



Cite this: *RSC Adv.*, 2017, 7, 25450

Received 16th March 2017

Accepted 8th May 2017

DOI: 10.1039/c7ra03116e

rsc.li/rsc-advances

Ultrathin Janus nanodiscs†

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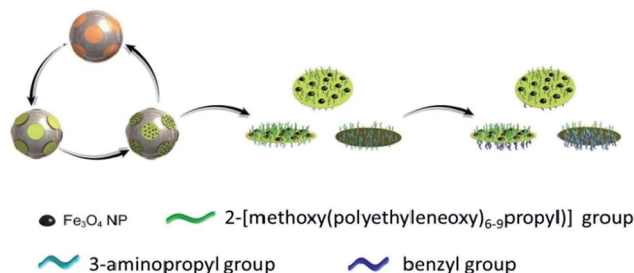
Ultrathin Janus nanodiscs with single molecular scale thickness are fabricated by self-organized sol–gel process against a patchy magnetic microsphere. Functional groups onto the patch domains can induce a favourable absorption of an amine. The morphology of Janus nanodiscs is adjusted by controlling the patchy regions on the surface of paramagnetic Fe₃O₄@SiO₂ core/shell microspheres. The as-used patchy C₈–(Fe₃O₄@SiO₂)–PhCHO microspheres serving as templates can be easily separated from the as-formed Janus nanodiscs and reused to fabricate other Janus nanodiscs. Functional compositions such as paramagnetic Fe₃O₄ nanoparticles and polymers with different wettability properties are introduced onto the different regions of Janus nanodiscs to achieve magnetic Janus nanodiscs. They are used as efficient solid surfactants to stabilize emulsion.

Introduction

Janus materials with two different compositions and properties distinctly compartmentalized onto the same surface of one object have gained growing academic and industrial interests. It is important to develop methods to tune their morphology, composition thus function spatial distribution.¹ Concerning with wettability difference of the two compositions, amphiphilic Janus materials can serve as a solid surfactant to stabilize immiscible liquids.² Among the representative shapes, such as 0-D (zero-dimensional) Janus spheres,³ 1-D Janus rods,⁴ 2-D Janus discs,⁵ and 3-D Janus cages,⁶ Janus discs are efficient solid surfactants for their anisotropic shapes. Serving as emulsion stabilizers, rotation of the Janus discs (or named sheets) with anisotropic shapes is restricted. So the orientation of Janus discs has definite direction, and the as-formed emulsion is very stable.⁷ So the as-stabilized emulsion is more stable than that upon using spherical Janus particles. But disc-like Janus materials are difficult to be obtained. Polymeric nano-sized Janus discs have been fabricated *via* self-assembly of block copolymers.⁸ But the narrow molecular weight is needed for the as-used block copolymers to self-assembly forming a layered structure. Recently, we have fabricated Janus nanosheets with molecular scale thickness by a surface sol–gel process of the self-assembled monolayer of an amphiphilic silane onto the template particles.⁹ For their ultrathin thickness, Janus nanosheets are flexible to tightly adhere onto the interface

with appropriate deformation. But in all these Janus discs, their shapes and sizes are difficult to be controlled because all of them are achieved by crushing process.

Herein, we report a novel approach towards Janus nanodiscs with single molecular scale thickness against a patchy Fe₃O₄@SiO₂ core/shell microsphere (Scheme 1). The aldehyde groups in the patchy domains can induce a favourable absorption of 3-aminopropyltrimethoxysilane (APTMS) *via* a dynamic imine bond. After removal residual APTMS, a monolayer of APTMS forms onto the patchy domain. The pedant silane groups direct outwardly, which can form a molecular thick silica layer after a sol–gel process. Under acidic conditions, when the imide bond is broken, the Janus nanodiscs are released from the Fe₃O₄@SiO₂ microspheres. Further, paramagnetic Fe₃O₄ nanoparticles and polymers with different wettability properties are introduced onto the different sides of the ultrathin Janus nanodiscs to achieve functional ultrathin Janus nanodiscs. They could be served as efficient solid surfactants to stabilize emulsion.



Scheme 1 Synthesis of ultrathin Janus nanodiscs. The patchy magnetic Fe₃O₄@SiO₂ core/shell microspheres as template can be recycled and the Janus nanodiscs are modified with Fe₃O₄ NPs and hydrophilic PEO group on the one side and hydrophobic benzyl group on the other side.

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† Electronic supplementary information (ESI) available: Fig. 1–9. See DOI: 10.1039/c7ra03116e



Experimental

Materials

Iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), iron chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), ethylene glycol (EG), sodium acetate trihydrate (NaAC), sodium citrate, hydrochloric acid (HCl), ammonium hydroxide (25 wt%), tetraethyl orthosilicate (TEOS), silver nitrate (AgNO_3), nitric acid (HNO_3), dimethyl sulphoxide (DMSO), potassium iodide (KI), sodium bicarbonate (NaHCO_3), benzaldehyde, paraffin (52–54 °C), tetrahydrofuran (THF), *N*-heptane, sodium borohydride (NaBH_4) and cyclohexane were purchased from Sinopharm Chemical Reagent. *N*-Butylamine was purchased from ACROS. 4-(chloromethyl)phenyltrimethoxysilane ($\text{PhCH}_2\text{Cl-TMS}$) were purchased from Alfa Aesar. *N*-Octyltrimethoxysilane ($\text{C}_8\text{-TMS}$), 3-aminopropyltrimethoxysilane (APTMS), fluorescein isothiocyanate isomer 1 (FITC) and coumarine-6 were purchased from J&K. 2-[Methoxy(polyethyleneoxy)_{6–9}propyl]trimethoxysilane (PEO-TMS) was purchased from Fluorochem.

Preparation of Fe_3O_4 microspheres. 3.76 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 10.03 g of NaAC were dispersed in 139 ml of EG under ultrasonic. Shifted them to hydrothermal reactor and sealed, heated to 200 °C for 8 h. Cooled it to room temperature and got precipitated black magnetic microspheres which were Fe_3O_4 microspheres.

Preparation of $\text{Fe}_3\text{O}_4@SiO_2$ core/shell microspheres. 0.1 g of Fe_3O_4 microspheres were dispersed in 20 ml of sodium citrate solution (10 wt%) for 0.5 h after being etched by 20 ml of HCl (2 M) solution for 2 min under ultrasonic. And then dispersed the Fe_3O_4 microspheres in the solution containing 54 ml of ethanol, 9 ml of water and 0.9 ml of ammonium hydroxide (25 wt%) under ultrasonic for 1 h. Added 0.3 ml of tetraethylorthosilicate (TEOS) and stirred them at room temperature for 10 h.

Preparation of patchy templated microspheres. Firstly, 150 mg of $\text{Fe}_3\text{O}_4@SiO_2$ core/shell microspheres were dispersed in 100 ml of ethanol under ultrasonic. 120 mg of AgNO_3 and 70 ml of *n*-butylamine were added into the mixture and stirred them for 50 min at 50 °C. Patchy ($\text{Fe}_3\text{O}_4@SiO_2$)-Ag microspheres were obtained. Secondly, 10 mg of patchy ($\text{Fe}_3\text{O}_4@SiO_2$)-Ag microspheres and 2 μl of $\text{C}_8\text{-TMS}$ were dispersed in 100 ml of ethanol, stirred them for 10 h at room temperature. Patchy $\text{C}_8\text{-(Fe}_3\text{O}_4@SiO_2\text{)-Ag}$ microspheres were obtained. Thirdly, 10 mg of patchy $\text{C}_8\text{-(Fe}_3\text{O}_4@SiO_2\text{)-Ag}$ microspheres were dispersed in 10 ml of HNO_3 (2 M) solution and stirred for 100 min at room temperature. Ag nanoparticles (NPs) were completely dissolved and got patchy $\text{C}_8\text{-(Fe}_3\text{O}_4@SiO_2)$ microspheres. Sequentially, 10 mg of patchy $\text{C}_8\text{-(Fe}_3\text{O}_4@SiO_2)$ microspheres were dispersed in 100 ml of ethanol, 2 μl of $\text{PhCH}_2\text{Cl-TMS}$ was added and stirred for 10 h at room temperature. Patchy $\text{C}_8\text{-(Fe}_3\text{O}_4@SiO_2\text{)-PhCH}_2\text{Cl}$ microspheres were obtained. Finally, 10 mg of patchy $\text{C}_8\text{-(Fe}_3\text{O}_4@SiO_2\text{)-PhCH}_2\text{Cl}$ microspheres, 1 mg of NaHCO_3 and 1 mg of KI were added into 60 ml of DMSO and stirred for 10 h at 90 °C. Patchy $\text{C}_8\text{-(Fe}_3\text{O}_4@SiO_2\text{)-PhCHO}$ microspheres were obtained.

Preparation of single molecular scale thickness Janus nanodiscs. 10 mg of patchy $\text{C}_8\text{-(Fe}_3\text{O}_4@SiO_2\text{)-PhCHO}$ microspheres were dispersed in 100 ml of toluene, and 2 μl of APTMS

was added and stirred for 6 h at room temperature. The product (S1) was washed by ethanol and dried in vacuum oven. Subsequently, 100 mg of S1 was added into the mixture containing 95 ml of ethanol and 5 ml of water and stirred them for 10 h at room temperature. Patchy $\text{C}_8\text{-(Fe}_3\text{O}_4@SiO_2\text{)-SiO}_2$ microspheres were obtained. Following, dispersed 10 mg of patchy $\text{C}_8\text{-(Fe}_3\text{O}_4@SiO_2\text{)-SiO}_2$ microspheres in the solution of 20 ml of ethanol and 20 μl of HCl (0.1 M) under ultrasonic for 2 min, single molecular scale thickness Janus nanodiscs were released from the patchy templated microspheres. The as-formed nanodiscs and magnetic templated microspheres were separated by magnet.

Preparation of functionalized Janus nanodiscs. Firstly, 100 mg of patchy $\text{C}_8\text{-(Fe}_3\text{O}_4@SiO_2\text{)-SiO}_2$ microspheres and 400 μl of ammonium hydroxide (25 wt%) were dispersed in 100 ml of ethanol under ultrasonic and strongly stirred at 70 °C. The solution containing with 1.2 ml of 0.1 M $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 1 ml of 0.2 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 50 ml of ethanol was dropped into the above mixture in 20 min. Patchy $\text{C}_8\text{-(Fe}_3\text{O}_4@SiO_2\text{)-SiO}_2\text{-Fe}_3\text{O}_4$ NPs microspheres (S2) were obtained. Secondly, 10 mg of S2 and 2 μl of PEO-TMS were dispersed in 100 ml of ethanol and stirred for 10 h at room temperature. The patchy $\text{C}_8\text{-(Fe}_3\text{O}_4@SiO_2\text{)-SiO}_2\text{-Fe}_3\text{O}_4$ NPs-PEO microspheres (S3) were obtained. Thirdly, S3 was dispersed in the solution of 20 ml of ethanol and 20 μl of HCl (0.1 M) under ultrasonic for 2 min, then Fe_3O_4 NPs-PEO modified Janus nanodiscs (S4) were obtained. Fourthly, 100 mg of S4 was dispersed in 100 ml of ethanol, 200 μl of benzaldehyde was added and stirred for 6 h at room temperature. The phenyl/ Fe_3O_4 NPs-PEO modified Janus composite nanodiscs (S5) were obtained. Finally, dispersed 100 mg of S5 in 100 ml of water, 1 mg of NaBH_4 was added and stirred for 2 h at room temperature. The benzyl/ Fe_3O_4 NPs-PEO composited Janus nanodiscs (S6) were obtained.

Label of functionalized Janus nanodiscs. 100 mg of S6 was dispersed in 100 ml of water. Then, 1 mg of FITC was added and stirred for 6 h at room temperature. FITC labelled S6 was obtained.

Emulsification with functionalized Janus nanodiscs. (1) 3 mg of S6 was added to the mixture containing 2 ml of water and 500 μl of *n*-heptane under ultrasonic for 3 min. The emulsion of *n*-heptane in water was formed. In order to observation, the *n*-heptane was dyed with coumarine-6; (2) 5 mg of labelled S6 was added to the mixture containing 1 g of paraffin and 8 g of water, sheered them at 2000 rpm for 10 min at 70 °C. The emulsion was achieved.

Characterization

Morphology of the samples were characterized by scanning electron microscopy (Hitachi S-4800 at 15 kV), which with an energy dispersive X-ray (EDX) analyser and transmission electron microscopy (JEOL1011 at 100 kV). The samples for SEM observation were ambient dried and vacuum sputtered with Pt. The samples for TEM observation were prepared by spreading very dilute emulsions in ethanol onto carbon-coated copper grids. FTIR spectroscopy was performed on the sample/KBR pressed pellets after scanning samples for 32 times using



a BRUKER EQUINOX55 spectrometer. Thickness and shape of the samples was measured by AFM of Bruker Multimode 8. Emulsion was characterized by inverted fluorescence microscopy (Olympus IX83) and Olympus optical microscope. Size contribution was measured by Zeta-sizer (Nano Series, Malvern Instruments) at 25 °C.

Results and discussion

The $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ microsphere is prepared by solvothermal method following a SiO_2 layer coating *via* sol-gel process.¹⁰ The representative Fe_3O_4 microsphere (200 nm in diameter) is selected as a paramagnetic core for easy separation (Fig. S1†). Onto the Fe_3O_4 microsphere surface, SiO_2 is detected by EDX (Fig. S2a and b†). The size contribution of Fe_3O_4 and $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ microspheres is measured by DLS, which is consistent with TEM results (Fig. S2c†). The thickness of SiO_2 layer is about 30–40 nm (Fig. S3a†). Onto the $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ microsphere, Ag NPs are achieved by reducing AgNO_3 with *n*-butylamine at 50 °C (Fig. S3b†).¹¹ The diameter of Ag NPs can be adjusted with reaction time. The exposed bare SiO_2 surface is treated to be hydrophobic with *n*-octyltrimethoxysilane ($\text{C}_8\text{-TMS}$). Then, a $\text{C}_8\text{-}(\text{Fe}_3\text{O}_4@/\text{SiO}_2)\text{-Ag}$ composite microsphere is achieved (Fig. 1a). Upon removal of Ag NPs by dissolution, surface of the microsphere becomes smooth, and fresh SiO_2 domains are exposed (Fig. S3c†). The fresh SiO_2 domains are further modified with 4-(chloromethyl)phenyltrimethoxysilane ($\text{PhCH}_2\text{Cl-TMS}$) to graft benzyl chloride groups (Fig. S3d†). Benzaldehyde groups are derived from the benzyl chloride groups by Kornblum oxidation.¹² A patchy $\text{C}_8\text{-}(\text{Fe}_3\text{O}_4@/\text{SiO}_2)\text{-PhCHO}$ microsphere is achieved (Fig. 1b). The surface remains smooth. 3-Aminopropyltrimethoxysilane (APTMS) can form a monolayer onto the patchy domains since the aldehyde group can form a dynamic imine bond with the functional amine-group of APTMS. The amine-groups are prevented thereby. The pedant silane groups can form a molecular thick silica layer *via* sol-gel

process. The sphere surface remains smooth (Fig. S3e and f†). After adding acid, the imine bond is broken. Then, the silica nanodiscs are released from the microsphere. Using a magnet, the patchy template microspheres are recycled, while the nanodiscs are purified.

The compositions of different microspheres are measured by FTIR spectrum (Fig. S4†). Characteristic peaks at 2840 cm^{-1} and 2920 cm^{-1} are respectively assigned to $-\text{CH}_3$ group and $-\text{CH}_2$ -group, which prove that the patchy $\text{C}_8\text{-}(\text{Fe}_3\text{O}_4@/\text{SiO}_2)$ microspheres are prepared. Characteristic peaks at $1600\text{--}1400\text{ cm}^{-1}$ are assigned to phenyl group, which proves that the patchy $\text{C}_8\text{-}(\text{Fe}_3\text{O}_4@/\text{SiO}_2)\text{-PhCH}_2\text{Cl}$ microspheres had been prepared. Meanwhile, the characteristic peak at 1750 cm^{-1} is assigned to $-\text{CHO}$ group, it is shown that the patchy $\text{C}_8\text{-}(\text{Fe}_3\text{O}_4@/\text{SiO}_2)\text{-PhCHO}$ microspheres are achieved. The peaks at 3404 cm^{-1} and 3520 cm^{-1} are assigned to $-\text{NH}_2$ group of APTMS which is grafted onto the $-\text{PhCHO}$ group region of patchy $\text{C}_8\text{-}(\text{Fe}_3\text{O}_4@/\text{SiO}_2)\text{-PhCHO}$ microspheres.

When pH is tuned to about 4.5, aminopropyl/hydroxyl composited Janus nanodiscs are released from the templated microspheres for the dynamic imine bond is cleaved. The average size of Janus nanodiscs is about 15 nm in diameter (Fig. 1c). The thickness of Janus nanodiscs is about 0.7 nm (Fig. 1d). Shape and size of the aminopropyl/hydroxyl composited Janus nanodiscs are uniform. Because of the as-formed Janus nanodiscs are too thin to observe in SEM, they can only be characterized by TEM and AFM in morphology. The compositions of the as-formed Janus nanodiscs are measured by FTIR spectrum (Fig. S5†). The peaks at 3448 cm^{-1} and 3360 cm^{-1} are assigned to $-\text{NH}_2$ group, the peaks 3155 cm^{-1} are assigned to $-\text{OH}$ group, and the peak at 1090 cm^{-1} are assigned to $-\text{Si-O-Si-}$ bond.

The single molecular scale thickness Janus nanodiscs are prepared from the domains where the Ag NPs are. So the size of Janus nanodiscs can be adjusted by controlling the size of Ag NPs. It is found that the Ag NPs grow bigger with the increase of reaction time. When the reaction time is 40 min, the diameters of Ag NPs are about 5 nm (Fig. S6a†). Then the as-formed Janus nanodiscs are about 5 nm in diameter (Fig. 2a). When the reaction time is increased to 60 min, the average diameters of both Ag NPs and as-formed Janus nanodiscs are about 25 nm (Fig. S6b,† and 2b). Thus, the size of the single molecular thickness Janus nanodiscs can be precisely controlled. However, the thickness of the Janus nanodiscs with different sizes remains 0.7 nm (Fig. 2c and d).

Two sides of the as-formed Janus nanodiscs are easily to be selectively modified with different compositions, respectively. Firstly, Fe_3O_4 NPs are grafted onto the hydroxyl group side by coprecipitation method.¹³ Fe_3O_4 NPs are barely recognized on the surface of patchy $\text{C}_8\text{-}(\text{Fe}_3\text{O}_4@/\text{SiO}_2)\text{-SiO}_2$ microsphere (Fig. 3a). When pH is tuned to about 4.5, aminopropyl/ Fe_3O_4 NPs composited Janus nanodiscs are released from the templated microspheres (Fig. 3b). It is easy to find the Fe_3O_4 NPs exist on the surface of the Janus composite nanodiscs. In order to enhancing hydrophilic property of the Janus composite nanodiscs, 2-[methoxy(polyethyleneoxy)₆-propyl]trimethoxysilane (PEO-TMS) are grafted on the Fe_3O_4 NPs side *via* sol-gel

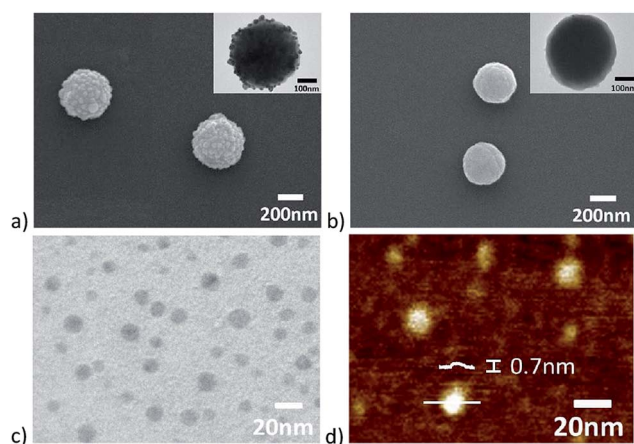


Fig. 1 Morphologies of paramagnetic microspheres and as-formed Janus nanodiscs: SEM and inset TEM images of (a) patchy $\text{C}_8\text{-}(\text{Fe}_3\text{O}_4@/\text{SiO}_2)\text{-Ag}$ microspheres; (b) patchy $\text{C}_8\text{-}(\text{Fe}_3\text{O}_4@/\text{SiO}_2)\text{-PhCHO}$ microspheres; TEM (c) and AFM (d) images of the as-formed Janus nanodiscs.



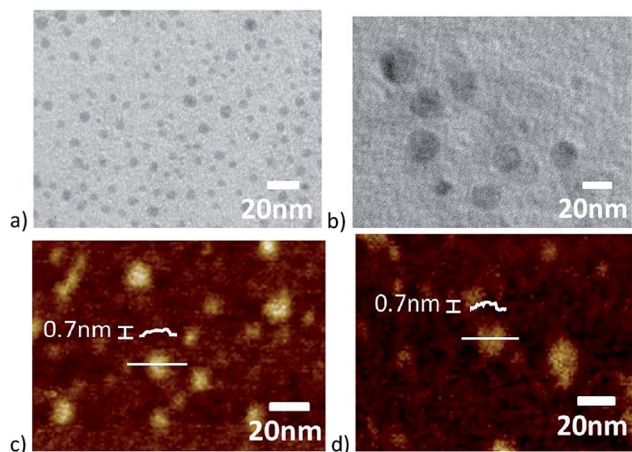


Fig. 2 Size control of the as-formed Janus nanodiscs. TEM and AFM images of the aminopropyl/hydroxyl composited Janus nanodiscs are achieved at different reaction time: (a) and (c) are at 40 min; (b) and (d) are at 60 min.

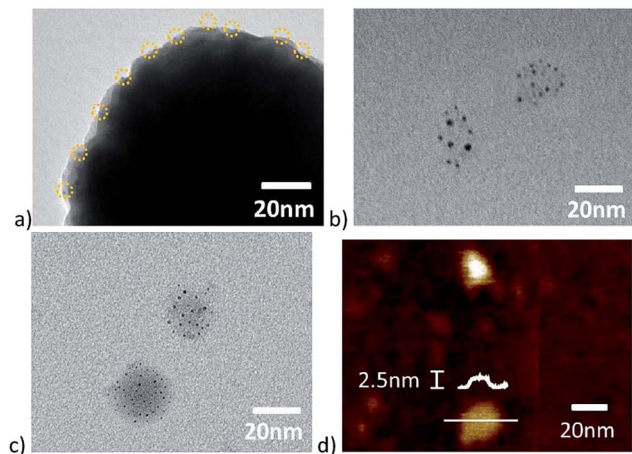


Fig. 3 Morphologies of different Janus nanodiscs: (a) TEM image of patchy $C_8-(Fe_3O_4@SiO_2)-SiO_2-Fe_3O_4$ NPs microsphere; (b) TEM image of Fe_3O_4 NPs modified Janus nanodiscs; TEM (c) and AFM (d) images of benzyl/ Fe_3O_4 NPs-PEO Janus composite nanodiscs.

reaction. The patchy $C_8-(Fe_3O_4@SiO_2)-SiO_2-Fe_3O_4$ NPs-PEO microspheres are achieved (Fig. S7†). Turn pH to about 4.5, the Fe_3O_4 NPs-PEO modified Janus composite nanodiscs are achieved from the templated microspheres. Then, benzaldehyde is grafted to the aminopropyl group *via* Schiff base reaction, and further imine bonds are reduce with $NaBH_4$. So the benzyl/ Fe_3O_4 NPs-PEO Janus nanodiscs are fabricated (Fig. 3c). Hydrophilic PEO group and hydrophobic benzyl group are respectively grafted onto the two sides of the as-formed Janus nanodiscs. For the existence of Fe_3O_4 NPs, PEO and benzyl groups, thickness of the Janus nanodiscs increase to about 2.5 nm (Fig. 3d). But the size of Janus nanodiscs does not change obviously. The compositions of different Janus nanodiscs are proved by FTIR spectrum (Fig. S8†). The character peak at 506 cm^{-1} indicates Fe-O bond, and peak at 1090 cm^{-1} indicates -Si-O-Si- bond. Meanwhile, the peaks at 1390 cm^{-1} and 1690 cm^{-1} respectively indicate C-N and C=N bonds.

In order to prove their amphiphilic property which originated from their Janus structures, aggregation structures of Janus nanodiscs in different solvents are studied. When the Janus nanodiscs are dispersed in selective solvent such as water, the hydrophobic benzyl side is stacked together while the hydrophilic PEO side exposes to the aqueous phase to form back-to-back stacked aggregates for their amphiphilic property originated from their Janus structure (Fig. S9a†). Similarly in cyclohexane, the hydrophilic PEO side is stacked together while the hydrophobic benzyl side exposes to the cyclohexane phase to form large size aggregates (Fig. S9b†). When the Janus nanodiscs are dispersed in co-solvent THF, Janus nanodiscs are mono-dispersed as single particles (Fig. S9c†). Meanwhile, DLS data shown that Janus nanodiscs aggregate together to form large size aggregated particles in selective solvents and are dispersed as single particles in co-solvent, respectively (Fig. S9d†).

For the magnetic responsive property of Fe_3O_4 NPs, the as-prepared Janus nanodiscs can be easily manipulated with external magnetic field (Fig. S9†). The as-prepared Janus nanodiscs can be employed as solid surfactants to stabilize emulsion. Taking water and *n*-heptane as immiscible solvents, they are emulsified to oil-in-water emulsion (Fig. 4a). For their magnetic property, Janus composite nanodiscs can be collected with magnet and reused. In order to observe the as-stabilized emulsion droplets more clearly, melt paraffin ($T_m = 52-54\text{ }^\circ\text{C}$) is used as oil phase. Then a paraffin-in-water emulsion forms upon $70\text{ }^\circ\text{C}$ and stirring at 2000 rpm for 10 min. The paraffin-in-water emulsion could be stable for several months and the diameter of paraffin droplets is 2–5 μm (Fig. 4b). After the emulsion is cooled down to room temperature, the paraffin is solidified (Fig. 4c). FITC is employed to observe the positions of as-used Janus nanodiscs in emulsion system. It is shown that all

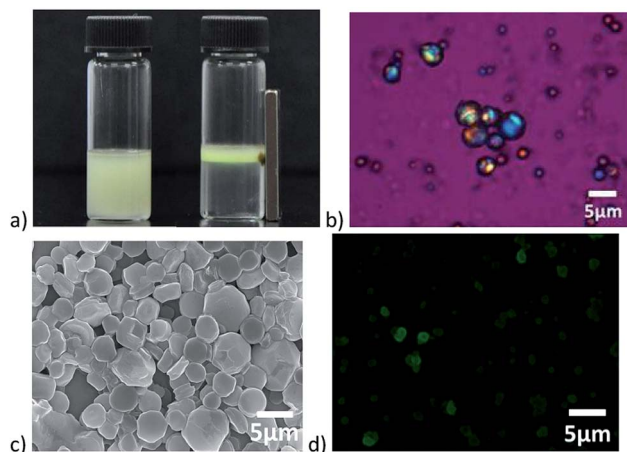


Fig. 4 Performance demonstration of the as-prepared Janus nanodiscs: (a) magnetic performance: the as-prepared Janus nanodiscs are served as solid surfactant in the *n*-heptane-in-water emulsion, the *n*-heptane is dyed by coumarine-6 (left), and the as-used Janus nanodiscs are easily collected by magnet (right); (b) polarizing optical image of the paraffin-in-water emulsion; (c) SEM image of the paraffin droplets; (d) inverted fluorescence microscope image of the paraffin-in-water emulsion.



the Janus nanodiscs aggregate at the interface of emulsion (Fig. 4d). So the as-prepared Janus nanodiscs are a kind of efficient solid emulsion stabilizer.

Conclusions

In summary, single molecular scale thickness Janus nanodiscs are successfully achieved from patchy $C_8-(Fe_3O_4@SiO_2)-PhCHO$ microspheres as template. The sizes of Janus nanodiscs can be controlled by tuning the patchy domains. Meanwhile, paramagnetic Fe_3O_4 NPs are introduced onto the hydrophilic side of the Janus nanodiscs thus achieving magnetic response. Further, benzyl groups and PEO groups are grafted respectively onto the hydrophobic and hydrophilic sides of the as-formed Janus nanodiscs to enhance their amphiphilic performance. The as-prepared Janus composite nanodiscs can be used as recyclable solid surfactants to stabilize emulsion. Most importantly, the patchy $C_8-(Fe_3O_4@SiO_2)-PhCHO$ templated microspheres can be easily recovered and reused to fabricate more Janus nanodiscs.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (51233007, 51622308).

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