Janus colloidal copolymers

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We propose a new type of nanocomposite that we call Janus colloidal copolymers (JCCPs). JCCPs have two different polymers conjugated on opposite sides of a nanosized colloid. Janus clusters of copolymer PS-*b*-PAA (where PS is polystyrene and PAA is poly(acrylic acid)) are self-organized within confined mesoporous silica channels onto the surface of iron oxide (Fe_3O_4) core particles by coordination-induced adsorption. PS-*c*PAA diblock JCCPs are fabricated by selective crosslinking of the nanosized PAA domains. In addition, the crosslinked PAA domains are terminated with amine-capped polyethylene glycol (PEG) to form PS-*c*PAA-PEG triblock JCCPs. The *c*PAA domain containing functional groups can serve as a nanoreactor to allow *in situ* preparation of functional materials. The composite JCCPs combine the functionality of nanosized colloids with the amphiphilic performance and self-organization capability of copolymers.

INTRODUCTION

Janus spheres with two different compositions and thus properties compartmentalized on the same surface are attracting growing academic and industrial interest [1–3]. It is strongly desired to synthesize Janus nanoparticles (NPs) with a diameter of 1–10 nm, because of their tunable composition and diverse performance [4]. Janus NPs with polymer chains conjugated onto one side or on opposite sides are a particularly attractive target. If the NP size is comparable with that of the polymer chains, they are coined Janus colloidal copolymers (JCCPs), and are analogous to functionalized copolymers. NPs render functionality, while the copolymers endow JCCPs with amphiphilic and self-organization capability. Unconventional new superstructures based on JCCPs are anticipated. As an example, large molecules like polyhedral oligomeric silsesquioxane, buckminsterfullerene and polyoxometalate can self-organize into new superstructures after conjugation of polymer chains onto one side by sequential “click” steps [5]. This approach relies on precise control of the number of clickable sites on the large molecules. The large molecules possess well-defined molecular structure, which ensures

their precise modification using traditional organic routes. However, such routes are inapplicable to NPs because their introduced clickable points are usually randomly distributed over their surface.

Although many attempts to synthesize Janus NPs have been reported, it remains challenging to develop methods to fabricate JCCPs. Selective growth of organic species on preformed NPs has been used extensively to synthesize Janus NPs. In the case of sufficiently small gold (Au) NPs, after a single NP is wrapped with an individual middle block of a triblock copolymer, the corresponding polystyrene (PS) and polyethylene oxide chains are present on opposite sides because of steric constraints [6,7]. Very small Janus Au NPs have also been synthesized following a kinetic approach by tethering as few as one single-stranded DNA molecule [8]. Both approaches are highly size selective and suitable for small NPs. In the case of large NPs, patchy NPs usually form when two types of ligands are randomly tethered onto their surface. By rearranging the ligands at a block copolymer interface, patchy NPs can be transformed into Janus NPs [9–11]. Similarly, Janus NPs can be formed at a binary component interface by substituting weak ligands from one side of the NPs in the corresponding phase [12,13]. It should be noted that such Janus NPs are usually metastable because ligand exchange/rearrangement is dynamic.

Solid-phase protection synthesis is another approach to fabricate Janus NPs. This approach involves selective growth of materials on the desired sides of NPs. To strongly anchor NPs onto the solid substrates through specific interactions, the NPs and substrates should possess suitably matched groups. For example, modified Wang resin spheres with desired groups have been used to fabricate Janus Au NPs by transfer of the organic species on the sphere surface onto the NP surface at the contact area, or by growth of another species on the exposed surface [14,15]. While poly(acrylic acid) (PAA)-capped NPs can be adsorbed onto a sphere surface via electrostatic interaction, amine group-terminated polymers can be covalently bound onto

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the exposed side of the NPs to produce Janus NPs [16]. In another example, using azido–alkynyl interactions, Janus NPs were prepared by mechanochemical deprotection after clicking azido group-terminated polymers onto NPs [17]. Similarly, Janus NPs with two kinds of oligonucleotides selectively conjugated on each side have been synthesized [18]. Besides the surfaces of spheres, functional groups like thiol-terminated polymer single crystals have been used to anchor Au NPs via chemisorption [19]. After grafting another polymer chain onto the exposed side of the tethered NPs, Janus NPs with two polymers conjugated on opposite sides are obtained. These Janus NPs are JCCPs. However, controlling the contact surface and thus protection degree of a solid NP on a solid substrate remains a problem, especially in the case of spherical shapes.

As an alternative, Janus NPs of copolymers are promising to produce JCCPs by *in situ* preferential growth of functional materials [2]. However, the conventional approach to obtain copolymer Janus NPs by disassembling supramolecular structures involves strict requirements including sufficiently narrow molecular weight (M_w) distribution of copolymers, particular composition and block fraction, and precise processing conditions. These strict requirements have delayed progress in the use of the Janus NPs of copolymers to derive JCCPs.

Herein, we report a simple approach to fabricate JCCPs starting from the synthesis of crosslinked Janus NPs of block copolymers within confined mesoporous silica ($mSiO_2$) channels (Scheme 1). This approach involves three main considerations. 1) The $mSiO_2$ layer serves as a mask to compartmentalize the iron oxide (Fe_3O_4) core surface into isolated nanoscale regions, which can induce preferential adsorption of desired materials. In a suitable solvent like tetrahydrofuran (THF), copolymer $PS_{5.2k}$ - b - PAA_{4k} is adsorbed within the channels. This allows PAA chains to

preferentially tether onto the Fe_3O_4 core surface via specific coordination. 2) After THF is substituted with a PS-selective solvent like toluene, phase separation occurs, forming a Janus cluster with PAA blocks collapsed on the core surface and PS blocks extended outwards. PAA chains are further covalently crosslinked with polyamines. The PS- $cPAA$ diblock JCCPs are obtained after etching $mSiO_2$. 3) Another polymer chain, such as amine-capped poly(ethylene glycol) (PEG), can be bound on the opposite side of the $cPAA$ colloidal domain by amidation to achieve a PS- $cPAA$ -PEG triblock JCCP. The $cPAA$ colloidal domains have residual carboxyl groups, which can serve as a nanoreactor, and thereby induce *in situ* growth of functional materials. The developed approach is robust, without specific requirements for copolymers and functional materials.

EXPERIMENTAL METHODS

Materials

Representative diblock copolymer $PS_{5.2k}$ - b - PAA_{4k} with a polydispersity index of 1.15 was purchased from Polymer Source, Inc. Amine-capped poly(ethylene glycol) (PEG- NH_2) ($M_w = 5 \text{ kg mol}^{-1}$), cetyltrimethylammonium bromide (CTAB), silver nitrate ($AgNO_3$), *n*-butylamine, *N*-3-dimethylaminopropyl-*N'*-ethylcarbodiimide hydrochloride (EDC-HCl), *N*-hydroxysuccinimide (NHS), and *N,N'*-dicyclohexylcarbodiimide (DCC) were purchased from Alfa Aesar. Tetraethoxysilane (TEOS), tetrabutyl titanate (TBT), acetic ether, cyclohexane, *N,N*-dimethylformamide (DMF), THF, toluene, ethanol, ethylene glycol, aqueous ammonia ($NH_3 \cdot H_2O$, 28 wt.%), sodium acetate, ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) and ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) were purchased from Sinopharm Chemical Reagent Beijing. PEG ($M_w = 20 \text{ kg mol}^{-1}$) and tetraethylene-pentamine (TEPA) were purchased from Xilong Chemical

Scheme 1 Synthesis of JCCPs. (a, b) In good solvents, such as THF, the diblock copolymer of PS- b -PAA is adsorbed within the mesoporous silica ($mSiO_2$) channels via coordination, where the PAA blocks are tethered onto the Fe_3O_4 core surface. After exchanging THF for a PS-selective solvent like toluene, phase separation occurs. This induces collapse of the PAA blocks onto the core surface and outward extension of the PS blocks. A Janus cluster forms within the $mSiO_2$ channel. After selectively crosslinking the PAA blocks, a robust PS- $cPAA$ diblock JCCP is obtained. (c) Individual PS- $cPAA$ JCCPs are obtained after release from the core surface by etching $mSiO_2$. (d) A PS- $cPAA$ -PEG triblock JCCP is prepared by conjugation of amine-capped PEG on the opposite side to the $cPAA$ colloidal domain. (e) A functional PS- $cPAA$ @X-PEG composite JCCP is derived by preferential growth of functional group X on the $cPAA$ domain.

Corporation. All reagents were used as received. NdFeB magnets (N35M) with a magnetic strength of 0.5 T were purchased from Beijing Link Technology Corporation. The magnetic field of 0.8 T was generated using two magnets.

Characterization

Sample morphology was characterized using a transmission electron microscope (TEM; JEOL 2100F at 200 kV) equipped with an energy-dispersive X-ray (EDX) analyzer, and a scanning electron microscope (SEM, S-4800, Hitachi, Japan) at 15 kV. Samples for SEM observation were prepared by vacuum sputtering with Pt after drying under ambient conditions. Samples for TEM observation were prepared by spreading very dilute dispersions of the materials onto carbon-coated copper grids. Samples were stained using 0.5% phosphotungstic acid (PTA) solution at pH 7.4 and ruthenium oxide (RuO_4). Size distribution and ζ potential of the samples were measured for aqueous dispersions using a Zetasizer (Nano Series, Malvern Instruments) at 25°C. To demonstrate the pH response of the samples, 1 mol L⁻¹ HCl or 1 mol L⁻¹ NaOH was used to adjust the pH of the dispersions. Fourier transform infrared (FT-IR) spectroscopy was performed with pressed KBr pellets using a Bruker Equinox 55 spectrometer with a horizontal attachment. Optical microscopy images were obtained with an Olympus optical microscope. Nitrogen adsorption isotherms were measured on a Micromeritics ASAP-2020M porosimeter.

Synthesis of Fe_3O_4 @ mSiO_2 spheres

The Fe_3O_4 @ mSiO_2 core/shell spheres were prepared as follows. Fe_3O_4 spheres (0.30 g) were treated with 0.1 mol L⁻¹ HCl aqueous solution (50.0 mL) under ultrasonication for 10 min. The spheres were separated and washed with water, then dispersed in a mixture of CTAB (0.45 g), water (525.0 mL), ammonia aqueous solution (15.0 mL), and ethyl acetate (25.0 mL). The mixture was homogenized for 1 h under ultrasonication. TEOS (0.53 g) was then added dropwise to the stirred dispersion. After reaction for 6 h, the product was collected with a magnet and washed with ethanol and water. The spheres were purified, redispersed in acetone (60.0 mL) and then heated under reflux at 80°C for 48 h to extract CTAB. The extraction was repeated three times. The solid was washed with water to obtain Fe_3O_4 @ mSiO_2 core/shell spheres.

Synthesis of PS-cPAA diblock JCCPs and composites

To a solution of $\text{PS}_{5.2k}$ -b- PAA_{4k} (5.0 mg) in THF (20.0 mL) was added Fe_3O_4 @ mSiO_2 spheres (20.0 mg). After stirring overnight at room temperature to saturate adsorption, the

spheres were collected with a magnet, washed with THF to remove the residual copolymer, and then dried at 30°C for 12 h. The spheres were redispersed in a mixture of DCC (5.0 mg), NHS (2.50 mg), TEPA (10.0 μL) and toluene (20.0 mL). After stirring overnight at room temperature, the product was collected with a magnet and washed with toluene, and then dried at 30°C for 12 h. PAA domains were selectively crosslinked. The mSiO_2 shell was etched by addition of 2 mol L⁻¹ NaOH aqueous solution (2.0 mL). The PS-cPAA diblock JCCPs were then collected by centrifugation.

PS-cPAA JCCPs (2.0 mg) were added to water (8.0 mL) containing $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (2.24 mg) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (4.32 mg). After vigorously stirring for 5 h, the mixture was centrifuged at 15,000 rpm to remove the residual iron ions. After dispersion in water (8.0 mL) under nitrogen, a desired amount of aqueous ammonia was added to adjust the pH to 10. After 5 h, the PS-cPAA@ Fe_3O_4 composite JCCPs were collected with a magnet.

PS-cPAA JCCPs (2.0 mg) were added to ethanol (1.5 mL) containing AgNO_3 (0.25 mg). After vigorously stirring for 8 h, the mixture was centrifuged at 15,000 rpm to remove residual silver ions. After dispersion in ethanol (1.5 mL), *n*-butylamine (2.0 μL) was added. The mixture was stirred at 50°C for 50 min. The PS-cPAA@Ag composite JCCPs were then collected by centrifugation.

Synthesis of PS-cPAA-PEG triblock JCCPs and composites

After the Janus nanosheets were dispersed in water under ultrasonication for 5 min, dispersions of various pH was stood for observation.

PS-cPAA JCCPs (2.0 mg) were dispersed in water (1.0 mL) containing cyclohexane (50.0 μL). After ultrasonication for 5 min, EDC·HCl (5.0 mg) and NHS (2.50 mg) were added. After stirring overnight at room temperature, PEG-NH₂ (2.0 mg) was added, and then the mixture was stirred for another 12 h. The product was washed with water to remove residual EDC·HCl and NHS, and then dried at 30°C for 12 h. The PS-cPAA-PEG triblock JCCPs were collected by centrifugation.

PS-cPAA-PEG JCCPs (2.0 mg) were added to toluene (1.5 mL) containing TBT (5.0 μL). After vigorously stirring for 8 h to saturate adsorption of TBT inside the cPAA domains, the mixture was centrifuged at 15,000 rpm to remove the residual TBT. Ethanol/water mixture (1:1 v/v, 2.0 mL) was added under stirring at ambient temperature for 2 h to induce the sol-gel process to form cPAA@ TiO_2 composite domains. The PS-cPAA@ TiO_2 -PEG composite JCCPs were collected by centrifugation.

PS-cPAA-PEG JCCPs (2.0 mg) were added to DMF

(10.0 mL) containing HAuCl_4 (0.1 g). Ethanol (50.0 μL) was added, and then the JCCPs were reduced at 60°C for 10 h. The PS-cPAA@Au-PEG composite JCCPs were collected by centrifugation.

Assembly of JCCPs

Water (0.8 mL) was added dropwise to a stirred dispersion of PS-cPAA-PEG or PS-cPAA@ TiO_2 -PEG JCCPs in THF (1 mg mL^{-1} , 0.2 mL) using a microsyringe at a rate of 2.0 mL h^{-1} . THF was slowly evaporated at 30°C over 12 h.

Emulsification of PS-cPAA-PEG JCCPs

PS-cPAA-PEG JCCPs (0.1 mg) were dispersed in water (2.0 mL). Wax (20.0 mg) with a melting temperature of $52\text{--}54^\circ\text{C}$ was added at 70°C . The mixture was vigorously shaken for 1 min to form a melted wax-in-water emulsion. When the emulsion was naturally cooled to room temperature, the melted wax solidified.

Adsorption of PS-cPAA-PEG JCCPs onto polydivinylbenzene (PDVB) nanofibers

PS-cPAA-PEG JCCPs (2.0 mg) and PDVB nanofibers (5.0 mg) were added to a mixture of THF (0.5 mL) and water (0.1 mL). Adsorption was performed for 6 h. After slow evaporation of THF, the PDVB nanofibers were filtered before TEM observation.

RESULTS AND DISCUSSION

Dissolution of CTAB from the mesostructured CTAB/silica thin layer on a Fe_3O_4 core particle produced transverse mSiO_2 channels with a pore capacity of $200\text{ cm}^3\text{ g}^{-1}$ (Fig. S1a) [20,21]. After adsorption of $\text{PS}_{5.2\text{k}}\text{-b-PAA}_{4\text{k}}$ in THF into the mSiO_2 channels, the pore capacity decreased dramatically to $45\text{ cm}^3\text{ g}^{-1}$ (Fig. S1b). The PAA blocks are preferentially anchored onto the Fe_3O_4 core surface via coordination. When THF is substituted with a PS-selective solvent (for example, toluene), a phase separation occurs that involves outward extension of the PS blocks and collapse of the PAA blocks onto the core surface. A Janus copolymer cluster is formed within the mSiO_2 channel. After the PAA blocks are selectively crosslinked with TEPA inside the mSiO_2 channel, a crosslinked PAA colloid (cPAA) is produced. New peaks consistent with amide groups ($-\text{CONH}-$) confirm this crosslinking (Fig. S2). Etching mSiO_2 with aqueous NaOH caused the PS-cPAA diblock JCCPs to detach from the core surface under sonication. The PS-cPAA JCCPs can be dispersed in good solvents such as THF (Fig. S3). After drying the dispersion in THF, individual particles with a diameter of about 6 nm are observed under SEM (Fig. S4). Under TEM, only the cPAA

domains with a diameter of about 3–5 nm are visible (Fig. 1a). This is consistent with the presence of more compact cPAA after crosslinking. Selective staining with PTA makes the cPAA domains much darker (Fig. 1b). Additional staining with RuO_4 to distinguish the PS domains reveals that they possess a loose parachute-like shape (Fig. 1c). No superstructures are found in selective solvents such as water (Fig. S5). After drying an aqueous dispersion of the JCCPs, the parachute-like PS domains become compact and able to be discerned by TEM without staining (Fig. S6a). The PS-cPAA JCCPs do not aggregate. The PS parachute-like shape becomes too disperse to visualize under TEM without staining after drying a dispersion of the JCCPs in a PS-selective solvent like toluene (Fig. S6b). In all cases, the cPAA domains are visible under TEM.

When the copolymer $\text{PS}_{2.3\text{k}}\text{-b-PAA}_{9\text{k}}$ with a longer PAA block than $\text{PS}_{5.2\text{k}}\text{-b-PAA}_{4\text{k}}$ is used, the cPAA domains become larger; about 5–7 nm in diameter (Fig. S7). In addition, the cPAA domains become larger at high pH (Fig. S8). The ζ potential of the aqueous dispersion strongly depends on pH, becoming very negative at high pH (Fig. S9a). When using PS-cPAA JCCPs as a surfactant to form a wax-in-water emulsion, the emulsion becomes unstable at low pH (for example, 2.0), but is very stable at high pH (Fig. S9b). This implies that the cPAA domains contain residual PAA groups. The cPAA domains can serve as a nanoreactor to induce *in situ* growth of functional materials. As proof of this concept, paramagnetic PS-cPAA@ Fe_3O_4 composite JCCPs are derived after preferential adsorption of ions and precipitation (Fig. 1d). Selected-area electron diffraction (SAED; inset of Fig. 1d) and EDX (Fig. S10) results confirm the presence of Fe_3O_4 . The composite JCCPs remain readily dispersible both in water and toluene. In addition, they are easily captured with a magnet (Fig. S11). After adsorption and reduction of AgNO_3 , PS-cPAA@Ag composite JCCPs are obtained (Fig. S12). This method is general and can be used to fabricate a huge family of composite JCCPs.

Residual carboxyl groups on the cPAA domains of the PS-cPAA diblock JCCPs facilitate the growth of another polymer. As an example, amine-capped PEG is used to terminate the opposite side of the cPAA domain by amidation to give a PS-cPAA-PEG triblock JCCP. Prior to the termination, cyclohexane was added to induce aggregation of the PS domains and confinement in an internal phase, while the other side of the JCCPs was exposed for termination. Otherwise, the PS domains would sterically constrain the termination of the opposite side of the JCCPs. After termination with PEG, the ζ potential of the JCCP aqueous dispersion became less dependent on pH (Fig. S13a). The emulsions remain stable independent of pH

Figure 1 TEM images of PS-cPAA diblock JCCPs (a) after drying a dispersion in THF, and after sequential staining with (b) PTA and (c) RuO₄. (d) TEM image of PS-cPAA@Fe₃O₄ composite JCCPs along with their SAED pattern (inset).

(Fig. S13b). This implies that no residual PAA groups are present at the colloidal domain surface after termination with PEG. DLS measurements reveal that the PS-cPAA-PEG JCCPs are larger than the PS-cPAA ones (Fig. S14), which is consistent with SEM and atomic force microscopy (AFM) results (Fig. S15). Under TEM, the dark domains correspond to cPAA (Fig. 2a). PEG domains are discerned as mushroom-like shapes after staining with PTA (Fig. 2b). After additional staining with RuO₄, the PS domains are distinguished as parachute-like shapes (Fig. 2c). The PEG and PS domains are distinctly compartmentalized on the opposite sides of the cPAA domains.

Many chemical approaches can be used to grow functional materials within the cPAA domains, providing access to an expansive family of composite JCCPs. For example, PS-cPAA@Au-PEG composite JCCPs may be synthesized by preferential adsorption of metallic ions and *in situ* reduction. Both PS and PEG domains are compartmentalized on the opposite sides of the cPAA@Au composite domains (Fig. 2d). Meanwhile, inorganic composite JCCPs like PS-cPAA@TiO₂-PEG can be synthesized by the sol-gel process (Fig. S16). Similarly, PS-cPAA@Fe₃O₄-PEG composite JCCPs have also been prepared (Fig. 2e). These JCCPs are readily dispersible in toluene and water. The

aqueous dispersion is transparent and slightly brown. The composite JCCPs can be completely collected with a magnet (Fig. 2f). Upon removal of the magnet, the JCCPs can be redispersed.

The PS-cPAA-PEG JCCPs are amphiphilic and able to self-organize into superstructures. After slow evaporation of THF from a dispersion of the JCCPs in THF/water (1/4 v/v), the solution becomes transparent but slightly blue. Dynamic light scattering (DLS) results reveal the formation of superparticles with a diameter of about 80 nm (Fig. S17), which is consistent with SEM observations (Fig. S18a). An AFM image reveals that the superparticles are composed of a number of JCCPs (Fig. S18b). To observe their internal structure under TEM, the composite PS-cPAA@TiO₂-PEG JCCPs are used. The superparticles are surrounded with black cPAA@TiO₂ domains (Fig. S19a). Staining with PTA reveals that the PEG domains are present at the surface of the JCCPs (Fig. S19b). After precipitation of the PS-cPAA-PEG JCCPs on a crosslinked PDVB nanofiber surface by slow evaporation of THF from their THF/water dispersion, the hydrophobic PS sides are exclusively anchored onto the nanofiber surface, while the cPAA domains are directed towards the external aqueous phase (Fig. S20a). Further staining with PTA reveals that all PS-cPAA-PEG JCCPs are

Figure 2 TEM images of PS-cPAA-PEG JCCPs (a) after drying a dispersion in THF, and after sequential staining with (b) PTA and (c) RuO₄. (d) TEM image of PS-cPAA@Au-PEG composite JCCPs after drying a dispersion in THF, and staining with RuO₄. (e) TEM image of PS-cPAA@Fe₃O₄-PEG composite JCCPs. (f) Photographs of the composite JCCP dispersion in water (left), and after magnetic manipulation (right).

oriented perpendicularly onto the PDVB nanofiber surface with the hydrophilic PEG sides directed towards the aqueous phase (Fig. S20b).

PS-cPAA-PEG JCCPs can lower the interfacial tension at oil/water interfaces like other copolymers (Fig. S21). Wax-in-water emulsions containing PS-cPAA-PEG JCCP as an emulsifier are formed at high temperature. The wax spheres become solid after cooling (Fig. 3a). The JCCPs form a monolayer at the sphere surface (Fig. 3b). No JCCPs are found in either the water or wax phase. Similarly, a wax/PEG blend is formed at high temperature. After dissolution of the continuous PEG phase in water, wax

spheres are obtained (Fig. S22a). After dissolution of wax from the fractured surface with *n*-hexane, many voids are left (Fig. S22b). A monolayer of the JCCPs is observed at the interface, and no JCCPs are found in either the wax or PEG phase. Similarly, a wax-in-water emulsion can form in the presence of PS-cPAA@Fe₃O₄-PEG composite JCCPs (left, Fig. S23). After the wax spheres are collected with a magnet, the continuous aqueous phase becomes colorless (right, Fig. S23). The emulsion remains stable after removal of the magnet. The composite JCCPs form a monolayer on the sphere surface (Fig. S24a). While water elutes under a magnetic field, the captured wax spheres are stable (left,

Figure 3 (a) SEM image of the wax spheres obtained after drying a wax-in-water (1:100 wt./wt.) emulsion (inset) stabilized with PS-cPAA-PEG JCCPs. (b) Magnified SEM image of the wax sphere surface. (c) Magnetic collection of the wax-in-water (1:3 wt./wt.) emulsion stabilized with PS-cPAA@Fe₃O₄-PEG composite JCCPs (left), and (right) magnetic field-induced de-emulsification under a stronger magnetic field.

Fig. 3c). At a higher magnetic field of about 0.8 T, the liquid wax begins to elute (right, Fig. 3c). Eventually, only a brown powder is left. An SEM image of the frozen sample reveals that the wax spheres start to coalesce to form larger aggregates during de-emulsification under the strong magnetic field (Fig. S24b). Few JCCPs are found on the aggregate surface (Fig. S24c). SEM analysis indicates that the brown powder is the composite JCCPs (Fig. S24d). This implies that the composite JCCPs can be withdrawn from the water/wax interface by a strong magnetic field. As a result, the emulsion becomes de-emulsified and the composite JCCPs can be recycled.

CONCLUSION

We developed a new Janus nanocomposite: JCCPs with two different polymers conjugated on opposite sides of a nanosized colloid. In the JCCPs, the functionality of colloids and performance of block copolymers are hybridized. Janus clusters of a copolymer are formed within mesoporous channels, while the PAA blocks are tethered on the core surface through coordination. The PS-cPAA diblock JCCPs are synthesized by selectively crosslinking the PAA blocks. After the cPAA domains are terminated with

amine-capped PEG chains, PS-cPAA-PEG triblock JCCPs are produced. The cPAA domain can serve as a nanoreactor to prepare functional materials *in situ*, providing opportunities to synthesize a huge family of composite JCCPs. The developed approach is essentially based on the specific interaction of one block of a copolymer with a core surface beneath a porous mask layer, and should be applicable to a broad composition range of copolymers and size/shape of JCCPs. JCCPs are a new genre of block copolymers to assist with organization of functional NPs into superstructures. When using the composite PS-cPAA@Fe₃O₄-PEG JCCPs as a magnetic-responsive surfactant, emulsions can be collected with a magnet and even de-emulsified under a strong magnetic field.

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Author contributions Yang Z proposed the project; Yang Z and Liang F designed the work; Zhou P synthesized the materials and measured their properties. All authors participated in the analysis of the experimental data and discussion of the results.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

Yang Zhenzhong was born in 1968. In 1997, he received his PhD degree from the Institute of Chemistry, Chinese Academy of Sciences (ICCAS). During 1997 and 1998, he undertook postdoctoral research at Badische Anilin-und-Soda-Fabrik (BASF), Ludwigshafen. Currently, he is a professor and director of the State Key Laboratory of Polymer Physics and Chemistry at ICCAS. His research goal is to develop methods to precisely tune the microstructure and spatial distribution of components and thus their performance within a given composite morphology. The composites include inorganic/polymer hollow spheres and capsules, and mesoporous and Janus materials.

中文摘要 本文提出了Janus胶体共聚物(JCCPs)纳米复合粒子概念,即在纳米胶体粒子两侧对称部分分别复合生长不同的聚合物。嵌段聚合物PS-*b*-PAA通过配位键选择性吸附在 Fe_3O_4 磁性微球表面后,在其外部孔道的受限空间内自组装。选择性交联PAA链段部分即可得到PS-*c*PAA两嵌段JCCPs。在交联的PAA另一侧接枝复合一端带 NH_2 基团的PEG从而制备得到PS-*c*PAA-PEG三嵌段JCCPs。部分交联的PAA链段部分有功能化基团可以作为纳米反应器进而原位选择性生长功能物质。JCCPs复合纳米粒子兼具纳米胶体颗粒的双亲性与共聚物的自组装特性。