

## Selective surface reactions for Janus ORMOSIL particles with multiple functional groups using an ordered monolayer film at liquid–liquid interface

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### ABSTRACT

Monodispersed, submicron-sized Janus ORMOSIL particles with multiple functional groups were prepared by the selective surface reaction of a monolayer film formed at a hexane–water interface. A well-ordered monolayer film was obtained by self-assembly of ORMOSIL particles with multiple functional groups at hexane–water interface. The photopolymerization of an ordered monolayer containing ORMOSIL particles yields a rigid film strong enough to maintain its integrity for transfer and further chemical reaction. The chemical reaction of this ordered film with organic and inorganic functional groups produced Janus ORMOSIL particles with multiple functional groups. The morphologies, structures, and chemical compositions of monolayer films and Janus ORMOSIL particles were characterized by FT-IR, solid state NMR, X-ray diffraction (XRD), optical microscopy (OM), electron microscopies (SEM and TEM), and confocal laser scanning microscopy.

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### 1. Introduction

Monodispersed colloidal particles with multiple functionalities and submicron sizes have potential for use in various types of industrial materials [1–3] and biological applications [4–6]. To be suitable for these applications, colloidal particles must possess specific chemical and physical properties such as controlled structures and chemical compositions. Several techniques have been developed for synthesizing a variety of submicron particles with proper structures and compositions, including core–shell synthesis, layer-by-layer techniques, multi-block polymer emulsifications, and surface modifications [7–11]. Colloidal silica particles have been extensively studied, as they can be easily synthesized with controlled sizes and shapes [12–14]. Organically modified silica (ORMOSIL) particles are hybrid materials that can be prepared by surface modification of silica particles from tetraethylorthosilicate (TEOS) or using an organo-silane monomer as a starting material [15,16]. However, these ORMOSIL particles usually contain only a single type of functional group. Therefore, multiple sequential modification steps must be employed to attach multitasking components such as imaging components, or drugs and targeting moieties. For wider biological applications, the development of a

simple and efficient preparation method for particles with various functionalities is of great importance.

Multiple functionalities of colloidal particles can also be provided by asymmetry in shape and/or chemical composition of the particles. Janus particles, which were first mentioned by de Gennes in 1991, are asymmetric and usually exhibit different physical/chemical properties on opposite sides [17]. Their asymmetric dual functionality makes them effective as solid surfactants in emulsion stabilization, imaging/targeting/delivery probes and sensors in biochemical applications, and as photonic or display materials in electronic devices, as well as making them good building blocks for complex structures [18–24]. Janus particles are generally prepared by direct syntheses or indirect chemical or physical modifications. Micro-fluidic methods, electrohydrodynamic jetting, and self-assembly of block copolymers are typical direct synthetic routes, while indirect chemical and physical modifications involve gel trapping methods, metal sputtering, and Pickering emulsion methods [25–32]. Although excellent control of shape and anisotropic features can be achieved using these methods, the submicron-size region is not readily accessible, and an inability to load chemical and biological components such as dyes, drugs, and image contrasting agents limits their use in biochemical applications. Therefore, the multiple chemical functionalities of Janus particles provide a great opportunity but raise significant challenges in the precise control of the dimensions, morphologies, and physicochemical properties of these asymmetric particles.

In this study, we describe the synthesis and the formation of an ordered monolayer with ORMOSIL particles with multiple

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functional groups, the photo-polymerization of a monolayer to generate a rigid film, and finally, the preparation of Janus particles using an asymmetric synthesis method. The synthetic method described in this study is very simple and produces monodispersed Janus ORMOSIL particles with homogeneously distributed multiple functional groups inside and outside of spherical particles. These Janus ORMOSIL particles are not only the first example of Janus particles with multiple functional groups, but also can be further modified by the simple surface reaction to provide versatile materials in nano- and bio-applications such as multicolor imaging, signal amplification, self-assembly to ordered structures, and multiplex tasking.

## 2. Experimental

### 2.1. Materials

Phenyltrimethoxysilane [PTMS] (94%, Aldrich), 3-mercaptopropyltrimethoxysilane [MPTMS] (97%, Fluka), 3-aminopropyltrimethoxysilane [APTMS] (99%, Aldrich), silver nitrate (99.8%, Junsei), iron (II) sulfate heptahydrate (98%, Sam Chun Chemicals), and hydrazine monohydrate (80%, Sam Chun Chemicals) were used without further purification. Ammonium hydroxide solution (30 wt.% as  $\text{NH}_3$ ), nitric acid (60%), hexane (95%), and methylmethacrylate [MMA] (99%) were obtained from Sam Chun Chemicals.

### 2.2. Preparation of ORMOSIL particles with tri-functional groups (phenyl, amine, and mercapto functionalities)

A 250-mL three-neck flask maintained at 40 °C was charged with 150 mL of deionized water, and 0.2 mL of nitric acid (2.67 mmol, 60 wt.%) was added while stirring at 300 rpm. 5 mL of PTMS (24.89 mmol) was injected into an acidic aqueous solution, followed by the addition of 0.5 mL APTMS (2.75 mmol) and 0.5 mL MPTMS (2.57 mmol). The resulting solution was stirred for 1 min to initiate the hydrolysis reaction, and then 40 mL of ammonium hydroxide (305 mmol, 30 wt.%) was added to induce condensation. The resulting solution became turbid and was stirred for an additional 4 h. The ORMOSIL particles with multiple functional groups obtained were filtered through a membrane filter and washed with 10 mL of deionized water and 10 mL of ethanol several times. The filtered particles were dried under vacuum and 2.8 g of ORMOSIL particles with phenyl–amine–thiol functional groups were obtained.

### 2.3. Preparation of a rigid monolayer film of ORMOSIL particles at a hexane–water interface

We added 400 mL of de-ionized water and 5 mL of hexane to a 500-mL beaker, and 0.3 g of ORMOSIL particles with phenyl, amine, and mercapto functional groups was dispersed in 5 mL of ethanol. Upon slow injection of 0.05 mL ethanol solution containing ORMOSIL particles into a hexane–water interface, the ORMOSIL particles were immediately diffused into the water phase and then a monolayer of ORMOSIL particles was formed at the interface within 10 min. After the formation of the ordered monolayer, 1 mL of an MMA monomer solution, prepared by mixing 1 mL of hexane, 9 mL of MMA, and 0.1 g of benzoyl peroxide, was slowly introduced into the upper layer of hexane. After photochemical polymerization of the MMA monomers using a UV lamp (1 kW, mercury lamp) for 30 min, a rigid monolayer film of ORMOSIL particles coated with PMMA was obtained.

### 2.4. Asymmetric synthesis for Janus ORMOSIL particles coated with metal nanoparticles

To the water phase of interface where a rigid monolayer film of ORMOSIL particles coated with PMMA was formed, 5 mL of de-ionized water containing silver nitrate (0.1 g, 0.59 mmol) was added, and then the reaction temperature was raised to 80 °C. After 2 h of aging to insure the attachment of Ag (I) ions onto the thiol functional groups in the ORMOSIL particles, the monolayer film was transferred onto a freshly prepared water phase using a glass substrate. To the water phase, added 5 mL of de-ionized water containing 0.05 mL of hydrazine monohydrate as a reducing agent for the reduction in silver ions. Finally, the monolayer film of Ag-coated Janus ORMOSIL particles was moved to another water phase using a glass substrate, and the monolayer film was sonicated for 10 min. The disassembled Janus ORMOSIL particles were filtered through a membrane filter and washed with 10 mL of deionized water several times. The filtered particles were dried under vacuum, and Ag-coated Janus ORMOSIL particles were obtained.

### 2.5. Asymmetric synthesis for Janus ORMOSIL particles coated with inorganic oxide nanoparticles

After the formation of a rigid monolayer film of ORMOSIL particles coated with PMMA at the interface, 5 mL of de-ionized water containing iron(II) sulfate heptahydrate (0.163 g, 0.59 mmol) was added to the water phase by syringe, then the reaction temperature was raised to 80 °C. After 2 h of aging to insure the attachment of Fe (II) ions onto the thiol functional groups in the ORMOSIL particles, the monolayer film was transferred onto a freshly prepared water phase using a glass substrate. Then, the solution of 0.05 mL of hydrazine monohydrate (80%) in 5 mL of water was added to water phase slowly, and the resulting reaction mixture was kept at room temperature for an hour. Finally, the monolayer film of  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ -coated Janus ORMOSIL particles was moved to another water phase using a glass substrate, and the monolayer film was sonicated for 10 min. The disassembled Janus ORMOSIL particles were filtered through a membrane filter and washed with 10 mL of deionized water several times. The filtered particles were dried under vacuum, and  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ -coated Janus ORMOSIL particles were obtained.

### 2.6. Characterizations

A Fourier transform infrared spectrometer (FT-IR, AAB FTLA 2000) and nuclear magnetic resonance spectrometer (NMR, Varian Unity Inova 300 and Bruker Avance 400) were used for the chemical characterization. An X-ray powder diffractometer (XRD, Rigaku, D/RAD-C diffractometer with  $\text{Cu K}\alpha$  radiation) was used to investigate the structures of the ORMOSIL particles after the asymmetric reaction. The sizes and morphologies of the ORMOSIL particles, monolayer films, and Janus ORMOSIL particles were examined with optical microscopy (OLYMPUS, BX51), field emission scanning electron microscopy (FE-SEM, JEOL JEM-6340F), and transmission electron microscopy (TEM, JEOL EM-2000EXII).

## 3. Results and discussion

Monodispersed, submicron-sized ORMOSIL particles having three different functional groups were synthesized by a simple one-pot method, and a well-ordered monolayer film made up of these ORMOSIL particles was prepared using a self-assembly process at the interface between water and hexane. To obtain a rigid monolayer film, photochemical polymerization of the methyl-

methacrylate monomers onto a monolayer formed with ORMOSIL particles was carried out by injecting the monomers into the top hexane layer. This polymeric network of poly-methyl-methacrylate (PMMA) was strong enough to maintain the morphology of the monolayer film even when subjected to small disturbances such as stirring, agitation, and reflux. Monolayer films of ORMOSIL particles with a rigid network have been used as templates for the asymmetric synthesis of Janus particles. Different types of Janus ORMOSIL particles such as organic–inorganic and organic–metallic biphasic colloidal particles were prepared by selective surface chemical modification of ORMOSIL particles at a liquid–liquid interface. The entire synthetic process for the formation of a monolayer film with ORMOSIL particles and the preparation of Janus ORMOSIL particles are presented in Scheme 1.

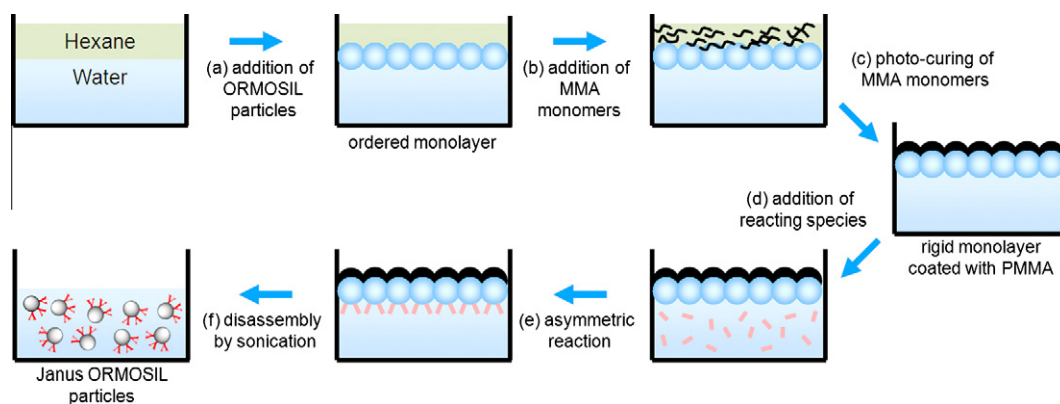
The monodispersed ORMOSIL particles with triple functional groups used in this study were synthesized using a two-step acid-base/hydrolysis-condensation process. A structural drawing and SEM image, as well as the spectroscopic data for the ORMOSIL particles with tri-functional groups (phenyl, thiol, and amine functionalities) are shown in Fig. 1. As shown in the SEM image, ORMOSIL particles with phenyl–amine–mercapto functional groups exhibit mono-dispersity and spherical morphologies. The IR spectra of these ORMOSIL particles exhibited characteristic stretching vibrational absorption peaks for the corresponding functional groups. For the phenyl, amine, and mercapto tri-functional ORMOSIL particles,  $\nu(\text{C}=\text{C})$ ,  $\nu(\text{S}-\text{H})$ , and  $\nu(\text{N}-\text{H})$ , stretching vibrational absorption peaks from each functional group were observed at 3100, 2550, and 3300  $\text{cm}^{-1}$ , respectively. Solid-state  $^{13}\text{C}$  NMR analysis also showed typical carbon resonance peaks for corresponding functional groups. For phenyl-, amine-, and mercapto-based ORMOSIL particles, strong absorption peaks near 135 ppm were observed from unsaturated carbons, while aliphatic carbon peaks between 0 and 50 ppm were observed for propyl–amine and propyl–mercapto functional groups. The solid-state  $^{29}\text{Si}$  NMR spectrum showed peaks at 78.1 and 69.4 ppm, indicating that the main structure of the ORMOSIL particles consisted of  $\text{T}^2$  and  $\text{T}^3$  networks.

An ordered monolayer of ORMOSIL particles with multiple functional groups was prepared using a self-assembly process at the hexane/water interface as shown in Scheme 1a. A colloidal dispersion of ORMOSIL particles in an ethanol solution was injected slowly at the interface. The ethanol suspension of ORMOSIL particles diffused into the liquid–liquid interface and then formed a self-assembled monolayer with a two-dimensionally ordered structure. Li et al., had prepared a monolayer of hydrophilic nanoparticles at an interface between toluene and water using ethanol as an induction solvent [33]. In this study, the ethanol was also used as a transfer medium for the colloidal particles at the interface

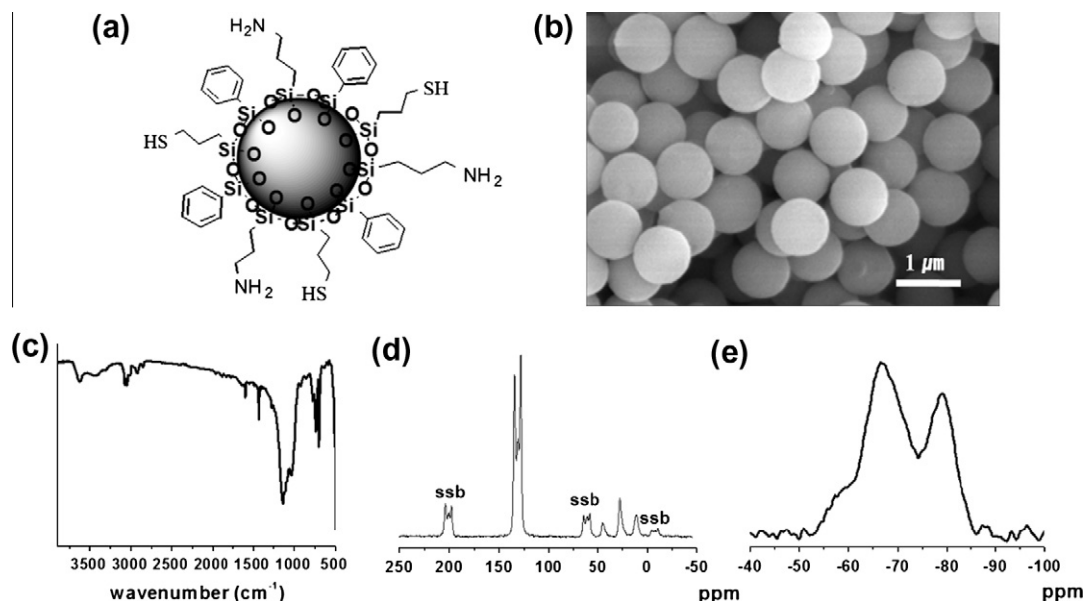
because of its miscibility to both hexane and water. The effect of the transfer medium on the formation of the monolayer was investigated. Irregularly shaped layers of ORMOSIL particles were formed when methanol was used instead of ethanol. An ordered monolayer was obtained when 2-propanol was used; however, some portion of the monolayer was covered by double or triple layers of small numbers of ORMOSIL particles (Supporting information). The greater miscibility of methanol to water than ethanol made the ORMOSIL particles diffuse further into the water phase, producing a layer of stacked ORMOSIL particles. The addition of lyophilic 2-propanol moved some ORMOSIL particles into the hexane layer, causing a number of the ORMOSIL particles to stack on the top of the monolayer. The top layer of hexane also had an important effect on the formation of an ordered monolayer. Only when hexane was used as a top layer could a two-dimensionally ordered monolayer be prepared. The difference in surface tension between hexane and ORMOSIL particles caused them to be regularly ordered at the interface (see Supplementary material).

In the next step, photochemical polymerization of the methyl-methacrylate monomers was carried out on the top surface of the ordered monolayer of ORMOSIL particles prepared at a liquid–liquid interface as shown in Scheme 1b and c. The ordered monolayer of ORMOSIL particles that was formed at the hexane–water interface by a self-assembly process was still labile, so the particles could rotate and move freely at the interface. To perform additional asymmetric chemical reactions for Janus particles, ORMOSIL particles in an ordered monolayer must be inert with respect to rotational and vibrational motion. The gel trapping technique and the LB film method are widely used to freeze the positions of the particles in a monolayer [25,26]. However, these methods are rather complicated and require a long preparation time. Compared to these methods, the photochemical polymerization used in this study is simple and convenient. Optical microscopy (OM) and SEM images of the rigid ordered monolayer films after a photochemical polymerization are shown in Fig. 2.

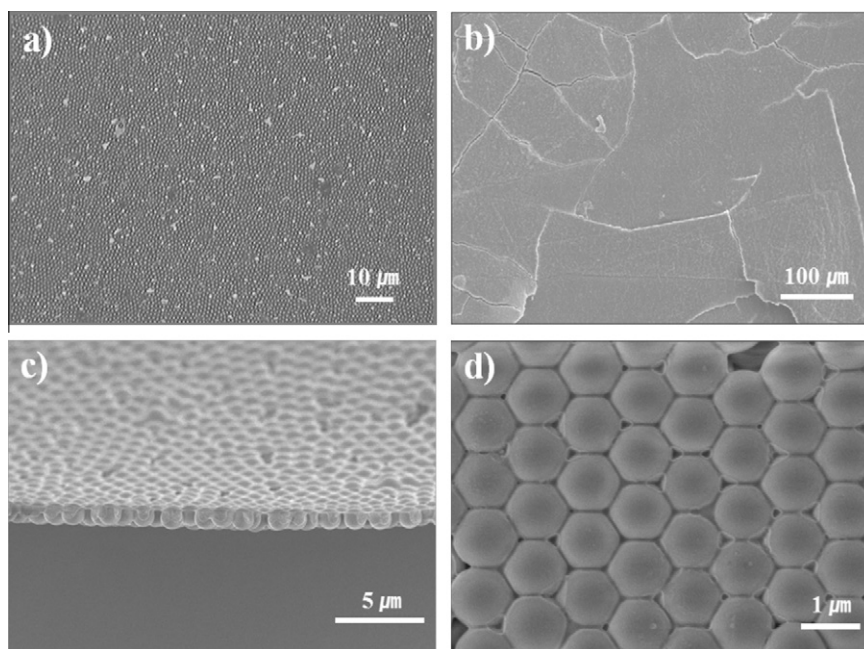
Perfectly ordered ORMOSIL particles with hexagonal structures were obtained with a single layer of stacking. To make a rigid monolayer by photochemical polymerization, a hexane solution of methyl-methacrylate monomers and an initiator were slowly added to the top hexane layer after the formation of an ordered monolayer of ORMOSIL particles. Then, UV light was irradiated onto the monolayer prepared at the liquid–liquid interface, where the formation of a poly-methyl-methacrylate (PMMA) film on top of the ordered monolayer resulted. The photochemically cured monolayer film was rigid enough to carry out further chemical reactions even with stirring or heating at high temperature. A PMMA film formed on the top of an ordered monolayer can be easily removed by simple sonication after further asymmetric chemical reactions if



**Scheme 1.** Formation of monolayer film of ORMOSIL particles and asymmetric reaction for Janus particles.



**Fig. 1.** (a) Structure drawing, (b) SEM image, (c) IR, CP/MAS (d)  $^{13}\text{C}$  NMR, and (e)  $^{29}\text{Si}$  NMR spectra of ORMOSIL particles with three different functional groups.



**Fig. 2.** OM and SEM images of an ordered monolayer film with ORMOSIL particles with different magnifications: (a) OM image and (b–d) SEM images.

needed. On the other hand, it was strong enough to maintain its integrity while being transferred to another interface using a glass substrate. When ORMOSIL particles with methyl-methacrylate functional groups were used, the photochemical polymerization produced a rigid monolayer film through a side-by-side connection of the methyl-methacrylate silane groups in the ORMOSIL particles, even without the addition of methyl-methacrylate monomers. The surface methyl-methacrylate functional groups on the ORMOSIL particles were inter-crosslinked to generate two-dimensional networks of ORMOSIL particles in an ordered monolayer. This network was strong enough to maintain the morphology of a monolayer film subjected to small disturbances such as stirring or agitating, but not to maintain the ordered monolayer during transfer. Sonication of the photochemically cured monolayer film of ORMOSIL particles

containing methyl-methacrylate functional groups produced ORMOSIL particles with several facets from the disassembly of the fused particles. The shapes of the facets formed on the ORMOSIL particles depended on the time of irradiation, where ORMOSIL particles with larger facet areas resulted from longer UV irradiation times. SEM images of the faceted ORMOSIL particles are shown in Fig. 3.

Photochemically cured, ordered monolayer films with a rigid network were used to produce Janus ORMOSIL particles with multiple functional groups through asymmetric reactions as shown in Scheme 1d and e. For an asymmetric modification, Janus ORMOSIL particles coated with Ag nanoparticles were prepared using the asymmetric reduction reaction of  $\text{AgNO}_3$  attached to a cured monolayer film with hydrazine at the interface. The dissolved Ag

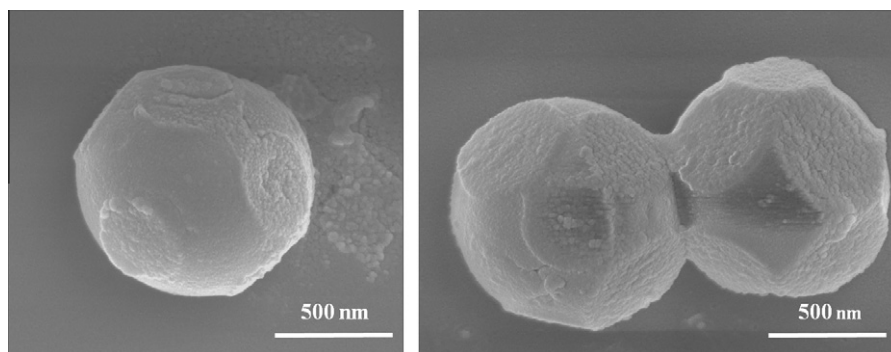


Fig. 3. SEM images of faceted ORMOSIL particles with methyl-methacrylate functional groups prepared at different photochemical polymerization time.

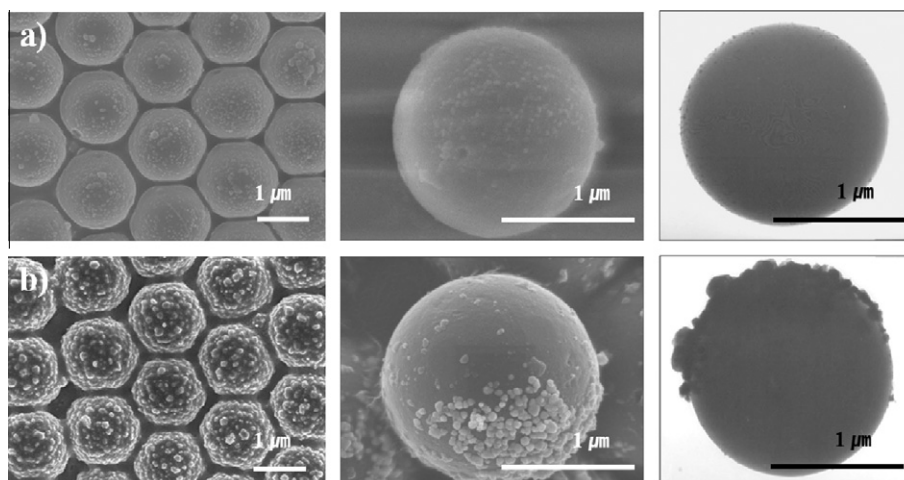
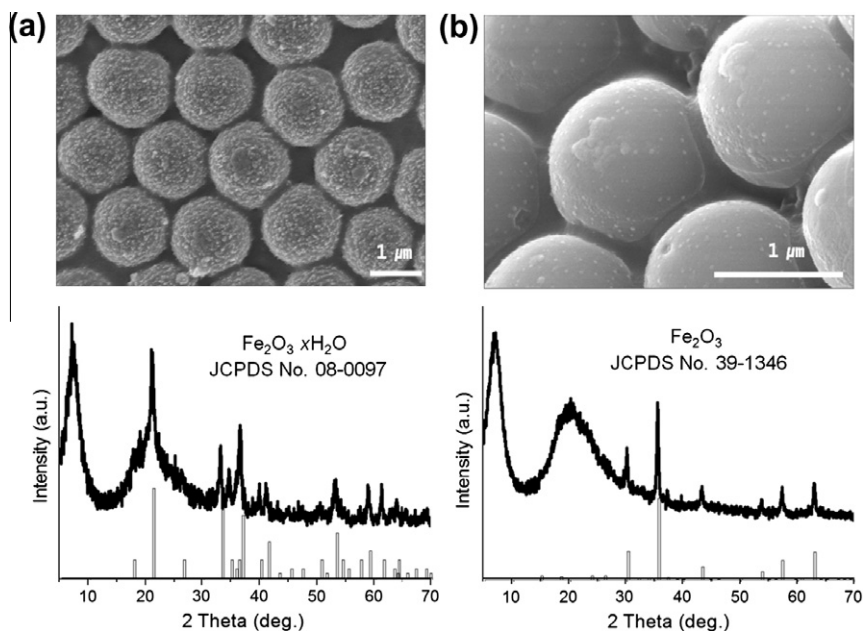


Fig. 4. SEM and TEM images of Ag-nanoparticle-coated Janus ORMOSIL particles prepared at 80 °C for (a) 2 h and (b) 7 h.

(I) ions were reacted with mercapto groups on the surfaces of the ORMOSIL particles located in the water phase. A cured monolayer film of ORMOSIL particles with a covering layer of PMMA maintained its integrity without any rotation or movement under mild stirring and heating conditions. After an hour of reaction, this monolayer film of ORMOSIL particles was transferred using a slide glass to a beaker, which contained a new water phase, and an aqueous hydrazine ( $\text{H}_2\text{NNH}_2 \cdot \text{H}_2\text{O}$ ) solution was added to the water phase to reduce the  $\text{Ag(I)}$  ions attached to the surface mercapto groups of the ORMOSIL particles in the monolayer film to metallic Ag particles. After the reduction reaction, the monolayer film decorated with Ag nanoparticles was moved again to a beaker containing freshly prepared water and Janus ORMOSIL particles coated with metallic Ag nanoparticles were obtained by the removal of the coated PMMA layer with sonication as shown in Scheme 1f. The X-ray diffraction pattern confirmed that the nanoparticles coated on Janus ORMOSIL particles were metallic Ag (JCPDS No. 04-0783). As the time and temperature of the reaction between the monolayer film and  $\text{AgNO}_3$  increased, so did the size and amount of metallic Ag particles on the surfaces of the ORMOSIL particles (see Supplementary material). During the entire reaction procedure, the network structures of the ORMOSIL particles in the monolayer film were maintained. This asymmetric preparation of Janus ORMOSIL particles was performed several times without disintegration of the ordered monolayer film. By repeating the sequential asymmetric reaction and transfer of the same monolayer, multiple coatings or consecutive reactions are possible. More cycles of the asymmetric reaction led to larger coated nano-

particles (see Supplementary material). The top side of the monolayer coated with PMMA was clean (without metallic Ag particles), while the bottom side showed attached metallic Ag particles (see Supplementary material). SEM and TEM images of the Janus ORMOSIL particles coated with Ag nanoparticles before and after the removal of the PMMA cover layer are shown in Fig. 4.

When iron(II) sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) was used as an inorganic precursor instead of silver nitrate ( $\text{AgNO}_3$ ), Janus ORMOSIL particles coated with hydrated iron-oxide ( $\text{Fe}_2\text{O}_3$ ) nanoparticles were obtained. We believe that either the Fe nanoparticles formed after the complete reduction of Fe(II) with hydrazine were converted to  $\text{Fe}_2\text{O}_3$  by instantaneous oxidation with  $\text{H}_2\text{O}$  and  $\text{O}_2$  or the reduction of Fe(II) with hydrazine was incomplete and some hydrazine was used to generate  $\text{OH}^-$  ions, resulting in the formation of hydrated iron-oxide ( $\text{Fe}_2\text{O}_3$ ) on the surfaces of the ORMOSIL particles. Further investigation is required to explain the exact mechanism for the formation of the hydrated iron-oxide ( $\text{Fe}_2\text{O}_3$ ) nanoparticles. The amount and size of the hydrated iron-oxide ( $\text{Fe}_2\text{O}_3$ ) nanoparticles increased as the reaction temperature and time increased, as in the case of the Ag nanoparticles (see Supplementary material). XRD analysis indicated that the major product coated on the ORMOSIL particles was iron-oxide hydrate ( $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ , JCPDS No. 08-0097) as shown in Fig. 5. In addition, iron-oxide ( $\text{Fe}_2\text{O}_3$ ) nanoparticles could be directly coated on one side of the monolayer film to produce Janus ORMOSIL particles simply by reacting mercapto functionalities on ORMOSIL particles with a suspension of iron-oxide nanoparticles. The iron-oxide nanoparticles were synthesized by the method of Wang's et al.



**Fig. 5.** SEM images and XRD patterns for (a) hydrated iron-oxide-nanoparticle-coated Janus ORMOSIL particles prepared by the reduction at 80 °C for 10 h, and (b) Janus ORMOSIL particles prepared by direct coating with iron oxides sol at 80 °C for 7 h.

[34], and the iron-oxide-coated Janus ORMOSIL particles were prepared by the reacting monolayer of mercapto functionalized ORMOSIL particles with the aqueous dispersion of iron-oxide nanoparticles as in the case of Janus ORMOSIL particles coated with hydrated iron-oxide ( $\text{Fe}_2\text{O}_3$ ) nanoparticles.

It is known that mercapto functional groups exhibit a good affinity to metals or metal oxides. The SEM images and XRD patterns of the Janus ORMOSIL particles indicated that the  $\text{Fe}_2\text{O}_3$  (JCPDS No. 39-1346) particles were successfully coated as shown in Fig. 5.

#### 4. Conclusions

In conclusion, monodispersed, submicron-sized Janus ORMOSIL particles with multiple functional groups were prepared by the asymmetric reaction of a monolayer film formed at a hexane–water interface. ORMOSIL particles with three different chemical functional groups were synthesized by a simple one-pot synthesis method. A well-ordered monolayer film was obtained by self-assembly of ORMOSIL particles with multiple functional groups at a hexane–water interface. The photochemical polymerization of MMA monomers in the hexane top layer produced a rigid monolayer covered with PMMA that could maintain an ordered monolayer structure of ORMOSIL particles for additional chemical reactions and easily be removed after the generation of Janus ORMOSIL particles with gentle sonication. Metals and metal oxides decorated the Janus ORMOSIL particles with multiple chemical functional groups were prepared using an asymmetric reaction of the monolayer film. With the controllable chemical and spatial compositions of their functional groups, these Janus ORMOSIL particles offer great promise in many nanoengineering and biochemical applications.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jcis.2011.09.079](https://doi.org/10.1016/j.jcis.2011.09.079).

#### References

- [1] J. Kim, J.E. Lee, J. Lee, Y. Jang, S.W. Kim, K. An, J.H. Yu, T. Hyeon, *Angew. Chem., Int. Ed.* 45 (2006) 4789.
- [2] S. Mornet, C. Elissalde, O. Bidault, F. Weill, E. Sellier, O. Nguyen, M. Maglione, *Chem. Mater.* (2007) 987.
- [3] L. Li, C. Tsung, T. Ming, Z. Sun, W. Ni, Q. Shi, G.D. Stucky, J. Wang, *Adv. Funct. Mater.* 18 (2008) 2956.
- [4] G.R. Reddy, M.S. Bhojani, P. McConville, J. Moody, B.A. Moffat, D.E. Hall, G. Kim, Y.L. Koo, M.J. Woolliscroft, J.V. Sugai, T.D. Johnson, M.A. Philibert, R. Kopelman, A. Rehemtulla, B.D. Ross, *Clin. Cancer Res.* 12 (2006) 6677.
- [5] O.C. Farokhzad, J. Cheng, B.A. Tepley, I. Sherif, S. Jon, P.W. Kantoff, J.P. Richie, R. Langer, *PNAS* 103 (2006) 6315.
- [6] L. Wang, W. Zhao, M.B. O'Donoghue, W. Tan, *Bioconjugate Chem.* 18 (2007) 297.
- [7] M. Green, *Small* 1 (2005) 684.
- [8] F. Caruso, *Adv. Mater.* 13 (2001) 11.
- [9] K.S. Soppimath, L. Liu, W.Y. Seow, S. Liu, R. Powell, P. Chan, Y.Y. Yang, *Adv. Funct. Mater.* 17 (2007) 355.
- [10] F. Hoffmann, M. Cornelius, J. Morell, M. Fröba, *Angew. Chem., Int. Ed.* 245 (2006) 3216.
- [11] S.I. Stoeva, F. Huo, J. Lee, C.A. Mirkin, *J. Am. Chem. Soc.* 127 (2005) 15362.
- [12] Z. Meng, C. Xue, Q. Zhang, X. Yu, K. Xi, X. Jia, *Langmuir* 25 (2009) 7879.
- [13] J.S. Park, H.J. Hah, S.M. Koo, Y.S. Lee, *J. Ceram. Proc. Res.* 7 (2006) 83.
- [14] F. Li, Z. Wang, A. Stein, *Angew. Chem., Int. Ed.* 46 (2007) 1885.
- [15] Z. Wu, H. Han, W. Han, B. Kim, K.H. Ahn, K. Lee, *Langmuir* 23 (2007) 7799.
- [16] M.H. Lim, A. Stein, *Chem. Mater.* 11 (1999) 3285.
- [17] P.G. de Gennes, *Rev. Mod. Phys.* 64 (1992) 645.
- [18] L. Hong, A. Cacciuto, E. Luijten, S. Granick, *Nano Lett.* 6 (2006) 2510.
- [19] S.C. Glotzer, *Science* 306 (2004) 419.
- [20] K.P. Yuet, D.K. Hwang, R. Haghgoie, P.S. Doyle, *Langmuir* 26 (2010) 4281.
- [21] S. Jiang, Q. Chen, M. Tripathy, E. Luijten, K.S. Schweizer, S. Granick, *Adv. Mater.* 22 (2010) 1060.
- [22] A. Perro, S. Reculosa, S. Ravaine, E. Bourgeat-Lami, E. Duguet, *J. Mater. Chem.* 15 (2005) 3745.
- [23] M.D. McConnell, M.J. Kraeutler, S. Yang, R.J. Composto, *Nano Lett.* 10 (2010) 603.
- [24] A. Walther, A.H.E. Müller, *Soft Matter* 4 (2008) 663.
- [25] R.T. Chen, B.W. Muir, G.K. Such, A. Postma, K.M. McLean, F. Caruso, *Chem. Commun.* 46 (2010) 5121.

- [26] S. Pradhan, L. Xu, S. Chen, *Adv. Funct. Mater.* 17 (2007) 2385.
- [27] M.A. Correa-Duarte, V. Salgueiriño-Maceira, B. Rodríguez-González, L.M. Liz-Marzán, A. Kosiorek, W. Kandulski, M. Giersig, *Adv. Mater.* 17 (2005) 2014.
- [28] Z. Li, D. Lee, M.F. Rubner, R.E. Cohen, *Macromolecules* 38 (2005) 7876.
- [29] D. Dendukuri, D.C. Pregibon, J. Collins, T.A. Hatton, P.S. Doyle, *Nat. Mater.* 5 (2006) 365.
- [30] K. Roh, D.C. Martin, J. Lahann, *Nat. Mater.* 4 (2005) 759.
- [31] T. Nisisako, T. Torii, T. Takahashi, Y. Takizawa, *Adv. Mater.* 18 (2006) 1152.
- [32] B. Liu, W. Wei, X. Qu, Z. Yang, *Angew. Chem., Int. Ed.* 47 (2008) 3973.
- [33] Y. Li, W. Huang, S. Sun, *Angew. Chem., Int. Ed.* 45 (2006) 2537.
- [34] S. Wang, H. Cao, F. Gu, C. Li, G. Huang, *J. Alloys Compd.* 457 (2008) 560.