Spatial Isolation of Carbon and Silica in a Single Janus Mesoporous Nanoparticle with Tunable Amphiphilicity

Tiancong Zhao,† Xiaohang Zhu,‡ Chin-Te Hung,† Peiyuan Wang,† Ahmed Elzatahry,‡ Areej Abdulkareem Al-Khalaf,§ Wael N. Hozzein,¶,‖ Fan Zhang,‖ Xiaomin Li,*‡† and Dongyuan Zhao*§†

†Department of Chemistry and Laboratory of Advanced Materials, State Key Laboratory of Molecular Engineering of Polymers, Collaborative Innovation Center of Chemistry for Energy Materials (2011-iChEM), Fudan University, Shanghai 200433, P.R. China
‡Materials Science and Technology Program, College of Arts and Sciences, Qatar University, P.O. Box 2713, Doha, Qatar
§Biology Department, College of Sciences, Princess Nourah Bint Abdulrahman University, Riyadh 11671, Saudi Arabia
Bioproducts Research Chair, Zoology Department, College of Science, King Saud University, Riyadh 11451, Saudi Arabia
¶Botany and Microbiology Department, Faculty of Science, Beni-Suef University, Beni-Suef, Egypt

ABSTRACT: Like surfactants with tunable hydrocarbon chain length, Janus nanoparticles also possess the ability to stabilize emulsions. The volume ratio between the hydrophilic and hydrophobic domains in a single Janus nanoparticle is very important for the stabilization of emulsions, which is still a great challenge. Herein, dual-mesoporous Fe3O4@mC@mSiO2 Janus nanoparticles with spatial isolation of hydrophobic carbon and hydrophilic silica at the single-particle level have successfully been synthesized for the first time by using a novel surface-charge-mediated selective encapsulation approach. The obtained dual-mesoporous Fe3O4@mC@mSiO2 Janus nanoparticles are made up of a pure one-dimensional mesoporous SiO2 nanorod with tunable length (50–400 nm), ∼100 nm wide and ∼2.7 nm mesopores and a closely connected mesoporous Fe3O4@mC magnetic nanosphere (∼150 nm diameter, ∼10 nm mesopores). As a magnetic “solid amphiphilic surfactant”, the hydrophilic/hydrophobic ratio can be precisely adjusted by varying the volume ratio between silica and carbon domains, endowing the Janus nanoparticles surfactant-like emulsion stabilization ability and recyclability under a magnetic field. Owing to the total spatial separation of carbon and silica, the Janus nanoparticles with an optimized hydrophilic/hydrophobic ratio show spectacular emulsion stabilization ability, which is crucial for improving the biphasic catalysis efficiency. By selectively anchoring catalytic active sites into different domains, the fabricated Janus nanoparticles show outstanding performances in biphasic reduction of 4-nitroanisole with 100% conversion efficiency and 700 h−1 high turnover frequency for biphasic cascade synthesis of cinnamic acid.

INTRODUCTION

Oil–aqueous biphasic reactions, despite being important for organic synthesis, petroleum processing, biorefineries, and enzymatic reactions, suffer from limited efficiencies due to the low reaction interface area caused by immiscibility between water and oil.1–10 Thus, formation of stabilized emulsions for a maximum interaction area is essential for improving their practicability. Solid nanoparticles, while stabilizing the biphasic system to form a Pickering emulsion like organic amphiphilic surfactants, have superior functionalities and recycling abilities.11–13 They can also serve as carriers of catalysts, which is very promising for enhancing the catalytic ability of biphasic reactions.9,10

Similar to traditional organic amphiphilic surfactants with hydrophilic/hydrophobic ends for stabilizing emulsions, asymmetric nanoparticles are much preferred for the stabilization of Pickering emulsions compared to normal homogeneous particles11–13 because the two sides of the Janus particles can be positioned in their respective affinitive phase (oil or water) to lower the thermo-dynamical energy. The emulsion stabilizing ability of molecular amphiphilic surfactants changes with different hydrophobic carbon chains and hydrophilic ionic heads. Correspondingly, the emulsifying ability of asymmetric particles also strongly depends on the volume ratio of their hydrophilic/hydrophobic domains on distinct ends.14–17 Yet, unlike organic amphiphilic surfactants, in which the hydrophilic/hydrophobic ratio can be adjusted by changing the hydrocarbon chain length, the precise tuning of asymmetric nanoparticles’ hydrophilic/hydrophobic ratio is rather difficult. Most of the existing asymmetric particles are made up of different nanocrystals or polymers with similar surface properties.18–21 Though several papers have reported the synthesis of Janus nanoparticles with different hydrophilic/
hydrophobic domains, these particles are based on anisotropic growth of periodic mesoporous organosilica (PMO) on SiO2 or resorcinol–formaldehyde resin (RF).22−26 Because PMO is a hybrid material with the organic/inorganic components homogeneously distributed over the whole framework, the obtained Janus PMO&mSiO2 (SiO2/C&mSiO2 after carbonization) or PMO&RF (C/SiO2&C after carbonization) nanoparticles are not absolutely asymmetric in compositions, narrowing the heterogeneity of asymmetric domains.24,26−28 Therefore, it is critically desired that the carbon (hydrophobic) and SiO2 (hydrophilic) sections are completely isolated in every single nanoparticle, so that the proportion of the hydrophilic/hydrophobic domains can be easily and precisely adjusted in a very broad range. Furthermore, the organic amphiphilic surfactants like “solid surfactants” can be easily functionalized with different inorganic nanocrystals (magnetic, optic, electric, etc.), showing great potential for applications in catalysis, adsorption, separation, and biomedicines.

Herein, we demonstrate the fabrication of dual-mesoporous Fe3O4@mC&mSiO2 Janus “magnetic solid surfactants” with absolute spatial isolation of carbon and silica at the single-nanoparticle level for the first time, which is based on a novel surface-charge-mediated selective encapsulation approach of mesoporous carbon shells on magnetic Fe3O4 cores. The obtained mesoporous Fe3O4@mC&mSiO2 Janus particles with a high surface area (~415 m2/g) are made up of a pure one-dimensional (1D) mesoporous SiO2 nanorod (tunable length in the range of 50−400 nm, ~100 nm wide) with highly ordered mesostructure (space group p6mm with 2.7 nm mesopores) and a closely connected ~150 nm core−shell structured Fe3O4@mC nanosphere with radial mesopores (~10 nm) at one end (Figure 1). Distinct from the PMO-based asymmetric nanoparticles with interfingering carbon and silica frameworks reported previously, the obtained magnetic Janus nanoparticles possess spatial isolation for carbon and silica, indicating the total separation of hydrophobic and hydrophilic domains in every single nanoparticle. Due to such isolation, the hydrophilic/hydrophobic ratio can be easily adjusted by changing the volume ratio between the carbon and silica domains, enabling the uniform Janus nanoparticles the ability to tune the stabilization of Pickering emulsions as amphiphilic “solid surfactants”. With further functioning with Fe3O4 nanoparticles, the “magnetic solid surfactants” with good recyclability under a magnetic field can be obtained. Owing to the distinct surface properties of carbon and silica, active catalytic sites, such as small noble nanocrystals, organic functional group, etc., can selectively be incorporated into the hydrophobic carbon or hydrophilic silica domains. With surfactant-like emulsion stability, the obtained asymmetric nanocatalysts show significantly high activity in not only biphasic reduction of 4-nitroanisole with 100% conversion efficiency but also biphasic cascade reactions for the synthesis of cinnamic acid, achieving turnover frequency as high as 700 h−1. The Janus structured “magnetic solid surfactants” with spatial isolation and tunable silica and carbon domain size, dual mesoporosity, high surface area, magnetic property, and easy functionalization can be utilized as a novel platform for various applications.

### EXPERIMENTAL SECTION

**Synthesis of Fe3O4 Nanocrystals.** Fe3O4 nanoparticles were prepared via a solvothermal method reported previously.27 In a typical synthesis of the magnetite Fe3O4 nanoparticles with an average diameter of ~100 nm, 3.25 g of FeCl3·H2O (20 mmol), 100 mL of ethylene glycol, 1.3 g of trisodium citrate (4.4 mmol), and 6.0 g of sodium citrate tribasic were mixed and sonicated for 1 h. The mixture was then transferred into a 200 mL Teflon-lined stainless-steel autoclave. The autoclave was heated at 200 °C and maintained for 10 h. After being cooled to room temperature, the products were washed with distilled water and ethanol and finally dispersed in ethanol for further use.

**Synthesis of Fe3O4&mSiO2 Janus Nanoparticles.** The mesoporous Fe3O4&mSiO2 Janus nanoparticles were fabricated with the surfactant-oriented anisotropic growth of mesoporous silica.28−30 In a typical fabrication of the mesoporous Fe3O4&mSiO2 Janus nanoparticles with mesoporous SiO2 rods with a length of 400 nm, 37.5 mg of the Fe3O4 nanoparticles obtained above was dispersed in 20 mL of distilled water, and 100 mg of CTAB was added. The mixture was then sonicated for 30 min and then transferred into an oil bath and heated at 40 °C. Next, 1.0 mL of ammonium hydroxide and 180 μL of TEOS were added stepwise. The mixture was allowed to react for 36 h and was then centrifuged and washed with water and ethanol. The final products were dispersed in 20 mL of ethanol solution.

**Synthesis of Dual-Mesoporous Fe3O4@mPDA&mSiO2 and Fe3O4@mC&mSiO2 Janus Nanoparticles.** Mesoporous polymeric dopamine (mPDA) coating on the obtained Fe3O4&mSiO2 Janus nanoparticles was realized through a selective encapsulation strategy. In a typical synthesis, 3.0 mg of the Fe3O4&mSiO2 Janus nanoparticles with 400 nm mesoporous SiO2 rods was dispersed in 25 mL of distilled water. Twenty milliliters of ethanol, 0.20 g of Pluronic F127, and 50 mg of dopamine hydrochloride were added to the solution and stirred to form a transparent solution. Next, 0.4 mL of TMB was then added, and the solution was stirred for 30 min. Thirty milligrams of tris(hydroxymethyl)aminomethane was further added, and the reaction was left to proceed for 4 h. The final products were centrifuged and washed with distilled water and ethanol. The

![Figure 1](Image)
obtained dual-mesoporous \( \text{Fe}_3\text{O}_4@\text{mPDA@mSiO}_2 \) Janus nanoparticles with spatial isolation of mPDA and mSiO2 domains were calcined in a nitrogen environment at 450 °C for 3 h to obtain the dual-mesoporous \( \text{Fe}_3\text{O}_4@\text{mC&mSiO}_2 \) Janus nanoparticles with spatial isolation of carbon and silica domains.

**RESULTS AND DISCUSSION**

As shown in Figure 1A, the \( \text{Fe}_3\text{O}_4 \) nanoparticles with a diameter of \( \sim 100 \) nm are first prepared via a solvothermal method (Figure S1).29 The uniform \( \text{Fe}_3\text{O}_4@m\text{SiO}_2 \) Janus nanoparticles with controllable length of the mesoporous silica rod domain are fabricated based on the anisotropic growth of the mesoporous nanocomposites reported previously (Figures S2–S4).30,31 Mesoporous polydopamine is selectively coated on the \( \text{Fe}_3\text{O}_4 \) nanoparticle side of the \( \text{Fe}_3\text{O}_4@m\text{SiO}_2 \) Janus nanoparticles to form the dual-mesoporous \( \text{Fe}_3\text{O}_4@m\text{PDA&mSiO}_2 \) asymmetric nanostructure with polymer and silica separation (Figures S5 and S6). The dual-mesoporous \( \text{Fe}_3\text{O}_4@m\text{C&mSiO}_2 \) Janus nanoparticles with spatial carbon and silica isolation at the single-particle level are finally obtained after carbonization.

The scanning electron microscopy (Figure 1B,C) and transmission electron microscopy (TEM) (Figure 1D,E) images show that the dual-mesoporous \( \text{Fe}_3\text{O}_4@m\text{C&mSiO}_2 \) Janus nanoparticles possess uniform asymmetric head–tail morphology and are made up of a mesoporous \( \text{Fe}_3\text{O}_4@m\text{C} \) core–shell structured nanosphere with a diameter of \( \sim 150 \) nm and one closely connected mesoporous \( \text{SiO}_2 \) nanorod with \( \sim 400 \) nm length and \( \sim 100 \) nm width. High-resolution TEM images show that the mesoporous \( \text{SiO}_2 \) nanorods have uniform hexagonal mesopores (space group \( \text{p6mm} \)) with a pore diameter of \( \sim 2.7 \) nm (Figure S2). The core–shell structured \( \text{Fe}_3\text{O}_4@m\text{C} \) nanospheres possess a magnetite \( \text{Fe}_3\text{O}_4 \) core with a diameter of \( \sim 100 \) nm, a mesoporous carbon shell with a thickness of \( \sim 30 \) nm and radial mesoporous channels with \( \sim 10 \) nm pore size (Figures S6 and S7). \( \text{N}_2 \) sorption isotherms of the obtained dual-mesoporous \( \text{Fe}_3\text{O}_4@m\text{C&mSiO}_2 \) Janus nanoparticles exhibit representative type-IV curves with a rapid increase in the adsorption branch at a relative pressure of 0.2–0.6, clearly indicating uniform mesopores (Figure 1F). The Brunauer–Emmett–Teller surface area of the dual-mesoporous \( \text{Fe}_3\text{O}_4@m\text{C&mSiO}_2 \) Janus nanoparticles is estimated to be \( \sim 415 \) m\(^2\)/g. Consistent with the results obtained from the TEM images, the pore size distribution curve obtained by the Barrett–Joyner–Halenda method shows that the \( \text{Fe}_3\text{O}_4@m\text{C} \) Janus nanoparticles exhibit dual-mesopore size distribution with an average diameter of \( \sim 2.7 \) nm and a broad size distribution in the range of 5–15 nm (Figure 1G), which are mainly derived from the ordered mesopores of the mesoporous \( \text{SiO}_2 \) nanorod domains and radial mesopore channels of the core@shell \( \text{Fe}_3\text{O}_4@m\text{C} \) mesoporous carbon domains, respectively. The obtained dual-mesoporous \( \text{Fe}_3\text{O}_4@m\text{C&mSiO}_2 \) Janus nanoparticles exhibit superparamagnetic properties with a high saturation magnetization value of \( \sim 30 \) emu/g (Figure S9), which is very important for the recyclability under the magnetic field. Elemental mapping images of one single nanoparticle clearly show the asymmetrically distributed compositions and Janus geometry (Figure 1H). All of the expected elements can be detected, and the segregation of carbon and silicon elements matches well with the relative positions in the Janus nanocomposites, clearly demonstrating the composition separation. This is the first realization of the spatial isolation of carbon and silica domains at the single-particle level.

The selective encapsulation of mPDA is crucial for spatial isolation of the carbon (polymer) and silica domains in Janus nanoparticles. It can be seen that, during the growth of mPDA, the tendency of mesoporous PDA assembly to avoid the mesoporous \( \text{SiO}_2 \) rods in \( \text{Fe}_3\text{O}_4@m\text{SiO}_2 \) Janus nanoparticles always exists, and distinct notches are formed at the boundary between the \( \text{PDA} \) and mesoporous \( \text{SiO}_2 \) rod domains (Figure S10). After selective etching of the \( \text{Fe}_3\text{O}_4 \) nanoparticles and mesoporous \( \text{SiO}_2 \) rods, only mesoporous mPDA bowls remain (Figure S11), further proving that mPDA molecules are not grown on the mesoporous \( \text{SiO}_2 \) rods. mPDA molecules do not grow on the mesoporous \( \text{SiO}_2 \) parts of the Janus nanoparticles even when an excess amount of dopamine is added (Figure S12) or when the reaction time is prolonged (Figure S13). The influence of other reagents in the reaction system is also investigated. Without the addition of the mesopore-directing agents, Pluronic \( \text{F}127 \) and 1,3,5-trimethylbenzene (TMB),32–34 nonporous PDA also does not grow on \( \text{SiO}_2 \), resulting in the formation of the mesoporous \( \text{Fe}_3\text{O}_4@m\text{PDA&mSiO}_2 \) Janus structures (Figures S14 and S15). Shifting the reaction medium (ethanol/water) or addition of surfactants can change the encapsulation behavior of PDA: changing the ratio of ethanol/water from 1 to 3 and the addition of cationic surfactant CTAB can induce the homogeneous coating of PDA on silica (Figures S16 and S18), thus a uniform coating is realized on both the \( \text{Fe}_3\text{O}_4 \) nanoparticle cores and mesoporous silica mSiO2 rods of the Janus \( \text{Fe}_3\text{O}_4@m\text{SiO}_2 \) nanoparticles (Figures S17 and S19).

Here, we consider that the selective encapsulation of PDA is mainly attributed to the surface charge repulsion between silica and dopamine molecules. In basic environments (Figure 2), hydroxyl groups on the silica surface can deprotonate, leaving negatively charged oxygen anions, which can be demonstrated by the \( \zeta \)-potential measurement (~43.6 eV). Dopamine molecules with phenolic hydroxyl groups also go through a similar process to acquire a negative charge. Thus, charge repulsion prevents the attachment of dopamine molecules on silica domains, resulting in self-nucleation (Figure S20 and Table S1). In contrast, the interaction between Fe3O4 nanoparticles and dopamine is very strong because of the coordination between the Fe3+ and dopamine molecules,35,36 which further induces the nucleation on Fe3O4 nanoparticles to form uniform core/shell structures (Figure S20). Thus, when the Fe3O4 nanoparticle and silica domains coexist in the

Figure 2. Schematic illustration of the surface-charge-controlled selective encapsulation of mPDA toward the mesoporous \( \text{Fe}_3\text{O}_4@m\text{SiO}_2 \) Janus nanoparticles to form a dual-mesoporous \( \text{Fe}_3\text{O}_4@m\text{PDA&mSiO}_2 \) Janus structure with particle level polymer and \( \text{SiO}_2 \) isolation.
solution, dopamine molecules selectively polymerize and encapsulate on magnetite Fe3O4 nanoparticles, resulting in the formation of the dual-mesoporous Fe3O4@mPDA@mSiO2 Janus structure (Figure 2). By shifting the reaction medium or adding cationic surfactants, the surface properties of nanomaterials are changed. It can be seen that the negative charge of both silica and dopamine is decreased (Table S1) when changing the ratio of ethanol/water from 1 to 3, meaning that the repulsive force between PDA molecules and silica is greatly suppressed. The addition of cationic CTAB can shift the surface charge of the silica domains to positive. Thus, PDA can grow on silica under these circumstances, achieving a homogeneous coating on whole Janus Fe3O4@mSiO2 nanoparticles. When such surface-charge-mediated selective encapsulation mechanisms are utilized, similar structures, such as Au@PDA@mSiO2 Janus nanoparticles and CdS@mPDA@mSiO2 Janus nanoparticles (Figure S22), can be fabricated, demonstrating universality of the methodology.

Due to the spatial isolation of the carbon and silica domains, the hydrophilic/hydrophobic ratio of the obtained asymmetric dual-mesoporous Fe3O4@mC@mSiO2 Janus nanocomposites can be easily adjusted by changing the volume ratio between the two domains. By adjusting the amount of the silica precursor during the anisotropic growth of the mesoporous silica nanorods (Figure 3A–D), the length of the SiO2 domain in the dual-mesoporous Fe3O4@mC@mSiO2 Janus nanoparticles can be varied from 50 to 400 nm (Figure 3E–H). This means that the hydrophilic/hydrophobic ratio of the mesoporous Fe3O4@mC@mSiO2 Janus nanoparticles can be easily tuned, which is very important for tuning the emulsion stability of different emulsion systems when using the dual-mesoporous Fe3O4@mC@mSiO2 Janus nanoparticles as an amphiphilic "solid surfactant". With the water/toluene oil-in-water emulsion system as an example, the stability of the toluene/water emulsion is quite different when the dual-mesoporous Fe3O4@mC@mSiO2 Janus nanoparticles with different hydrophilic domain size (mesoporous SiO2 rod length) are used as the stabilizer (Figure 3I). The biphasic system can be stabilized by the dual-mesoporous Fe3O4@mC@mSiO2 Janus nanoparticles with a 400 nm mesoporous SiO2 rod to form a very stable emulsion. The emulsion can last as long as 12 h, indicating spectacular surfactant-like emulsion stability. Oil-in-water droplets are clearly observable under an optical microscope, and the fluorescence of oil-soluble fluorescence dye further demonstrates the formation of the stable oil-in-water emulsion (Figure 3J,K). In contrast, when the length of the mesoporous SiO2 nanorods decreases (e.g., 200, 100, 50 nm), due to the insufficient size of hydrophilic domain, the hydrophilic/hydrophobic ratio is too small to stabilize the emulsions, resulting in phase separation in no more than 6 h. In addition to the hydrophilic part, the presence of hydrophobic domains in the Janus nanoparticles is also very important: without hydrophobic carbon domains, the mesoporous Fe3O4@mSiO2 nanoparticles are unable to stabilize the biphasic system. The thickness of the mesoporous carbon shells can be tuned from 10 to 30 nm by varying the reaction time (Figure S23). Compared with that of hydrophilic mesoporous SiO2 rod, the variation range for the hydrophobicity of the mesoporous carbon domain is too narrow to tune the amphiphilicity of the Janus nanoparticles. Therefore, the adjustment of emulsion stability is mainly realized by changing the length of the mesoporous SiO2 nanorod domains. In addition to oil-in-water systems, the dual-mesoporous Fe3O4@mC@mSiO2 Janus nanoparticles can also be used to stabilize water-in-oil emulsions, showing a good stabilization ability (Figure S24). It can be concluded that the superior emulsion stabilizing ability of the dual-mesoporous Fe3O4@mC@mSiO2 Janus nanoparticles is attributed to not only the spatial isolation of carbon and silica domains but also the appropriate hydrophilic/hydrophobic ratio of the two domains in every single particle. This hydrophilic/hydrophobic ratio determined that the emulsion stabilizing ability of the dual-mesoporous Fe3O4@mC@mSiO2 Janus nanoparticles is similar to that of organic amphiphilic surfactants with different hydrocarbon chain length, which can be determined as "solid surfactants".

As "magnetic solid surfactants", in addition to functioning as surfactants, the mesoporous Fe3O4@mC@mSiO2 Janus nanoparticles can also selectively be loaded with active catalytic sites (e.g., small noble nanocrystals, organic functional groups, etc.) to catalyze the biphasic reaction. Due to the coordination interactions between dopamine and metal species, Pt4+ ions can be coordinated in the frameworks of polydopamine during mPDA selective encapsulation. As observed from TEM images (Figure 4A,B) and element mappings (Figure 4C), the Pt nanocrystals with an average diameter of 3–5 nm are selectively and homogeneously implanted within the carbon domains of the Janus nanoparticles after further calculation.

Figure 3. TEM images of the mesoporous Fe3O4@mSiO2 (A–D) and Fe3O4@mC@mSiO2 (E–H) Janus nanoparticles with different mesoporous silica rod length: (A,E) 400 nm, (B,F) 200 nm, (C,G) 100 nm, (D,H) 50 nm (all denoted as mC@mSiO2-X, where X is the length of the mesoporous silica domain). (1) Digital photos of the Pickering emulsion solution of toluene and water in the presence of the obtained dual-mesoporous Fe3O4@mC@mSiO2 Janus nanoparticles with different mesoporous silica rod length. Nile red is added for coloration. The mixture solutions were sonicated to form an emulsion and then set still for observation; photos were taken at 0.5, 6, and 12 h after emulsifying. (1) Optical micrograph image and (K) fluorescent optical micrograph image of the toluene-in-water emulsion stabilized by the dual-mesoporous Fe3O4@mC@mSiO2 Janus nanoparticles with a length of 400 nm for the mesoporous silica rods. The oil phase is dyed by fluorescein isothiocyanate to fluoresce.
Subsequently, the obtained Pt-nanoparticle-loaded Pt/Fe3O4@mC&mSiO2 Janus nanocomposites are used for biphase reduction of 4-nitroanisole (Figure 4D). As shown in Figure 4E, the conversion efficiency of the dual-mesoporous Pt/Fe3O4@mC&mSiO2 Janus nanoparticles reaches more than 70% in the initial 3 h due to the formation of a stable emulsion (Figure S27). In stark contrast, the Pt-loaded mesoporous Fe3O4@mC core−shell or Fe3O4@mSiO2 Janus nanoparticles (Figure S28), which are unable to stabilize the emulsion with only hydrophilic or hydrophobic domains, show a very low conversion efficiency (<10%) in the same time period (Figure S29). Such a significant difference in catalytic efficiency is mainly attributed to the surfactant-like property of the dual-mesoporous Pt/Fe3O4@mC&mSiO2 Janus nanoparticles for the stabilization of the biphase emulsion reaction system, which can increase the reactive interface area and kinetics. In addition, with the advantage of the magnetic Fe3O4 nanoparticles, the well-designed dual-mesoporous Pt/Fe3O4@mC&mSiO2 Janus nanocatalysts are easily collected by external magnetic force for reuse (Figure S31). The results show that the dual-mesoporous Pt/Fe3O4@mC&mSiO2 Janus nanoparticles exhibit almost constant catalyst efficiency during the tested 10 cycles, indicating the stable interfacial activity and satisfying recovery ability (Figure 4F).

A cascade reaction, a consecutive chemical transformation, involves the design of a multistep reaction in a sequence, making the approach economical and environmentally friendly.55 Yet, the design of catalytic cascades is often hindered by the random interactions between reagents and catalysts of different reactions, leading to unwanted by-products. One ideal solution is the Janus-nanoparticle-stabilized oil/water biphasic system.39−41 In a Pickering emulsion stabilized by the Janus nanoparticles with suitable hydrophilic/hydrophobic domain ratio, oil-soluble reagents and catalysts loaded on the hydrophobic side of the Janus nanoparticles always stay in the oil phase. Similarly, the active sites on the hydrophilic domain of the particles and water-dispersible reactants are kept in the water phase, thus allowing controllable interactions between reagents and catalysts.12−24 Therefore, such a system can achieve the spatial isolation of sequential catalyst reactions, allowing the design of complex cascade reactions.

The obtained dual-mesoporous Pt/Fe3O4@mC&mSiO2 Janus nanoparticles are further treated with aminoisobutane to form the mesoporous Pt/Fe3O4@mC&mSiO2/NH2 Janus nanocomposites with Pt nanoparticles in hydrophobic carbon domains and −NH2 active groups in hydrophilic mesoporous mSiO2 domains (Figure S32). The fabricated dual-mesoporous Pt/Fe3O4@mC&mSiO2/NH2 Janus nanocomposites are used for the cascade synthesis of cinnamic acid, which is an important ingredient for chemical engineering, food, and drug industries. A traditional synthetic route of cinnamic acid fabricated via multiple homogeneous phase reactions requires complicated and repeated purification processes to transfer intermediates between different reaction systems, resulting in economic inefficiency,45−47 which could be solved by designing “solid surfactant”-catalyzed biphasic cascade reactions (Figure 5A). In this reaction, under the catalysis of −NH2

Figure 5. (A,B) Schematic illustration of the catalytic cascade reaction over the uniform dual-mesoporous Pt/Fe3O4@mC&mSiO2/NH2 Janus-nanocomposite-stabilized biphasic catalysis system. (C) Cinnamic acid’s production turnover frequency of the cascade reaction using different functionalized nanoparticles as catalysts: the dual-mesoporous Fe3O4@mC&mSiO2 Janus nanoparticles without functionalization (Fe3O4@mC&mSiO2), Fe3O4@mC&mSiO2 Janus nanoparticles with only Pt nanocrystals loaded in the carbon domain (Pt/Fe3O4@mC&mSiO2), Fe3O4@mC&mSiO2 Janus nanoparticles with both Pt nanocrystals loaded in the mesoporous carbon domain and −NH2 groups functioning in the mesoporous SiO2 domain (Pt/Fe3O4@mC&mSiO2/NH2), and Fe3O4@mC&mSiO2 Janus nanoparticles with only −NH2 groups functioning in the SiO2 domain (Fe3O4@mC&mSiO2/NH2). Benzaldehyde and acetaldehyde can first react with each other under the catalysis of −NH2 groups in the aqueous phase at 50 °C to form oil-soluble trans-cinnamaldehyde, and then trans-cinnamaldehyde is oxidized by Pt nanocrystals in the oil phase at 50 °C to form cinnamic acid.
active groups on the surface of the hydrophilic mesoporous silica (mSiO2) domains, aqueous-phase soluble reagents benzaldehyde and acetaldehyde first react with each other to form trans-cinnamaldehyde according to the aldol condensation. Cinnamaldehyde molecules are then transported to the oil phase due to the limited aqueous solubility and go through an oxidation reaction through catalysis of Pt nanoparticles on the hydrophobic carbon domains of the dual-mesoporous Pt/Fe3O4@mC&mSiO2/NH2 catalysts, resulting in the final production of cinnamic acid (Figures S8 and S33). As shown in Figure 5C, the turnover frequency of the spatially functionalized Pt/mC&mSiO2−NH2 Janus nanoparticles can reach as high as ~700 h−1, which is far beyond that of other nanocatalysts without the cascade catalytic activity (e.g., Pt/Fe3O4@mC&mSiO2, Fe3O4@mC&mSiO2/NH2, Fe3O4@mC&mSiO2, etc.), clearly demonstrating the advantage of stabilized emulsion and functional spatial isolation of the Janus nanoparticles in biphasic cascade reactions. As the dual-mesoporous Fe3O4@mC&mSiO2 Janus nanoparticles can be spatially functionalized by different catalyst sites, the Janus nanoparticles may be used as universal platforms for designing various cascade reactions. The biphasic catalytic sequential reactions stabilized by the novel solid surfactant promise the possibility of greatly increasing economic and marketing efficiency in industrial production, even allowing new design protocols of the synthesis routes in industrial fields.

**CONCLUSIONS**

In conclusion, uniform dual-mesoporous Fe3O4@mC&mSiO2 Janus nanoparticles as “magnetic solid surfactants” have successfully been designed and fabricated, and for the first time ever, absolute separation of carbon and silica domains at the single-particle level has been realized. The Janus Fe3O4@mC&mSiO2 nanoparticles with high surface area of ~415 m2/g are made up of a pure 1D mesoporous SiO2 nanorod with tunable length (50−400 nm), ~100 nm width, and ~2.7 nm mesopores and a closely connected mesoporous Fe3O4@mC magnetic nanosphere (~150 nm in diameter, ~10 nm mesopores). The key to the successful synthesis of the dual-mesoporous Janus nanoparticles is the surface-charge-mediated selective encapsulation of dopamine molecules on magnetic Fe3O4 cores. Due to the spatial isolation of carbon and silica, the ratio of hydrophobic/hydrophilic domains can be tuned easily like amphiphilic molecular surfactants, enabling the nanoparticles to be “solid surfactants”. In addition, due to the magnetic functionality, the “solid surfactants” exhibit excellent recyclability under magnetic field. Spatial functionalization of the mesoporous Janus nanoparticles can ensure fabulous catalytic efficiency at the aqueous−oil biphasic interface not only in biphasic reduction of 4-nitroanisole with 100% conversion efficiency but also in biphasic cascade reactions for the synthesis of cinnamic acid, achieving a very high turnover frequency of 700 h−1. Such Janus nanoparticles with tunable hydrophilic/hydrophobic compartment and selective functionalization are highly extendable and have great potential of being multifunctional platforms not only for catalysts but also for diagnosis, therapy, energy storage, battery, sensing, and environmental remediation.
(37) Yang, Z.; Wei, J.; Sobolev, Y.; Grzybowski, B. Nature 2018, 553, 313.
(42) Wu, J.; Ma, G. Small 2016, 12, 4633.