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# Redox-Responsive, Reconfigurable All-Liquid Constructs

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**KEYWORDS:** *Structured liquids; host-guest chemistry; nanoparticle surfactants; jamming; liquid-liquid interfaces*

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**ABSTRACT:** Using host-guest chemistries in a biphasic system, a novel supramolecular nanoparticle surfactant (s-NPS) with redox-responsiveness is presented to structure liquids. The *in-situ* assembly/jamming and disassembly/unjamming of s-NPSs at the oil-water interface, are reversibly controlled by a switchable redox process, imparting a nanoscale redox-responsiveness, affecting the assemblies on all length scales. “Smart” all-liquid constructs including structured emulsions and programmable liquid devices are easily prepared, showing promising applications in responsive delivery, release and reaction systems.

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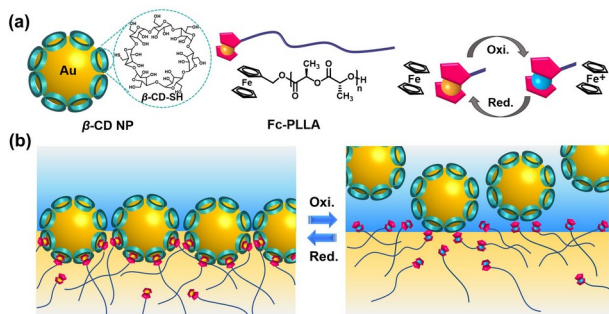
The structuring of liquids can be achieved by the formation, assembly, and jamming of nanoparticle surfactants (NPSs), where nanoparticles (NPs) and polymer ligands bind with each other dynamically at the interface between two immiscible liquids.<sup>1, 2</sup> The jamming of the NPSs kinetically traps the liquids in highly nonequilibrium shapes, while the desirable characteristics of liquids, e.g. transport and mobility, are retained. By using external fields, e.g. electric, magnetic or shear fields, to manipulate the shapes of the liquids, complex, reconfigurable all-liquid systems can be generated in a simple way, showing tremendous potential applications in encapsulants, delivery systems and microreactors.<sup>3-7</sup> The electrostatic interactions between NPs and functionalized ligands has frequently been used to generate NPSs at the oil-water interface, forming a monolayer to minimize interfacial tension. This reversible, dynamic, noncovalent interaction not only endows the NPSs with self-regulating properties to maximize the reduction in the interfacial tension, in terms of the number of ligands that attach to each NP, but also gives the resultant liquid constructs a stimuli-responsiveness, for example, to changes in pH and ionic strength.<sup>8-11</sup> By using electrostatic interactions at the interface, a variety of NPSs

with different dimensions and functions have been explored, significantly broadening potential applications of structured liquids.<sup>12-14</sup> However, generating NPSs and, by default, structured liquids that are responsive to multiple stimuli has received little attention.

Among the different noncovalent interactions, host-guest interactions provide a promising approach to construct supramolecular systems with excellent stimuli-responsive features.<sup>15-18</sup> Significant progress has been made in generating materials that are “smart” on multiple length scales based on host-guest chemistries, including micelles, microcapsules and hydrogels.<sup>19-21</sup> Inspired by this, very recently, we introduced the host-guest interaction between  $\alpha$ -cyclodextrin and azobenzene into biphasic systems, generating a supramolecular NPS (s-NPS) at the oil-water interface. The jammed and unjammed states of s-NPSs could be reversibly controlled by photoswitching, toggling the liquids from a nonequilibrium state to an equilibrium state in a reproducible manner, opening a pathway for the fabrication of multiresponsive all-liquid constructs.<sup>22</sup>

Herein, we report the formation, assembly and jamming of a new type s-NPS, based on the molecular recognition of ferrocene (Fc) and  $\beta$ -

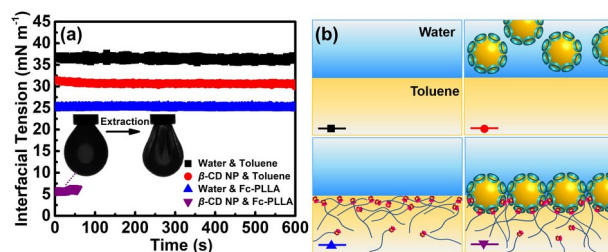
cyclodextrin ( $\beta$ -CD) at the oil-water interface. Normally, uncharged Fc is strongly bound in the cavity of  $\beta$ -CD by host-guest recognition, whereas the charged  $\text{Fc}^+$  dissociates rapidly.<sup>23-25</sup> This association and dissociation effect can be reversibly manipulated by a redox process (Figure 1). As a result, a desirable assembly/jamming and disassembly/unjamming of NPSs is achieved, leading to an efficient encapsulation and release of cargo. Moreover, the s-NPSs exhibit remarkably high interfacial activity. The *Plateau-Rayleigh* (PR) instabilities of a free-falling water jet can be completely suppressed, allowing the 3D printing of “smart” all-liquid devices that are stabilized with s-NPSs jammed at the interface.



**Figure 1.** (a) Chemical structures of the designed  $\beta$ -CD NP and Fc-PLLA (left); reduced and oxidized state of Fc (right). (b) Schematic representation of the reversible assembly and disassembly of s-NPSs at the oil-water interface in a redox process.

Prior to preparing the redox-responsive s-NPSs, water soluble  $\beta$ -CD-modified gold NPs ( $\beta$ -CD NPs),  $\sim 5$  nm in diameter, and oil-soluble Fc-terminated poly(l-lactide) (Fc-PLLA,  $M_w = 3.0$  K) were designed and synthesized, respectively (Figure S1-S5). The kinetics of the cooperative assembly of  $\beta$ -CD NPs and Fc-PLLA at the water-toluene interface was monitored by pendant drop tensiometry. As shown in Figure 2, with  $\beta$ -CD NPs dispersed in the aqueous phase against pure toluene, the equilibrium interfacial tension is  $\sim 30$   $\text{mN m}^{-1}$ , slightly lower than that for the pure water-toluene system ( $\sim 36$   $\text{mN m}^{-1}$ ), indicating the weak interfacial activity of  $\beta$ -CD NPs, arising from the amphiphilicity of  $\beta$ -CD. However, when the volume and, therefore, surface area of the droplet is reduced to compress the interfacial assembly, no wrinkles are observed on the droplet surface, indicating that the binding energy of  $\beta$ -CD NPs at the interface is not sufficient to hold the particles at the interface when compressed, and the droplet assumes its equilibrium shape (Video S1). However, when Fc-PLLA is dissolved in the toluene, an obvious reduction in the interfacial tension against water from  $\sim 36$  to  $\sim 24$   $\text{mN m}^{-1}$  is observed, indicating the surfactant nature of Fc-PLLA, due to the hydrogen bonding between PLLA carbonyl groups and water. Wrinkling is only observed after a significant contraction of the droplet, but disappears rapidly due to a

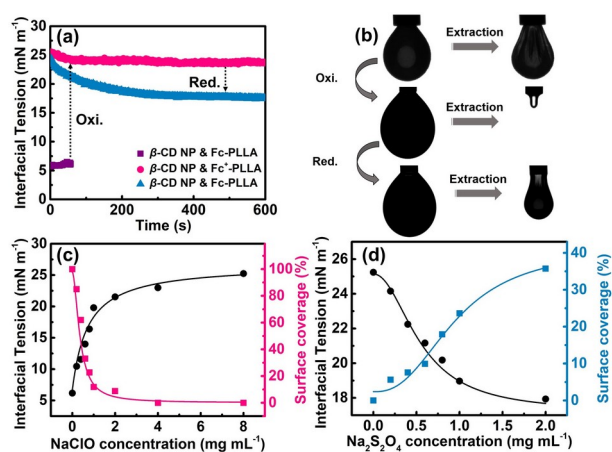
reorganization of Fc-PLLA at the interface (Video S2). With  $\beta$ -CD NPs dispersed in the water and Fc-PLLA dissolved in toluene, the interfacial tension rapidly decreases to  $\sim 6.0$   $\text{mN m}^{-1}$ , and the interface rapidly saturates ( $\sim 70$  s), reaching full coverage, then a deformation of the droplet is observed. The Young-Laplace equation is no longer valid and the interfacial tension cannot be measured by the shape of the pendant drop (Video S3). These results give clear evidence that the host-guest interactions between  $\beta$ -CD and Fc are triggered at the interface, leading to the *in-situ* formation and assembly of s-NPSs with high interfacial activity. With hydrogen bonding, the terminal Fc groups and  $\beta$ -CD NPs can locate at the oil-water interface, reducing the interfacial energy, and significantly enhancing the probability of collision between Fc and  $\beta$ -CD NPs. Moreover, the hydrogen bonding promotes water penetration into the oil phase close to the interface, presenting a high energy environment to Fc near the interface, leading to the triggering of molecular recognition (Figure S6). Systematic experiments and discussions on the interactions at the oil-water interface can be found in the supporting information (Figure S7-S9).



**Figure 2.** (a) Time evolution of interfacial tension of different oil-water systems including water/toluene,  $\beta$ -CD NP @water/toluene, water/Fc-PLLA@toluene and  $\beta$ -CD NP @water/Fc-PLLA@toluene, [ $\beta$ -CD NP] =  $1.0$   $\text{mg mL}^{-1}$ , [ $\text{Fc-PLLA}$ ] =  $1.0$   $\text{mg mL}^{-1}$ . (b) Schematics of different oil-water systems in (a).

The redox-responsiveness of s-NPSs is investigated by using sodium hypochlorite ( $\text{NaClO}$ ) as the oxidant and sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ) as the reductant. By adding  $4.0$   $\text{mg NaClO}$  directly into  $1.0$   $\text{mL Fc-PLLA}$  toluene solution ( $[\text{Fc-PLLA}] = 1.0$   $\text{mg mL}^{-1}$ ), the hydrophobic Fc group is oxidized to hydrophilic  $\text{Fc}^+$ . With  $\text{Fc}^+$ -PLLA dissolved in toluene and  $\beta$ -CD NPs dispersed in water, an interfacial tension of  $\sim 23$   $\text{mN m}^{-1}$  is obtained, which is significantly higher than the value of  $\sim 6.0$   $\text{mN m}^{-1}$  measured with Fc-PLLA as the ligand, indicating the disassembly of s-NPSs at the interface, due to the low affinity between  $\text{Fc}^+$  and  $\beta$ -CD (Figure 3a). As a result, no wrinkles are observed when contracting the droplet (Video S4). The oxidized  $\text{Fc}^+$ -PLLA can be reduced again by adding  $2.0$   $\text{mg Na}_2\text{S}_2\text{O}_4$  into  $1.0$   $\text{mL } \beta$ -CD NP aqueous solution. The Fc group reinserts into the cavity of  $\beta$ -CD, causing the re-formation and re-assembly of s-

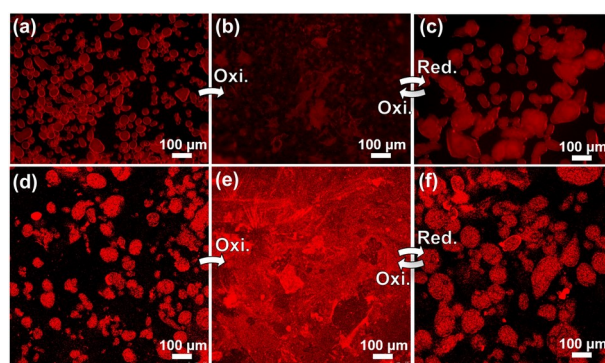
NPSs, reducing the interfacial tension to  $\sim 17$  mN  $m^{-1}$ . When contracting the droplet, the s-NPSs jam again and wrinkles return (Video S5). It should be noted that the interfacial tension is relatively higher in comparison to the original state ( $\sim 6.0$  mN  $m^{-1}$ ) with a decreased surface coverage of s-NPSs, indicating that the reduction of Fc<sup>+</sup>-PLL A is insufficient. Since the reduction only occurs at the water-toluene interface, the reaction area is limited, leading to a low reaction efficiency. By changing the amount of NaClO and Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, the extent of disassembly and assembly of the s-NPSs can be effectively controlled, as evidenced by the interfacial tension and surface coverage (Figure 3c-d, Figure S10). Furthermore, by using ferric chloride (FeCl<sub>3</sub>) as the oxidant and sodium borohydride (NaBH<sub>4</sub>) as the reductant, a redox-responsiveness of s-NPSs can also be realized (Figure S11).



**Figure 3.** (a) Time evolution of interfacial tension in a redox process. [ $\beta$ -CD NP] = 1.0 mg mL<sup>-1</sup>, [Fc-PLL A] = 1.0 mg mL<sup>-1</sup>, [NaClO] = 4.0 mg mL<sup>-1</sup>, [Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>] = 2.0 mg mL<sup>-1</sup>. (b) Redox-switchable reconfiguration of pendent droplets between jammed and unjammed states. (c, d) The evolution of interfacial tension and surface coverage as a function of oxidant and reductant concentrations.

Vigorously homogenizing the mixture of water with dispersed  $\beta$ -CD NPs and toluene with dissolved Fc-PLL A results in the formation of stable water-in-oil (w/o) Pickering emulsions at a water/oil ratio of 1:6. Due to the interfacial jamming of the s-NPSs in the shear field, all the droplets have highly irregular shapes (Figure 4a and 4d). The droplet size can be adjusted from several tens to hundreds of microns by varying the concentrations of either  $\beta$ -CD NP or Fc-PLL A (Figure S12). Remarkably, by taking advantage of the redox-responsiveness of s-NPSs, a switchable emulsification/demulsification can be easily achieved, showing a promising application for encapsulation and release. As shown in Figure 4, with the addition of NaClO to the emulsions loaded with Rhodamine B, a disassembly/unjamming of the s-NPSs occurs, leading to a rapid disruption of droplets and

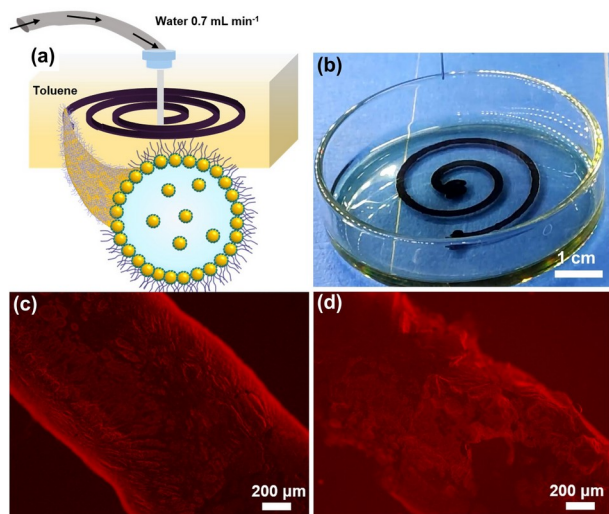
complete cargo release (Figure 4b and 4e). The released cargo can be re-encapsulated by adding Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> to the de-emulsified system, then homogenizing. s-NPSs assemble and jam again at the interface, leading to the re-formation of the droplets (Figure 4c and 4f). Due to the insufficient reduction of Fc<sup>+</sup>-PLL A, less s-NPSs are formed to stabilize the interface. As a result, the droplet size increases slightly. This switchable emulsification/demulsification can be repeated multiple times, recycling the loading and release of cargoes (Figure S15).



**Figure 4.** (a-c) Fluorescence and (d-f) laser confocal microscope images showing the redox-switchable encapsulation and release of cargoes via an emulsification/demulsification process. [ $\beta$ -CD NP] = 1.0 mg mL<sup>-1</sup>, [Fc-PLL A] = 1.0 mg mL<sup>-1</sup>, [NaClO] = 4.0 mg mL<sup>-1</sup>, [Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>] = 2.0 mg mL<sup>-1</sup>, [Rhodamine B] = 0.5 mg mL<sup>-1</sup>.

The high interfacial activity and redox-responsiveness of s-NPSs make it possible to construct “smart” all-liquid devices. By using all-liquid 3D printing,<sup>6</sup> i.e. printing one liquid in another incompatible liquid phase, stable aqueous tubules with a programmed spatial arrangement are produced in a low viscosity toluene solution (Figure 5a-b, Figure S17, Video S6). s-NPSs form *in-situ*, assemble rapidly at the interface, significantly reducing the interfacial tension, and completely suppressing the PR instabilities of the water jet.<sup>26</sup> When jammed, an elastic film with exceptional mechanical strength is generated, allowing the stabilization of tubular structures. The rigid liquid device can be used for mass storage and transmission, while retaining the redox-responsiveness of the s-NPSs. As shown in Figure 5c-d, in an oxidation process by adding NaClO to the toluene solution, the channel collapses in a short time, releasing the Rhodamine B loaded in the aqueous channel to the oil phase (Figure S18, Video S7). More importantly, due to the inherent functionality of the s-NPS wall, numerous potential applications including advance catalysis, chemical separations can be realized. We also note that complex liquid devices can be prepared by a molding strategy (Figure S19).





**Figure 5.** (a) Schematic of 3D printing of s-NPS-stabilized aqueous tubules in toluene. (b) Optical image of an aqueous spiral printed in toluene. (c) Fluorescence image of the tubule channel encapsulating Rhodamine B. (d) Fluorescence image showing the collapse of the tubule channel and release of Rhodamine B in an oxidation process. [ $\beta$ -CD NP] = 20 mg mL<sup>-1</sup>, [Fc-PLLA] = 20 mg mL<sup>-1</sup>.

In summary, we have successfully demonstrated a redox-responsive s-NPS, by using inclusion complexes between  $\beta$ -CD and Fc at the oil-water interface. Due to the dynamic nature of this supramolecular interaction, the assembly/jamming and disassembly/unjamming of s-NPS can be reversibly switched in a redox process, endowing the resultant assemblies with multiple stimuli responsiveness. Taking advantage of the dynamic s-NPSs, reconfigurable droplets with structural stability can be prepared, and used to reversibly encapsulate and release cargoes via a redox stimulus. Using all-liquid 3D printing, complex, programmable liquid devices with supramolecular function can be easily generated in a low viscosity system, showing tremendous potential applications in responsive soft-matter delivery and chemical systems.

## ASSOCIATED CONTENT

**Supporting Information.** This material is available free of charge via the Internet at <http://pubs.acs.org>. Experimental details and characterization data

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