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Gated Molecular Diffusion at Liquid-Liquid Interfaces

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Abstract: The jamming of nanoparticle surfactants (NPSs) at liquid-liquid interface imparts attractive properties to the interfacial assemblies and enables the structuring of liquids. Here, we report photoresponsive supramolecular microcapsules with jammed NPS assemblies at the oil-water interface, taking advantage of host-guest molecular recognition. The permeability of the colloidal membrane can be effectively manipulated by switching the NPSs from a jammed state to an unjammed state with a photo trigger, leading to a controlled molecular diffusion and release, affording a versatile platform for the construction of next generation smart microcapsule systems.

Colloidal microcapsules stabilized by nanoparticles (NPs) provide access to a variety of applications as drug delivery vehicles, microreactors, and encapsulants.[1,2] The inherent properties of the individual NPs can be integrated into the resultant assemblies, endowing the microcapsules with responsiveness to magnetic, electronic and optical triggers.[3-5] Such systems can be constructed by using emulsions as the soft templates, where the NPs tend to be localized at liquid–liquid interfaces to minimize the interfacial energy.[6,7] However, in comparison to micron-sized colloidal particles, the adsorption of NPs at the interface is usually dynamic and, therefore, the thermal fluctuations can easily displace NPs from the interface, leading to unstable emulsions.[8-13] To prepare robust and stable microcapsules, strategies based on either covalent or noncovalent crosslinking of NPs at the oil-water interface have been explored to facilitate the stabilization of the NP assemblies.[14-20]

Nanoparticle surfactants (NPSs) provides an alternative strategy to construct interfacial NP assemblies by dispersing NPs in one liquid and dissolving functionalized polymer ligands in a second liquid immiscible with the first.[21,22] NPSs form *in-situ* at the interface by the electrostatic interactions between NPs and polymer ligands, assemble into a monolayer and, when jammed, generate a robust assembly with exceptional mechanical properties.[23-26] By taking advantage of the interfacial jamming of NPSs, liquids can be sculpted into complex shapes using all-liquid molding and 3D printing,[27,28] showing tremendous potentials for all-liquid microfluidics, biphasic micro-reactors and chemical separation systems.[29-32] On the other hand, with NPSs, ultra-stable, structured Pickering emulsion can be produced via a simple shearing process, that can be used as templates to fabricate microcapsules and 3D porous materials.[33,34] Owing to the dynamic interactions between NPs and polymer ligands, the jamming-to-unjamming transition of NPSs can be reversibly manipulated with a pH trigger, switching the assemblies from a nonequilibrium state to an equilibrium state.[35,36] This unique dynamic jamming of NPSs give us inspiration to control the diffusion and release of molecules at the interface, opening a pathway to generate smart microcapsule systems. Recently, by using Janus zwitterionic nanoplates, Cheng et al reported an electrostatic-driven dynamic jamming interfacial system, achieving a pH-responsive molecular diffusion at the oil-water interface.[37] However, the pH responsiveness usually requires the addition of acid or base to the system, which is undesirable for producing a mild microcapsule environment, in particular, for biological applications.

Here, we report a direct, versatile approach to generate photoresponsive microcapsules by assembling supramolecular NPSs (s-NPSs) at the oil-water interface. Different from traditional NPSs, mainly formed by electrostatic interactions, the s-NPSs used here consist of water soluble α-cyclodextrin (α-CD) modified gold NPs (α-CD NPs) and oil-soluble azobenzene terminated poly-L-lactide (Azo-PLLA).[38] The host-guest molecular recognition between the α-CD and Azo functionalities can be dynamically controlled by using light as an external trigger, toggling the assemblies encapsulating the microcapsules from a jammed state to an unjammed state, enabling a jamming-controlled diffusion and release of cargoes dispersed in the droplets (Figure 1a). Since the size of the droplet can be arbitrarily large or small, this fascinating behavior can also be realized in macroscopic structured liquids having a cubic shape, where the shape of liquids can be changed from a highly nonequilibrium shape to the classic spherical shape with no change in the volume by the jamming-to-unjamming transition of the interfacial assembly of s-NPSs (Figure 1b).

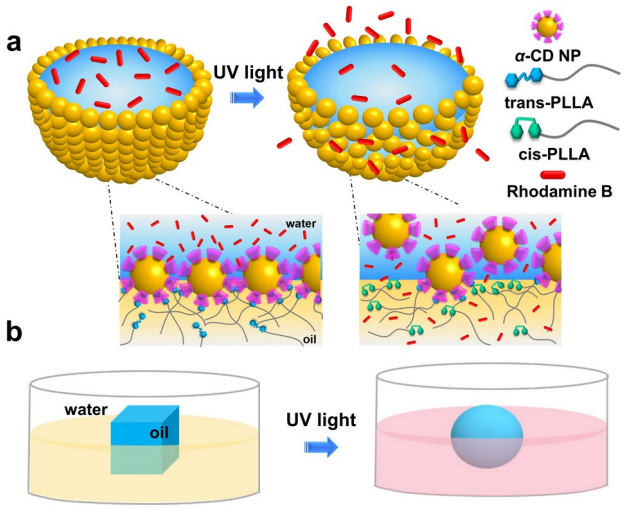

Figure 1. Schematics of (a) photoresponsive microcapsules and (b) jamming-controlled cubic to spherical shape change of the capsule with controlled cargo release.

The microcapsules are prepared using an emulsion-templated strategy. Stable water-in-oil (w/o) Pickering emulsions can be obtained by vigorously homogenizing a mixture of an aqueous dispersion of α-CD-functionalized NP and a toluene solution of Azo-PLLA at a water/oil ratio of 1:8. By changing the concentration of α-CD NP or Azo-PLLA, the emulsion size can be effectively tuned from several tens to hundreds of microns (Figure S2-3). The cooperative assembly kinetics of α-CD NP or Azo-PLLA has been studies in our previous report.[38] Azo-PLLA acts as a surfactant and assembles at the oil-water interface initially, triggering the molecular recognition of α-CD and Azo rapidly, leading to the *in-situ* formation and assembly of s-NPSs (Figure S4). When Rhodamine B is dissolved in the aqueous solution, fluorescence images in Figure 2a clearly shows the encapsulation of Rhodamine B in the microcapsules. The non-spherical shapes of the droplets indicate a jammed state of s-NPSs at the interface, greatly enhancing the mechanical strength of microcapsules. The structural integrity of the microcapsule is retained during drying (Figure 2b-c), and AFM measurements show that the thickness of the membrane is ~ 42.5 nm (Figure 2d-e).

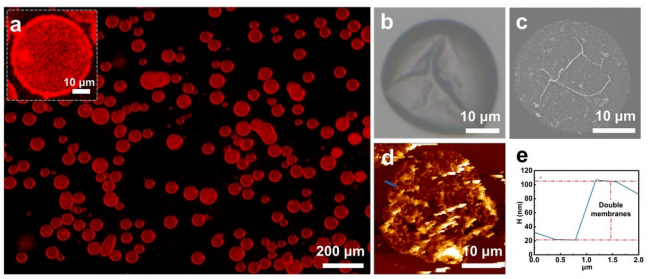

Figure 2. (a) Fluorescence image and confocal fluorescence image (inset) of microcapsules showing the encapsulation of Rhodamine B. (b) Optical microscopy image of the microcapsule after partial drying in air. (c) SEM image of the microcapsule after drying. (d) AFM image and (e) corresponding height profile along the trace that traverses double membrane thicknesses. [α-CD NP] = 1.0 mg mL^{-1}, [Azo-PLLA] = 1.0 mg mL^{-1}, [Rhodamine B] = 1.0 mg mL^{-1}, w/o = 1:8, speed = 15000 rpm, shear time = 2.0 min.

The jamming-controlled molecular diffusion is first investigated by using a pendant droplet in the jammed state. As shown in Figure 3a, aqueous solution of α-CD NPs and Rhodamine B is injected slowly into a toluene solution of Azo-PLLA to form a pendant droplet. The surrounding toluene solution is a light yellow in color, due to the Azo moieties. By reducing the droplet volume to compress the interfacial assemblies, wrinkles are observed on the droplet surface, indicating a jamming transition of the s-NPSs at the interface. Under visible light, there is no change in the wrinkles and the color of the toluene solution, indicating the binding energy of α-CD NPs at the interface is sufficiently high and the jammed α-CD NPs form a good barrier, preventing the diffusion of Rhodamine B into the oil phase. However, under UV irradiation, the wrinkles gradually disappear, and the shape of the contracted droplet returns to a classic droplet shape, indicating the jamming-to-unjamming transition of s-NPSs at the interface. An obvious color change of the surrounding toluene phase from light yellow to orange red is also observed, indicating the release of Rhodamine B (Video S1). Upon exposure to UV light, the trans-Azo-PLLA photo-isomerizes to cis-Azo-PLLA, leading to the dissociation of Azo from α-CD and reduction in the binding energy of α-CD NPs. The in-plane compressive load on the assembly at the interface forces an ejection of some of the α-CD NPs into the aqueous phase, relaxing the stress on the assembly, and changing the assemblies from a jammed state to an unjammed state. As a result, the permeability of the colloidal interface increases, and Rhodamine B passes through the interface. This jamming-controlled molecular diffusion can also be achieved by constructing a 2D colloidal membrane, macroscopic droplet and microcapsules in biphasic systems. As shown in Figure S5, with a jammed 2D colloidal membrane at the water-toluene interface as a barrier with Rhodamine B dissolved in the aqueous phase, no color change is observed in the upper oil phase using visible light. Also, the membrane shows excellent mechanical strength to support the water droplet (Figure S6). However, under UV irradiation, a clear color change is achieved in the oil phase within 5.0 min, indicating the diffusion of Rhodamine B from water to oil (Figure 3b). By suspending an aqueous droplet with dispersed α-CD NPs in a toluene/CCl_4 mixed solution with dissolved Azo-PLLA, a directed diffusion of Rhodamine B into the upper toluene phase is observed under UV irradiation, which is due to the higher solubility of Rhodamine B in toluene (Figure 3c, Video S2 and Figure S7). This jamming-controlled diffusion can also be obtained in the case of microcapsules settled at the bottom, that are fabricated by the w/o emulsion templating approach (Figure 3d).

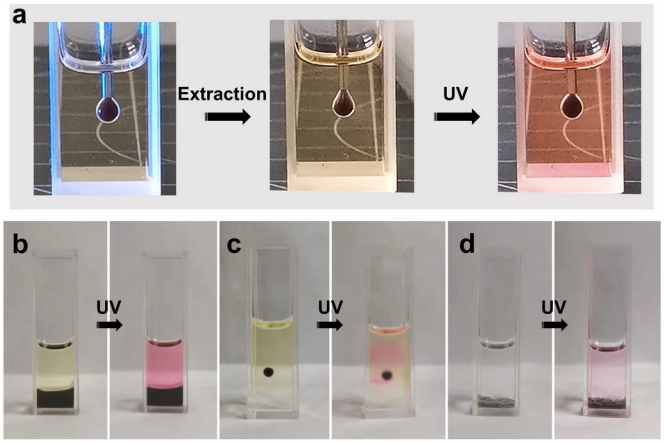

Figure 3. Optical image of (a) pendant droplet, (b) 2D colloidal membrane, (c) single droplet and (d) microcapsule showing the jamming-controlled diffusion of Rhodamine B under 365 nm UV light irradiation. [α-CD NP] = 1.0 mg mL^{-1}, [Azo-PLLA] = 1.0 mg mL^{-1}, [Rhodamine B] = 1.0 mg mL^{-1}.

Fluorescence images clearly show the diffusion of Rhodamine B from the microcapsules into the surrounding environment after UV irradiation (Figure 4a). The release of Rhodamine B from the microcapsules was quantitatively investigated by exposing the microcapsules to UV irradiation as a function of time. As shown in Figure 4b, almost 80% of Rhodamine B is released after 1 h UV exposure. A control experiment shows that, absent UV light, only 18% of the Rhodamine B is released during the same time period, due almost enttirely to the dissolution of a small quantity of Rhodamine B in the toluene during the preparation of microcapsules (Figure S8). By producing a 2D colloidal membrane at the oil-water interface, the release of Rhodamine B was found to be effectively controlled by the photoswitchable jamming-to-unjamming transition. As shown in Figure 4c-d and Figure S11, ~ 30% of Rhodamine B is released after UV irradiation for 2.0 min. When UV irradiation is removed, the s-NPSs jam again under visible light and the release of Rhodamine B is arrested immediately. Further release of Rhodamine B can be achieved by exposing the system to UV irradiation, showing a unique photo-controlled molecular diffusion.

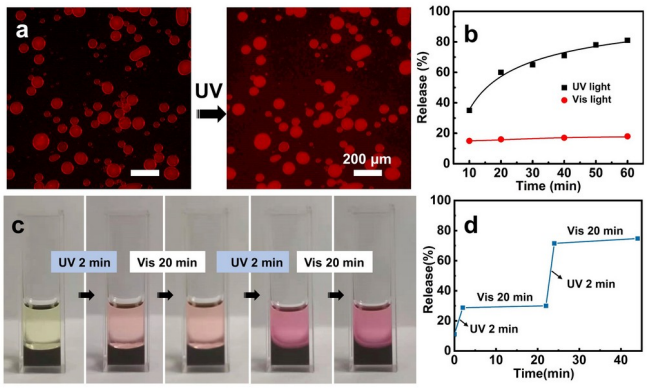

Figure 4. (a) Fluorescence image showing the release of Rhodamine B from microcapsules under UV irradiation. (b) Time-resolved Rhodamine B release profiles under UV (black line) or visible (red line) irradiation in microcapsule-based biphasic system. (c-d) Photo-controlled molecular diffusion in 2D colloidal membrane-based biphasic system. [α-CD NP] = 1.0 mg mL^{-1}, [Azo-PLLA] = 1.0 mg mL^{-1}, [Rhodamine B] = 1.0 mg mL^{-1}.

The jamming-controlled cargo release can also be achieved in all-liquid constructs with more complex shapes. As shown in Figure 5 and video S3, a water cube is prepared using all-liquid molding.[28] Under UV irradiation, an obvious change in the shape of the water shape from cubic to spherical is observed, indicating the jamming-to-unjamming transition of s-NPSs at the interface and, as a result, the water cube tends to return to its equilibrium state. At the same time, the loaded Rhodamine B is released from the aqueous phase, as evidenced by the color change of the surrounding oil phase (video S4).

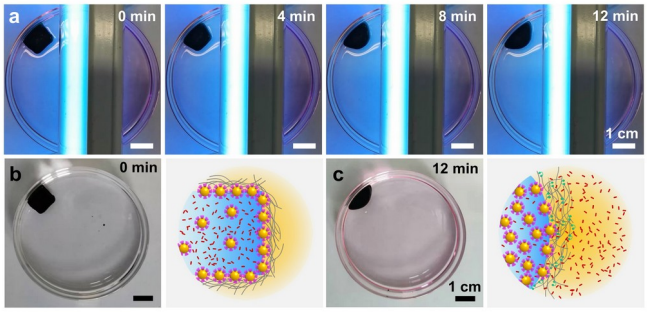

Figure 5. (a) Optical images showing the deformation of a water cube and the cargo release under UV irradiation. (b) Optical image of the water cube under visible light (left) and the schematic of the jammed interface (right). (c) Optical image of the deformed water after 12 min UV exposure (left) and the schematic of the unjammed interface (right). [α-CD NP] = 2.0 mg mL^{-1}, [Azo-PLLA] = 2.0 mg mL^{-1}, [Rhodamine B] = 1.0 mg mL^{-1}.

In summary, we demonstrate a simple approach for the preparation of micro- and macrocapsules using the interfacial jamming of photo-responsive nanoparticle surfactants at liquid-liquid interface. Photoresponsive s-NPSs are produced using the host-guest molecular recognition as the building block of the membrane encapsulating the fluid domains. A dynamic jamming of s-NPSs at the interface has been achieved by using light as an external trigger, leading to a jamming-controlled molecular diffusion at the interface, that shows promising applications for drug delivery, cosmetics and biphasic reactors.

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Keywords: nanoparticle surfactants • jamming • host-guest chemistry • microcapsules • interface

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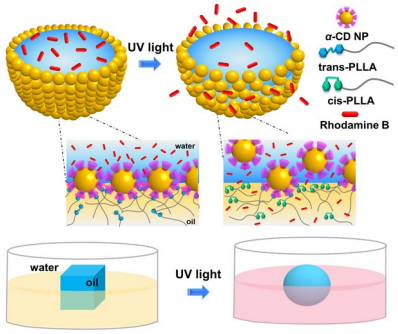

By taking advantage of host-guest molecular recognition at the oil-water interface, photoresponsive interfacial assemblies with jammed nanoparticle surfactants (NPSs) are present. The permeability of the colloidal membrane can be effectively manipulated by switching the NPSs from a jammed state to an unjammed state with a photo trigger, leading to a controlled molecular diffusion and release, affording a versatile platform for the construction of next generation smart interfacial systems.