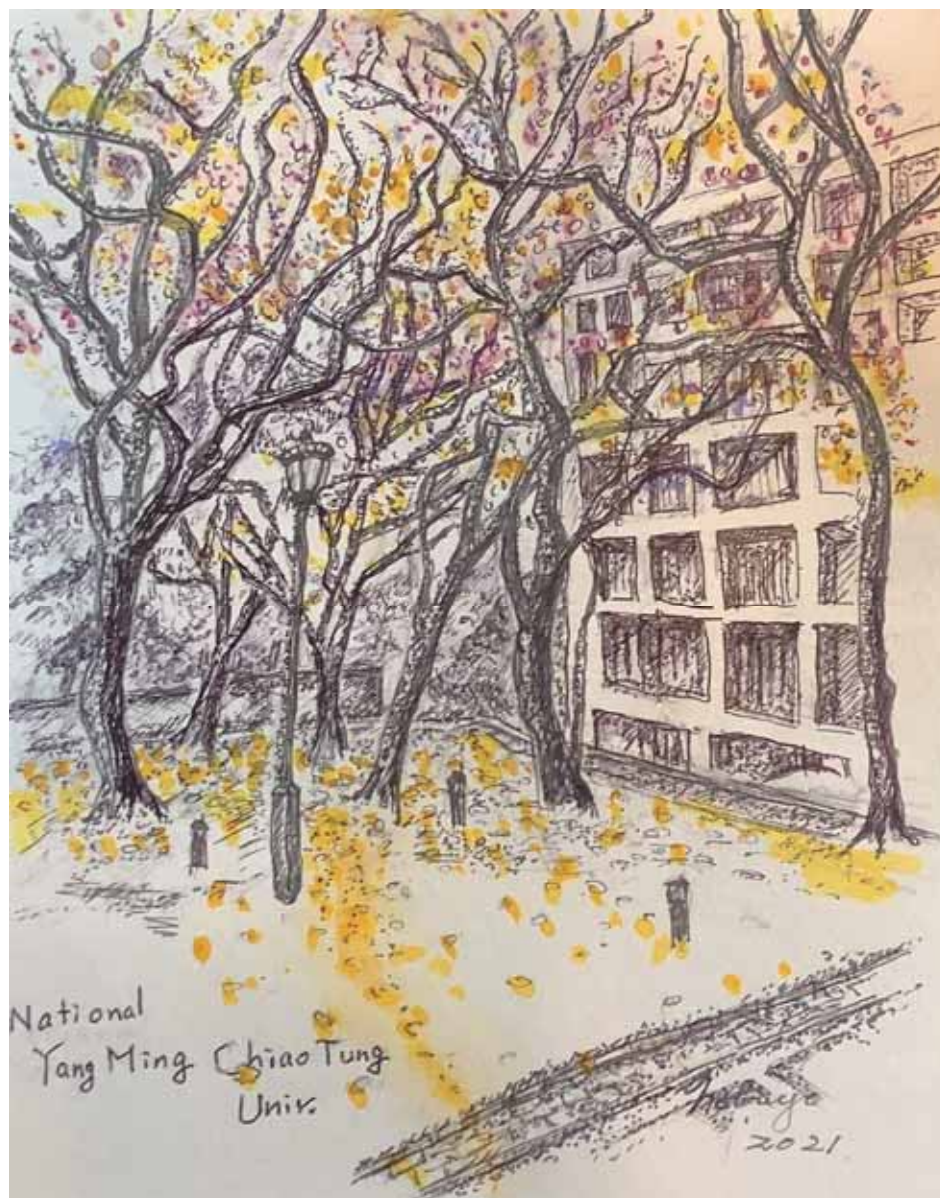
some certain reasons. Prof. Lee, “So I asked him, why don’t you come to Taiwan instead? I believed that he also found it unbelievable himself.”

With the support from the President of NCTU, Mr. Chong-Yu Wu, on one hand, and enough funds from the Ministry of Education on the other, he went on continuing contact with Prof. Masuhara. Not only providing research funds, but Prof. YP Lee also committed to Prof. Masuhara that he will maintain the Japanese System, which is to keep “a research team” as a unit for him as much as he can. Prof. Lee, “It is different in Japan. In Japan, apart from a Professor, a research team also includes an Associate Professor and an Assistant Professor. So, we kept this system for him.” It only took about nearly two months to went from coming to an agreement to going through all the DAC procedures and preparing a lab. “I believe his contribution will be extraordinary after he joins us,” said Prof. Lee. While Prof. Masuhara continues to his research, he also pulls strings for the young researchers in Taiwan with the ones in Japan, have them to join international conferences in Japan, and even recommended awards. Prof. Lee mentioned that Prof. Masuhara guides a research team in Japan as well, which has about 30 to 40 young researchers. “He had all these 30 to 40 researchers come to Taiwan for meeting because he thinks that the young generations should take the chance to know more about Taiwan, learn from each other, or make friends.”

In the past few years, Prof. Masuhara has put his influence on “research” to the “education” level. He called out to the teachers and students of science high schools in Japan and had them come to visit NCTU and join a seminar. Prof. Lee, “Not just one high school, but 2 to 3 high schools, which includes 80 to over 100 people.” He also hosts a Summer Course every year inviting various top foreign professors to join and give a lecture. We had 25 Japanese students joined us last year, this year, we even had students from Australia as well. This is a great opportunity for our students to build up their international connections. Prof. Lee was impressed to say, “His energy is really something, and these international experiences is a good thing for our students.”

Little by little, this academic exchange mode has opened its publicity, and we have even more Japanese Professors joining us, and more people in Japan recognizes NCTU. These top researchers have brought us a great amount of energy in research, and for them, coming to Taiwan and continue on their research life is also a good way to go. One of our NCTU students is now an Assistant Professor in Japan.

After more than a decade, this win-win path is still been carried on through succeeding Deans with great supports from the past Principles. As a pioneer, Professor Yuan-Pern Lee didn't take it all for himself but to give all the credits to others. "This requires the right time, the right place, and the right people. It needs NCTU's open atmosphere and the flexible administration to achieve; and nothing can be done without the 500 million in 5 years from the Ministry of Education. I am truly grateful to our President, Mr. Chong-Yu Wu, and the following two as well, Ms. Yan-Hwa Wu, Mr. Mau-Chung Chang. With their 100% of trust and fully support, I can go ahead and do it without asking everything one by one."





學而優則仕，這條路徑不只是古代讀書人的「指定賽道」，在今日台灣亦為學界鉅子拓展事業第二春的熱門選項。但也有一群「學術狂人」，若擔任行政顯要是「江山」，研究與教學是「美人」，他們肯定直奔美人懷抱。交大理學院的箇中代表人物，無非是在海內外獲頒榮譽無數的中研院院士——李遠鵬，交通大學理學院第十任院長。李遠鵬人如其名，志在更寬廣的科學殿堂，行政工作關不住他的翅膀。然而與他共事的同仁都知道，他的行政能力高超，沒有續任院長不是「不能」，而是「不願」。

李遠鵬雖自承對行政「沒興趣」，卻在院長三年任期做了相當十年的重要工作：設立前瞻跨領域基礎科學中心、理學院學士學位學程班、完成科三館興建構想書及設計、整修科一、科二館、支持新創開放式課程（OCW）、以及透過高強度的國際合作等方式，拉拔理學院迅速壯大。

### 轉任交大還接院長，清華同仁：跌破眼鏡

回首 14 年前，當李遠鵬要從清大化學系轉往交大任職時，他的同仁對此「搬遷」是相當錯愕。「很多人覺得不可思議，為什麼我從一個那時候比較好的系跑到一個比較差的系。」誠如眾人之惑，客觀來看當年台灣的理學院，交大的理科研究無論是 paper 的發表數目、成就、國際名聲等等，都遠遠落在台大、清大之後。那李遠



#### ——關於 李遠鵬

第十任院長（2005 — 2008）

##### ■ 學歷

加州大學柏克萊分校化學博士（1979）

台灣大學化學系學士（1973）

##### ■ 經歷

新世代功能性物質研究中心主任

（2018 — 2019）

前瞻跨領域基礎科學中心主任（2006 — 2017）

交通大學理學院院長（2005 — 2008）

交通大學分子科學所所長（2004 — 2007）

交通大學應化系、分子科學所講座教授

（2004 — ）

東京大學講座教授（1997）

中央研究院原子與分子科學研究所合聘研究員

（1988 — ）

清華大學化學系教授（1985 — 2004）

清華大學化學系副教授（1981 — 1985）

美國海洋及大氣總署環境研究所研究員

（1979 — 1981）

鵬為什麼會做此決定呢？他解釋，時任校長張俊彥請了中研院院院士林明璋來到應

這兩項都經由學校獲得教育部的補助，理學院從 2006 年起上緊發條，開始急起直追。

當外界還在用刻板印象說著「理科」清大、「工科」交大的時候，交大應化系所教員的年發表論文總數已在 2009 年超越清大，目前和台大不相上下。交大物理領域以凝態物理為首，在國際主流期刊上的凝態物理發表數亦在國內大學之中領先。李遠鵬憶起剛來到交大應化系時，化學領域的論文產量甚至不到清大的一半，「在這十幾年來，我相信理學院的表現是突飛猛進。」

### 「國際化」之路，日籍權威學者全時進駐

曾有後來的院長說，李遠鵬在任內三年期間，做了超過十年的事情。其中最為人津津樂道的，也許是科三館完善規劃，也許是跨領域中心表現驚人。但若是最具代表性、值得全校甚至全國大學院所借鏡學習的，無非是從他任內開始，在應化、電物系所推動的深度國際交流。其中，又以和日本的合作最為透徹、緊密。不過，說起李遠鵬最初開始推動「國際化」的契機，卻要從「分子所」說起。

「我來的時候張校長想要設分子所，然後有四個名額可以給我們聘。那時候我們聘的人，以當時別人的角度來看，可能會覺得很奇怪。」這四位教授，有原先在物理領域任教的電機博士孫建文、在工研院專攻生醫領域的廖奕翰、物理出身的中裔日籍教授朱超原，以及波蘭籍量子化學博士魏恆理。「都不是一般人會預期的人吧？魏恆理教授也打開我們開始聘外國人

的大門。後來又聘了日籍的重藤真介。」李遠鵬幽微一笑，對於這份聘用名單沒有再多做解釋。但其實回到今日來看，理學院走向跨領域與國際化的齒輪，早已從那時起就開始轉動。即便他笑而不語，這十多年的成果自會說話。

攤開應化系師資陣容，以榮膺「日本天皇紫綬褒章」的教授增原宏、濱口宏夫為首，多位日籍教授全時駐系；電物系也不惶多讓，早期世界著名的超快雷射專家小林孝嘉已在交大深耕逾十年、去年低溫物理專家河野公俊也到系上駐點研究。他提到，會能夠積極開拓這條路徑，原因之一是受到了校長張俊彥的啟發。

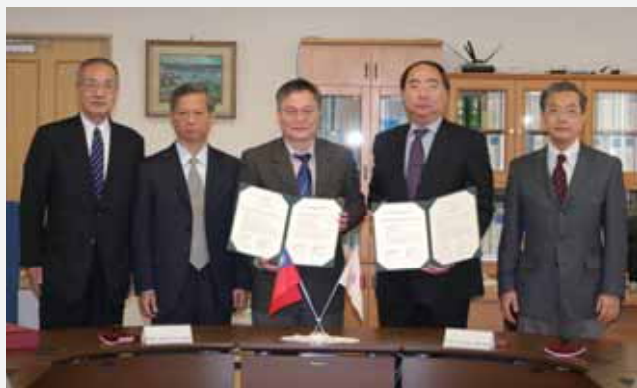


2007 年與東京大學理學院院長 Yasuhiro Iwasawa 簽訂合作協定。濱口宏夫教授（圖中）為促成此事之最大助力。（圖片來源 / 李遠鵬提供）

當時張俊彥希望能邀請小林孝嘉退休後前來交大，但因他在日本又拿到了一項大型計畫，便無法全時駐台。這個預料之外的變動，讓李遠鵬原先有點懊惱。「可是張校長說，沒關係啊，他這麼大牌的人，只要他願意來，他一年要來三個月也好半年也好，我們都要去接受他。」爾後，聘任的模式一直在變化。李遠鵬解釋，早期



漸漸地，在這套交流互惠模式打開知名度後，越來越多日籍教授加入行列，也越來越多日本人認識交通大學。這些國際級學者為我們注入豐沛的研究能量，同時對他們而言，能夠來台延續研究生涯，亦不失為一個好選擇。而我們的學子，已有一位因為此種交流，現已在日本擔任助理教授。



2011 年理學院幸由太田信廣教授（左一）作媒，與北海道大學電子研究所所長三澤宏明簽訂合作協定。交大代表團為太田信廣教授、李遠鵬前院長（左二）以及時任院長莊振益（左三）。（圖片來源 / 李遠鵬提供）



2012 年李遠鵬參加第七屆亞洲及大洋洲光化學會，受邀參加開酒儀式；2018 年更榮獲「亞洲及大洋洲光化學會增原宏講座」。（圖片來源 / 李遠鵬提供）

十多年了，這條雙贏之路仍透過後繼院長們接續耕耘著，並得到歷任校長們的大力支持。李遠鵬是開路先鋒，他卻把功勞都「推」給別人。「這個也是要天時地

利人和，要有交大開放的風氣及靈活的行政才可以做成；若沒有教育部的五年 500 億，也不可能做成。我也很感謝吳重雨校長以及其後的吳妍華、張懋中校長，他們給我完全的信任及大力的支持，所以我不用事事都請示，可以放心去做。」

## 在研究狂熱中，用規劃平衡生活

春秋以來我們從幽默的孔先生那裡得知，做學問有「止飢、解憂、抗老化」的神奇功效。在這方面，李遠鵬恐怕更勝一籌。他曾風趣地對辦公室同仁說，每當覺得有感冒跡象時，只要進實驗室便「不藥而癒」了。「因為我喜歡研究工作啦，注意力轉移了之後，身體的一些不適就拋到腦後去了！」李遠鵬對做研究樂此不疲，他笑說即使到了現在，每週一、四仍鑽研到半夜才離開學校。「因為南大門要關了，所以我只能待到半夜，如果有選擇的話也許我會待更晚，因為跟老婆請假，兩小時也算一次，六小時也算一次。」此話驚為天人，莫非他竟會如學生一般熱血「看日出」？原來純屬俏皮的玩笑一場，他直言「倒是不會做到天亮，身體還是重要，年輕的時候我也不是會任意熬夜做事情的人。」想不到以嚴謹形象示人的李遠鵬，其實有這活潑靈轉的一面。

「我想我對時間的規劃及掌控都還不錯，他們應該很少看到我焦頭爛額、超過期限才交卷的時候。」李遠鵬在當院長時，發表的論文數也絲毫沒有減少。他表示，當事情都按部就班地照規劃走，自然能平衡工作和生活。同仁吳盈熹也回憶道，李遠鵬雖然公務、研究繁忙，仍不忘陪伴家

# Thirteen Years Research Life in Taiwan and COVID-19

Hiroshi MASUHARA

Chair Professor, Department of Applied Chemistry,  
National Chiao Tung University (NCTU), Taiwan

## 1. Introduction

I have been staying and extending research on "Optical Force Chemistry at Solution Surface" in NCTU after I retired from Osaka University in 2008. Also, I have devoted a lot of effort to make NCTU more visible in Science and in Japan. My life and research are based on frequent international travels. However, everything has been changing much, and those nice days seem to have passed away. With COVID-19 spreading all over the world, universities, academies, their ideals and evaluations are changing and will change significantly. Taiwan is now attracting worldwide attention as a democratic country with minimal COVID-19. The current COVID-19 situation makes me, as a researcher who has been looking at Japan and Taiwan, think about the future development of society, customs, universities, and international relations. Fortunately, I would like to take the opportunity to write about Taiwan's dynamism in the society, science and technology, and academia.

## 2. The dynamism of Taiwanese society and its anti-COVID-19 measures

I am writing this manuscript in December 2020. Taiwan has a population of 23 million people, and the number of COVID patients to date is about 760. Among democratic

countries where people can behave freely and selfishly, Taiwan is a rare country that has succeeded in anti-COVID-19 measures. The author has frequently traveled back and forth between Japan and Taiwan for the past 13 years. When I returned to Taiwan at the end of February this year, and was preparing to start classes for the new semester, I was suddenly told, "You can't hold classes or seminars for two weeks after entering Taiwan." When I went to the hospital about a week after I arrived in Taiwan, the receptionist scanned my health insurance card and immediately said, "It's been less than two weeks since you returned to Taiwan from abroad. Therefore, you cannot see a doctor. Please go home soon." In Taiwan, insurance card data exchanges link with passport data. At that time, I lived in a staff dormitory on campus. A dormitory assistant usually works from 8 am to 5 pm. She takes a rest on Saturdays and Sundays. However, the university suddenly increased the number of assistants, and the assistant stayed there all day long after Covid-19. It is a quick response. Shortly after the beginning of March, the assistant started measuring our temperature every morning. If I have no fever, they will give us a small sticker. I put this on a prominent place on my shirt, and then I could enter any building in the school, a cafeteria, or a convenience store. If not put, a staff member will measure my temperature each time I enter any buildings. One day, when I forgot to measure the temperature

and went to the laboratory, I received a confirmation call from the dormitory.



(Photo1) Stickers that people can get if they are OK with the temperature check. Colors and numbers change every day. This system was terminated around May when the safety of Taiwan was confirmed.

The color of the sticker changes every day, so the check is perfect. Photo1 shows a collection of stickers for several weeks. While regulations such as temperature measurement, masks (Photo2), and Social Distance have begun, the iRun campaign to run the campus together once a week also started. I said "iWalk" and walked around the campus for two laps, 2.1 kilometers each time. I participated more than ten times (Photo3), so I got an iRun T-shirt. In Taiwan, while

strict regulation of daily activities, exercise events for health are planned. When I told my American friend about this, she said, "Your University is cool." Regulations have been relaxed since summer, but the school shuttle bus and city bus are not available to people without masks still in December. The Central Epidemic Command Center (CECC) of the Ministry of Health and Welfare seems to have ordered such quick responses to COVID-19. Mr. Chen Shih-Chung, Minister of Health and Welfare, Taiwan, held press conferences many times a day. He became a hero of the time, along with Audrey Tang, 41 years old, a digital minister.



(Photo2) Masks purchased online with health insurance card and credit card numbers. 9 masks per person per two weeks for 52 NTD (1 NTD is about 3,5 JPY), delivered to the nearest convenience store in the school.

I returned to my home in Osaka in mid-September. After I quarantined at home for two weeks, I worked for a week and returned to Taiwan. I experienced a two-week quarantine life in Hsinchu's apartment again. By comparing the two quarantine lives in Japan and Taiwan, we can see the difference in the two countries' management systems. In Japan, people somehow loosely monitor each other. And it is mainly due to self-regulation that comes from the national character of hating to bother others. Taiwan,

on the other hand, is taking dynamic organizational measures. When I returned to Japan from Taiwan, I went to Taiwan Taoyuan Airport. At the time of departure, it was no difference from usual. Of course, the Japanese can return to Japan without any problems. Taiwan is not a dangerous area, so the Japanese government does not request us anything before departure. After arriving at Kansai International Airport, I lined up for a PCR test using saliva and waited for the results. Two hours after landing, I finished everything I had to do, and I could go outside. Arrived people are told not to use public transport, but no one manages it. I had an acquaintance pick me up. Every day from the next morning, the Ministry of Health, Labor and Welfare returnee follow-up staff asked questions on the app and inquiries by phone. My interaction with them lasted for two weeks. However, how you actually act is entirely up to your personal conscience.

On the other hand, when I returned to Taiwan, the person who had an Alien Residence Certificate did not need a PCR test in advance, so I went to Kansai International Airport without doing anything. At the same time as showing my passport at the check-in counter, an airline officer asked me to open the LINE on my smartphone, download the Taiwanese Quarantine Electronic Report Certificate, and enter my personal information in it. When I arrived at Taiwan Taoyuan Airport, the airport officer asked me to connect my smartphone to the internet. Looking at the line on my smartphone, I had already received a "COVID 19 Health Declaration and Home Quarantine Notice" and a "Health Declaration Certificate". I showed this to the airport officer and proceeded to the quarantine station, and

entered Taiwan smoothly. When I picked up my luggage and went outside, an officer led me to a quarantine taxi stand. Here, an officer disinfected not only the big baggage but also all clothes and the soles of shoes. The Taiwanese government paid a little less than half the quarantine taxi fare. Arriving in front of the apartment, I went straight to my room and started a two-week quarantine life.



Photo3

(Photo3) Every Wednesday, between 3:30 p.m. and 5:30 p.m., you can get a stamp for every 2.1 km, and if you participate 10 times, you can get a T-shirt with "iRun" on it. I received two stamps at a time. I got two stamps at a time, i.e. 4.2km at a time, but I enjoyed the iWalk, not the iRun.



The next day, I started to report my health status to CECC every morning at 10:00 am on LINE. Meanwhile, a foreign affairs police officer in Hsinchu City sent me her identification on LINE and asked me to send my passport photo on LINE. That morning, two female police officers came to my room with a grocery set distributed by the government (Photo4), which is useful for quarantine life. They took a picture of my face from outside the door. They also asked me to fill out a health status form and send it to them every day. Every afternoon I wrote on the form that there was no change in my health status, took a picture of it, and sent it on LINE. The officer in charge was a woman, and each time I sent it, I received a thank you response with a cute stamp. It was a relaxing moment. A week later, halfway through the quarantine period, the CECC and the foreign affairs police officer called me to confirm my health status and then came to my house again to take another face photo. They were very kind, and I was glad to have someone to talk to for a moment during the quarantine. After two weeks, I was able to get out of my room. However, I still needed to spend one more week before I go to the university. During this week, I could not have any classes or seminars. The university has been very thorough in its response. The Taiwanese government has prepared such responses based on its experience during the severe pneumonia SARS epidemic of 2002-2003. During the quarantine, I felt stressed that the government was monitoring me and restricting my behavior. However, I could feel their compassion. I was strongly impressed by the Taiwanese government's dynamic and proactive management for COVID-19, as well as the Taiwanese community's willingness to cooperate.

### 3. COVID-19 will change the research world, and a generational shift is underway

Local wars, terrorism, earthquakes, typhoons, floods put people's lives in danger and severely damage their surroundings. The damage, however, is still limited to the people involved. COVID-19 is experienced by the entire world simultaneously. In almost every country in the world, people are stopping traveling and visiting simultaneously, losing their jobs simultaneously, people's research activities are stopping simultaneously, schools are changing to online classes at the same time. It is happening all over the world at the same time, and everyone is experiencing it simultaneously. And the economy is getting worse, companies are losing money, and the country's income is decreasing. Suppose this situation continues for a few years longer. In that case, I believe that society, economy, population, technology, academia, and universities will suffer the same level of severe damage as in World War II. After the end of World War II, our generation grew up hearing people say, "I grew up before the war, so...", "I grew up during the war, so..." or "I grew up after the war, so...". In the same way, after 20 years, we will probably hear the same lines. "I grew up before COVID-19, so...", "I grew up during COVID-19, so...", or "I grew up after COVID-19, so...". I think we are at such a significant turning point in time. What will happen to chemical research then? I will try to remember the old days.

Before and for a while after World War II, people said that chemical research was a

study of experience. However, that changed dramatically with World War II. The elders quickly lost their power, and up-and-coming young professors in their thirties began to emerge. Chemical research was transformed into a logical discipline based on quantum mechanics. However, on further reflection, the logic of the discipline was not changed by the war. It was always in that trend. World War II seems to have been the catalyst for a great acceleration of that trend not only in Japan but also in Europe and the United States. Now let's consider the future of chemistry research by analogy. I think that COVID-19 will realize what I have predicted about the future development of chemistry. COVID-19 will accelerate the trend of academics, and there will be a great leap forward. People say that one of them is AI-based chemical research after COVID-19. Just as there was a shift from the chemistry of experience before the war to the chemistry of quantum mechanics-based logic after the war, I predict that main stream of chemistry research will move toward AI-based studies after COVID-19.

On the other hand, how will COVID-19 change the international collaborative research system, which is especially essential for basic research in Taiwan. After World War II, the internationalization of research has been a consistent trend that can never reverse. I also think so and have worked hard to develop my research life in such a way and to accelerate it in Taiwan. I started my research in Taiwan in 2008. During the next three years, I also had a laboratory at Nara Institute of Science and Technology. The simultaneous pursuit of overlapping topics in Taiwan and Japan has been very effective in both research and graduate education. This

situation also gave me the experience of double funding. Later, I promoted Double Degree programs with the Katholieke Universiteit of Leuven in Belgium, Saitama University, and Nara Institute of Science and Technology in Japan, etc. Besides, I believe that Double Appointment should be realized. In Taiwan, NCTU has established the deepest and most extensive research collaboration with Japanese universities.<sup>1)</sup> Many young Japanese people have worked here at NCTU for a few years. They have taken their experience as a career path<sup>2)</sup> to return to their universities in Japan to develop their research. I have invited many Japanese professors to Taiwan, set up summer courses in collaboration with Japan's Grant-in-Aid for Scientific Research (Kakenhi), and offered a research school for Japanese graduate students.<sup>3)</sup> I have also recommended young Taiwanese professors to be invited to international conferences and laboratory seminars in Japan. In the past few years, about 130 students from Super Science High School in Japan have been visiting NCTU every year for overseas study. We have made NCTU more visible in Japan.<sup>4)</sup> I attended as many meetings in Japan as I could from Taiwan as if I were coming to Tokyo or Sapporo from Osaka. The flight from Taiwan to Osaka only takes a little over two hours. The flight time is comparable to the flight time from Osaka to Sapporo. But that still takes time, so I have been trying to buy time by living in campus housing and working on weekends. However, my internationalization strategy is no longer possible with COVID-19.

As long as the current situation does not return to what it was before COVID-19, my model for the existing internationalization



before COVID-19 will not be viable. Even if COVID-19 disappears in a few years, society, academia, universities, and research conditions will not retrieve the former state. Predicting post-war society during World War II would have been difficult. Also, Predicting and preparing for post-COVID-19 research and education in the midst of COVID-19 is not easy. For the time being, people have no choice but to get through this situation by having discussions and meetings in Zoom. But in this way, people can not do more than keep their existing relationships. There are master students who can only experience presentations online. Unfortunately, I can not give them the reality of an international conference. They will join the company next summer without any real experience of attending international conferences and start manufacturing online or doing business online. After all, we cannot raise a child online. Research and education cannot be done online forever. As long as I am in Taiwan, I want to continue to try to understand what Taiwanese dynamism is and prepare for post-COVID-19.

#### 4. What COVID-19 suggests

Taiwan has succeeded in minimizing the damage of COVID-19 while protecting its free democratic society. At first, I thought it was just a success against infectious diseases. As time passed, it has turned out to be a remarkable success in Taiwanese society. Needless to say, Taiwan is a free society with a democratic rule of law. However, I think that democracy in Taiwan is different from the liberalism of southern Europe, where people oppose the lockdown and say, "I want to go out for dinner or a drinking party at night". In Taiwan, there seems to be some

great mechanism. Although Japan is a democratic country and people are serious about obeying the law, the situation changes during the debate about how to do it fairly, equally, and without fail. Their measures often fall behind. Fortunately, the relationship is so strong in Japanese society that the situation is never the worst. In Taiwan, society changes quickly. Taiwanese society is capable of quickly detecting changes in circumstances. Those in authority are also always sensitive to change and have the dynamism to take action ahead of time. As a Japanese researcher, I will keep a close eye on the development of Taiwanese society and Taiwanese science and technology during and after COVID-19.

Another significant world change that has come to be understood by the coronavirus epidemic has a lot to do with Taiwan's choice. Taiwan has many science parks around the country. The oldest and most famous is the Hsinchu Science Park. Among them are the NCTU, National Tsing Hua University, National Synchrotron Radiation Research Center, National Center for High-performance Computing, and Taiwan Instrument Research Institute. In this aspect, the Hsinchu Science Park is similar to the Tsukuba Science Park. The difference is that Taiwan Semiconductor Manufacturing Company, Ltd., and other leading Taiwanese electronics companies have not only their laboratories but also manufacturing plants. We can learn about the latest global trends in science and technology at the Science Park in Hsinchu.<sup>5)</sup> Why? Taiwan is basically in line with the U.S. global strategy in science and technology. In the 80s, IBM stopped manufacturing personal computers by themselves. After that, the United States

decided to manufacture their hearts in the United States, their peripherals in Taiwan, and assemble them in China. In Taiwan, the Hsinchu Science Park was responsible for manufacturing the peripherals for personal computers. Since then, Taiwan's electronics industry has developed dramatically and surpassed Japan's. Nowadays, there is a global competition for 5G dominance, AI technology, and internet technology. Looking at the United States' recent global strategic measures, I feel that "something" reminiscent of the United States' decisions in the 80s is going on in the United States under the current COVID situation. The reconfiguration of the supply chain is an example of "something" that is easy for us to understand.

I have written about my thoughts while comparing the experiences in Japan and Taiwan under the COVID-19 epidemic, which is comparable to the devastation by World War II. In the era of significant changes caused by COVID-19, the sooner we detect and respond to them, the better our chances of survival after COVID-19. I hope that the flexible nature and the academics of NCTU will create a new path suitable for the post-COVID-19 era and take the leadership of the post-COVID-19 world as quickly as possible.

## References

- 1) Yuan-Pern Lee, *40<sup>th</sup> Anniversary Book of Department of Applied Chemistry*, NCTU, 111-115, 2019
- 2) Maki Kawai, "Passport to an international career - True globalism", The Chemical Society of Japan, *Chemistry, and Industrial Chemistry*, 64, 763-765, 2011
- 3) Grant-in-Aid for Scientific Research on Innovative Areas, MEXT, Japan "Nano-Material Manipulation and Structural Order Control with Optical Forces", News Letter Special Issue, "Masuhara Summer Course & Workshop", 2017
- 4) Laser Bio-Nano Science Laboratory, Department of Applied Chemistry, NCTU, *Research Activity Report*, 2018
- 5) *30<sup>th</sup> Anniversary Book of Hsinchu Science Park*, The Hsinchu Science Park. Taiwan 2010



Photo 4) Those who enter Taiwan must be quarantined at home or in a designated hotel for two weeks. If they step out of the quarantine area, they can be fined between 350,000 and 3.5 million JPY. On the first day of quarantine, two female policewomen of the Hsinchu City Foreign Affairs Police gave me this bag and took my mug shot. From left to right: garbage bag, thermometer, face mask. From top right: canned foods, drip coffees, crackers, retort pouch curry, and Instant noodles.

# From Nanosecond Photochemistry to Optical Force Chemistry: My Journey

Hiroshi Masuhara<sup>\*[a]</sup>

**Abstract:** Laser was invented in 1960 and soon introduced to chemistry research. We started time-resolved spectroscopy and photochemistry and initial trial was focused to nanosecond and then picosecond electronic absorption spectroscopy for studying molecular electronic excited states, charge separation in molecular complexes, and intermolecular electron transfer in solution. We considered that not only time-resolved but also space-resolved chemistry would be important for future laser-based chemistry and combined pulsed lasers with optical microscopes. Spectroscopy, photochemistry, ablation, and spatial arrangement of single microparticles and microdroplets in solution were carried out. Further we shifted from micro to nano and opened a new field covering spectroscopy, ablation, phase transition, crystallization, patterning, and fabrication. The progress is summarized and discussed as time-resolved nano spectroscopy, ablation nano dynamics, and optical force chemistry.

**Keywords:** Ablation, laser chemistry, nanoparticles, optical force, photochemistry

## 1. Starting Chemistry in Sendai, Japan

Laser oscillation was first achieved for ruby laser by Mainman in 1960 and introduced to wide fields of science and technology. It is indeed influential and innovative, which no one doubts now. Characteristic nature of laser light such as monochromaticity, short pulse, directionality, and so on has given many breakthroughs in chemistry. Still in 1985 laser was nominated as an indispensable tool for chemistry research with synchrotron and computer.<sup>[1]</sup> In my research life I feel its reality, utilize high potential of laser, and understand how laser enables us to develop new methodologies, explore new chemical phenomena, and propose new concepts. Here I summarize our past and present experimental studies by following my research experience, which would be one research example of a chemist working in Japan and Taiwan for 1960's–2020's.

[a] H. Masuhara

Department of Applied Chemistry and Center for Emergent Functional Matter Science, National Chiao Tung University, 1001 Ta Hsueh Rd., Hsinchu 30010, Taiwan  
E-mail: masuhara@masuhara.jp

I entered Tohoku Univ. in 1962 and joined the laboratory of Prof. Masao Koizumi (Late Emeritus Prof. of Tohoku Univ.) of Physical Chemistry and Photochemistry in the fourth year of undergraduate. I was trying to read “The Nature of the Chemical Bond” written by Pauling and translated into Japanese by Prof. Koizumi, and his large book “Survey of Photochemistry” (Figure 1). At that time, Profs. Tetsuo Nozoe and Koji Nakanishi were two giants in organic chemistry at Tohoku Univ. and had a strong presence in the field of Natural Products Chemistry. However, I thought that the intermediate between physics (research on the theory of things) and chemistry (research on the abundance of things) was very interesting, and it fitted me. That is the reason I choose physical chemistry and I felt Prof. Koizumi was a sincere scientist and real gentleman. However, his research life was more than what I, a vague young man, had thought. Every morning, he walked from his home in Yagiyama to the Faculty of Science in Katahira campus and worked on a well-prepared schedule, while he sometimes rushed to the toilet with his shirt outside on his back. I remember, like as if it were just yesterday, that I had a strong impression from him about what research is and what research life is.

In 1968, I went on to a doctoral program at the Faculty of Engineering Science, Osaka Univ., and decided to try to get a



**Figure 1.** (Left) L. Pauling, “The Nature of the Chemical Bond”. (Translated to Japanese by M. Koizumi), Kyoritsu Shuppan, Tokyo, **1962**. (Middle) M. Koizumi, “Survey of Photochemistry” (in Japanese), Asakura Shoten, Tokyo, **1963**. (Right upper) N. Mataga, “Introduction to Photochemistry” (in Japanese), Kyoritsu Shuppan, Tokyo, **1975**. (Right lower) N. Mataga, T. Kubota, “Molecular Interactions and Electronic Spectra”, Marcel-Dekker, **1970**.

Ph.D. degree under the supervision of Prof. Noboru Mataga (Late Emeritus Prof. of Osaka Univ.). In front of the nanosecond ruby laser installed in that year, Prof. Mataga told me, “Lasers will replace all light sources in the future, and photochemical research using lasers will have unlimited possibilities.” I was so excited by his words. I became the first graduate student at Mataga Lab who obtained a degree in laser-based research. My first work was to oscillate a nanosecond ruby laser stably. I realized I could be awarded Ph.D. if I could write papers unique to nanosecond lasers. So, I was very free to choose a theme. At this time, I think that I enjoyed the real (true) fun of exploratory research. Since then, I have been studying molecular systems unique to lasers and working in the so-called interdisciplinary area, belonging to the departments of chemistry, synthetic chemistry, polymer science, applied physics, life science, materials science, and applied chemistry. However, my research has been consistently laser-based molecular science and photochemistry. I think that there is no other field that enables pioneering research and gives the real thrill of physics and chemistry as much as physical chemistry. In 2020 I turned 76 years old. I am still conducting

exploratory research using lasers and microscopes at the National Chiao Tung Univ. (NCTU) in Hsinchu, Taiwan.

## 2. Dye Photochemistry and Flash Photolysis Method at Koizumi Lab, Tohoku University (1965–1968)

I heard that Prof. Koizumi considered on critical energy problem of future Japan after the World War II, as we had and have no natural resource, and decided to study photo-oxidation and -reduction reactions of dye molecules aiming solar energy utilization. When I joined his laboratory, two methods were introduced and utilized to identify photochemical intermediates directly; one was rigid matrix isolation method and the other was flash photolysis method. The former is carried out with ESR spectroscopy by Prof. Michio Okuda (Late Chief Researcher of the Inst. of Environmental Science, Environment Agency) and Dr. Shigeya Niizuma (Emeritus Prof. of Iwate Univ.). Prof. Okuda gave me the theme of stably capturing the pi-radical of the dye intermediates in rigid solvent, measuring their absorption spectra, and



Hiroshi Masuhara received his B.S. and M.S. degrees from Tohoku University and started his Ph.D. work on nanosecond laser photochemistry at the laboratory of Prof. Noboru Mataga in Osaka University. Following his Ph.D degree in 1971, he extended there a systematic study on nanosecond and picosecond dynamics and mechanism of electron donor-acceptor systems. In 1984 he was promoted as a full professor of Kyoto Institute of Technology and started time-resolved reflection spectroscopy and laser ablation of organic materials. Then he combined pulsed laser with optical microscopes and opened a new field of laser microchemistry. After moving to Department of Applied Physics of Osaka university, He developed a systematic study on nano spectroscopy, nano ablation, and nano manipulation of organic molecules and materials by exploring new laser-induced molecular phenomena and elucidating their dynamics and mechanism. Since 2008 he is working in Taiwan to open a new research field of optical force chemistry at solution surfaces. He is awarded Chemical Society of Japan Award, Porter Medal, The Medal of Purple Ribbon, and The Order of the Sacred Treasure-Gold Rays with Neck Ribbon, and many others, as well as serves as foreign fellows of Royal Flemish Academy of Belgium and National Academy of Sciences India.



assigning its electronic absorption bands. At that time all computer programs calculating for molecular electronic structure and electronic transition must be developed by ourselves. Learning a lot from the books and reviews written by Profs. Saburo Nagakura, Kenichi Fukui, and Haruo Hosoya groups, I developed a program for calculating the open-shell electronic structure of the Pariser-Parr-Pople formulation.

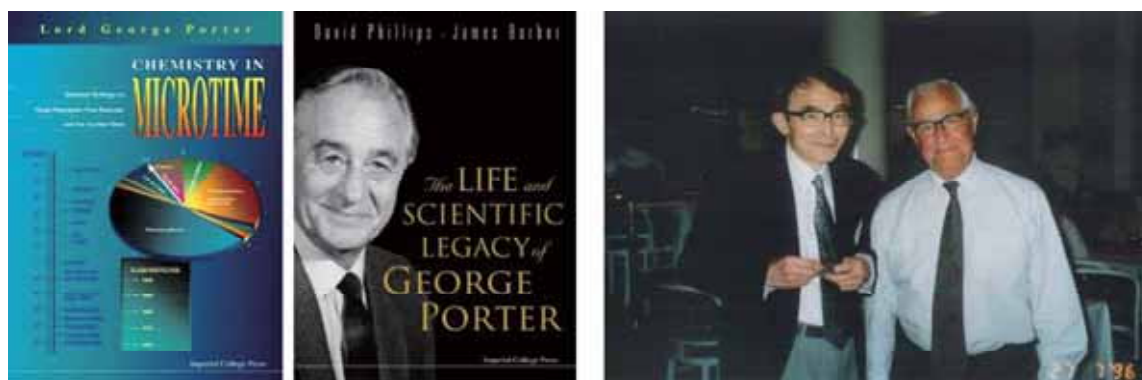
Flash photolysis method was instrumented by utilizing home-made flash lamp and pulse circuit using vacuum tubes. In 1959, Drs. Shunji Kato (Late Emeritus Prof. of Osaka Univ.), Kengo Uchida (Emeritus Prof. of Hirosaki Univ.) and Masao Koizumi reported the first transient absorption spectra of dyes intermediates in *Nature*.<sup>[2]</sup> In the flash photolysis where the first flashlight forms excited states of dyes and the second flashlight monitors the induced photoreaction. It was proposed by Late Dr. Ronald G. W. Norrish and Late Dr. George Porter (Figure 2), and they were awarded the Nobel Prize in 1967 together with Late Dr. Manfred Eigen, the developer of the stopped flow method. In late 1960' Dr. Yoshiharu Usui (Emeritus Prof. of Ibaragi Univ.), Mr. Akira Kira (Emeritus Researcher of RIKEN, Former Director of Japan Synchrotron Radiation Research Inst.), Mr. Masaharu Morita (Late Prof. of Matsumoto Dental College), and Mr. Koichi Kikuchi (Emeritus Prof. of Kitasato Univ.) were engaged in the flash photolysis studies. It was developed to a luminescence absorption flash method (named by Prof. Koizumi),<sup>[3]</sup> which was a simultaneous measurement of delayed fluorescence and absorption. According to Dr. Keitaro Yoshihara (Emeritus Prof. of Inst. for Molecular Science),<sup>[4]</sup> the flash photolysis system was also in operation in the Laboratory of Prof. Saburo Nagakura (Late Emeritus Prof. of the Univ. of Tokyo, Former director of Inst. for Molecular Science) at the Inst. for Solid State Physics, the Univ. of Tokyo. In the early days, time-resolved spectroscopy was technically possible only for the

molecular electronic spectral measurement in the visible wavelength, although it is now commonplace in all wavelength regions from X-ray to terahertz spectroscopy.

### 3. Nano-picosecond Laser Photochemistry at Mataga Laboratory, Osaka University (1968–1984)

Prof. Mataga became a Professor of the newly established Faculty of Engineering Science of Osaka University when he was already known worldwide as the proposer of the Mataga-Lippert equation<sup>[5]</sup> and the Mataga-Nishimoto approximation<sup>[6]</sup> at that time. Two reports on these works were later cited in Iwanami's "50 Years of Japanese Scientific Papers" (Iwanami Shoten, Publishers.),<sup>[7]</sup> which summarizes typical postwar research examples. In addition, Prof. Mataga published a famous paper in 1968 that proposed the concept of molecular ferromagnetism.<sup>[8]</sup> I consider these three papers the most notable work by Prof. Mataga before entering the brilliant laser photochemistry era. A little bit later two books on the electronic state and photochemistry of molecules were written by Prof. Mataga (Figure 1).

My work was to operate the laser and enable the nanosecond time-resolved electronic absorption spectroscopy first in Japan. I started experimenting with making and running the equipment from scratch. We managed to operate a ruby laser to measure nanosecond transient absorption spectra while learning vacuum tube circuits from Mr. Tadashi Okada (Emeritus Prof. of Osaka Univ.). After that, a picosecond ruby laser was introduced and managed by Mr. Nobuaki Nakashima (Emeritus Prof. of Osaka City Univ.). These ruby lasers could oscillate every 3 min, we adjusted the optical system without a viewer to look at the beam, we measured transient absorption spectra and rise and decay



**Figure 2.** (Left) G. Porter, "Chemistry in Microtime: Selected Writings on Flash Photolysis, Free Radicals, and the Excited State", Imperial College Press, London, 1977. (Middle) D. Phillips, J. Barber, "The Life and Scientific Legacy of George Porter", Imperial College Press, London, 2006. (Right) Profs. Noboru Mataga (left) and George Porter (right) at IUPAC Symposium on Photochemistry in Helsinki in 1996. Prof. Mataga was awarded the Porter Medal directly from Prof. Porter. The photo was taken by Prof. Iwao Yamazaki (Emeritus Prof. of Hokkaido Univ.).

curves of absorption band with photographic film, and ran into a dark room for developing the film.<sup>[9,10]</sup> After that, we could know whether it worked well or not, and we performed this procedure for longer than 10 hours every day. Windsor,<sup>[11]</sup> Albrecht,<sup>[12]</sup> and Porter<sup>[13]</sup> groups had already reported the nanosecond absorption spectra of the excited singlet state of  $\pi$ -electronic molecules. Our target was intermolecular charge transfer and electron transfer processes in solution, that is, Prof. Mataga's specialty. Fluorescence spectra of such electron donor-acceptor system cover all the visible wavelength, so that it was not easy to measure the absorption spectra of the fluorescent state. Proposing re-absorption method, we successfully measured a charge-transfer complex of s-tetracyanobenzene and toluene, whose excited-state absorption,  $S_1$ - $S_n$  absorption, was very similar to that of the anion of the electron acceptor s-tetracyanobenzene.<sup>[14]</sup> We were surprised to see that Ottolenghi also reported the similar spectra in the same volume of Chem. Phys. Lett.<sup>[15]</sup> This direct indication that the excited state of charge transfer complex is an electronic state similar to an ion pair received much attention, and the result became one of the topics at that time.

Sincere discussion was extended world widely, including exciplexes that form a charge-transfer complex only in an excited state. At the time, those were called hetero-excimer by Prof. Mataga, while excimers were formed between the same molecules. He considered that electronic structure of donor-acceptor system is determined by interaction with solvent and the charge transfer degree gradually changes depending solvent polarity.<sup>[16]</sup> Another idea was that the charge separation and recombination leading to non-radiative relaxation compete with each other and its ratio depends on solvent polarity. This issue was developed from intermolecular to intramolecular systems, leading to the discussion on twisted intramolecular charge transfer dynamics. I remember fruitful discussion among Profs. Mataga,<sup>[17]</sup> Ottolenghi, Weller,<sup>[18]</sup> Nagakura,<sup>[19]</sup> De Schryver,<sup>[20]</sup> Grabowski,<sup>[21]</sup> Rettig,<sup>[21]</sup> Verhoeven,<sup>[22]</sup> Zachariasse,<sup>[23]</sup> et al.

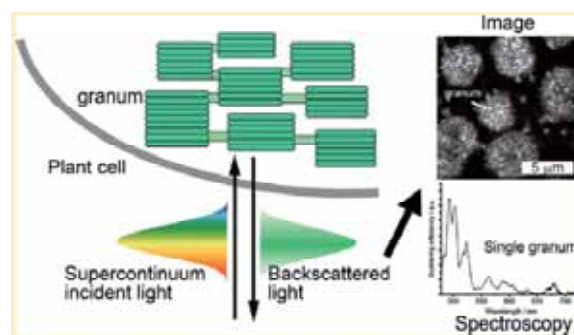
In the early 1980s, we were able to install a picosecond Nd:YAG laser at Mataga Lab with the JSPS grants. With the laser oscillating at 10 Hz, streak cameras, and diode array detectors, we were a bit relieved that we had finally reached some level in front of these modern advanced laser spectroscopy systems. Its optical set up for picosecond transient absorption spectroscopy<sup>[24]</sup> was introduced as a representative in the textbook written by Fleming.<sup>[25]</sup> Many researchers not only in physical chemistry but also in organic chemistry, polymer chemistry, photobiology, and solid state physics highly evaluated the research of electron and charge transfer dynamics and developed collaborative studies with Mataga Lab. I think Prof. Mataga has just proved this proverb; the peach and the plum do not speak and try hard to appeal to

people, yet a path is born beneath them because of their flower and fruit.<sup>[26]</sup>

Prof. Mataga did not say anything about my research trial, but when I came to his office with the data, he always discussed on the progress for hours. After explaining and discussing the experiment results, I had more time to talk with him about what to do next and what might be the future of the research. Prof. Mataga was often silent for a while. Still, on the other hand, the conversation with him flourished, and I was sometimes moved to tears. I think that this discussion-style with the manuscript that was turned red by Prof. Mataga became the basis for my research life. His seminal work was highly evaluated and he was awarded the Purple Ribbon Medal in 1995, Porter Medal in 1996 (Figure 3), Japan Academy Prize in 2006, and many others.

#### 4. Time-resolved Nano Spectroscopy

In 1984 I was appointed as Prof. of the Department of Polymer Science, Faculty of Textile Science, Kyoto Inst. of Tech., and started nanosecond diffuse reflectance spectroscopy of light scattering powder system, referring the first paper by Wilkinson.<sup>[27]</sup> I remember the discussion with Prof. Kazuhito Hashimoto (currently Dean of NIMS, Japan) about the future possibility of laser study on nanoparticles. I talked on high potential of laser spectroscopy in studying organic solids, while he was negative to use lasers. Laser means usually high intensity irradiation, limiting the development of photochemistry, as role of light in nature is always with weak intensity. That was his opinion, on which he has developed his way to contribute to environmental and sustainable research. My direction toward measuring and elucidating dynamics of nano films, nano surface of solid, and nanoparticles was settled in this way.



**Figure 3.** Illustration of light scattering spectroscopy of a single granum, the light scattering image of grana, and light scattering spectrum of a single granum. These are observed for a fresh leaf of *Egaria densa*. Reproduced with permission from Reference 37; Copyright 2017 American Chemical Society



In 1991 I shifted to Department of Applied Physics, Osaka University, when we improved the time resolution of diffuse reflectance spectroscopy to femtosecond and studied TiO<sub>2</sub> powders.<sup>[28]</sup> Although many mechanistic studies were extended, fundamental analysis based on direct spectroscopic measurement was limited so that our paper is still contributing to the relevant field. Also, we applied the spectroscopy to photochromic molecular crystal powders and proposed cooperative photochromic reaction mechanism where high density of chemical intermediates enables their conformational change.<sup>[29]</sup> The cooperativity is indeed one of key viewpoints to understand laser-induced photochemistry of molecular solids. Further, we developed femtosecond regular/specular reflection spectroscopy and applied it to probe photothermal relaxation dynamics of dye films.<sup>[30]</sup> In general reflection spectroscopy was established in 1960's mainly by physicists, while its time-resolution had not received much attention and was not improved. As a chemistry group we developed initially nanosecond and later femtosecond reflection spectroscopy systems and applied them to representative polymer films and nanopowders.

By combining pulsed lasers and microscope, we developed femtosecond single crystal absorption spectroscopy and single nanoparticle light scattering spectroscopy, with which measurements relaxation dynamics of perylene crystal<sup>[31]</sup> and gold nanoparticle<sup>[32]</sup> were clarified, respectively. Also, we launched a new system by combining an optical microscope and AFM, and clarified the correlation between the morphology of individual organic nanoparticles and their fluorescence/light scattering spectroscopic data.<sup>[33]</sup> These results indicate the size effect of the electronic spectrum of organic solids, and we proposed "structural confinement" instead of "electronic confinement" for semiconductor nanocrystals. Usually time- and space-resolved spectroscopy is developed and applied to a target in laboratory, however, direct application to real world like fabrication process,<sup>[34,35]</sup> working device,<sup>[36]</sup> living cell and natural plant is important and promising in future. Here we introduce our single nanoparticle light scattering spectroscopy to *Egaria densa*, a typical example plant in research.<sup>[37]</sup> As shown in Figure 3, a single granum consists of many thylakoids and its scattering spectrum changes as a function of the size, giving a new insight.

## 5. Ablation Nano Dynamics

High intensity laser pulse irradiation induces materials ablation, which has high potential in cutting and welding of metals, fabrication of various materials, medical operation, and electronics lithography were proposed.<sup>[35,38–41]</sup> Laser is a useful light source for fragmentation of targets for mass spectrometer, which led to Nobel Prize in Chemistry 2002. In microscopic

level the ablation seemed very complex to understand, while we performed our studies to understand ablation processes in terms of photoexcitation, vibrational relaxation, and the following processes. This was started in 1985, when Dr. Hiroyuki Hiraoka invited me as a Summer Faculty Fellow at the IBM Almaden Research Center for three months. We decided to extend a spectroscopic study of laser ablation of aromatic molecule-doped polymer film as new nonlinear photochemical processes. Already Srinivasan (IBM Thomas J Watson Research Center) wrote a famous paper on polymer ablation in 1982,<sup>[42]</sup> but there had been no fundamental examination of the molecular electronic levels. I posted the results at IBM to Prof. Mitsuo Ito (Late Emeritus Prof. of Tohoku Univ.),<sup>[43]</sup> who was editing Chem. Phys. Lett. I wondered if this was not physical chemistry and would be refused by Prof. Ito. However, he accepted this as being new physical chemistry. I think that my research attitude may have been more conservative if Prof. Ito refused at that time.

We developed nanosecond interferometry and femtosecond surface light scattering imaging and applied them together with conventional transient absorption and fluorescence spectroscopies.<sup>[35]</sup> This enables us to correlate photophysical processes with expansion and contraction dynamics of polymer films and with fragmentation of dye films. As a nonlinear electronic absorption process we could propose that cyclic multiphotonic absorption of the excited singlet state during its lifetime is critical for laser ablation.<sup>[44]</sup> Further we succeeded in proving that gradual temperature rise in nanosecond ablation and abrupt local pressure increase in femtosecond ablation are the keys to understanding ablation dynamics and mechanism of organic materials.<sup>[34,35]</sup> These results are base for developing new applications; nanoparticle fabrication, protein crystallization, and non-destructive manipulation of living cells.

Laser ablation of organic crystals results in formation of fragments which are usually ejected in vacuum chamber or in air. Contrarily we carried out nanosecond and femtosecond laser ablation in aqueous solution, and found that the ejected nanoparticles were dispersed homogeneously. We confirmed their size distributing from a few tens to a few hundreds of nanometers, namely, solution ablation is a best laboratory scale fabrication method of organic nanocrystals.<sup>[33]</sup> The colloidal solution of nanoparticles is easy to handle for the next applications such as nanodrug preparation, device fabrication, and so on.

It is well known that femtosecond laser ablation of solution results in bubble formation. We found for the first time that this ablation in supersaturated aqueous protein solution leads to protein crystallization.<sup>[45]</sup> The bubble formation and shrinking concentrates proteins and induces nucleation, which is considered to be spatio-temporal crystal formation. Various experiments were designed and performed to confirm the mechanism, while its practical application was realized by

organizing a spin-out company. Recently we extended this method to prepare protein amyloid fibril, another non-crystal aggregation,<sup>[46]</sup> which is considered to cause of Alzheimer's and Parkinson's diseases. Its result is shown in Figure 4.

The femtosecond laser-induced bubbling expands quickly, generating shockwaves and inducing convection flow. As a result, living cells located around the laser focus receive mechanical force. We utilized this bubbling phenomenon to freely manipulate the single cells in solution. Since the cells are not illuminated directly by laser, no photo-decomposition is induced, which is extremely important for manipulating bio-samples. This performance was demonstrated with using protein- and macromolecule-patterned glass substrates. Heterologous cells are manipulated individually and arranged arbitrarily on the patterns in a non-contact and non-destructive manner. We have reported various trials to realize particular functions of cells based on the spatial arrangement, on which we set the goal of producing biosensors and biodevices arranging living cells.<sup>[47]</sup>

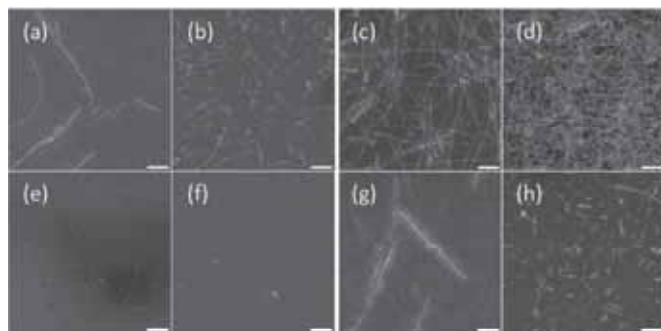
## 6. Optical Force Chemistry

Light-material interactions in spectroscopy and ablation studies are absorption, emission, scattering, and diffraction of photons by materials. Another interaction is momentum transfer from photons to materials, and we can load mechanical force on micrometer-sized targets by irradiating a focused laser beam under a microscope. Ashkin proposed optical tweezers based on this principle and was awarded the Nobel Prize in Physics 2018. This opened new research area of optical manipulation<sup>[48–50]</sup> and their application to single living cells, bacteria, DNA strands, and so on is intensively extended. Optical manipulation was also introduced to chemistry research and various kinds of molecules and nanomaterials

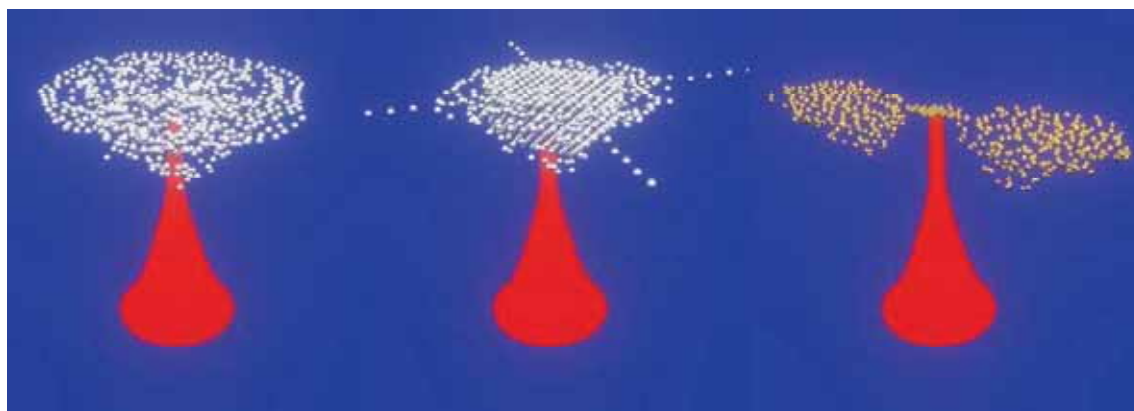
have been widely studied in solution. We combined optical manipulation with fluorescence spectroscopy, time-resolved absorption spectroscopy, micro-electrochemistry, laser ablation, and photopolymerization, and reported various chemical phenomena for individual microparticles and microdroplets. Further by integrating these approaches with surface micro-machining by scanning microscope and CVD, we were ahead of laser microchemistry. To show this research stream, we organized an international conference on microchemistry in Brussels in 1993 with excellent cooperation by Profs. F. C. De Schryver, G. Whiteside, M. S. Wrighton, A. J. Bard, J. Klafter, R. Srinivasan, D. D. Dlott, I. Tanaka, K. Honda, et al.<sup>[51]</sup> We could launch a new research area of time- and space-resolved chemistry to the world. Indeed, these results were introduced as optical trapping-based microchemistry by Ashkin.<sup>[52]</sup> In parallel with our approach, microchemistry research has been developed also in organic photochemistry and analytical chemistry, where microchannels and micro-fluidics are coupled with light emitting diode (LED).<sup>[53,54]</sup>

Laser trapping of micrometer-sized targets are interpreted by Mie theory and geometrical optics, optical force exerted on nanometer-sized is understood in the framework of light scattering theory and point dipole approximation.<sup>[55]</sup> It consists of scattering and gradient forces and, in case that the latter is stronger than that of the former, optical trapping is realized. As the effective volume of the laser focus is much larger compared to molecules and nanoparticles, a number of them are confined and interact with each other in an optical potential, leading to efficient formation of a single characteristic assembly. We have been studying the trapping and assembling phenomena, which is introduced and discussed here. The first is on femtosecond laser trapping of nanoparticles in solution. We demonstrated that nanoparticles are gathered within the focus, forming an assembly, and ejected upon its size increase. It is worth noting that the ejection takes place in the direction perpendicular to laser polarization and alternatively switched from one side to the other.<sup>[56]</sup> This is never observed with CW laser and indicates a high potential of pulsed optical force in exploring new chemical processes. Indeed, femtosecond laser induces temporal force in addition to gradient and scattering forces, and efficient multiphoton absorption results in optical resonance effect in optical trapping and sometimes in laser ablation.

The second is on optical trapping-induced molecular crystallization at solution surface. As local concentration of molecules at and around the focus becomes high, association, aggregation, and cluster formation of molecules are made possible and nucleation can be triggered. It is surprising to see that crystallization is achieved even in unsaturated solution.<sup>[57,58]</sup> Also we proposed a crystal growth mechanism in which focused trapping light is scattered and propagated through the prepared crystal. Recently Prof. T. Sugiyama is



**Figure 4.** SEM images of insulin amyloid fibrils obtained under laser irradiation and incubation (a–d) and under incubation only as controls (e–h). Femtosecond laser ablation of insulin solution leads to enhancement of amyloid fibril formation. Reproduced with permission from Reference 46; Copyright 2017 American Chemical Society.



**Figure 5.** Illustrations of the focused trapping laser and the expanded distribution of nanoparticles. (Left) a single disc-like assembly of 200 nm polystyrene nanoparticles at solution surface, (middle) a single assembly of 500 nm polystyrene nanoparticles well arranged with horn-like elongated linear aggregates at a solution/glass interface, and (right) 200 nm Au nanoparticles at a solution/glass interface. The top of each illustration corresponds to flat interface. The focal volume of the 1064 nm trapping laser is approximately  $1\ \mu\text{m}^3$ , while the optically evolving assemblies reach a few tens of micrometers. The expansion direction depends on the laser polarization.

extending new trials by introducing plasmonics to lower the threshold of laser power required for crystallization, to realize chiral crystallization, and to control crystal morphology. The chirality control in crystallization is currently receiving much attention, through which optical trapping will be recognized as a new methodology in chemistry.

The third is on optically evolving assembling and swarming of nanoparticles at solution surfaces. A single disc-like assembly of polystyrene particles of 200 nm in diameter is formed at the surface, expanding to 8 micrometers from the focus. Polystyrene particles of 500 nm at solution-glass interface give a well-arranged assembly with tetragonal and hexagonal packing depending linearly and circularly polarized trapping laser, respectively. Further we found a new phenomenon of swarming in the case of gold nanoparticles where the scattering is very strong. Gold nanoparticles interact with each other to form a periodic structure, and scatter trapping laser light far away like the Yagi-Uda antenna. Then, many gold nano-

particles gathered and moved like a group of bees. We name these phenomenon optical assembling and swarming and are studying their dynamics and mechanism.<sup>[58]</sup> We conclude that all these optical trapping behaviors are characteristic of solution surface and interface. Our understanding is illustrated in Figure 5, where optical potential can be expanded by scattering of the trapping laser by nanoparticles. Also, we consider that optical scattering and absorption forces contribute to immobilize particles at interfaces, which opens a new avenue for optical force chemistry.

## 7. Summary

We have described our research stream where development of new methodologies, exploration of new chemical phenomena, and elucidation of their microscopic dynamics and mechanism have been performed by utilizing advancing lasers. Initially nanosecond and picosecond, and later femtosecond spectroscopy and photochemistry were our interest, and then we shifted to space-resolved chemistry, initially micrometer and then nanometer in 1980's. Thus, our research is often regarded as one of nanoscience and nanotechnology researches. Still, nanotechnology began to gain social attention because the US President Clinton issued a textbook in 2000<sup>[59]</sup> and invested in research. Already we were heading toward nano by integrating lasers and optical microscopes earlier before the 2000s. At Osaka Univ. Profs. Satoshi Kawata, Toshio Yanagida, and Tomoji Kawai were playing leading roles in the world of nanoscience and nanotechnology, while we could demonstrate our uniqueness by focusing on lasers and molecular systems.<sup>[60–63]</sup> Our activity was recognized in photochemistry and physical chemistry worlds, and a special issue for my



**Figure 6.** (Left) H. Fukumura, F. Wilkinson, Edt., “Special Issue of Life and Research of Prof. Hiroshi Masuhara”, Photochemical and Photobiological Sciences, Royal Society of Chemistry, **2005**, 4, 1–164. (Right) P. F. Barbara, J. Hofkens, H. Misawa, K. Murakoshi, T. Asahi, and H. Miyasaka, Edt., “The Hiroshi Masuhara Festschrift: Exploration with Lasers into New Areas of Molecular Photoscience”, J. Phys. Chem. C, American Chemical Society, **2009**, 113 (27), 11425–11974





**Figure 7.** Group photo of Laser Bio/Nano Science Laboratory at NCTU in August 2020. The author and Prof. Sugiyama are the 1st and the 2nd from the left on the top row, respectively. Dr. Kudo is the 4th from the left on the middle row. Dr. Shun-Fa Wang is the far right on the back row.

60 years birthday was published in *Photochem. and Photobiol. Sci.* in 2005. Further Profs. G. Schatz and P. Kamat, Editors-in-Chief of *J. Phys. Chem.* issued my Festschrift in December 2009 (Figure 6). I clearly remember the old day in late 1960's when I read *J. Phys. Chem.* at Department of Chemistry in Katahira campus of Tohoku Univ. during my master's course. At that time, I wondered if I could submit a paper to this journal in future.

Our study of optical force chemistry at NCTU in Taiwan is still very unique in the world, and our laboratory would be the largest group in the relevant research fields (Figure 7). Our research is exactly on exploration and elucidation of new molecular phenomena induced by lasers. Many professors and researchers have come from this field, and we expect many more in the future.

### Acknowledgements

In the past few decades, our work has been supported by JSPS, JRDC, JST, and NEDO in Japan and by MOST and MOE in Taiwan. Our recent activity is due to MOST (MOST-109-2634-F-009.028) and the Center for Emergent Functional Matters Science of NCTU from the Future Core Research Center Program within the frame work of the Higher Education SPROUT Project by MOE in Taiwan.

### References

- [1] Committee to Survey Opportunities in the Chemical Sciences, National Research Council, "Opportunity in Chemistry (Pimentel Report)", National Academy Press, **1986**.
- [2] S. Kato, K. Uchida, M. Koizumi, *Nature* **1959**, *184*, 1620–1621.
- [3] K. Kikuchi, H. Kokubun, M. Koizumi, *Photochem. Photobiol.* **1968**, *7*, 499–501.
- [4] K. Yoshihara, *Molecular Science* **2011**, *5*, A0037.
- [5] N. Mataga, Y. Kaifu, M. Koizumi, *Bull. Chem. Soc. Jpn.* **1955**, *29*, 465–470.
- [6] N. Mataga, K. Nishimoto, *Z. Physik. Chem.* **1957**, *13*, 140–157.
- [7] "50 Years of Japanese Scientific Papers", Iwanami publish, Tokyo, **1980**.
- [8] N. Mataga, *Theor. Chim. Acta* **1968**, *10*, 372–376.
- [9] H. Masuhara, M. Shimada, N. Tsujino, N. Mataga, *Bull. Chem. Soc. Jpn.* **1971**, *44*, 3310.
- [10] N. Nakashima, M. Murakawa, N. Mataga, *Bull. Chem. Soc. Jpn.* **1976**, *49*, 854–858.
- [11] J. R. Novak, M. W. Windsor, *J. Chem. Phys.* **1967**, *47*, 3075.
- [12] D. S. Kliger, A. C. Albrecht, *J. Chem. Phys.* **1969**, *50*, 4109.
- [13] G. Porter, M. R. Topp, *Proc. R. Soc. A* **1970**, *315*, 163–184.
- [14] H. Masuhara, N. Mataga, *Chem. Phys. Lett.* **1970**, *6*, 608–610.
- [15] R. Potashnik, M. Ottolenghi, *Chem. Phys. Lett.* **1970**, *6*, 525–528.
- [16] N. Malaga, Y. Murala, *J. Am. Chem. Soc.* **1969**, *91*, 3144–3152.
- [17] N. Mataga, T. Okada, H. Masuhara (Eds.), "Dynamics and Mechanisms of Photoinduced Electron Transfer and Related Phenomena", North Holland, Elsevier **1992**.
- [18] H. Beens, A. Weller, "Absorption spectra of CT complexes in their lowest excited singlet states" In *Organic Molecular Photo-physics*; J. W. Birks, Ed., J. Wiley & Sons: London, **1975**, Vol. II, Chapter 4.
- [19] S. Nagakura, In *Excited States*; E. C. Lim, Ed., Academic Press, New York, **1975**, Vol. 2, p 322.
- [20] A. Onkelinx, F. S. De Schryver, L. Viaene, M. Van der Auweraer, K. Iwai, M. Yamamoto, M. Ichikawa, H. Masuhara, M. Maus, W. Rettig, *J. Am. Chem. Soc.* **1996**, *118*, 2892–2902.
- [21] Z. R. Grabowski, K. Rotkiewicz, W. Rettig, *Chem. Rev.* **2003**, *103*, 3899–4031.
- [22] J. W. Verhoeven, *J. Photochem. Photobiol. C* **2006**, *7*, 40–60.
- [23] S. I. Druzhinin, V. A. Galievsky, A. Demeter, S. A. Kovalenko, T. Senyushkina, S. R. Dubbaka, P. Knochel, P. Mayer, C. Grosse, D. Stalke, K. A. Zachariasse, *J. Phys. Chem. A* **2015**, *119*, 11820–11836.
- [24] H. Miyasaka, H. Masuhara, N. Mataga, *Laser Chem.* **1983**, *1*, 357–386.



- [25] G. R. Fleming, "Chemical Applications of Ultrafast Spectroscopy", Oxford University Press, New York, **1996**.
- [26] For the more profound meaning, this idiom represents that if someone has high merit, honest, and straightforward, he/she does not need to advocate or tell people around. Everyone respects and thinks highly of him/her.
- [27] F. Wilkinson, *J. Chem. Soc. Faraday Trans. 2*, **1986**, 82, 2073–2081.
- [28] A. Furube, T. Asahi, H. Masuhara, H. Yamashita, M. Anpo, *J. Phys. Chem. B* **1999**, 103, 3120–3127.
- [29] T. Asahi, M. Suzuki, H. Masuhara, *J. Phys. Chem. A* **2002**, 106, 2335–2340.
- [30] M. Ichikawa, H. Fukumura, H. Masuhara, *J. Phys. Chem.* **1995**, 99, 12072–12075.
- [31] N. Tamai, C. Porter, H. Masuhara, *Chem. Phys. Lett.* **1993**, 211, 364–370.
- [32] T. Itoh, T. Asahi, H. Masuhara, *Appl. Phys. Lett.* **2001**, 79, 1667–1669.
- [33] T. Asahi, T. Sugiyama, H. Masuhara, *Acc. Chem. Res.* **2008**, 41, 1790.
- [34] Hosokawa, M. Yashiro, T. Asahi, H. Masuhara, *J. Photochem. Photobiol. A* **2001**, 142, 197–207.
- [35] H. Masuhara, *Bull. Chem. Soc. Jpn.* **2013**, 86, 755–783.
- [36] A. Furube, Z.-S. Wang, K. Sunahara, K. Hara, R. Katoh, M. Tachiya, *J. Am. Chem. Soc.* **2010**, 132, 6614–6615.
- [37] T. Uwada, L. T. Huang, P. Y. Hee, A. Usman, H. Masuhara, *J. Phys. Chem. B* **2017**, 121, 915–922.
- [38] D. Bäuerle, "Laser Processing and Chemistry", Springer, Berlin, **2000**.
- [39] T. Lippert, J. T. Dickinson, *Chem. Rev.* **2003**, 103, 453.
- [40] R. Srinivasan, B. Braren, *Chem. Rev.* **1989**, 89, 1303.
- [41] A. Vogel, V. Venugopalan, *Chem. Rev.* **2003**, 103, 577.
- [42] R. Srinivasan, W. J. Leigh, *J. Am. Chem. Soc.* **1982**, 104, 6784.
- [43] H. Masuhara, H. Hiraoka, E. E. Martinero, *Chem. Phys. Lett.* **1986**, 135, 103–108.
- [44] H. Fukumura, H. Masuhara, *Chem. Phys. Lett.* **1994**, 221, 373–378.
- [45] H. Y. Yoshikawa, R. Murai, H. Adachi, S. Sugiyama, M. Maruyama, Y. Takahashi, K. Takano, H. Matsumura, T. Inoue, S. Murakami, H. Masuhara, Y. Mori, *Chem. Soc. Rev.* **2014**, 43, 2147.
- [46] T.-H. Liu, K. Yuyama, T. Hiramatsu, N. Yamamoto, E. Chatani, H. Miyasaka, T. Sugiyama, H. Masuhara, *Langmuir* **2017**, 33, 8311.
- [47] K. Okano, H.-Y. Hsu, Y.-K. Li, H. Masuhara, *J. Photochem. Photobiol. C* **2016**, 28, 1–28.
- [48] A. Ashkin, J. M. Dziedzic, J. E. Bjorkholm, S. Chu, *Opt. Lett.* **1986**, 11, 288–290.
- [49] J. R. Moffitt, Y. R. Chemla, S. B. Smith, C. Bustamante, *Annu. Rev. Biochem.* **2008**, 77, 205–228.
- [50] K. Dholakia, P. Reece, M. Gu, *Chem. Soc. Rev.* **2008**, 37, 42–45.
- [51] H. Masuhara, F. C. De Schryver, N. Kitamura, N. Tamai (Eds.), "Microchemistry: Spectroscopy and Chemistry in Small Domains", North Holland, **1944**.
- [52] A. Ashkin, *Proc. Natl. Acad. Sci. USA* **1997**, 94, 4853–4860.
- [53] D. Cambié, C. Bottecchia, N. J. W. Straathof, V. Hessel, T. Noël, *Chem. Rev.* **2016**, 116, 10276–10341.
- [54] H. Nakazato, H. Kawaguchi, A. Iwabuchi, K. Hane, *Lab Chip* **2012**, 12, 3419–3425.
- [55] Y. Harada, T. Asakura, *Opt. Commun.* **1996**, 124, 529–541.
- [56] W.-Y. Chiang, J. J.-K. Chen, A. Usman, T. Kudo, K. Xia, J. Su, T. Sugiyama, J. Hofkens, H. Masuhara, *J. Phys. Chem. C* **2019**, 123, 27823–27833.
- [57] T. Sugiyama, K. Yuyama, H. Masuhara, *Acc. Chem. Res.* **2012**, 45, 1946–1954.
- [58] H. Masuhara, K. Yuyama, *Annu. Rev. Phys. Chem.* **2020**, accepted.
- [59] National Nanotechnology Initiative: The Initiative and its Implementation Plan, USA National Science and Technology Council Committee on Technology, Subcommittee on Nano-scale Science, Engineering and Technology July **2000**.
- [60] H. Masuhara, S. Kawata (Eds.), "Nanophotonics", Elsevier, **2004**.
- [61] S. Kawata, H. Masuhara (Eds.), "Nanoplasmonics: From Fundamentals to Applications", Elsevier, **2006**.
- [62] H. Masuhara, S. Kawata, F. Tokunaga (Eds.), "Nano Biophotonics: Science and Technology", Elsevier, **2007**.
- [63] H. Fukumura, M. Irie, Y. Iwasawa, H. Masuhara, K. Uosaki (Eds.), "Molecular Nano Dynamics Vol. 1 & 2", VCH-Wiley, Berlin, **2009**.

Manuscript received: November 17, 2020

Revised manuscript received: February 18, 2021

Version of record online: March 3, 2021

# Optical Force-Induced Chemistry at Solution Surfaces

Hiroshi Masuhara<sup>1</sup> and Ken-ichi Yuyama<sup>2</sup>

<sup>1</sup>Department of Applied Chemistry and Center for Emergent Functional Matter Science, National Chiao Tung University, Hsinchu 30010, Taiwan; email: masuhara@masuhara.jp

<sup>2</sup>Department of Chemistry, Osaka City University, Osaka 558-8585, Japan; email: yuyama@sci.osaka-cu.ac.jp

Annu. Rev. Phys. Chem. 2021. 72:565–89

First published as a Review in Advance on February 10, 2021

The *Annual Review of Physical Chemistry* is online at physchem.annualreviews.org

<https://doi.org/10.1146/annurev-physchem-090419-044828>

Copyright © 2021 by Annual Reviews.  
All rights reserved

## Keywords

optical trapping, molecular crystallization, nanoparticles, surface, interface, assembly formation

## Abstract

When an intense 1,064-nm continuous-wave laser is tightly focused at solution surfaces, it exerts an optical force on molecules, polymers, and nanoparticles (NPs). Initially, molecules and NPs are gathered into a single assembly inside the focus, and the laser is scattered and propagated through the assembly. The expanded laser further traps them at the edge of the assembly, producing a single assembly much larger than the focus along the surface. Amino acids and inorganic ionic compounds undergo crystallization and crystal growth, polystyrene NPs form periodic arrays and disklike structures with concentric circles or hexagonal packing, and Au NPs demonstrate assembling and swarming, in which the NPs fluctuate like a group of bees. These phenomena that depend on laser polarization are called optically evolved assembling at solution surfaces, and their dynamics and mechanisms are elucidated in this review. As a promising application in materials science, the optical trapping assembly of lead halide perovskites, supramolecules, and aggregation-induced emission enhancement–active molecules is demonstrated and future directions for fundamental study are discussed.

## ANNUAL REVIEWS CONNECT

[www.annualreviews.org](http://www.annualreviews.org)

- Download figures
- Navigate cited references
- Keyword search
- Explore related articles
- Share via email or social media

## 1. INTRODUCTION

The laser (light amplification by stimulated emission of radiation) has been contributing to the development of physical chemistry since its invention in 1960 (1). Coherent oscillation from a cavity shows characteristics of light such as monochromaticity, pulse mode, and directionality. This allows light–matter interactions to be studied in more detail and the microscopic nature of molecules to be clarified. The monochromaticity has opened state-to-state chemistry in which a particular rotational, vibrational, and electronic level of the molecule is excited, and the resulting excited state in a specific rotational, vibrational, and electronic energy level undergoes selective relaxation and reaction. This fundamental chemistry on isolated molecules in the gas phase has been one of the major research areas in physical chemistry (2). The pulsed laser was soon introduced to time-resolved spectroscopy, which was originally called flash photolysis before the use of the laser was introduced (3). Nanosecond, picosecond, and then femtosecond chemistry have received a great amount of attention as new frontiers in physical chemistry (4–6). Because the laser can be well focused under a microscope, this allowed the development of many innovative tools and studies, such as optical imaging, super-resolution microscopy, single-molecule fluorescence spectroscopy, and multiplane observation (7–11). In all of this research, laser light is used as an energy source for molecular reactions or as a light source for monitoring physical and chemical processes; in these studies, laser light is generally absorbed, scattered, and/or diffracted. However, light was not widely recognized as a source of mechanical force, and many scientists did not expect chemistry by optical force even when Ashkin and colleagues (12) proposed optical tweezers.

Upon light–matter interaction, the momentum of photons can be transferred to the material, exerting mechanical force on it. This idea was first experimentally tested by Lebedev (13). A large yet lightweight target set in vacuum showed a small tilt when it was irradiated by a conventional light. Now the high-intensity light of lasers can be focused on a small area so that a large transfer of momentum from light to matter is possible. This opens up the new research area of optical manipulation (14–31). Ashkin first demonstrated that a polymer microparticle (MP) can be pushed, levitated, and transferred by two counterpropagating continuous-wave (CW) laser beams in 1970 (32) and proposed optical tweezers by tightly focusing a single laser beam on a single MP (12, 33). This technique was soon applied to biological targets such as living single cells, bacteria, and DNA (34–37). One of the authors of this review (H. Masuhara), with colleagues (38, 39), introduced a Galvano mirror set to microscopic systems and achieved free manipulation of single MPs and single liquid droplets in the focal plane. This idea was then integrated with fluorescence spectroscopy (40), time-resolved absorption spectroscopy (41), microelectrochemistry (42), laser ablation (43), and photopolymerization (44) to explore and analyze various chemical phenomena by utilizing optical force. The results for single MPs and single microdroplets based on optical trapping were summarized by our research groups (45, 46) and then Ashkin (47, 48) introduced the research area called optical trapping–based microchemistry.

In optical manipulation, the smallest target is atoms, and indeed, atom trapping is made possible by laser cooling (49). For the nanometer-sized targets between MPs and atoms, various kinds of molecules and nanomaterials have been widely studied; typical examples are molecular clusters (50–53), aggregates (54, 55), polymers (56–61), supramolecules (62–64), DNA molecules (65), carbon nanotubes (66, 67), micelles or vesicles (68–70), quantum dots (71–73), nanodiamonds (74), nanowires (75–77), polymer nanoparticles (NPs) (78, 79), and metal NPs (80–85). In this review, these targets are called generally referred to as NPs. To provide background for this discussion, we first summarize the theoretical framework for how mechanical force is loaded onto NPs based on Rayleigh scattering and point-dipole approximation (86).

When the radius of an NP is sufficiently smaller than the wavelength of the laser, this approximation can be used to describe the behavior of the NP in an electromagnetic wave. An NP is treated as an induced, simple point dipole, and optical force is exerted on this dipole. The force can be divided into two components: a scattering force component ( $F_{\text{scat}}$ ) and a gradient force component ( $F_{\text{grad}}$ ). The scattering force is associated with the momentum change of the electromagnetic wave. Upon laser irradiation, light scattering is induced by the dipole, and the momentum of the incident light is transferred to an NP. Due to this momentum change, the scattering force ( $F_{\text{scat}}$ ) is exerted on an NP. This force is given by the equation

$$F_{\text{scat}}(r) = \frac{C_{\text{scat}} \cdot \langle S(r, t) \rangle_{\text{T}}}{c/n_2}, \quad 1.$$

where  $n_2$  is the refractive index of a surrounding medium,  $c$  is the speed of light in a vacuum,  $C_{\text{scat}}$  is the scattering cross section of an NP, and  $\langle S(r, t) \rangle_{\text{T}}$  is the time-averaged Poynting vector at position  $r$ . When the radius of the NP ( $a$ ) is used, the scattering force increases in proportion to  $a^6$ .

The gradient force is associated with a Lorentz force that acts on a dipole located in an inhomogeneous electromagnetic field. The gradient force that an NP experiences in a steady state is given by

$$F_{\text{grad}}(r) = \pi n_2^2 \varepsilon_0 a^3 \left( \frac{m^2 - 1}{m^2 + 2} \right) \nabla |E(r)|^2, \quad 2.$$

where  $\varepsilon_0$  is the dielectric constant in the vacuum,  $m$  is the relative refractive index of the NP, and  $E(r)$  is the electric-field vector. The intensity of the laser,  $I(r)$ , is defined as

$$I(r) = \frac{1}{2} n_2 \varepsilon_0 c |E(r)|^2. \quad 3.$$

Given this definition, the gradient force is then calculated in terms of the intensity distribution of the beam by

$$F_{\text{grad}}(r) = \frac{2\pi n_2 a^3}{c} \left( \frac{m^2 - 1}{m^2 + 2} \right) \nabla I(r). \quad 4.$$

Considering the relationship between force and potential, the optical potential energy well is described by

$$U_{\text{grad}}(r) = -\frac{2\pi n_2 a^3}{c} \left( \frac{m^2 - 1}{m^2 + 2} \right) I(r). \quad 5.$$

Different from the scattering force, the gradient force is proportional to  $a^3$ . In an optically evolved phenomenon, assembly size increases with time so that the balance between the scattering force and gradient force is dynamically changed.

The optical forces that are exerted on NPs consist of gradient and scattering forces. When the gradient force is larger than the scattering force, optical trapping is possible. This is generally true in bulk solution; however, the situation is different at liquid/air, liquid/liquid, and liquid/solid interfaces, where the scattering forces toward the interfaces can also immobilize the object. Thus, even small objects can be trapped at an interface with relatively weak gradient forces, leading to new optical assembling phenomena.

We usually use a 1,064-nm CW laser as a trapping light source, as its long wavelength tends to hamper multiphoton excitation of the trapping targets. NPs are much smaller than the focal area, so a number of NPs can be confined in a given potential. The NPs physically and chemically interact with one another, producing various phenomena under optical trapping. As the local concentration of NPs in the confined potential increases above a certain level, association, aggregation,



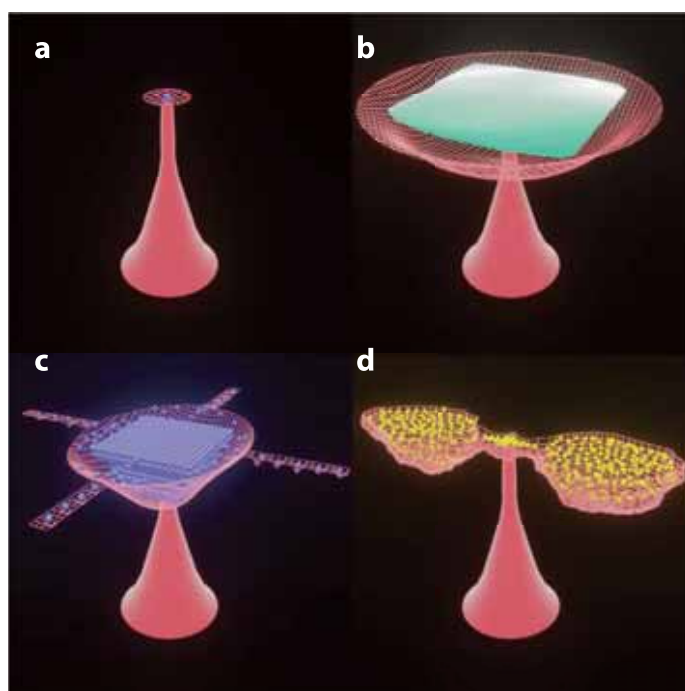
cluster formation, and even nucleation can be induced. The range of phenomena produced can be expanded. If the trapping laser light is absorbed by solvent molecules through their vibrational overtone mode, the local temperature becomes elevated. For example, an elevation of 22 K per 1 W of laser power is estimated for 1,064-nm laser trapping in aqueous solution (87). The temperature distribution is wider than the focal volume due to thermal conduction. Therefore, a thermal phase transition that starts at the focus expands into the area where the temperature is high. In these cases, the optical potential only triggers the phenomena, and the assembly expands outside of the focus following thermodynamic conditions determined by temperature, concentration, and other factors.

At the surface and interface, the trapping laser at the focus is strongly scattered by the trapped NPs and is propagated through the gathered NPs, forming an attractive potential at their edge. The multiple scattering results in a decrease in the laser's intensity; however, a small gradient force is usually enough to immobilize the NPs. Also, the scattering force pushes NPs toward the surface and interface, contributing to their immobilization. As a result, a single assembly of NPs can grow to become much larger than the focus along the solution surface and interface. In the past decades, we have demonstrated various interesting phenomena that we call optically evolved assembling, and we have been elucidating their dynamics and mechanisms that are characteristic of solution surface and solution/glass interfaces.

In this review, we mainly summarize our seminal research and discuss the evolved trapping of molecules and NPs at solutions and interfaces. Our viewpoint for comprehensively understanding their dynamics and mechanisms is based on optical trapping potential expansion by nonlinearly evolving interactions between the trapping laser and the NPs. The Gaussian beam potential is tightly focused on a solution surface and interface where a single NP is trapped (**Figure 1a**). When the NP concentration of the mother solution is high, many NPs are confined, triggering cluster formation, crystallization, and crystal growth of molecules as well as phase transition of the polymer solution, phenomena that are similar to those observed under conventional thermodynamic conditions. In the case of low solute concentration, the trapping potential does not change much. The advantage of optical trapping is its high spatiotemporal controllability. When the trapping laser light is scattered by the trapped NPs at a surface and interface, the laser propagates through the trapped NPs and they interfere with one another, expanding the optical trapping potential. Optically evolving crystallization, periodic arrangement of polystyrene (PS) NPs, and the assembly and swarm of Au NPs, which are never observed in solution, are illustrated in **Figure 1b–d**, respectively. In the following sections, we present how new molecular and NP phenomena are induced at a solution interface by optical force, propose their dynamics and mechanisms, and describe possible applications.

## 2. CHEMICALLY EXPANDING ASSEMBLY OF MOLECULES AND POLYMERS IN SOLUTION

Under the optical conditions in our group's experiments, the effective focal volume is diffraction limited so that the attractive potential size is about 1  $\mu\text{m}$ . Conventional organic molecules and inorganic compounds are small, so the exerted optical force is weak and does not stop vigorous Brownian motion in solution at room temperature. Their movement is just slowed down, which is called biased diffusion (88–90). Our optical trapping experiments have shown that a few nanometers and 20 nm are the necessary diameters for metal and organic NPs, respectively. One example is shown in **Figure 2a** (58), in which polymers were trapped at a focus and aggregated with each other, producing a single assembly. The assembly, which was saturated by radiation, was about 1  $\mu\text{m}$  in size, similar to its focal volume. In this case, the gradient force overcame the scattering



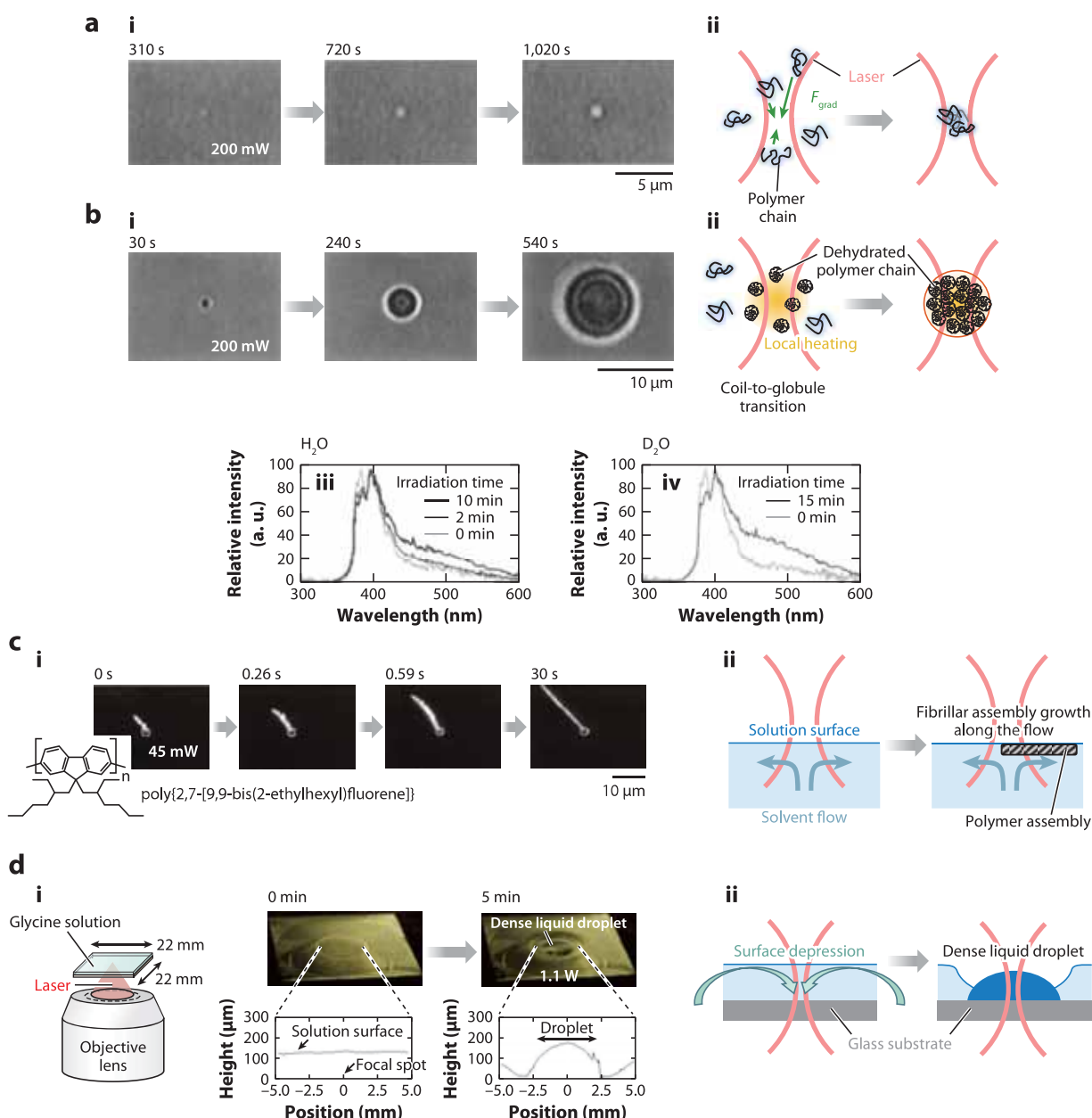
**Figure 1**

Illustrations of optically evolved assembly. The modification of optical potential and the expansion of the distribution of molecules and nanoparticles (NPs) are induced by interactions between the trapping laser and the NPs. (a) A single NP at a solution surface, (b) a single crystal of L-phenylalanine at a solution surface, (c) a single assembly of polystyrene (PS) NPs with hornlike elongated linear aggregates at a solution/glass interface, and (d) Au NPs at a solution/glass interface. As NPs are distributed only below the solution surface and interface, the top of each illustration is flat. The focal volume of the 1,064-nm trapping laser is approximately  $1\ \mu\text{m}^3$ , while the optically evolving molecular crystal shown in panel b, the periodic arrangement of PS NPs with four horns in panel c, and the two swarms of Au NPs in panel d reach a few tens of micrometers.

force in the focal volume; however, for a larger trapped aggregate, the scattering force can be stronger than the gradient force. In the latter case, the aggregate was then ejected from the focus. This is one reason why an assembly in solution usually has a size similar to that of the focal volume. This behavior is quite common in solutions and has been systematically confirmed for poly(*N*-isopropylacrylamide) (PNIPAM) and its family (56, 57).

The 1,064-nm trapping laser excites the overtone vibrational mode of  $\text{H}_2\text{O}$ , leading to local laser heating (87) and subsequent thermal conduction. In the case of PNIPAM in aqueous solution, the polymer changes from random coil to globule conformation with prolonged irradiation, exhibiting a sol–gel phase transition. Indeed, one assembly observed at the focus reached a size of  $10\ \mu\text{m}$ , much larger than the focal volume, reflecting the heated area (56). To monitor the local structures of polymers, pyrene-labeled PNIPAM (Py-PNIPAM) was studied, as shown in **Figure 2b** (57). Dimer fluorescence around 480 nm reflects a high local concentration of dimer configurations in the ground state, while the vibrational structure of pyrene fluorescence indicates local polarity. Both photothermal and optical trapping effects determine the assembly structure in  $\text{H}_2\text{O}$ , but the former effect is hampered in  $\text{D}_2\text{O}$  and the characteristic spectral change indicates strong packing of PNIPAM by optical trapping.

Another example shown in **Figure 2c** is the formation of ordered fibril- and particle-like assemblies during the solvent evaporation process on a glass substrate (60). This is achieved by combining laser irradiation with convection flow in the cast solution. When the viscous drag of the solution in the convection is stronger than the optical force, fibril-like assemblies can form. The molecular orientation in these assemblies differs from that in self-assembled fibril-like structures, and such orientation can be controlled by the polarization direction of the focused laser



(Caption appears on following page)

**Figure 2** (Figure appears on preceding page)

Optical trapping and assembling phenomena coupled with thermal effects. (*Left, i*) Illustrations of the experiments. (*Right, ii*) Schematic illustrations of respective laser trapping behaviors. The laser power is given in corresponding optical images. (*a*) Laser trapping behavior of poly(*N*-vinylcarbazole) in *N,N*-dimethylformamide. (*i*) Optical transmission micrographs around the focal spot, showing a particle-like molecular assembly. Panel *a* subpanel *i* adapted with permission from Reference 58; copyright 1998 American Chemical Society. (*b*) Fluorescence analysis of laser trapping of pyrene-labeled poly(*N*-isopropylacrylamide) in H<sub>2</sub>O and D<sub>2</sub>O. (*i*) Optical transmission micrographs around the focal spot in H<sub>2</sub>O, producing (*ii*) a large molecular assembly due to photothermal effects. (*iii, iv*) Normalized fluorescence spectra, which were obtained by laser trapping in (subpanel *iii*) H<sub>2</sub>O and (subpanel *iv*) D<sub>2</sub>O solutions, are shown at the different irradiation times. Panel *b* subpanels *i, iii, and iv* adapted with permission from Reference 57; copyright 1997 American Chemical Society. (*c*) Laser trapping behavior of poly[2,7-[9,9-bis(2-ethylhexyl)fluorene]] in tetrahydrofuran. (*i*) Fluorescence images and (*ii*) illustrations show the fibril-like assembly growing along the solvent flow. The chemical structure of the polymer is given in the inset to subpanel *i*. Panel *c* subpanel *i* adapted with permission from Reference 60; copyright 2007 American Chemical Society. (*d*) A millimeter-scale dense liquid droplet of glycine (23 wt%) formed under focused laser irradiation of a thin film of the D<sub>2</sub>O solution. (*i, Top*) Optical micrographs are shown of the sample and (*bottom*) the corresponding solution surface profiles before and after irradiation. Panel *d* adapted with permission from Reference 95; copyright 2012 American Chemical Society.

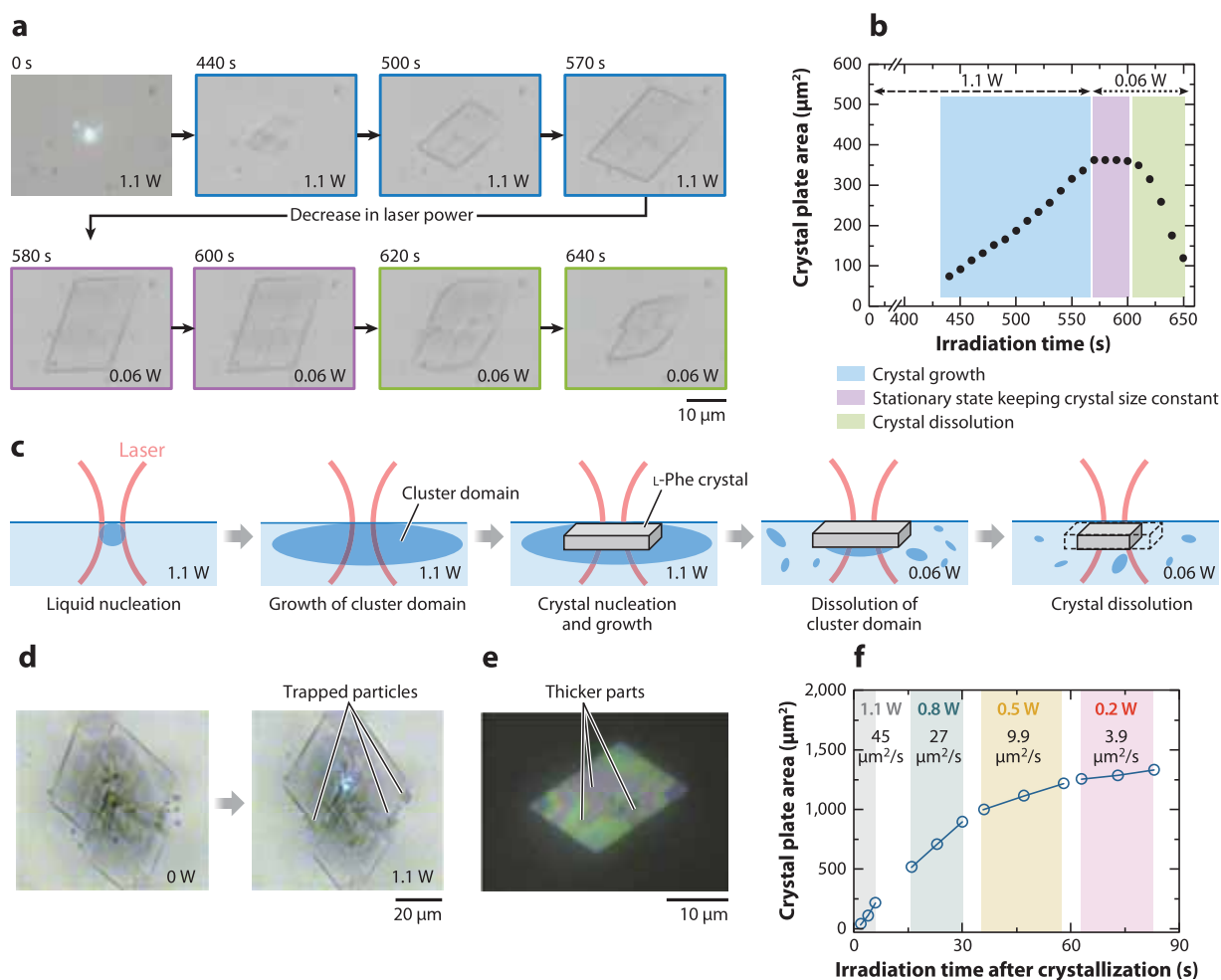
beam. When the viscous drag of the convection solution is weak, particle-like assemblies form in which polymer orientation is still controllable by the polarization direction of the trapping laser.

Heat generated at the focal spot diffuses to the surroundings, and surface tension decreases with increasing temperature. Due to the resultant inhomogeneous distribution of surface tension, the solution surface becomes depressed around the laser focus (91, 92), leading to the formation of an ultrathin film just a few micrometers in thickness. In parallel, convection flow transports solutes to the depressed area upon which optical force is acting (93). As a result, the efficient optical trapping of transported solutes is achieved, and the local solute concentration quickly increases, resulting in nucleation for liquid–liquid phase separation (LLPS). In fact, a dense liquid droplet is formed through phase separation in a thin film of a supersaturated D<sub>2</sub>O solution of glycine (94, 95). Liquid nucleation takes place after the surface depression occurs, and the liquid nucleus grows increasingly larger by absorbing solutes from the surrounding solution. As shown in **Figure 2d**, the droplet takes on a thin convex shape with a diameter of 5 mm, which is 5,000× larger than the focal spot (about 1 μm in diameter). The saturation degree of the droplet is 2.7, but it remains a liquid without crystallization under laser irradiation. Similar droplet formation is observed for other amino acids, potassium chloride, and urea. As introduced in **Figure 2b–d**, optical trapping occasionally accompanies thermal effects, such as the phase transition of polymers, convection flow, and surface deformation, through which a unique molecular assembly with a size much larger than that of the focal volume is formed in a spatially and temporally controlled manner.

### 3. OPTICALLY EVOLVING CRYSTALS AT THE SOLUTION SURFACE

During laser trapping at a solution surface, molecular or ionic crystals are formed at the focal spot. This crystallization was first demonstrated for glycine in 2007 (96). Since then, it has been observed for other amino acids (97–105), potassium chloride (106), sodium chlorate (107), and lead halide perovskites (108, 109). Laser trapping locally and transiently increases the concentration of solutes not only at but also around the focus. Therefore, crystallization can be induced even in an unsaturated solution. A representative example is given in **Figure 3a** (101). The trapping laser was focused onto the surface of an unsaturated solution of L-phenylalanine (L-Phe). The initial solution has a saturation degree of 50%, a situation that never exhibits spontaneous crystallization. After several minutes of irradiation, crystallization is induced at the focal spot. The resultant plate-like L-Phe crystal is stably trapped at the focus and continuously grows larger. This crystal growth pauses when the laser power is decreased to one-twentieth of the original value. The crystal is stably trapped even at this low laser power but starts to dissolve after a certain amount of





**Figure 3**

Laser trapping-induced crystallization of L-phenylalanine (L-Phe) in  $\text{H}_2\text{O}$ . (a) Optical transmission micrographs around the focal spot and (b) a graph of time evolution of the crystal plate area during laser trapping at the air/solution interface. Panels a and b adapted with permission from Reference 104; copyright 2018 American Chemical Society. (c) A schematic illustration of laser trapping dynamics at 1.1 and then 0.06 W. (d) Optical micrographs of particles around an L-Phe crystal. Panel d reproduced with permission from Reference 101; copyright 2013 American Chemical Society. (e) An optical reflection image of an L-Phe crystal. Panel e reproduced with permission from Reference 105; copyright 2019 The Japan Society of Applied Physics. (f) A graph showing the temporal change in the crystal plate area upon the step-by-step decrease of laser power. The 2D crystal growth rate at each laser power is shown. Panel f adapted with permission from Reference 103; copyright 2016 American Chemical Society.

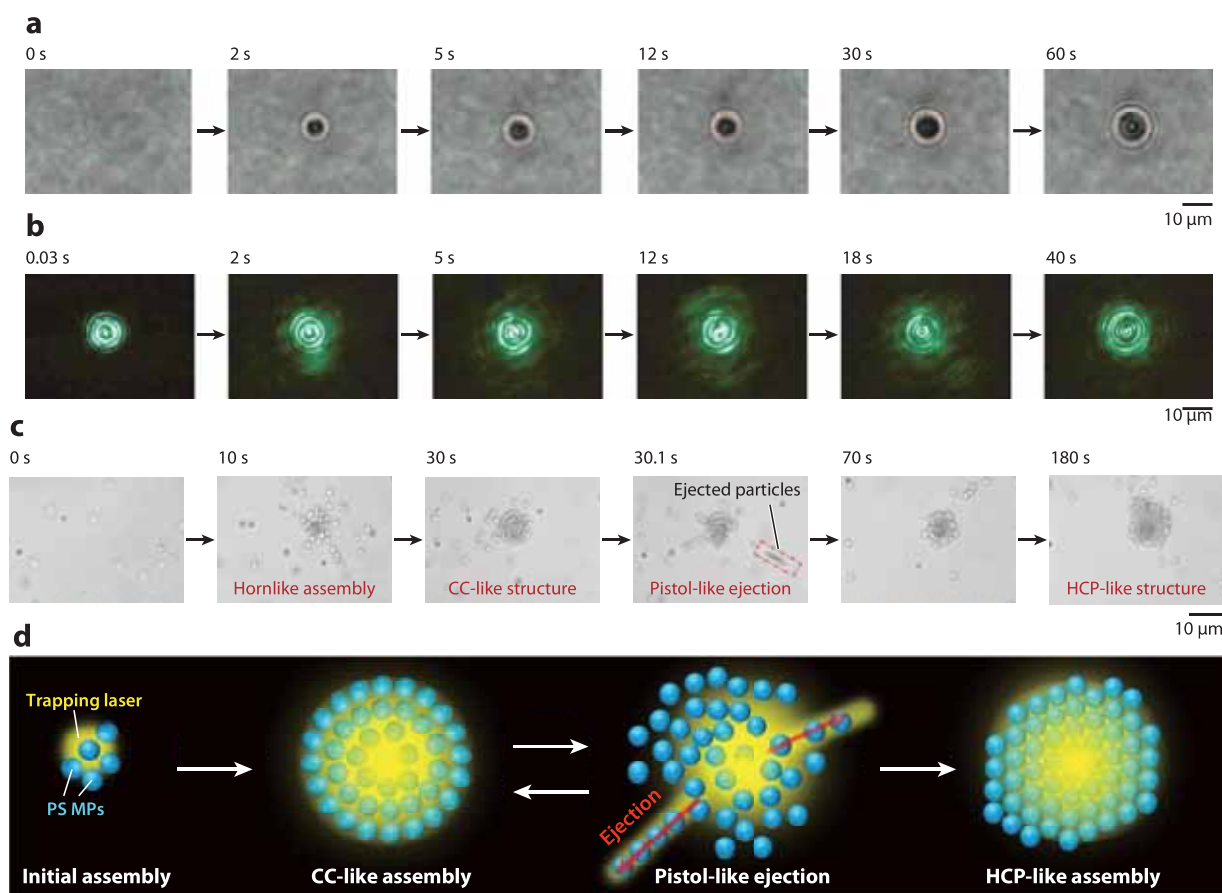
time (Figure 3a,b). The stationary state keeping crystal size constant can be explained by assuming a highly concentrated area of solute around the crystal (Figure 3c). This dense area gradually diffuses into the surrounding solution during the laser irradiation at low power. As a result, the surrounding solution is homogenized, and the crystal is exposed to the unsaturated solution, initiating crystal dissolution. Indeed, the crystal quickly dissolves when it is optically manipulated to a position far from the original focal spot. The size of the highly concentrated area was estimated by the optical manipulation experiment to be a few tens of micrometers.

The mechanism of formation of a highly concentrated, large area of L-Phe may be similar to that of the dense liquid droplet of glycine (**Figure 3c**). L-Phe liquid-like clusters, in which solute and solvent molecules are associated with weak interactions, are attracted by optical force and merge with each other, forming larger clusters. Through this process, the optical potential becomes increasingly deeper, and the local concentration is gradually increased. As a result, liquid nucleation takes place at the focal spot. While being irradiated, the resulting liquid nucleus is more energetically favorable than the surrounding solution and so enlarges through spontaneous growth. We call the dense area a cluster domain, as it is formed by the association of L-Phe liquid-like clusters. Actually, two order parameters and a concentration of solutes with their associated structures are known to be necessary for crystallization. Before crystallization, the optical potential forms only at the focal spot, and the shape of the potential reflects the intensity distribution of the incident laser beam. In contrast, the optical potential is spatially modified after crystallization, as illustrated in **Figure 1b**. The potential is extended to the outside of the focal spot, which enables optical trapping at the edge of the crystal.

The expansion of optical potential is visually confirmed by trapping PS MPs with a diameter of 1  $\mu\text{m}$ . Upon focused laser irradiation, the MPs gather at the edge of an L-Phe crystal. The MPs are closely arranged at the crystal edge, although they are not directly irradiated by the laser (**Figure 3d**). After switching off the laser, the gathered MPs start to diffuse into the surrounding solution, meaning that the particles are transiently attracted by the laser irradiation. This remote trapping at the crystal edge can be explained by an optical mechanism. The laser light sent into the center of the crystal propagates inside the crystal outward from the focus and forms an optical potential at the crystal edge. This extended optical potential attracts MPs to the crystal from the surrounding solution. Similarly, L-Phe in a surrounding cluster domain is also trapped at the crystal edge, which leads to continuous crystal growth even in the unsaturated solution. The mechanism of light propagation is supported by the observed framework-like structure of the crystal. We investigated the crystal growth behavior of L-Phe with reflection microscopy under laser trapping conditions. L-Phe crystals appear to be colored in reflection micrographs due to the interference of white light being reflected at the upper and lower crystal faces. The interference is strongly dependent on crystal thickness, so the inhomogeneity of crystal thicknesses is visualized. We found that a framework-like structure with a wider thickness is formed from the focus toward the crystal edge (**Figure 3e**). This structure likely acts as a waveguide to propagate the laser outward from the focal point, and the propagated light modifies the optical potential, enabling the optical trapping of L-Phe and MPs at the crystal edge. How L-Phe molecules are trapped and concentrated at and around the focus is dependent on the power of the laser. Thus, the 2D growth rate of plate-like L-Phe is slowed down by a decrease in the input laser power (**Figure 3f**). Therefore, crystal growth can be optically controlled by tuning the laser power.

#### 4. OPTICALLY EVOLVING ASSEMBLY OF POLYMER NANOPARTICLES AT THE SOLUTION SURFACE

The optical assembly of PS NPs is itself an interesting topic in colloid science and technology and is also considered to be a useful reference for the optically evolving crystallization of molecules. In the case of 200-nm PS NPs at a solution surface (110), a disklike assembly is formed and continuously grows, keeping a circular shape during the irradiation as shown in **Figure 4a**. The trapping laser seems to gather NPs, propagate through the formed NP assembly, and expand the trapping potential further, thus growing the aggregates outward at the solution surface. NPs confined in focal volume induce the scattering of the trapping laser, and the surrounding NPs propagate the scattered laser, forming a potential just outside the circular assembly. PS NPs are trapped in the



**Figure 4**

(a) Optical transmission micrographs and (b) backscattering images from the optical trapping of 200-nm PS NPs at an aqueous solution surface after switching on the trapping 1,064-nm laser. Panels *a* and *b* adapted with permission from Reference 110; copyright 2016 American Chemical Society. (c) Optical transmission micrographs and (d) a schematic illustration for the optical trapping-induced assembly and rearrangement of 1- $\mu$ m PS MPs at a D<sub>2</sub>O solution surface. Hornlike assembly, CC-like structure, pistol-like ejection (outlined by red rectangle), and HCP-like structures are indicated in corresponding images. Panels *c* and *d* adapted with permission from Reference 111; copyright 2020 American Chemical Society. Abbreviations: CC, concentric circle; HCP, hexagonal close-packed; MP, microparticle; NP, nanoparticle; PS, polystyrene.

potential, increasing the circular assembly size. This optically evolved assembling proceeds until the formed optical potential becomes shallow, comparable to the thermal energy of NPs. To confirm this idea, we monitored the backscattering pattern from the assembly. **Figure 4b** shows the time evolution of the backscattering images from the 1,064-nm trapping laser, in which the concentric circle (CC) pattern extends continuously and symmetrically into the surrounding solution. The growth of the circular shape of backscattered light corresponds well to the images shown in **Figure 4a**.

How intense laser irradiation traps NPs and MPs at the focus in a solution has been studied by many groups, but it is not widely accepted that optical force is useful for forming a large disk-like assembly of molecules and NPs at the solution interface. To visualize the trapping assembly dynamics, we have sampled 1- $\mu$ m PS MPs (111). When the 1,064-nm laser is focused, the MPs

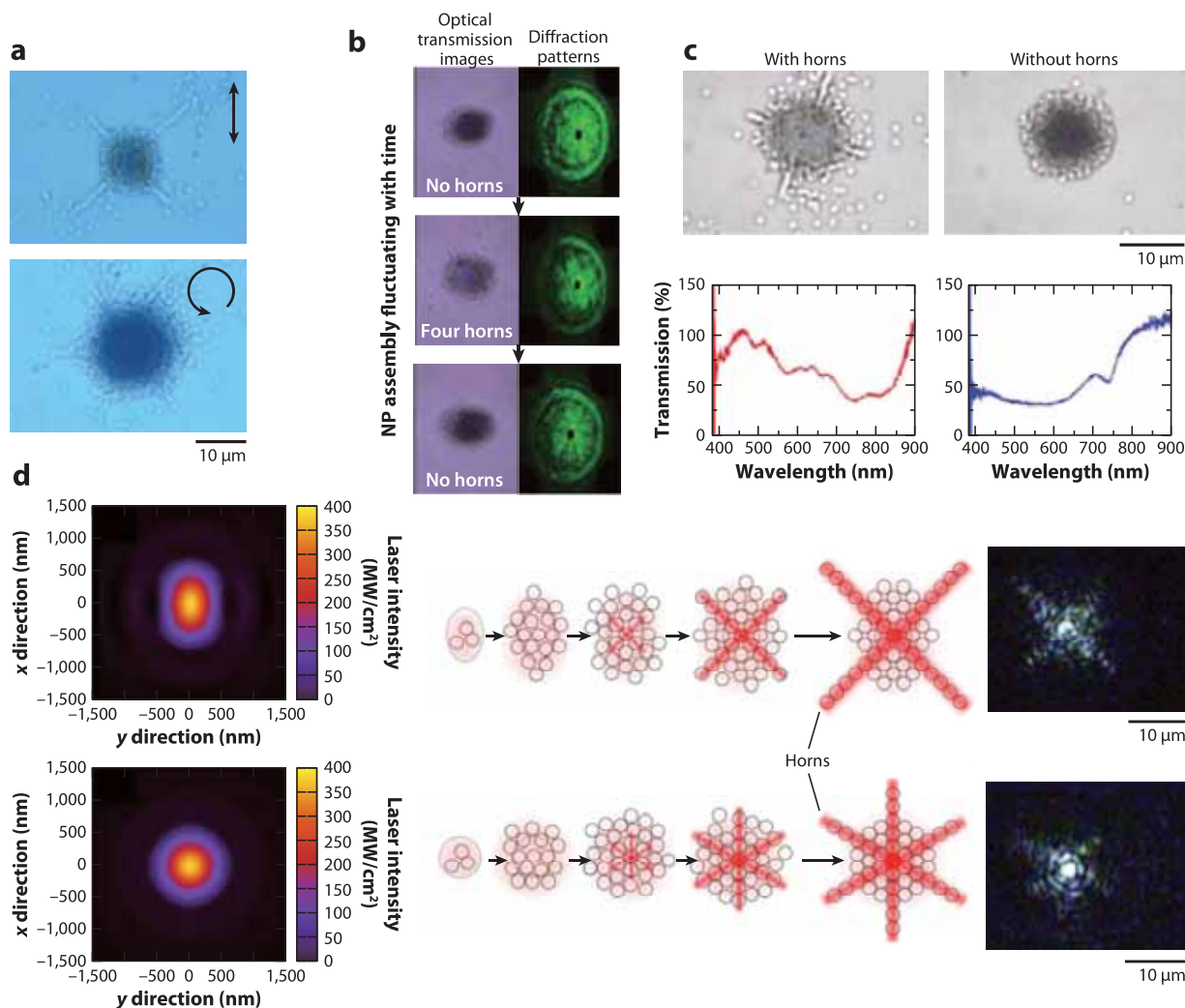
gather far from the focus, leading to the formation of a single large assembly with CC-like packing. The assembly evolves with the irradiation time, exhibiting an increase in lateral size, producing the pistol-like ejection of several MPs in a linearly aligned manner, rearranging to another CC-like assembly, and eventually forming a hexagonal close-packed (HCP) structure of PS MPs. Representative sequential transmission optical micrographs are shown in **Figure 4c**. The CC-like structure is considered to be kinetically prepared, while the 2D HCP structure is thermodynamically favored at the interface (112, 113). This is an experimental model of what happens microscopically at the solution surface upon optical trapping. The behavior presently observed with continuous irradiation is illustrated in **Figure 4d**.

Pistol-like ejection is always induced radially from the center to the outside, so we think that the light scattering and propagation of the trapping laser inside the CC assembly has an important role in this process. Occasionally, we observed that the 1- $\mu\text{m}$  PS MPs were radially extended, forming a line, and then they were ejected. This occurred along the scattering lines of the trapping laser from the focus, as similarly observed for 200-nm PS NPs at the solution surface (114) and for 500-nm PS NPs at the solution/glass interface (115). Here the 1- $\mu\text{m}$  PS MPs in the line were ejected when the incoming MPs collided with the assembly, as illustrated in **Figure 4d**. We observed that the laser scattering always looked like multiple radial white streams expanding from the center of the CC-like structure. This supports our idea that the scattered light of the trapping laser from the central part of the CC-like assembly and its directional propagation through the structure is the origin of pistol-like ejection at the solution surface. Quantitative analysis of pistol-like ejection is being performed; for example, the ejection speed for the highest laser power (1.4 W) was estimated to be 200  $\mu\text{m/s}$ , and the ejection angle was tilted by 11–15° from the solution surface.

## 5. OPTICALLY EVOLVING ASSEMBLY OF POLYMER NANOPARTICLES AT THE SOLUTION/GLASS INTERFACE

Light scattering and propagation of the trapping laser are critical for molecular crystallization and disklike assembly formation of NPs, which is directly demonstrated by the periodic assembly formation of 500-nm PS NPs at the solution/glass interface (**Figure 5a**) (115). Compared to that with the solution surface, the interface with glass is rigid, so PS NP packing is more stable, leading to an arrangement that allows more efficient scattering and propagation of the trapping laser. The single lateral assembly is deformed and becomes elongated along the linear polarization direction of the trapping laser. This is due to the high numerical aperture of the objective lens used. For the circularly polarized laser, the assembly shape is circular. A long period of irradiation with a linearly and circularly polarized laser produces elongated and circular assemblies with four and six horns at their edges, respectively. The packing structure at the center determines the expanding assembly shape by propagating the trapping laser. The tetragonal and hexagonal packing structures at the assembly center, which correspond to four and six horns, respectively, are monitored by diffraction pattern measurement, as shown in **Figure 5b**. In addition, **Figure 5c** shows the transmission spectra for four and no horns, which agree well with the images of these structures. This polarization-dependent assembly is well explained by theoretical calculation of the laser beam profiles at a focal plane. The calculated profiles in **Figure 5d** match the shapes of the corresponding NP assemblies, so the PS NPs seem to be arranged according to the trapping laser intensity distribution. The results confirm that propagation of light from the trapping laser through packed PS NPs yields the horns, which is illustrated in **Figure 1c**. This mechanism has great potential for assembling and fabricating fascinating materials.



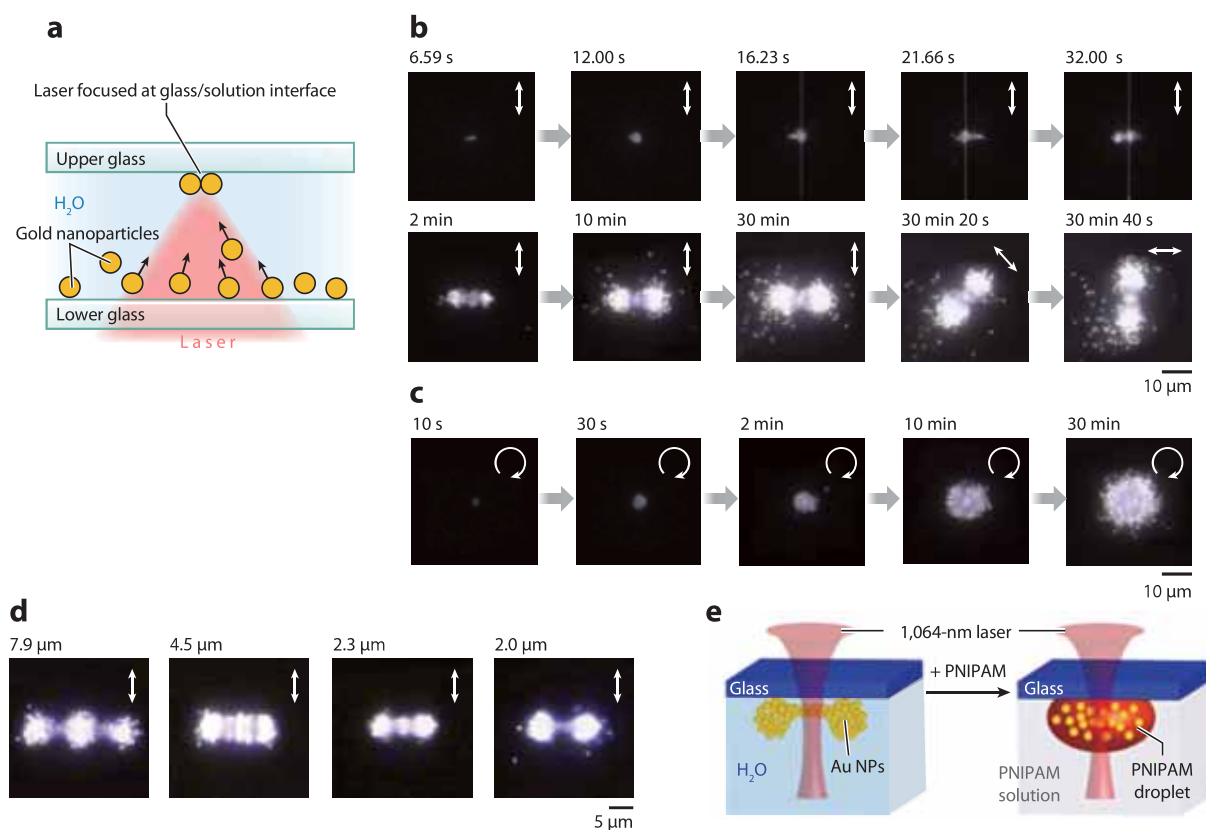


**Figure 5**

(a) Optical transmission micrographs of the optical trapping of 500-nm polystyrene (PS) nanoparticles (NPs) at an aqueous solution/glass interface. (Top) Linearly and (bottom) circularly polarized lasers produce four and six hornlike structures, respectively, at the edges of the single disklike assemblies. The polarization is shown by straight and circular black arrows. (b) Temporal changes in optical transmission micrographs and diffraction patterns of the optical trapping of 500-nm PS NPs at an aqueous solution/glass interface with the linearly polarized laser. (c) Optical transmission micrographs of NP assemblies (left) with horns and (right) without horns and the corresponding transmission spectra measured at the focus. These assemblies are formed at different times during the optical trapping of 500-nm PS NPs at an aqueous solution/glass interface with a linearly polarized laser. (d, left) Images and illustrations showing the spatial distribution of calculated laser intensity with a high-numerical aperture lens for linearly and circularly polarized lasers. (Middle) Schematic illustrations showing assembly growth of 500-nm PS NPs with (top) tetragonal and (bottom) hexagonal structures for linearly and circularly polarized trapping lasers, respectively. The trapping laser propagates along the structures, producing either four or six horns. (Right) Backscattering images of the trapping laser observed from the assembly. Images in panels a and d reproduced with permission from Reference 115; copyright 2016 American Chemical Society.

## 6. OPTICALLY EVOLVING SWARMING OF GOLD NANOPARTICLES AT THE SOLUTION/GLASS INTERFACE

Recently, we have extended these experiments at the solution/glass interface to gold (Au) NPs, and we have found a new phenomenon that is characteristic of their inherent surface plasmon resonance (SPR) (116). The heavy 200-nm Au NPs sink to the bottom of the sample but are lifted upward upon trapping laser irradiation, as shown in **Figure 6a**. Initially, a few Au NPs are trapped at the focal spot at the interface and efficiently scatter the trapping laser light. With linearly polarized laser irradiation, dipolar scattering of Au NPs renders the light distribution perpendicular to the direction of laser polarization. The scattered light expands the optical potential and collects more Au NPs at both sides of the assembly outside the focal spot (**Figure 6b**). The NPs fluctuate as a group like flying bees and form a dumbbell-shaped assembly of about  $5 \times 10 \mu\text{m}^2$  at the solution/glass interface. In the case of circularly polarized laser irradiation (**Figure 6c**), the



**Figure 6**

(a) A schematic illustration of the optical trapping and swarming of 200-nm Au NPs at an aqueous solution/glass interface. Au NPs sink to the bottom of the sample cell and are then lifted up by trapping laser irradiation. (b,c) Temporal change in light-scattering images showing the optical trapping or swarming of Au NPs with a linearly (panel b) or circularly (panel c) polarized laser. Panels b and c adapted with permission from Reference 116; copyright 2018 American Chemical Society. (d) Light-scattering images of Au NP trapping and swarming using two linearly polarized trapping laser beams of equal power. The distance between the centers of the two laser beams is given in the images. (e) Schematic illustrations of Au NPs first swarming and then stopped in a single microdroplet of PNIPAM, which is prepared by local phase transition due to photothermal heating of the NPs. Abbreviations: NP, nanoparticle; PNIPAM, poly(*N*-isopropylacrylamide).

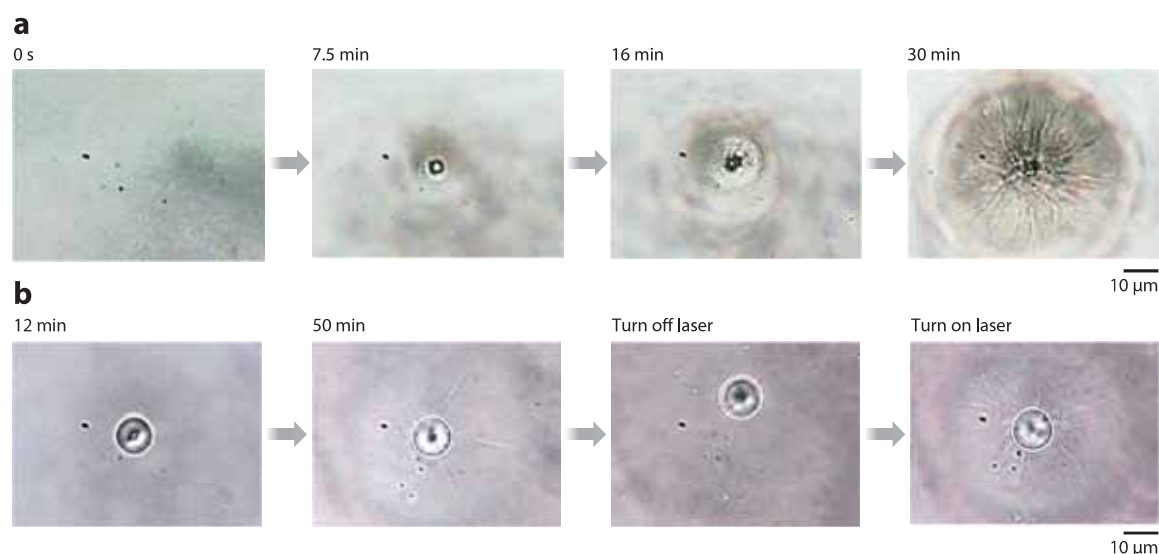
trapping laser expands isotopically in all directions, and consequently a circular swarming assembly is formed. The Au NPs undergo vigorous fluctuation, and back-and-forth movement between left and right swarms is observed. Multiple scattering among multiple NPs must be intrinsic, and the position of NPs can be replaceable, that is, one NP can be replaced with another. To demonstrate this characteristic, we split the trapping laser into two and manipulated the NPs freely with a Galvano mirror. **Figure 6d** shows that the number of swarms and the distance between them can be controlled by changing the distance between the foci of the two trapping lasers.

Au NPs efficiently scatter the trapping laser, which leads to larger NP swarms when the laser wavelength matches the SPR band (117). In the beginning of this section, we described the results of trapping 200-nm Au NPs with a 1,064-nm laser. Under the same conditions, the swarm is not found when the diameter of the NPs is smaller than 200 nm. The SPR band shifts to a shorter wavelength when the Au NP size decreases; as a result, the 1,064-nm laser becomes off-resonance for the smaller NPs. In other words, the swarming assembly for smaller Au NPs should be observed if the laser wavelength is shifted toward the SPR band. Of course, a larger swarm could be achieved if the wavelength is exactly resonant to the SPR band. Optically evolved assembling and swarming are considered to be complex behaviors, and a large number of Au NPs interact with each other through attractive multiple light scattering and electrostatic repulsion, which expands the effective optical trapping potential, as illustrated in **Figure 1d**. Brownian motion, hydrodynamic interaction, and thermal heating must be coupled with the swarming (118); however, the swarming surely starts from the scattered light of Au NPs, and matching the trapping laser with the SPR band is critical.

In general, heating and convection induced by the laser irradiation of Au NPs have been extensively studied (119, 120), and these modes should be involved in the present assembly and swarming phenomena. One important issue to examine is how the dumbbell-shaped swarm depends on the heating and convection caused by irradiation of Au NPs. We designed an experiment to add PNIPAM to an aqueous solution of Au NPs. As mentioned previously, this polymer is soluble in water but undergoes LLPS above its lower critical solution temperature (32°C) (121, 122). This behavior is locally achieved by irradiating a single Au NP under a microscope (123, 124). In the case of Au NPs in PNIPAM solution, trapping, local heating, and local LLPS develop simultaneously, as they are coupled with each other (118). The Au NPs are embedded in the prepared droplet of PNIPAM and no longer show swarming, as illustrated in **Figure 6e**. The observation and analysis of such dynamically evolving processes provide information on the morphology and sizes of swarms and assemblies.

## 7. MECHANISM AND APPLICATION OF OPTICALLY EVOLVED ASSEMBLING AT SOLUTION SURFACES AND INTERFACES

We have described the optical force-induced assembling phenomena of molecules and NPs at solution surfaces and interfaces, showing that the assembly size is much larger than the focus. Our proposed mechanism is supported by direct observation of light scattering and propagation of the trapping laser, and we know that surface tension, convection flow, and thermophoretic effects (125–127) are all involved to various degrees. We plan to integrate all possible dynamics and mechanisms to enable a comprehensive understanding of this process. Here we introduce our recent results on the optical trapping and assembling of 100-nm PS NPs at the solution surface and point out a new possible mechanism. Upon irradiation of a 1- $\mu\text{m}$  focal spot, we found a single large, disklike assembly a few tens of micrometers in diameter around the spot (**Figure 7a**). Apparently, this assembly is similar to that produced by 200-nm PS NPs; however, needlelike structures expanding radially out of the focus are also formed (128). After switching off the trapping laser,



**Figure 7**

(a) Optical transmission micrographs of the optical trapping of 100-nm polystyrene (PS) nanoparticles (NPs) at an aqueous solution surface. (b) Optical transmission micrographs of the optical trapping of 100-nm PS NPs around an optically trapped 10-μm PS microparticle at the surface of a D<sub>2</sub>O solution. Micrographs in figure reproduced with permission from Reference 128; copyright 2020 American Chemical Society.

the assembly dissolves and the needlelike structures disappear while the highly concentrated NP domain slowly dissipates. If the trapping laser is switched on again soon, the domain shifts back toward the focus, the disklike assembly is restored, and even the needles reform.

We have designed a new experiment to hamper the light scattering of the trapping laser from the focus, that is, the optical trapping of 100-nm PS NPs around a single optically trapped 10-μm PS MP at a D<sub>2</sub>O solution surface. Surprisingly, a similar disklike assembly of NPs as well as needlelike structures forms outside the large 10-μm PS MP (**Figure 7b**). A similar behavior is observed when switching on and off the laser sequentially. Most of the trapping light irradiates the big MP while the surrounding area is affected by leaked trapping light. These needlelike structures are similar to a discharge pattern from material after a high voltage is applied to its center. The power of the 1,064-nm trapping laser, which is 1.4 W, is focused onto a small 1-μm<sup>2</sup> area so that the laser fluence is roughly 140 MW/cm<sup>2</sup>. This power density may result in an optical Kerr effect in which the optical properties of materials are changed; such changes are conventionally examined by irradiating with a nanosecond to femtosecond laser pulse (129, 130). In our case, CW high-power irradiation may orient phenyl substituents and modify the segment structures inside the PS MP, accompanied by a change in surface charge; consequently, water molecules, being coupled with rearrangement of the 100-nm PS NPs, are dynamically reoriented.

In fact, the assembly of 1-μm PS MPs and the formation of needlelike structures both start at the MP surface. The simulation study reports that the dielectric particles are rearranged in a linear manner under electrical and magnetic fields (131). At the molecular level, these behaviors should be assisted by charge transfer and electron transfer through the hydrogen-bonding network of water molecules. The collected 100-nm PS NPs must be coupled with this network, which induces the electronic polarization of water molecules. We infer that the radially expanding assembly of 100-nm PS NPs may be ascribed to the formation of a giant dipole consisting of water

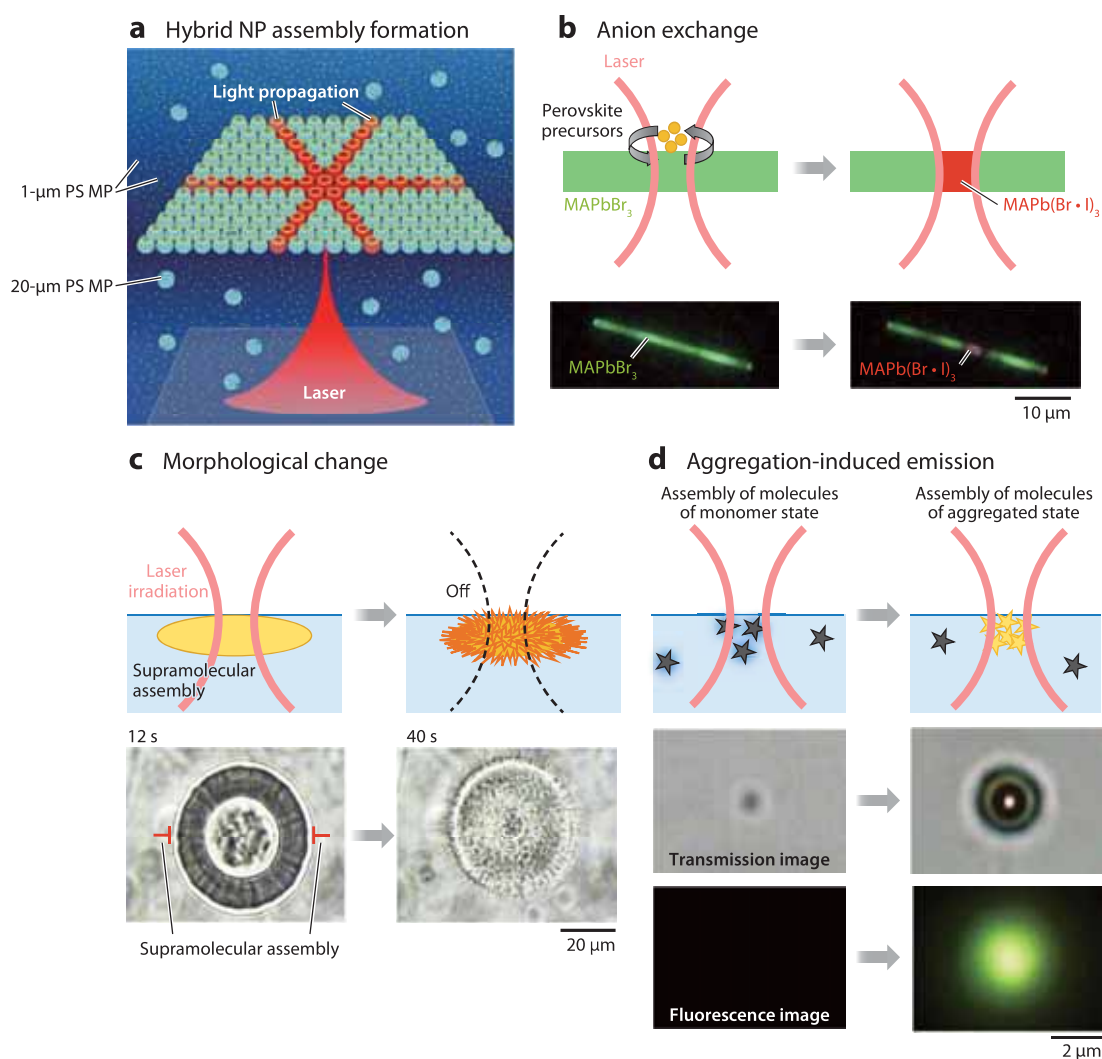


molecules and the small NPs at the solution surface. The giant dipole and needlelike structures might enable the local electrostatic effect to propagate further than a few tens of micrometers. Such an electrostatic effect may be coupled with the light scattering and propagation.

As previously discussed, optical trapping is usually limited to the area of focus, conventionally about  $1\ \mu\text{m}^2$ , but at solution surfaces and interfaces the area affected by irradiation expands into an area with a diameter of a few tens of micrometers, which suggests the great potential of optically evolved assembly in materials applications. The first example of an application is the preparation of a large assembly of MPs, such as our recent successful fabrication of a submillimeter disklike assembly of 20- $\mu\text{m}$  PS MPs with a necklace-like structure of 1- $\mu\text{m}$  PS MPs (132). In the initial solution, 1- $\mu\text{m}$  MPs are homogeneously dispersed in  $\text{D}_2\text{O}$  but 20- $\mu\text{m}$  MPs float on the solution surface due to their having a lesser density than the solvent. Upon trapping a 20- $\mu\text{m}$  MP, 1- $\mu\text{m}$  MPs gather at the surface of the trapped MP and arrange into a circular pattern, forming a necklace-like structure. With further irradiation, more 1- $\mu\text{m}$  MPs are trapped in a concentric manner, producing multiple necklace-like structures at the surface of the 20- $\mu\text{m}$  MP. This hybrid colloidal assembly is shown in **Figure 8a** expanding to 150  $\mu\text{m}$  away from the focal spot, although the focal spot diameter is approximately 1  $\mu\text{m}$  as usual. The extension of the optical potential coupled with a specific light propagation mode such as the whispering gallery mode gives us an opportunity to fabricate such a large millimeter-scale assembly with a unique structure.

The second example is the application to lead halide perovskites, a new class of semiconductor materials for next generation optoelectronic devices (108, 133). Optical trapping occurs at the air/solution interface of unsaturated precursor solutions  $\{\text{MABr}/\text{PbBr}_2/\text{MAI}/\text{PbCl}_2$  [MA (methylammonium) =  $\text{CH}_3\text{NH}_3^+$ ] in a mixture of DMSO (dimethyl sulfoxide)/DMF (dimethylformamide)]. After laser irradiation for a few minutes, a single perovskite crystal ( $\text{MAPbBr}_{3-n}\text{Cl}_n$ ) is formed at the focal spot. This is due to a local increase in the concentration of perovskite precursors. Indeed, the precursor solutions remain unsaturated after irradiation. Laser trapping of perovskite precursors also enables control of the halide exchange reaction. In the process of trapping MAI (methylammonium iodide) at the surface of a  $\text{MAPbBr}_3$  crystal, an exchange reaction of  $\text{MAPbBr}_3$  with iodide ions is induced, and  $\text{MAPbBr}_{3-n}\text{I}_n$ , which has a narrower band gap, is formed only around the focal spot. Photoluminescence at the trapping site gradually changes to red from green, while the nonirradiated parts continue to emit green light, as shown in **Figure 8b**. The optically controlled anion exchange offers a new methodology for the band gap tuning of perovskite crystals, enabling the fabrication of a heterogeneous or gradient band gap structure with unique optical and electronic properties.

The third example involves the use of supramolecular gels derived from low-molecular-mass compounds that are formed through the self-assembly of molecules with multiple noncovalent weak interactions such as hydrogen bonding, dipole–dipole interactions, van der Waals forces, and solute–solvent interactions. The transition from solution to gel occurs at an elevated solute concentration, so optical force acts as a new perturbation for assembling gelator molecules. Supramolecular gelators with an azobenzene-based bisalix[4]arene exhibit unique assembly formation (63), which accompanies the morphological change into the assembly (**Figure 8c**). In optical trapping at the solution surface, a supramolecular assembly is formed at the focal spot. The strong optical force results in a specific molecular association structure, and the resultant stable assembly spontaneously increases in size. Upon switching off the laser, needle-like structures are generated at the assembly surface, transforming it into a structure with a stable sea urchin-like morphology. The molecular association pinned at the focal spot undergoes relaxation, and the constituent molecules reorient due to their intrinsic weak intermolecular interactions, producing a morphological change in the assembly. This shows that laser trapping is a new and promising



**Figure 8**

(a) Schematic illustration of a huge submillimeter-scale arrangement of a necklace-like hybrid colloidal assembly of 1-μm and 20-μm polystyrene (PS) microparticles (MPs) by optical trapping. (b) Illustration and micrographs of a site-specific halide exchange reaction by optical trapping perovskite [MA(methylammonium)PbBr<sub>3</sub>]. Panel b adapted with permission from Reference 133; copyright 2020 American Chemical Society. (c) Illustration and micrographs of the formation of a supramolecular assembly accompanying morphological change after switching off the trapping laser. Panel c adapted with permission from Reference 63; copyright 2017 American Chemical Society. (d) Illustration and micrographs of an aggregation-induced emission during laser trapping. Panel d adapted with permission from Reference 134; copyright 2020 John Wiley & Sons.

approach for preparing a single spherical assembly of supramolecules, analyzing its assembly dynamics, and fabricating microstructures from single assemblies.

The fourth application involves an aggregation-induced emission enhancement (AIEE) of a tetraphenylethylene (TPE) derivative known as AIEE-active dye. Upon laser irradiation, TPE monomers undergo conformational transformation, and photoexcitation energy is dissipated via a nonradiative pathway. As a result, TPE monomers exhibit weak, almost negligible, emission. When

the monomers are densely aggregated and their conformational transformation is restricted, their fluorescence is greatly enhanced. This emission behavior can be used to investigate the dynamics of molecular assembly under optical trapping conditions. Upon the trapping of TPE at the solution surface, a small molecular assembly is formed at the focal spot after a few minutes (134). The small assembly has a weak, almost negligible, fluorescence. This shows that the TPE molecules constituting the small assembly continue the conformational transformation that accompanies the dissipation of the photoexcited energy. With further irradiation, the assembly continuously increases in size and suddenly strong fluorescence is generated, as shown in **Figure 8d**. This fluorescence enhancement indicates that the assembly has changed into a densely packed aggregate in which the intrinsic repulsive force of the protonated TPE is overcome by the strong optical force. In laser trapping at an interface, local TPE concentration is efficiently increased, and intrinsic attractive and repulsive interactions are modified by the strong optical force, resulting in the formation of unique molecular assemblies.

## 8. CONCLUDING REMARKS

The optical trapping dynamics and mechanisms of molecules, polymers, and NPs at solution surfaces are completely different from those of conventional ones inside the solution, and their assembly sizes reach a few tens of micrometers larger than the focus. Optically evolving molecular crystals, PS NP assemblies, and Au NP swarms at surfaces are described and discussed, in which the gathering, trapping, arrangement, ejection, repulsion, and swarming processes are all driven by optical force. This review indicates that a new chemistry field is being paved by optical trapping at solution surfaces and that new applications are possible.

The development of optically evolved assembling is being advanced by designing new experiments. One is plasmonic trapping, which is currently receiving a large amount of attention because of the recent enhancement of optical force itself (135–141). In such experiments, metal nanostructures and semiconductor needles are fabricated on their substrates. The surface and interface leading to scattering and propagation of the trapping laser may also be involved in plasmonic trapping. For example, morphology control and enantioselectivity in molecular crystallization are being demonstrated by plasmonic trapping at the solution surface.

Another way to enhance optical force is to use the optical resonance effect in which the trapping laser wavelength matches the electronic transitions of molecules and NPs in the trapping target (142–144). In this method, optical stiffness and trapping time are used as measures of enhancement. Usually this technique is carried out in solution, but its extension to the solution/glass interface should enable us to study the optical resonance effect of not only the gradient force but also the scattering and absorption forces. This is due to the NPs being immobilized at the interface by being pushed by scattering and absorption forces.

The introduction of various microscopic techniques should allow the optically evolving assembly and swarming of molecules and NPs to be studied more widely and in greater detail. Single-molecule fluorescence microscopy and super-resolution analysis should enable us to extend dynamics and mechanism studies to nanometer-scale resolution (9, 10). Multiplane microscopy will provide 3D information on optical trapping dynamics (145), while dynamic differential microscopy will be useful to elucidate 2D assembling dynamics, as in **Figure 7** (146).

Further, pulsed lasers are useful to explore new optically evolved assembling and swarming phenomena. We have extended femtosecond studies on the optical trapping dynamics of PS NPs in solution, found trapping and ejection behavior, and proposed a mechanism based on the transient assembly formation of PS NPs in the optical potential (147–150). The assembly becomes large, the scattering force overcomes the gradient force, and then the assembly is ejected from the

optical potential. Such femtosecond optical trapping can be extended to solution surfaces, which will enable us to explore new optical force-induced molecular phenomena. Thus, the study of the optically evolved assembling of molecules and NPs is fundamentally important and provides promising materials applications that will be more fully developed by new types of microscopy and related tools and by theoretical analysis. We hope that our viewpoint, illustrated in **Figure 1**, will be more widely developed and more deeply elucidated and that a new research field of optical force-induced chemistry will open up.

## DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holding that might be perceived as affecting the objectivity of this review.

## ACKNOWLEDGMENTS

This review is dedicated to the late Arthur Ashkin for his pioneering work on optical trapping and his kind understanding of our extensive use of optical trapping techniques in the field of microchemistry. The authors would like to express their sincere thanks to Teruki Sugiyama of National Chiao Tung University in Taiwan and Tetsuhiro Kudo of Toyota Technological Institute in Japan for their long-term collaborations and invaluable discussions. Thanks are also due to Abdullah Kamit for his kind help with preparation of the manuscript. This work is supported by the Ministry of Science and Technology, Taiwan (grant MOST 109-2634-F-009-028) and the Center for Emergent Functional Matter Science of the National Chiao Tung University from The Featured Areas Research Center Program within the framework of the Higher Education Sprout Project by the Ministry of Education in Taiwan. Thanks are also due for funding from the Ministry of Science and Technology (MOST) of Taiwan (grant MOST 109-2113-M-009-022 to H.M.), to the Japan Society for the Promotion of Science (grant JSPS-KAKENHI JP20K05242 to K.Y.), and to the Japan Science and Technology Agency (grant JST-CREST JPMJCR1903 to K.Y.).

## LITERATURE CITED

1. Maiman TH. 1960. Stimulated optical radiation in ruby. *Nature* 187:493–94
2. Moore CB. 1971. Lasers in chemistry. *Annu. Rev. Phys. Chem.* 22:387–428
3. Porter G, Topp MR. 1970. Nanosecond flash photolysis. *Proc. R. Soc. A Math. Phys. Eng. Sci.* 315:163–84
4. Novak JR, Windsor MW. 1967. Laser photolysis and spectroscopy in the nanosecond time range: excited singlet state absorption in coronene. *J. Chem. Phys.* 47:3075–76
5. Eisert WG, Degenkolb EO, Noe LJ, Rentzepis PM. 1979. Kinetics of carboxymyoglobin and oxymyoglobin studied by picosecond spectroscopy. *Biophys. J.* 25:455–64
6. Potter ED, Herek JL, Pedersen S, Liu Q, Zewail AH. 1992. Femtosecond laser control of a chemical reaction. *Nature* 355:66–68
7. Wang XF, Herman B, eds. 1996. *Fluorescence Imaging Spectroscopy and Microscopy*. Vol. 137. New York: John Wiley & Sons
8. Rigler R, Orrit M, Basché T, eds. 2001. *Single Molecule Spectroscopy: Nobel Conference Lectures*. Springer Ser. Chem. Phys. Vol. 67. Berlin/New York: Springer
9. Sauer M, Hofkens J, Enderlein J, eds. 2011. *Handbook of Fluorescence Spectroscopy and Imaging: From Ensemble to Single Molecules*. Hoboken, NJ: John Wiley & Sons
10. Masters BR. 2020. *Superresolution Optical Microscopy: The Quest for Enhanced Resolution and Contrast*. Springer Ser. Opt. Sci. Vol. 227. Cham, Switz.: Springer
11. Moerner WE. 2002. A dozen years of single-molecule spectroscopy in physics, chemistry, and biophysics. *J. Phys. Chem. B* 106:910–27



12. Ashkin A, Dziedzic JM, Bjorkholm JE, Chu S. 1986. Observation of a single-beam gradient force optical trap for dielectric particles. *Opt. Lett.* 11:288–90
13. Lebedev PN. 1901. Experimental examination of light pressure. *Ann. Phys.* 6:433
14. Grier DG. 2003. A revolution in optical manipulation. *Nature* 424:810–16
15. Neuman KC, Block SM. 2004. Optical trapping. *Rev. Sci. Instrum.* 75:2787–809
16. Moffitt JR, Chemla YR, Smith SB, Bustamante C. 2008. Recent advances in optical tweezers. *Annu. Rev. Biochem.* 77:205–28
17. Dholakia K, Reece P, Gu M. 2008. Optical micromanipulation. *Chem. Soc. Rev.* 37:42–45
18. Padgett M, Bowman R. 2011. Tweezers with a twist. *Nat. Photon.* 5:343–48
19. Juan ML, Righini M, Quidant R. 2011. Plasmon nano-optical tweezers. *Nat. Photon.* 5:349–56
20. Sugiyama T, Yuyama K, Masuhara H. 2012. Laser trapping chemistry: from polymer assembly to amino acid crystallization. *Acc. Chem. Res.* 45:1946–54
21. Maragò OM, Jones PH, Gucciardi PG, Volpe G, Ferrari AC. 2013. Optical trapping and manipulation of nanostructures. *Nat. Nanotechnol.* 8:807–19
22. Woerdemann M, Alpmann C, Esseling M, Denz C. 2013. Advanced optical trapping by complex beam shaping. *Laser Photon. Rev.* 7:839–54
23. Lehmuskero A, Johansson P, Rubinsztein-Dunlop H, Tong L, Käll M. 2015. Laser trapping of colloidal metal nanoparticles. *ACS Nano* 9:3453–69
24. Daly M, Sergides M, Chormaic SN. 2015. Optical trapping and manipulation of micrometer and sub-micrometer particles. *Laser Photon. Rev.* 3:309–29
25. Spesyvtseva SES, Dholakia K. 2016. Trapping in a material world. *ACS Photon.* 3:719–36
26. Rodríguez-Sevilla P, Labrador-Páez L, Jaque D, Haro-González P. 2017. Optical trapping for biosensing: materials and applications. *J. Mater. Chem. B* 5:9085–101
27. Gao D, Ding W, Nieto-Vesperinas M, Ding X, Rahman M, et al. 2017. Optical manipulation from the microscale to the nanoscale: fundamentals, advances and prospects. *Light Sci. Appl.* 6:e17039
28. Bradshaw DS, Andrews DL. 2017. Manipulating particles with light: radiation and gradient forces. *Eur. J. Phys.* 38:034008
29. Bradac C. 2018. Nanoscale optical trapping: a review. *Adv. Opt. Mater.* 6:1800005
30. Zemánek P, Volpe G, Jonáš A, Brzobohatý O. 2019. Perspective on light-induced transport of particles: from optical forces to phoretic motion. *Adv. Opt. Photon.* 11:577–678
31. Bustamante C, Alexander L, Maciuba K, Kaiser CM. 2020. Single-molecule studies of protein folding with optical tweezers. *Annu. Rev. Biochem.* 89:443–70
32. Ashkin A. 1970. Acceleration and trapping of particles by radiation pressure. *Phys. Rev. Lett.* 24:156–59
33. Ashkin A. 1980. Application of laser radiation pressure. *Science* 210:1081–88
34. Ashkin A, Dziedzic JM. 1987. Optical trapping and manipulation of viruses and bacteria. *Science* 235:1517–20
35. Ashkin A, Dziedzic JM, Yamane T. 1987. Optical trapping and manipulation of single cells using infrared laser beams. *Nature* 330:769–71
36. Smith SB, Cui Y, Bustamante C. 1996. Overstretching B-DNA: the elastic response of individual double-stranded and single-stranded DNA molecules. *Science* 271:795–99
37. Wang MD, Yin H, Landick R, Gelles J, Block SM. 1997. Stretching DNA with optical tweezers. *Biophys. J.* 72:1335–46
38. Sasaki K, Koshioka M, Misawa H, Kitamura N, Masuhara H. 1991. Laser-scanning micromanipulation and spatial patterning of fine particles. *Jpn. J. Appl. Phys.* 30:L907
39. Sasaki K, Koshioka M, Misawa H, Kitamura N, Masuhara H. 1992. Optical trapping of a metal particle and a water droplet by a scanning laser beam. *Appl. Phys. Lett.* 60:807–9
40. Kim H-B, Hayashi M, Nakatani K, Kitamura N, Sasaki K, et al. 1996. In situ measurements of ion-exchange processes in single polymer particles: laser trapping microspectroscopy and confocal fluorescence microspectroscopy. *Anal. Chem.* 68:409–14
41. Tamai N, Asahi T, Masuhara H. 1993. Femtosecond transient absorption microspectrophotometer combined with optical trapping technique. *Rev. Sci. Instrum.* 64:2496–503

42. Nakatani K, Uchida T, Funakura S, Sekiguchi A, Misawa H, et al. 1993. Control of a dye formation reaction in a single micrometer-sized oil-droplet by laser trapping and microelectrochemical methods. *Chem. Lett.* 22:717–20
43. Misawa H, Koshioka M, Sasaki K, Kitamura N, Masuhara H. 1991. Three-dimensional optical trapping and laser ablation of a single polymer latex particle in water. *J. Appl. Phys.* 70:3829–36
44. Ito S, Tanaka Y, Yoshikawa H, Ishibashi Y, Miyasaka H, Masuhara H. 2011. Confinement of photopolymerization and solidification with radiation pressure. *J. Am. Chem. Soc.* 133:14472–75
45. Masuhara H, De Schryver FC, Kitamura N, Tamai N, eds. 1994. *Microchemistry: Spectroscopy and Chemistry in Small Domains*. North-Holland Delta Ser. Amsterdam: Elsevier Sci.
46. Masuhara H, De Schryver FC, eds. 1999. *Organic Mesoscopic Chemistry*. Malden, MA: Blackwell Sci.
47. Ashkin A. 1997. Optical trapping and manipulation of neutral particles using lasers. *PNAS* 94:4853–60
48. Ashkin A. 2000. History of optical trapping and manipulation of small-neutral particle, atoms, and molecules. *IEEE J. Sel. Top. Quantum Electron.* 6:841–56
49. Lett PD, Julienne PS, Phillips WD. 1995. Photoassociative spectroscopy of laser-cooled atoms. *Annu. Rev. Phys. Chem.* 46:423–52
50. Tsuboi Y, Shoji T, Kitamura N. 2007. Crystallization of lysozyme based on molecular assembling by photon pressure. *Jpn. J. Appl. Phys.* 46:L1234
51. Tsuboi Y, Shoji T, Nishino M, Masuda S, Ishimori K, Kitamura N. 2009. Optical manipulation of proteins in aqueous solution. *Appl. Surf. Sci.* 255:9906–8
52. Tsuboi Y, Shoji T, Kitamura N. 2010. Optical trapping of amino acids in aqueous solutions. *J. Phys. Chem. C* 114:5589–93
53. Shoji T, Kitamura N, Tsuboi Y. 2013. Resonant excitation effect on optical trapping of myoglobin: the important role of a heme cofactor. *J. Phys. Chem. C* 117:10691–97
54. Tanaka Y, Yoshikawa H, Masuhara H. 2006. Two-photon fluorescence spectroscopy of individually trapped pseudocyanine J-aggregates in aqueous solution. *J. Phys. Chem. B* 110:17906–11
55. Mototsuji A, Shoji T, Wakisaka Y, Murakoshi K, Yao H, Tsuboi Y. 2017. Plasmonic optical trapping of nanometer-sized J-/H- dye aggregates as explored by fluorescence microspectroscopy. *Opt. Express* 25:13617–25
56. Hofken J, Hotta J, Sasaki K, Masuhara H, Iwai K. 1997. Molecular assembling by the radiation pressure of a focused laser beam: poly(*N*-isopropylacrylamide) in aqueous solution. *Langmuir* 13:414–19
57. Hofkens J, Hotta J, Sasaki K, Masuhara H, Taniguchi T, Miyashita T. 1997. Molecular association by the radiation pressure of a focused laser beam: fluorescence characterization of pyrene-labeled PNIPAM. *J. Am. Chem. Soc.* 119:2741–42
58. Borowicz P, Hotta J, Sasaki K, Masuhara H. 1998. Chemical and optical mechanism of microparticle formation of poly(*N*-vinylcarbazole) in *N,N*-dimethylformamide by photon pressure of a focused near-infrared laser beam. *J. Phys. Chem. B* 102:1896–901
59. Smith TA, Hotta J, Sasaki K, Masuhara H, Itoh Y. 1999. Photon pressure-induced association of nanometer-sized polymer chains in solution. *J. Phys. Chem. B* 103:1660–63
60. Masuo S, Yoshikawa H, Nothofer HG, Grimsdale AC, Scherf U, et al. 2005. Assembling and orientation of polyfluorenes in solution controlled by a focused near-infrared laser beam. *J. Phys. Chem. B* 109:6917–21
61. Singer W, Nieminen TA, Heckenberg NR, Rubinsztein-Dunlop H. 2007. Collecting single molecules with conventional optical tweezers. *Phys. Rev. E* 75:011916
62. Gould OEC, Qiu H, Lunn DJ, Rowden J, Harniman RL, et al. 2015. Transformation and patterning of supermicelles using dynamic holographic assembly. *Nat. Commun.* 6:10009
63. Yuyama K, Marcelis L, Su PM, Chung WS, Masuhara H. 2017. Photocontrolled supramolecular assembling of azobenzene-based biscalix[4]arenes upon starting and stopping laser trapping. *Langmuir* 33:755–63
64. Gould OEC, Box SJ, Boott CE, Ward AD, Winnik MA, et al. 2019. Manipulation and deposition of complex, functional block copolymer nanostructures using optical tweezers. *ACS Nano* 13:3858–66
65. Katsura S, Hirano K, Matsuzawa Y, Mizuno A, Yoshikawa K. 1998. Direct laser trapping of single DNA molecules in the globular state. *Nucleic Acids Res.* 26:4943–45

66. Tan S, Lopez HA, Cai CW, Zhang Y. 2004. Optical trapping of single-walled carbon nanotubes. *Nano Lett.* 4:1415–19
67. Rodgers T, Shoji S, Sekkat Z, Kawata S. 2008. Selective aggregation of single-walled carbon nanotubes using the large optical field gradient of a focused laser beam. *Phys. Rev. Lett.* 101:127402
68. Hotta J, Sasaki K, Masuhara H. 1996. A single droplet formation from swelled micelles by radiation pressure of a focused infrared laser beam. *J. Am. Chem. Soc.* 118:11968–69
69. Kitamura N, Sekiguchi N, Kim HB. 1998. Optical transformation and fission of single giant vesicles in water by radiation pressure. *J. Am. Chem. Soc.* 120:1942–43
70. Murshid N, Yuyama K, Wu SL, Wu KY, Masuhara H, et al. 2016. Highly-integrated, laser manipulable aqueous metal carbonyl vesicles (MCsomes) with aggregation-induced emission (AIE) and aggregation-enhanced IR absorption (AEIRA). *J. Mater. Chem.* 4:5231–40
71. Pan L, Ishikawa A, Tamai N. 2007. Detection of optical trapping of CdTe quantum dots by two-photon-induced luminescence. *Phys. Rev. B* 75:161305(R)
72. Jauffred L, Oddershede LB. 2010. Two-photon quantum dot excitation during optical trapping. *Nano Lett.* 10:1927–30
73. Chiang WY, Okuhata T, Usman A, Tamai N, Masuhara H. 2014. Efficient optical trapping of CdTe quantum dots by femtosecond laser pulses. *J. Phys. Chem. B* 118:14010–16
74. Pin C, Otsuka R, Sasaki K. 2020. Optical transport and sorting of fluorescent nanodiamonds inside a tapered glass capillary: optical sorting of nanomaterials at the femtonewton scale. *ACS Appl. Nano Mater.* 3:4127–34
75. Pauzauskie PJ, Radenovic A, Trepagnier E, Shroff H, Yang P, Liphardt J. 2006. Optical trapping and integration of semiconductor nanowire assemblies in water. *Nat. Mater.* 5:97–101
76. Yan Z, Jureller JE, Sweet J, Guffey MJ, Pelton M, Scherer NF. 2012. Three-dimensional optical trapping and manipulation of single silver nanowires. *Nano Lett.* 12:5155–61
77. Yan Z, Pelton M, Vigdeman L, Zubarev ER, Scherer NF. 2013. Why single-beam optical tweezers trap gold nanowires in three dimensions. *ACS Nano* 7:8794–800
78. Hosokawa C, Yoshikawa H, Masuhara H. 2005. Cluster formation of nanoparticles in an optical trap studied by fluorescence correlation spectroscopy. *Phys. Rev. E* 72:021408
79. Hosokawa C, Yoshikawa H, Masuhara H. 2004. Optical assembling dynamics of individual polymer nanospheres investigated by single-particle fluorescence detection. *Phys. Rev. E* 70:061410
80. Ito S, Yoshikawa H, Masuhara H. 2002. Laser manipulation and fixation of single gold nanoparticles in solution at room temperature. *Appl. Phys. Lett.* 80:482–84
81. Tanaka Y, Yoshikawa H, Itoh T, Ishikawa M. 2009. Laser-induced self-assembly of silver nanoparticles via plasmonic interactions. *Opt. Express* 17:18760–67
82. Jiang Y, Narushima T, Okamoto H. 2010. Nonlinear optical effects in trapping nanoparticles with femtosecond pulses. *Nat. Phys.* 6:1005–9
83. Urban AS, Lutich AA, Stefani FD, Feldmann J. 2010. Laser printing single gold nanoparticles. *Nano Lett.* 10:4794–98
84. Ohlinger A, Nedev S, Lutich AA, Feldmann J. 2011. Optothermal escape of plasmonically coupled silver nanoparticles from a three-dimensional optical trap. *Nano Lett.* 11:1770–74
85. Kyrsting A, Bendix PM, Oddershede LB. 2013. Mapping 3D focal intensity exposes the stable trapping positions of single nanoparticles. *Nano Lett.* 13:31–35
86. Harada Y, Asakura T. 1996. Radiation forces on a dielectric sphere in the Rayleigh scattering regime. *Opt. Commun.* 124:529–41
87. Ito S, Sugiyama T, Toitani N, Katayama G, Miyasaka H. 2007. Application of fluorescence correlation spectroscopy to the measurement of local temperature in solutions under optical trapping condition. *J. Phys. Chem. B* 111:2365–71
88. Chiu DT, Zare R. 1996. Biased diffusion, optical trapping, and manipulation of single molecules in solution. *J. Am. Chem. Soc.* 118:6512–13
89. Osborne MA, Balasubramanian S, Furey WS, Klennerman D. 1998. Optically biased diffusion of single molecules studied by confocal fluorescence microscopy. *J. Phys. Chem. B* 102:3160–67
90. Chirico G, Fumagalli C, Baldini G. 2002. Trapped Brownian motion in single- and two-photon excitation fluorescence correlation experiments. *J. Phys. Chem. B* 106:2508–19

91. Nabetani Y, Yoshikawa H, Grimsdale AC, Müllen K, Masuhara H. 2007. Effects of optical trapping and liquid surface deformation on the laser microdeposition of a polymer assembly in solution. *Langmuir* 23:6725–29
92. Louchev OA, Juodkazis S, Murazawa N, Wada S, Misawa H. 2008. Coupled laser molecular trapping, cluster assembly, and deposition fed by laser-induced Marangoni convection. *Opt. Express* 16:5673–80
93. Bartkiewicz S, Miniewicz A. 2015. Whirl-enhanced continuous wave laser trapping of particles. *Phys. Chem. Chem. Phys.* 17:1077–83
94. Yuyama K, Sugiyama T, Masuhara H. 2010. Millimeter-scale dense liquid droplet formation and crystallization in glycine solution induced by photon pressure. *J. Phys. Chem. Lett.* 1:1321–25
95. Yuyama K, Rungsimanon T, Sugiyama T, Masuhara H. 2012. Formation, dissolution, and transfer dynamics of a millimeter-scale thin liquid droplet in glycine solution by laser trapping. *J. Phys. Chem. C* 116:6809–16
96. Sugiyama T, Adachi T, Masuhara H. 2007. Crystallization of glycine by photon pressure of a focused CW laser beam. *Chem. Lett.* 36:1480–81
97. Rungsimanon T, Yuyama K, Sugiyama T, Masuhara H, Tohnai N, Miyata M. 2010. Control of crystal polymorph of glycine by photon pressure of a focused continuous wave near-infrared laser beam. *J. Phys. Chem. Lett.* 1:599–603
98. Rungsimanon T, Yuyama K, Sugiyama T, Masuhara H. 2010. Crystallization in unsaturated glycine/D<sub>2</sub>O solution achieved by irradiating a focused continuous wave near infrared laser. *Cryst. Growth Des.* 10:4686–88
99. Yuyama K, Rungsimanon T, Sugiyama T, Masuhara H. 2012. Selective fabrication of  $\alpha$ - and  $\gamma$ -polymorphs of glycine by intense polarized continuous wave laser beams. *Cryst. Growth Des.* 12:2427–34
100. Yuyama K, Ishiguro K, Sugiyama T, Masuhara H. 2012. Laser trapping dynamics of L-alanine depending on the laser polarization. In *Proceedings SPIE 8458: Optical Trapping and Optical Micromanipulation IX*, ed. K Dholakia, GC Spalding, pp. 84582D-1–7. Bellingham, WA: SPIE
101. Yuyama K, Sugiyama T, Masuhara H. 2013. Laser trapping and crystallization dynamics of L-phenylalanine at solution surface. *J. Phys. Chem. Lett.* 4:2436–40
102. Yuyama K, Wu CS, Sugiyama T, Masuhara H. 2014. Laser trapping-induced crystallization of L-phenylalanine through its high-concentration domain formation. *Photochem. Photobiol. Sci.* 13:254–60
103. Yuyama K, George J, Thomas KG, Sugiyama T, Masuhara H. 2016. Two-dimensional growth rate control of L-phenylalanine crystal by laser trapping in unsaturated aqueous solution. *Cryst. Growth Des.* 16:953–60
104. Yuyama K, Chiu DS, Liu YE, Sugiyama T, Masuhara H. 2018. Crystal growth and dissolution dynamics of L-phenylalanine controlled by solution surface laser trapping. *Cryst. Growth Des.* 18:7079–87
105. Chen JJ-K, Yuyama K, Sugiyama T, Masuhara H. 2019. In situ reflection imaging and microspectroscopic study on three-dimensional crystal growth of L-phenylalanine under laser trapping. *Appl. Phys. Express* 12:112008
106. Cheng AC, Masuhara H, Sugiyama T. 2020. Evolving crystal morphology of potassium chloride controlled by optical trapping. *J. Phys. Chem. C* 124:6913–21
107. Niinomi H, Sugiyama T, Miyamoto K, Omatsu T. 2018. “Freezing” of NaClO<sub>3</sub> metastable crystalline state by optical trapping in unsaturated microdroplet. *Cryst. Growth Des.* 18:734–41
108. Yuyama K, Islam MJ, Takahashi K, Nakamura T, Biju V. 2018. Crystallization of methylammonium lead halide perovskites by optical trapping. *Angew. Chem. Int. Ed.* 57:13424–28
109. Islam MJ, Yuyama K, Takahashi K, Nakamura T, Konishi K, Biju V. 2019. Mixed-halide perovskite synthesis by chemical reaction and crystal nucleation under an optical potential. *NPG Asia Mater.* 11:31
110. Wang SF, Kudo T, Yuyama K, Sugiyama T, Masuhara H. 2016. Optically evolved assembly formation in laser trapping of polystyrene nanoparticles at solution surface. *Langmuir* 32:12488–96
111. Lu JS, Kudo T, Louis B, Bresoli-Obach R, Scheblykin IG, et al. 2020. Optical force-induced dynamics of assembling, rearrangement, and three-dimensional pistol-like ejection of microparticles at the solution surface. *J. Phys. Chem. C* 124:27107–17
112. Nam HJ, Jung D-Y, Yi G-R, Choi H. 2006. Close-packed hemispherical microlens array from two-dimensional ordered polymeric microspheres. *Langmuir* 22:7358–63



113. Shoji T, Shibata M, Kitamura N, Nagasawa F, Takase M. et al. 2013. Reversible photoinduced formation and manipulation of a two-dimensional closely packed assembly of polystyrene nanospheres on a metallic nanostructure. *J. Phys. Chem. C* 117:2500–6
114. Wang SF, Yuyama K, Sugiyama T, Masuhara H. 2016. Reflection microspectroscopic study of laser trapping assembling of polystyrene nanoparticles at air/solution interface. *J. Phys. Chem. C* 120:15578–85
115. Kudo T, Wang S-F, Yuyama K, Masuhara H. 2016. Optical trapping-formed colloidal assembly with horns extended to the outside of a focus through light propagation. *Nano Lett.* 16:3058–62
116. Kudo T, Yang S-J, Masuhara H. 2018. A single large assembly with dynamically fluctuating swarms of gold nanoparticles formed by trapping laser. *Nano Lett.* 18:5846–53
117. Huang C-H, Kudo T, Bresolí-Obach R, Hofkens J, Sugiyama T, Masuhara H. 2020. Surface plasmon resonance effect on laser trapping and swarming of gold nanoparticles at interface. *Opt. Express* 28:27727–35
118. Aibara I, Huang C-H, Kudo T, Bresolí-Obach R, Hofkens J, et al. 2020. Dynamic coupling of optically evolved assembling and swarming of gold nanoparticles with photothermal local phase separation of polymer solution. *J. Phys. Chem. C* 124:16604–15
119. Kuppe C, Rusimova KR, Ohnouteck L, Slavov D, Valev VK. 2020. “Hot” in plasmonics: temperature-related concepts and applications of metal nanostructures. *Adv. Opt. Mater.* 8:1901166
120. Setoura K, Ito S, Miyasaka H. 2017. Stationary bubble formation and Marangoni convection induced by CW laser heating of a single gold nanoparticle. *Nanoscale* 9:719–30
121. Heskins M, Guillet JE. 1968. Solution properties of poly(N-isopropylacrylamide). *J. Macromol. Sci. A* 2:1441–55
122. Hashimoto C, Ushiki H. 2006. Graphical analysis for gel morphology. III. Gel size and temperature effects on the volume phase transition of gels. *J. Chem. Phys.* 124:044903
123. Aibara I, Mukai S, Hashimoto S. 2016. Plasmonic-heating-induced nanoscale phase separation of free poly(N-isopropylacrylamide) molecules. *J. Phys. Chem. C* 120:17745–52
124. Aibara I, Chikazawa JI, Uwada T, Hashimoto S. 2017. Localized phase separation of thermoresponsive polymers induced by plasmonic heating. *J. Phys. Chem. C* 121:22496–507
125. Braun D, Libchaber A. 2002. Trapping of DNA by thermophoretic depletion and convection. *Phys. Rev. Lett.* 89:188103
126. Young JB. 2011. Thermophoresis of a spherical particle: reassessment, clarification, and new analysis. *Aerosol Sci. Technol.* 45:927–48
127. Leng J, Guo Z, Zhang H, Chang T, Guo X, Gao H. 2016. Negative thermophoresis in concentric carbon nanotube nanodevices. *Nano Lett.* 16:6396–402
128. Wu CL, Wang SF, Kudo T, Yuyama K, Sugiyama T, Masuhara H. 2020. Anomalous large assembly formation of polystyrene nanoparticles by optical trapping at solution surface. *Langmuir* 36:14234–42
129. Taschin A, Bartolini P, Eramo R, Righini R, Torre R. 2014. Optical Kerr effect of liquid and supercooled water: the experimental and data analysis perspective. *J. Chem. Phys.* 141:084507
130. Garetz BA, Aber JE, Goddard NL, Young RG, Myerson AS. 1996. Nonphotochemical, polarization-dependent, laser-induced nucleation in supersaturated aqueous urea solution. *Phys. Rev. Lett.* 77:3475–76
131. Maloney RC, Hall CK. 2020. Clustering and phase separation in mixtures of dipolar and active particles in an external field. *Langmuir* 36:6378–87
132. Lu J-S, Wang H-Y, Kudo T, Masuhara M. 2020. A large submillimeter assembly of microparticles with necklace-like patterns formed by laser trapping at solution surface. *J. Phys. Chem. Lett.* 11:6057–62
133. Islam MJ, Shahjahan M, Yuyama K, Biju V. 2020. Remote tuning of bandgap and emission of lead perovskites by spatially controlled halide exchange reactions. *ACS Mater. Lett.* 2:403–8
134. Wang S-F, Lin J-R, Ishiwari F, Fukushima T, Masuhara H, Sugiyama T. 2020. Spatiotemporal dynamics of aggregation-induced emission enhancement controlled by optical manipulation. *Angew. Chem. Int. Ed.* 59:7063–68
135. Kawata S, Masuhara H, eds. 2006. *Nanoplasmonics: from Fundamentals to Applications*. Amsterdam: Elsevier
136. Tsai W-Y, Huang J-S, Huang C-B. 2014. Selective trapping or rotation of isotropic dielectric microparticles by optical near field in a plasmonic Archimedes spiral. *Nano Lett.* 14:547–52

137. Shoji T, Saitoh J, Kitamura N, Nagasawa F, Murakoshi K, et al. 2013. Permanent fixing or reversible trapping and release of DNA micropatterns on a gold nanostructure using continuous-wave or femtosecond-pulsed near-infrared laser light. *J. Am. Chem. Soc.* 135:6643–48
138. Kotsifaki DG, Chormaic SN. 2019. Plasmonic optical tweezers based on nanostructures: fundamentals, advances and prospects. *Nanophoton* 8:1227–45
139. Shoji T, Itoh K, Saitoh J, Kitamura N, Yoshii T, et al. 2020. Plasmonic manipulation of DNA using a combination of optical and thermophoretic forces: separation of different-sized DNA from mixture solution. *Sci. Rep.* 10:3349
140. Shoji T, Mototsuji A, Balčytis A, Linklater D, Juodkakis S, Tsuboi Y. 2017. Optical tweezing and binding at high irradiation powers on black-Si. *Sci. Rep.* 7:12298
141. Hanasaki I, Shoji T, Tsuboi Y. 2019. Regular assembly of polymer nanoparticles by optical trapping enhanced with a random array of Si needles for reconfigurable photonic crystals in liquid. *ACS Appl. Nano Mater.* 2:7637–43
142. Hosokawa C, Yoshikawa H, Masuhara H. 2006. Enhancement of biased diffusion of dye-doped nanoparticles by simultaneous irradiation with resonance and nonresonance laser beams. *Jpn. J. Appl. Phys.* 45:L453
143. Kudo T, Ishihara H. 2012. Proposed nonlinear resonance laser technique for manipulating nanoparticles. *Phys. Rev. Lett.* 109:087402
144. Kudo T, Ishihara H, Masuhara H. 2017. Resonance optical trapping of individual dye-doped polystyrene particles with blue- and red-detuned lasers. *Opt. Express* 25:4655–64
145. Louis B, Camacho R, Bresolí-Obach R, Abakumov S, Vandrale J, et al. 2020. Fast-tracking of single emitters in large volumes with nanometer precision. *Opt. Express* 28:28656–71
146. Hanasaki I, Okano K, Yoshikawa HY, Sugiyama T. 2019. Spatiotemporal dynamics of laser-induced molecular crystal precursors visualized by particle image diffusometry. *J. Phys. Chem. Lett.* 10:7452–57
147. Usman A, Chiang W-Y, Masuhara H. 2012. Optical trapping and polarization-controlled scattering of dielectric spherical nanoparticles by femtosecond laser pulses. *J. Photochem. Photobiol. A Chem.* 234:83–90
148. Chiang W-Y, Usman A, Masuhara H. 2013. Femtosecond pulse-width dependent trapping and directional ejection dynamics of dielectric nanoparticles. *J. Phys. Chem. C* 117:19182–88
149. Muramatsu M, Shen T-F, Chiang W-Y, Usman A, Masuhara H. 2016. Picosecond motional relaxation of nanoparticles in femtosecond laser trapping. *J. Phys. Chem. C* 120:5251–56
150. Chiang W-Y, Chen JJ-K, Usman A, Kudo T, Xia K, et al. 2019. Formation mechanism and fluorescence characterization of a transient assembly of nanoparticles generated by femtosecond laser trapping. *J. Phys. Chem. C* 123:27823–33

Nanoparticle Assembling Dynamics  
Induced by Pulsed Optical ForceJim Jui-Kai Chen,<sup>[a]</sup> Wei-Yi Chiang,<sup>\*[a, b]</sup> Tetsuhiro Kudo,<sup>[a]</sup> Anwar Usman,<sup>\*[c]</sup> and  
Hiroshi Masuhara<sup>\*[a, d]</sup>

**Abstract:** Femtosecond (fs) laser trapping dynamics is summarized for silica, hydrophobically modified silica, and polystyrene nanoparticles (NPs) in aqueous solution, highlighting their distinct optical trapping dynamics under CW laser. Mutually repulsive silica nanoparticles are tightly confined under fs laser compared to CW laser trapping and, upon increasing laser power, they are ejected from the focus as an assembly. Hydrophobically modified silica and polystyrene (PS) NPs are sequentially ejected just like a stream or ablated, giving bubbles. The ejection and bubbling take place with the direction perpendicular to laser polarization and its direction is randomly switched from one to the other. These characteristic features are interpreted from the viewpoint of single assembly formation of NPs at an asymmetric position in the optical potential. Temporal change in optical forces map is prepared for a single PS NP by calculating scattering, gradient, and temporal forces. The relative contribution of the forces changes with the volume increase of the assembly and, when the pushing force along the trapping pulse propagation overcome the gradient in the focal plane, the assembly undergoes the ejection. Further fs multiphoton absorption is induced for the larger assembly leading to bubble generation. The assembling, ejection, and bubbling dynamics of NPs are characteristic features of pulsed optical force and are considered as a new platform for developing new material fabrication method.

**Keywords:** Optical trapping, optical assembling, optical force, nanoparticle, femtosecond laser

## 1. Introduction

Laser was introduced to chemistry research soon after its invention in 1960<sup>[1]</sup> and has been widely used because of its superior nature such as monochromaticity, short pulse, high light energy per unit area, and directionality. A particular rotational, vibrational, and electronic energy levels of molecules can be selectively excited, and a produced state of specific rotational, vibrational, and electronic levels were analyzed. This systematic research formed a new field called state-to-state chemistry.<sup>[2]</sup> The pulsed laser has enabled time-resolved spectroscopy and chemistry to describe the ultrafast processes with initially nanosecond and recently attosecond time resolution.<sup>[3–6]</sup> In addition to high resolutions with respect to energy and time, highly focused and directionally stable lasers have brought innovative development in optical microscopy. Single molecule fluorescence spectroscopy, super resolution spectroscopy, and multiplane microscopy are of representative examples.<sup>[7–10]</sup> In most cases laser light is absorbed by

[a] Mr. J. Jui-Kai Chen, Dr. W.-Y. Chiang, Dr. T. Kudo,  
Prof. H. Masuhara  
Department of Applied Chemistry, National Chiao Tung University,  
1001 Ta Hsueh Rd., Hsinchu 30010, Taiwan

[b] Dr. W.-Y. Chiang  
Department of Chemistry, Rice University, 6100 Main St., Space  
Science and Technology Building, Houston, TX 77005, USA  
E-mail: weiyichiang@gmail.com

[c] Prof. A. Usman  
Department of Chemistry, Faculty of Science, Universiti Brunei  
Darussalam, Jalan Tungku Link, Gadong BE1410, Negara Brunei  
Darussalam  
E-mail: anwar.usman@ubd.edu.bn

[d] Prof. H. Masuhara  
Center for Emergent Functional Matter Science, National Chiao  
Tung University, 1001 Ta Hsueh Rd., Hsinchu 30010, Taiwan  
E-mail: masuhara@masuhara.jp



Jim Jui-Kai Chen studied laser trapping chemistry under the supervision of Prof. Masuhara in National Chiao Tung University, Taiwan. During this period, he received his B.S. in 2016 and M.S. degree in 2018. After graduation, he joined Prof. Ming Tao Lee's lab as a research assistant in life science group of National Synchrotron Radiation Research Center (NSRRC), Taiwan in 2018. Since 2020, he became a beamline manager of X-ray Scattering in NSRRC.



Wei-Yi Chiang earned a B.S. in Chemistry in 2010 from National Sun Yat-sen University and joined Masuhara Lab at National Chiao Tung University, where he obtained a M.S. in Applied Chemistry in 2012. He received dual Ph.D. degree from National Chiao Tung University and Katholieke Universiteit Leuven in 2017 under supervision of Professor Hiroshi Masuhara and Professor Johan Hofkens. After military service, he came back to Masuhara Lab as a postdoc fellow in 2018 and continued his research of a systematic study on femtosecond laser trapping dynamics and mechanism of nanoparticle trapping. He studied novel phenomena where nanoparticles are trapped and subsequently ejected, which had never been observed for continuous wave laser trapping. Following these skills, he is interested in extending femtosecond laser trapping to include time-resolved pump-probe spectroscopy/microscopy of nanoparticles. Since 2019, he has shifted to the U.S. and is currently an associate postdoc fellow under Professor Stephan Link in Department of Chemistry at Rice University.



Tetsuhiro Kudo studied photophysics at Osaka Prefecture University, Japan where he received his Ph.D. in 2014 for a theory of laser manipulation and trapping with resonant excitation. Following this he moved to National Chiao Tung University, Taiwan as JSPS (Japan Society for the Promotion Science) Overseas Research Fellow, Postdoc and Assistant Research Fellow (2014–2020). He started experimental research on the laser trapping at an interface under various resonance conditions. In 2020 he became a Lecturer at Toyota Technological Institute, Japan starting his exploratory research on Laser Trapping Science. He received two Young Scientist Awards from the Physical Society of Japan and Inoue Foundation of Science.



Dr. Anwar Usman got his Ph.D. from Tohoku University (Japan), and extended his research in several places, including Universiti Sains Malaysia (Malaysia), Max-Born-Institut für Kurzzeitspektroskopie, Berlin (Germany), Osaka University (Japan), and École Normale Supérieure du Chimie, Paris (France), National Chiao Tung University, Hsinchu (Taiwan), and King Abdullah University of Science and Technology, Thuwal (Saudi Arabia). He closely worked with Masuhara group on femtosecond laser trapping of Rayleigh particles. Since 2015, he is an associate professor at Department of Chemistry, Universiti Brunei Darussalam. He may be contacted at Email: [anwar.usman@ubd.edu.bn](mailto:anwar.usman@ubd.edu.bn).



Hiroshi Masuhara studied physical chemistry with Prof. Masao Koizumi in Tohoku University and received his B.S. and M.S. degrees in 1966 and 1968, respectively. He started his Ph.D. with nanosecond laser with Prof. Noboru Mataga in Osaka University and received the degree in 1971. Following a postdoctoral fellow and Research Associate there, he had his own laboratory in Kyoto Institute of Technology in 1984. He is a physical chemist extending interdisciplinary areas by exploring new laser-induced molecular phenomena and elucidating their dynamics and mechanism. Since 2008 he shifted to Taiwan and has opened a new research field of optical force chemistry at solution surfaces. He is awarded Chemical Society of Japan Award, Porter Medal, The Medal of Purple Ribbon, and The Order of the Sacred Treasure-Gold Rays with Neck Ribbon, and serves as foreign fellows of Royal Flemish Academy of Belgium and National Academy of Sciences India.



molecules, nanoparticles, and so on and its energy is used to excite them electronically, which enables spectroscopy, photo-physics, photochemistry, photothermal heating, ablation, patterning, photobiology, phototherapy, and photomedicine studies.

Recently laser receives much attention as a light source for exerting mechanical force on small microparticles and living cells, particularly after Ashkin was awarded the Nobel Prize in Physics 2018. He proposed optical tweezers by tightly focusing a single laser beam to a single microparticle (MP).<sup>[11]</sup> This is completely different light-matter interactions, as photons are not absorbed by the target. Large photon momentum of the laser is transferred to the target by scattering, refraction, and reflection, and mechanical force is loaded on the MP under a microscope. We know that this concept of photon pressure itself was experimentally examined by Lebedev<sup>[12]</sup> much before ruby laser was oscillated. Now we have laser and its high intensity can be focused to a small area, so that large momentum transfer from light to matter is achieved. This enables scientists to open a new research area of optical manipulation.<sup>[13–25]</sup> It was soon applied to biological targets such as single living cell, bacterium, DNA strand, and so on.<sup>[26–28]</sup>

Optical manipulation was also extended to chemistry research. Various kinds of molecules and nanomaterials have been widely studied in solutions. Molecular clusters<sup>[18,29]</sup> and aggregates,<sup>[30,31]</sup> polymers,<sup>[32–34]</sup> DNA strands,<sup>[35]</sup> micelles and vesicles,<sup>[36]</sup> nanomaterials,<sup>[37–41]</sup> polymer NPs,<sup>[42]</sup> and metal NPs<sup>[43]</sup> are those of typical examples. One of the authors (H.M.) introduced a Galvano mirror set to microscope systems and achieved free manipulation of single MPs and single liquid droplets in solution.<sup>[44]</sup> Fluorescence spectroscopy,<sup>[45]</sup> time-resolved absorption spectroscopy,<sup>[46]</sup> micro-electrochemistry,<sup>[47]</sup> laser ablation,<sup>[48]</sup> and photopolymerization,<sup>[49]</sup> and various chemical phenomena were explored for individual MPs and microdroplets and were analyzed as a new physical chemistry. These results were introduced as optical trapping-based micro-chemistry by Ashkin.<sup>[50,51]</sup>

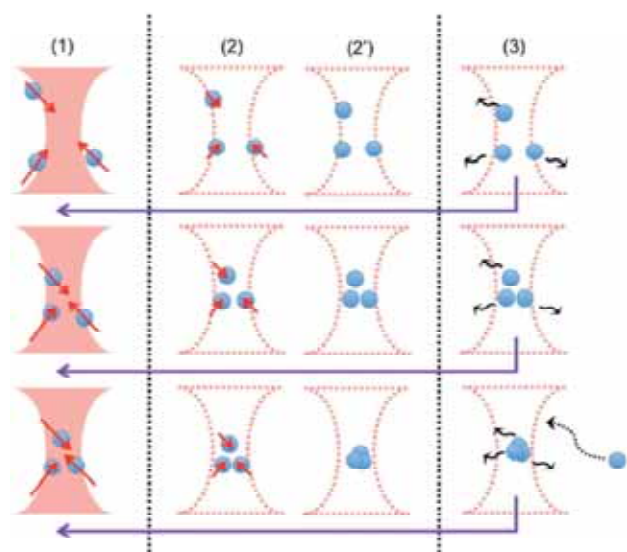
When trapping laser is focused at solution surface and glass/solution interface, completely different phenomena are observed for molecules and NPs. A single assembly of them is initially prepared inside the focus, and it scatters and propagates the trapping laser, growing the assembly larger than the focal volume. The scattered and propagated laser through the assembly are further able to trap molecules and NPs at the edge of the assembly. In the cases of amino acids and inorganic ionic compounds, nucleation takes place during the growing and it undergoes crystallization and crystal growth.<sup>[18]</sup> In the case of polystyrene (PS) nanoparticles (NPs) their periodical array and disc-like structure with concentric circle or hexagonal packing are formed.<sup>[52,53]</sup> Interestingly, Au NPs demonstrate assembling and swarming at glass/solution interface, where the

NPs fluctuate like a group of bees.<sup>[54,55]</sup> We call these phenomena “optically evolved assembling and swarming”, and we have elucidated their dynamics and mechanism.<sup>[56]</sup> As the promising application of optical trapping at solution surfaces to material science, halide perovskite,<sup>[57]</sup> supramolecule,<sup>[58]</sup> and aggregation-induced emission enhancement (AIEE)-active molecule have received much attention.<sup>[59]</sup>

Most of the above chemistry research has been carried out by focusing a 1064 nm CW laser into the small area of  $\sim \mu\text{m}^2$ . Usually light power as high as  $1 \text{ W}/\mu\text{m}^2$  is used for optical trapping of NPs in solution, so that we notice about  $100 \text{ MW}/\text{cm}^2$  is continuously irradiated on the focus area. Once the trapping laser is turned on, NPs in the irradiated area receive optical force and move toward the focal center, and there they are trapped. With the irradiation, NPs are trapped in the optical potential and form a single assembly, being accompanied with local heating, convection flow, phoretic effect, and so on. All processes occur cooperatively and continuously. In the case of pulsed laser irradiation this trapping behavior is changed. Usually femtosecond (fs) Ti:sapphire laser is utilized in optical trapping, whose characteristics are typically the wavelength of 800 nm, the pulse width of 100 fs, and the repetition rate of 80 MHz. Optical force is loaded on NPs in the irradiated area only during the pulse irradiation, and then the NPs start free diffusion till the next pulse comes. The high peak intensity laser transiently gives a large momentum, pushing the NPs toward the focus during the 100 fs and for a while even after the pulse passed through. This loading of the high attractive force and free movement are repeated with 80 MHz as illustrated in Figure 1, which leads to unique trapping and assembling dynamics of NPs. The trapped NPs form a single assembly, growing to a certain size. Since the scattering force overcomes the gradient force for a large assembly, it is ejected and dissociated to smaller aggregates. Also, bubbles are generated and ejected, which is ascribed to laser ablation of the single assembly of NPs by the trapping laser itself. For a larger assembly, more efficient multiphoton absorption of the trapping laser is possible, enabling laser ablation to occur. It is well known that laser ablation of molecules and NPs in solution induces bubbling.<sup>[60]</sup> These results indicate that the assembly formation of NPs is a key process to understand trapping dynamics by pulsed optical force. In this Accounts we summarize our results on NP assembling dynamics of the representative dielectric NPs<sup>[61–68]</sup> and consider the characteristic mechanism.

## 2. Optical Trapping of Silica Nanoparticles by Pulsed and Continuous-wave Lasers

Since Ashkin reported optical tweezers by using PS MPs in water, this solution has been used for demonstrating new



**Figure 1.** Schemes of optical trapping of nanoparticles by repetitive femto-second laser pulses. (1) Within the femto-second laser pulse, impulsive trapping force toward the focal point (shown in red arrows) is exerted on the nanoparticles. (2) Even after the pulse has passed away, nanoparticles are pushed to the focal point with the given inertia force (shown in red arrows). (2') The inertia force loaded on the nanoparticles is decreased by the collision with solvent molecules. (3) During the following time period before the next pulse comes, nanoparticles undergo dispersion (shown in black arrows) from the focal volume. In parallel, some nanoparticles are translated into the focal volume from outside through Brownian motion (shown in black dotted arrows). Reproduced with permission of ref. [63]. Copyright 2016 American Chemical Society.

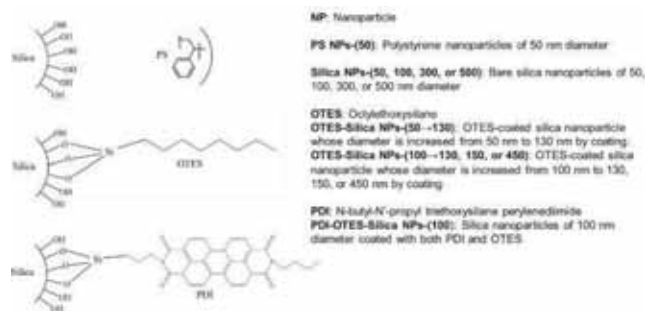
optical trapping phenomena and for proposing new manipulation methods. PS MPs and NPs are stable, while their surface can be chemically modified and functionalized. The size-controlled MPs and NPs are commercially available. No electronic absorption band is located at the trapping laser wavelength. The polymer particles are partially oxidized in air and probably  $-\text{COOH}$  groups are prepared for PS MPs and NPs, so they are charged more or less and well dispersed in water. They can be good models for optical trapping of living cells and organic matters. Silica particles have roughly similar optical properties to the polymer particles, and have been used as well. Their surface is hydrophilic and the particles are well dissolved in water, which makes the particles biocompatible. Metal MPs and NPs are also very popular and commercially prepared. Mutual optical interactions between metal particles are strong, modifying the trapping laser intensity distribution and changing optical trapping phenomena. Thus, PS and silica particles have been generally used and we find that their unique trapping behaviors are induced by fs laser irradiation.

Optical trapping is made possible by focusing tightly an intense trapping laser under a microscope, so the effective diameter is usually less than  $1\ \mu\text{m}$ . Thus, one MP is trapped at the focus, which is the cases of Ashkin's early demonstration

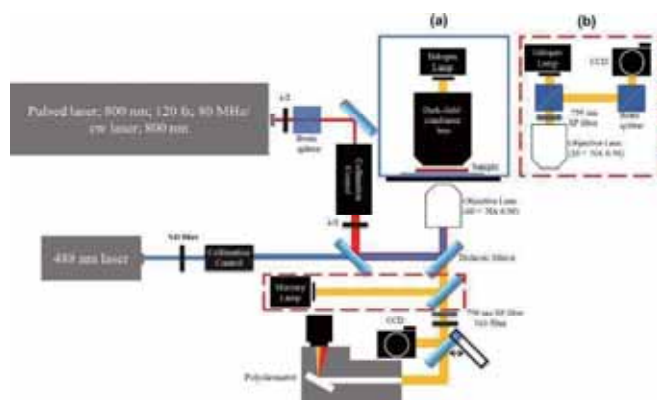
and the following many applications to living cells. In the case of NPs, however, plural particles are confined in a space of focus, about  $1\ \mu\text{m}^3$ , and their mutual interaction is intrinsically important. The samples discussed here are listed in Figure 2. PS and silica NPs are used as hydrophobic and hydrophilic NPs, respectively. PS NPs in aqueous solution may be associated, aggregated, or even assembled with each other when confined in an optical trap. Similarly, silica particles can be trapped in a small potential, but they are relatively repulsive and distributed separately due to its negatively charged surface. The modification of silica NPs with octylethoxysilane (OTES) increases their surface hydrophobicity and enhances interparticle association.<sup>[65]</sup> N-butyl-N'-propyl triethoxysilane perylene-3,4,9,10-tetracarboxylic diimide (PDI) is a most frequently used chromophore in single molecular spectroscopy, as it is very stable and has high fluorescence quantum yield. Further its fluorescence property is well known, so that PDI is introduced to the surface of silica NPs and its density is controlled.<sup>[64]</sup>

Optical setup consists of trapping lasers, optical microscopes, lenses, lamps, CCD cameras, related optical components, computers, and displays as usual. Spectrometers and fluorescence excitation lasers are also necessary. A representative arrangement is shown in Figure 3, where two observation methods are possible. Light scattering images are obtained with a dark-field condenser lens (Figure 3(a)) whose focus is set on the plane where the trapping laser is introduced. Transmission images are available when the dark-field lens is removed. The dynamics is in principle three-dimensional, so we introduce a dual objective lens microscope (Figure 3(b)) and monitor the optical trapping dynamics not only at the focal plane but also above and below it.

In the case of CW laser, trapping optical force and its spatial distribution are constant with respect to time. On the other hand, the pulsed optical force forms an attractive potential temporarily changing and propagating along the trapping optical beam axis. How this difference is reflected in the trapping dynamics of NPs is an interesting and important subject. Since light scattering intensity is proportional to the

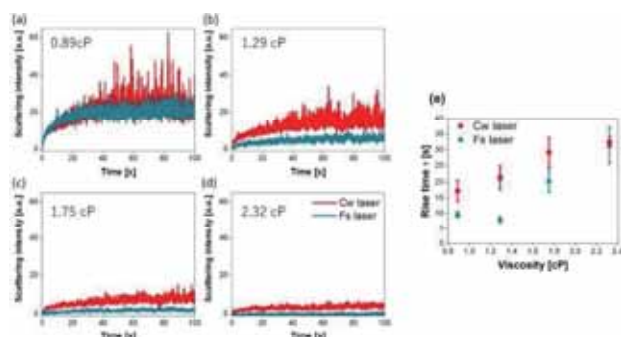


**Figure 2.** Illustrations of synthesized and commercial nanoparticles as well as their surface chemical structures. Their abbreviation is summarized.



**Figure 3.** Experimental setup for optical trapping of nanoparticles in solution by femtosecond laser. The pulsed Ti:Sapphire laser is sometimes replaced by a CW one. The wavelength of both lasers is 800 nm. (a) Dark-field scattering imaging with a conventional microscope with one objective lens. Halogen lamp from the upper or 488 nm laser from the bottom is used as a light source for scattering measurement. (b) Transmission imaging by a dual objective lens microscope. Mercury lamp from the bottom is used as a light source.

number of NPs, gathering and trapping of Silica NPs-(50) at the focus are measured by back scattering imaging and compared for femtosecond and CW laser as in Figure 4. In aqueous solution, light scattering intensity at the focal point increases with the irradiation time and saturated around 40 s after switching the laser on. This means that the number of the trapped NPs increases monotonously, which is common to both laser modes. It is noticeable, however, that the intensity fluctuation is large for CW laser as shown in Figure 4(a), although almost same number of Silica NPs-(50) are trapped. Many NPs come to the focus even after 40 s but are repelled soon, which repetition gives the fluctuation. On the other hand, the movement of NPs in the pulsed optical potential is



**Figure 4.** The trapping dynamics of Silica NPs-(50) trapped at the focus in aqueous solution by femtosecond and CW laser trapping. The laser of 350 mW power is turned on at 0 s. (a–d) Scattering light intensity increase in mixed solution with different viscosity. (e) The rise time obtained by analyzing the results of (a–d) (see text). Reproduced with permission of ref. [64]. Copyright 2019 American Chemical Society.

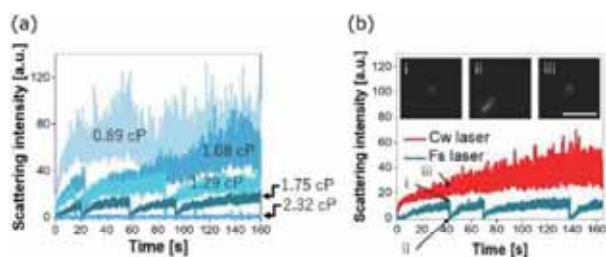
relatively small during the trapping. The NPs should be more stably trapped, although the impulsive force of femtosecond laser pulse might induce more fluctuation. We consider that the repulsive force between silica NPs is suppressed by intense pulsed optical force, and as a result they are better confined in the pulsed potential. Indeed, the peak power of the 100 fs pulse is  $10^5$  times higher than that of the corresponding CW laser. This is the first feature of NPs trapping behavior by pulsed optical force.

In general, NPs undergo directional diffusion in solution following optical gradient force, reflecting the viscosity. We tuned the solution viscosity by adding ethylene glycol (EG) with viscosity of 18.38 cP and summarized the obtained results in Figure 4(b)–(d). The scattering light intensity of both fs and CW laser trapping decreases with the increase in viscosity. Namely, trapping is hampered more with the viscosity increase. The trapping efficiency of the NPs depends on the refractive index of medium, and the value of EG (1.43) is higher than that of water (1.33). The efficiency is usually expressed by a dimensionless value as  $Q=F/(c/nP)$ ,<sup>[69,70]</sup> where  $F$  is the net trapping force,  $P$  is the incident power,  $n$  is the refractive index of a medium, and  $c$  denotes the speed of light in vacuum. By adding EG, effective refractive index of the mixed solution increases compared to pure water. The optical force exerted on Silica NPs is diminished, decreasing trapping efficiency.

By fitting the rise in the light scattering intensity to an exponential rise curve, we estimate the rise time in the femtosecond and CW laser trapping, as shown in Figure 4(e). Following the increase in viscosity, the rise time in CW laser trapping shows monotonic increase with viscosity. This is consistent with conventional understanding on viscosity effect. The diffusion of NPs becomes slow, giving the larger rise time, in more viscous solution. In the case of femtosecond trapping, however, the rise times in pure water (0.89 cP) and mixed solution (1.29 cP) are about 10 s and do not show large difference. After that the rise time increases and is almost similar to that of the CW laser trapping at high viscosity of 2.32 cP. The viscosity dependence of trapping behavior with femtosecond laser is different from that in CW laser trapping, in which clarification needs more systematic examination. Anyway, viscosity dependence is the second feature of NPs trapping behavior by pulsed optical force.

By increasing the laser power to 400 mW, we find interesting phenomenon that the scattering light intensity of Silica NPs-(50) at the focus changes rapidly. As shown in Figure 5(a), scattering intensity fluctuates more vigorously and sometimes shows a sudden decrease to zero at higher viscosity. This means the NPs are ejected from the focus. After that the scattering intensity recovers, indicating that many NPs are again trapped from the outside. The behavior is clearly confirmed in the solution with the viscosity of 1.29 and





**Figure 5.** The rise curve showing the increase of Silica NPs-(50) trapped at the focus in mixed solution with different viscosity by femtosecond and CW laser trapping. Sometimes sudden decrease is observed, showing the trapped NPs are ejected from the focus. The laser is turned on at 0 s, and its power is increased to 400 mW. (a) Scattering light intensity change at the focus by femtosecond laser trapping. (b) Scattering light intensity at the focus in the mixed solution with the viscosity of 1.75 cP by femtosecond and CW laser trapping. The scattering light images (i), (ii), and (iii) inserted in the upper are observed at the time noted as (i), (ii), and (iii) in the lower scattering light intensity change, respectively. The scale bar in the image is 10  $\mu\text{m}$ . Reproduced with permission of ref. [64] Copyright 2019 American Chemical Society.

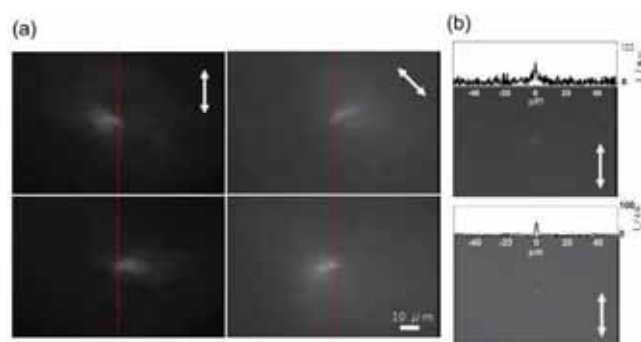
1.75 cP. When the number of the NPs at the focus reaches a certain value, the ejection of NPs from the focus take place occasionally. The behavior of Silica NPs-(50) is studied in more detail for this solution of 1.75 cP and compared for CW and fs lasers as in Figure 5(b). The number of the trapped NPs in the CW case is larger than that in the case for femtosecond, and the scattering intensity fluctuates showing a slow rise up to 160 s. However, the quick drop to zero is never observed. The unique trapping behavior and ejection behavior is the third feature of NPs trapping by pulse optical force.

We consider that a trapping status of Silica NPs-(50) at the focus is changed at laser power higher than 400 mW. The repulsion between the NPs is suppressed by this intense pulsed optical force and a single assembly of the gathered NPs is formed. It is well known that the scattering force is more nonlinearly increased with the assembly volume compared to the gradient force. When the assembly comes to a certain size, scattering force overcomes the gradient force, leading to the ejection. When the scattering intensity becomes zero, the NPs are all removed at once and not partly remained at the focus. The phenomenon of trapping and ejection can be explained in terms of the formation of a single assembly and its following ejection. This idea is directly confirmed by observing the scattering images included in Figure 5(b) (i)–(iii). In images (i) and (iii), one scattering white spot is observed at the focus, while the scattering flowing out from the focus is observed in the image (ii). These images can be correlated to the temporal scattering intensity rise and drop. The image (ii) corresponds to the zero value, while (i) represents gathered NPs at the focus and is similar to (iii) of CW laser trapping. It is interesting and important to propose that the pulse optical force assembles

even repulsive silica NPs, forms their single assembly, and ejects it.

### 3. Optical Assembling and Ejection of Hydrophobic Silica Nanoparticles

Our result is that repulsive Silica NPs-(50) are packed with each other by pulsed intense force, indicates that surface chemical modification of silica NPs will modify their trapping and ejection behavior. We synthesize OTES-modified silica NPs with different thicknesses of OTES layer. The results on their fs laser trapping experiment show more distinct ejection behavior. (OTES)-Silica NPs-(50 $\rightarrow$ 130) give a stream-like light scattering pattern, as shown in Figure 6(a). This stream suggests that the ejection like Figure 5(b) (ii) takes place sequentially. As the reference, the light scattering images of Silica NPs-(50 and 100) are shown in Figure 6(b), where the NPs are just trapped. As described above, these NPs are packed, forming a single assembly, and the latter is ejected from the focus after some irradiation time. The assembly formation of hydrophobic (OTES)-Silica NPs-(50 $\rightarrow$ 130) is efficient compared to Silica NPs-(50), so the ejection is speedily and repeatedly during the irradiation. The ejected assemblies scatter the light of halogen lamp, which is the origin of the streaming pattern. It is worth noting that the ejection direction is roughly perpendicular to linearly polarized laser and the direction is alternatively switched. When the polarization vector of the trapping laser was rotated ejection direction was also rotated, keeping its perpendicular relation to

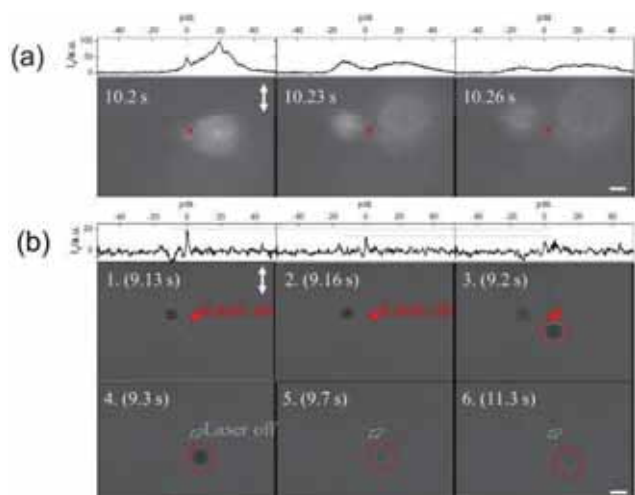


**Figure 6.** Optical trapping and ejection of various Silica NPs by femtosecond laser. The laser power is 350 mW. The double-headed arrow indicates the direction of laser polarization. (a) Light scattering images of OTES-Silica NPs-(50 $\rightarrow$ 130) showing the ejection from the focus of which direction is perpendicular to laser polarization and alternatively switched from one direction to the other. The white bar corresponds to 10  $\mu\text{m}$ . (b) Trapping of Silica NPs-(50) (upper) and Silica NPs-(100) (lower), showing no ejection. Line profiles represent scattering intensity distribution along the line through the focal spot perpendicular to laser polarization. Reproduced with permission of ref. [65] Copyright 2018 American Chemical Society.



the polarization vector. This is the fourth feature of NPs trapping behavior by the pulse optical force.

The unique trapping and the following ejection behavior of OTES-Silica NPs-(100→130, 150, and 450) depend on the thickness of OTES layer and the NP size. They gave a sphere-like light scattering pattern which is ejected one by one, whose representative example is given in Figure 7(a). This is obtained only after a certain irradiation time. The light scattering sphere is ejected from the focus and flown out, expanding its size and reducing scattering intensity. The behavior is much different compared to OTES-Silica NPs-(50→130). With the increase in the OTES layer thickness, the ejection behavior is phenomenologically switched from the scattering stream to scattering sphere. One may doubt that the optical refractive index is changed by OTES coating and the trapping efficiency  $Q$  is changed. Fortunately, the refractive index of OTES (1.42) is almost the same to that of silica, and the coating leads just to volume expansion. Since the volume of (OTES)-silica NPs-(100→450) is comparable to that of Silica NPs-(500), the volume expansion is not a major factor. We tried to interpret that the OTES surface assists association of the NPs, resulting in the formation of a single assembly and the latter looks as the scattering sphere upon its ejection.



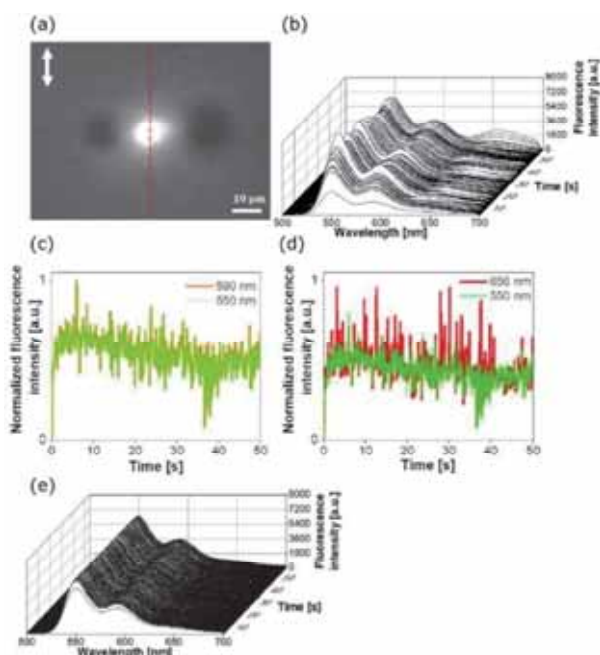
**Figure 7.** Optical trapping and ejection dynamics of OTES-Silica NPs-(100→450) by femtosecond laser. The red arrow indicates the focus and the white bar corresponds to 10  $\mu\text{m}$ . The laser power is 350 mW and the white double-headed arrow show the laser polarization. (a) Light scattering images observed at 10.2–10.26 s after starting the irradiation. Scattering spheres correspond to the bubbles formed by ablation of assembled NPs. Line profiles represent scattering intensity distribution passing through the focal spot perpendicular to laser polarization. (b) Transmission images observed at 9.13–9.2 s after starting the laser irradiation. The black spheres correspond to the bubbles formed by ablation of assembled NPs. Line profiles represent transmission intensity distribution passing through the focal spot perpendicular to laser polarization. The trapping laser is switched off at 9.3 s when the focus is shown by the white dotted arrow. Reproduced with permission of ref. [65]. Copyright 2018 American Chemical Society..

The corresponding transmission images are given in Figure 7(b), where a dark sphere appears and moves out from the focal area. Its size is smaller than that of the scattering sphere. One possible explanation for these OTES-Silica NPs-(100→450) behaviors is that the NPs assembled largely and ejected without dissociation to the component NPs. Another is that a single assembly of OTES-Silica NPs-(100→450) is formed and ablated by the trapping laser, producing bubbles one by one. By close examination of Video1 (Supporting Information), we find that the dark spheres become large after shifting from the focus, always keeping their sphere shape. They are ejected upward three-dimensionally away from the trapping site. We have to consider that the bubble formation takes place, which is eventually ascribed to multiphoton absorption of the trapping laser by the assembly of the NPs. It is well known that larger solid in solution has a lower ablation threshold.<sup>[65]</sup> The production and movement of the scattering sphere observed in Figure 7(a) correspond to those of the dark sphere of the bubbles in Figure 7(b) 1–3. The behavior of this OTES-Silica NPs-(100→450) during the laser irradiation (upper pictures) and after switching off the laser (lower pictures) are compared with each other in Figure 7(b). The size of the black sphere changes with time probably due to the diffusion and floating of the bubbles out from the focal plane. Thus, the assembling and bubbling is the fifth features of NPs trapping behavior by pulsed optical force.

#### 4. Assembly Formation and its Fluorescence Characterization of Silica Nanoparticles

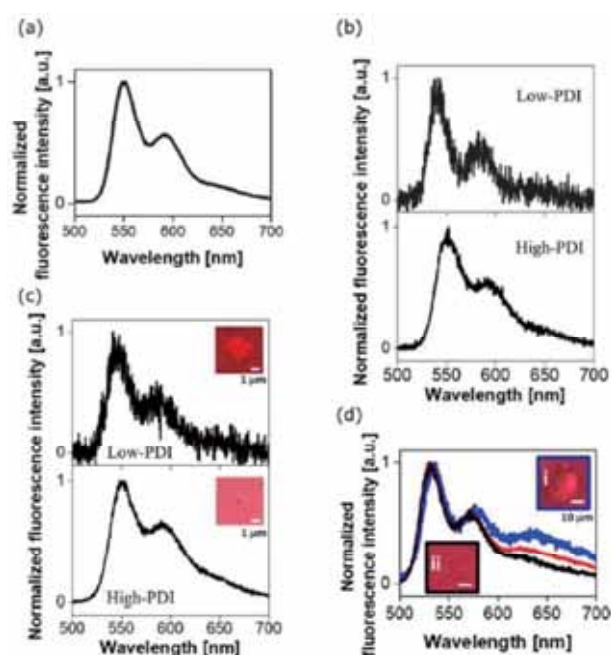
It is important to confirm spectroscopically the assembly formation of silica NPs. We design and synthesize a PDI-OTES-Silica NPs-(100) by introducing PDI chromophore (Figure 2). The PDI monomer fluorescence with vibronic bands at 550 and 590 nm are always observed, but the band intensity at 656 nm is increased upon the dimer formation. We prepare several silica NPs samples including low and high density PDI. The transmission image is given in Figure 8(a), where the central bright area is ascribed to PDI fluorescence induced by two-photon excitation by the trapping femtosecond 800 nm laser. Its fluorescence spectra are measured during the trapping and displayed as a function of irradiation time in Figure 8(b).

As a reference we measure this PDI-OTES-Silica NPs-(100) under various conditions and summarize them in Figure 9. In aqueous solution of PDI-OTES-Silica NPs-(100) with low PDI density, only monomer fluorescence is observed. This spectrum is also obtained for a single PDI-OTES-Silica NP-(100) with low (upper) and high (lower) PDI density on a glass substrate. The results mean that PDI chromophores on one PDI-OTES-Silica NP-(100) do not interact with each



**Figure 8.** Transient assembly formation of PDI-OTES-Silica NPs-(100) in aqueous solution in femtosecond optical trapping. (a) A transmission image obtained by overlaying two alternative directional ejections of the black sphere due to a bubble. The bright fluorescence of PDI chromophores is observed at and around the focus by two-photon excitation with the femtosecond 800 nm trapping laser. (b) Temporal change of the PDI fluorescence spectra during the trapping. (c–d) Temporal change of PDI monomer (550 and 590 nm) and excimer (656 nm) fluorescence intensity during the trapping. The excimer is ascribed to the association of PDI chromophores belonging to different NPs, indicating transient assembly formation of the NPs (see text). (e) Temporal change of PDI fluorescence spectra obtained by one-photon excitation with CW 488 nm laser during the 800 nm CW laser trapping. All the spectra are obtained by accumulating the fluorescence for 1 s. Reproduced with permission of ref. [64]. Copyright 2019 American Chemical Society.

other, namely the distance between them is too long for  $\pi$ - $\pi$  electronic interaction. When PDI-OTES-Silica NPs-(100) are assembled on a glass, the interaction between PDI chromophores belonging to different silica NPs is in principle possible. We prepare aggregates of these NPs by casting or spin-coating of their solution and measure the PDI fluorescence. It gives only monomer fluorescence and no enhancement of the dimer emission is detected. Then we centrifuge the solution and form aggregates of PDI-OTES-Silica NPs-(100) with low (upper) and high (lower) PDI density on a glass substrate. We find the excimer band in the assembly of PDI-OTES-Silica NPs-(100) with low PDI density, which means that the PDI-chromophores belonging to different NPs, are stacked with each other. This means a transient assembly with the stacked PDI chromophores is formed. Thus, we conclude that pulsed optical force is comparable to that of centrifuge force and forms a strongly packed NPs assembly upon femtosecond laser trapping NPs. The fluorescence spectra of the NPs during the

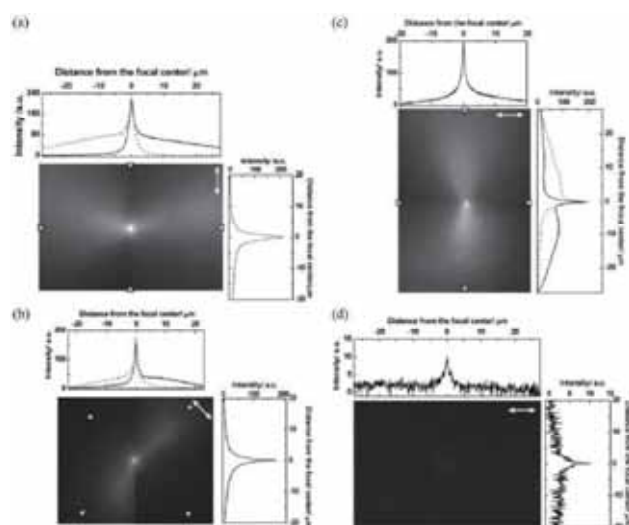


**Figure 9.** Reference PDI fluorescence spectra used for concluding the transient assembly formation of PDI-OTES-Silica NPs-(100) in aqueous solution by femtosecond optical trapping. The 488 nm laser is used for fluorescence excitation. (a) Monomer fluorescence spectrum of PDI-OTES-Silica NPs-(100) with low PDI density (see text) in aqueous solution. (b) Fluorescence spectra (upper and lower) of the assembled PDI-OTES-Silica NPs-(100) with low and high PDI density on a glass substrate, respectively. (c) Fluorescence spectra (upper and lower) of a single PDI-OTES-Silica NP-(100) with low and high PDI density on a glass substrate, respectively. The corresponding transmission images, where the single NP is selected and measured, are inserted. (d) Fluorescence spectra of the centrifuged PDI-OTES-Silica NPs-(100) with low PDI density (see text). (Blue spectrum) Monomer and excimer bands at the central assembly, (red spectrum) monomer and a little excimer bands at the high NP density, and (black spectrum) only monomer band at the low NP density. Reproduced with permission of ref. [64]. Copyright 2019 American Chemical Society.

CW laser trapping always consist of the monomer band, as shown in Figure 8(e), which is an important reference.

## 5. Optical Assembling and Ejection of Polystyrene Nanoparticles

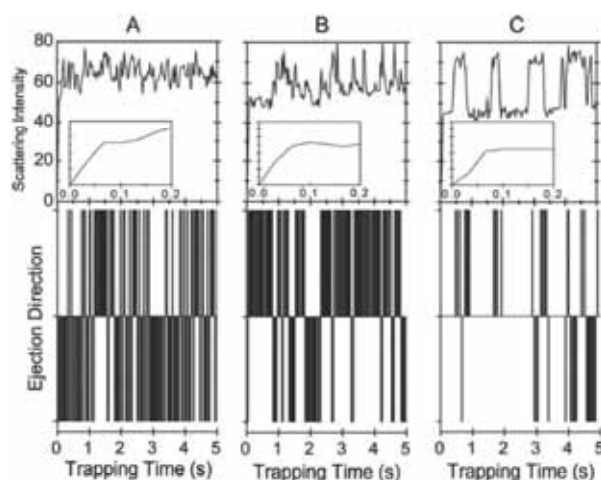
Another representative NPs studied in our group is PS NPs-(50) in aqueous. Their surface is hydrophobic and assembly formation by the pulsed optical force is shown in Figure 10. We observed a bright spot at the focus with the femtosecond laser and its intensity is much higher than that obtained with the CW laser of the same power. In addition, a white scattering stream-like pattern is similar to Figure 6(a), which can be ascribed to the PS NPs-(50) continuously ejected from the focus to the outside. This takes place only to one direction and switched alternatively. Thus, two oppositely extending fan



**Figure 10.** Optical trapping and ejection dynamics of PS NPs-(50) in aqueous solution by femtosecond laser. (a–c) The PS NPs are ejected to right or left direction perpendicular to laser polarization, giving a scattering image of half-opened fan shape. Its intensity distribution is taken from one line passing through the focal point in parallel and perpendicular to the polarization direction, and given in the graph above or side the corresponding image. The combination of two images showing opposite ejection direction is given for different laser polarization. Double-headed arrow represent the direction of laser polarization. A bright dot at the focus is ascribed to scattered light due to the assembled PS NPs and their benzene excimer fluorescence obtained with three-photon excitation of femtosecond trapping laser (See text). (d) The dark-field image of PS NPs trapped at the focus by CW 800 nm laser. The laser power is 350 mW after the objective lens. The arrow in each panel indicates polarization direction of the laser. Reproduced with permission of ref. [61]. Copyright 2012 Elsevier.

patterns are combined and overlaid as a pair in Figure 10(a)–(c). We rotate the polarization direction of the trapping laser, and then the ejection direction follows the rotation. The central spot is very bright with the fs laser compared to the CW laser, although the laser power is same 350 mW. We consider that optical trapping is more efficient by femtosecond laser and benzene excimer emission of PS excited by three-photon absorption of the 800 nm laser is overlapped.

The NP concentration dependence is studied on PS NPs-(50). In upper panels of Figure 11, the scattering intensity at the focus is plotted as a function of irradiation time, namely, how the trapped PS NPs-(50) increase at the focus and fluctuate through their ejection. At  $15.2 \times 10^2 \text{ NPs}/\mu\text{m}^3$  (Figure 11A), the trapping site is filled quickly within a few tens ms and keeps the high number of PS NPs. The NPs are continuously ejected out of the focus and supplied soon from the surrounding, which corresponds to two alternatively switched directions perpendicular to the laser polarization. At  $1.1 \times 10^2/\mu\text{m}^3$  (Figure 11C), however, the number of the NPs at the focus stochastically appears at a high level and turns suddenly to a low level, which repeats in the same manner on a second scale. An intermediate behavior is observed for the



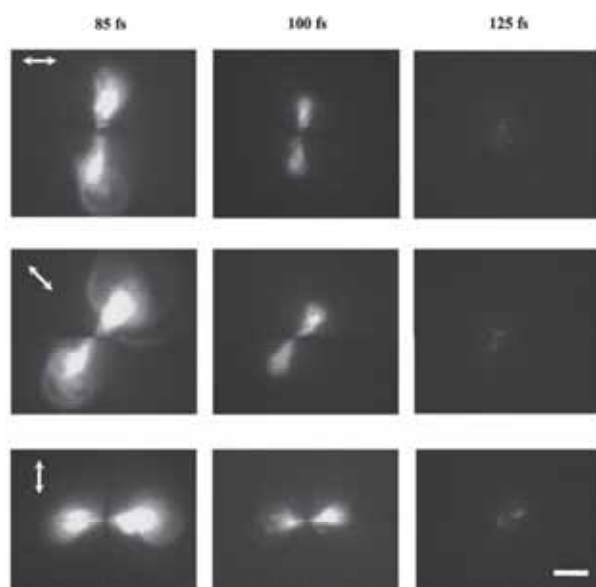
**Figure 11.** NPs concentration dependence of optical trapping and ejection dynamics in aqueous solution by femtosecond laser. PS NPs-(50) ejection is attained when their number at the focus reaches a certain value. The concentration is (A)  $15.2 \times 10^2/\mu\text{m}^3$ , (B)  $3.8 \times 10^2/\mu\text{m}^3$ , and (C)  $1.1 \times 10^2/\mu\text{m}^3$ . (Upper panels) Scattering light intensity change at the focal spot for 0–5 s after starting the trapping, and the intensity in the inserted graphs are enlarged for 0–0.2 s. (Lower panels) Illustrative representation of ejection direction and frequency. Direction switching takes place randomly, and ejection frequency is reduced for lower concentration. Reproduced with permission of ref. [61]. Copyright 2013 American Chemical Society.

concentration of  $3.8 \times 10^2/\mu\text{m}^3$  (Figure 11B). In the lower panels the ejection direction perpendicular to the laser polarization direction is illustrated up or down. The ejection occurs sequentially for high concentration, but it becomes seldom for low concentration.

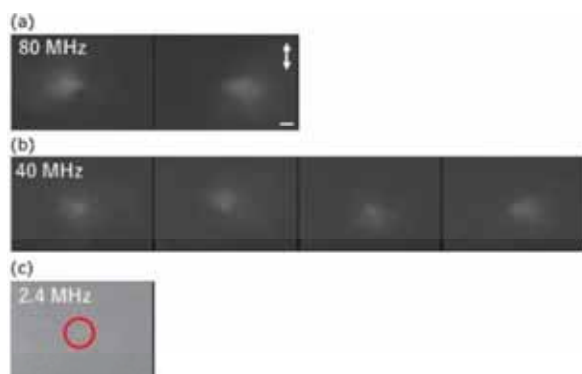
Characteristic behavior of trapping and ejection of PS NPs-(50) is examined by changing the pulse width. The very critical dependence is made clear, as demonstrated in Figure 12. The scattering images of two overlaid partially opened folding fans are brighter with the shorter pulse width, while its directionality is confirmed for all the pulse width. The gathering of PS NPs toward the focus during the laser pulse is due to directional transport, and much different from conventional diffusion and that under the CW laser trapping. It is estimated, using the diffusion coefficient of a  $10^{-10} \text{ m}^2/\text{s}$  (for a NP radius of 57 nm,<sup>[71]</sup> that PS NPs of 57 nm diameter travel only the distance of  $\sim 3 \text{ nm}$  and  $\sim 1 \text{ nm}$  within the 100 fs pulse and during the interval of 12.5 ns, respectively. The diffusion length during the pulse width is not changed much from 125 fs to 85 fs, so that the dependence is probably ascribed to pulsed optical force, which is critically determined as nonlinear optical effect. The NPs are more efficiently trapped and scattering with shorter pulse.

The repetition rate dependence is also critical, which is summarized in Figure 13. In the standard case of 80 MHz, the ejection is alternatively switched along the perpendicular direction to the laser polarization. By reducing the rate,





**Figure 12.** Pulse-width and polarization dependences of optical trapping and ejection of PS NPs-(50) in solution by femtosecond laser trapping. The light scattering images are obtained by combining two oppositely ejected half-opened fun-like patterns. The polarization direction is indicated by the double-headed arrow in each row, and the pulse width is tuned to 85, 100, and 125 fs is indicated on the top of each column. The scale bar of 10  $\mu\text{m}$  is applied for all images. Reproduced with permission of ref. [62]. Copyright 2013 American Chemical Society.

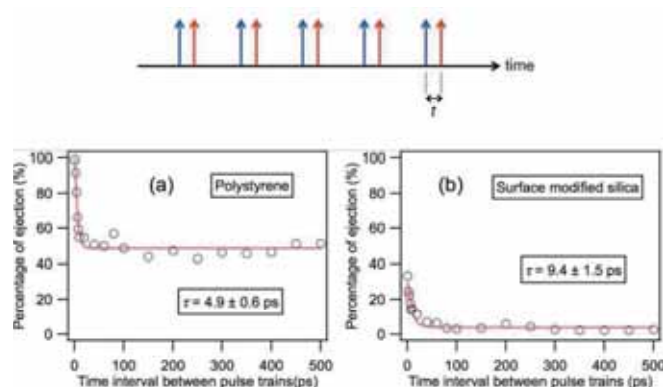


**Figure 13.** Repetition rate dependence of optical trapping and ejection dynamics of PS NPs-(50) by femtosecond laser. The NPs concentration is  $3.8 \times 10^2 \text{ NPs}/\mu\text{m}^3$ , and the white double-headed arrow indicates the direction of laser polarization. A small ejection is found in the red circle for 2.4 MHz. Reproduced with permission of ref. [61, 64]. Copyright 2013 & 2019 American Chemical Society.

however, ejection takes place to the random direction and the scattering intensity becomes weak. Namely the number of the NPs undergoing trapping and ejection is less. During the pulse interval the assembly of NPs becomes small, the packing of formed assembly is weak, and its dissociation from its edge to the surrounding leads to the decrease in size. The assembly

volume governs trapping force, so that smaller size of assembly receives weaker scattering force, which results in the short ejection distance. When the repetition rate is further decreased to 2.4 MHz, the estimated diffusion distance of NPs during the relaxation time is  $\sim 40$  times longer than that in the original 80 MHz. This results in the small size of the assembly, leading to the weak beam pattern of PS NPs.

One direct information of the transient assembly dynamics in the framework of Figure 1 is obtained by designing a new double pulse train experiment. The 80 MHz fs pulse train is split into double pulse trains, both are linearly polarized as usual, and the time interval between double pulses is tuned in the picosecond time region, as shown in upper panel of Figure 14. Compared to the 80 MHz pulse train with the laser power of the sum of two trains, the ejection by the double pulse trains is less frequent. In the lower panel of Figure 14, the ejection frequency of PS NPs-(50) and OTES-Silica-NPs is plotted against the interval of the double pulse. It consists of two components; one is flat, showing no decay in the sub-nanosecond time region, and the other is fitted to an exponential decay curve. Sometimes the single assembly survives up to the next double pulse comes, or the single assembly decays with the time constant of a few ps. The single assembly formation is stochastic, and its size and location may fluctuate from pulse to pulse. The NPs may be enough strongly packed and stable in the sub-nanosecond region, or may dissociate to the component NPs. The formation probability of both assemblies is half and half. This explanation is consistent with stochastic nature of the trapping phenomena.



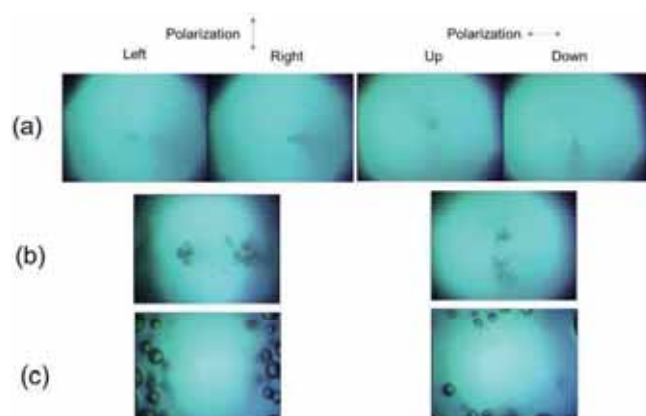
**Figure 14.** Optical trapping and ejection dynamics by femtosecond double pulse experiment. (Upper) The time interval between the double pulse ( $t$ ) is controlled with keeping laser power and repetition rate of 80 MHz. (a) Ejection frequency of PS NPs-(50) in aqueous solution as a function of the time interval. (b) Ejection frequency of OTES-Silica NPs-(50) in aqueous solution as a function of the time interval. Total laser power of the double pulse is 200 mW. The obtained relaxation time is given in the graph. Reproduced with permission of ref. [63]. Copyright 2016 American Chemical Society.



## 6. Optical Assembling, Ejection, and Ablation of Nanoparticles

We have described the characteristic features of NPs dynamics by pulsed optical force and their possible interpretation. A scattering stream extending from the focus to the outside is observed for OTES-Silica NPs (50→130) and PS NPs-(50), which is ascribed to the ejection of the NPs, while a scattering sphere for OTES-Silica NPs (100→130, 150, and 450) is assigned to the bubbles prepared by ablation of the assembled NPs. These phenomena have been obtained by a conventional dark field microscope, although they are in principle three-dimensional. Recently we have introduced a double objective lens microscope and observed transmission images of their behaviors at different focal planes. When the observation objective lens is set at the same plane to the trapping objective lens, small dark dots streaming from the focus to the outside is observed for PS NPs-(50) (Figure 15(a), Video 2 (Supporting Information)), which corresponds well to the ejection in the light scattering images of Figure 10(a)–(c).

After moving up the observation plane by several tens  $\mu\text{m}$  higher, bubbles are observed, while dark dots are also identified. It is interesting to note that the bubbles are ejected also perpendicular to the laser polarization. The bubbles are alternatively generated from one side to the other and move up due to buoyancy by increasing their volume (Figure 15(b)). Shifting the monitoring objective lens to the upper solution-glass interface, we find many bubbles are repeatedly prepared and stay longer in both sides (Figure 15(c)). When the monitoring objective lens is shifted several  $\mu\text{m}$  below the focal plane of the trapping objective lens, we observed the scattering stream of dots, which is quite similar to the results of



**Figure 15.** Optical trapping, ejection, and bubbling dynamics of PS NPs-(50) in aqueous solution observed by transmission images with dual objective lens microscope. The images are observed (a) at the same focal plane with trapping, (b) between the focal plane and upper solution surface, and (c) at upper solution surface. Polarization direction of the femtosecond trapping laser is vertical and horizontal in left right images, respectively.

Figure 10(a)–(c). One may consider that the streaming dots are ascribed to the sphere bubbles located at different focal planes in upper solution. However, it is not probable that a defocused image of a sphere bubble is observed as a stream of dots. The fs laser irradiation to the bulk solution induces bubbling is well known,<sup>[60]</sup> and it happens randomly to all directions. Thus, we examine PS NPs-(500) under the same condition as a standard reference of fs laser bubbling. The PS NPs-(500) show benzene excimer fluorescence and bubble generation, however, obvious directionality is not observed. In this case assembly formation within the potential is difficult because of its large size comparable to the focal area. It is considered that the directionality of PS NPs-(50) bubbling ascribed to the characteristic formation process of the assembly.

## 7. Directional Ejection and Ablation Mechanism of Polystyrene Nanoparticles

Here, we describe our theoretical consideration on trapping and assembling dynamics of NPs by summarizing the relevant theory and numerical calculation of force maps of the pulsed optical force. This is carried out for a single NP. As the diameter of a NP is sufficiently smaller than the wavelength of the laser, a single NP is treated as a simple point dipole on which optical force is exerted. The force consists of gradient and scattering components. The gradient force is associated with Lorentz force that acts on a dipole locating in an inhomogeneous electromagnetic field, and is proportional to  $a^3$ , where  $a$  is the radius of the NP. The scattering force is associated with momentum change of the electromagnetic wave, which is proportional to  $a^6$ . This understanding is generally established and explains many trapping phenomena induced by CW laser. In case of femtosecond laser trapping, temporal force should be involved additionally. The time-dependent electromagnetic field of the introduced pulsed laser linearly along the x-axis is given by,<sup>[72]</sup>

$$E_x = E_0 \frac{i}{(i + 2\xi)} \exp[i(\omega_0 t - kz - 2\xi\rho^2 / (1 + 4\xi^2))] \exp[-\rho^2 / (1 + 4\xi^2)] \exp(-t^2/\tau^2) \quad (1)$$

where  $E_0$  is the impulsive electric field of the laser pulse,  $\rho^2 = \xi^2 + \eta^2$ ,  $\xi = x/w_0$ ,  $\eta = y/w_0$ , and  $\xi = z/(kw_0^2)$  are the normalized spatial coordinates in the focal spot,  $w_0$  is beam waist,  $\omega_0$  is light frequency of the laser beam, and  $\tau$  is the pulse duration. It is important to emphasize that optical trapping in our work utilizes high numerical aperture objective lens. It tightly focuses the intense beam and also diffuses partially the linear polarized beam into the transverse and

longitudinal components.<sup>[73,74]</sup> Based on paraxial approximation, the transverse and longitudinal components are given by

$$E_z = (-i/k) \partial_x E_x \quad (2)$$

$$E_y = (1/k^2) \partial_y \partial_x E_x \quad (3)$$

With the existences of transverse and longitudinal fields in the focal spot, the optical forces exerted on the NPs in the trapping spot should be the three-dimensional. The optical gradient, scattering, and temporal ( $F_{grad}$ ,  $F_{scat}$ , and  $F_{temp}$ ) forces exerted on the NPs which can be treated as point dipole small, are approximately expressed as

$$\begin{aligned} \vec{F}_{grad} = & -\{\hat{x}(\xi/((1+4\xi^2)^2) + (K^4\xi^3\eta^2)/((1+4\xi^2)^4) - \\ & \frac{K^4\xi\eta^2}{2(1+4\xi^2)^3} + (K^2\xi^3)/((1+4\xi^2)^3) - (K^2\xi)/(2(1+4\xi^2)^2)) \\ & \hat{y}(\eta/((1+4\xi^2)^2) + (K^4\xi^2\eta^3)/((1+4\xi^2)^4) - \\ & (K^4\xi^2\eta)/(2(1+4\xi^2)^3) + (K^2\xi^2\eta)/((1+4\xi^2)^3)) + \\ & \hat{z}\left(\frac{2\xi}{(1+4\xi^2)^2}\right) \left[1 - \frac{2(\xi^2 + \eta^2)}{(1+4\xi^2)}\right] + \frac{6K^4\xi^2\eta^2\xi}{(1+4\xi^2)^4} - \\ & (4K^4\xi^2\eta^2(\xi^2 + \eta^2)\xi)/((1+4\xi^2)^5) + \\ & (4K^2\xi^2\xi)/((1+4\xi^2)^3) - (4K^2\xi^2(\xi^2 + \eta^2)\xi)/ \\ & ((1+4\xi^2)^4))\} \times (n_m^2 \epsilon_0 \alpha E_0^2)/w_0 \times \exp[-2(\xi^2 + \eta^2)/ \\ & (1+4\xi^2)] \times \exp[-2t^2/\tau^2] \end{aligned}$$

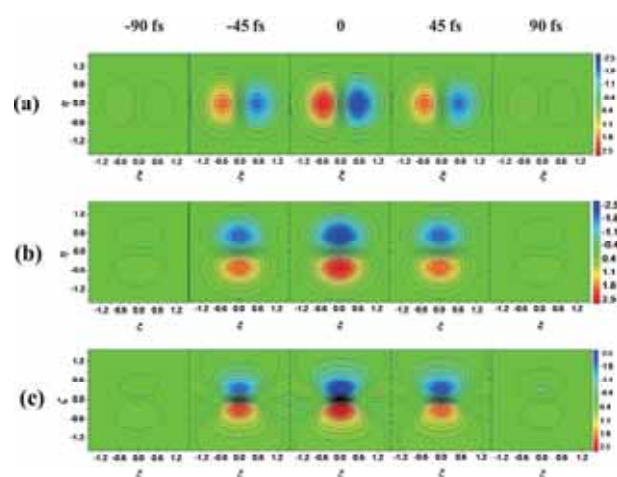
$$\begin{aligned} \vec{F}_{scat} = & \{\hat{x}[(K^4\xi^2\eta^2)/((1+4\xi^2)^3) + 2K\xi\xi/((1+4\xi^2)^2)] + \\ & \hat{y}[(K^2\xi^2)/((1+4\xi^2)^2) + (4K^2\xi\eta\xi)/((1+4\xi^2)^3)] + \\ & \hat{z}[1/((1+4\xi^2)) - (K^3\xi^2\eta)/((1+4\xi^2)^3)]\} \times \\ & (n_m^2 \epsilon_0 \sigma_p E_0^2)/2 \times \exp[-2(\xi^2 + \eta^2)/(1+4\xi^2)] \\ & \times \exp[-2t^2/\tau^2] \end{aligned} \quad (4)$$

$$\begin{aligned} \vec{F}_{temp} = & \{\hat{x}[(K^4\xi^2\eta^2)/((1+4\xi^2)^3) + 2K\xi\xi/((1+4\xi^2)^2)] + \\ & \hat{y}[(K^2\xi^2)/((1+4\xi^2)^2) + (4K^2\xi\eta\xi)/((1+4\xi^2)^3)] + \\ & \hat{z}[1/((1+4\xi^2)) - (K^3\xi^2\eta)/((1+4\xi^2)^3)]\} \times \\ & (-2n_m^3 \alpha \epsilon_0 E_0^2 t)/(c\tau^2) \times \exp[-2(\xi^2 + \eta^2)/(1+4\xi^2)] \times \\ & \exp[-2t^2/\tau^2] \end{aligned} \quad (6)$$

The notation  $K = 2/kw_0$  is a value related to numerical aperture of an objective lens,  $n_m$  is refractive index of medium,  $\epsilon_0$  is the vacuum permittivity,  $c$  is the speed of light,  $\alpha$  is polarizability, and  $\sigma_p = k^4 \alpha^2 / 6\pi$  is the scattering cross section of the individual NPs. Here, the absorption cross section is negligible for NPs having diameter much smaller compared

with the polarization vector. It is important to note that  $F_{grad}$  and  $F_{scat}$  exerted on NPs generated by pulsed laser are similar to those of CW laser, except the additional temporal term,  $\exp[-2t^2/\tau^2]$ , while  $F_{temp}$  is solely attributed to the pulsed laser.

Figure 16 illustrates the spatio-temporal maps of the  $\vec{F}_x$ ,  $\vec{F}_y$ , and  $\vec{F}_z$  components of  $F_{grad}$ ,  $F_{scat}$ , and  $F_{temp}$  exerted on a PS NP-(50) optically trapped with laser pulses of 800 nm,  $\tau = 90$  fs, and 80 MHz. It is tightly focused by an objective lens with the numerical aperture of 0.90. Figure 16 Panel (a) indicates that the  $\vec{F}_x$  acts as an attractive force directing the NPs toward the focal point. This attractive force increases rapidly in the first half of the pulse envelope, reaches a maximum magnitude on the scale of nN, and then decreases at the second half of the pulse envelope. Such the magnitude of the ultrafast impulsive attractive force is extremely higher than the constant attractive forces of pN scales which are loaded on gold NPs by CW laser beams.<sup>[75]</sup> Similarly in Figure 16 Panel (b),  $\vec{F}_y$  also pushes the particles toward the focal centre. Thus, for every single pulse passing the focal spot, the generated  $\vec{F}_x$  and  $\vec{F}_y$  acts as attractive forces directing the NPs toward the focal point. The magnitude of the generated forces depends on the relative position of the particular NP with respect to the beam centre in the focal spot, and the general maps indicate that  $\vec{F}_y$  is just slightly lower than  $\vec{F}_x$ . This suggests that the force on the xy-plane is actually elliptical with the major axis being along the polarization of the incident light. Namely,

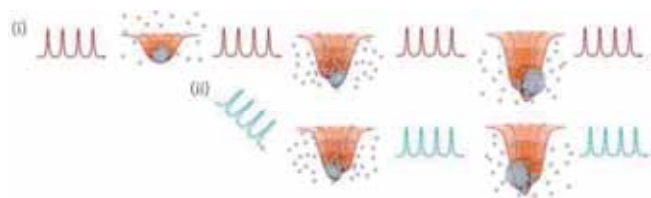


**Figure 16.** Spatio-temporal optical force maps of  $\vec{F}_x$ ,  $\vec{F}_y$ , and  $\vec{F}_z$ , consisting of optical gradient, scattering, and temporal ( $F_{grad}$ ,  $F_{scat}$ , and  $F_{temp}$ ) forces. They are exerted on a single PS NP-(50) which are optically trapped with laser pulses (800 nm,  $\tau = 90$  fs, 80 MHz). The normalized spatial coordinates of  $\rho^2 = \xi^2 + \eta^2$ ,  $\xi = x/w_0$ ,  $\eta = y/w_0$ , and  $\xi = z/kw_0^2$ , are used, where  $w_0$  is beam waist (See text). Calculated  $F_x$  on the xy-plane (a),  $F_y$  on the xy-plane (b), and  $F_z$  on the xz-plane (c). The forces are in the range of  $-2.5$  to  $2.5$  nN as indicated. The temporal change of the maps at the focal plane is given from left to right, where the time 0 correspond to the time when the femtosecond laser pulse passes just on the plane.

optical potential is relatively elongated along the x-axis compared to y-axis, and relatively sharp along the y-axis compared to x-axis. This means that NPs can be more easily packed in the y-direction. In Figure 16 Panel (c) shows that  $\vec{F}_z$  increases along the positive z-axis during the first half of the pulse envelope and turns into the opposite direction in the second half. The magnitude of  $\vec{F}_z$  is asymmetrical with respect to the pulse propagation with a maximum value of +0.46 nN at  $t = -0.5\tau$  in the first half and -0.34 nN at  $t = 0.5\tau$  in the second half of the pulse envelope. Namely a repulsive force rather than an oscillating force is generated along the z-axis. Thus,  $\vec{F}_z$  induces intrinsically the ejections of a single NP out from the focal spot along the beam propagation, which can be applied to a single assembly of the NPs.

The ejection direction is perpendicular to linear polarization of the trapping laser, which can be explained qualitatively, but alternative behaviour not rationalized. The force is always symmetric with respect to x and y axes, so that the assembly of the NPs should be located equally at the both sides along the y-axis. It is necessary to introduce a new viewpoint, that is, the stochastic nature of single NPs trapping. If a single NP trapped at the plus position along the y-axis and packed to a single assembly there, it becomes large at that position and ejected to the upper left. If trapped and grown at the minus position, the ejection takes place toward to the upper right. This is illustrated in Figure 17, which should be precursor assembly formation dynamics before Figure 6(a), Figure 10(a)–(c), and Figure 15(a).

When the assembly becomes larger, multi-photon absorption of the trapping laser by the assembly is made more possible, as its absorption is proportional to the volume. One single assembly increases its volume by adsorbing new NPs packed by pulsed optical force, and then absorbs the trapping laser densely. It is well studied that the densely excited states in solid leads to ablation generating bubbles in solution.<sup>[60]</sup> Thus the ejection and bubbling can be competitive, and which



**Figure 17.** The illustration of a single optically evolving assembly of NPs in solution by femtosecond laser pulses, where the laser polarization is vertical to the paper plane. Once the assembly is prepared at the right side in the optical trap, it grows at the right side, giving ejection and bubbling to the right side. When the assembly is at the left, the ejection and bubbling to the left. The initial small assembly is born stochastically at the right or left side in the potential, evolves there, and undergoes ejection and bubbling. Reproduced with permission of ref. [64]. Copyright 2019 American Chemical Society.

behavior is first induced depends on their threshold. In the case of OTES-Silica NPs-(100→130, 150, and 450), ablation is induced earlier than the ejection is. The opposite behaviour is observed for OTES-Silica NPs-(50→130). The bubble formation is well known in laser ablation studies, however, its directionality with respect to the laser polarization has never been reported as far as we know. We consider that the pushing force exerted on the ablated assembly is responsible to the bubbling direction. Indeed, we find alternatively ejected bubbles by a dual objective lens between the focal plane and upper solution surface as in Figure 15(c).

## 8. Summary and Perspective

What is the main difference of laser trapping between CW and pulsed lasers is one of the general questions, and physicists and optical scientists have answered it theoretically and demonstrated typical behaviors of micrometer-sized targets.<sup>[76]</sup> It is considered from chemical viewpoints that the pulsed laser-induced trapping behaviors of molecules, polymers, supramolecules, DNAs, biopolymers, semiconductor quantum dots, and NPs are diverse and depend on material properties. We have studied silica and PS NPs as representative example in this size domain by utilizing fs laser. Various features of the NPs trapping are interpreted in terms of evolving processes of trapping, ejection, and bubbling in the pulse optical potential. The key point of our understanding is that NPs are confined in the optical potential and associated as a single assembly. As its size becomes larger, the scattering force overcomes the gradient force, leading to ejection of the assembly. Simultaneously the multiphoton absorption of the trapping laser is more probably induced, resulting in ablation and bubbling. We explain the perpendicular direction of ejection and bubbling with respect to laser polarization by theoretically considering the temporal change of optical force map. In addition, its alternative behavior of switching direction is ascribed to stochastic nature of the assembling growth in the pulse optical potential.

The importance of NPs assembling by optical force was first demonstrated for CW laser trapping at solution surface and solution/glass interface. The initially trapped NPs in the optical potential form an assembly and scatter the trapping laser to the outside. Consequently, the trapping laser is scattered and propagated through the assembled NPs, generating attractive potential at the edge of the assembly. The NPs coming from the outside are trapped there, leading to the expansion of the assembly, which we call optically evolved assembling.<sup>[52,56]</sup> The assembling and rearrangement of NPs are driven by optical force, which is made possible by CW laser.<sup>[77]</sup> It will be fruitful to study these processes at solution surfaces by femtosecond laser. How the characteristic features of NPs



trapping by the pulsed optical force will be modified and enhanced at solution surface or completely new phenomena will be clarified? This will be one interesting topic following the present Review.

The assembly formation of NPs by femtosecond laser in single NPs level is studied by Goswami et al. They manipulated dye-doped 250 nm PS NPs and constructed a specific 3D geometry,<sup>[78,79]</sup> where two-photon fluorescence is used for tracking the movement of individual NPs and for analyzing their geometry.<sup>[80]</sup> Even hierarchical self-assembly was demonstrated and discussed,<sup>[81]</sup> which will be a useful reference for fabricating the assembly as the bottom-up approach. They reported that not only optical trapping potential shape but also the assembly of NPs can be controlled by femtosecond laser polarization. Their approach will be integrated with our study on many NPs systems, and the complex behavior here will be understandable by correlating to individual construction toward the formation of a big assembly.

It is well known that the enhancement of optical force is achieved with optical resonance effect. The trapping laser wavelength is matched to electronic transition of molecules and NPs in the trapping target,<sup>[82,83]</sup> and optical stiffness and trapping time are measured. Usually it is mainly studied by CW laser trapping in solution, but its extension to pulsed laser trapping is being performed. As multiphoton absorption is made possible, multiphoton resonance effect is easily induced. We mention here our results as examples. Picosecond 1064 nm laser was applied as a trapping light source and the number of the trapped NPs is confirmed to increase when the laser wavelength matches well with absorption of the doped dye.<sup>[66,68]</sup> In the case of CdTe quantum dots the luminescence intensity was measured as a function of laser power.<sup>[84]</sup> The trapping efficiency is enhanced, while its quantitative examination is not easy. The number of the trapped quantum dots increases nonlinearly with the laser power for pulsed lasers, two-photon resonance effect is in principle shows the square dependence, and produced excited states linearly absorbs the trapping laser. Thus, the intensity dependence is expected to be super-linear, but the saturation effect in the dependence was observed for CdTe quantum dots.<sup>[85]</sup> It may be promising to study resonance effect in individual NPs level and to compare the experimental results with theoretical simulation, which is carried out for CW laser trapping.<sup>[83]</sup>

Technical trend in optical trapping study should involve various microscope techniques. Single molecular fluorescence microscope and super-resolution analysis enables us to extend the dynamics and mechanism study with real nanometer resolution.<sup>[9,10]</sup> Multiplane microscope shows the three-dimensional information on optical trapping dynamics as mentioned above.<sup>[86]</sup> Dynamic differential microscope will be useful to two-dimensionally elucidate the assembling dynamics, as optical trapping affects up to a few tens micrometer at solution

surfaces. The combination of pulsed lasers with these modern microscopes will open a new field of spatio-temporal control of optical trapping.

Optical trapping study of molecules and NPs is now regarded as one of the advanced studies on physical chemistry<sup>[56]</sup> and nanophotonics. Indeed, not only fundamental studies on dynamics and mechanism but also potential application is now being extended by CW laser trapping. Halide perovskites receive much attention as a new class of semiconductor materials for next generation opto-electronic devices.<sup>[87,88]</sup> Their crystallization and in-situ functional modification are demonstrated. Aggregation-induced emission enhancement (AIEE) of molecules is due to their concentration increase, which is now performed by laser trapping. Namely spatio-temporal control of AIEE is reported for a representative molecule, a tetraphenylethene derivative.<sup>[59]</sup> Another chemical application is on photoreactive supramolecules which forms gels through self-assembly of molecules with multiple non-covalent weak interactions such as hydrogen bonding, dipole-dipole interactions, van der Waals force, and solute-solvent interactions.<sup>[58]</sup> As optical trapping potential is comparable to those interactions, the gel formation can be controlled by optical force. These behaviors are demonstrated at solution surface by CW laser, while the introduction of fs laser is expected to develop these and related applications further.

The high peak intensity of femtosecond laser enables multiphoton excitation and the produced excited state density is extremely high, leading to ablation. In our study reported here the laser power of 100 MW/cm<sup>2</sup> is irradiated to the focal area of about 1  $\mu\text{m}^2$ , so that laser ablation is easily induced if the targets have some absorption at the wavelength. Even multiphoton absorption can induce laser ablation, which is the cases we have described here. It is usually considered that ablation and trapping are in the relation of trade-off, however, we have confirmed a clear example where assembling and ejection develop to ablation, keeping the alternatively switched directionality of the ejection in ablation. This will be a new methodology to control spatio-temporal characteristic of ablation. Until now the controllability of sequential trapping and ablation are demonstrated by changing the target material, while tuning optical parameters and applying different laser modes like Laguerre-Gaussian will make it more controllable, which will be very useful for future material fabrication.

### Acknowledgements

This work is supported by Ministry of Science and Technology, Taiwan (grant No. MOST 109-2634-F-009-028) and the Center for Emergent Functional Matter Science of National Chiao Tung University from The Featured Areas Research



Center Program within the framework of the Higher Education Sprout Project by the Ministry of Education (MOE) in Taiwan. Thanks are also due to funding by Ministry of Science and Technology (MOST) of Taiwan (MOST 108-2113-M-009-015- and 109-2113-M-009-022- to H.M. and MOST 108-2112-M-009-008- to T.K.). W.-Y. C. acknowledges the funding supports from the Ministry of Science and Technology (MOST) in Taiwan (MOST 107-2113-M-009-013-), the financial support from NCTU through the scholarship of 2016 Global Networking Talent Program, and the KU Leuven research council through the IDO program (interdisciplinary research IDO/13/008) for a personal grant.

## References

- [1] T. H. Maiman, *Nature* **1960**, *187*, 493.
- [2] C. B. Moore, *Annu. Rev. Phys. Chem.* **1971**, *22*, 387.
- [3] J. R. Novak, M. W. Windsor, *J. Chem. Phys.* **1967**, *47*, 3075.
- [4] W. G. Eisert, E. O. Degenkolb, L. J. Noe, P. M. Rentzepis, *Biophys. J.* **1979**, *25*, 455.
- [5] E. D. Potter, J. L. Herek, S. Pedersen, Q. Liu, A. H. Zewail, *Nature* **1992**, *355*, 66.
- [6] H. Niikura, F. Légaré, R. Hasbani, M. Y. Ivanov, D. M. Villeneuve, P. B. Corkum, *Nature* **2003**, *421*, 826.
- [7] R. Rigler, M. Orrit, T. Basché, *Single Molecule Spectroscopy*, Springer-Verlag Berlin Heidelberg, Berlin, Heidelberg, **2001**.
- [8] W. E. Moerner, *J. Phys. Chem. B* **2002**, *106*, 910.
- [9] M. Sauer, J. Hofkens, J. Enderlein, *Handbook of Fluorescence Spectroscopy and Imaging: From Single Molecules to Ensembles*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, **2011**.
- [10] D. K. Tiwari, Y. Arai, M. Yamanaka, T. Matsuda, M. Agetsuma, M. Nakano, K. Fujita, T. Nagai, *Nat. Methods* **2015**, *12*, 515.
- [11] A. Ashkin, J. M. Dziedzic, J. E. Bjorkholm, S. Chu, *Opt. Lett.* **1986**, *11*, 288–290.
- [12] P. N. Lebedev, *Ann. Phys.* **1901**, *6*, 433.
- [13] D. G. Grier, *Nature* **2003**, *424*, 810.
- [14] K. C. Neuman, S. M. Block, *Rev. Sci. Instrum.* **2004**, *75*, 2787.
- [15] J. R. Moffitt, Y. R. Chemla, S. B. Smith, C. Bustamante, *Annu. Rev. Biochem.* **2008**, *77*, 205.
- [16] K. Dholakia, P. Reece, M. Gu, *Chem. Soc. Rev.* **2008**, *37*, 42.
- [17] M. L. Juan, M. Righini, R. Quidant, *Nat. Photonics* **2011**, *5*, 349.
- [18] T. Sugiyama, K. Yuyama, H. Masuhara, *Acc. Chem. Res.* **2012**, *45*, 1446.
- [19] O. M. Maragò, P. H. Jones, P. G. Gucciardi, G. Volpe, A. C. Ferrari, *Nat. Nanotechnol.* **2013**, *8*, 807.
- [20] A. Lehmuskero, P. Johansson, H. Rubinsztein-Dunlop, L. Tong, M. Käll, *ACS Nano* **2015**, *9*, 3453.
- [21] M. Daly, M. Sergides, S. Nic Chormaic, *Laser Photonics Rev.* **2015**, *9*, 309.
- [22] S. E. S. Spesvytseva, K. Dholakia, *ACS Photonics* **2016**, *3*, 719.
- [23] D. S. Bradshaw, D. L. Andrews, *Eur. J. Phys.* **2017**, *38*, 034008.
- [24] C. Bradac, *Adv. Opt. Mater.* **2018**, *6*, 1800005.
- [25] P. Zemánek, G. Volpe, A. Jonáš, O. Brzobohatý, *Adv. Opt. Photonics* **2019**, *11*, 678.
- [26] A. Ashkin, J. M. Dziedzic, *Science* **1987**, *235*, 1517.
- [27] A. Ashkin, J. M. Dziedzic, T. Yamane, *Nature* **1987**, *330*, 769.
- [28] S. B. Smith, Y. Cui, C. Bustamante, *Science* **1996**, *271*, 795.
- [29] Y. Tsuboi, T. Shoji, N. Kitamura, *J. Phys. Chem. C* **2010**, *114*, 5589.
- [30] Y. Tanaka, H. Voshikawa, H. Masuhara, *J. Phys. Chem. B* **2006**, *110*, 17906.
- [31] A. Mototsuji, T. Shoji, Y. Wakisaka, K. Murakoshi, H. Yao, Y. Tsuboi, *Opt. Express* **2017**, *25*, 13625.
- [32] P. Borowicz, J.-I. Hotta, K. Sasaki, H. Masuhara, *J. Phys. Chem. B* **1998**, *102*, 1896.
- [33] T. A. Smith, J.-I. Hotta, K. Sasaki, H. Masuhara, Y. Itoh, *J. Phys. Chem. B* **1999**, *103*, 1660.
- [34] S. Masuo, H. Yoshikawa, H.-G. Nothofer, A. C. Grimsdale, U. Scherf, K. Müllen, H. Masuhara, *J. Phys. Chem. B* **2005**, *109*, 6917.
- [35] S. Katsura, K. Hirano, Y. Matsuzawa, A. Mizuno, K. Yoshikawa, *Nucleic Acids Res.* **1998**, *26*, 4943.
- [36] J.-I. Hotta, K. Sasaki, H. Masuhara, *J. Am. Chem. Soc.* **1996**, *118*, 11968.
- [37] S. Tan, H. A. Lopez, C. W. Cai, Y. Zhang, *Nano Lett.* **2004**, *4*, 1415.
- [38] T. Rodgers, S. Shoji, Z. Sekkat, S. Kawata, *Phys. Rev. Lett.* **2008**, *101*, 127402.
- [39] L. Jauffred, L. B. Oddershede, *Nano Lett.* **2010**, *10*, 1927.
- [40] P. J. Pauzauskie, A. Radenovic, E. Trepagnier, H. Shroff, P. Yang, J. Liphardt, *Nat. Mater.* **2006**, *5*, 97.
- [41] Z. Yan, M. Pelton, L. Vigdeman, E. R. Zubarev, N. F. Scherer, *ACS Nano* **2013**, *7*, 8794.
- [42] C. Hosokawa, H. Yoshikawa, H. Masuhara, *Phys. Rev. E* **2005**, *72*, 021408.
- [43] A. Ohlinger, S. Nedev, A. A. Lutich, J. Feldmann, *Nano Lett.* **2011**, *11*, 1770.
- [44] K. Sasaki, M. Koshioka, H. Misawa, N. Kitamura, H. Masuhara, *Appl. Phys. Lett.* **1992**, *60*, 807.
- [45] H.-B. Kim, M. Hayashi, K. Nakatani, N. Kitamura, K. Sasaki, J.-I. Hotta, H. Masuhara, *Anal. Chem.* **1996**, *68*, 409.
- [46] N. Tamai, T. Asahi, H. Masuhara, *Rev. Sci. Instrum.* **1993**, *64*, 2496.
- [47] K. Nakatani, T. Uchida, S. Funakura, A. Sekiguchi, H. Misawa, N. Kitamura, H. Masuhara, *Chem. Lett.* **1993**, *22*, 717.
- [48] H. Misawa, M. Koshioka, K. Sasaki, N. Kitamura, H. Masuhara, *J. Appl. Phys.* **1991**, *70*, 3829.
- [49] S. Ito, Y. Tanaka, H. Yoshikawa, Y. Ishibashi, H. Miyasaka, H. Masuhara, *J. Am. Chem. Soc.* **2011**, *133*, 14472.
- [50] A. Ashkin, *Proc. Natl. Acad. Sci. USA* **1997**, *94*, 4853.
- [51] A. Ashkin, *IEEE J. Sel. Top. Quantum Elec.* **2000**, *6*, 841.
- [52] S.-F. Wang, T. Kudo, K. Yuyama, T. Sugiyama, H. Masuhara, *Langmuir* **2016**, *32*, 12488.
- [53] T. Kudo, S.-F. Wang, K. Yuyama, H. Masuhara, *Nano Lett.* **2016**, *16*, 3058.

- [54] C.-H. Huang, T. Kudo, R. Bresolí-Obach, J. Hofkens, T. Sugiyama, H. Masuhara, *Opt. Express* **2020**, 28, 27735.
- [55] I. Aibara, C.-H. Huang, T. Kudo, R. Bresolí-Obach, J. Hofkens, A. Furube, H. Masuhara, *J. Phys. Chem. C* **2020**, 124, 16604.
- [56] H. Masuhara, K.-I. Yuyama, *Annu. Rev. Phys. Chem.* **2021**, in press.
- [57] M. J. Islam, M. Shahjahan, K.-I. Yuyama, V. Biju, *ACS Materials Lett.* **2020**, 2, 403.
- [58] K.-I. Yuyama, L. Marcelis, P.-M. Su, W.-S. Chung, H. Masuhara, *Langmuir* **2017**, 33, 755.
- [59] S. Wang, J. Lin, F. Ishiwari, T. Fukushima, H. Masuhara, T. Sugiyama, *Angew. Chem. Int. Ed.* **2020**, 59, 7063.
- [60] H. Masuhara, *Bull. Chem. Soc. Jpn.* **2013**, 86, 755.
- [61] A. Usman, W.-Y. Chiang, H. Masuhara, *J. Photochem. Photobiol. A* **2012**, 234, 83.
- [62] W.-Y. Chiang, A. Usman, H. Masuhara, *J. Phys. Chem. C* **2013**, 117, 19182.
- [63] M. Muramatsu, T.-F. Shen, W.-Y. Chiang, A. Usman, H. Masuhara, *J. Phys. Chem. C* **2016**, 120, 5251.
- [64] W.-Y. Chiang, J. J.-K. Chen, A. Usman, T. Kudo, K. Xia, J. Su, T. Sugiyama, J. Hofkens, H. Masuhara, *J. Phys. Chem. C* **2019**, 123, 27823.
- [65] W.-Y. Chiang, A. Usman, T. Sugiyama, J. Hofkens, H. Masuhara, *J. Phys. Chem. C* **2018**, 122, 13233.
- [66] A. Kittiravechote, W.-Y. Chiang, A. Usman, I. Liao, H. Masuhara, *Laser Phys. Lett.* **2014**, 11, 076001.
- [67] A. Usman, W.-Y. Chiang, H. Masuhara, *Sci. Prog.* **2013**, 96, 1.
- [68] A. Kittiravechote, A. Usman, H. Masuhara, I. Liao, *RSC Adv.* **2017**, 7, 42606.
- [69] H. Felgner, O. Müller, M. Schliwa, *Appl. Opt.* **1995**, 34, 977.
- [70] A. Ashkin, *Biophys. J.* **1992**, 61, 569.
- [71] P.-O. Gendron, F. Avaltroni, K. J. Wilkinson, *J. Fluoresc.* **2008**, 18, 1093.
- [72] L.-G. Wang, C.-L. Zhao, *Opt. Express* **2007**, 15, 10615.
- [73] L. Novotny, B. Hecht, *Principles of Nano-Optics*, Cambridge University Press, **2006**.
- [74] K. Sasaki, M. Tsukima, H. Masuhara, *Appl. Phys. Lett.* **1997**, 71, 37.
- [75] T. Uwada, T. Sugiyama, H. Masuhara, *J. Photochem. Photobiol. A* **2011**, 221, 187.
- [76] J. C. Shane, M. Mazilu, W. M. Lee, K. Dholakia, *Opt. Express* **2010**, 18, 7554.
- [77] J.-S. Lu, T. Kudo, B. Louis, R. Bresolí-Obach, I. G. Scheblykin, J. Hofkens, H. Masuhara, *J. Phys. Chem. C* **2020**, 124, 27107.
- [78] D. Mondal, S. Dinda, S. N. Bandyopadhyay, D. Goswami, *Sci. Rep.* **2019**, 9, 700.
- [79] D. Roy, D. Mondal, D. Goswami, *Sci. Rep.* **2016**, 6, 23318.
- [80] D. Mondal, D. Goswami, *Methods Appl. Fluoresc.* **2016**, 4, 044004.
- [81] D. Mondal, S. N. Bandyopadhyay, D. Goswami, *PLoS One* **2019**, 14, e0223688.
- [82] T. Kudo, H. Ishihara, *Phys. Rev. Lett.* **2012**, 109, 087402.
- [83] T. Kudo, H. Ishihara, H. Masuhara, *Opt. Express* **2017**, 25, 4664.
- [84] L. Pan, A. Ishikawa, N. Tamai, *Phys. Rev. B* **2007**, 75, 161305.
- [85] W.-Y. Chiang, T. Okuhata, A. Usman, N. Tamai, H. Masuhara, *J. Phys. Chem. B* **2014**, 118, 14010.
- [86] B. Louis, R. Camacho, R. Bresolí-Obach, S. Abakumov, J. Vandaele, T. Kudo, H. Masuhara, I. G. Scheblykin, J. Hofkens, S. Rocha, *Opt. Express* **2020**, 28, 28671.
- [87] K. Yuyama, M. J. Islam, K. Takahashi, T. Nakamura, V. Biju, *Angew. Chem.* **2018**, 130, 13612.
- [88] M. J. Islam, K. Yuyama, K. Takahashi, T. Nakamura, K. Konishi, V. Biju, *NPG Asia Mater.* **2019**, 11, 31

Manuscript received: January 7, 2021

Revised manuscript received: February 23, 2021

Version of record online: March 4, 2021



Chair Professor Hiroshi MASUHARA  
Department of Applied Chemistry  
Center for Emergent Functional Matter Science  
National Yang Ming Chiao Tung University  
Ta Shueh Road 1001, Hsinchu City 30010, Taiwan

増原 宏  
講座教授、工学博士  
国立陽明交通大學 理学院応用化学系  
国立陽明交通大學 新世代功能性物質研究中心  
〒30010 台湾新竹市大學路 1001  
masuhara@masuhara.jp  
<https://masuhara.lab.nycu.edu.tw/>  
<http://www.masuhara.jp/>  
+886-(0)983-811-798