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Published in:
Macromolecular Chemistry and Physics

DOI:
[10.1002/macp.201800267](https://doi.org/10.1002/macp.201800267)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2018

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Yang, Q., Miao, X., & Loos, K. (2018). Fabrication of Nano-Sized Hybrid Janus Particles from Strawberry-Like Hierarchical Composites. *Macromolecular Chemistry and Physics*, 219(19), [1800267].
<https://doi.org/10.1002/macp.201800267>

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Fabrication of Nano-Sized Hybrid Janus Particles from Strawberry-Like Hierarchical Composites

Qiuyan Yang, Xiaoming Miao, and Katja Loos*

Janus nanoparticles possess amphiphilic properties and thus exhibit vast applications in the field of catalysis, drug delivery, displays, and surface/interface stabilizers. Despite several successful approaches, that were developed for micro-sized Janus particle fabrication, the achievement of nano-sized Janus particles is still facing challenges due to the difficulty with nanoscale processing. Here, new options for the preparation of Janus nanoparticles are demonstrated from strawberry-like hierarchical composites with designed surface functional groups for both “satellites” and spherical “core.” The “satellites” of the hierarchical composites can be freely varied, from iron oxide to silica nanoparticles. Results from transmission electron microscopy, fourier transform infrared spectroscopy, and thermal gravimetric analysis measurements clearly prove the successful production of hybrid Janus silica nanoparticles coated by polystyrene and poly(acrylic acid). This technique demonstrates the vast flexibility of the abovementioned technique in terms of size, type, and surface chemistry design of Janus nanoparticles, which thus offers an additional approach to the current synthesis library of hybrid Janus nanoparticles.

1. Introduction

Janus particles, materials with two or more distinct surfaces/shapes in one particle and thus anisotropic properties, attracted great interest in various fields including catalytic applications,^[1,2] drug delivery,^[3] and display technologies.^[4,5] They are particularly found to work as effective solid surfactants for stabilizing polymer blends, emulsions, etc.^[6–10] In this regard, several approaches were developed for the fabrication of Janus particles with different sizes, shapes, and also surface chemistry. Although self-assembly

methods and surface nucleation strategies were proposed for the synthesis of organic^[11,12] and inorganic nano-sized Janus particles (JPs),^[13,14] respectively, nano-sized hybrid Janus particles are still challenging to achieve due to technical difficulties of nano-scale processing.

In our previous work, a masking strategy was proposed to prepare Janus particles by the embedding of rigid “satellites” on soft spherical polymeric “cores” using carbon dioxide (sc CO₂) (Scheme 1).^[15] The ratio between two distinct surfaces was tunable with proper control on the embedding degree of the “satellites” on the soft “core.” Ideally, the sizes of both the “core” and the “satellites” can be varied over a wide range according to the practical needs. However, so far the size of Janus particles achieved was limited to macro-sized objects being dependent on the degree of “satellites” immersing into the substrate. With a further

investigation on surface movement of polystyrene (PS) in sc CO₂, we were able to show that the embedding depths are controllable even in a range from several to tens nanometer,^[16] providing the possibility to design JPs on the nano-scale.^[17] Here, as a further proof of concept, sub-20 nm sized hybrid JPs were particularly fabricated via the similar strategies. Two coupling strategies are further shown here from tunable surface functionalized nanoparticles, proving the great flexibility of above mentioned technique for the design of JPs.

2. Results and Discussion

Hierarchical composite structures with spherical “cores” and “satellites” were employed for the embedding of nanoparticles in this system (Scheme 1), in which case “satellites” and soft “core” can be easily tuned. For instance, in addition to previously reported gold nanoparticles (NPs) coated silica Janus particles,^[15] magnetic silica Janus particles (500 nm) can also be achieved with simply taking place of the gold NPs by magnetic Fe₃O₄ NPs, as shown in Figure 1. Results from magnetization measurements indicate that the obtained Janus particles demonstrate superparamagnetic properties, with which Janus particles are expected to be stimuli-responsive when external fields are applied.^[18–22] Although the preparation of micrometer-sized magnetic JPs is out of our scope in this paper, it is interesting to notice that Janus particles demonstrated different morphologies with the variation of dispersing solvents. As shown in

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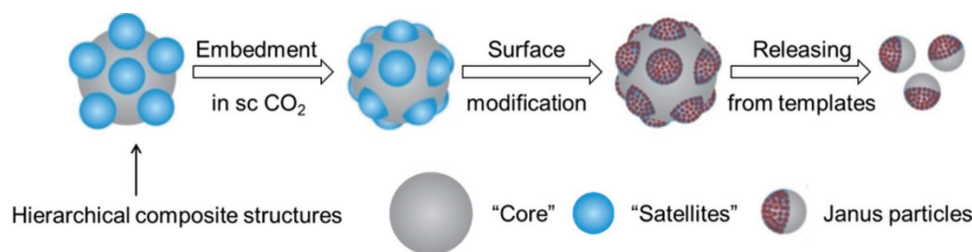
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DOI: 10.1002/macp.201800267



Scheme 1. The strategy to fabricate Janus particles from hierarchical composite structures.^[15,17]

Figure 1b,c, one hemi-surface of Janus particles was found to be coated with a layer of polymers when samples were dried from DMF. However, local aggregation of PS, exhibited as pitch-like morphology, was formed on the same hemisphere of Janus particles while an antisolvent of PS (such as water in Figure 1e,f) was present during the preparation of samples for imaging. Such results provided one direct proof that PS was successfully coated on the embedded site “satellites” after the removal of PS templates. In other words, directly releasing the embedded “satellites” from the PS “core” templates without any further surface modification on the exposed surface can still achieve JPs, which are solely coated by PS on one hemisphere.

Motivated by such positive results and the previous work that proved the possibility to control the embedding depth of “satellites” on the PS substrate in the scale of sub-ten nanometers,^[17] we had the ambition to prepare much smaller Janus particles, like tens or even several nanometers nanoparticles. In such cases, the surface chemistry of “satellites” and “core” plays a key role for the preparation of hierarchical composites and the

further structure design of Janus nanoparticles. Proper playing on them provides various possibilities. The materials of “satellites” are thus also not only limited to silica. **Figure 2a,b** demonstrated two trial coupling strategies for the design of JPs with adjustment on the surface chemistry of the Fe_3O_4 NPs “satellites” and soft PS “core” (200 nm). Two types of Fe_3O_4 NPs functionalized with $-\text{NH}_2$ or $-\text{CHO}$ groups were synthesized based on ligand exchange methods (detail synthesis methods and related results can be found in supporting information).^[23,24] TEM images inset in the left part of Figure 2 show their size are homogeneously distributed in the range of 6–7 nm. Typical absorption peaks of C=O stretch at 1712 cm^{-1} , N–H bend at 1602 cm^{-1} , and N–O absorption at 1283 cm^{-1} were observed from fourier transform infrared spectroscopy (FTIR) spectra in Figure 2c, indicating the successful ligand exchange of $-\text{NH}_2$ or $-\text{CHO}$ groups from oleate (OA) onto Fe_3O_4 NPs. The ligand coverage on Fe_3O_4 NPs close to $0.87\text{--}1.01\text{ nm}^{-2}$ was calculated based on the thermal gravimetric analysis (TGA) results in Figure S5, Supporting Information (details on quantification

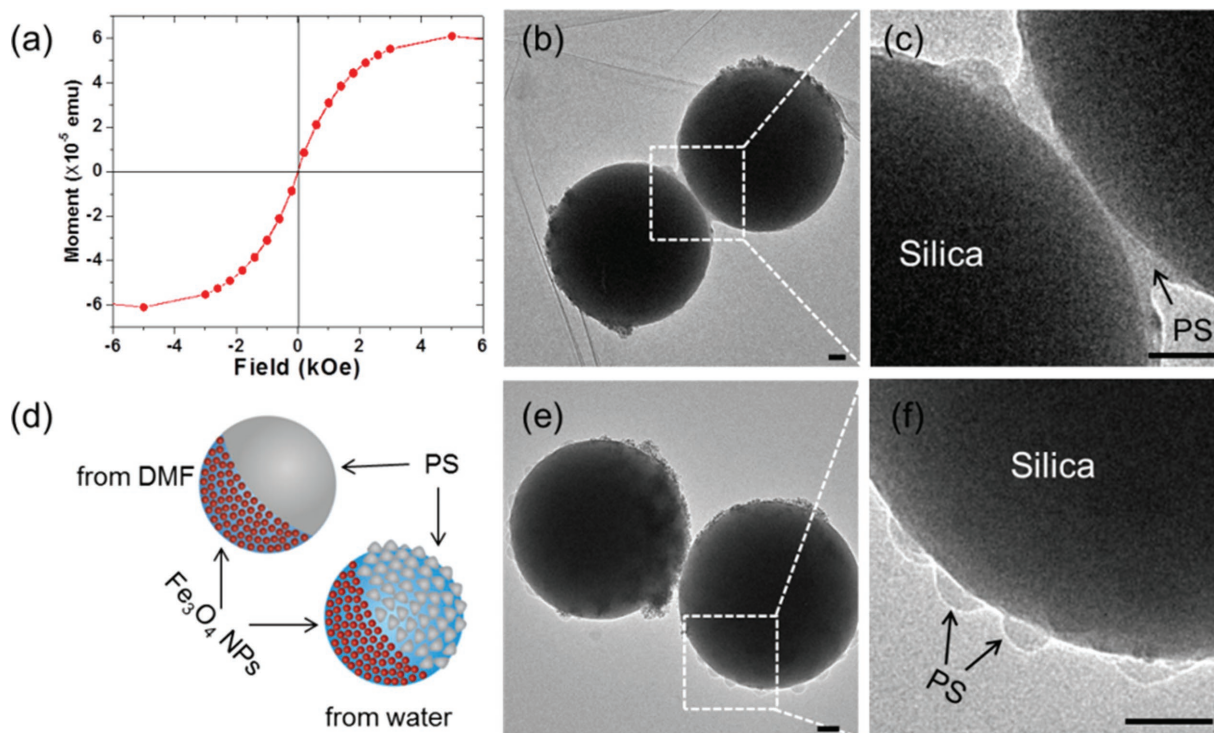


Figure 1. a) Magnetic properties b,c,e,f) TEM images, and d) cartoon of Fe_3O_4 nanoparticle coated SiO_2 JPs: (b,c) samples dried from DMF; (e,f) samples dried from water. Scale bar: 50 nm.

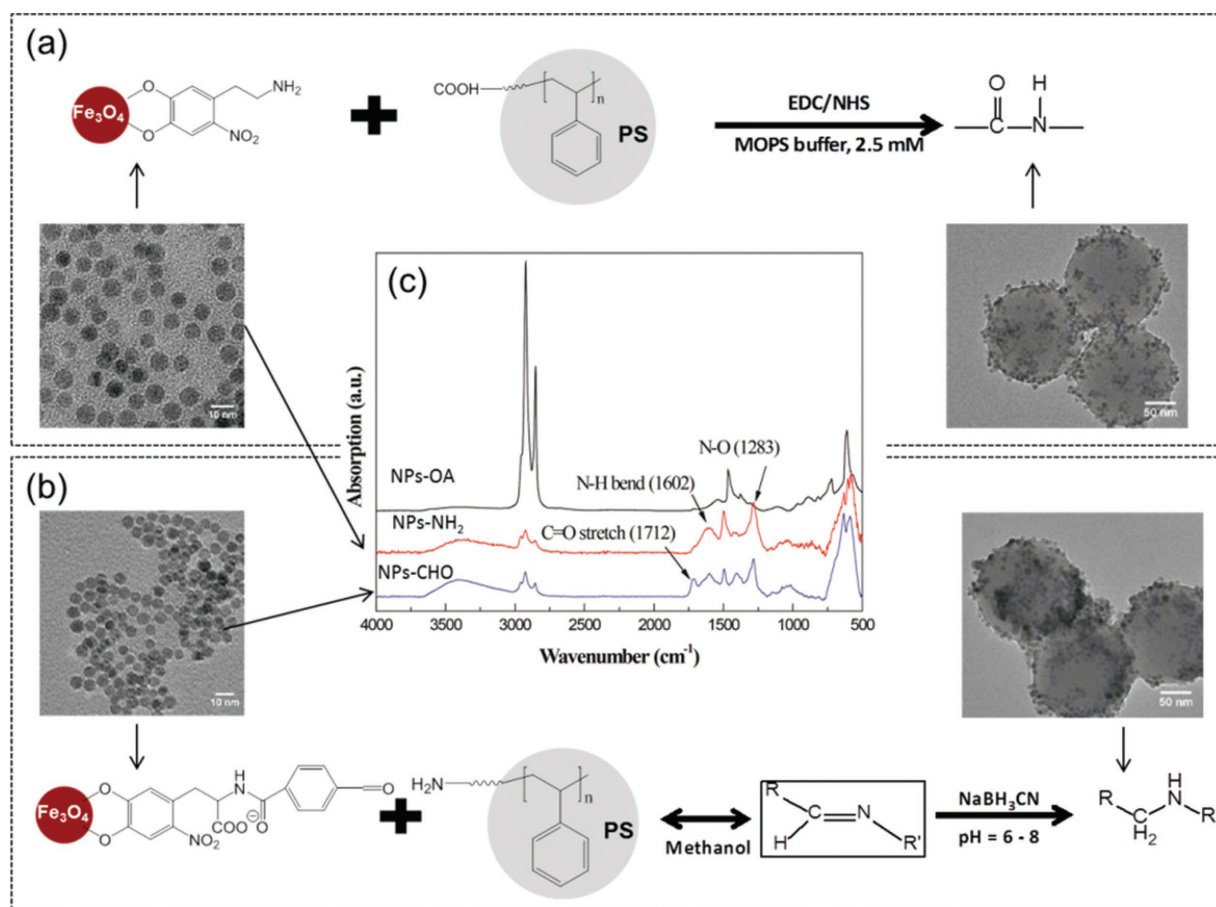


Figure 2. a) Coupling reaction of nitrodopamine anchored iron oxide nanoparticles (left TEM image) and 200 nm -COOH surface functionalized PS spheres; (right inset) TEM image shows the successful coupling. b) Coupling reaction of -CHO groups anchored iron oxide nanoparticles (left TEM image) with 200 nm NH₂ surface functionalized PS spheres; (right inset) TEM image are the coupling results. c) FTIR spectra of iron oxide nanoparticles with different surface functional groups of OA, -NH₂, and -COOH ligands.

methods of the ligand density on iron oxide nanoparticles can be found in the supporting information). In the case of -NH₂ group-functionalized Fe₃O₄ NPs, a carbodiimide-assisted reaction was conducted to couple with -COOH surface functionalized PS spheres (Figure 2a). Another alternative reaction between -CHO and -NH₂ groups was also possible in the presence of reductive agent, like sodium cyanoborohydride (Figure 2b). The right inset TEM images in Figure 2a,b demonstrated the successful adsorption of Fe₃O₄ NPs on the surface of PS spheres in both cases, confirming the flexibility to achieve hierarchical composites even on micro scale.

As one way to achieve nano-sized JPs from smaller sized strawberry-like hierarchical composites, in addition to previously reported PS and PVP-coated JPs,^[17] in Figure 3, we showed another example of successful fabrication of amphiphatic JPs functionalized by poly(acrylic acid) (PAA) and PS on their two sides, respectively. In this case, -NH₂ surface-functionalized silica NPs with an average size of 10 nm were firstly coupled and subsequently embedded onto 200 nm PS microspheres at sc CO₂. The exposed surface of the silica particle was subsequently coupled to PAA chains via carbodiimide-based reactions. After dissolving the PS templates, hybrid Janus silica NPs coated by PAA and PS—on the respective sides—were

successfully synthesized. The TEM image in Figure 3c clearly shows the hybrid structure of the produced silica JPs coated by PAA and PS on its two opposite hemi-surfaces. The dark closed packed dots on the silica JPs (right side in Figure 3c) are contributed to randomly reacted PAA, and the low contrast coating on the left side are PS chains detached from the PS template.

FTIR spectra of the JPs in Figure 4a exhibit both an absorption peak of C=O stretches of PAA in the wavenumber range from 1700 to 1750 cm⁻¹ and absorptions peaks of the benzene rings in the region of 1400–1600 cm⁻¹ contributed to PS, confirming the presence of both PAA and PS onto hybrid silica JPs. The composition of PAA, PS, and silica NPs in JPs can be further verified by the TGA measurements (Figure 4b). The total weight loss of Janus silica nanoparticles is higher as compared to that of the nanoparticles solely modified by PS and also the bare silica particles, suggesting the presence of both PS and PAA chains after modification. The weight loss of PS is calculated to be 15.8% from the TGA measurements (Figure 4b), which is much higher than 11.0% of PAA, indicating a higher mass loading of PS than PAA on the surface of JPs. Considering the fact that the molecular weight of the PS template (as measured by GPC in DMF, Figure S6 and Table S1, Supporting Information) is even a bit smaller than that of PAA

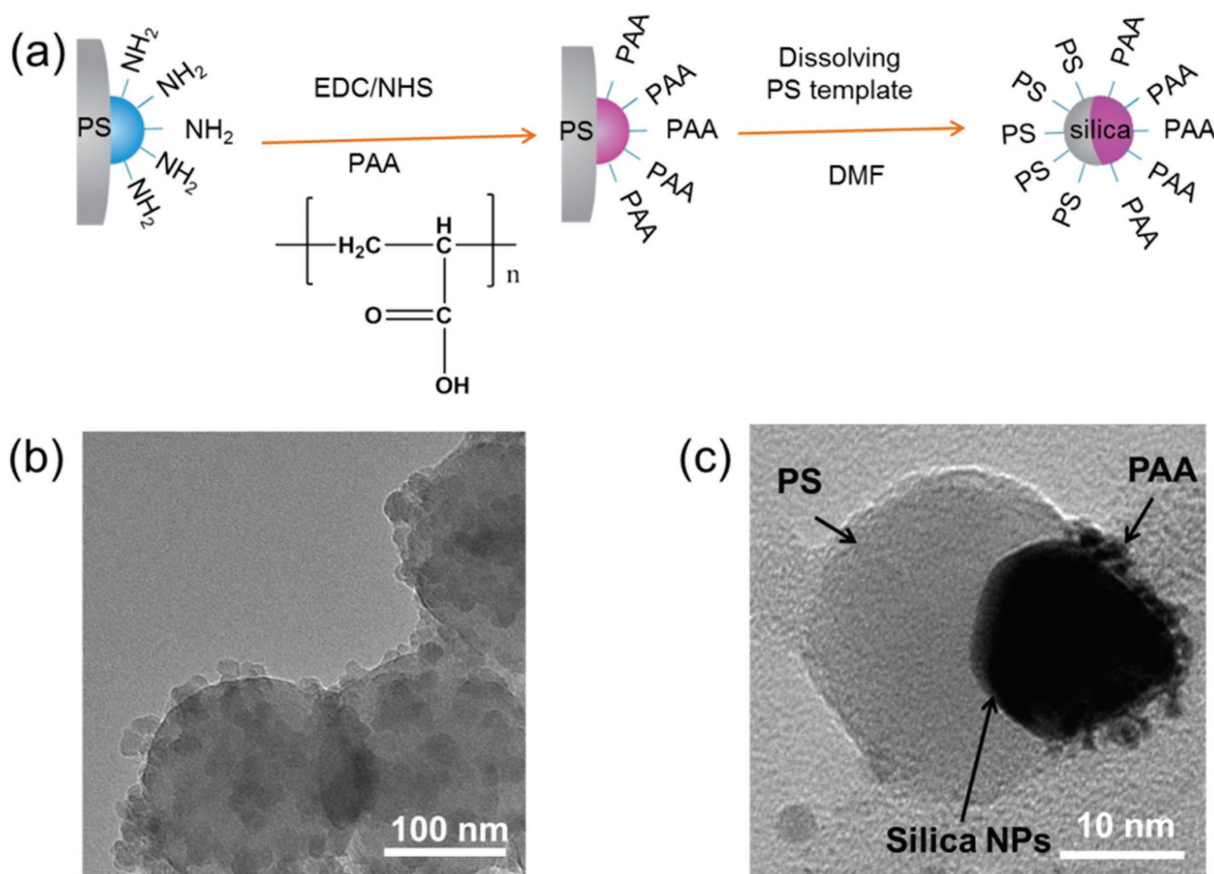


Figure 3. a) Scheme for the fabrication of nano-sized JPs coated by PAA and PS on its two opposite hemi-surfaces; b) TEM image of $\text{SiO}_2\text{-NH}_2$ particles embedded on the PS spherical templates; c) TEM of Janus PS- SiO_2 -PAA nanoparticles with PS (right, lighter part) and PAA (left, dark dots) modified on two sides.

(average $M_w \approx 100,000$) and that the embedding depth is supposed to be 3–4 nm under the embedding treatment condition of 40 °C, 60 bar for 140 min,^[16] that is, no more than the half area of silica nanoparticles was coated by PS, the lower amount of PAA molecules coating on the silica surfaces is due to the higher amount of functional $-\text{COOH}$ groups per PAA chain involved in the reaction with silica surfaces than that of solely surface-functionalized PS spheres.

3. Conclusions

In summary, a strategy from strawberry-like hierarchical composites for fabrication of nano-sized silica hybrid JPs was demonstrated with an embedding treatment on soft PS “cores” and a subsequent surface modification treatment. Several examples demonstrate great flexibility of the provided strategy in the design of JPs with various sizes (from micro to nano), materials

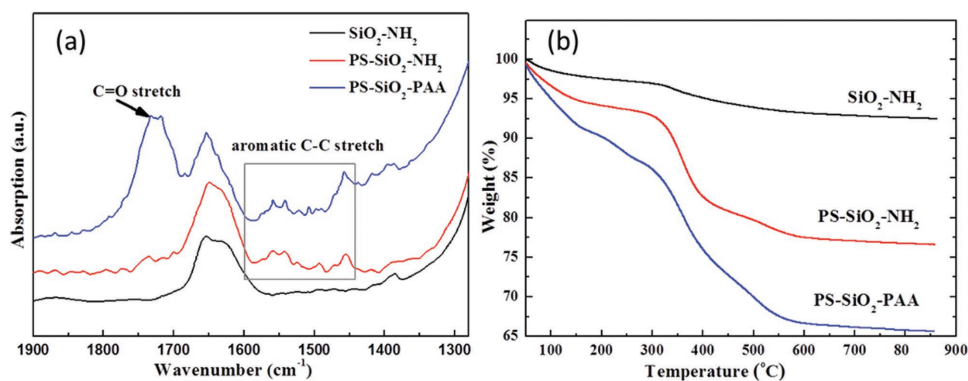


Figure 4. a) FTIR spectra and b) TGA curves of as synthesized silica nanoparticles with different surface functionalization, including amino groups functionalized silica, PS-coated nano-sized silica JPs, and both PAA- and PS-coated silica JPs.

(iron oxide or silica nanoparticles), and surface chemistries via such a technique. As another proof of concept, nano-sized Janus particles coated by PS and PAA on each side were achieved, of which the Janus structure were further proven by TEM, FTIR, and TGA measurements. Therefore, the fabrication approach of nano-sized Janus particles from strawberry-like hierarchical composites offers various possibilities to achieve structures for different applications in polymer blending, pickering emulsion, drug delivery, etc.

4. Experimental Section

Materials: Aqueous suspensions of 200 nm polystyrene microspheres functionalized with carboxyl and amine groups (2.6 w/v%) were obtained from Polyscience Inc. N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC, protein seq. grade), N-hydroxysuccinimide (NHS, 98%), 3-(N-morpholino)propanesulfonic acid (MOPS), poly(acrylic acid) solution (average Mw \approx 100,000, 35 wt% in H₂O), sodium chloride (>99.0%), iron(III) chloride (>99.0%), oleic acid (>99.0%), sodium nitrite, dopamine, dopa, sulfuric acid, 4-formylbenzoic acid, sodium hydroxide, and hydrochloric acid were purchased from Sigma-Aldrich. Hydrophilic polycarbonate membrane filters (pore size 100 nm with diameter 47 mm) were purchased from Sterlitech Corporation. All solvents were of analytical grade.

Adsorption of Silica Nanoparticles on PS Template: An excess amount of silica-NH₂ spheres were dispersed in 10 mL MOPS buffer (pH = 6.4, 0.025 M) and then the PS-COOH spheres were added to the solution.^[15,17] This suspension was sonicated for approximately 10 min to completely mix the spheres. 0.1 g EDC and 0.03 g NHS in 10 mL of MOPS buffer (pH = 6.4, 0.025 M) was then added to the mixture, followed by slow rotation for 24 h. The colloidal solutions were centrifuged and washed with water several times to remove unreacted chemicals, followed by a filtration treatment using hydrophilic polycarbonate membranes with pore sizes of 0.1 micron to remove excess silica particles.

Adsorption of Iron Oxide Nanoparticles on PS Template: Synthesis of iron oxide nanoparticles was synthesized using a modified literature method.^[23] Detail information can be found in the supporting document. Hierarchical composites based on the coupling of -COOH-functionalized PS templates (200 nm, 10 μ L, 2.6 w/v%) with -NH₂-functionalized iron oxide NPs (\approx 7 nm, 50 μ L, 1 mg mL⁻¹) were prepared via the same method as for the PS/silica system. The other coupling between -NH₂-functionalized PS spheres (200 nm, 30 μ L, 2.6 w/v%) with -CHO-functionalized iron oxide NPs (\approx 7 nm, 1.5 mL, 0.3 mg mL⁻¹) was performed in a total amount of 1.8 mL methanol with 20 mg sodium cyanoborohydride by shaking for several hours.

Embedding Treatment of Hierarchical Composites: As-prepared samples with hierarchical structures were first added to the cylinder (50 mL). The temperature was then set to the desired value by heating the controller (Eurotherm controller, The Netherlands) and the setup was refreshed with CO₂ for at least 10 s to flush the air out; after this CO₂ was added using a membrane pump (Lewa, USA) to the cylinder until the desired pressure was reached. After keeping the sample inside CO₂ for a certain time, the pressure was slowly released by venting and the sample was kept for further analysis.^[15-17] sc CO₂ treatment conditions for the smaller hierarchical system with 200 nm PS "cores" and nano-sized "satellites" and the bigger ones with 10 μ m PS "cores" and 500 nm silica particles were 40 °C, 60 bar for 140 min and 60 °C, 126 bar for 480 min, respectively.

Preparation of PS- and PAA-Coated JPs: Twenty milligrams of embedded PS/silica hierarchical composites was first mixed with extra amount PAA in 15 mL MOPS buffer (pH = 6.0, 2.5 mM) by sonicating for 15 min. Ninety milligrams of EDC and 54 mg NHS dispersed in 15 mL MOPS buffer (pH = 6.4, 2.5 mM) were subsequently added into the mixture, followed by stirring for 24 h. Samples were washed several

times with water, centrifuged, and dried under vacuum overnight and then dissolved in DMF to remove the PS templates.

Characterization: Transmission electron microscopy (TEM) was carried out on a Philips CM12 transmission electron microscope operating at an accelerating voltage of 120 kV. A droplet of diluted sample was dried on carbon-coated copper grid for imaging. TGA measurements were performed on a Perkin-Elmer thermogravimetric analyzer under air atmosphere in a temperature range of 50–800 °C and with a heating rate of 10 °C min⁻¹. FTIR measurements were performed using KBr pellets in VACUO in transmission mode on a Bruker FIS88 spectrometer with a DTGS detector in the range of 4000 and 700 cm⁻¹ at a resolution of 4 cm⁻¹.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by the Netherlands Organization for Scientific Research (NWO) and the China Scholarship Council. The authors greatly appreciate Piotr Nowak for the discussion and suggestions on the synthesis of iron oxide nanoparticles.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

hierarchical composites, hybrid materials, Janus nanoparticles, magnetic properties, masking techniques

Received: June 22, 2018
Revised: August 5, 2018
Published online: September 6, 2018

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