International Collaboration on Optically Evolving Assembling at Solution Interface

DAC/COS Hiroshi Masuhara

Optical trapping of small objects by a focused laser beam receives much attention in physics and bio-science since 2018 when A. Ashkin was awarded the Nobel Prize in Physics. We started optical trapping study in chemistry in 1988 and, in NYCU, we have been exploring new chemical phenomena, elucidating their dynamics and mechanism, and developing innovative optical methods fabricating particles, proteins, and biomolecules for the past 14 years. The representative results are on nanoparticle assembling, molecular crystallization, amyloid fibril formation, AIEE (aggregation-induced emission enhancement), and so on. Most of these phenomena are achieved at solution interfaces and based on the common mechanism which we have proposed as "Optically Evolved Assembling". Trapping laser focused at 1 micrometer volume is scattered, reflected, propagated, and interfered through gathered small objects and expands optical potential, forming molecular and nanoparticle assemblies with the size of 10 micrometer to submillimeter. Our study is paving a new way to manipulate and fabricate soft matters, and we are carrying out international collaboration with Japan, Belgium, Spain, and Sweden. Here we report the collaboration research with Katholieke Universiteit Leuven (KUL) in Belgium which is supported by the bilateral funding.

The collaboration aims to develop a new optical methodology to assemble and fabricate various nanomaterials at interfaces, and is strengthening the scientific and formative long-term relation between NCTU and KUL. Several research stays are planned (including one double degree PhD student in an international context (other collaborators from Spain and Japan).

<u>Bilateral Funding</u>

This collaboration was started in 2018 and is formally supported by MOST and FWO (Belgian funding agency) bilateral project for 2021-2022. Dr. Roger Bresoli-Obach of KUL stayed for 6 months in our laboratory as Visiting Assistant Research Fellow (2020.Feb. – 2020.Jan). Hiroshi Masuhara staryed in KUL for 2 weeks in 2019.

<u>Students Performing Experiments:</u>

2018.05.05-2018.05.27, KUDO in KUL
2018.10.01-2018.12.09, Chih-Hao HUANG in KUL
2019.05.06-2019.06.07, Ian LU in KUL
2019.07.01-2019.09.02, Chih-Hao HUANG in KUL
2019.07.22-2019.07.28, Abdullah Kamit in KUL
2021.10.01-2021.12.15, Po-Wei Yi in KUL
2021.10.01-2021.12.15, Yu-Chia Chang in KUL

<u>Organizing Workshops on COODy-Nano (Collective Optofluidic Dynamics on Nano Materials)</u>

2018.10.05-2018.10.06, 1st in San Sebastian, Spain
2019.05.30-2019.05.31, 2nd in Leuven, Belgium
2019.11.14-2019.11.15, 3rd in Kobe, Japan
2020.11.27-2020.11.28, 4th in Hsinchu, Taiwan (Postponed because of the Covid-19)

Mechanism of Optically Evolved Assembling

1. <u>Photon momentum dictates the shape of assembling and swarming gold nanoparticles (Supplemental cover of J. Phys. Chem. C)</u>

Optical trapping at interfaces assists the gathering and assembling of particles, inducing the optically evolved assembling, that can expand outside the laser focus due to a multiple scattering process. In previous works, we described that the Au nanoparticles dynamic evolved assembly has a dumbbell morphology, where the Au nanoparticles fluctuate as a group like a swarm of bees. The shape and the size of such assembly can be controlled from a chemical point of view, considering the intrinsic surface plasmon resonance properties of Au nanoparticles. However, we focus on the optical condition as an alternative approach for controlling its morphology. Strikingly, we observe two new states with ellipse and ring distribution morphologies by shifting the axial position of the trapping laser focus. Indeed, we can modify the morphology of such unique assembly by displacing the dynamic equilibrium between the different "optically evolved assembly" states. Moreover, the morphology of the dumbbell state can be further controlled by the incident and the focusing angles of the trapping laser. The results are elucidated in terms of the overwhelming scattering force that arises from the momentum transfer between photons and Au nanoparticles. We show the importance of the momentum direction of incident photons, establishing the critical steps to comprehensively control the "optical evolved assembling" phenomena, which has a large potential in other research fields such as soft mater or colloidal chemistry.

2. <u>Optical assembling, ejection and rea-arangement of microparticles (Figure 1)</u>

Optical trapping and assembling dynamics of polystyrene (PS) microparticles (MPs) of 1 µm diameter is studied at its solution-air surface using a widefield microscope. Upon switching on the intense 1064 nm laser, the MPs are gathered, forming a single concentric circle (CC)-like assembly larger than the focus. It consists of a few tens of MPs and the central part of the assembly shows structural color, which indicates that the assembly is also growing in the axial direction. The MPs are dynamically fluctuating in ~~inside~~ the assembly, and some of them are ejected when newly coming MPs collide with the CC-like assembly from the bulk solution. The MPs speedily leaving the assembly are aligned in a linear manner, which we refer to as "pistole-like ejection". The three-dimensional (3D) dynamics was elucidated by changing laser power, MP concentration, and surface chemical property. It is directly observed that the trapping laser was scattered radially from the CC-like assembly and the ejection was induced along the scattered laser path. This pistol-like ejection is stochastically repeated upon the collision. After prolonged irradiation, the assembly rearranges to a hexagonal close packing (HCP)-like assembly, in which no pistol-like ejection was observed. We note that our observation is characteristic of the solution surface and were never observed in bulk solution. We conclude that the kinetically driven assembly formation gives rise to a CC-like structure which is meta-stable and shows the pistol-like ejection phenomenon. Later, the assembly rearranges to a thermodynamically stable HCP-like assembly. The assembling, pistol-like ejection, and its rearrangement are all driven by optical force, which is common for optical trapping-induced molecular crystallization and optically evolved assembling and swarming of gold nanoparticles (NPs).

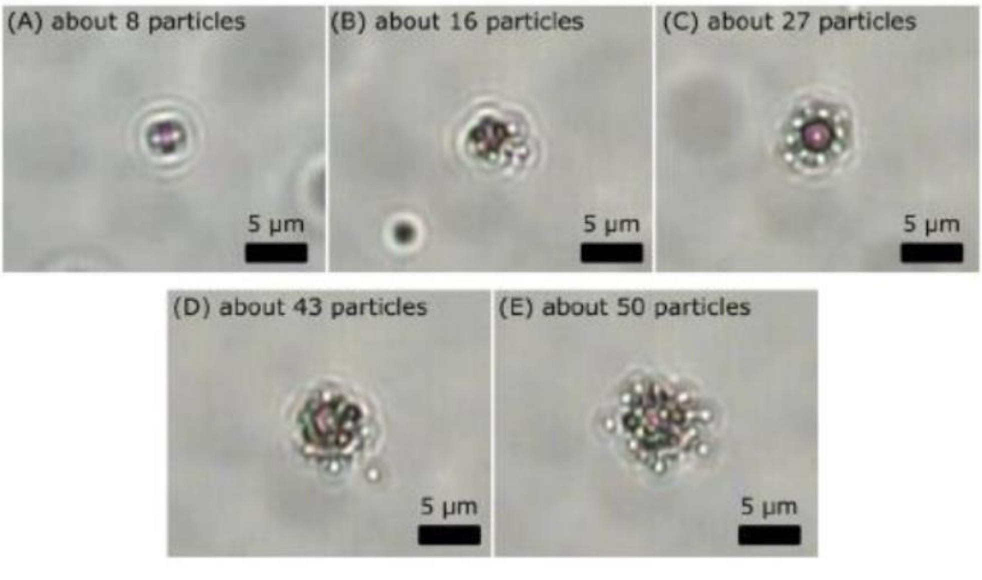


Figure 1. Optical assembling of polystyrene microparticles where individually trapped particles are counted leading to a new assembly.

Application of Optically Evolved Assembling

1. A single sub-millimeter assembly of protein by optical trapping (Figure 2)

Optical trapping of dielectric and metal particles yields different types of "optically evolving assembly" at air/solution and glass/solution interfaces. However, all these structures are in common that the trapping laser is scattered and propagated through the assembly, expanding from the focus up to a few tens of micrometers. We fabricate a single sub-millimeter linear assembly of polystyrene microparticles starting from the surface of a concentrated lysozyme D_2O solution. Such assembly has a three-dimensional linear structure composed by a single microparticle aggregate without folding and bending. Indeed, it is prepared along the lysozyme assembly which is also generated by optical trapping. The cooperative trapping of the microparticle and lysozyme did not arrange as a homogeneously distributed assembly. Instead a unique anomalously long assembly of microparticles and a densely, widely, and deeply expanded lysozyme layer were simultaneously prepared. Their morphology was reconstructed by shifting the imaging plane immediately after switching off the trapping laser. Independently, the lysozyme assembly was also confirmed by fluorescence imaging and Raman scattering spectroscopy. Thus, we consider that the described cooperative "optically evolved assembling" has a large potential to fabricate hybrid materials with applications in different fields such as colloid science, protein chemistry, and soft matter.

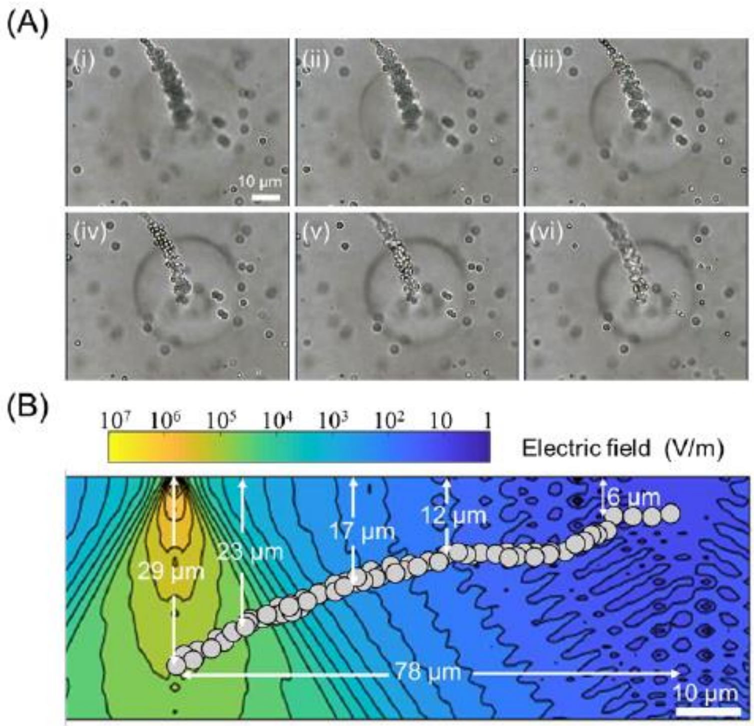
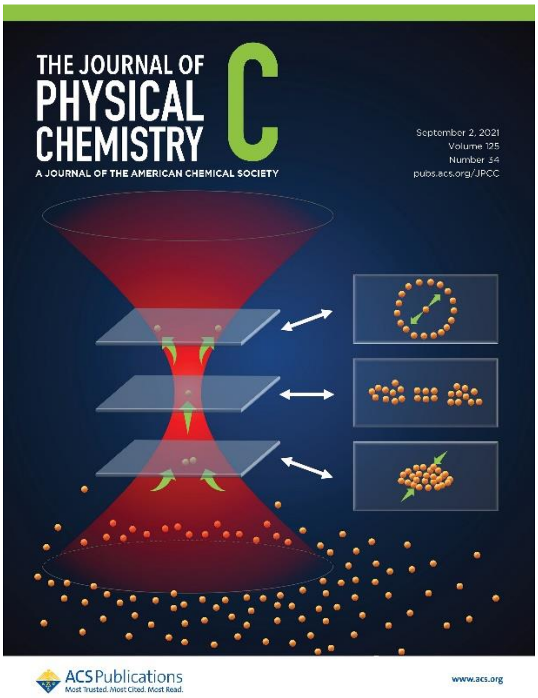


Figure 2. Optical trapping of lysozyme at solution surface, which is monitored by cooperatively trapped polystyrene microparticles.

2. Control of local phase separation of polymer solution (Cover of J. Phys. Chem. C)

Optical trapping of gold nanoparticles (Au NPs) at a glass/solution interface initially generates a periodically aligned structure of a few NPs along the direction perpendicular to linearly polarized laser. When the number of NPs was increased, this alignment was expanded to the outside of the irradiated focus, forming a single large assembly where the Au NPs dynamically fluctuated like a swarming of bees. The morphology was dumbbell-shape, consisting of two swarms at both sides of the focus, and its size reached about 10 μm. This optically evolved assembling and swarming was studied in poly(*N*-isopropylacrylamide) (PNIPAM) solution, where liquid-liquid phase separation (LLPS) was induced by photothermal heating of the trapped Au NPs forming a microdroplet of highly concentrated PNIPAM. Dynamic coupling of the NPs assembling and swarming with the droplet formation of PNIPAM leads to cooperative optical evolution, through which the assembly was embedded in the single microdroplet.



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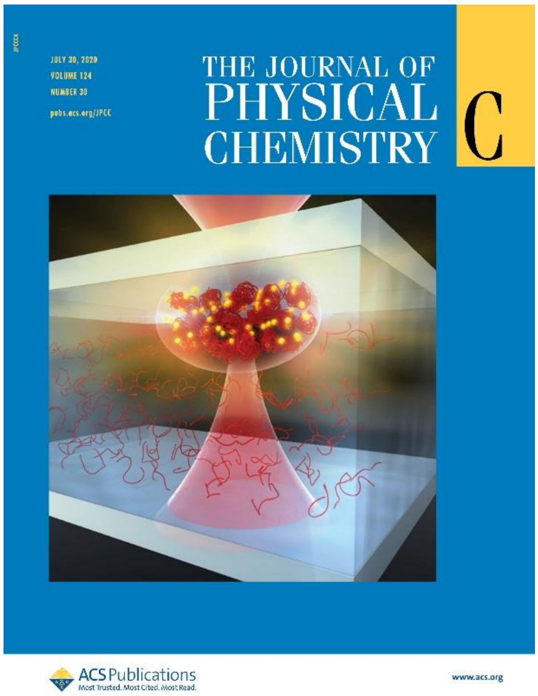

Cover of J. Phys. Chem. C.

Collaboration Articles

1. Chih-Hao Huang, Tetsuhiro Kudo, Teruki Sugiyama, Hiroshi Masuhara, Johan Hofkens, Roger Bresoli-Obach, "Photon Momentum Dictates the Shape of Swarming Gold Nanoparticles in Optical Trapping at an Interface", *The Journal of Physical Chemistry C,* (2021) Accepted
2. Po-Wei Yi, Wei-Hsiang Chiu, Tetsuhiro Kudo, Teruki Sugiyama, Roger Bresoli-Obach, Johan Hofkens, Eri Chatani, Ryohei Yasukuni, Yoichiroh Hosokawa, Shuichi Toyouchi, Hiroshi Masuhara, "Cooperative Optical Trapping of Polystyrene Microparticle and Protein Forming a Sub-millimeter Linear Assembly of Microparticle", *The Journal of Physical Chemistry C*, (2021), Accepted
3. Abdullah Kamit, Ching-Shiang Tseng, Tetsuhiro Kudo, Teruki Sugiyama, Johan Hofkens, Roger Bresoli-Obach, Hiroshi Masuhara, "Unravelling the 3D morphology and dynamics of the optically evolving polystyrene nanoparticle assembly using dual objective lens microscopy", *The Journal of Chinese Chemistry Society.*, (2021), Accepted
4. Roger Bresolí-Obach, Tetsuhiro Kudo, Boris Louis, Yu-Chia Chang, Ivan G. Scheblykin, Hiroshi Masuhara, and Johan Hofkens, "Resonantly Enhanced Optical Trapping of Single Dye-Doped Particles at an Interface", *ACS Photonics*, 8, 6, 1832–1839 (2021).

DOI:10.1021/acsphotonics.1c00438

5. Jia-Syun Lu, Tetsuhiro Kudo, Boris Louis, Roger Bresolí-Obach, Ivan G. Scheblykin, Johan Hofkens, and Hiroshi Masuhara,“Optical Force-Induced Dynamics of Assembling, Rearrangement, and Three-Dimensional Pistol-like Ejection of Microparticles at the Solution Surface”, *The Journal of Physical Chemistry C*, 124, 49, 27107–27117 (2020). DOI:10.1021/acs.jpcc.0c07735
6. Boris Louis, Rafael Camacho, Roger Bresolí-Obach, Sergey Abakumov, Johannes Vandaele, Testsuhiro Kudo, Hiroshi Masuhara, Ivan G. Scheblykin, Johan Hofkens, and Susana Rocha, “Fast-tracking of single emitters in large volumes with nanometer precision”, *Optics Express*, 28 (19), 28656-28671 (2020). DOI:10.1364/OE.401557
7. Chih-Hao Huang, Tetsuhiro Kudo, Roger Bresolí-Obach, Johan Hofkens, Teruki Sugiyama, and Hiroshi Masuhara, “Surface plasmon resonance effect on laser trapping and swarming of gold nanoparticles at an interface”*Optics Express*, 28 (19), 27727-27735 (2020). DOI:10.1364/OE.401158
8. Aibara, I.; Hunag, C.-H.; Kudo, T.; Bresoli-Obach, R.; Hofkens, J.; Furbe, A.; Masuhara, H. “Dynamic Coupling of Optically Evolved Assembling and Swarming of Gold Nanoparticles with Photothermal Local Phase Separation of Polymer Solution”, *The Journal of Physical Chemistry C*, 124, 30, 16604–16615(2020).