Macromolecules
ARTICLE

Large Scale Synthesis of Janus Submicrometer Sized Colloids by Seeded Emulsion Polymerization

Chen Tang, Chengliang Zhang,* Jiguang Liu, Xiaozhong Qu, Jiaoli Li, and Zhenzhong Yang*

State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

Received February 24, 2010; Revised Manuscript Received May 5, 2010

ABSTRACT: We present a facile approach to produce submicrometer sized Janus PAN/PS polymer colloids by seeded emulsion polymerization. Both high cross-linking degree and slow feeding monomer are crucial to control the resultant anisotropic structure. The PAN seed is cross-linked, ensuring that the formed PS bulge contains no PAN. The two different polymers are distinct compartmentalized onto the surface. Other Janus composite colloids with varied composition and microstructure are derived by selective modification of desired polymer part and following favorable growth of other materials therein. The Janus colloids can serve as solid surfactants to emulsify oil/water immiscible mixtures, which have a well-defined orientation at the interface. The method can be scaled up to produce large quantity of submicrometer sized Janus colloids.

1. Introduction

Controlling microstructure of colloids is important to gain additional performances of composite materials. Janus colloids[1] with compositions or properties compartmentalized onto their surface are promising in many applications.[2] For example, at a Janus material stabilized oil/water interface biphasic catalysis has been reported, in which location control of catalytic nanoparticles if facing toward the oil phase or the aqueous phase becomes determinative in the reaction.[2e] Many methods have been proposed to prepare Janus particles. Although the method by selective growth of materials onto the exposed part while the other part is protected is universal,[3,4] the synthesis efficiency remains rather low even in the case of Pickering emulsion interface.[4] In order to massively synthesize the Janus materials with decreased characteristic dimension, supramolecular structures from block copolymers are used to derive the Janus objects, including directly from microphase separation in mixed micelles,[5a−c] and template synthesis using supramolecular structures.[5d,e] However, the polymer structure, especially block copolymers, is strictly required. Although microfabrication including microfluidics[6] and electrospinning[7] can massively produce Janus particles, it is rather difficult to control their size below 1 μm. Janus metal or metal oxides nanoparticles can be synthesized from two components with mismatched lattice spacing and phase transition temperature.[8] The components are greatly restricted, and the solid content is rather low. Phase separation during emulsion polymerization usually gives many interesting anisotropic particles such as snowman-like, acorn-like, and dumbbell-like.[9] One-step seeded emulsion polymerization is usually employed to achieve micrometer sized anisotropic particles. The method fails in the synthesis of submicrometer sized anisotropic colloids. Recently, Ballauff et al. have reported an alternative effective approach toward submicrometer sized dumbbell-like anisotropic PMMA/PS colloids. The key point is to feed the monomer slowly dropwise rather than one-batch feeding.[10] Since the PMMA seed

is linear polymer, it is inevitable that the newly formed major PS bulge contains minor PMMA after phase separation (vice versa). Furthermore, the PMMA core is also covered with a layer of PS. Although the colloids look dumbbell-like and anisotropic in geometry, two polymers are not distinct compartmentalized onto the surface. In this case, to speak strictly, the reported dumbbell-like anisotropic colloids are not Janus in chemistry. It remains challenging to large scale produce submicrometer sized Janus polymer colloids with two different components distinct compartmentalized onto the surface.

Herein, we present a facile approach to large scale produce submicrometer sized Janus polymer colloids by seeded emulsion polymerization against a cross-linked polymer hollow colloid seed as illustrated in Scheme 1. An example submicrometer cross-linked polyacrylonitrile (PAN) hollow colloid is used as a seed (Figure 1a).[11] A monomer mixture of styrene/divinylbenzene (St/DVB) is slowly dropped into the seed emulsion accompanying with polymerization at high temperature, which is essentially different from the reported one-step seeded emulsion polymerization.[9] PAN and PS are typically immiscible, and PS phase separates from the PAN shell especially driven by polymer network elastic−retractile force during cross-linking. So Janus PAN/PS polymer colloids are obtained. Since the PAN shell is cross-linked, in principle, no PAN is present in the PS bulge phase. Functional groups such as carboxylic acid (−COOH) are derived by selective hydrolysis of PAN, which facilitates a further favorable growth of other materials, thereby forming Janus composite colloids.

2. Experimental Methods

Materials. Styrene (St), acrylonitrile (AN), sodium dodecyl benzenesulfonate (SDS), potassium persulfate (KPS), benzoyl peroxide (BPO), tetraethyl orthosilicate (TEOS), ferrous chloride tetrahydrate (FeCl$_2$−4H$_2$O), ferric chloride anhydrous (FeCl$_3$), *N*,*N*′-dimethylformamide (DMF), aqueous ammonia (NH$_3$−H$_2$O, 28 wt %), concentrated sulfuric acid (H$_2$SO$_4$, 98 wt %), sodium hydroxide (NaOH), trisodium citric, nitric acid, acetone, hexane, and ethanol were analytical grade and purchased from Sinopharm Chemical Reagent Beijing Co. Ltd. (SCRC). Divinylbenzene (DVB) was purchased from Fluka.

 *Corresponding author. E-mail: zhangcl@iccas.ac.cn (C.Z.), yangzz@iccas.ac.cn (Z.Y.).

Scheme 1. Schematic Synthesis of Janus Colloids[a]
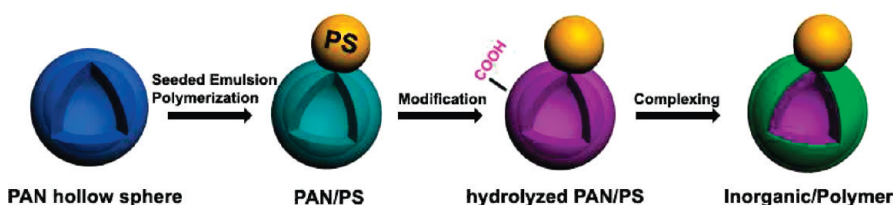
[a] Janus PAN/PS colloids are prepared by seeded emulsion polymerization against the cross-linked PAN hollow seed spheres. By alkaline hydrolysis of PAN shell of the colloids, hydrolyzed PAN/PS colloids with functional groups such as carboxylic acid are derived. By favorable growth of other materials, for example silica by a sol–gel process, Janus inorganic/polymer composite colloids are synthesized.
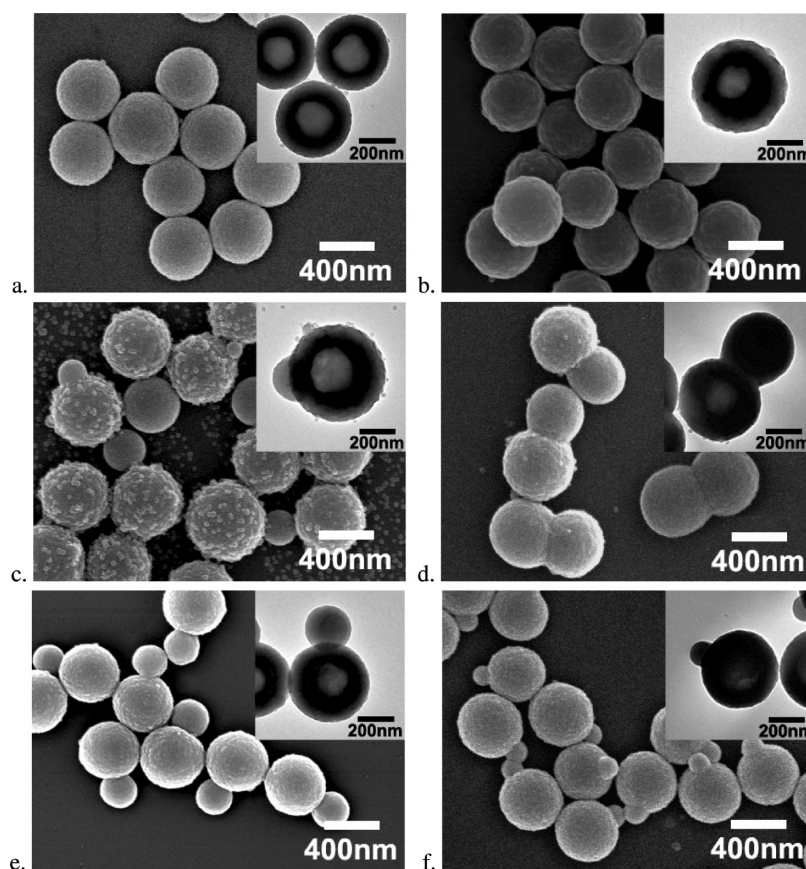

Figure 1. SEM and inset TEM images of some representative polymer colloids: (a) cross-linked PAN hollow seed colloids; (b, c) Janus PAN/PS polymer colloids prepared by one-step batch seeded emulsion polymerization at different cross-linking agent DVB content: (b) St/PAN seed = 2:1; (c) (St + DVB)/PAN seed = (0.5 + 1.5):1; (d–f) Janus PAN/PS polymer colloids prepared by slowly feeding monomer dropwise at decreased monomer/PAN seed weight ratio: 4:1, 2:1, and 1:1, respectively, and the DVB/St weight ratio is kept at 3:1.

St and DVB were destabilized over Al_2O_3 column (SCRC) and then stored at low temperature. All other reagents were used as received.

The cross-linked PAN hollow spheres with 50 wt % DVB were prepared as following.[11] 5 g of freeze-dried powder of parent polystyrene (PS) hollow spheres HP-433 (a Rohm & Haas product) with an outer diameter of 400 nm and cavity diameter of 250 nm was dispersed in 100 g of water. 0.1 g of SDS was added as surfactant. 5 g of AN/DVB (1:1 w/w) and 0.05 g of BPO were added and emulsified under ultrasonication for 10 min. The mixture was held under stirring at ambient temperature for 6 h to swell the shell with the monomers and initiator. Afterward, the emulsion was heated to 80 °C to initiate the polymerization in nitrogen for 6 h. The resultant cross-linked PAN/PS hollow spheres were washed with excess DMF to remove the linear polymer and freeze-dried for use.

The paramagnetic Fe_3O_4 nanoparticles (Fe_3O_4 NPs) were synthesized by coprecipitation of $FeCl_3$ and $FeCl_2$ aqueous solution. 10 mL of 1 M $FeCl_3$ solution and 11 mL of 0.5 M $FeCl_2$ solution were mixed, then added into 100 mL of deoxygenated 5 M NaOH solution, and stirred for 1 h at room temperature in N_2 and for another 1 h at 90 °C. 100 mL of 0.5 M chitosan solution was added, and the mixture was stirred for 30 min. After being precipitated with acetone, Fe_3O_4 NPs were washed with water and separated with a magnet and redispersed into water for use. The diameter of Fe_3O_4 NPs was about 5–10 nm.

Methods.   *Synthesis of Janus PAN/PS Colloids.* An example recipe was given as following. 0.5 g of freeze-dried cross-linked PAN hollow powder was dispersed in 15 g of water as a seed emulsion under stirring at 80 °C. 0.25 g of St, 0.75 g of DVB, 0.5 g of initiator solution (1 wt % KPS), 0.6 g of surfactant NPS25 (gifted by BASF), and 15 g of water were emulsified at room temperature under ultrasonication for 10 min. The monomer emulsion was slowly dropped into the seed emulsion within 1.5 h. Afterward, the emulsion was held for further polymerization at
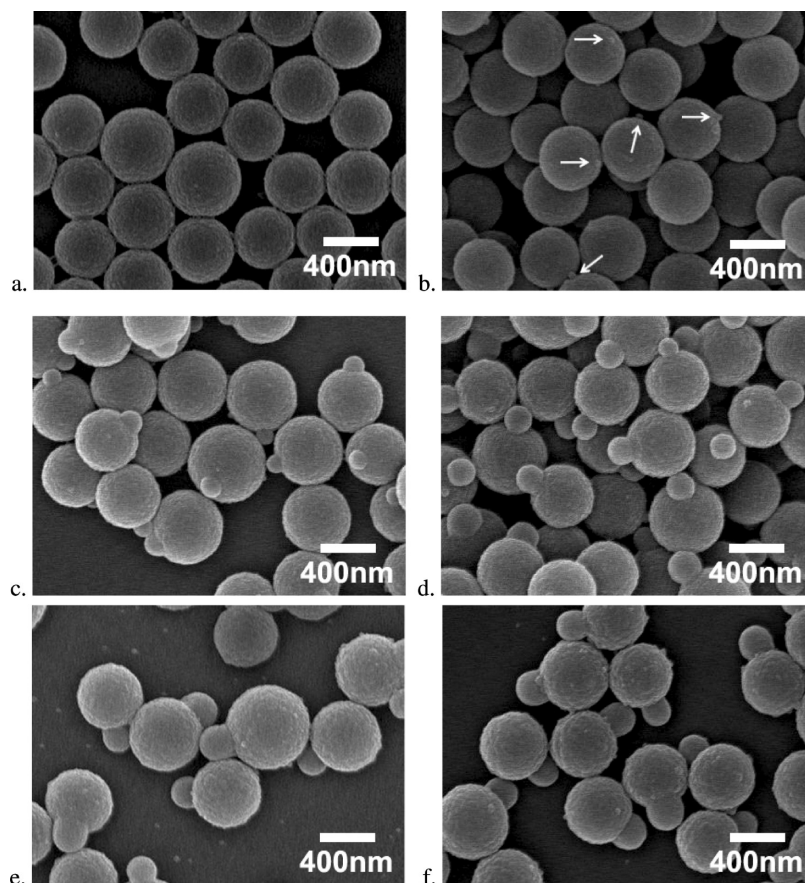
Figure 2. Morphological evolution of the Janus PAN/PS polymer colloids with reaction time: (a) 20 min; (b) 40 min; (c) 60 min; (d) 90 min (monomer feeding is completed); (e) 6 h; (f) 12 h. The monomer/PAN seed colloid weight ratio is 2:1, and DVB/St weight ratio is 3:1.

80 °C for another 6 h. Janus PAN/PS polymer colloids were obtained by centrifugation.

As comparison with the above monomer feeding dropwise seeded emulsion polymerization, one-step batch seeded emulsion polymerization was also carried out after the monomer emulsion was added into the seeded emulsion in one step at 80 °C.

Janus Hydrolyzed PAN/PS Colloids. 1.0 g of freeze-dried powder of the Janus PAN/PS polymer colloids was dispersed in 200 g of 5 wt % aqueous NaOH. The mixture was refluxed under stirring for 24 h to selectively hydrolyze the PAN shell. After wash until the continuous phase was neutral, the Janus hydrolyzed PAN/PS polymer colloids were obtained after centrifugation.

Janus Fe_3O_4/PS Composite Colloids. 0.1 g of freeze-dried powder of the Janus hydrolyzed PAN/PS polymer colloids was dispersed in 5 g of water. After 10 g of Fe_3O_4 NPs aqueous dispersion (0.5 wt %) was added under stirring for 10 min, the Janus Fe_3O_4/PS composite colloids were obtained after centrifugation.

Janus Silica/PS Composite Colloids. 0.1 g of freeze-dried powder of the Janus hydrolyzed PAN/PS polymer colloids was dispersed in 20 g of ethanol containing 0.5 g of aqueous ammonia (28 wt %). A mixture of 0.1 g of TEOS and 5 g of ethanol was added into the dispersion. A sol−gel process was carried out under stirring for 8 h at room temperature. After centrifugation and wash with ethanol, the Janus silica/PS composite colloids were obtained.

Silica/Sulfonated PS Composite Colloids. 0.1 g of freeze-dried powder of the Janus silica/PS colloids was dispersed in 10 g of 98 wt % concentrated H_2SO_4. The mixture was held at 40 °C for 6 h under stirring. After removing residual H_2SO_4 by centrifugation and rinsing with water, the silica/sulfonated PS composite colloids were obtained.

Janus OTS Modified Silica/Sulfonated PS Composite Colloids. 0.1 g of freeze-dried powder of the silica/sulfonated PS colloids was dispersed in 10 g of hexane, and 1 g of *n*-octyltrichlosilane (OTS, Alfa Aesar) was added. The mixture was held under stirring at room temperature for 24 h. After removing residual OTS by centrifugation and rinsing with hexane, the Janus OTS modified silica/sulfonated PS composite colloids were obtained.

Janus Titania/PS Composite Colloids. 0.1 g of freeze-dried powder of the Janus hydrolyzed PAN/PS colloids was dispersed in 20 g of water, 5 g of 2 M nitric acid was added under stirring at 65 °C, and then 0.2 g of titanium isopropoxide (TTIP, Fluka) dispersed in 5 g of ethanol was added slowly. After the dispersion was stirred in air for 24 h, the Janus titania/PS composite colloids were obtained.

Janus β-FeOOH/PS Composite Colloids. 0.1 g of freeze-dried powder of the Janus hydrolyzed PAN/PS colloids was dispersed in 10 g of water, and then 10 g of $FeCl_2$ (1.842 g)/$FeCl_3$ (1.5 g) aqueous solution was added. The mixture was held under stirring in nitrogen for 24 h. After centrifugation and rinsing with water, the resultants were redispersed in 10 g of water, and then 4 g of 2 M aqueous NaOH was added under stirring in nitrogen at 65 °C for 1 h. After centrifugation and rinsing with water, the Janus β-FeOOH/PS composite colloids were obtained.

Emulsification Using the Janus Composite Colloids. The Janus silica/PS composite colloids were washed with DMF to remove the surfactant and linear polymers. 0.02 g of freeze-dried powder of the Janus silica/PS composite colloids was dispersed in 13 g of water, followed by adding 0.5 g of wax (T_m: 52−54 °C). The mixture was vigorously stirred at 80 °C for 30 min, and then the formed emulsion was naturally cooled down to room temperature.
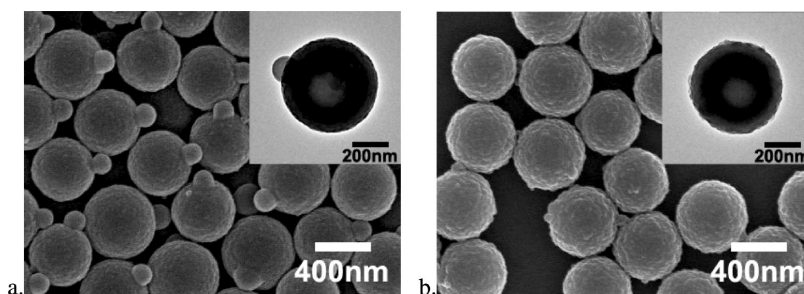
Figure 3. SEM and inset TEM images of the PAN/PS polymer colloids prepared by slowly feeding monomer dropwise with decreased DVB content: (a) DVB:St = 1:3; (b) without DVB. Monomer/PAN seed weight ratio is kept at 2:1.

Characterization. Morphology of the Janus colloids was characterized using transmission electron microscopy (JEOL 1011 at 100 kV) and scanning electron microscopy (Hitachi S-4300 at 15 kV). The samples for SEM observation were prepared by vacuum sputtering with Pt on the ambient dried samples. The samples for TEM observation were prepared by spreading very dilute emulsions in ethanol onto carbon-coated copper grids. FT-IR spectroscopy was performed using a Bruker EQUINOX 55 spectrometer with the samples/KBr pressed pellets. The crystallinity of materials was characterized by wide-angle X-ray powder scattering (Rigaku D/max-2500).

3. Results and Discussion

For the first experiment, one-step batch seeded swell emulsion polymerization was carried out against the cross-linked PAN seed colloids (Figure 1a) using St along the reported procedure for micrometer sized anisotropic particles.[9] No anisotropic colloids were prepared but hollow spheres with a thicker shell (from 100 to 150 nm) and smaller cavity (from 200 to 150 nm) (Figure 1b). This indicates that St mainly polymerized within the PAN shell. In order to enhance the phase separation by increasing polymer network elastic−retractile force, cross-linking agent DVB was added to St at a sufficiently high weight ratio, for example DVB:St = 3:1. Onto the PAN hollow sphere surface, a large bulge coexists with some smaller ones (Figure 1c). These anisotropic colloids are not strictly Janus. Meanwhile, many free PS particles formed in the continuous phase. Removal of free PS particles from the emulsion involves additional procedure to purify the colloids. Theoretic analysis predicates an equilibrium phase separation by lowering monomer−polymer mixing force.[9a,b] The experiments have also confirmed that slow feeding monomer dropwise is effective to synthesize submicrometer sized anisotropic colloids.[10] In our case, we carried out all the other experiments by slowly feeding the monomer dropwise to the seed emulsion, ensuring monomer content at a very low level. Relatively uniform Janus PAN/PS polymer colloids were indeed synthesized with only one solid PS bulge (Figure 1d), whose size is about 400 nm and comparable with the PAN part. No free PS particles were observed in the continuous phase. Size ratio between PS and PAN parts was decreased by lowering the monomer feeding amount. For example, the bulge size is further decreased from 200 to 100 nm (Figure 1e,f). In order to elucidate the formation process, morphological evolution of the Janus polymer colloids with reaction time was monitored (Figure 2). At the early stage during monomer feeding hollow colloids with smooth surface formed, indicating that all the monomer swelled the shell and polymerized therein (Figure 2a). From thermodynamic consideration, the PS fraction is insufficient to drive the phase separation and coexists as a minor phase with the PAN major phase. Along with further increasing monomer feeding amount, a small PS bulge emerged onto the hollow sphere surface (Figure 2b), corresponding to the onset of phase separation of PS from PAN matrix. In this case, fraction of the PS is sufficient to drive the
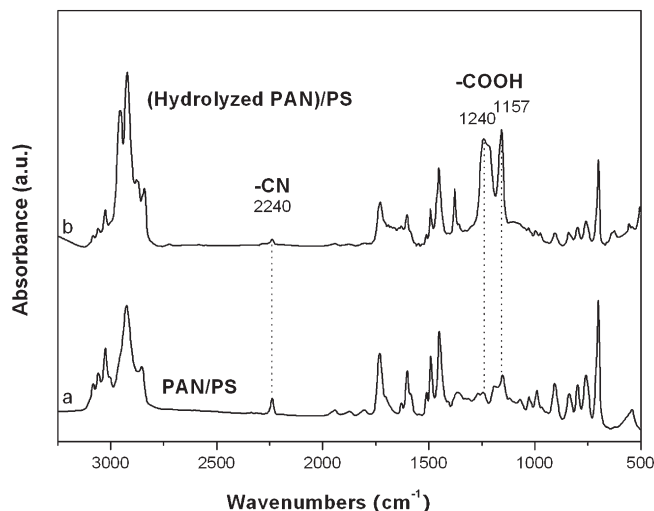

Figure 4. FT-IR spectra of (a) the Janus PAN/PS polymer colloids and (b) the Janus hydrolyzed PAN/PS polymer colloids.

phase separation. At the linkage site, the PS bulge and PAN are physically interpenetrated, forming an interpenetration polymer network. Afterward, the fed monomer preferentially swelled the PS bulge and polymerized therein; size of the PS bulge was increased progressively until completion of monomer feeding (Figure 2c,d). With further prolonging reaction time, size increment was not remarkable (Figure 2d−f). The PS bulge is tightly linked with the PAN part, which cannot be detached under vigorous ultrasonication. Besides thermodynamic consideration, to control kinetic variables for example cross-linking agent DVB content is also important to achieve the anisotropic structure. The PS bulge size is decreased with a decrease in DVB content, for example DVB:St = 1:3 (Figure 3a). In the absence of DVB, only hollow spheres with thicker shell and small cavity were prepared (Figure 3b). Careful observation indicates that some tiny PS bulges are present on the surface, meaning that PS tends to phase separate from the PAN shell. Because of insufficient elastic force of PS network in the absence of cross-linking agent DVB, the grown bulges are not well developed.

Since PAN shell has already been cross-linked, the PS bulge has no PAN. Functional groups can be derived by selective modification of both parts. For example, the Janus PAN/PS polymer colloid was treated in alkaline to selectively hydrolyze PAN forming a hydrogel.[11,12] New bands assigned to carboxylic acid (−COOH) appear while the band attributed to −CN group becomes weakening (Figure 4). Onto the hydrolyzed PAN region, paramagnetic Fe_3O_4 nanoparticles with the chitosan corona were used to complex by selective adsorption. They were predominantly adsorbed onto the hollow shell surface, while no nanoparticles were observed onto the PS bulge (Figure 5a). Other materials can be further grown selectively in the hydrolyzed PAN
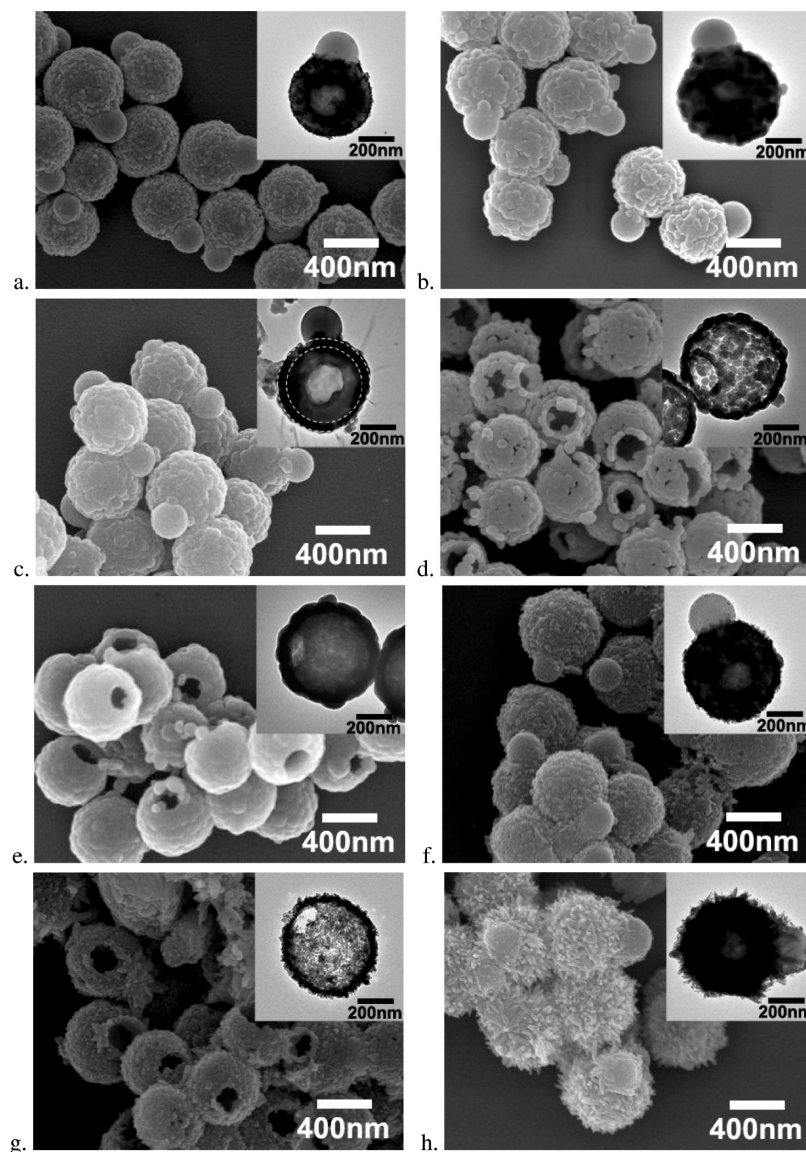
Figure 5. SEM and (inset) TEM images of some representative samples: (a) the Janus hydrolyzed PAN/PS colloids with Fe_3O_4 nanoparticles preferentially labeled onto the hydrolyzed PAN part; (b, c) the Janus silica/PS composite colloids at varied TEOS/hydrolyzed colloids weight ratio (1:1 and 5:1) (inset (c): cross-section TEM image); (d, e) the silica hollow colloids with a single hole after the samples in (b, c) are calcined in air at 450 °C for 2 h; (f) the Janus titania/PS composite colloids; (g) the titania hollow colloids with a single hole after the samples in (f) are calcined in air at 450 °C for 2 h; (h) the Janus β-FeOOH/PS composite colloids.

part of the Janus colloids. As the first example, a sol−gel process of TEOS forming silica occurred mainly within the hydrogel shell. At a low silica content (TEOS/colloid weight ratio 1:1), the hydrogel shell surface was partially covered with silica (Figure 5b). At a high silica content (TEOS/colloids weight ratio 5:1), the hydrogel shell was more compacted covered with silica (Figure 5c). The cross-section TEM image (inset Figure 5c) shows that the silica was mainly grown onto the exterior surface of hydrogel shell. After the polymers were calcined in air, the corresponding hollow silica spheres with a single hole were obtained. Their shell microstructure could be controlled to be porous or compacted due to different silica coverage (Figure 5d,e). Formation of the single hole in the shell is consistent with the IPN structure at the PAN/PS linkage site. Although some anisotropic SiO_2/PS composite colloids have been reported, the silica surface remains covered with a layer of PS besides the PS bulge.[13] Therefore, the two compositions are not distinctly compartmentalized onto the anisotropic colloid surface. To speak strictly, they are not Janus in chemistry. In our case, the SiO_2/PS composite colloids have two different compositions distinctly compartmentalized onto

the surface besides the asymmetric geometry. Another feature lies that the PAN part possesses a hollow cavity, and the corresponding performances of hollow spheres may be introduced into the Janus colloids. Similarly, the corresponding Janus titania/PS colloids were prepared by a favorable sol−gel process in the hydrolyzed PAN part (Figure 5f). After calcination in air, the corresponding titania hollow spheres with a single hole were derived (Figure 5g). Such hollow spheres with a single hole will serve as a microcontainer with potential applications in vehicles and reactors.[14] As another example, after iron ions were favorably absorbed by the hydrogel followed by a reduction, the Janus β-FeOOH/PS composite colloids were prepared (Figure 5h). β-FeOOH appears in the form of nanosized needle, and their crystal structure is verified by XRD (Figure S1).

Interfacial properties of the Janus colloids were demonstrated as solid surfactants by emulsifying oil/water (O/W) mixture. In order to clarify orientation of the Janus colloids at the emulsion interface, wax with a melt temperature about 52−54 °C was used as an example oil. In the presence of 0.15 wt % the Janus silica/PS composite colloids (as shown in Figure 5c), a wax-in-water
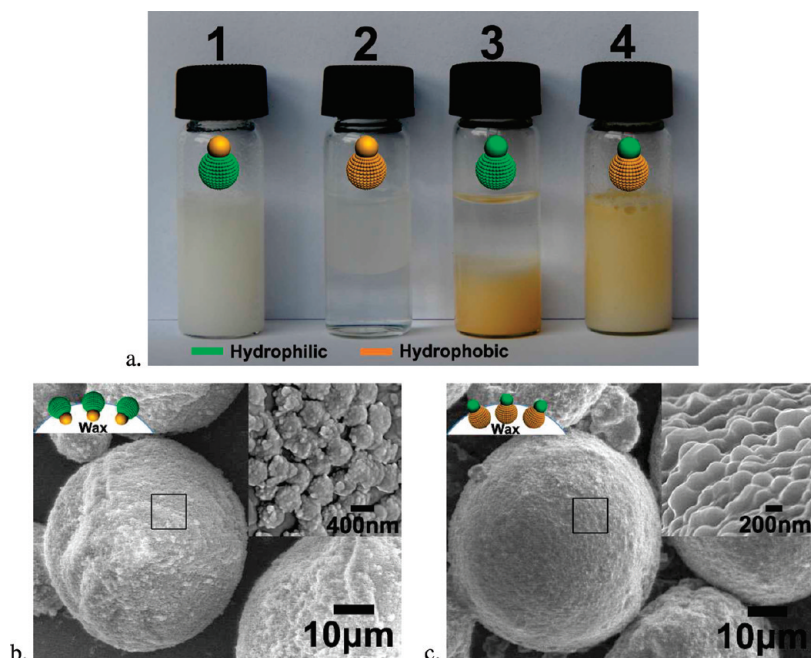
Figure 6. (a) Interfacial properties of some representative composite colloids at 80 °C: (1) O/W emulsion stabilized by the Janus silica/PS composite colloids, (2) the OTS-modified silica/PS composite colloids only dispersible in top oil phase, (3) the silica/sulfonated PS composite colloids only dispersible in bottom water phase, (4) O/W emulsion stabilized by the Janus OTS modified silica/sulfonated PS composite colloids. (b) Frozen wax/water emulsion stabilized by the Janus silica/PS composite colloids; the coarse silica side facing toward the external water phase. (c) Frozen wax/water emulsion stabilized by the Janus OTS-modified silica/sulfonated PS composite colloids; the smooth sulfonated PS side facing toward the external water phase.
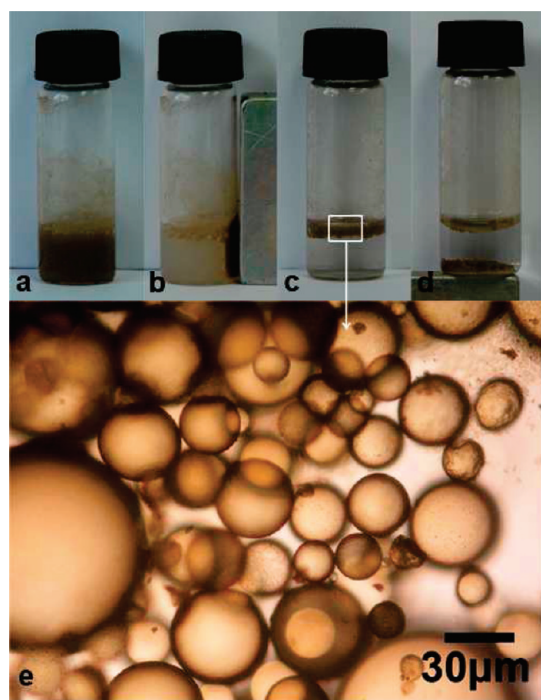

Figure 7. (a) Paramagnetic Janus composite colloids (shown in Figure 5a) dispersed in water. (b) Collecting the paramagnetic Janus composite colloids with a magnet. (c) Toluene/water emulsion stabilized by the paramagnetic Janus composite colloids. (d) Driving the dispersed droplets with a magnet. (e) Optical microscopy image of the toluene/water emulsion.

indicates that the Janus composite colloids have a well-defined orientation at the interface. In comparison, those homogeneous colloids at a Pickering emulsion interface rotate without any defined orientation.[4] Wettability of the two parts of the Janus composite colloids can be tuned by simple modification. After the hydrophilic silica part of the Janus silica/PS composite colloids was modified with *n*-octadecyltrichlorosilane (OTS), the colloids became hydrophobic and only dispersible in the oil (Figure 6a-2). Similarly, when the Janus silica/PS composite colloids were sulfonated, the colloids became hydrophilic and only dispersible in the aqueous phase (Figure 6a-3). When the sample as shown in Figure 6a-2 was further sulfonated, the colloids became Janus again. It is noticed that wettability of two parts is reversed from the original Janus silica/PS composite sample. The successful chemical modification is confirmed by the FT-IR spectra (Figure S2). A wax-in-water emulsion also formed (Figure 6a-4) but with the smooth hydrophilic sulfonated PS bulge facing toward the aqueous phase (Figure 6c). Additional performance can be integrated with the Janus colloids. As an example, the Janus composite colloids with the paramagnetic nanopaticles (as shown in Figure 5a) favorably absorbed onto the hydrogel part remained dispersible in both water (Figure 7a) and oil. The Janus composite colloids were easily collected for example from their aqueous emulsion by a magnet (Figure 7b). The Janus composite colloids were used to stabilize a toluene-in-water emulsion (Figure 7c), and the dispersed droplets could be driven and collected by a magnet (Figure 7d). Upon removal of the magnet, the emulsion remained stable and floated on the top layer again. There is no coalescence between the individual droplets; their droplets are tens micrometers in size (Figure 7e).

4. Conclusion

In conclusion, we have synthesized submicrometer sized anisotropic Janus polymer colloids by seeded emulsion polymerization. Polymerization induced phase separation is mainly responsible for the growth of the Janus colloids. Slow feeding

emulsion was formed at high temperature (Figure 6a-1). Upon cooling to room temperature, orientation of Janus colloids was frozen at the interface. The exposed hydrophilic coarse silica part faces toward the external aqueous phase (Figure 6b). This

monomer dropwise is important to achieve the small anisotropic colloids. Sufficient cross-linking of the formed polymer is required to drive a more complete phase separation. It is key that the seed PAN colloid is cross-linked; no PAN is present in the formed PS bulge. In principle, it is guaranteed that two parts of the anisotropic colloids are distinct compartmentalized in chemistry. By simple selective modification of one part of the Janus polymer colloids and further favorable growth of other materials, composition and microstructure of the Janus colloids are controlled; meanwhile, their interfacial performance is tuned. The Janus colloids can be used as solid surfactants to easily emulsify oil/water mixture, which have a preferential orientation at the interface. The method is facile and can be scaled up for massive production of Janus colloids. This is important to systematically characterize properties of Janus colloids and further explore their practical applications.

Supporting Information Available: XRD spectrum of Janus β-FeOOH/PS composite colloids and FT-IR spectra of some representative samples. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) de Gennes, P. G. *Rev. Mod. Phys.* **1992**, *64*, 645.

(2) (a) Perro, A.; Reculusa, S.; Ravaine, S.; Bourgeat-Lami, E.; Duguet, E. *J. Mater. Chem.* **2005**, *15*, 3745. (b) Yang, S. M.; Kim, S. H.; Lim, J. M.; Yi, G. R. *J. Mater. Chem.* **2008**, *18*, 2117. (c) Walther, A.; Müller, A. H. E. *Soft Matter* **2008**, *4*, 663. (d) Wurm, F.; Kilbinger, A. F. M. *Angew. Chem., Int. Ed.* **2009**, *48*, 8412. (e) Crossley, S.; Faria, J.; Shen, M.; Resasco, D. E. *Science* **2010**, *327*, 68.

(3) (a) Love, J. C.; Gates, B. D.; Wolfe, D. B.; Paul, K. E.; Whitesides, G. M. *Nano Lett.* **2002**, *2*, 891. (b) Lu, Y.; Xiong, H.; Jiang, X.; Xia, Y.; Prentiss, M.; Whitesides, G. M. *J. Am. Chem. Soc.* **2003**, *125*, 12724. (c) Koo, H. Y.; Yi, D. K.; Yoo, S. J.; Kim, D. Y. *Adv. Mater.* **2004**, *16*, 274. (d) Paunov, V. N.; Cayre, O. J. *Adv. Mater.* **2004**, *16*, 788. (e) Ling, X. Y.; Phang, I. Y.; Acikgoz, C.; Yilmaz, M. D.; Hempenius, M. A.; Vancso, G. J.; Huskens, J. *Angew. Chem., Int. Ed.* **2009**, *48*, 7677.

(4) (a) Pickering, S. U. *J. Chem. Soc. Trans.* **1907**, *91*, 2001. (b) Dinsmore, A. D.; Hsu, M. F.; Nikolaides, M. G.; Marquez, M.; Bausch, A. R.; Weitz, D. A. *Science* **2002**, *298*, 1006. (c) Aveyard, R.; Binks, B. P.; Clint, J. H. *Adv. Colloid Interface Sci.* **2003**, *100*, 503. (d) Hong, L.; Jiang, S.; Granick, S. *Langmuir* **2006**, *22*, 9495. (e) Liu, B.; Wei, W.; Qu, X.; Yang, Z. *Angew. Chem., Int. Ed.* **2008**, *47*, 3973.

(5) (a) Erhardt, R.; Zhang, M.; Böker, A.; Zettl, H.; Abetz, C.; Frederik, P.; Krausch, G.; Abetz, V.; Müller, A. H. E. *J. Am. Chem. Soc.* **2003**, *125*, 3260. (b) Wurm, F.; König, H. M.; Hilf, S.; Kilbinger, A. F. M. *J. Am. Chem. Soc.* **2008**, *130*, 5876. (c) Cheng, L.; Zhang, G.; Zhu, L.; Chen, D.; Jiang, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 10171. (d) Walther, A.; André, X.; Drechsler, M.; Abetz, V.; Müller, A. H. E. *J. Am. Chem. Soc.* **2007**, *129*, 6187. (e) Nie, L.; Liu, S.; Shen, W.; Chen, D.; Jiang, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 6321.

(6) (a) Dendukuri, D.; Pregibon, D. C.; Collins, J.; Hatton, T. A.; Doyle, P. S. *Nature Mater.* **2006**, *5*, 365. (b) Nie, Z.; Li, W.; Seo, M.; Xu, S.; Kumacheva, E. *J. Am. Chem. Soc.* **2006**, *128*, 9408. (c) Nisisako, T.; Torii, T.; Takahashi, T.; Takizawa, Y. *Adv. Mater.* **2006**, *18*, 1152. (d) Nisisako, T.; Torii, T. *Adv. Mater.* **2007**, *19*, 1489. (e) Kim, S. H.; Jeon, S. J.; Jeong, W. C.; Park, H. S.; Yang, S. M. *Adv. Mater.* **2008**, *20*, 4129. (f) Shah, R. K.; Kim, J. W.; Weitz, D. A. *Adv. Mater.* **2009**, *21*, 1949. (g) Prasad, N.; Perumal, J.; Choi, C. H.; Lee, C. S.; Kim, D. P. *Adv. Funct. Mater.* **2009**, *19*, 1656.

(7) (a) Roh, K. H.; Martin, D. C.; Lahann, J. *Nature Mater.* **2005**, *4*, 759. (b) Roh, K. H.; Martin, D. C.; Lahann, J. *J. Am. Chem. Soc.* **2006**, *128*, 6796.

(8) (a) Giersig, M.; Ung, T.; Liz-Marzán, L. M.; Mulvaney, P. *Adv. Mater.* **1997**, *9*, 570. (b) Gu, H.; Zheng, R.; Zhang, X.; Xu, B. *J. Am. Chem. Soc.* **2004**, *126*, 5664. (c) Wang, C.; Xu, C.; Zeng, H.; Sun, S. *Adv. Mater.* **2009**, *21*, 3045.

(9) (a) Sheu, H.; Ei-Aasser, M.; Vanderhoff, J. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 629. (b) Sheu, H.; Ei-Aasser, M.; Vanderhoff, J. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 653. (c) Kim, J. W.; Larsen, R. J.; Weitz, D. A. *J. Am. Chem. Soc.* **2006**, *128*, 14374. (d) Kim, J. W.; Larsen, R. J.; Weitz, D. A. *Adv. Mater.* **2007**, *19*, 2005. (e) Kim, J. W.; Lee, D.; Shum, H. C.; Weitz, D. A. *Adv. Mater.* **2008**, *20*, 3239. (f) Ahmad, H.; Saito, N.; Kagawa, Y.; Okubo, M. *Langmuir* **2008**, *24*, 688.

(10) Hoffmann, M.; Lu, Y.; Schrinner, M.; Ballauff, M.; Harnau, L. *J. Phys. Chem. B* **2008**, *112*, 14843.

(11) Zhang, C.; Ding, S.; Li, J.; Xu, H.; Sun, L.; Wei, W.; Li, C.; Liu, J.; Qu, X.; Lu, Y.; Yang, Z. *Polymer* **2008**, *49*, 3098.

(12) (a) Bu, H.; Rong, J.; Yang, Z. *Macromol. Rapid Commun.* **2002**, *23*, 460. (b) Wei, W.; Yang, Z. *Adv. Mater.* **2008**, *20*, 2965.

(13) (a) Reculusa, S.; Poncet-Legrand, C.; Perro, A.; Duguet, E.; Bourgeat-Lami, E.; Mingotaud, C.; Ravaine, S. *Chem. Mater.* **2005**, *17*, 3338. (b) Perro, A.; Reculusa, S.; Pereira, F.; Delville, M. H.; Mingotaud, C.; Duguet, E.; Bourgeat-Lami, E.; Ravaine, S. *Chem. Commun.* **2005**, 5542. (c) Ge, J.; Hu, Y.; Zhang, T.; Yin, Y. *J. Am. Chem. Soc.* **2007**, *129*, 8974. (d) Nagao, D.; Hashimoto, M.; Hayasaka, K.; Konno, M. *Macromol. Rapid Commun.* **2008**, *29*, 1484.

(14) (a) Im, S.; Jeong, U.; Xia, Y. *Nature Mater.* **2005**, *4*, 671. (b) Han, J.; Song, G.; Guo, R. *Chem. Mater.* **2007**, *19*, 973.