Opto-thermophoretic assembly of colloidal matter

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Colloidal matter exhibits unique collective behaviors beyond what occurs at single-nanoparticle and atomic scales. Treating colloidal particles as building blocks, researchers are exploiting new strategies to rationally organize colloidal particles into complex structures for new functions and devices. Despite tremendous progress in directed assembly and self-assembly, a truly versatile assembly technique without specific functionalization of the colloidal particles remains elusive. We develop a new strategy to assemble colloidal matter under a light-controlled temperature field, which can solve challenges in the existing assembly techniques. By adding an anionic surfactant (that is, cetyltrimethylammonium chloride), which serves as a surface charge source, a macro ion, and a micellar depletant, we generate a light-controlled thermoelectric field to manipulate colloidal atoms and a depletion attraction force to assemble the colloidal atoms into two-dimensional (2D) colloidal matter. The general applicability of this opto-thermophoretic assembly (OTA) strategy allows us to build colloidal matter of diverse colloidal sizes (from subwavelength scale to micrometer scale) and materials (polymeric, dielectric, and metallic colloids) with versatile configurations and tunable bonding strengths and lengths. We further demonstrate that the incorporation of the thermoelectric field into the optical radiation force can achieve 3D reconfiguration of the colloidal matter. The OTA strategy releases the rigorous design rules required in the existing assembly techniques and enriches the structural complexity in colloidal matter, which will open a new window of opportunities for basic research on matter organization, advanced material design, and applications.

INTRODUCTION

Colloidal particles exhibit collective behaviors beyond their individual properties when the particles are built into colloidal matter (1). For example, colloidal matter, which consists of particles with sizes comparable to or below optical wavelength, has been explored as photonic crystals and meta-materials with unique properties such as optical bandgap and negative refractive index. Rationally designed assemblies of colloidal atoms, such as plasmonic superstructures (2, 3), Janus particle clusters (4–7), and chiral clusters (8), feature various emerging physical and chemical performances. However, challenges in the precise engineering of attractive interactions to induce bonding between colloidal atoms have limited the construction of colloidal matter of any desired properties. Both intrinsic interparticle attractive force and external attractive force have been exploited in current techniques for colloidal bonding. The former includes electrostatic attraction (9) and hydrophobic attraction (4, 10, 11). The latter includes depletion attractive interaction by mixing colloidal atoms with nonadsorbed polymers or small particles (12). These techniques feature high throughput but with limited structural configurations. Much effort has been exerted to enrich the configurations of colloidal matter. For example, patchy colloids can achieve directional bonding to break symmetry in colloidal superstructures. Patchy colloids include colloidal atoms region-selectively modified with organic or biological molecules (for example, DNA) (13–20) and those with modified surface geometry (21, 22). Directed motion of active colloidal atoms under external fields, including electric fields (23, 24), magnetic fields (5, 8, 25), and electromagnetic fields (26, 27), has been further explored to achieve colloidal assembly in a controllable and programmable manner. However, manipulation via external fields is highly material-dependent and only works for colloidal particles with specific electric, magnetic, or optical properties, limiting its broader applications to general colloidal particles.

With an ever-increasing interest in enriching the structures of colloidal matter for new properties and in understanding the factors that determine its structures and dynamics, a versatile on-demand technique that can construct colloidal matter of arbitrary structures with colloidal atoms of a wide range of sizes, materials, and surface chemistry is highly desired. Developing such a technique will require progress in both colloidal manipulation and colloidal bonding. Optical tweezers have proved effective in colloidal manipulation (28). However, trapping and manipulation of nanoscale colloids and anisotropic particles with optical tweezers are challenging. Specifically, trapping of metal nanoparticles via optical tweezers requires even higher optical power because of the optical heating of trapped particles and possible light-particle coupling. Plasmonic tweezers can capture nanoscale particles using the plasmon-enhanced optical force but lack the capability to perform dynamic manipulation (29). We have also reported the reversible assembly of plasmonic nanoparticles using plasmon-enhanced thermophoresis, whereas the configuration of the assemblies was not controllable in building colloidal superstructures. To overcome the limitations of current methods, we developed a new strategy, termed opto-thermophoretic assembly (OTA), to manipulate and construct colloidal matter based on ionic depletants under a light-controlled temperature field. Because of its low-power operation, wide range of colloidal sizes and materials, and flexibility in orientation control of anisotropic particles, the OTA strategy allows a versatile assembly of colloidal matter with diverse compositions, configurations, and bonding lengths and strengths.

RESULTS

General concept of OTA

The general concept of OTA strategy is shown in Fig. 1. Colloidal atoms of different sizes and materials are dispersed in water (solvent), serving
as building blocks (Fig. 1A). The ionic surfactant cetyltrimethylammonium chloride (CTAC), whose concentration is above its critical micelle concentration ($c_{\text{cmc}}$; 0.13 to 0.16 mM), was added to the colloidal dispersion to enable controllable optothermal response of the colloidal atoms. The CTAC molecules adsorb onto the colloidal particles through electrostatic interaction and/or hydrophobic interaction to obtain positively charged surfaces (fig. S1), with the positive and hydrophilic head groups pointing to the solvent. Meanwhile, above $c_{\text{cmc}}$, surfactant molecules form positively charged micelles with a hard sphere radius (without consideration of the electrostatic interaction) of several nanometers (Fig. 1B). Although the micelles are much larger than common ions, their high charge density makes it possible for them to serve as “macro ions.” On the other hand, the micelles are significantly smaller than the colloidal atoms studied here, making them a natural choice as “micellar depletants.” To optically manipulate the colloidal atoms, we used a continuous-wave laser and an Au thin film (porous or continuous) as the optothermally responsive substrate to convert photon energy to thermal energy (Fig. 1C). Spatial separation of CTAC micelles and counterions creates a localized electric field to confine the colloidal atoms at the thermal hot spot. The colloidal atoms are further driven dynamically by steering the laser beam. The optical intensity that we typically use to manipulate colloidal atoms under a light-controlled thermoelectric field is $0.08 \text{ mW}/\mu \text{m}^2\text{ while the optical intensity that we typically use to manipulate colloidal atoms under a light-controlled thermoelectric field is } 0.08 \text{ mW}/\mu \text{m}^2 \text{ while the optical intensity that we typically use to manipulate colloidal atoms under a light-controlled thermoelectric field is } 0.08 \text{ mW}/\mu \text{m}^2$.

**Optical trapping and dynamic manipulation of colloidal atoms under a light-controlled thermoelectric field**

Under an externally controlled temperature gradient, colloidal particles (or molecules) will drift from hot to cold regions or from cold to hot regions, a process that is usually described as thermophoresis or the Soret effect. The drift velocity is given by $v_T = -D_T \nabla T$, where $D_T$ is the thermophoretic mobility and $\nabla T$ is the temperature gradient. At steady state, the concentration gradient of the colloidal particles is written as $\nabla c = -c S_T \nabla T$, where $c$ is the particle concentration and $S_T = D_T/D$ is the Soret coefficient ($D$ is the diffusion coefficient). One of the underlying physical mechanisms of thermophoresis is the thermoelectric effect (30–32). The different $S_T$ values of the positive and negative ions arising from their different sizes and solvation energies lead to the spatial separation of these ions under the temperature gradient, generating a thermoelectric field to drive the charged colloids along the temperature gradient.

Here, we demonstrate that the CTAC micelles can be used as positive macro ions to create a thermoelectric field for optical trapping of colloidal atoms. Figure 2A shows the working principle of optical trapping under a thermoelectric field. A green laser is directed from the bottom of a porous Au film for optical heating. The simulated temperature gradient along the $z$ axis irradiated by a laser beam, which is $2 \mu \text{m}$ in diameter and $0.253 \text{ mW}$ in optical power, is embedded in the scheme of Fig. 2A. A maximum temperature gradient of $-1.8 \times 10^3 \text{ K/m}$ is obtained. Under the temperature gradient, both the CTAC micelles and Cl$^-$ ions are driven to the cold region. By treating the CTAC micelles as macro ions, we calculate the thermoelectric field using the equation (32)

$$E_T = \frac{k_B T \nabla T}{e} \sum_i Z_i n_i S_{Ti}$$

where $k_B$ is the Boltzmann constant, $e$ is the elemental charge, $i$ is the ionic species (that is, CTAC micellar ions or Cl$^-$ ions), and $n_i$ and $S_{Ti}$ are the corresponding ionic concentration and Soret coefficient. The extremely small $S_T$ value of Cl$^-$ ions ($7.8 \times 10^{-4} \text{ 1/K}$) gives a positive sign of $\sum_i Z_i n_i S_{Ti}$. Thus, the electric field has the same direction as $\nabla T$ and points from cold to hot regions, which leads to the trapping of the positively charged colloidal atoms at the thermal hot spot. The trapping velocity of the colloidal particles can be calculated using the Helmholtz-Smoluchowski electrophoretic mobility $\varepsilon \zeta/\eta$ (33)

$$v = \varepsilon E_T \zeta/\eta$$

where $\varepsilon$ is the dielectric constant of the solvent, $\eta$ is the viscosity, and $\zeta$ is the $\zeta$ potential of the particles. To illustrate the role of the thermoelectric field in optical trapping, we carried out a control experiment using both anionic surfactant (that is, SDS) and nonionic surfactant (that is, Triton X-100). We observed the repelling of PS beads, instead of trapping by the laser beam, using 10 mM SDS. The use of Triton X-100 led to neither trapping nor repelling of the particles. Instead,

**Fig. 1. Schematic illustration of the concept of OTA. (A) Dispersion of colloidal atoms in solvents. (B) CTAC surfactants adsorbed on the surface of the colloidal particles form molecular double layers, generating a positive and hydrophilic surface. Meanwhile, the CTAC molecules self-assemble into CTAC micelles with high surface charge density. (C) Manipulation of the colloidal atoms with the light-directed dynamic temperature field, and bonding of the closely positioned colloidal atoms with depletion attraction. (D) Construction of colloidal atoms into one-dimensional (1D) and 2D assemblies.**
the particles illuminated by the laser beam went upward following the thermal convective flow, indicating the absence of the thermoelectric field (movie S1).

To demonstrate the parallel manipulation of colloidal atoms, we used a digital micromirror device (DMD) to generate and project multiple laser beams on the substrate to simultaneously capture and arrange PS beads with diameters of 2 and 0.96 μm in designed patterns, as shown in Fig. 2A. With the light-controlled temperature field, dynamic manipulation of the PS beads is achieved (see fig. S2 and movies S2 and S3). This provides the possibility of manipulating colloidal atoms in a programmable manner. Furthermore, we demonstrate the orientational control of nonspherical particles. We fabricated the anisotropic PS particles using microsphere lithography (see Materials and Methods and fig. S3 for details). We used the DMD to create a 1D optical image to trap and align the anisotropic PS particles (fig. S4). By rotating the 1D optical image, we have achieved the rotation of the anisotropic particles.

To further evaluate trapping capability, we trapped single colloidal particles using a laser beam and introduced a Stokes drag force to release the particles by setting a certain value for the moving velocity of the motorized sample stage. The critical velocity at which the maximum trapping force of the particle is balanced by the drag force is defined as escape velocity (see also Materials and Methods for details). It can be estimated using the equation

$$qE_T^{m} = 6\pi \eta a v_e \phi(h)$$

where $q$ is the surface charge of the particles, $E_T^{m}$ is the thermoelectric field at the maximum in-plane temperature gradient, $\eta$ is the viscosity of the solvent, $a$ is the radius of the particle, $v_e$ is the escape velocity, and $\phi(h)$ is the correction factor that accounts for the hydrodynamic boundary effect, which is a function of the particle-substrate distance $h$. The left term is the maximum trapping force in the thermoelectric field, and the right term is the fluidic drag force. Figure 2 (C to E) summarizes the measured escape velocities of the trapped PS beads as a function of optical intensity and CTAC concentration. An increase in optical intensity increases the escape velocity because of the increased temperature gradient $\nabla T$ (Fig. 2, C to E, purple lines). An increase in CTAC concentration increases the $\zeta$ potential of the PS beads but decreases the Soret coefficient of the CTAC micelles. The former increases the electrophoretic mobility of the colloidal atoms, whereas
the latter decreases the intensity of the electric field, leading to a maximum escape velocity of ~1 mM CTAC. Surprisingly, the escape velocity and trapping stability significantly increase when the size of the trapped particles is decreased, which is attributed to the increased temperature gradient around the smaller particles (fig. S5). Therefore, a light-controlled thermoelectric field can manipulate nanoscale particles at a much lower optical power than optical tweezers.

**Assembly of colloidal matter using OTA**

Accompanied by the manipulation of colloidal atoms, an attraction force between the colloidal atoms is induced to bond them together. The bonding mechanism is shown in Fig. 3A. Without any external energy, both the CTAC micelles and the colloidal atoms are dispersed in the solvent in their free forms. Spontaneous self-assembly of the colloidal atoms may occur if the depletants are driven outside the depletion region by thermal perturbations and entropy. However, the process of bonding and assembly is slow. When the laser beam illuminates two colloidal atoms (Fig. 3A, middle), laser heating causes thermophoresis. Under the temperature field, the CTAC micelles migrate to the cold region, and the colloidal atoms migrate to the hot region with a trapping force $F_T$. As a result, thermophoresis depletes the micelles at the particle-particle spacing with a depletion volume $V_{pp}$. The bonding mechanism is shown in Fig. 3A. Without any external energy, both the CTAC micelles and the colloidal atoms are dispersed in the solvent in their free forms. Spontaneous self-assembly of the colloidal atoms may occur if the depletants are driven outside the depletion region by thermal perturbations and entropy. However, the process of bonding and assembly is slow. When the laser beam illuminates two colloidal atoms (Fig. 3A, middle), laser heating causes thermophoresis. Under the temperature field, the CTAC micelles migrate to the cold region, and the colloidal atoms migrate to the hot region with a trapping force $F_T$. As a result, thermophoresis depletes the micelles at the particle-particle spacing with a depletion volume $V_{pp}$.

**Fig. 3. Physical principle of bonding in OTA.** (A) Schematics of the depletion attraction between two colloidal atoms, which is enhanced by the light-controlled temperature field. Middle: The green arrows indicate that thermophoresis drives the CTAC micelles from hot to cold regions. $F_T$ is the trapping force, $F_{adv}$ is the van der Waals force, and $F_e$ is the electrostatic repulsive force. Right: $V_{pp}^W(r)$ is the depletion volume, which is indicated with dashed circles, and $\Delta T$ is the osmotic pressure difference between the bulk region (cold region) and the depletion region (hot region). In all panels, the gray rings around the micelles indicate an effective depletion size. (B to D) Calculated interaction potential between two PS beads and optical images of colloidal superstructures of beads of different diameters: 2 μm (B), 0.96 μm (C), and 500 nm (D). In (C), the optical images (from left to right) are recorded, where the distances between the focus plane of the 100x objective (numerical aperture (NA), 0.9) and the substrate are 12.275, 13.125, and 13.950 μm, respectively. Scale bars, 5 μm (B) and 2 μm (C and D).
for the stability of the colloidal matter. At 10 mM, the 2D assembly can
influence the particle-particle interaction potential, should also be considered
when balance is achieved, the interaction potential after optical
photolysis remained after the laser was turned off. Because the micellar de-
pletion interaction measured by TIRM (see Materials and Methods for details) and fitted
theoretical models to the measurement results. The particle-particle
interaction of silica particles was obtained using the particle-particle
excluded volume term. The fitted parameters were used to calculate the particle-particle interaction potential of PS beads, which have
Hamaker constants and potentials similar to those of the silica
particles. The theoretical model has been proven to work for the micelle
deployment interaction measured by TIRM. The measurements
and models are detailed in note S1. We introduce the micelle-particle
electrostatic interaction with an effective micellar radius and the compressibility factor of the micelles with a depletion fraction to calculate
the interaction potential. The accuracy of the theoretical models was further verified by Monte Carlo simulations of the TIRM experiments, which
produced a quantitative agreement of both the interaction potentials and 2D crystallization behavior with the experimental results (note S1). This model only works when the size of the micellar depletants is significantly smaller than that of the colloidal atoms. In addition, we have also excluded other possible bonding mechanisms in CTAC surfactants, as discussed in note S2. The calculated results for PS beads of different sizes are summarized in Fig. 3 (B to D). A decreased minimum interaction potential occurs at a shorter bonding length when the CTAC concentration is increased, which increases the osmotic pressure difference \(\Delta \Pi\) and the ionic strength. This provides opportunities to tune the bonding length and bonding strength by changing the CTAC concentration. The thresholds of CTAC concentration for stable colloidal assemblies are 8, 15, and 40 mM for colloidal sizes of 2 \(\mu\)m, 0.96 \(\mu\)m, and 500 nm, respectively. For 2-\(\mu\)m PS beads (Fig. 3B), stable colloidal bonding occurs when the CTAC concentration is \(\sim 10 \text{mM}\). The bonding becomes stronger with a shorter bonding length when the CTAC concentration is further increased.

Using the light-controlled colloidal manipulation and bonding, we have demonstrated the construction of the thermodynamically stable, close-packed colloidal assembly of 2-\(\mu\)m PS beads in a 10 mM CTAC solution, as shown in the left panel of Fig. 3B. The assembly process via a single laser beam is demonstrated in movie S4. The colloidal structure remained after the laser was turned off. Because the micellar depletants cannot diffuse into the particle-particle gap, which is smaller than the effective sizes of the CTAC micelles, the depletion attraction interaction can be maintained when the temperature gradient disappears. When balance is achieved, the interaction potential after optical heating is the same as that without optical heating. The substrate-particle interaction potential, which is about two times higher than the particle-particle interaction potential, should also be considered for the stability of the colloidal matter. At 10 mM, the 2D assembly can be further manipulated by the light-controlled thermoelectric field.

For example, we used a single laser beam for translation of the 2D assembly and a 1D optical image to rotate the 2D assembly (movie S5). It is also possible to assemble a thermodynamically unstable colloidal structure. To improve the stability of the colloidal structures, we increased the CTAC concentration for stronger particle-particle and particle-substrate interactions. In the middle and right panels of Fig. 3B, we demonstrate the assembly of 2-\(\mu\)m PS beads into a 1D chain using a 1D optical image (see also fig. S6 and movie S6) and into a 2D chiral structure using a single beam (fig. S7), respectively.

As discussed in note S1, the interaction potential is highly dependent on the size of the colloidal atoms. For smaller PS beads (Fig. 3, C and D), the critical CTAC concentration for stable colloidal bonding is increased. We built a heptamer with 0.96-\(\mu\)m PS beads at a CTAC concentration of 20 mM. As shown in the right panels of Fig. 3C, the heptamer of colloidal atoms exhibits light transmission and focusing properties, where the observed color of transmitted light depends on the objective (or detector) location. The optical transmission characteristics of the heptamer arise from the interaction between the spherical PS beads, which can be treated as microlenses. In note S3, we decompose the recorded optical images with different color channels (blue, green, and red). When the substrate-objective distance is 12.275 \(\mu\)m, an enhanced transmission is observed in the blue channel, whereas no obvious enhanced transmission in the green channel and a suppressed transmission in the red channel are observed, which leads to a blue color in the optical image that is composed of all the three channels. When the substrate-objective distance is increased, the wavelength of the extracted light makes a red shift with an enhanced transmission in the green and red regions, leading to intense green and orange colors through the PS beads. The improved light extraction efficiency will find potential applications in photovoltaics and flat optics. To demonstrate the bonding between nanoscale colloidal atoms, we assembled 500-nm PS beads into various thermodynamically unstable colloidal superstructures in a 50 mM CTAC solution, as shown in the right panels of Fig. 3D.

To better understand the stability of colloidal superstructures, we built a heptamer with 2-\(\mu\)m PS beads in different CTAC concentrations and examined the time response after the laser was turned off, as shown in fig. S8. At a low CTAC concentration (below 5 mM), the colloidal structure changed at 9 s because the interaction potential was too shallow and the thermal fluctuation could easily change the configuration of the colloidal superstructure. An increase in CTAC concentration improves the bonding strength between the colloidal atoms, as shown in Fig. 3B, and the colloidal superstructure becomes more stable. At 8 mM, the heptamer can be maintained for more than 2 hours without reconfiguration. We further show the time response of a thermodynamically unstable colloidal superstructure (fig. S9), which was assembled in a 20 mM CTAC solution. Because of the strong particle-particle and particle-substrate interactions, the superstructure was very stable (that is, without significant structural change after 2 hours). Furthermore, we demonstrate that the construction of colloidal superstructures is highly repeatable because of the precise control of colloidal atoms under the light-controlled thermoelectric field. As an example, we carried out multiple experiments during which we built the same type of thermodynamically unstable colloidal superstructures six times. As shown in fig. S10, the superstructures show excellent repeatability.

**Diversity of colloidal matter built via OTA**

To examine the general applicability of OTA, we built diverse colloidal superstructures of complex configurations using colloidal atoms of a
a wide range of materials and sizes. Figure 4 (A to C) shows a 1D hybrid chain, a 2D hybrid lattice, and a 2D double-layer “Saturn ring” built from PS beads that are 2 and 0.96 μm in diameter (see also fig. S11). Beyond spherical particles, we also assembled nonspherical particles into 2D colloidal matter. One of the challenges in the assembly of anisotropic particles is the precise orientational control. We overcome this challenge by using the 1D optical image (fig. S4). In Fig. 4D, we used a single 2-μm Gaussian laser beam to assemble a heptamer with 2-μm PS beads, and a 1D optical image to trap, align, and assemble the anisotropic PS particles. The tips of the anisotropic particles were controlled to point toward the center of the heptamer. A CTAC concentration of 15 mM was chosen for stable bonding among the particles. Another challenge in the assembly of anisotropic particles arises from the different curvature radii at different locations of the anisotropic particles. As shown in Fig. 3 (B to D), the interaction potential highly depends on the radius of the colloidal atoms, indicating that the critical CTAC concentration depends on the orientation of the anisotropic particles when bonding. In fig. S12, we built the

**Fig. 4. General applicability of the OTA strategy.** (A) 1D hybrid assembly of 2- and 0.96-μm PS beads. The assembly was achieved by adding the 2- and 0.96-μm PS beads alternatively. (B) 2D hybrid square assembly of 2- and 0.96-μm PS beads. Each 0.96-μm PS bead was added at the interface between two 2-μm PS beads and then confined by two other 2-μm PS beads. (C) 2D hybrid assembly of a double-layer Saturn-ring structure with 2- and 0.96-μm PS beads. The structure was built layer by layer from the inside out. (D) 2D hybrid assembly of 2-μm PS beads and anisotropic PS particles. The anisotropic particles were aligned with a 1D optical image and inserted into the heptamer. (E) 3D assembly and manipulation of four 500-nm PS beads. (F) 2D hybrid superlattice of 2-μm PS, 0.96-μm PS, 2-μm silica, and 1-μm silica beads. The assembly process is similar to (B), whereas half of the PS beads were replaced with silica beads. (G) 2D assembly of a star pattern of 2-μm silica beads. The structure was built layer by layer from top to bottom. (H) A heterogeneous dimer consisted of a 500-nm PS bead and a 200-nm Au nanosphere. (I) 2D assembly of a Saturn-ring structure with 2- and 0.96-μm PS beads. The 0.96-μm PS beads were added around the 2-μm PS bead to obtain the structure. (J) 2D assembly of a 0.96-μm PS with three 500-nm PS beads as satellites. The three 500-nm PS beads were added around the 0.96-μm PS at the specific location with a rotation angle of 120°. (K) An Au dimer consisted of two 200-nm Au nanospheres. (A to F, I, and J) Schematics and bright-field optical images of colloidal superstructures. (G) Bright-field and dark-field optical images of the superstructure. (H and K) Schematics and dark-field optical images of the colloidal atoms and dimers. Arrows in the optical images of (K) indicate the use of different incident light polarizations. Scale bars, 5 μm (A to D, F, and G) and 2 μm (E and H to K).
hybrid assemblies of spherical and anisotropic particles, where the tips of anisotropic particles point away from the assembly of 2-µm PS beads (see also movie S7). The assembly can be stable at a lower CTAC concentration (that is, 10 mM). Thus, the CTAC concentration should be carefully chosen according to the minimum curvature radius at the bonding sites.

To achieve 3D manipulation of the colloidal structures, we incorporated optical scattering force into the thermo-electric field to provide both out-of-plane and in-plane manipulations of the colloidal atoms using a 100× objective (NA, 0.9). As shown in movie S8 and note S4, we aligned the colloidal atoms into an out-of-plane 1D chain using the optical scattering force and steered the location of the laser beam to drag individual colloidal atoms from the chain to modify the configuration. The different configurations of four 500-nm PS beads are summarized in Fig. 4E. Increasing the number of colloidal atoms can improve the challenge of manipulation because multiple colloidal atoms around the laser beam have similar responses to the thermo-electric field. In Fig. S13, we demonstrated the 3D manipulation of six 500-nm PS beads. These 3D assemblies can find applications in 3D plasmonic and chiral meta-materials.

Because the CTAC surfactants can be widely applied to different colloidal suspensions to modify the surface charges of the colloidal atoms, the OTA strategy can be used to construct colloidal super-structures of various materials. Considering the material-dependent parameters, including the ħ potential of the colloidal atoms and the Hamaker constant, we slightly modify the CTAC concentration to obtain stable colloidal bonding. In Fig. 4F, we selectively picked up 2-µm PS, 0.96-µm PS, 2-µm silica, and 1-µm silica from the colloidal suspensions to build a 2D hybrid superlattice, where the different beads are arranged in a precisely controlled fashion. Figure 4G shows both bright-field and dark-field optical images of a large-area star pattern of 2-µm SiO₂ colloids assembled in a 10 mM CTAC solution. We have also demonstrated the assembly of an Au nanoparticle and a PS bead into a heterogeneous dimer (Fig. 4H), which is also known as an optoplasmic molecule, where photonic-plasmonic coupling can lead to interesting optical phenomena (41).

Furthermore, we study the applicability of the OTA strategy in different colloidal sizes. In Fig. 4 (I and J), we show the Saturn-ring structures with PS beads of different sizes by adding the smaller PS beads surrounding the bigger ones (fig. S14). Finally, we demonstrate the assembly of a metallic dimer with plasmonic coupling using OTA. The precise control of particle-particle gap from several nanometers to tens of nanometers is critical to control the resonant peak location and local electric field intensity in the plasmonic dimers. Figure 4K shows the dark-field optical images of an Au nanoparticle dimer assembled in a 50 mM CTAC solution and a single Au nanoparticle when the polarization of the incident light is vertical and parallel to the dimer axis, respectively. Enhanced light scattering by the dimer is observed for the parallel incidence due to the near-field plasmonic coupling. Because of tunable bonding length and hence interparticle distance, we expect to precisely control the plasmonic coupling in the colloidal assemblies, which underpins an emerging field of meta-surfaces and meta-materials (42). The assembly of sub-100-nm colloidal atoms using OTA remains challenging. Although the optical manipulation of sub-100-nm colloidal atoms can still be achieved using a low-power laser beam, depletion attraction cannot provide sufficient bonding strength for stable assembly because the size of the micellar depletants is not significantly smaller than that of the sub-100-nm colloidal atoms.

DISCUSSION

In conclusion, we mimic atomic systems to develop the OTA strategy to build diverse colloidal matter based on the opto-thermo-fluidic platform. Because of the thermal transport of ions (including micellar macro ions) under the temperature field, we generate a light-controlled thermo-electric field for versatile manipulation of colloidal atoms and interlocking of the arranged colloidal atoms with depletion attraction. This OTA strategy features a wide range of colloids, leading to complex colloidal superstructures with tunable bonding strength and length between the colloidal atoms.

The advantages of the OTA strategy over optical tweezers include its manipulation capability for a wider range of colloidal materials, sizes, and shapes; low-power and invasive operation; tunable bonding length and strength; and flexible control of anisotropic colloids, which markedly enrich the geometry and functions of colloidal superstructures. Specifically, the capability to manipulate and assemble subwavelength colloids with controllable interparticle coupling is extremely important for material applications. Because of their strong interaction with light and unique optical response, the subwavelength colloids provide tremendous opportunities to build colloidal photonic materials with on-demand tunable optical properties. Therefore, OTA will overcome the limitation of optical tweezers in the assembly of functional colloidal nanomaterials. Although current results are demonstrated based on PS, SiO₂, and Au nanospheres, the CTAC surfactants can be widely applied to different colloidal suspensions with good stability. Thus, the OTA concept can be easily extended to a bundle of many other colloids such as Si nanoparticles, metal oxide nanoparticles, and nanowires to build diverse functional materials and devices.

The throughput of the OTA strategy is lower than that of some self-assembly techniques, which can create large-scale ordered colloidal assemblies. However, OTA has the advantage of providing precise control of colloidal assembly configuration and interparticle interaction, which is critical in tuning coupling between colloidal atoms and thus the functions of the assemblies. In addition, the flexibility in light management and the low-power requirement for the thermophoretic manipulation will allow parallel operation of the colloidal construction with improved throughput and lead to a programmable platform for the construction of designer colloidal matter.

On the basis of our current understanding and demonstration, the OTA strategy can be widely applied to colloidal atoms with sizes ranging from the micrometer scale to ~100 nm. Assembly of sub-100-nm colloidal atoms remains challenging because of their relevance to the size of the micellar depletants. Although we have demonstrated that reconfigurable 3D assembly is achievable by incorporating the optical scattering force into the OTA strategy, the configuration of the 3D assemblies and the number of colloidal atoms in the 3D assemblies are still limited. One of the potential strategies to improve the upper limit is to use multiple laser beams to manipulate and assemble colloidal atoms in parallel.

The understanding of colloid science and opto-thermo-fluidics in the OTA strategy paves the way toward precisely tuning and reconfiguring the structures and properties of colloidal matter. The versatile construction of optical matter with enriched structures and reconfigurability, in combination with real-space imaging of the motions of individual particles by optical microscopy, will also advance the understanding of the general principles of self-assembly. Eventually, the scale-up of the directed assembly for a large quantity of designer structures and materials will lead to a wide range of technical applications of colloidal matter.
MATERIALS AND METHODS
Materials and sample preparation
The substrates were prepared by depositing 4.5-nm Au thin films on glass slides under thermal deposition (Denton thermal evaporator; base pressure, 9 × 10⁻⁶ torr) followed by thermal annealing at 550°C for 2 hours. The PS beads and silica beads (purchased from Bangs Laboratories Inc.) were dispersed in the CTAC solutions at a volume ratio of 1:20,000. The 200-nm Au nanospheres in phosphate-buffered saline (0.1 mM; purchased from Sigma-Aldrich) were centrifuged for 10 min (4500 rpm) and redispersed in the CTAC solutions at a volume ratio of 1:1000. The particle concentration in the colloidal suspensions was diluted to 5 × 10⁵ to 5 × 10⁶ particles/ml to avoid spontaneous aggregation. For the assembly of hybrid colloidal structures, the PS beads, silica beads, or centrifuged Au nanospheres were codispersed in the CTAC solutions. The colloidal dispersions were added to the substrates in a 1-mm-thick chamber.

The anisotropic PS microparticles were fabricated by reactive ion etching of close-packed PS microsphere bilayers. The colloidal solution of PS microspheres (9.6%) with a diameter of 5.31 μm was purchased from Bangs Laboratories Inc. The PS microspheres were first concentrated by centrifugation and then dispersed in ethanol at a volume fraction of 33%. The PS microspheres were then spin-coated (1500g; 5 min) on a clean glass substrate to form close-packed bilayers. Before spin coating, the glass substrate was cleaned by ultrasonication in acetone, methanol, and deionized (DI) water. The substrate was further cleaned for 10 min in an ultraviolet ozone system to obtain a hydrophilic surface. Reactive ion etching was performed in a plasma etching system (March Plasma CS170IF) with O₂ plasma (100 W, 30 sccm, 600 s). The etched PS microspheres were collected by ultrasonication of the glass substrate in DI water for 2 min.

Optical setup
A 532-nm diode-pumped solid-state laser (Genesis MX STM-1 W; Coherent) was expanded with a 5x beam expander and projected onto the DMD. The optical images reflected off the DMD were focused onto the DMD. The optical images reflected off the DMD were focused onto the DMD and the condenser to control the incident light polarization. Either a polarizer (Thorlabs Inc.) was inserted between the white light source and the condenser, or a 40x objective (Nikon; NA, 0.75) in an inverted microscope. For dark-field imaging, an air condenser was used to focus the illumination light into the sample. The size of the beam was reduced by 200 times after being relayed by a 200-mm doublet lens, an infinity-corrected 1000-mm doublet lens, a 200-mm doublet lens, an infinity-corrected tube lens, and a 40x objective (Nikon; NA, 0.75) in an inverted microscope. For dark-field imaging, an air condenser was used to focus the illumination light into the sample. The size of the beam was reduced by 200 times after being relayed by a 200-mm doublet lens, an infinity-corrected 1000-mm doublet lens, a 200-mm doublet lens, an infinity-corrected tube lens, and a 40x objective (Nikon; NA, 0.75) in an inverted microscope. For dark-field imaging, an air condenser was used to focus the illumination light into the sample. The size of the beam was reduced by 200 times after being relayed by a 200-mm doublet lens, an infinity-corrected 1000-mm doublet lens, a 200-mm doublet lens, an infinity-corrected tube lens, and a 40x objective (Nikon; NA, 0.75) in an inverted microscope. For dark-field imaging, an air condenser was used to focus the illumination light into the sample. The size of the beam was reduced by 200 times after being relayed by a 200-mm doublet lens, an infinity-corrected 1000-mm doublet lens, a 200-mm doublet lens, an infinity-corrected tube lens, and a 40x objective (Nikon; NA, 0.75) in an inverted microscope. 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Measurement of interaction potentials
TIRM was used to directly measure the evolution of colloid-surface depletion attraction at different CTAC concentrations. The experi-
movie S4. Assembly process of a 2D thermodynamically stable structure with 2-μm PS beads.
movie S5. Manipulation of the 2D assembly of 2-μm PS beads.
movie S6. Trapping, rotation, and bonding of the 1D assembly of 2-μm PS beads.
movie S7. Assembly of anisotropic PS particles.
movie S8. Manipulation of the 3D assembly of 500-nm PS beads.

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Author contributions: L.L. and Y.Z. conceived the idea for this study. L.L., X.P., and Z.W. prepared the materials. L.L. worked on the experiments and collected the data. J.Z. and M.A.B. measured the interaction potentials. L.L., J.Z., and M.A.B. calculated the interaction potentials. A.C.H.C. and J.Z. measured the interaction potentials. L.L. and Y.Z. conducted the computational fluid dynamics simulations. All authors discussed the results and wrote the manuscript.

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