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Nanoparticle surfactants and structured liquids

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Abstract

Materials are usually classified as solids or liquids, based on their structural stability, dynamic response, and rheological properties. Structured liquid, a new state of matter, has attracted much attention in recent years. Different with either solid or liquid, structured liquid combines the desirable characteristics of fluids with the structural stability of a solid, showing a myriad of potential applications in encapsulation, biphasic reactors, and programmable liquid constructs. Here, a brief review is given, by introducing a new strategy to structure liquids based on the formation, assembly, and jamming of nanoparticle surfactants (NPSs) at liquid-liquid interfaces. The interfacial packing of the NPSs can be effectively manipulated using external triggers, endowing the structured liquids with adaptiveness and responsiveness to changes in their external environment.

Keywords Nanoparticle surfactants · Interfacial assembly · Structured liquids

Introduction

When it comes to liquids, the first words that come to mind are soft, flowing, and shapeless. These properties distinguish liquids from solids, which, in turn, make liquids difficult to be processed and molded. Imagine how wonderful it would be if liquids could be shaped as desired. In this case, the structures of liquids can be manipulated to complex geometries and can be further used for the construction of complex liquid devices for charge and mass transduction, compartmentalized reac- tion, encapsulation, and delivery. Recently, by taking advan- tage of the jamming of colloidal particles at the liquid-liquid interface, a new kind of soft material, termed structured liq- uids, has been put forward. This field emerged from bicontinuous interfacially jammed emulsion gels, or bijels [1, 2], which are prepared by using the spinodal decomposition of a binary liquid mixture in the presence of the colloidal particles. These particles are trapped at the interface without imposing any preferred interfacial curvature. As phase separation proceeds, the system attempts to reduce the interfacial area, the packing of the particles at the interface densifies, and the particles jam; not allowing the interfacial area to decrease further, phase separation is arrested. And the bicontinuous structure characteristic of spinodal phase separation is locked in [3–6]. However, to obtain stable bijel structure, it usually requires the particles to be strictly neutral wetting at the liquid-liquid interface, which can be a time- consuming and difficult chemical challenge to meet [7]. These disadvantages become increasingly more significant as the size of the particles decreases to the nanoscopic level. Since the size of the particles are small, the binding energy of the particles to the interface is small, and, as a consequence, the compressive force associated with the reduction in the interfacial area can easily cause the nanoparticles to be ejected from the interface [8, 9]. In addition, the number of fluids that undergo spinodal phase separation is not limitless, and, hence, this rather intriguing behavior becomes less general in applicability.

In this review, we will introduce an alternative strategy to structure liquids by using nanoparticle surfactants (NPSs), where functionalized NPs dispersed in one liquid and polymer/oligomer ligands dissolved in the second liquid inter- act at the interface between the liquids. The energy holding each NP at the interface can be significantly increased by the self-regulated number of ligands anchored to the NPs. Under

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the influence of an external field, such as electric field, jetting, and confinement, liquids can be manipulated to arbitrary shapes, showing promising potential applications in encapsu- lation, delivery systems, and unique microfluidic devices [9].

Assembly and jamming of nanoparticles at liquid-liquid interfaces

The thermodynamics of solid particles at the interface was first described by Pieranski [10], by studying the self-assembly of polystyrene spheres at the water-air interface. This theory illuminates that the reducing free energy is the main driving force for the interfacial assembly of particles and also applies to particles at the liquid-liquid interface, e.g., oil-water interface (Fig. 1) [11, 12]. For example, when placing a spherical particle of radius r from one phase (oil or water) to the interface, the change in the interfacial energy, ΔE, can be calculated by the following equation:

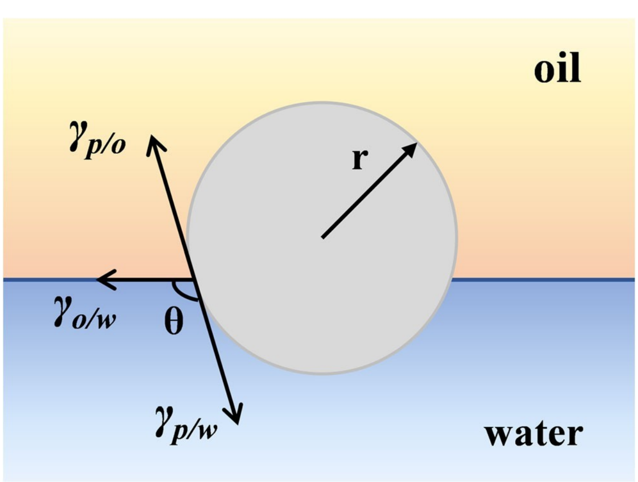
$$\Delta E = E_{min} - E_0 = -\frac{\pi r^2}{\gamma_{o/w}}\left[\gamma_{o/w} - \left(\gamma_{p/w} - \gamma_{p/o}\right)\right]^2 \quad (1)$$

where $\gamma_{p/o}$, $\gamma_{p/w}$, and $\gamma_{o/w}$ are the interfacial tensions of the particle-oil, particle-water, and oil-water interfaces, E_{min} is the minimum energy when NP is located at the interface, and E_0 is the energy when NP is located in the oil or water phase. Along with Young's equation,

$$\gamma_{p/o} - \gamma_{p/w} = \gamma_{o/w} \cos\theta \quad (2)$$

where θ is the contact angle of particles at the interface [9, 12–14] and ΔE also can be expressed as

$$\Delta E = -\pi r^2 \gamma_{o/w}\left(1 - |\cos\theta|\right)^2 \quad (3)$$



From Eqs. 1 and 3, it is clear that, for a given system, the particle stabilization at the oil-water interface is strongly size- dependent. The reduction in the interfacial energy is propor- tional to the square of the particle radius r. For micrometer- sized particles, the decrease in total free energy is ~ 10^7 k_BT (k_B is the Boltzman constant, T is the Kelvin temperature), much larger than thermal energy, leading to an effective con- finement of large colloids to the interface [9, 13–18]. However, for nanometer-sized particles, or NPs, the energy reduction is closed to thermal energy (several k_BT). As a re- sult, thermal fluctuation can easily detach NPs from the inter- face, leading to a dynamic or "liquid-like" nature of the assemblies.

As the density of particles at the liquid-liquid interface is increased, the particles will gradually become crowded, forming a particle monolayer in a jammed state at the interface eventually. In this case, the interfacial particles lose mobility and the mechanical properties of the interfacial assemblies are enhanced, showing a "solid-like" nature. More interestingly, the interfacial jamming of particles provides a pathway to shape the liquid-liquid interface in a biphasic system, or in other words, liquids can be structured to different shapes, just like the solid materials. However, in comparison with micrometer-sized particles, it is difficult to achieve structured liquids using NPs, due to the low interfacial energy of each

Fig. 1 A spherical particle at the oil-water interface

NP. Thus, the NPs can be easily ejected from the interface, unable to maintain the nonequilibrium liquid shapes.

Nanoparticle surfactants

By dispersing carboxylated polystyrene NPs in water and dis- solving amine-terminated polydimethylsiloxane (PDMS- NH_2) in oil, Cui et al. developed a method for constructing "Janus-like" nanoparticle surfactants (NPSs) at the oil-water interface [19]. The electrostatic interactions between -COO^- and -NH_3^+ drive the segregation of NPs to the interface, forming a monolayer of NPs. When an electric field was ap- plied, the spherical droplet suspended in oil was deformed into an ellipsoid, exposing more interfacial area, leading to the assembly of more NPSs at the interface. When the electric field was removed, the droplet attempted to return to its spher- ical shape with the lowest energy (Fig. 2a). However, during the decrease of the interfacial area, NPSs jammed at the inter- face, arresting the further change of the droplet shape, kineti- cally trapping the drop into a highly nonequilibrium shape, which can be stable for months (Fig. 2b). The shape of the droplet can be further reconfigured by applying sequential electric fields in the same or different directions, where the NPSs at the interface undergo a local unjamming and jam- ming process. On the other hand, by using PDMS capped with two amine end groups, the interfacial NPs could be cross-linked, suppressing the deformation of the droplet shape.

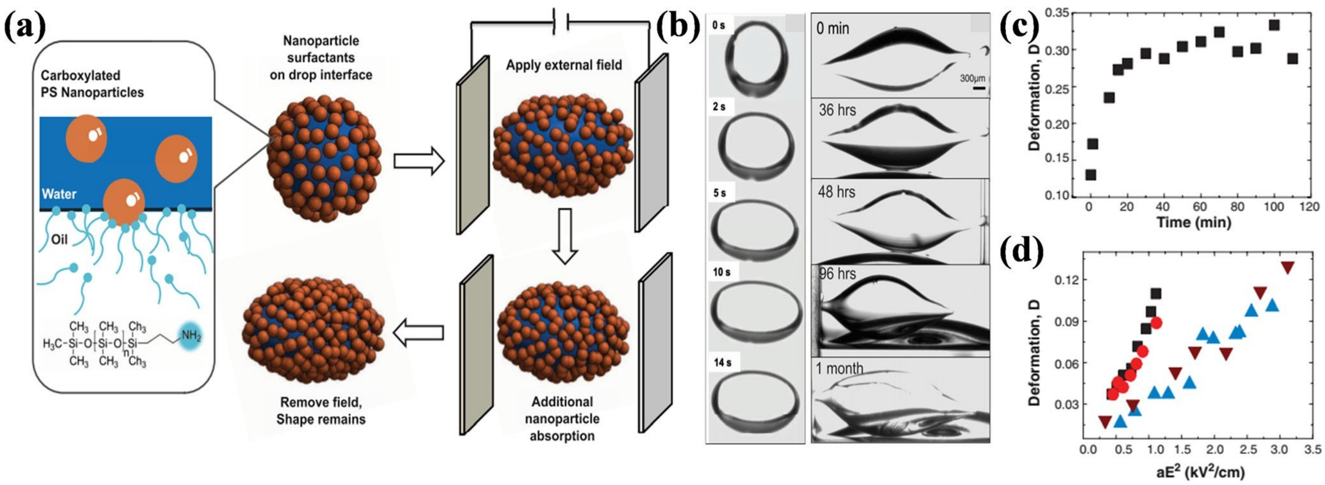


Fig. 2 (a) The schematics of structuring the droplet by an electric field.
(b) The deformation and stability of droplets with NPSs assembled at the interface. (c) The deformation of the water droplet with time. (d) The linear relationship between the D and aE^2 under various conditions. Reproduced with permission [19]. Copyright 2013, The American Association for the Advancement of Science

The assembly kinetics of NPSs was tracked by investigat- ing the relationship between the deformation (D) of the drop- let and aE^2 under different conditions, where $D \approx aE^2/\gamma$, a is the radius of the initial drop, E is the electric field, and γ is the interfacial tension (Fig. 2d). With only NPs dispersed in aque- ous phase against pure oil, the droplet deformation was almost the same as the pure water-oil system. With PDMS-NH_2 dis- solved in the oil against pure water, the rate at which D changed with E^2 increases, indicating that PDMS-NH_2 is a surfactant, and the interfacial tension is decreased. However, when removing the field, the droplet returned to its spherical shape. With NPs dispersed in the aqueous phase and PDMS- NH_2 dissolved in the oil, the rate at which D changed with E^2 increases further, indicating the formation of the NPSs at the interface and the further reduction in the interfacial tension. These results demonstrate the mechanism of the assembly and formation of the NPSs; that is, the NPs alone are not interfacially active, whereas the PDMS-NH_2 is. As a result, PDMS-NH_2 assembles at the oil-water interface first and then the NPs diffuse to the interface, interacting with PDMS-NH_2, leading to the formation of the NPSs. The assembly kinetics of NPSs at the water-oil interface can also be probed by tracking the dynamic interfacial tension using pendant drop tensiometry.

By taking advantage of the cooperative interfacial assem- bly between NPs and polymer ligands, the interfacial assem- bly as well as the packing of NPSs can be effectively adjusted by tuning parameters such as the pH, the concentration of NPs/ligands, and the ionic strength of aqueous phase [8, 20]. Huang et al. systematically investigated the effect of pH on the formation and assembly of NPSs, by using carboxylated NPs dispersed in water and PDMS-NH_2 dissolved in toluene [21]. Since the pK_a of carboxyl group was ~ 4.2 and the pK_a of the amine group was ~ 9.0, in the pH range of 4.2 and 9.0, the deprotonated carboxyl groups and protonated amine groups interacted strongly at the interface, leading to the formation of the NPSs. The equilibrium interfacial tension decreased with decreasing pH (Fig. 3a). However, it does not mean that at lower pH, more NPSs form at the interface. When the pH was close to the pK_a of the carboxyl groups, both carboxyl groups and amine groups were highly protonated, and the reduction in the interfacial tension mainly arose from the protonated amine groups. By estimating the interfacial coverage of NPs at different pH and constructing ellipsoidal droplets with an electric field, it showed that when pH > 5.0, the interfacial coverage of NPs was high and the deformed droplet could be trapped after removing the electric field. In the pH range of 4.3–5.0, the interfacial coverage of NPs decreased and the deformed droplet relaxed to some extent. When the pH was lower than 4.3, the carboxyl groups were almost fully proton- ated and the electrostatic interactions became weak. The de- formed droplet completely returned to spherical shape after removing the electric field (Fig. 3b). By taking advantage of this pH responsiveness, the jamming and unjamming of NPSs at the interface can be reversibly controlled, providing a sim- ple way to reconfigure the structured liquids. After adding base into the water droplet, the droplet could be deformed again with an electric field and maintained in the nonequilibrium shape.

The assembly behavior of NPSs at the oil-water interface can also be controlled by tuning the ionic strength of the aque- ous phase. Generally, the charge density of charged particles can be effectively reduced by increasing the ion strength in solution. The electrostatic repulsion between particles can be weakened, leading to an enhanced interfacial activity of par- ticles. This effect is also applicable to NPSs. By increasing the ionic strength of the aqueous phase dispersing carboxylated NPs, Chai et al. obtained a denser packing of NPSs at the oil- water interface and demonstrated the transformation of the interfacial assemblies form liquid-like to solid-like (Fig. 4a)

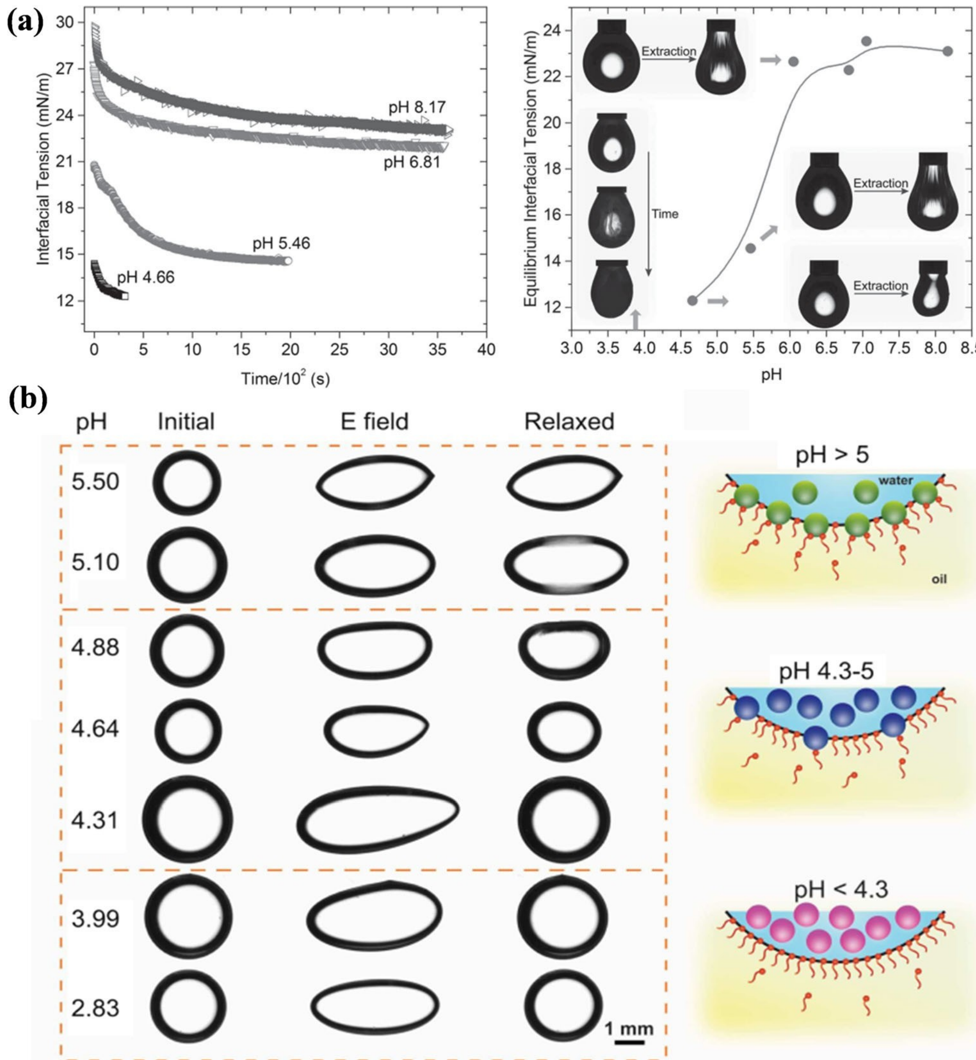


Fig. 3 (a) pH-Dependent assem- bly of NPSs at the water-oil in- terface. (b) Structuring and restructuring liquids through pH- controlled assembly of NPSs. Reproduced with permission [21]. Copyright 2016, Wiley-VCH

[22]. Also, by taking advantage of the in situ AFM, a densely packed state of NPSs at the interface was observed, with crystalline-like arrays in some areas (Fig. 4b).

In general, NPSs provide a simple and universal strategy to realize the stable assembly of NPs at the liquid-liquid interface. The assembled NPs at the interface can be in either

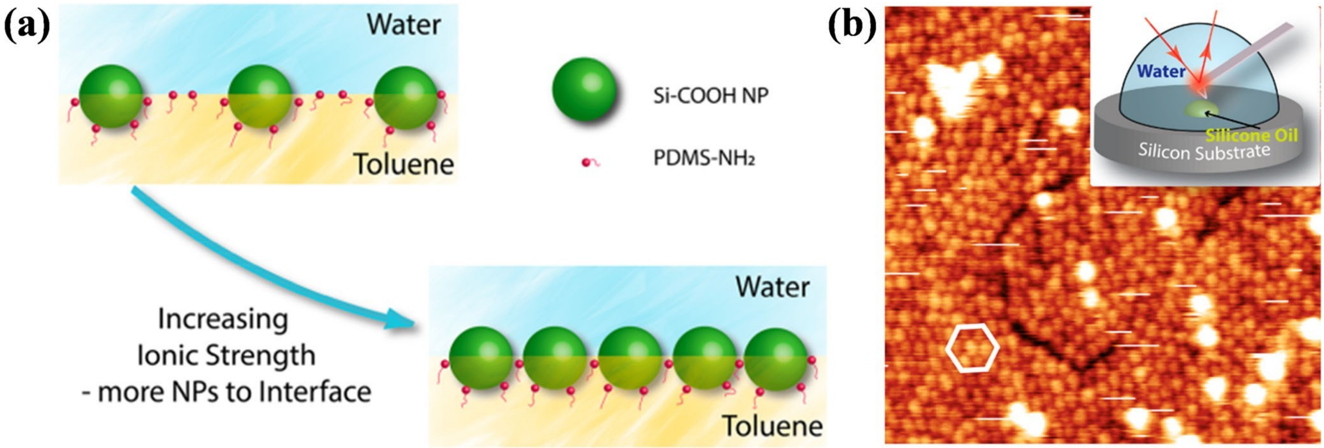


Fig. 4 (a) Schematic diagram of the NPSs assembled at the water-oil interface with increasing ionic strength. (b) In situ AFM image of the interfacial NPS assemblies at 100-mM NaCl. Reproduced with permission [22]. Copyright 2017, American Chemical Society unjammed or jammed states, which can be readily switched using external triggers such as pH and ionic strength. The mechanical properties of the interfacial assemblies can be ef- fectively tuned by varying the concentration of NPs/ligands, the type of NP/ligand, the NP size, and the ligand molecular weight.

Construction of structured liquids

All-liquid 3D printing

Traditional 3D printing technology is an additive manufacturing process to make solid objects. The 3D printer nozzle is controlled by the computer software to stack molten raw ma- terials layer by layer according to the designed spatial path and finally cool down to make solid parts. The prototype of a 3D- printed object can be derived from a spatial scanning model or electronic data designed by other software, and the 3D object can be processed to any geometric feature [23]. By combining 3D printing with the concept of structured liquids, it would be fascinating if the liquid could be printed using the same design and control methods, which opens a pathway to construct a complex liquid device, where the liquids retain the inherent mobility and transport characteristics yet would permit flow by tailored pathways.

All-liquid 3D printing refers to the technology of printing one liquid with a programmed spatial arrangement in another incompatible liquid phase. To achieve all-liquid 3D printing, an effective suppression of the Plateau-Rayleigh (PR) insta- bilities of liquid flow is important [24]. In a previous study, the effect of NPSs on PR instabilities was investigated by injecting an aqueous jet dispersed carboxylated NPs into the oil dissolving PDMS-NH_2. In comparison with the control experiments without NPSs at the interface, longer jet breakup lengths were observed, indicating the significant reduction in the interfacial tension [20, 25, 26]. Later, by using the coop- erative assembly of rod-like cellulose nanocrystals (CNCs), and amine-terminated polystyrene (PS-NH_2), Liu et al. report- ed the formation and assembly of cellulose nanocrystal sur- factants (CNCSs) [27]. The interfacial activity of CNCSs could be significantly enhanced by decreasing the pH, leading to a rapid formation of a CNC monolayer at the interface (Fig. 5a and b). Since jet formation occurs rapidly, this high rate of CNCS formation and assembly is essential to arrest PR insta- bilities and stabilize the tubular structures. At a certain flow rate, a clear dripping-to-jetting transition was achieved with decreasing pH. By varying parameters such as the concentra- tion of CNC/PS-NH_2, the flow rate, and the molecular weight of PS-NH_2, continuous tubular structures could be obtained. In the subsequent work, using a 3D printer, Forth et al. real- ized the printing of the liquids in high-viscosity silicone oil [28]. Complex liquid devices including sigmoidal and branched structures were prepared, which could be used for the mass transmission and chemical reactions (Fig. 5c). Further, by using the novel 2D transition metal carbides and nitrides (MXenes) [30–33], Cain et al. presented the creation of all-liquid 3D-printed devices with MXene surfactants, showing potential applications in all-liquid electrochemical and energy storage devices (Fig. 5d) [29].

All-liquid molding

Similar with 3D printing, the traditional molding method, which is a standard procedure to process polymers in industry, also provides a way of constructing structured liquids. Using the interfacial assembly and jamming of CNCSs, Shi et al. introduce the strategy of all-liquid molding, to produce struc- tured liquids that retain the shape and details of the mold [34]. In this strategy, a 3D printer is used to produce the mold with a patterned trench. The mold is made of hydrophobic polylactic acid (PLA). After prewetting the mold with the PS-NH_2 solution in CCl_4, an aqueous CNC dispersion is placed into the mold. Without prewetting, the aqueous solu- tion would stick to the corners of the cavity, leading to an unfixed liquid in the trench. After that, the filled mold is im- mersed into CCl_4 solution dissolving PS-NH_2, and CNCSs are formed rapidly on the exposed surface. Due to the higher density of CCl_4 than water, the aqueous phase rises out of the mold, with more CNCSs assembled and formed at the interface. In the process of rising, the interface area decreased, leading to a jammed state of CNCSs, arresting further varia- tion of the liquid shape (Fig. 6a).

As we discussed above, pH has significant effects on the interfacial activity of CNCS as well as the structuring of the aqueous phase. As shown in Fig. 6b, with the increase of the pH from 3.0 to 7.0, the fidelity of the molding decreased, and at the pH of 9.0, only spherical droplet could be achieved. Moreover, if the pH was further decreased to 1.2, the CNCs began to aggregate, forming a hydrogel network. Using all- liquid molding, a shaped CNCS-coated gel was prepared with a high fidelity, generating an interfacial bulk gel composite (Fig. 6c).

Bijels

Huang et al. reported a simple method for preparing bijels by solution shearing at room temperature using NPSs (Fig. 7a) [35]. In this strategy, carboxylated polystyrene NPs were dis- persed in water and two different molecular weights of PDMS-NH_2 were dissolved in the oil phase to prepare bijels. By varying the concentration of NPs and polymer ligands, the water/oil ratio, and other factors, the characteristic size of the bijels could be effectively adjusted, and channel width as low as 500 nm could be achieved (Fig. 7b and c). In comparison with bijels produced via spinodal decomposition, this strategy

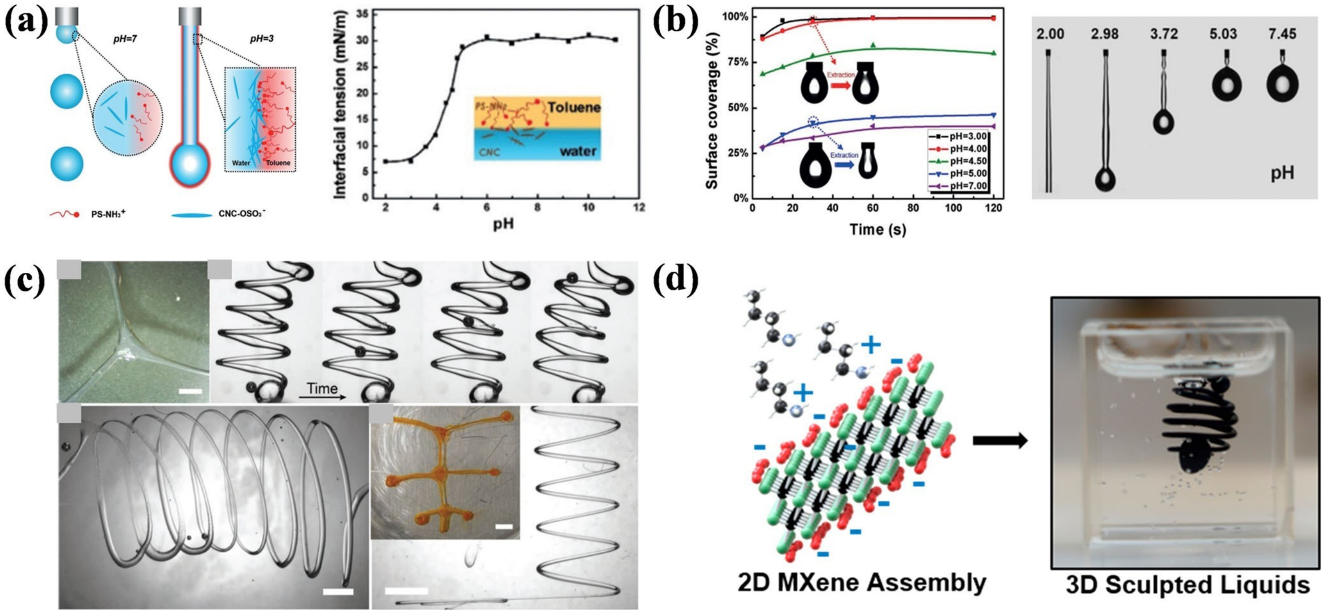
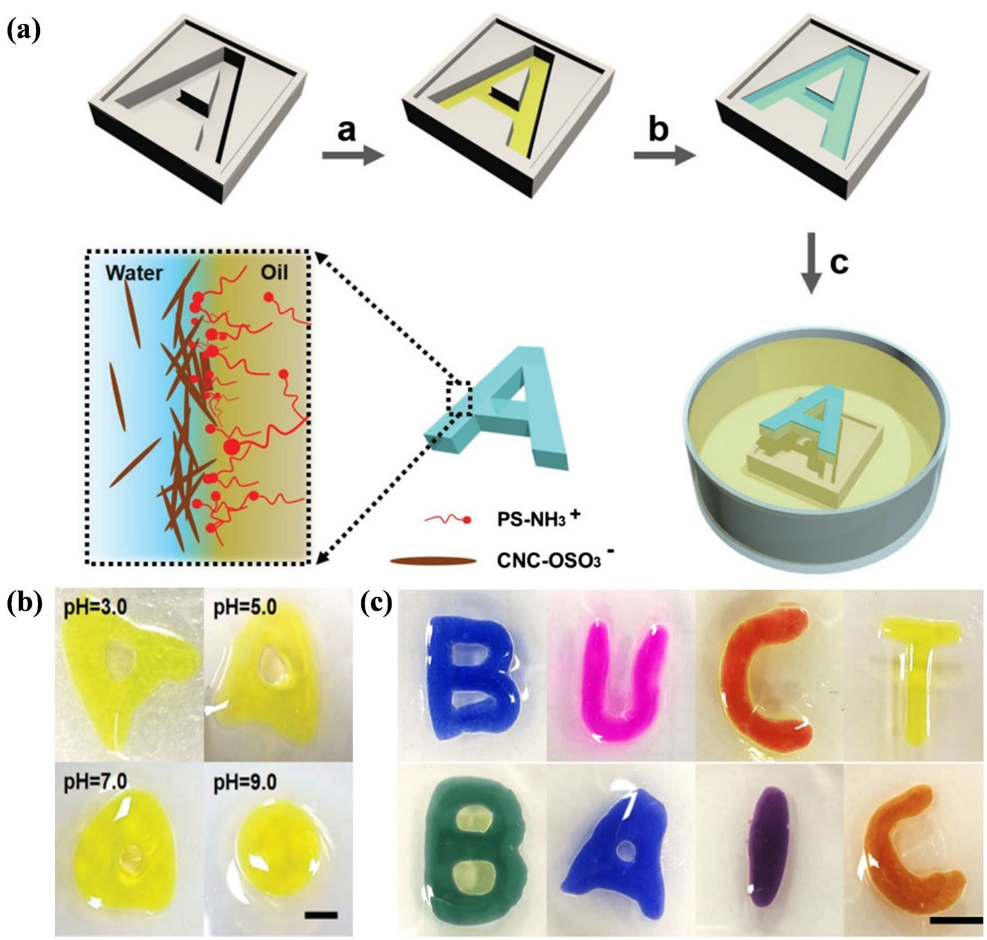


Fig. 5 (a) Schematics of the formation of tubule liquids using CNCSs (left) and interfacial activity of CNCSs at different pH (right). (b) Surface coverage variation of the droplet with time (left) and breakup length variation of the water jet at different pH (right). Reproduced with permis- sion [27]. Copyright 2017, Wiley-VCH. (c) All-liquid 3D-printed systems. Reproduced with permission [28]. Copyright 2018, Wiley-VCH. (d) All-liquid 3D-printed devices using MXene surfactants. Reproduced with permission [29]. Copyright 2019, American Chemical Society

Fig. 6 (a) Schematics of all-liquid molding process. (b) Dyed liquid letter molded in different pH. (c) Dyed gel letters molded in pH of
1.2. Scale bar = 5 mm. Reproduced with permission [34]. Copyright 2018, Wiley-VCH



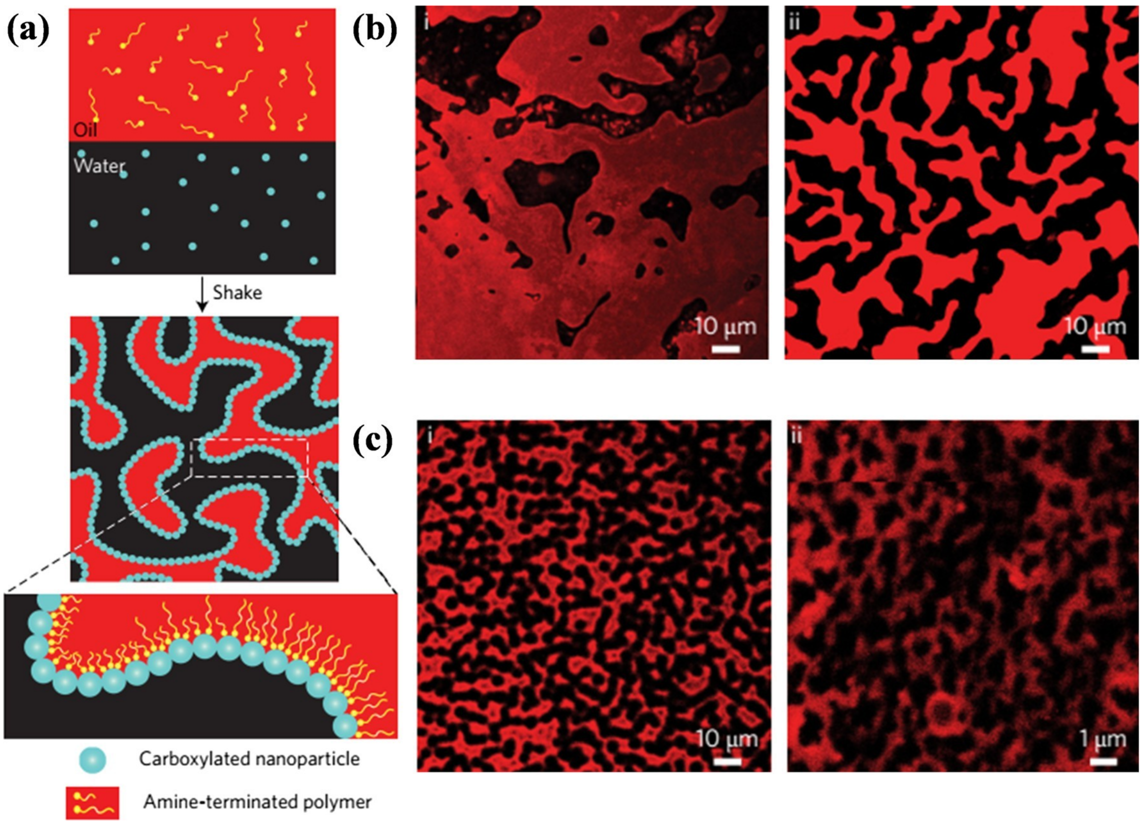


Fig. 7 (a) The preparation of bijels using NPSs at the oil-water interface.
(b) Bicontinuous structures formed by NPSs with different NP concentrations at a fixed concentration of PDMS-NH_2. (c) Bicontinuous structures formed by NPSs at constant particle concentration with differ- ent concentrations of PDMS-NH_2. Reproduced with permission [35]. Copyright 2017, Springer Nature.

is much easier and universal, which can be used to produce bijel structures using a range of chemistries, where the solvents, particles, and polymer ligands can all be changed.

Applications

All-liquid microfluidics

Microfluidics, also known as lab-on-a-chip or microfluidic lab, refers to the technology that processes or manipulates tiny fluids using fluidic channels (tens to hundreds of micrometers in size) [36]. Microfluidics have the ability to miniaturize the basic functions of the laboratory, such as biology and chem- istry, onto a few square centimeters chip, and can complete all the steps of sample pretreatment, separation, dilution, mixing, chemical reaction, and detection, so it is also called miniature full-analysis system.

Structured liquids provide a new strategy for the fabrication of all-liquid microfluidic devices. Feng et al. constructed a specific shape of aqueous fluidic channels in the oil phase using nanoclay surfactants and superhydrophobic- superhydrophilic micropatterned substrates (Fig. 8a) [37]. The fluidic channel based on NPSs is a semipermeable membrane structure with a negative charge on the hydrophilic side of the surface, which can be used to absorb, transport, and separate substances. When the channel was injected in a mixed aqueous solution dissolving neutral and anionic dye molecules, due to the different affinity of the two dyes in water and oil, the neutral dye molecule could be selectively removed through the walls of the microchannel into the oil phase, and the anionic dye continuously flowed in the channel, which can be collected at the exit, achieving the separation of dye mol- ecules. On the other hand, using the negative charges on the surface of the channel, positively charged dye molecules, bi- ological enzymes, or NPs were successfully adsorbed onto the inner wall of the channel in the process of transmission, endowing the microfluidic devices with functionalities, which can be used as microreactors (Figure 8b and c).

In addition, all-liquid 3D printing can be used to build a "bridge" between independent channels, while the "bridge" can be cut off to restore their independence. The cut channels are self- healing since NPSs can rapidly form and assemble at the inter- face (Fig. 8d). Based on the characteristics of self-healing and reconfiguration, programmable chemical logic reactors with complex structures can be constructed, and selective transport of reactants in different chemical reactors can be realized by cutting or building bridges between different reactors.

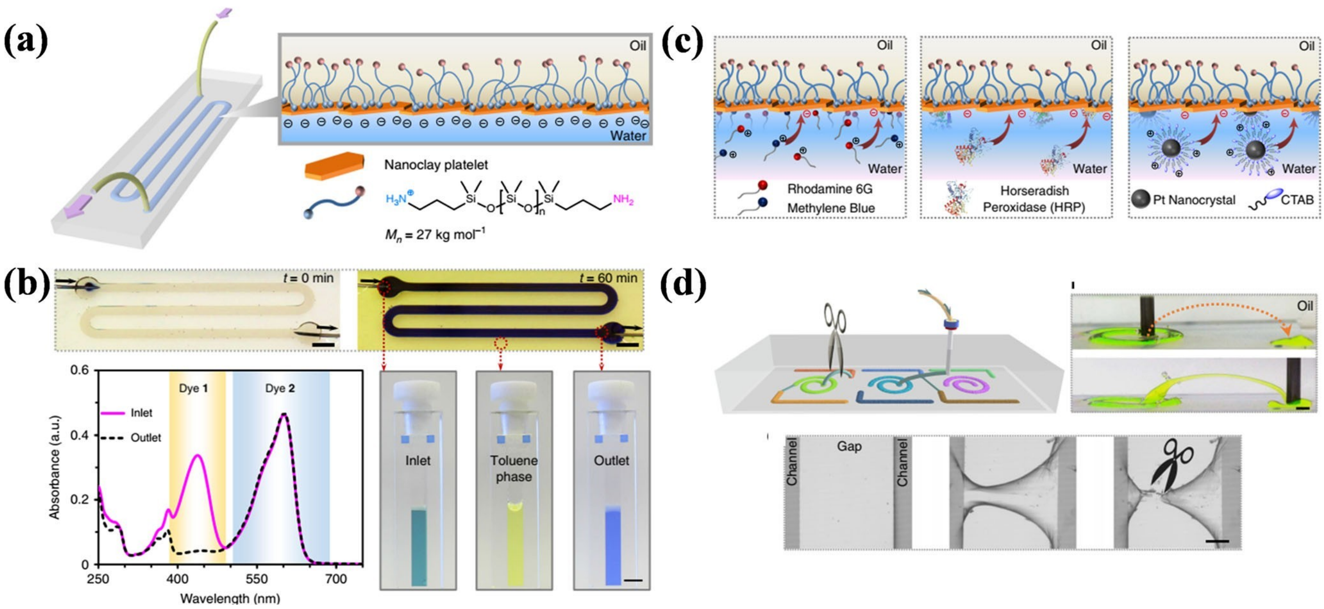


Fig. 8 (a) Schematics of all-liquid microfluidic devices. (b) Mass sepa- ration of different dye molecules in fluidic channels. (c) The functionalization of the anionic NPS film using cationic molecules, enzymes, and nanocrystals. (d) Reconfiguration and self-healing of all- liquid microfluidic devices. Reproduced with permission [37]. Copyright 2019, Springer Nature

Pickering emulsions and polymer nanocomposites

NPS also provides an easy way to fabricate Pickering emul- sions with functionalities [38–42]. Using carboxylated silica NPs or polystyrene NPs dispersed in aqueous phase and oil- soluble polymer ligands such as PDMS-NH_2, NH_2-PDMS-NH_2, or poly[dimethylsiloxane-co-(3-aminopropyl) methylsiloxane] copolymer, Toor et al. successfully produced NPS-stabilized aqueous droplets using a microfluidic device (Figure 9a and b) [43]. The mechanical properties of the in- terfacial assemblies can be effectively manipulated by using different types of polymer ligands or varying the molecular weight of polymer ligands. Due to the presence of NPS layer at the interface, the coalescence of the droplet can be arrested, preventing the exchange of materials across interfaces. NPs, dyes, and proteins with diameters in the 2.4 − 30 nm range can be encapsulated successfully (Fig. 9c, d, and e).

By mechanically shearing the suspension of CNC in the water phase and PS-NH_2 in the toluene phase, Li et al. pre- pared o/w Pickering emulsions stabilized by CNCSs (Figure 10a) [44]. By varying pH, the size and morphology of the emulsions can be effectively manipulated. It is interest- ing that at a low pH, structured emulsions could be prepared, due to the interfacial jamming of the CNCSs during homoge- nization. No structured emulsions were achieved at higher pH, indicating the loose packing of CNCSs at the interface. Using the concentrated emulsions stabilized by CNCSs as templates, a dry CNC/PS composite foam was fabricated by freeze-dry- ing. The pore size and shape of the foam cell could be effec- tively controlled, which were commensurate with the emul- sion droplets (Fig.10b). Also, the prepared foam was responsive to pH, which could keep its stability in the acid environment and be destroyed in the basic environment.

This strategy can be used for a broad range of nanomaterials. In the subsequent study, Shi et al. used MXene ($Ti_3C_2T_x$) and amine-functionalized polyhedral olig- omeric silsesquioxane (POSS-NH_2) to form MXene surfac- tants (MXSs) at the oil-water interface [45]. Stable w/o Pickering emulsions could be easily prepared using MXSs, and lightweight MXene aerogels with excellent mechanical properties could be achieved (Fig. 10c, d, and e). The as- prepared MXene aerogels showed excellent oil absorbency, and the fabricated MXene/epoxy nanocomposites showed good performance in the EMI shielding (Fig.10f and g).

Ferromagnetic liquid droplets

When magnetic nanoparticles (MNPs) are dispersed in carried fluids, paramagnetic ferrofluids are formed [46–50]. On the oth- er hand, if the Brownian motion of the MNPs is suppressed, the transformation of a ferrofluid into a ferromagnetic material can be achieved [51]. Recently, by taking advantage of the jamming of MNP surfactants (MNPSs) at the oil-water interface, Liu et al. reported a simple strategy to realize a paramagnetism to ferro- magnetism transformation at room temperature [52]. In this study, they used an aqueous dispersion of carboxylated MNPs (Fe_3O_4-COOH) and a solution of POSS-NH_2 in oil to form MNPSs at the oil-water interface. When the MNPSs jam at the interface, the ferrofluid droplet transforms into a ferromagnetic liquid droplet, which is confirmed by the magnetic hysteresis loops (Fig. 11a). By combining all-liquid 3D printing with microfluidic technology, ferromagnetic liquid cylinders were

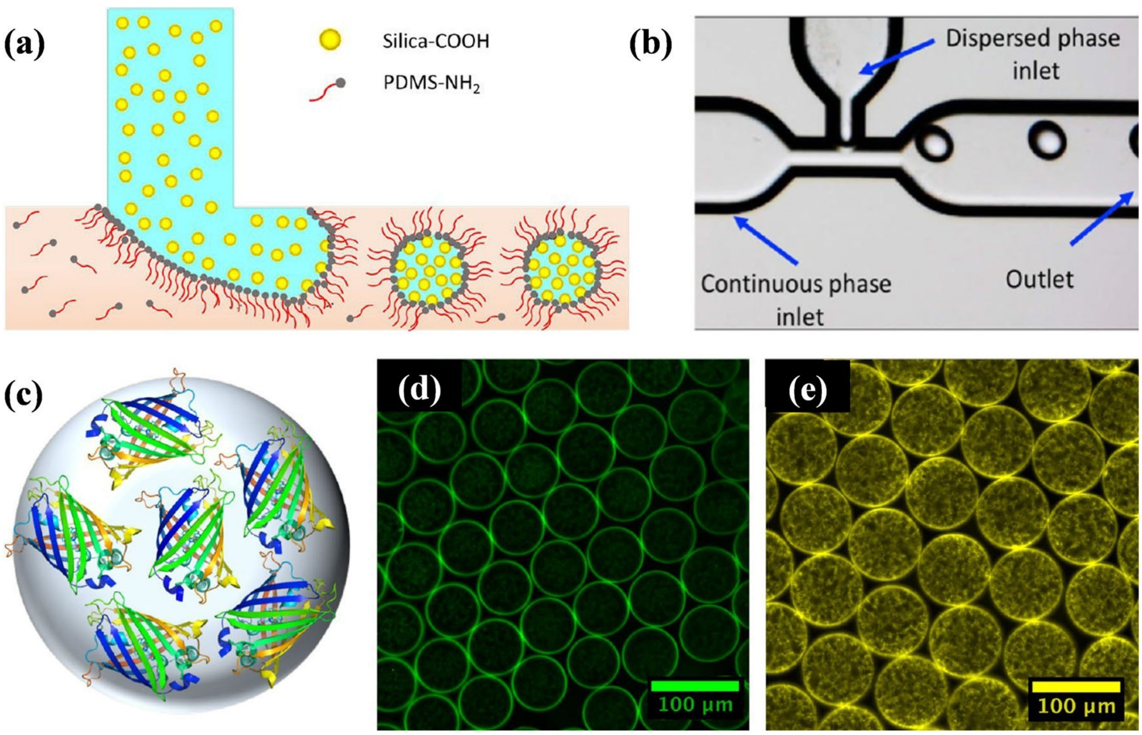


Fig. 9 (a, b) Schematics of the formation of w/o droplets in a microfluidic T-junction. (c) Schematic of an NPS-stabilized water droplet containing fluorescent proteins. (d, e) Confocal laser scanning microscopy images showing encapsulation of enhanced green fluorescent protein and yellow fluorescent protein. Reproduced with permission [43]. Copyright 2018, American Chemical Society

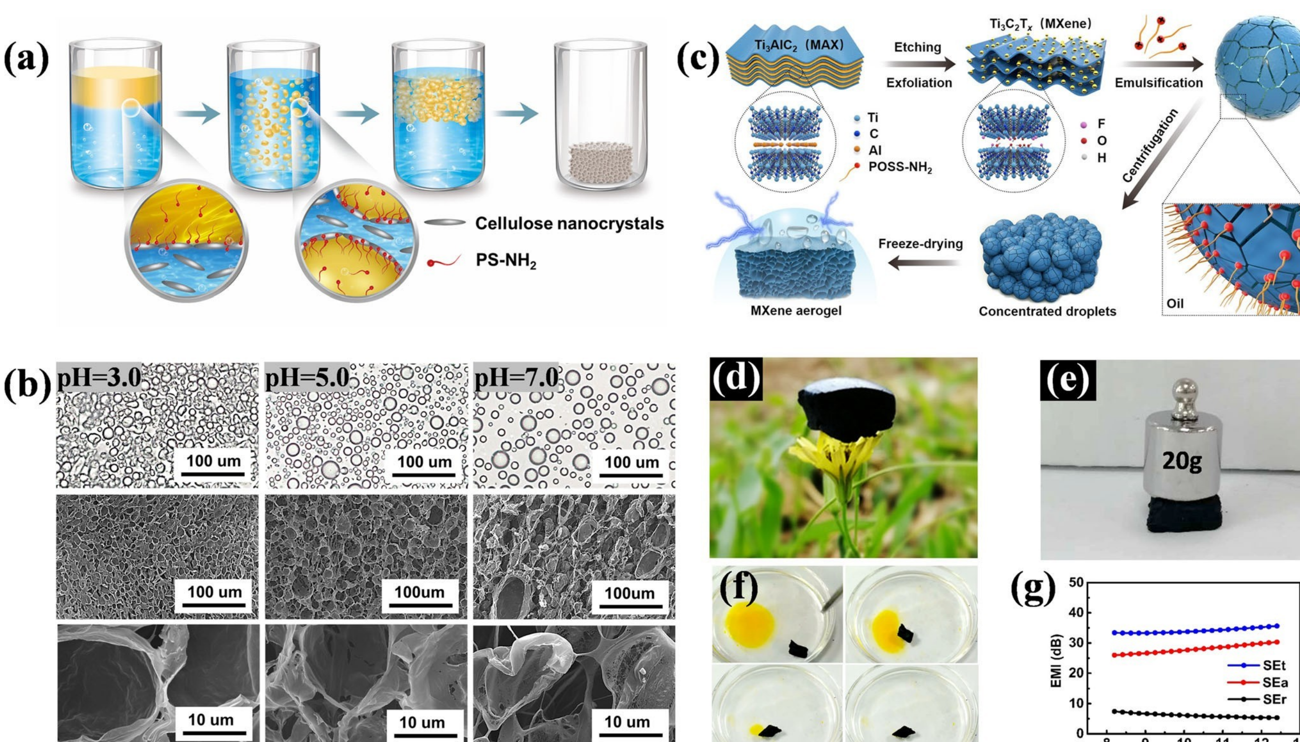


Fig.10 (a) Schematics of the preparation of the CNCS-based emulsions and foams. (b) Optical micrographs of Pickering emulsion droplets sta- bilized by CNCSs at different pH. Reproduced with permission [44]. Copyright 2018, Wiley-VCH. (c) Schematic showing the construction of Pickering emulsions and MXene aerogels via MXSs. (d, e) A small piece of MXene aerogel on a flower and a small piece of aerogel (~ 6.4 mg) supporting a 20-g weight. (f, g) Oil absorption of MXene aerogel and EMI shielding performance of MXene/epoxy nanocomposite. Reproduced with permission [45]. Copyright 2019, Wiley-VCH produced. In a magnetic field gradient generated by the alumi- num solenoid, a liquid cylinder was magnetized and pulled into the solenoid (Fig. 11b). The magnetized liquid cylinders behave like solid magnets, and N-N, S-S, and N-S dipole interactions can be obtained (Fig. 11c).

The prepared ferromagnetic liquid droplets show both the fluid characteristics of liquids and the magnetic properties of solids, with excellent reconfiguration (Fig. 11d and e). Taking advantage of these intriguing properties, separation and pat- terning of ferromagnetic liquid droplets could be easily achieved. As shown in Fig. 11f and g, in comparison with the ferrofluid droplets, the ferromagnetic liquid droplets were attracted much more strongly to a static bar magnet and could rotate when using a rotating magnet.

Photoresponsive structured liquids

As discussed above, the assembly and formation of NPSs mainly depend on electrostatic interactions between ion pairs (e.g., - COO^- and $_3NH^+$), and only pH responsiveness of the interfacial assemblies can be obtained, which limits the construction of structured liquids with complex multiple responsiveness. Recently Sun et al. reported the construction of photoresponsive NPSs as well as structured liquids using the host-guest interac- tions between α-cyclodextrin (α-CD) and azobenzene (Azo) at the oil-water interface (Fig. 12a) [53]. In this system, α-CD-modified gold NP with low interfacial activity was dispersed in water and Azo-terminated poly-L-lactide (Azo-PLLA) were dis- solved in toluene. NPSs were formed in situ at the interface. It should be noted that Azo-PLLA behaves like a surfactant. The carbonyl groups in Azo-PLLA could hydrogen bond with water, locating the terminal Azo groups at the interface, which played an important role in triggering the molecular recognition of α- CD and Azo at the interface (Fig. 12b). 2D films can be easily prepared at the oil-water interface and TEM image shows a monolayer of close-packed Au-NPs (Fig. 12c).

The photoresponsiveness of the NPSs was investigated by using a wrinkled droplet, where the NPSs were in a jammed state. No change of the droplet shape was observed under vis- ible light. However, under ultraviolet (UV) irradiation, the wrinkled droplet gradually relaxed and returned to a spherical shape, indicating the jamming-to-unjamming transformation of the NPSs. This transformation is reversible and the NPSs could be re-jammed when UV irradiation was stopped (Fig. 12d).

Summary and prospect

NPSs provide a new strategy for the design and construction of complex structured liquids. This review mainly summarizes the formation mechanism of NPSs, the construction of structured liquids, and applications. The assembly and packing behavior of NPs at the interface can be effectively manipulated by

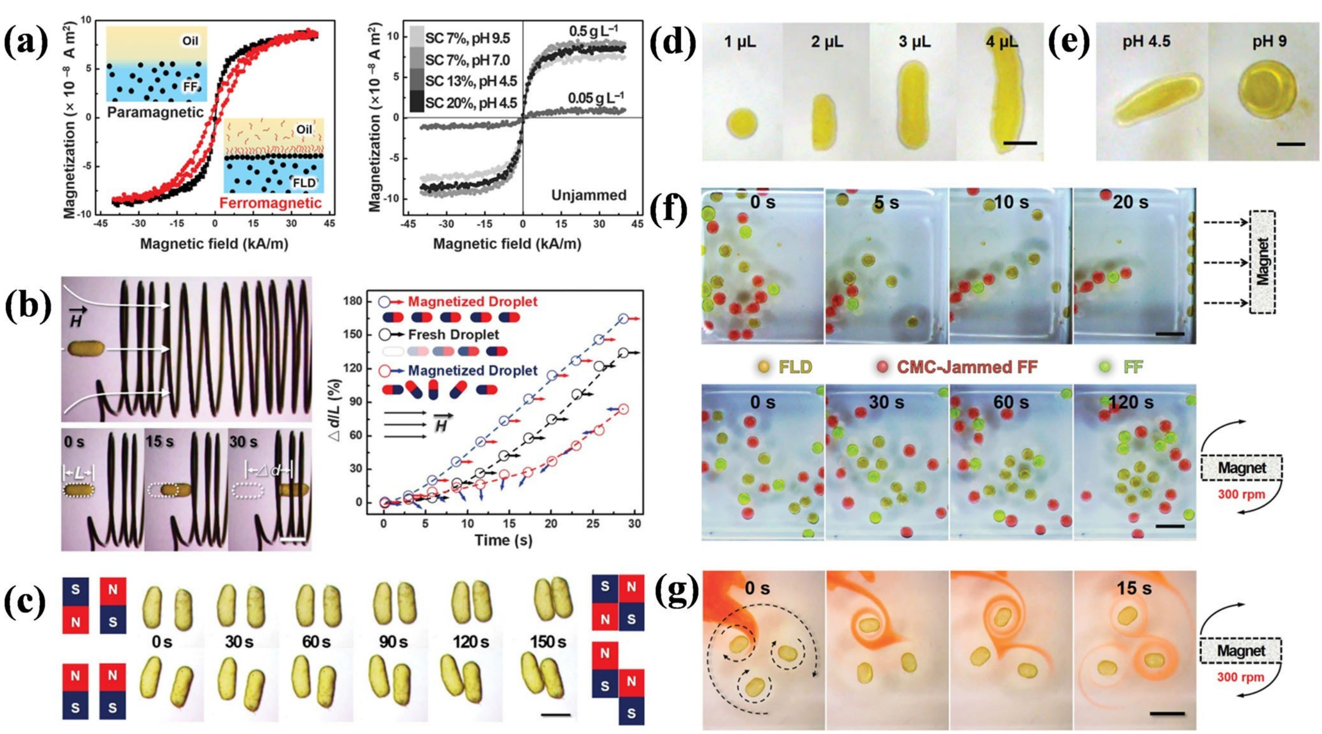


Fig. 11 (a) Magnetic hysteresis loops of droplets with and without jammed MNPSs at the interface. (b) The motion of a magnetized liquid cylinder in a magnetic field gradient, generated by the aluminum sole- noid. (c) Dipole interaction between two magnetized liquid cylinders. (d) Droplets of different aspect ratios. (e) Reconfiguration of the droplet by tuning the pH. (f and g) Sorting FLDs by using static and rotational magnetic fields. Reproduced with permission [52]. Copyright 2019, The American Association for the Advancement of Science.

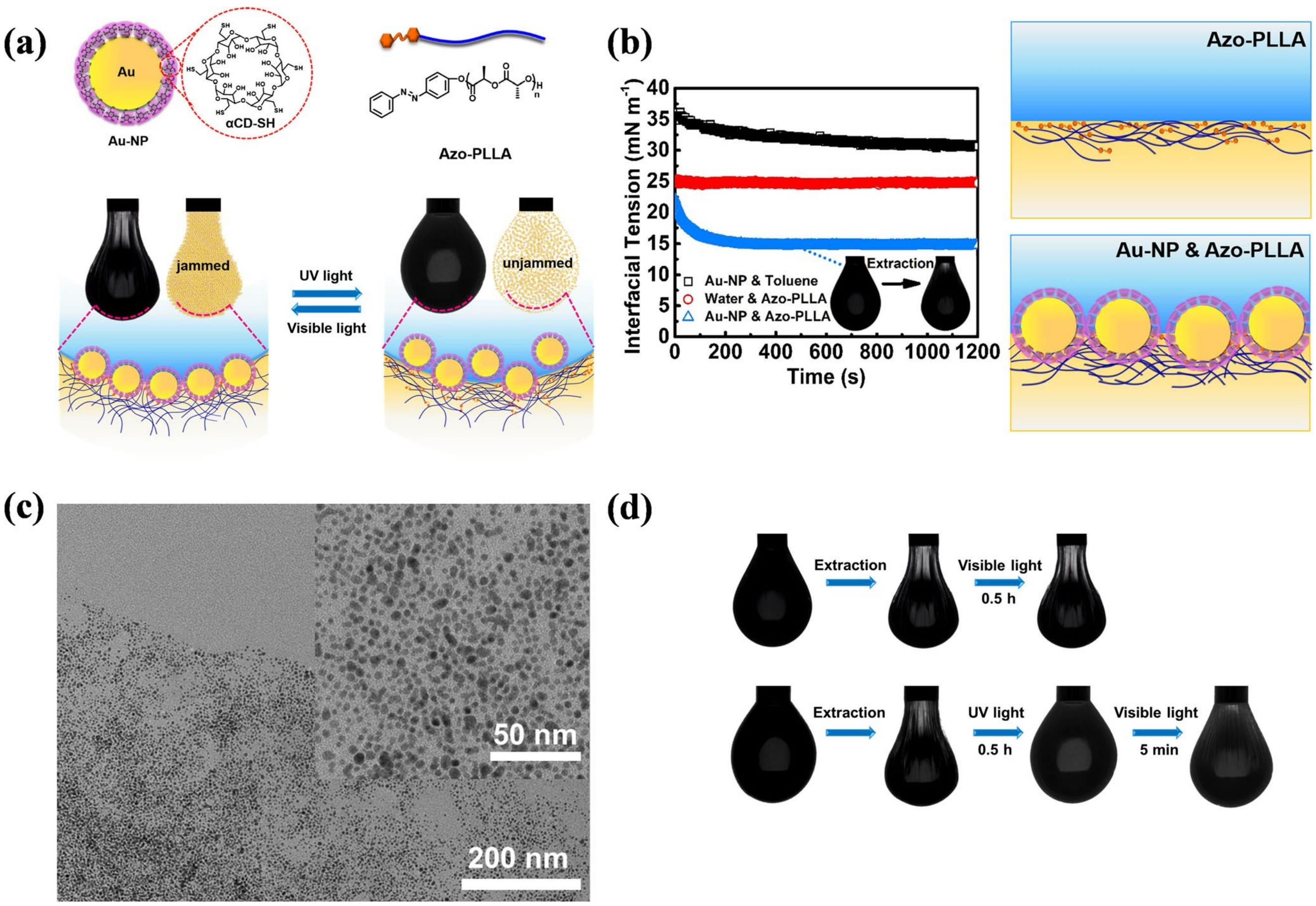


Fig. 12 (a) Schematics of the photoresponsive NPSs at the oil-water interface. (b) Assembly kinetics of the photoresponsive NPSs at the oil- water interface. (c) TEM image of 2D films assembled at the interface. (d) Photoresponsiveness of the wrinkled droplet. Reproduced with permission [53]. Copyright 2020, American Chemical Society

adjusting the two parts of NPS (NP and polymer/oligomer li- gand). Using external field and jammed NPSs at the interface, liquids can be printed or molded to desired shapes, just like solid materials, with responsiveness to the environment.

There is much we do not understand with this behavior and the field is wide open for further exploration. NPs such as carbon nanotube, graphene oxide, fullerene, and polyoxometalate can be used to construct functional assemblies including colloidosome, 2D nanofilms, polymer nanocomposites and structured liquids [20, 25, 29, 54, 55]. The concept of NPSs can be further extended to other systems without NPs, such as polyelectrolyte and even small molecule systems. For example, recently we obtained a fibrous supramolecular structure at the oil-water interface using water-soluble porphyrins assembled with polymer ligands [56]. Also, by using the cooperative assembly of polyelectrolyte and ligands, we put forward the concept of polyelectrolyte surfactants (PESs) [57, 58]. On the other hand, different liquid systems, e.g., aqueous two-phase system and oil/oil system, can be used to construct structured liquids [59–62]. The generation of multiple stimuli-responsive structured liquids is an emerging field just started, which can be achieved either by exploring new interactions at the interface [56, 63–65] or synthesizing NPs and functional polymer/oligomer ligands [66–70].

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest

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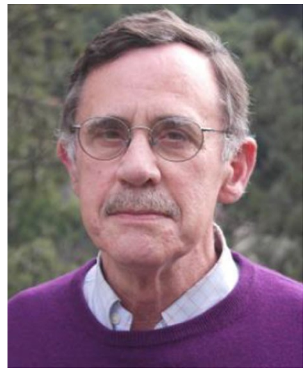

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