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Photoresponsive Structured Liquids Enabled by Molecular Recognition at Liquid−Liquid Interfaces

Huilou Sun, Lianshun Li, Thomas P. Russell,* and Shaowei Shi*

ABSTRACT: Using host−guest molecular recognition at the oil−water interface, a new type of photoresponsive nanoparticle surfactant (NPS) was designed and prepared to structure liquids. With the help of a polymeric surfactant, the interfacial host−guest interactions can be significantly enhanced, leading to the rapid formation and assembly of a NP monolayer and offering sufficient binding energy to hold the NPs in a jammed state. The assembly of the NPSs can be reversibly manipulated via a photoswitchable jamming-to-unjamming transition, endowing the interface as well as the macroscopic assemblies with responsiveness to the external trigger (photons). This study for the first time opens a pathway for the construction of multiresponsive, structured all-liquid systems by introducing host−guest chemistry, showing promising potential applications in encapsulation, delivery systems, and unique microfluidic devices.

The self-assembly of nanoparticles (NPs) at liquid−liquid interfaces (e.g., the oil−water interface) provides a powerful strategy to construct hierarchical structures with functionalities.[1−4] In general, NPs segregated to the interface form disordered or "liquid-like" assemblies that show mobility in the plane of the interface.[5−7] If the concentration of NPs at the interface is increased, dense packing of NPs in the plane of the interface can be achieved, known as interfacial jamming, leading to a transformation of the assembly from "liquid-like" to "solid-like" with significantly enhanced mechanical proper- ties.[8,9] When jammed, percolated pathways of NPs in close contact can bear load and prevent further volume reduction of the biphasic systems, opening the possibility to manipulate liquids into highly nonequilibrium shapes, such as bicontin- uous interfacially jammed emulsion gels, or bijels.[10,11] However, since the reduction in the interfacial energy for each NP is close to the thermal energy, the in-plane compressive forces can result in the NPs being easily ejected from the interface, causing the nonequilibrium liquid shapes to become spherical, with the lowest interfacial area for a given volume.[12−15] Thus, to achieve long-term stability of the structured liquids, neutral wetting conditions of NPs at the interface are essential, which are time-consuming and procedurally complex to attain.

An alternative strategy developed recently to overcome this obstacle is to use nanoparticle surfactants (NPSs), where functionalized NPs dispersed in one liquid and oligomeric/polymeric ligands dissolved in the second liquid interact at the interface between the liquids.[16]

The number of ligands anchored to the NPs is self-regulated, leading to a significant increase in the energy holding each NP at the interface. Exploiting the mechanics of NPS-stabilized interfaces, flow fields,[17−19] electric fields,[16,20] confinement,[21] and extrusion[22,23] have been utilized to shape interfaces into complex geometries, showing tremendous potential applications in areas such as all- liquid reaction vessels, microfluidic devices, and energy storage

materials.[24,25] To date, however, the generation of multiple- stimuli-responsive structured liquids is relatively unexplored and also challenging. Since the NPSs form mainly by electrostatic interactions between ion pairs (e.g., ammo-nium−carboxylate), only pH responsiveness can be achieved to realize the reconfiguration of liquids.[20]

Host−guest chemistries provide an important step in fabricating multifunctional systems with efficient stimuli-responsiveness.[26−28] There have been several reports on the fabrication of colloidal microcapsules by using interfacial molecular recognition, but these systems generally involved liquid-like NP assemblies at the interface.[29−32] Here, by using the classic photocontrolled molecular recognition of α-cyclodextrin (α-CD) with azobenzene (Azo), we present a simple strategy to build photoresponsive NPSs at the oil− water interface, where the trajectories between the jammed (solid-like) and unjammed (liquid-like) states of NPSs can be reversibly manipulated, endowing the resultant structured liquids with intriguing photoresponsiveness (Figure 1).

As a proof of concept, we began by designing and preparing α-CD-modified gold NPs (Au-NPs), ~10 nm in diameter, that are dispersed in water (Figures S1−S4) and two oil-soluble polymeric ligands, Azo-terminated polystyrene (Azo-PS, M_w = 3.3 K) and Azo-terminated poly-$_L$-lactide (Azo-PLLA, M_w = 3.6 K). The kinetics of different ligands assembled with Au- NPs at the water−toluene interface was probed by tracking the dynamic interfacial tension (γ) using pendant drop tensiom-etry. As shown in Figure 2a, with Au-NPs dispersed in water
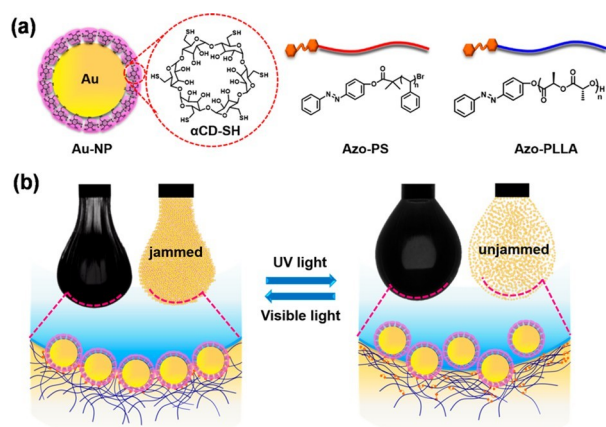
Figure 1. (a) Chemical structures of the designed Au-NPs, Azo-PS, and Azo-PLLA. (b) Schematic representation of the photoresponsive NPSs at the oil−water interface from the jammed state to the unjammed state.
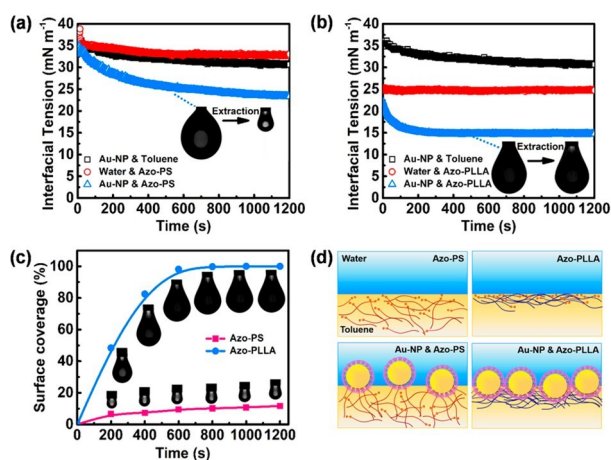

Figure 2. (a, b) Time evolution of interfacial tension of different polymeric ligands assembled with Au-NPs. (c) Interfacial coverage of NPSs as a function of time with different polymeric ligands. (d) Schematics of different polymeric ligands assembled with Au-NPs at the water−toluene interface. [Au-NP] = 1.0 mg mL^{-1}, [Azo-PS] = 1.0 mg mL^{-1}, [Azo-PLLA] = 1.0 mg mL^{-1}.

dissolved in the toluene, a further reduction in the interfacial tension is observed, indicating the formation and assembly of the NPSs at the interface by molecular recognition between the α-CD moieties anchored to the Au-NPs and the

against pure toluene, the equilibrium interfacial tension is ~31 mN m^{-1}, which is decreased slightly compared with the pure water−toluene system (35 mN m^{-1}). This low interfacial activity of Au-NPs can be attributed to the amphiphilic property of α-CD, which has a hydrophobic inner cavity and a hydrophilic exterior. In addition, unlike carboxylic acid-functionalized NPs, the Au-NPs used here are not charged, and there is no barrier impeding their interfacial assembly. However, the binding energy is still not sufficient to withstand the compressive force when the interfacial area decreases, and the interfacial assemblies show liquid-like behavior (Video S1). Azo-PS also shows no interfacial activity when dissolved in the toluene, which is due to the highly hydrophobic backbones (the slight reduction in the interfacial tension is due to the carbonyl group in the initiator, which can hydrogen bond with water). However, with Au-NPs dispersed in the water and Azo- PS

Azo end functionality on the PS. When the interface is compressed, wrinkles are observed on the droplet surface, indicating jamming of NPSs at the interface, causing a reduction in the mobility of the NPSs at the interface, which now exhibits solid-like characteristics (Video S2). Similar behavior can be achieved when using Azo small molecule dissolved in the toluene (Figure S8a and Video S3). On the other hand, Azo-PLLA does behave as a surfactant because of the formation of hydrogen bonding between numerous carbonyl groups and water, achieving a reduced interfacial

tension of ~25 mN m^{-1} (Figure 2b). With Azo-PLLA

dissolved in the toluene, the interfacial activity of NPSs is

evident by the rapid reduction in the interfacial tension and the development of wrinkles on the droplet surface with only a very small compression (Video S4). By tracking of the interfacial coverage (C) of NPSs with time (as estimated from the volume at which wrinkles appear to the initial volume), the rate at which NPSs form and assemble at the interface can be estimated (Figure 2c).[33] Relative to NPSs with Azo-PS, Azo-PLLA-based NPSs form and assemble at the interface much more rapidly, and the interface can be saturated, reaching nearly full coverage (ca. 100%) within 600 s.

It should be noted that Azo-PLLA can hydrogen-bond with both water and the hydroxyl groups of α-CD. To ensure the existence of molecular recognition between α-CD and the Azo group in Azo-PLLA-based NPSs, pure PLLA (M_w = 3.0 K) was used as a control. As shown in Figure S8b, upon the formation of hydrogen bonds with Au-NPs at the interface, the interfacial tension decreases. However, when the droplet is compressed, no wrinkling behavior is seen (Video S5), indicating that the binding energy of Au-NPs is too low to support a load at the interface, even with the hydrogen bonding. On the basis of the above, we find that hydrogen bonding plays an important role in driving the formation and assembly of NPSs by molecular recognition. Without this driving force, although NPSs can be formed at the interface, the interfacial activity is very low. The realization of molecular recognition depends only on random collisions between the host and guest units, as in Azo-PS-based

NPSs. However, with hydrogen bonding, the terminal Azo groups and Au-NPs can locate at the oil−water interface, significantly enhancing the probability of collision, leading to

rapid triggering of molecular recognition, as in Azo-PLLA- based NPSs (Figure 2d). In the following studies, we take Azo- PLLA-based NPSs as the model system, since it is easier to generate robust interfacial assemblies and to structure liquids. To further understand the

kinetics of the formation and assembly of the NPSs at the interface, the influence of the Au-NPs and Azo-PLLA concentrations was investigated. As shown in Figure S10, the interfacial activity of the NPSs can be markedly enhanced by increasing the concentration of either Au-NPs or Azo-PLLA. The initial reduction in the interfacial tension increases, with an equilibrium interfacial tension that proportionately decreases. Nevertheless, the interfacial cover- age of NPSs at equilibrium increases with increasing concentration of Au-NPs or Azo-PLLA, which agrees with the decrease in the equilibrium interfacial tension. 2D macroscopic films are produced at the oil−water interface

that can be transferred to a solid substrate (Figures 3a and

S11).[33] Transmission electron microscopy (TEM) imaging of these transferred films shows monolayers of randomly close- packed Au-NPs over large areas (Figure 3b). With NPS assemblies at the interface, when the pendent droplet is
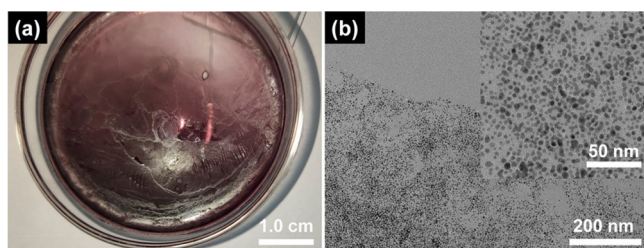
Figure 3. (a) Optical images (top view) of Au-NP films prepared at the oil−water interface. (b) TEM image of a thin film of Au-NPs transferred from the interface. [Au-NP] = 1.0 mg mL^{-1}, [Azo-PLLA] = 1.0 mg mL^{-1}.

brought into contact with a second droplet at the bottom of the container, coalescence of the droplets does not occur, even after the pendent droplet compresses the second droplet, reflecting the exceptional mechanical strength and elasticity of the interfacial assemblies (Figure S12).

The photoresponsiveness of the NPSs and their assemblies was studied by using a pendent droplet in the jammed state. As shown in Figure 4a and Video S6, under visible light, no
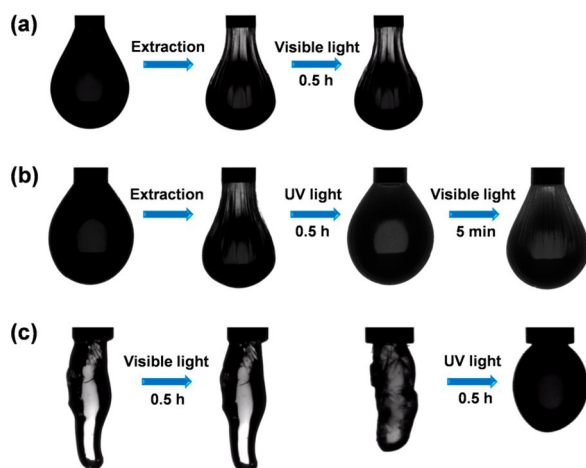

Figure 4. Morphology evolution of the pendent droplet with jammed NPSs at the interface (a) under visible light or (b) under UV irradiation and then under visible light. (c) Morphology evolution of the highly deformed droplet with jammed NPSs at the interface under
visible light or UV irradiation. [Au-NP] = 1.0 mg mL^{-1}, [Azo-PLLA] = 1.0 mg mL^{-1}.

change in the wrinkles is observed after half an hour. However, under UV irradiation (wavelength: 365 nm), the wrinkles gradually disappear, and the shape of the contracted droplet returns to a classic droplet shape, characteristic of unjamming of the NPS assembly and relaxation of the droplet shape. (Figure 4b). It is interesting to note that when UV irradiation is stopped, wrinkling of the droplet occurs spontaneously in visible light, with a slight deformation of the droplet (Figure 4b and Video S7). This jamming-to-unjamming-

to-rejamming transition of NPSs can be repeated multiple times by gradually decreasing the droplet volume (Figure S14). Here, with the trans form of Azo-PLLA dissolved in the oil phase, the jammed NPSs are strongly held at the interface because of the increased surfactancy (increased binding energy) of the NPS. Upon exposure to UV light, the *trans*-Azo-PLLA photoisomerizes to *cis*-Azo-PLLA, which is forced out of the pocket in the α-CD. As a consequence, the binding energies of the NPSs decrease,

the (now) NPs are rejected from the interface, and the shape of the droplet (i.e., the wrinkles) relaxes, decreasing the interfacial area. However, because of the hydrogen bonding, a monolayer of Au-NPs still remains at the interface.

When the Azo-PLLA is transformed from cis to trans under visible light, NPSs again form by host−guest interactions, decreasing the gain in interfacial energy for each NPS, and a reorganization of the Au-NPSs is triggered to allow more Au- NPSs to form and assemble at the interface, rejamming the

assembly. We note that the volume of the droplet remains constant. We also note that the ligands involved in the molecular recognition place further constraints on the lateral arrangement of the NPSs, which also contributes to the wrinkling behavior. This photoresponsive behavior is also observed in more complex structured liquids that were produced by extracting the aqueous phase in the droplet using the injection needle and then reinjecting the aqueous phase to the original volume (Figure 4c). Furthermore, by the use of a vigorous homogenization process, a stable water-in-oil Pickering emulsion can be obtained, containing droplets with highly irregular shapes. Under UV irradiation, these structured emulsions can be converted into spherical emulsions. Since the binding energy of the (now) NPs has decreased, coalesce of these droplets occurs, breaking the emulsion. If the UV irradiation is stopped, the system can be re-emulsified. This ability to reversibly make and break emulsions opens some rather interesting applications for delivery (Figure S15).

In summary, we have investigated photoresponsive NPSs by host−guest molecular recognition at the oil−water interface. Our results show that the interfacial assembly of NPSs between the jammed and unjammed states can be reversibly controlled by photoswitching, toggling the assemblies from a non- equilibrium state to an equilibrium state in a reproducible manner. This is an essential first step in establishing the bridge between jammed systems and host−guest chemistry, which can be further extended to the fabrication of multiresponsive

all-liquid objects. This ease of switching and the changes in shapes and states of dispersion of the droplets open numerous potential applications for capture and release, sequestration, and delivery in fluid systems.

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