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Interfacial Basicity-Guided Formation of Polydopamine Hollow Capsules in Pristine O/W Emulsions – Toward Understanding of Emulsion Template Roles

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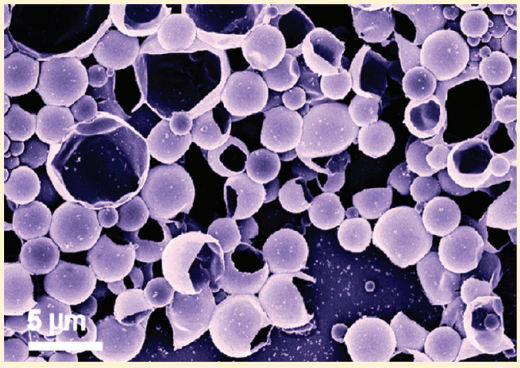
Supporting Information

ABSTRACT: In this article, alkane-in-water emulsions have been utilized as templates for polymerization of 3,4-dihydroxyphenylethylamine (dopamine) and L-3,4-dihydroxyphenylalanine (L-dopa). The resulting polymer structures are clearly dependent on the concentration of OH ions, i.e., pH, on the surfaces of the oil droplets, while show little dependence on the electrostatic or hydrophobic interactions between the resulting polymers and the surfaces of the oil droplets. Pristine alkane droplets, stabilized solely by OH ions, have templated formation of hollow capsules due to selective oxidation and self-polymerization of the monomers on the OH ion-rich surfaces of the pristine oil droplets. In contrast, macroporous structures have been obtained when either cationic or anionic surfactants were used to stabilize alkane droplets to lower the concentration of OH ions on the droplet surfaces.



KEYWORDS: *pristine o/w emulsions, oil/water interfaces, hollow capsules, macroporous structures, dopamine, and L-dopa*

INTRODUCTION

Oil-in-water emulsions have been widely employed as reaction media to sculpture various organic and inorganic materials into macroporous structures.[1−9] But they have been rarely used to template formation of hollow capsules.[7−9] The main reason should be that in an oil-in-water emulsion, precursors transform into targeted materials usually by reaction with water or active species in water, so there is no preference for the oil/water interface over the bulk aqueous phase to dictate the targeted materials to grow on the oil droplets. Selective growth and efficient accumulation of targeted materials at the oil/water interface is prerequisite for individual emulsion droplets to template formation of hollow capsules. To achieve that, one has to employ water-in-oil emulsions as templates, in which targeted materials are selectively formed at the oil/water interfaces only when their hydrophobic precursors in bulk organic phase interact with water or reactive species dissolved in the water droplets.[10] Recently, Xu et al. have used cyclohexane-in-water emulsion droplets, stabilized by nonionic polyglycol, as templates to synthesize hollow nickel capsules and they rationalized the formation of the hollow capsules as a result of a strong coordination between the polyglycol coating and nickel ions.[7] Zoldesi and Imhof have used surfactant-free dimethyldiethoxysilane(DMDES)-in-water emulsion droplets as templates to produce hollow silica capsules.[8] Later on, Zoldesi et al. have indicated a noticeable influence of the types of surfactants used to stabilize DMDES oil droplets on the wall thickness of the hollow silica capsules obtained in DMDES oil-in-water emulsions; anionic surfactant, sodium dodecylsulfate (SDS) significantly reduced the silica wall thickness, whereas nonionic surfactant, Triton X-100, caused little variation.[9] Possibly because of the complicated chemical composition of the silane oil droplets and other additive used, the underlying mechanism of hollow silica capsules has been little discussed in these studies. To address this issue, we employ pristine alkane-in-water emulsions, stabilized solely by OH ions, as templates for polymerization of 3,4-dihydroxyphenylethylamine (dopamine) and L-3,4-dihydroxyphenylalanine (L-dopa) (see the Supporting Information, Scheme S1) in order to study how the surfactant-free nature of the oil droplets affect the structures of the resulting polymers.

It has been clearly documented that oil-in-water emulsions can be generated in the absence of any surfactant – known as pristine emulsions – as a result of spontaneous enrichment of OH ions at the oil/water interfaces.[11−13] The surfaces of the oil droplets, stabilized by OH ions, are therefore negatively charged and their pH are much higher than that in bulk water. For instance, when the pH in bulk water is 9, the zeta potential of pristine hexadecane oil droplets is −105 mV, the surface charge density of hexadecane/water interfaces in the absence of surfactants can be as high as −4.9 μC cm^{-2} and the pH at the interfaces can be as high as 14.[12] Owing to the

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peculiar surface chemistry character, pristine oil-in-water emulsions should provide the simplest model to study the template effect of emulsion droplets, but, up to date, they have been rarely used to template formation of nanostructured materials. In this work, we used pristine alkane-in-water emulsions to template self-polymerization of pH-sensitive monomers. This should be the first report on careful correlation of the OH ion-enriched interfacial character of surfactant-free (pristine) oil-in-water emulsions with their template effect.

Inspired by mussels, increasing attention has been paid to dopamine and polydopamine (PDA) because of their peculiar adhesive and biocompatible properties.[14−19] PDA films have demonstrated strong adhesion to any substrate and immense flexibility for a range of chemical reactions to diversify the functionality of the surfaces coated by them.[14,16,20] PDA nanoparticles have exhibited excellent stability and biocompatibility in biological media, and very efficient free radical scavenging activity.[19] A number of techniques have been successfully developed to employ colloidal particles to template the formation of hollow PDA capsules.[17,18,21−24] Postma and Caruso used SiO_2 particles as template to prepare PDA hollow capsules. Zhou et al. reported that PDA capsules, obtained by silica particle templating synthesis have outstanding unidirectional loading and releasing ability of specific materials, thus suggesting of potential application of PDA hollow capsules in biomedicine.[21] $CaCO_3$ particles have also been applied as templates to produce PDA hollow capsules for construction of multienzyme or drug systems.[24] Jiang et al. recently developed a method to prepare PDA-inorganic hybrid microcapsules by the combination of biomineralization and manipulation of the metal-coordination interactions between inorganic layer and PDA layer. The obtained hybrid hollow capsules showed much higher mechanical stability and surface reactivity than pure inorganic capsules, which can be used as constructed multienzyme system for biocatalysis with desired activity and stability.[23] Similar to the work of Zoldesi and Imhof,[8] Cui et al. used monodisperse and stable DMDES-in-water emulsion droplets as templates to produce PDA hollow capsules with tailored size and shell thickness.[22] This method allowed loading of hydrophobic nanoparticles into the resulting PDA hollow capsules. Herein, pristine oil-in-water emulsions are utilized as template to fabricate PDA hollow capsules. The advantage of this method is that the reaction system is simple and versatile, only oil, water and OH^- are involved in the formation of emulsion template. In principle, all the hydrophobic oil can be stabilized solely by OH ions and server as template for PDA growth. Furthermore, because of the simple interfacial chemical milieu of pristine emulsion, it provides an ideal model to study the template effect of interfaces.

EXPERIMENTAL SECTION

Materials. Dopamine hydrochloride, L-dopa, hexadecane, hexane, octane, 1-octadecene, sodium dodecylsulfate (SDS), cetyltrimethylammonium bromide (CTAB), NaOH, and Nile red were purchased from Sigma-Aldrich and used without purification. Milli-Q water used has a resistance of higher than 18.2 MΩ cm.

Oxidation and Self-Polymerization of Dopamine in Water. Kinetic study of the oxidation and polymerization of dopamine in water: 1.5 mg of dopamine was dissolved in 10 mL of water. The pH of the resulting dopamine solutions was adjusted to 4.2, 6.3, 8.1, 8.5, and 9.2 by using 0.02 M NaOH. The reaction kinetics of dopamine oxidation and self-polymerization in water was monitored by UV−vis absorption spectroscopy.

Study of the morphology of the PDA obtained in water: 5 mg of dopamine was added to 10 mL of water. The pH of the resulting solution was adjusted to 8.2 by using the aqueous solution of NaOH (0.02 M). After being shaken for 1, 2, 7, and 24 h, the resulting solutions were directly used for characterization without further purification.

Using Pristine Oil-in-Water Emulsions to Template Self-Polymerization of Dopamine and L-dopa. Pristine oil-in-water emulsions, stabilized solely by OH ions, were obtained according to the protocol reported by Beattie and Djerdjev.[12] Typically, 0.2 mL of hexadecane, hexane, octane, or 1-octadecene and 0.6 mL of the aqueous solution of NaOH (0.02 M) were consecutively added to 9.8 mL of water. The resulting mixture was homogenized to produce pristine oil-in-water emulsions. Afterward, 3 or 5 mg of dopamine or 5 mg of L-dopa was added to the resulting pristine emulsions. The pH value of the emulsion solution was then adjusted to 8.2, followed by shaking for 1, 2, 3, 5, 7, and 24 h at ambient conditions. The resulting dispersions were directly used for characterization without further purification. In order to visualize the oil droplets, the alkane solvents used were stained by Nile red. The oil droplet templates were washed away with ethanol 3 times with the help of centrifugation.

Using Surfactant-Stabilized Oil-in-Water Emulsions to Template Self-Polymerization of Dopamine. Two-tenths of a milliliter of hexadecane and 0.6 mL of the aqueous solution of NaOH (0.02 M) were consecutively added into 9.8 mL of the aqueous solutions of SDS (2 mg/mL) or CTAB (0.8 mg/mL), followed by homogenization at ambient conditions. Subsequently, 5 mg of dopamine was added into the resulting emulsions. The pH of the resulting emulsion solution was then adjusted to 8.2, identical to that of pristine oil-in-water emulsions obtained above, followed by 24 h shaking at ambient conditions.

Characterization. UV−vis absorption spectra were recorded with a Cary 50 UV−vis absorption spectrophotometer. Transmission electron microscopy (TEM) imaging was implemented with a Zeiss EM 912 Omega microscope operated at an acceleration voltage of 120 kV. Scanning electron microscopy (SEM) imaging was conducted with a Gemini LEO 1550 instrument operated at 10 kV. The optical and fluorescent images were recorded by Leica DM IRBE confocal laser scanning microscope with excitation wavelength of 350 nm. Atomic force microscopy (AFM) images were obtained by a MultiMode 8 AFM (Bruker) in a scanning mode.

RESULTS AND DISCUSSION

Figure 1a shows the temporal evolution of the absorption spectra of an aqueous solution of dopamine at pH 9.2. According to the literature,[25] the appearance of the absorption band in the wavelength range of 300−308 nm suggests oxidation of dopamine into dopachrome and dopaindole. The following self-polymerization leads to a pronounced adsorption in the visible wavelength range (400−700 nm) and its intensity increases with time, which is accompanied by the color change of the reaction solutions from colorless to black. The intensity increase in the absorption at 400 nm with time was utilized to evaluate the polymerization rate of dopamine. Figure 1b indicates that the increase of the environmental pH can significantly accelerate dopamine oxidation and self-polymerization. The morphology of the PDA obtained in water (pH 8.2) was analyzed by SEM, indicating formation of PDA small particles with sizes of about 260 nm after 1 h (Figure 2a). The amount of the PDA particles increased with the reaction time while their size and the morphology remains little change (Figure 2b−d).

When self-polymerization was carried out in pristine hexadecane-in-water emulsions with the water phase pH of 8.2, SEM images of the resulting solutions indicate that microparticles with sizes of 1.3−7.5 μm were obtained after 1 h reaction instead of PDA small particles (Figure 3a); some

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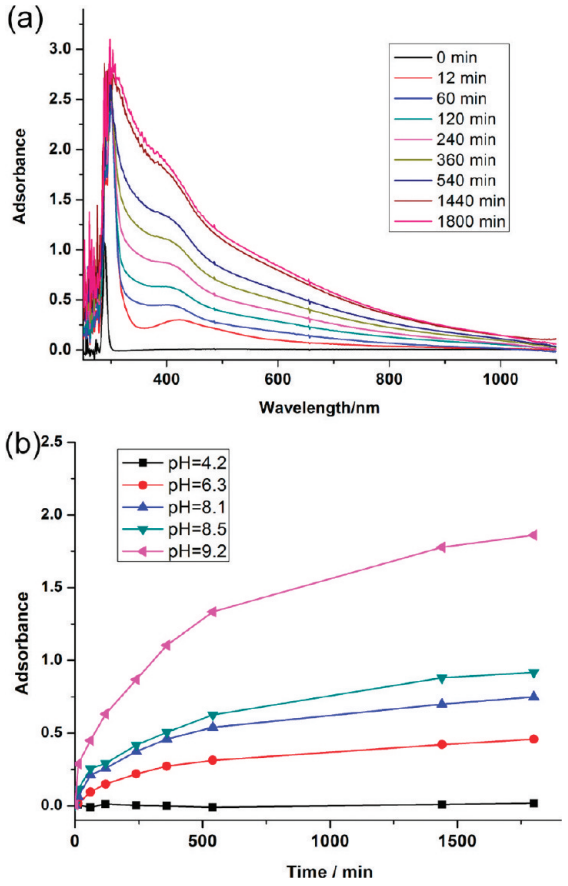

Figure 1. (a) UV−vis spectra of an aqueous solution of dopamine during oxidation and self-polymerization in water at pH 9.2. (b) Temporal evolution of the absorbance of the aqueous solution of dopamine at 400 nm at different pH. To avoid the formation of PDA precipitates, the dopamine concentration in water is as low as 0.15 mg/mL.

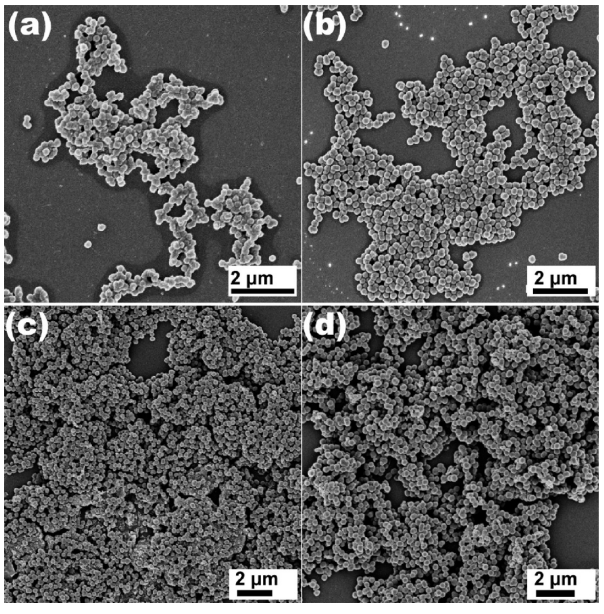

Figure 2. SEM images of PDA particles obtained via (a) 1, (b) 2, (c) 7, and (d) 24 h self-polymerization of dopamine in water at pH 8.2. The dopamine concentration in water is 0.5 mg/mL.

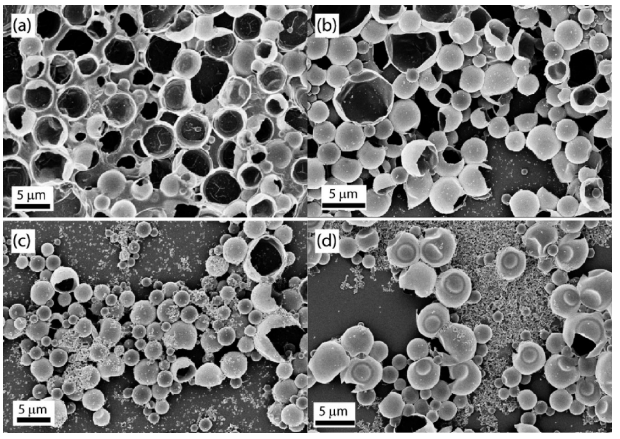

Figure 3. SEM images of PDA hollow capsules obtained via (a) 1, (b) 3, (c) 5, and (d) 24 h self-polymerization of dopamine in pristine hexadecane-in-water emulsions. The pH of the bulk water phase is 8.2 and the dopamine concentration in the emulsion is 0.5 mg/mL. The hexadecane core templates are not removed via washing.

broken particles revealed the resulting particles were hollow capsules. The amount, size and morphology of hollow capsules were little changed with the reaction time (Figure 3b−d). The hollow character of the resulting capsules was further confirmed by their TEM images, in which the capsules exhibit a dark edge and light center, further justifying the hollow character (Figure

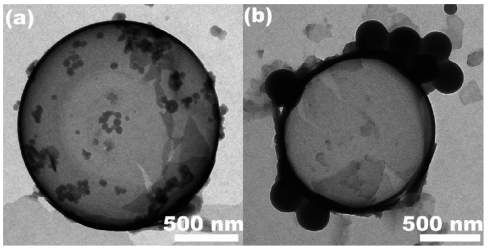

Figure 4. TEM images of PDA hollow capsules obtained via (a) 3 and (b) 7 h self-polymerization of dopamine in pristine hexadecane-in-water emulsions. The pH of the bulk water phase is 8.2 and the dopamine concentration in the emulsion is 0.5 mg/mL. The hexadecane core templates are not removed via washing.

4). In Figures 3 and 4, it is clearly visible that small particles with sizes of around 260 nm are formed and their amount significantly increases with the reaction time, similar to those observed in Figure 2. Note that the reaction solutions were directly used for SEM and TEM imaging without any purification. Formation of PDA small particles indicates that the pH of the bulk water phase of the pristine alkane-in-water emulsions is sufficiently high to trigger self-polymerization of dopamine to form PDA small particles in the bulk water phase. However, PDA small particles noticeably appeared after 5 h reaction in pristine alkane-in-water emulsions, rather slower than those formed in pure water.

The spherical shape of the resulting hollow capsules, shown in Figure 3 and especially Figure 4, suggests the presence of hexadecane inside because of its poor volatility. To remove the oil template, the resulting PDA hollow capsules were separated from the reaction solutions with the help of centrifugation and washed by ethanol for 3 times. Images a and b in Figure 5 show that collapsed hollow capsules are visible after drying at ambient conditions, suggesting removal of hexadecane. Note

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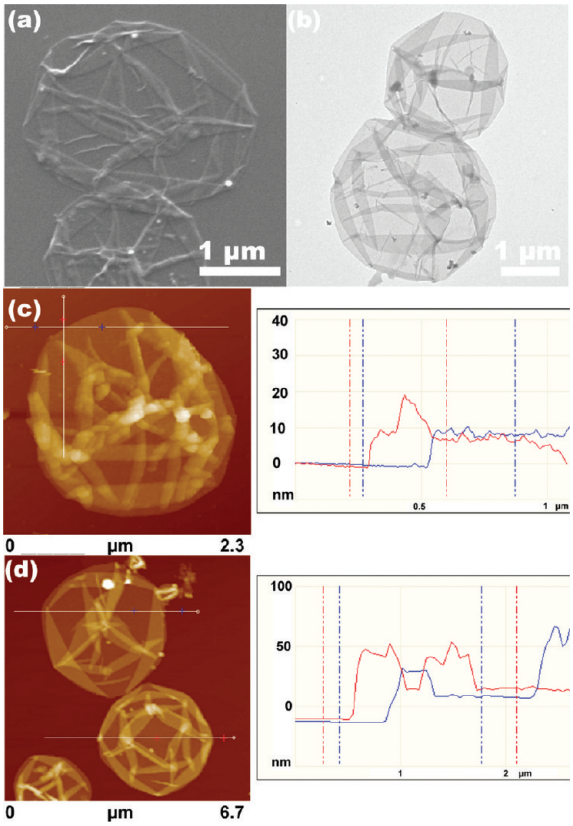

Figure 5. (a) SEM and (b) TEM images of PDA hollow capsules obtained via 24 h self-polymerization of dopamine in pristine hexadecane-in-water emulsions. The hexadecane core templates are removed via washing with ethanol. The pH of the bulk water phase is 8.2 and the dopamine concentration in the emulsion is 0.5 mg/mL. AFM images of the PDA hollow capsules obtained via (c) 2 and (d) 24 h self-polymerization of dopamine in the aforementioned pristine emulsions and the corresponding cross-section profiles of these capsules.

that after removal of the oil templates, broken capsules were hardly observed. The collapsed capsules allowed accurate measurement of their shell thickness by the means of AFM. The shell thickness of the PDA hollow capsules obtained after 2 h reaction is about 4 nm (Figure 5c). Twenty-four hour self-polymerization led to the maximum PDA shell thickness; it was about 10 nm (Figure 5d). Further prolongation of the reaction led to little change in the shell thickness (see the Supporting Information, Figure S1). The shell thickness increase should enhance the mechanical robustness of the resulting PDA hollow capsules, which was reflected by decrease in the number of broken capsules (unwashed), resulting from high vacuum SEM measurement with the reaction time shown in Figure 3. Similar PDA hollow capsules were also obtained when self-polymerization of dopamine were carried out in other pristine oil-in-water emulsions in which the oil phase was hexane, octane, or 1-octadecene instead of hexadecane (see the Supporting Information, Figure S2). This underlines that formation of PDA hollow capsules is independent of the chemical nature of the oil phase.

Formation of PDA hollow capsules suggests dominant self-polymerization of dopamine at the interfaces in pristine oil-in-water emulsions. It should be rationalized by the fact that the surfaces of pristine oil-in-water emulsion droplets have a pH much higher than that of bulk water phase by several orders of magnitude, which according to Figure 1b could significantly accelerate oxidation and self-polymerization of dopamine. We stained the alkane droplets in pristine alkane-in-water emulsions with a lipophilic dye, Nile red and in turn employed confocal laser scanning microscopy (CLSM) to in situ monitor the droplets and their surfaces over the course of self-polymerization of dopamine. CLSM imaging demonstrated that after self-polymerization of dopamine in pristine alkane-in-water emulsions was carried out in less than 3 h, the alkane droplets nonuniformly shrunk upon slight drying and wrinkles were clearly visible on the droplet surfaces, indicating formation of closed PDA shells enclosing the alkane droplets (see the Supporting Information, Figure S3). Furthermore, TEM and SEM imaging clearly indicates there is no PDA small solid particles formed during 3 h reaction (Figures 3 and 4). As such, we can conclude that self-polymerization of dopamine was preferentially carried out on the surfaces of the alkane droplets, thus leading to PDA shells enclosing the alkane droplets. When the concentration of dopamine in pristine emulsions was reduced to 0.3 mg/mL, the resulting PDA hollow capsules exhibited the sizes and shell thickness fairly similar to those obtained at the dopamine concentration of 0.5 mg/mL, but the amount of PDA small particles was significantly reduced (see the Supporting Information, Figure S4). This further confirms that most dopamine monomer, dissolved in bulk water phase, is consumed mainly for self-polymerization on the surfaces of the alkane droplets rather than in the bulk water phase.

Because the pK_a of the amine group of dopamine is 8.9,[26] the high basicity of the surfaces of pristine alkane droplets can readily deprotonate the PDA chains formed atop and turn them more hydrophobic. Thus, the hydrophobic interaction between deprotonated PDA chains would be taken into account for selective growth of PDA shells on the surfaces of pristine alkane-in-water emulsion droplets. To address this point, we used a derivative of dopamine, L-dopa, instead of dopamine. L-dopa has a molecular structure the same to dopamine except bearing amino acid terminal group rather than amine one (see the Supporting Information, Scheme S1). Because of its zwitterionic nature, the amino acid group renders L-dopa neutral or negatively charged and in turn the resulting poly(L-dopa) hydrophilic in a broad pH range (pH >2) according to the pK_a values of L-dopa.[27] Thus, the hydrophobic attraction between the poly(L-dopa) chains should be rather weak. On the other hand, the surfaces of pristine oil-in-water emulsion droplets in water are knownto be negatively charged because of the enrichment of OH ions.[11−13] The Zeta potential of the pristine alkane-in-water emulsions utilized in the current work was measured as high as −92 mV. An electrostatic repulsion should therefore be expected between L-dopa and the surfaces of pristine alkane droplets, which should be not favorable for poly(L-dopa) selective growth on the droplet surfaces to form the hollow capsules. However, images a and b in Figure 6 indicate the formation of poly(L-dopa) hollow capsules with sizes in the range of 0.6−3.6 μm after self-polymerization of L-dopa in pristine alkane-in-water emulsions. This underlines that the electrostatic and hydrophobic interactions between L-dopa and the surfaces of the pristine alkane droplets have little influence on the interfacial selectivity of the L-dopa self-polymerization. In the current work, self-polymerization of L-dopa was carried out for 7 days in order to achieve the maximum thickness of the resulting poly(L-dopa) shells on the alkane droplets because we found that self-polymerization of L-dopa was slower than dopamine (see the Supporting

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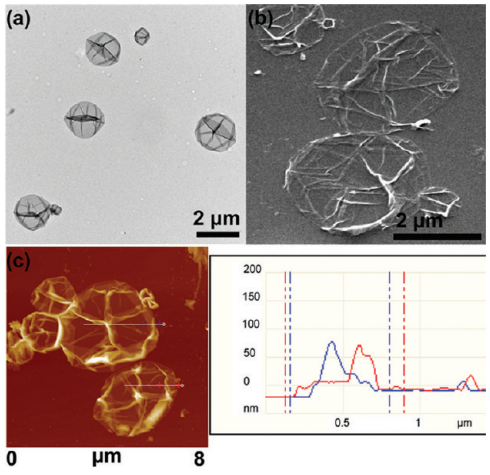


Figure 6. (a) TEM and (b) SEM images of poly(L-dopa) hollow capsules obtained via 7 days self-polymerization of L-dopa in pristine hexadecane-in-water emulsions. The pH of the bulk water phase is 8.2 and the L-dopa concentration in the emulsion is 0.5 mg/mL. The hexadecane core templates are removed via washing with ethanol. (c) AFM image of the aforementioned capsules and their cross-section profile.

Information, Figure S5). AFM imaging indicates the maximum shell thickness of the resulting poly(L-dopa) hollow capsules is about 6 nm (Figure 6c), which is about half of the maximun thickness of PDA hollow capsules (Figure 5d and Figure S1 in the Supporting Information). This thickness difference between poly(L-dopa) capsules and PDA ones should be due to the fact that the poly(L-dopa) is more hydrophilic than PDA formed on the surfaces of pristine alkane droplets

Conventionally used emulsion templates are those stabilized by surfactants. As such, we carried out self-polymerization of dopamine in alkane-in-water emulsions, stabilized by SDS or CTAB, and adjusted the pH of the bulk water phase to 8.2, identical to that of pristine alkane-in-water emulsions used above. As shown in Figure 7, self-polymerization of dopamine

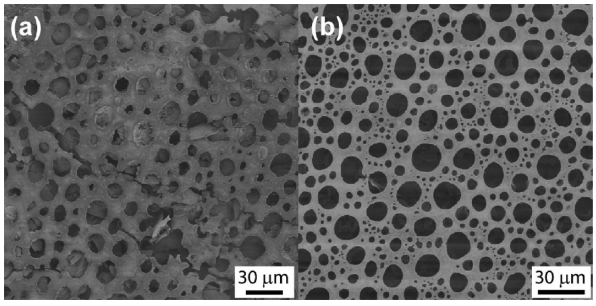


Figure 7. SEM images of the macroporous structures of PDA obtained via 24 h self-polymerization of dopamine in hexadecane-in-water emulsions stabilized by (a) SDS and (b) CTAB. The pH of the bulk water phase is 8.2 and the dopamine concentration in the emulsion is 0.5 mg/mL.

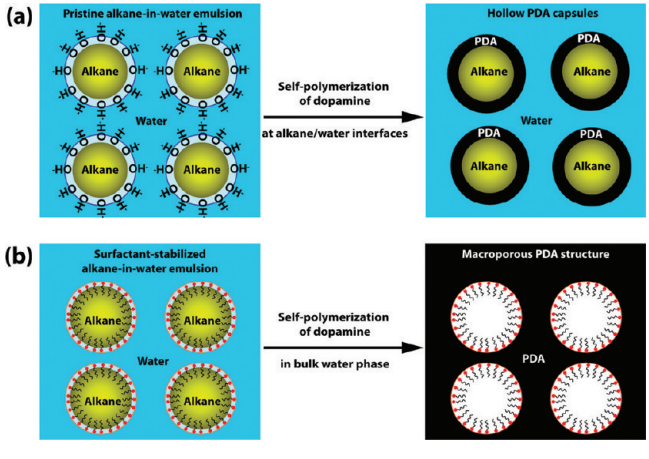
in surfactant-stabilized emulsions yields macroporous structures with the pore sizes in the range of 1−20 μm and the spacing distances of 7−8 μm between next-nearest neighboring pores, which is hardly dependent on the nature of the surfactants used for emulsion stabilization. No hollow capsules are visible in the resulting samples. According to the literature,[1−3] formation of macroporous structures can be easily elucidated as a result of accumulation of the resulting PDA in the void spaces between the emulsion droplets during drying. Although we cannot completely rule out the effect of the surface chemistry of the surfactant-stabilized alkane droplets on the kinetics of dopamine self-polymerizations, it is definitely not that pronounced as that of pristine alkane droplet surfaces. In other words, the presence of surfactants noticeably smears out the interfacial preference of self-polymerization of dopamine. Recently, Beattie and Djerdjev have reported that addition of surfactants to pristine hexadecane-in-water emulsions caused increase of the pH in the bulk water phases, indicated that the OH ions enriched on the surfaces of the alkane droplets were displaced by the surfactants and released to the bulk water.[12] In this scenario, therefore, the surface pH of oil-in-water emulsion droplets, stabilized by surfactants, is expected lower than that of pristine alkane-in-water emulsion droplets, stabilized solely by OH ions. In consideration of its pronounced pH dependence, therefore, self-polymerization of dopamine should be significantly suppressed on the surfactant-stabilized surfaces of alkane droplets.

Because the interfacial basicity of surfactant-stabilized alkane-in-water emulsions was significantly reduced, dopamine could remain slightly positively charged when the pH of the bulk water phase was lower than the dopamine pK_a (8.9). In this scenario, one should expect an electrostatic attraction between dopamine and the surfaces of SDS-stabilized alkane droplets, which should drive self-polymerization of dopamine selectively occurring on the droplet surfaces to form PDA hollow capsules. Nonetheless, only PDA macroporous structures were visible in our work (Figure 7a). This implies that as compared with the interfacial basicity in alkane-in-water emulsions, the electrostatic attraction between dopamine and alkane droplets has an insignificant contribution to the interfacial preference of dopamine self-polymerization.

CONCLUSION

In summary, we have successfully employed the strong interfacial basicity of pristine oil-in-water emulsions to direct oxidation and self-polymerization of dopamine selectively occurring on the surfaces of the oil droplets, leading to PDA hollow capsules. In this scenario, individual pristine oil droplets, stabilized solely by OH ions, play the template role (Scheme

Scheme 1. Schematic Illustration of Self-Polymerization of Dopamine in (a) Pristine Alkane-in-Water Emulsions and (b) Surfactant-Stabilized Alkane-in-Water Emulsions



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1a), which stems dominantly from the enrichment of OH ions on the surfaces of pristine oil droplets. The electrostatic and hydrophobic interactions between the droplet surfaces and dopamine have little contribution to the interfacial selectivity of the dopamine self-polymerization and formation of PDA hollow capsules. The hydrophobic interaction should have a non-negligible contribution of the accumulation of the resulting PDA chain to form thicker shells on the droplet surfaces. In contrast to pristine ones, oil-in-water emulsions, stabilized by ionic surfactants, have rather weak interfacial basicity, which cannot endorse the preference of self-polymerization of dopamine on the surfaces of the oil droplets, thus leading to macroporous structures. In this case, the ensemble of the oil droplets, stabilized by ionic surfactants, acts as a spatial skeleton to template PDA, formed in the bulk water phase to fill the interstitial space between the droplets in particular during drying (Scheme 1b). The present study therefore leads to clear implication that the difference of the template effect between surfactant-free and surfactant-stabilized oil-in-water emulsions, reported in the literature, should arise from the difference of the interfacial chemistry, for instance the pH, between these two emulsions. The interfacial basicity of pristine oil-in-water emulsions should be also expected for nonionic surfactant-stabilized emulsions, provided the nonionic surfactants can selectively adsorb and enrich OH ions on the surfaces of the oil droplets, which should be strongly dependent on the chemical nature of the surfactant hydrophilic groups for instance the affinity to proton. To achieve a better understanding of the template effect of different types of emulsions, our current effort is devoted to study of the enrichment of different ions on the surfaces of the emulsion droplets and careful interrogation of its correlation with the chemistry nature of the surfactants and its influence of the kinetics of material synthesis and accumulation.

From the standpoint of materials science, the present work has demonstrated a simple and surfactant-free strategy to produce hollow capsules by using pristine oil-in-water emulsions as templates. Any water immiscible organic solvent can be used to produce pristine oil-in-water emulsions. Using organic solution of functional lipophilic molecules, polymers, and inorganic nanoparticles instead of pure organic solvents allows efficient encapsulation of these functional substances, thus diversifying the functionality of the resulting capsules and broadening their application spectrum. Self-polymerization of dopamine and L-dopa is just a typical example for concept proof. Our approach should be extendable to other pH regulated reaction, such as sol−gel of metal oxides, which is the focus of our ensuing research.

■ ASSOCIATED CONTENT

Supporting Information

The illustration of the molecular structures of dopamine and L-dopa, AFM image of PDA capsules obtained via 7 day self-polymerization of dopamine in pristine hexadecane-in-water emulsions, SEM images of PDA capsules obtained from 24 h self-polymerization of dopamine in pristine alkane-in-water emulsions, confocal microscopy images of PDA encapsulated 1-octadecene droplets labeled with Nile red, and kinetic of oxidation and polymerization of L-dopa. This material is available free of charge via the Internet at http://pubs.acs.org/.

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