**Optical Binding**

**Light-Driven Self-Healing of Nanoparticle-Based Metamolecules**

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**Abstract:** Metamolecules and crystals consisting of nanoscale building blocks offer rich models to study colloidal chemistry, materials science, and photonics. Herein we demonstrate the self-assembly of colloidal Ag nanoparticles into quasi-one-dimensional metamolecules with an intriguing self-healing ability in a linearly polarized optical field. By investigating the spatial stability of the metamolecules, we found that the origin of self-healing is the inhomogeneous interparticle electrodynamic interactions enhanced by the formation of unusual nanoparticle dimers, which minimize the free energy of the whole structure. The equilibrium configuration and self-healing behavior can be further tuned by modifying the electrical double layers surrounding the nanoparticles. Our results reveal a unique route to build self-healing colloidal structures assembled from simple metal nanoparticles. This approach could potentially lead to reconfigurable plasmonic devices for photonic and sensing applications.

Self-healing is one of the most outstanding properties of living organisms, and is highly desirable in artificial systems. Extensive efforts have been made to develop self-healing materials, including metals, ceramics, and polymers. Self-healing has both extrinsic and intrinsic aspects. Extrinsic self-healing is based on external healing components embedded in the materials, such as micro- or nanocapsules. Intrinsic self-healing can occur in the self-assembly of molecules, in which the minimization of total energy is the driving force for the process. For example, micelles, phospholipid membranes, and thiol monolayers can self-heal after mechanical damage because of their tendency to minimize the surface free energy. However, self-healing in colloidal particle systems is rarely reported, except for tolerance of defects in microgel crystals. To realize a self-healing colloidal particle system that can recover from severe damage, the system needs to have pathways to access the global minimum of the potential energy surface while being protected from impact-induced instability. Therefore, in response to perturbations, the disturbed state is still within the basin of the potential well, and the system can recover. These conditions are usually hard to satisfy in hard-sphere colloidal microparticle systems, where defects can readily induce solid-solid phase transitions or even melting of colloidal crystals.

In this study, we discovered a novel self-healing characteristic in quasi-one-dimensional metamolecules formed by light-induced self-organization of Ag nanoparticles with strong optical binding interactions (i.e., nanoscale optical matter). The metamolecules can have several different configurations (i.e., isomers) with the same number of constituent nanoparticles. Upon external perturbation, for example, a change of the polarization state of the trapping laser beam or the introduction of another laser with a different wavelength, the metamolecules will deform or even disassemble. However, certain metamolecules can restore their initial configuration when the perturbations are removed. Our results show that a self-healing metamolecule is a unique configuration with minimal free energy among various isomers, whereby the formation of nanoparticle dimers inside a quasi-one-dimensional metamolecule can significantly improve the spatial stability of the structure, thus leading to restoration of the same configuration even if the system is totally destroyed.

The experiments were conducted in an optical tweezers system using a laser beam with a wavelength of 800 nm. The laser beam propagates along the z-axis with a linear polarization along the y-axis. The diameter of the laser spot is approximately 13 μm, which allows the confinement of multiple nanoparticles in the transverse (x-y) plane near a coverslip surface owing to the laser radiation pressure. As shown in the first column of Figure 1a,b, silver-nanoparticle-based metamolecules will form along the x-direction (the orientation of the metamolecules can be controlled by the polarization direction, see Figure S1 in the Supporting Information). The metamolecules have an average interparticle separation of approximately 570 nm along the x-direction, while the separation of the dimers along the y-direction is approximately 330 nm. The formation of a dimer is caused by the combination of electrodynamic and electrostatic interactions between two nanoparticles, as we found recently (see also Figure S2). However, the self-healing behavior was not observed in our previous report, in which the self-assembled structures were very unstable because isolated nanoparticles (not assembled into metamolecules) always existed. These isolated nanoparticles can disturb the ordered structures already assembled during the experiments, thus preventing the formation of stable metamolecules. In this study, we overcame this challenge by introducing a Stokes drag force into the trapping environment once isolated nanoparticles appeared by using a x-y translational stage to move the coverslip. For the constituent particles of metamolecules, the optical trapping and binding forces are large enough to balance the additional drag force, while the isolated nanoparticles are released from the optical field owing to the weak trapping forces. As a result, we could fabricate stable...
metamolecules of different lengths and controlled dimer numbers.

We began by investigating the self-healing ability of two different metamolecules in response to external perturbations (Figure 1a,b). A full-wave liquid-crystal variable retarder was used to change the polarization state of the light to introduce perturbations into the trapping system. As shown in the second and third columns of Figure 1a,b, the metamolecules immediately vanished and transformed into unstable structures with totally different configurations in circularly polarized light.

Strikingly, as the light was changed back to the linearly polarized state (columns 4–7), the particles immediately transformed into chain structures with at least one dimer unit (fourth and fifth columns), whereas the remaining single nanoparticles were attracted by the metamolecules \( t = 3.23 \text{ s in Figure 1a and } t = 0.99 \text{ s in Figure 1b} \) to form triangular structures owing to the optical binding potential wells generated by the adjacent subunits of the metamolecule.\(^{12}\) However, these potential wells are not deep enough to resist Brownian fluctuations. Eventually, the single nanoparticles paired together and formed stable dimers (column 7 of Figure 1a,b). The reconstructed metamolecule was different from the initial one in Figure 1a, whereas the metamolecule in Figure 1b was the same as the previous one. That is, the initial metamolecule in Figure 1b has self-healing ability (the final metamolecule in Figure 1a also has self-healing ability, see Figure S3), which was further demonstrated by repeated self-healing processes (see Video S1 in the Supporting Information) and the corresponding trajectories of the Ag nanoparticles in three different stages (Figure 1c). Furthermore, self-healing metamolecules could restore their initial configuration even if the light was suddenly turned off (structure disassembles) and then turned on again (see Figure S4). The recovery of metamole-

Figure 1. Light-driven self-healing of quasi-one-dimensional silver-nanoparticle-based metamolecules. a,b) A series of dark-field optical images that show several Ag nanoparticles (150 nm in diameter) self-assembled into metamolecules in a linearly polarized optical field (first column), then transformed into unstable structures upon external perturbation (by changing of the polarization state from linear to circular, second and third columns), and finally reconstructed into a) a shorter metamolecule with two dimer units and b) the same configuration as the initial metamolecule when the polarization is changed back to the linearly polarized state (columns 4–7). Scale bar: 1 \( \mu \text{m} \); laser power: 3.76 mW \( \mu \text{m}^2 \).

(c) Trajectories of eight Ag nanoparticles that show the self-healing behavior in response to external perturbations. For clarity, the trajectories exclude the structure transitions between two different polarization states. The trajectories of the particles in each plot are obtained from 300 dark-field images taken in 1 s.
cule structures was still observed when we used another laser beam (λ = 405 nm) to perturb the metamolecules while keeping the linearly polarized optical assembly field (λ = 800 nm) unchanged (see Figure S5). These observations clearly reveal the self-healing behavior of specific metamolecules, while other metamolecules lack this ability.

Light-induced self-organization of colloidal nanoparticles can lead to various equilibrium configurations with the same number (N) of nanoparticles.[11–13] Typical isomers of optical-matter structures are shown in Figure 2, but only one structure for a certain N value has self-healing ability (marked by stars). We find that all self-healing metamolecules satisfied one rule: they must have \( N_{s}\) = floor \((N/2 – 1)\) dimers that are all connected and not at the termini of the metamolecules (see Figure S6 for the self-healing of a three-nanoparticle-based metamolecule). For metamolecules with an odd number of nanoparticles, self-healing metamolecules satisfying the rule will have one single nanoparticle at one terminus and two at the other, and such metamolecules have mirror-image configurations (i.e., flipped horizontally; see Video S2). When considering the self-healing effect, these mirror-image configurations are treated as the same. For a metamolecule with a dimer number \( N_d < N_{s} \), the reconstructed metamolecule is different from the initial metamolecule (Figure 1a; see also Figure S7). These observations strongly suggest that dimers are not stable at the termini, and that the formation of dimers inside the metamolecules can minimize the free energy of the whole structure, thus leading to self-healing of certain configurations. Additionally, by categorizing the isomers based on the total number \( N_i \) of subunits along the long axes of the metamolecules, whereby either a single nanoparticle or a dimer is counted as one subunit, we find more properties of the metamolecules: For a given \( N_i \) value, the length of the metamolecule slightly decreases as the number of dimers increases (see Figure S8), and as \( N_i \) increases, the interparticle separation of the dimers increases and the thermal fluctuation decreases (see Figure S9). Therefore, longer metamolecules with more dimers become more stable.

To investigate the intrinsic self-healing behavior of the Ag metamolecules, we analyzed their spatial stability by measuring the trapping stiffness at each particle position. As a representative example, we consider three different metamolecules with \( N_i = 4 \). Figure 3a shows the measured trapping stiffness as a function of the particle index (see the inset dark-field images). The trapping stiffness of all the particles along the x-direction (long axis) is much larger than that along the y-direction (short axis), and the y-direction trapping stiffness of the inner particles is much larger than that of the terminal particles. For the paired particles in the dimers, their trapping stiffness is nearly the same (second and third columns of Figure 3a). Moreover, the addition of a new particle will increase the trapping stiffness of other particles. These results suggest that the spatial stability of a metamolecule is anisotropic owing to the anisotropic nature of the optical binding interactions[8c,14] and that the formation of one dimer would lead to the formation of more dimers, thus leading to self-replication of dimer units. We also examined the stability (i.e., the average standard deviation \( \bar{\sigma} \) of fluctuations of all the particles around their equilibrium positions) of a single particle chain and a dimer metamolecule illuminated by a laser at different powers. The results showed that the dimer metamolecule had much higher stability than the single particle chain (see Figure S10).

To understand our experimental observations, we performed electrodynamic simulations using the finite-difference time-domain (FDTD) method.[10] The simulations assume that the separation of paired nanoparticles in dimers is fixed at 330 nm in the y-direction, whereas the separation of the nanoparticles in the x-direction varies in the range of 500–700 nm (the equilibrium optical binding separation is ca. 600 nm). The optical force on each particle at a certain position is obtained by integrating the Maxwell stress tensor over a surface surrounding the nanoparticle. As a result, the position-dependent optical force around each equilibrium position can be used to calculate the trapping stiffness along the x- or y-direction. The calculated trapping stiffness of particles located at different positions of the metamolecules is shown in Figure 3b, where the spatial variation of the stability agrees very well with our experimental result.

We further analyzed the stability of optical isomers with the same number of particles \( N \), Two cases were considered: optical isomers with i) different numbers of subunits \( N_i \) and ii) the same \( N_i \) value but different spatial arrangements. Note that the existence time for all configurations is large enough (several seconds) for the analysis. For a better comparison, we used \( \bar{\sigma} \) to evaluate the stability of a metamolecule. Figure 3c shows \( \bar{\sigma} \) as a function of the dimer number for isomers with \( N = 6, 7, \) and 8. We found that the formation of more dimers

![Figure 2. Isomers of silver-nanoparticle-based metamolecules; the special configurations with self-healing ability are marked with red stars. Metamolecules with self-healing ability have long-term stability (could exist for several minutes), whereas other isomers are unstable (exist up to a few seconds). Scale bar: 1 μm.](image-url)
leads to higher stability of the metamolecules, and the specific metamolecule with self-healing ability is the most stable of the different isomers. These observations clearly reveal that with a fixed particle number, the light-driven self-organization of Ag nanoparticles always tends to form metamolecules with as many dimers as possible.

Moreover, the configuration matters even with the same number of dimers ($N_d$). By comparing the stability of each particle position in two metamolecules with the same $N_d$ and $N_s$ values but different configurations (see Figure S11 and Video S3), we found that when one dimer (close to one terminus of the metamolecule) dissociates and another dimer (near the center of the metamolecule) unites, the $y$-direction stability of nearly all nanoparticles is enhanced by this transition. This result suggests that dimer units that are all connected rather than separated by single nanoparticles could lead to higher stability of the metamolecule (also see Figure 1b, two dimer units are all connected before the third one joins during the self-healing processes).

The structures and self-healing behavior of metamolecules can be further tuned by changing the chemical environment near the nanoparticle surface. The interparticle separation of these Ag nanoparticles is influenced by the electrostatic repulsion induced by their negatively charged polyvinylpyrrolidone surface coating.\[10\] When the cationic surfactant cetyltrimethylammonium bromide (CTAB) is added to the solution, the electrostatic screening and electrical double layers surrounding the nanoparticles are changed owing to net reduction of the negative charge, which causes a decrease in interparticle separation. The orientation of a dimer is perpendicular to the polarization direction in the absence or with a low concentration ($0–1$ mM) of CTAB (Figure 4a, I). However, in a $5$ mM CTAB solution, the orientation of the dimer is parallel to the light polarization (Figure 4a, II). The average interparticle separation of the dimer decreased to approximately $250$ nm as the CTAB concentration increased to $5$ mM (Figure 4b). In this case, the near-field interactions dominate; thus, nanoparticles align themselves along the polarization direction ($y$-axis).\[15\] There is always a large jump from region I to II, even if the concentration of CTAB is changed continuously, as determined by the electrodynamic potential energy surface of a two particle system.\[12a\]

When sodium chloride was added to the solution, the average interparticle separation of two Ag nanoparticles also decreased as the concentration of NaCl increased (see Figure S12).

Figure 4c shows several typical metamolecules with self-healing ability in a $5$ mM CTAB solution. Interestingly, stable dimers can now exist at the termini of the metamolecules, which is forbidden in the previous cases (Figure 2). A series of dark-field images in Figure 4d further show the deformation and restoration of two metamolecules in response to external perturbations.

The authors declare no conflict of interest.

The development of colloidal synthesis has increased the availability of nanocrystals with well-controlled sizes and shapes, yet it is still a fundamental challenge to precisely control and assemble those nanocrystals. Addressing this challenge is important not only for nanoscience, but also for many branches of chemistry, in which nanoparticle is used for various purposes. Free-standing metamolecules formed by self-assembled gold nanoparticles conjugated by DNA or small-molecule cross-linkers have led to plasmonic nanostructures with novel optical properties, such as tunable circular dichroism and magnetic response at optical frequencies.[10] The interparticle separation of the building blocks in those metamolecules is typically less than 100 nm owing to the size of the molecules.[16–d] On the other hand, metal-nanoparticle chains and arrays with interparticle separations of hundreds of nanometers can support tunable surface lattice resonances (SLRs),[17] which have wide application, for example, in photovoltaics, biosensing, and visible lasing involving gain materials.[18] Such structures are mainly fabricated on substrates by lithographic techniques, which are static and lack tunability. Moreover, a significant challenge in the soft-matter field is the anisotropic organization of colloidal particles.[19] Conventional approaches based on van der Waals or electrostatic forces usually lack the ability to drive the system into an anisotropic assembly. Our study not only reveals a dissipative way to direct the anisotropic assembly of nanoparticle-based metamolecules with novel self-healing ability, but also provides a promising approach to the fabrication of free-standing plasmonic nanostructures with large interparticle separations (tuned by changing the surrounding solvents or light wavelengths)[20] to fulfill the critical conditions for generating SLR modes.[7]

In conclusion, we have fabricated quasi-one-dimensional silver-nanoparticle-based metamolecules with self-healing ability in an optical field. By analyzing the spatial stability of the nanoparticle building blocks, we found that the stability of the metamolecules is significantly increased as single nanoparticles group into dimer units aligned in parallel along the backbone of the metamolecules. A metamolecule with the maximum number of dimers has the highest stability and reaches the global minimum of the potential energy surface, which is the origin of the self-healing behavior. Moreover, by chemical modification of the electrical double layers surrounding the nanoparticles in solution, the self-healing structures can be tailored to a large extent. Our results provide new insight into the assembly of self-healing colloidal particle systems, which will benefit the fabrication of smart and reconfigurable optical and sensing devices.

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Conflict of interest

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