Breathing Demulsification: A Three-Dimensional (3D) Free-Standing Superhydrophilic Sponge
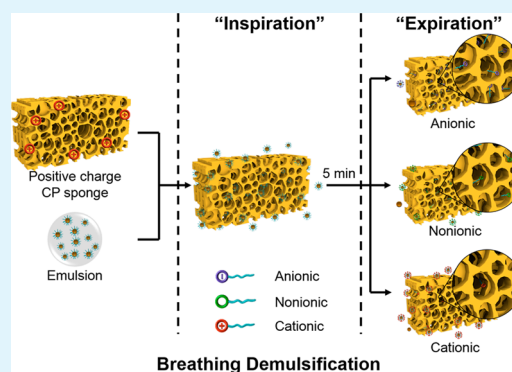
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S *Supporting Information*

ABSTRACT: A novel three-dimensional (3D) free-standing superhydrophilic sponge for industrial wastewater treatment was formed by combining chitosan and linear polyacrylamide (PAM). When the chitosan−PAM sponge is immersed into an oil-in-water emulsion, the milky white emulsion containing surfactant turns clear and clarified. Demulsification efficiency, capacity, and recyclability of this positively charged chitosan−PAM sponge to oil-in-water emulsions stabilized by different types of surfactants including anionic, nonionic, and cationic surfactants, has been investigated for further practical evaluation. A "breathing demulsification" mechanism is presented to explain this attractive demulsified process. The effective contact area between emulsion and sponge is increased by the microcomposite and nanocomposite hierarchical structure of the chitosan−PAM free-standing sponge. Then, interfacial interactions, size effect, and strain act as the driving force for the demulsification of the emulsified droplets at the surface of the sponge.

KEYWORDS: composite materials, sponge, demulsification, surfactant, absorption, extrusion

1. INTRODUCTION

New energy-efficient solutions to separate oil/water mixtures, especially those stabilized by surfactants, are major issues to be addressed.[1−3] Petrochemical, smelting, chemical, and mineral industry produce large number of emulsified wastewater, and bring a truly serious environmental pollution.[4,5] According to the statistics of the International Tanker Owners Pollution Federation (ITOPF), ~1800 large- and medium-sized oil tanker accidents occurred from 1970 to 2014.[6] These accidents were the causes for collisions, groundings, hull failures, equipment failures, fires, and explosions, resulting in ~5.74 million tons of oil spills.[6] By integrating physical, chemical, electrochemical, and biochemical technologies, separation methods including flotation, flocculation, electrocatalysis, and biofiltration are developed as traditional methodologies for separation of immiscible oil/water mixtures.[5] However, these traditional methods are ineffective in treating surfactants-stabilized emulsions.[7] It is highlighted the difficulty of the demulsification of surfactant-stabilized emulsions because dispersed droplets has lower surface tension than the surfactant-free ones.[8,9] Conventional demulsification relies solely on implementing an electric field or adding chemicals that cannot meet the higher requirement of an ecological environment. Moreover, these treatments also involve high energy consumption, poor efficient separation, and secondary pollution.[10−12] Hence, it is a critical need for the development of efficient emulsion separation.

To date, both zero-dimensional (0D) magnetic demulsifier[13−15] and two-dimensional (2D) filtration membranes[16−28] have been widely noted as innovative technologies to demulsify emulsions. Poly(N-isopropylacrylamide) grafted magnetic composite particles have been prepared as demulsifiers, which constitute Pickering emulsions for the harvesting of oil and demulsification.[14] For now, 2D membrane filtration techniques, especially microfiltration and ultrafiltration, are feasible solutions to separate emulsions and have been widely employed in industrial technology, because they can continuously remove emulsified oil droplets from oily wastewater. A superhydrophobic/superoleophilic poly(vinylidene fluoride) membrane is fabricated for the emulsion separation, with high permeation flux and separation efficiency, solely powered by gravity.[19] However, most polymer membranes are inevitably fouled by oil, because of the oleophilicity of C−H structures in the polymer chain. The oil fouling will significantly reduce performance in permeation flux and separation efficiency.[29−34] Therefore, research and development of facile, efficient, cost-effective separation materials for the demulsification of various emulsions, especially emulsions containing surfactants, is greatly desired.
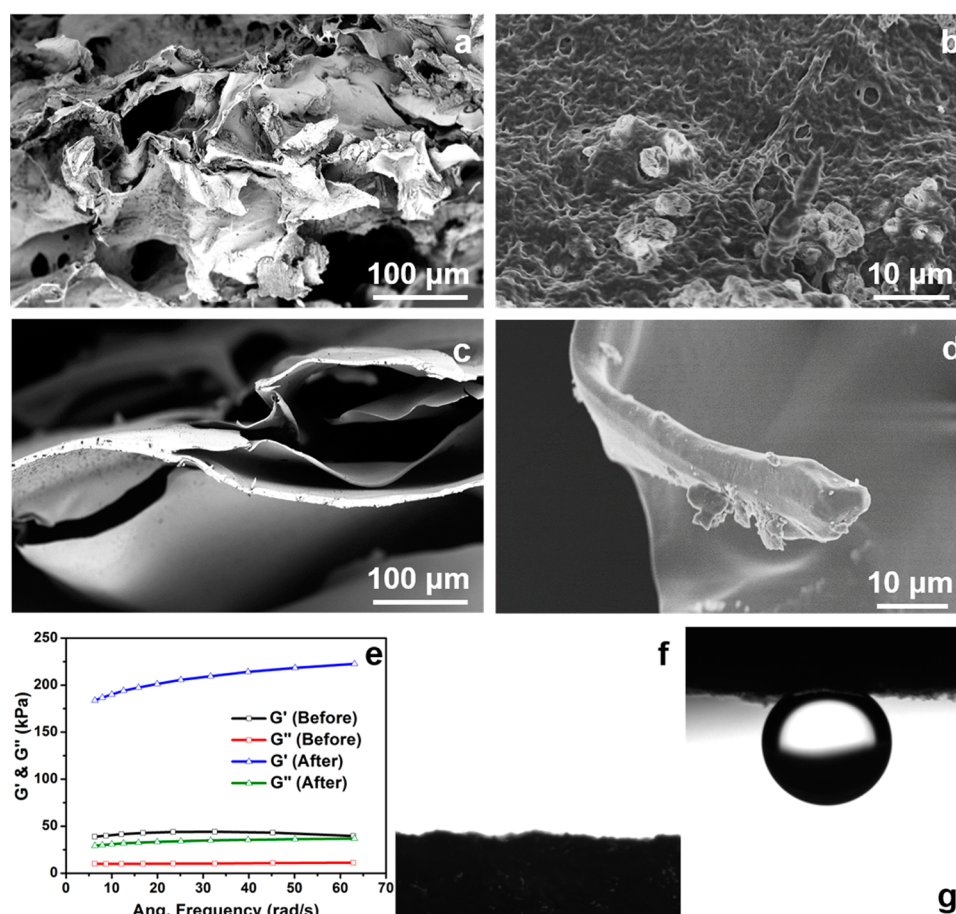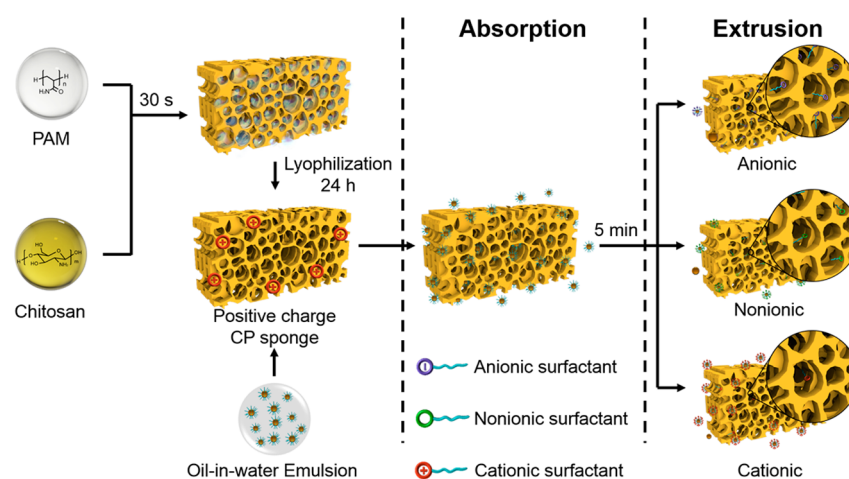
Herein, we develop a three-dimensional (3D) free-standing superhydrophilic sponge for industrial wastewater treatment by
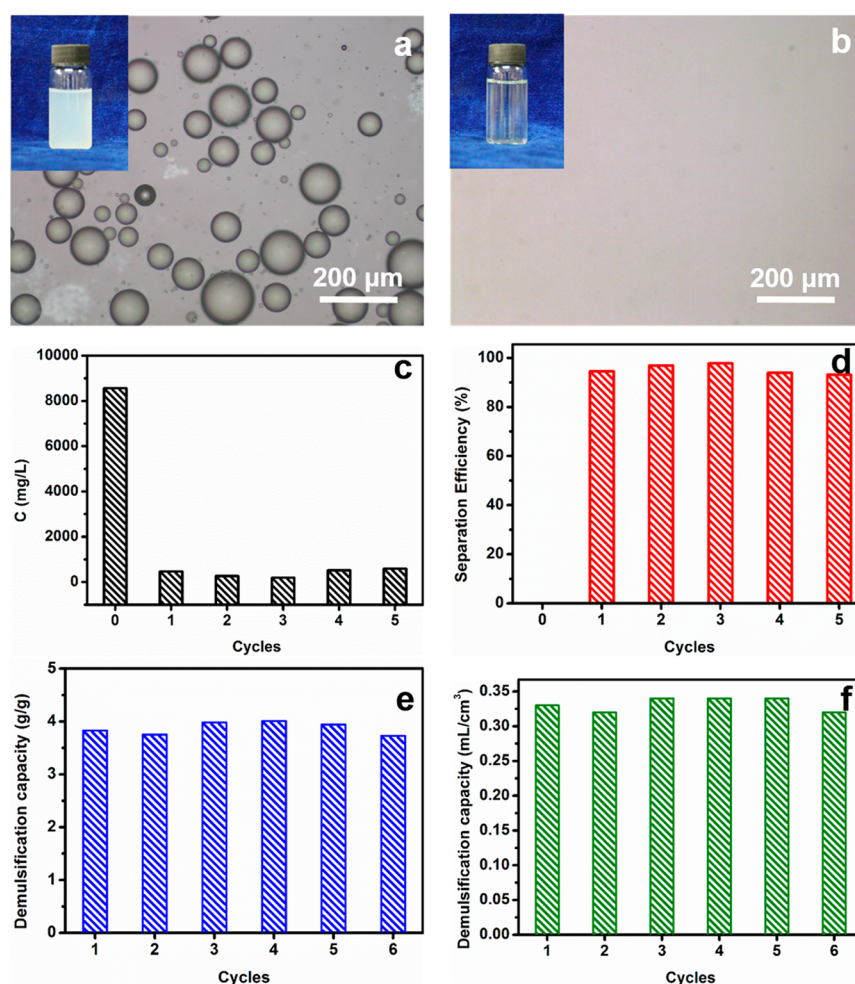
Scheme 1. Diagram Showing the Preparation of a CP Free-Standing Sponge, Exhibiting New Demulsification Phenomenon during the "Absorption–Extrusion" Process

Figure 1. SEM images of the as-prepared sponge: (a, b) lyophilized CP sponge; (c, d) lyophilized chitosan solution as a control sample; (e) storage modulus G' and loss modulus G'' analyses of the CP sponge at 25 °C before and after lyophilization (the CP sponge shows special wettability); (f) a water droplet (2 μL) that has spread and permeated quickly on the CP sponge; (g) photograph of a gasoline droplet (2 μL) on CP sponge with an oil contact angle of 134.77° ± 4.84°. [WCA, water contact angle; OCA, oil contact angle; oil, gasoline.]

combining chitosan and linear polyacrylamide (PAM), which is highly effective, with regard to the demulsification of emulsions stabilized by various surfactants. Instead of conventional filtering demulsification, the sponge achieves demulsification via an "absorption–extrusion" process for the first time. We propose a new "breathing demulsification" mechanism to explain this attractive demulsified process based on sufficient

data and detailed analysis. The microcomposite and nanocomposite hierarchical structure of the chitosan-PAM free-standing sponge (CP sponge) increases the effective contact area between the emulsion and the sponge. Then, interfacial interactions act as the driving force for the demulsification of these emulsified droplets at the surface of the sponge. In contrast, the separation effect of CP sponge to anionic

Figure 2. Separation studies of highly stabilized oil-in-water emulsion: (a, b) after the CP sponge was immersed in the Tween-20-stabilized toluene-in-water emulsion for 5 min, the emulsion turn from milky white to clear and becomes clarified (the optical microscopy images of toluene-in-water emulsions (a) before and (b) after demulsification show the break of emulsified toluene droplets); (c) the toluene concentration obviously decreases after demulsification, compared to the original toluene concentration of oil/water mixture, even after five cycles of use; and (d) the demulsification efficiency remains high after five cycles of use by taking Tween-20-stabilized oil-in-water emulsion as an example. Also shown is the recyclability investigation of the demulsification capacity of the CP sponge via the "absorption−extrusion" process, calculated by (e) mass ratio and (f) volume ratio.

surfactant-stabilized emulsions is better than cationic and nonionic surfactant-stabilized ones, because of the stronger interaction between the positive charges of chitosan and the negative charges of anionic surfactant. We expect that this outstanding material is an ideal candidate for wastewater treatment, the cleanup of oil spills, and the separation of commercially relevant emulsions.
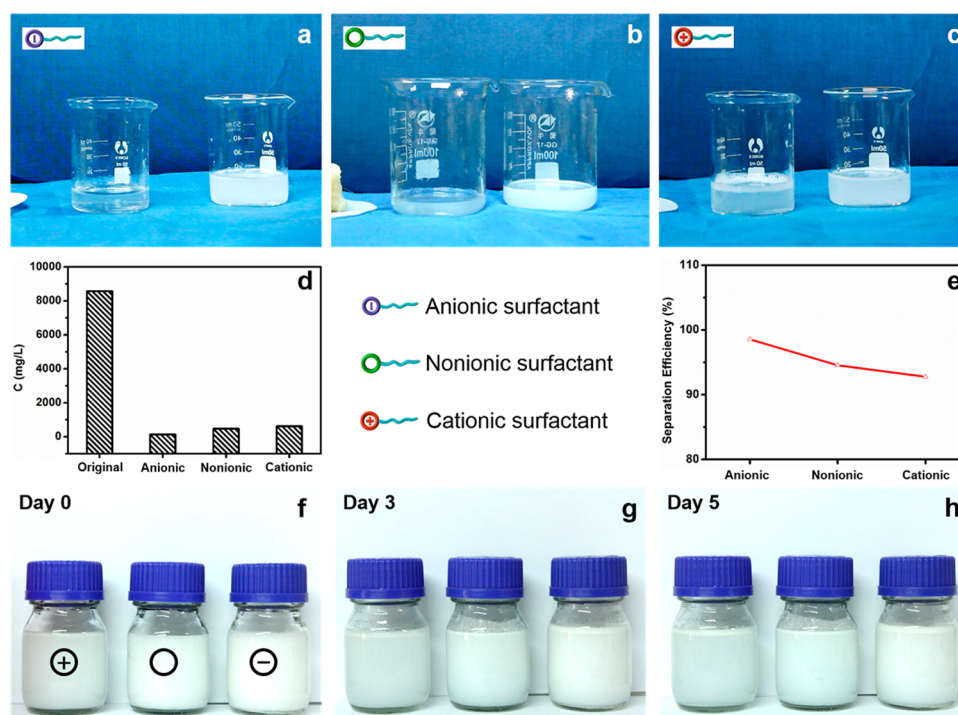
2. RESULTS AND DISCUSSIONS

2.1. Experimental Design of the 3D Free-Standing CP Sponge. The CP sponge is prepared by blending chitosan and linear PAM, as shown in Scheme 1. A 3% (w/w) 60 mPa s chitosan ethyl acetate solution and 10% (w/w) PAM solution is mixed in a beaker to fabricate a hydrogel within <30 s at ambient temperature. In this hydrogel, PAM is used as an adhesive to link the molecular chains of chitosan.[34] The water-filled hydrogel is lyophilized for 24 h to obtain the CP sponge. When the CP sponge is immersed in the anionic, nonionic, and cationic surfactants for 5 min, respectively, the stable oil-in-water emulsion changes from milky white to transparent. The porous microstructure of the CP sponge increases interfacial

interactions between the emulsion and the sponge, leading to the demulsification of these emulsified droplets at the surface of the sponge. The stronger interfacial interaction serves as the driving force of demulsification between the positive charges of the chitosan and the negative charges of the anionic surfactant. Hence, the CP sponge performs better in anionic surfactant-stabilized emulsions than cationic and nonionic surfactant-stabilized ones. As a typical "absorption−extrusion" process, the CP sponge adsorbs emulsified droplets when it is immersed in emulsion. After immersion for 5 min, CP sponge is removed and extruded to achieve demulsification.

2.2. Morphology and Wettability of the 3D Free-Standing CP Sponge. Typical scanning electron microscopy (SEM) images of the lyophilized CP sponge and lyophilized chitosan solution are shown in Figure 1. Compared with lyophilized chitosan, the CP sponge has a remarkably rough structure with tiny (200 nm) holes and 10−100 μm gaps (see Figures 1a and 1b). These microcomposite and nanocomposite hierarchical structures increase the effective contact area between the emulsion and the sponge. Thus, the demulsification of emulsified droplets occurs at the surface of the CP

Figure 3. Studies of highly stabilized toluene-in-water emulsions stabilized by (a) an anionic surfactant (sodium dodecylbenzenesulfonate (SDS)), (b) a nonionic surfactant (Tween 20), and (c) a cationic surfactant (cetyltrimethylammonium bromide (CTAB)). (d) Toluene concentration of the demulsified emulsion stabilized by SDS, Tween 20, and CTAB, showing an obvious decrease after demulsification, compared to the original toluene concentration of toluene-in-water emulsion. (e) Plot showing that the separation efficiency of the CP sponge to anionic CTAB-stabilized emulsions is better than that of the cationic SDS-stabilized and nonionic Tween-20-stabilized emulsions. Also shown are stability tests of the surfactant-stabilized emulsions after standing for (f) 0 days, (g) 3 days, and (h) 5 days. In panels f, g, and h, the three bottles, from left to right, are emulsions stabilized by CTAB, Tween-20, and SDS, respectively.

sponge, driven by the interfacial interaction of the sponge and the emulsion. In comparison, the lyophilized chitosan has a smooth surface and a highly ordered architecture (see Figures 1c and 1d), which cannot be employed as an emulsion separation material, because of its partial dissolution in water and poor mechanical strength.

The storage and loss modulus of the CP free-standing sponge is measured by rheological analysis, which can reflect the change in structure and identify whether it is solid or not (Figure 1e). Before the hydrogel has been lyophilized, the storage modulus (G') of hydrogel is 38.94 kPa and the loss modulus (G'') is 10.1 kPa. The result $G' > G''$ confirms the formation of hydrogel. The storage modulus G' obviously increases to 183.70 kPa and loss modulus G'' changes to 29.17 kPa after lyophilization. It means the sponge becomes stronger due to the formation of molecular chain microcrystal, as well as water content decreases. Respectable mechanical strength of free-standing sponge makes it keep integral under the "absorption−extrusion" process of demulsification.

To characterize the surface wettability transition of the CP sponge, the water contact angle (WCA) in the air and oil contact angle of the CP sponge under water have been measured. The wetting and permeating behavior on the CP sponge is illustrated in Figure 1f, in which the WCA in the air of CP sponge is 0°. When a water droplet touches the CP sponge, it can quickly spread and permeate the sponge. Meanwhile, Figure 1g displays the shape of a gasoline droplet under the CP sponge, showing that the oil contact angle under the water is 134.77° ± 4.84°. Combining the WCA and oil contact angle demonstrates that the CP sponge is an

outstanding superhydrophilic and oleophobic water-absorbing material. The intrinsic superhydrophilicity of CP sponge makes it a good candidate to adsorb the hydrophilic segments of surfactant, and enhances the ability of demulsification to surfactant-stabilized oil-in-water emulsions. The superhydrophilicity also results in its anti-oil fouling and easy cleaning for repetitive demulsification. The XPS and FT-IR spectra of the chitosan, PAM, and CP sponge are carried out and further clarify the formation of the CP sponge (see Figures S1 and S2 in the Supporting Information).

2.3. 3D Free-Standing Superhydrophilic Sponge for Demulsification. Highly stabilized toluene-in-water emulsions have been prepared to test the demulsified capability of the CP sponge. The nonionic surfactant-stabilized emulsion contains 1% toluene and 0.50 mg mL^{-1} Tween 20 is vigorously stirred in a beaker flask for 24 h. Twenty milliliters (20 mL) of the as-prepared emulsion is poured into each of two beakers, and then the CP sponge is immersed in the left beaker. After immersion for 5 min, the CP sponge is removed and extruded (see Figures 2a and 2b, as well as Movie S1 in the Supporting Information). Through the "absorption−extrusion" process, the hierarchical-structured surface of the porous CP sponge adsorbs the surfactant-stabilized emulsion. Intermolecular forces between the superhydrophilic sponge and the hydrophilic surface of emulsified oil-in-water droplets act as demulsification driving forces. These intermolecular forces, including hydrogen bonding and van der Waals forces, then break the stable emulsions. The strain of emulsified droplets during the "absorption−extrusion" process also increases the destabiliza-tion of the emulsion. Consequently, the milky white emulsion

containing nonionic surfactant turns clear and becomes clarified, which means successful demulsification of the surfactant-stabilized emulsion occurs in one step. Images of the toluene-in-water emulsion before and after demulsification are obtained using a polarizing optical microscope, further confirming the extreme purity of the demulsification (see Figures 2a and 2b). The toluene-in-water emulsion that has been stabilized by nonionic surfactant contains plenty of globules with diameters ranging from several micrometers to hundreds of micrometers. Therefore, the macrocomposite and nanocomposite hierarchical-structured surface of the CP sponge can contact sufficiently with these emulsified droplets. The appropriate size effect between the emulsion and the sponge also leads to effective separation of the oil-in-water emulsion (see Figure S3 in the Supporting Information).

The water purity and separation efficiency are evaluated for demulsification application, by using an infrared oil analyzer to test the content of toluene in the demulsified emulsion. The toluene concentration in the demulsified emulsion is significantly less than the original toluene concentration of the oil/water mixture, even after the CP sponge has been reused five times for demulsification (Figure 2c). In addition, the average toluene concentration of the five repetitive water samples is ~406 mg L^{-1}. The separation efficiency is determined by the toluene rejection rate (R (%)), which can be calculated according to the expression

$$R\ (\%) = \left(1 - \frac{C_d}{C_0}\right) \times 100 \tag{1}$$

where C_0 represents the toluene concentration of the original oil-in-water emulsion and C_d stands for the amount of water collected after demulsification. The separation efficiency of the CP sponge for the surfactant-stabilized toluene-in-water emulsion is >93% (Figure 2e). Water purity and separation efficiency of the CP sponge express the good repetitive usability that is due to the respectable mechanical strength, anti-oil fouling, and easy cleaning of the CP sponge. The demulsification capacity of the superhydrophilic CP sponge is measured to evaluate the practical value. The gravimetric demulsification capacity is greatly dependent on the bulk density, more than the porosity of bulk material. So the volumetric demulsification capacity is also notable. Figures 2e and 2f reveal that the demulsification capacities of the CP sponge for the toluene-in-water emulsion are ~4 times its own weight and one-third of its own volume. Therefore, this CP sponge is an outstanding hierarchical-structured and superhydrophilic sponge, with good separation capability and stable repetitive usability, for the demulsification of nonionic surfactant-stabilized oil-in-water emulsions.
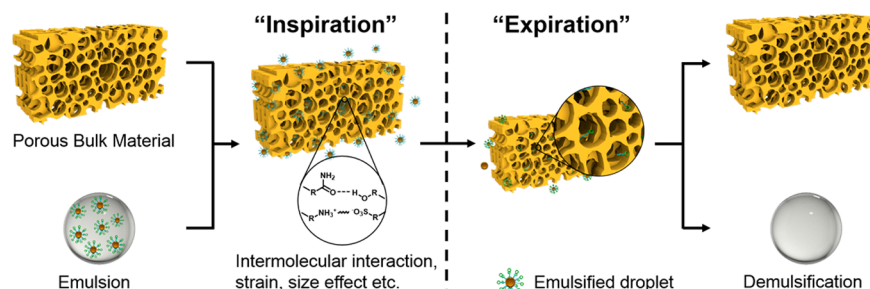
2.4. Influence of 3D Free-Standing Superhydrophilic Sponge for Different Types of Surfactant-Stabilized Emulsions. By adjusting the intensity of interfacial interaction, the influence of CP sponge for different types of surfactant-stabilized emulsions is investigated for further research of "absorption−extrusion"- type demulsification mechanisms. Anionic sodium dodecylbenzenesulfonate (SDS), nonionic Tween 20, and cationic cetyltrimethylammonium bromide (CTAB) are respectively selected as anionic, nonionic, and cationic surfactants for toluene-in-water emulsions (see Figures 3a, 3b, and 3c, respectively). The SDS-stabilized emulsion has a negative charge on the surface of the emulsified droplets, with good stability; the Tween 20-stabilized emulsion has no electric

charge in the emulsion and minimizes hazards; and the CTAB-stabilized emulsion has good bactericidal ability, because of the plentiful amount of positive charges in the emulsion. When the SDS-stabilized emulsion is absorbed into the CP sponge, the strong electrostatic interaction between the positive charges of chitosan and the negative charges of the anionic surfactant promotes the formation of ionic bonds. It becomes the driving force for the destabilization of the emulsion, consequently improving demulsification, and increases the separation efficiency, compared to the emulsion stabilized by nonionic Tween 20 (see Figures 3d and 3e). In contrast, the CP sponge is immersed in a beaker containing a CTAB-stabilized emulsion. Electrostatic repulsion takes place between the positive charges of chitosan and the positive charges of the cationic surfactant. It decreases the contact probability of the sponge and emulsified droplets, as well as the separation efficiency, with Tween 20-stabilized emulsion, as a comparison (see Figures 3d and 3e). Hence, the intensity of interfacial interaction is positively related to the demulsification efficiency of the oil-in-water emulsion. When the interfacial interaction between the CP sponge and emulsified droplets is enhanced, the demulsification efficiency decreases in this case and vice versa.

In addition, emulsion stability has been tested to prove the difficulty of the demulsification of surfactant-stabilized emulsions. In Figures 3f, 3g, and 3h, three bottles are respectively full of emulsions stabilized by CTAB, Tween-20, and SDS. All of the bottles can maintain milky white for at least 5 days without any disturbance. The stability of the emulsion that contains surfactant signifies that the CP sponge is an effective demulsification material, from another aspect.

2.5. Breathing Demulsification Mechanism in Porous Bulk Materials. The reported separation efficiency of conventional demulsification methods, including the demulsifier and the filtration membrane, are listed in Table S2 in the Supporting Information, as a comparison to the "absorption−extrusion"-type demulsification. Magnetic microspheres and microparticles are familiar demulsifiers, with >95% demulsification efficiency, which result from the use of Fe_3O_4 or Fe particles (see Table S2). It is worth noting that the hydrophilic demulsifier has an effect on oil-in-water emulsions and inverse is observed in 0D demulsification systems, because the hydrophilic (hydrophobic) nature of magnetic microparticles makes them disperse well in the oil-in-water (water-in-oil) emulsion. Thereby, the microparticles adsorb emulsified droplets and act as the driving force for the destabilization of the emulsion to achieve demulsification. Finally, these magnetic microparticles are collected for reuse under a static magnetic field. Two-dimensional (2D) microfiltration and ultrafiltration membranes are highly efficient for emulsion and have been applied to industrial sewage treatment, because of their continuous processing power. It is similar to the demulsifier that the hydrophilic filtration membranes function well in oil-in-water emulsions and, conversely, during the filtration process, good wettability between the hydrophilic membrane and the oil-in-water emulsion results in the formation of hydrogels in the pore. Then, the hydrogels prevent the emulsified droplets from permeating the member. The high demulsification efficiency of filtration membranes is >98%, which benefits from the plentiful amount of tiny micropores and nanopores in the membranes (see Table S2). Different from these conventional demulsification methods, the porous CP sponge or another sponge is immersed in the oil-in-water

Scheme 2. Mechanism of the Breathing Demulsification in Hierarchical-Structured Porous Bulk Material

emulsion and absorbs the emulsified droplets into the porous structure. Next, the intermolecular interaction, strain, and size effects between emulsified droplets and sponge lead to the break in the emulsion structure. The "absorption−extrusion"-type demulsification has a demulsification efficiency ranging from 92% to 98%, according to the different types of demulsification materials and emulsions.

Based on the above experimental data and detailed analysis, a new demulsification mechanism to describe this attractive demulsified process, called "breathing demulsification", is presented; this is a new demulsification method that uses the adsorption and extrusion of porous bulk material to demulsify the emulsion. When the oil-in-water emulsion is absorbed into the porous bulk material, the microcomposite and nano-composite hierarchical structure result in the large surface of porous bulk material (Scheme 2). It will contact sufficiently with the emulsion to increase the collision rate of emulsified droplets and porous bulk material. This absorption process is similar to the inspiration of humans, in that fresh air enters the lungs, which are full of plenty alveoli. Then, the intermolecular interaction, including hydrogen bonds, ionic bonds, and van der Waals forces, in the interface acts as a major driving force for the destabilization of the emulsion, consequently inducing demulsification of emulsified droplets.[14,34] Finally, the demulsified mixture is removed via an extrusion process, which completes its "expiration". In the demulsification, the strain of emulsified droplets during the "breathing" process and the size effect of the emulsion and porous bulk materials play inevitable roles.[22]

Additional demulsified data of polyurethane sponge system in the Supporting Information (Schemes S1 and S2, Figures S4−S9, and Tables S3−S7) also verified the rationality of addressed demulsification mechanism. The demulsification efficiency of the superhydrophilic PU sponge is greatly than that of the hydrophobic PU sponge. The difference may be caused by the better wettability between the oil-in-water emulsion and the hydrophilic surface than that between the oil-in-water emulsion and the hydrophobic surface. Breathing demulsification of the porous bulk materials is very different from conventional demulsification of filtration membranes and magnetic particles. Porous block materials are applied extensively in packaging, furnishing, automobile, and battery industry.[35−42] Based on the phenomenon of breathing demulsification, a huge number of porous block materials will create a new research area for emulsion separation in chemical, materials, and energy science.

3. CONCLUSION

In summary, a novel superhydrophilic hierarchical structured free-standing sponge has successfully developed for industrial

wastewater treatment. It has facile manufacture, simple operation, and high efficiency for demulsification via combining chitosan and PAM. The CP sponge can effectively separate the stable oil-in-water emulsions containing different types of surfactants, including anionic, nonionic, and cationic surfactants, with >92% demulsification efficiency. Moreover, the demulsification capacities of the CP sponge for toluene-in-water emulsions are ∼4 times its own weight and one-third of its own volume. Furthermore, a new "breathing demulsification" mechanism has been presented to explain this attractive demulsification process and it exercises influence for emulsion separation in chemical, materials, environmental, and energy science.

4. EXPERIMENTAL SECTION

4.1. Materials and Characterization. Chitosan (degree of deacetylation = 85%, viscosity = 60 mPa s; Jinan Haidebe Bioengineering, China) was used as purchased. Other reagents including polyacrylamide (molecular weight of MW ≥ 3 000 000), sodium dodecylbenzenesulfonate (SDS), Tween 20, and cetyltrimethylammonium bromide (CTAB) from Sinopharm Chemical Reagents are analytical grade and used without further purification.

Rheology analyses were obtained by using a rheometer (TA Instruments, Model AR-G2) with parallel plate geometry (40 mm in diameter) at 25 °C. The SEM images were obtained using a field-emission SEM system (Hitachi, Model S8010). The SEM specimens were prepared by dry meshes covered with platinum. Contact angles were taken on a DataPhysics Model OCA20 machine at ambient temperature. The contact angle was defined as the average value of five measurements, as determined at different positions on the mesh. Optical microscopy images were performed via polarizing optical microscopy (Nikon, Model ECLIPSE LV100POL). The oil content in the emulsified water was determined by using an infrared spectrometer oil analyzer (Huaxiakechuang, Model OIL480).

4.2. Experiment. *Preparation of Sponge.* The CP sponge was prepared by blending of chitosan solution and PAM solution. A 3% (w/w), 60 mPa s chitosan solution was obtained by dissolving certain amounts of chitosan in 2.1% (w/w) acetic acid aqueous solution. A 10% (w/w) PAM solution was prepared by dissolving 2.0 g of the polymer in 18.0 g of deionized water. As a typical sponge preparation, PAM solution (20 mL) was added to chitosan solution (80 mL) at 25 °C, and then the mixture was stirred for 20−30 s to obtain hydrogels. After the hydrogel was lyophilized for 24 h, it changed to a porous sponge for emulsion separation.

Rheology Test. the mechanical properties of hydrogel and sponge were tested through the rheology analyses. Typically, 1 cm³ of the as-prepared sponge was laid on a parallel plate (40 mm in diameter). The storage moduli (G') and loss moduli (G'') were measured as a function of frequency.

Demulsification Experiment. The nonionic surfactant-stabilized oil-in-water emulsion was prepared by mixing 1% toluene and 0.50 mg mL^{-1} Tween 20 in a beaker flask. The as-prepared emulsion was poured into two beakers, and then the CP sponge was immersed in the left beaker. After immersion for 5 min, the CP sponge was removed

and extruded to demulsification. The anionic and cationic surfactant-stabilized emulsions are addressed as described above.

■ **ASSOCIATED CONTENT**

Ⓢ Supporting Information

. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b07530.

> XPS and FT-IR spectra of chitosan, PAM and CP sponge, demulsification capacity data of the CP sponge, demulsified data of a polyurethane sponge system including SEM images, contact angle data, demulsification of a superhydrophilic polyurethane sponge and a highly hydrophobic polyurethane sponge (PDF)
> Immersion, removal, and extrusion of the CP sponge (AVI)

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Notes
The authors declare no competing financial interest.

■ **ABBREVIATIONS**

TOPF, International Tanker Owners Pollution Federation; PAM, polyacrylamide; CP sponge, Chitosan-PAM free-standing sponge; SDS, sodium dodecylbenzenesulfonate; CTAB, cetyltrimethylammonium bromide

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