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 Fe3-O4@SiO2 core 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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Experimental

Materials
Iron(III) chloride hexahydrate (FeCl₃·6H₂O), iron chloride tetrahy-
dratre (FeCl₄·4H₂O), ethylene glycol (EG), sodium acetate trihydrate
(NaAc), sodium citrate, hydrochloric acid (HCl), ammonium
hydroxide (25 wt%), tetraethyl orthosilicate (TEOS), silver nitrate
(AgNO₃), nitric acid (HNO₃), dimethyl sulphoxide (DMSO), potas-
sium iodide (KI), sodium bicarbonate (NaHCO₃), benzaldehyde,
paraffin (52–54 °C), tetrahydrofuran (THF), N-heptane, sodium
borohydride (NaBH₄) and cyclohexane were purchased from Sinopharm
Chemical Reagent. N-Butylamine was purchased from ACROS.
4-(chloromethyl)phenyltrimethoxysilane (PhCH₂Cl·TMS) was pur-
blished from Alfa Aesar. N-Octytrimethoxysilane (C₈-TMS), 3-
aminopropyltrimethoxysilane (APTMS), fluorescein iso-
thiocyanate isomer 1 (FITC) and coumarine-6 were purchased from
J&K. 2-[Methoxy(polyethyleneoxy)]₆-propyltrimethoxysilane (PEO-
TMS) was purchased from Fluorochem.

Preparation of Fe₃O₄ microspheres. Firstly, 10 mg of patchy C₈
microspheres were dispersed in 100 ml of ethanol, stirred for
10 h at room temperature. Patchy C₈-(Fe₃O₄@SiO₂)–SiO₂ microspheres
were obtained. Following, dispersed 10 mg of patchy C₈-(Fe₃-
O₄@SiO₂)–SiO₂ 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 C₈-(Fe₃O₄@SiO₂)–SiO₂ 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 FeCl₃·4H₂O, 1 ml of
0.2 M FeCl₃·6H₂O and 50 ml of ethanol was dropped into the
above mixture in 20 min. Patchy C₈-(Fe₃O₄@SiO₂)–SiO₂–Fe₃O₄
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 C₈-(Fe₃O₄@SiO₂)–
SiO₂–Fe₃O₄ 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 Fe₃O₄ 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 tempera-
ture. The phenyl/Fe₃O₄ NPs-PEO modified Janus composite
nanodiscs (S5) were obtained. Finally, dispersed 100 mg of S5 in
100 ml of water, 1 mg of NaNH₄ was added and stirred for 2 h at
room temperature. The benzyl/Fe₃O₄ NPs-PEO composites
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 emul-
sion 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 Fe$_3$O$_4$@SiO$_2$ microsphere is prepared by solvothermal method following a SiO$_2$ layer coating via sol–gel process. The representative Fe$_3$O$_4$ microsphere (200 nm in diameter) is selected as a paramagnetic core for easy separation (Fig. S1†). Onto the Fe$_3$O$_4$ microsphere surface, SiO$_2$ is detected by EDX (Fig. S2a and b†). The size contribution of Fe$_3$O$_4$ and Fe$_3$O$_4$@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 Fe$_3$O$_4$@SiO$_2$ microsphere, Ag NPs are achieved by reducing AgNO$_3$ with n-butylamine at 50 °C (Fig. S3b†). The diameter of Ag NPs can be adjusted with reaction time. The exposed bare SiO$_2$ surface is treated to be hydrophobic with 1-octyltrimethoxysilane (C$_8$–TMS). Then, a C$_8$–(Fe$_3$O$_4$@SiO$_2$)–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 (PhCH$_2$Cl–TMS) to graft benzyl chloride groups (Fig. S3d†). Benzaldehyde groups are derived from the benzyl chloride groups by Kornblum oxidation. A patchy C$_8$–(Fe$_3$O$_4$@SiO$_2$)–PhCHO microsphere is achieved (Fig. 1b). The surface remains smooth. 3-Aminopropyltrimethoxysilane (APMTS) 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 –CH$_3$ group and –CH$_2$– group, which prove that the patchy C$_n$–(Fe$_3$O$_4$@SiO$_2$) microspheres are prepared. Characteristic peaks at 1600–1400 cm$^{-1}$ are assigned to phenyl group, which proves that the patchy C$_n$–(Fe$_3$O$_4$@SiO$_2$)–PhCH$_2$Cl microspheres had been prepared. Meanwhile, the characteristic peak at 1750 cm$^{-1}$ is assigned to –CHO group, it is shown that the patchy C$_n$–(Fe$_3$O$_4$@SiO$_2$)–PhCHO microspheres are achieved. The peaks at 3404 cm$^{-1}$ and 3250 cm$^{-1}$ are assigned to –NH$_2$ group of APTMS which is grafted onto the –PhCHO group region of patchy C$_n$–(Fe$_3$O$_4$@SiO$_2$)–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 theaminopropyl/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 –NH$_2$ group, the peaks 3155 cm$^{-1}$ are assigned to –OH group, and the peaks at 1090 cm$^{-1}$ are assigned to –Si–O–Si– bond.

The single molecular scale thickness Janus nanodiscs are prepared from the domains where the Ag NPs are. 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†). 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$_3$O$_4$ NPs are grafted onto the hydroxyl group side by coprecipitation method. Fe$_3$O$_4$ NPs are barely recognized on the surface of patchy C$_n$–(Fe$_3$O$_4$@SiO$_2$)–SiO$_2$ microsphere (Fig. 3a). When pH is tuned to about 4.5, aminopropyl/Fe$_3$O$_4$ NPs composited Janus nanodiscs are released from the templated microspheres (Fig. 3b). It is easy to find the Fe$_3$O$_4$ NPs exist on the surface of the Janus composite nanodiscs. In order to enhance hydrophilic property of the Janus composite nanodiscs, 2-[methoxy(polyethylenoxy)]$_n$-propyltrimethoxysilane (PEO-TMS) are grafted on the Fe$_3$O$_4$ NPs side via sol–
reaction. The patchy C₆–(Fe₃O₄@SiO₂)–SiO₂–Fe₃O₄ NPs-PEO microspheres are achieved (Fig. S7†). Turn pH to about 4.5, the Fe₃O₄ 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 NaBH₄. So the benzyl/Fe₃O₄ 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 Fe₃O₄ 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 Fe₃O₄ 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 °C) is used as oil phase. Then a paraffin-in-water emulsion forms upon 70 °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
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$_3$O$_4$@SiO$_2$)–PhCHO microspheres as template. The sizes of Janus nanodiscs can be controlled by tuning the patchy domains. Meanwhile, paramagnetic Fe$_3$O$_4$ 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$_3$O$_4$@SiO$_2$)–PhCHO templated microspheres can be easily recovered and reused to fabricate more Janus nanodiscs.

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**Notes and references**