Amine/acid composite Janus nanosheets

Yijiang Liu, Qian Wang, Xiaozhong Qu, Fuxin Liang* and Zhenzhong Yang*

Janus materials have witnessed fast development due to their diversified promising performances and practical applications. Compared with their spherical counterparts, Janus nanosheets have gained more concerns for their highly anisotropic shape besides chemistry. Herein, 3.5 nm ultrathin and flexible Janus nanosheets with carboxyl group terminated onto one side are fabricated by surface sol-gel process of the self-assembled monolayer of an amphiphilic silane onto the template CaCO_3 particle firstly. Amine/acid composite Janus nanosheets are further derived from these carboxyl group terminated silica Janus nanosheets by selective conjugation with amine groups onto the other side. The amine/acid composite Janus nanosheets are dually pH responsive, and well dispersible in aqueous solution at both low and high pH levels. The nanosheets are aggregated forming multi-layered face-to-back superstructures at intermediate pH levels. This is originated by the opposite electrostatic interaction between the carboxyl and the amine groups. This approach can be extended to other silanes, and a huge family of Janus nanosheets is expected with tunable composition and performance.

INTRODUCTION

Janus materials, which consist of two different compositions compartmentalized on one object, have been shown to have diverse potential applications, such as solid surfactants, building blocks for superstructures, and self-propellant motors [1–6]. Shape control is important in determining the performances of these materials. Janus nanosheets are particularly interesting because of their highly anisotropic shape besides their asymmetric chemistry. As the rotation of Janus nanosheets at an interface is restricted, the nanosheets appear to form mosaics on the interface that can better stabilize emulsions [7,8]. It would thus be useful to develop methods to synthesize Janus nanosheets with tunable thickness and composition.

Polymeric Janus nanosheets have been synthesized by delaminating supramolecular structures formed from alternating layers of block copolymers [9,10]. This method requires a sufficiently narrow molecular-weight distribution to ensure uniformity in the supramolecular structure. If this is not the case, the layered structure will coexist with other structures. Janus polymer single crystal nano-

plates have been generated by evaporation-induced crystallization of carboxyl-capped poly(ϵ -caprolactone) at a planar water/pentyl acetate interface [11]. Inorganic Janus nanosheets have been prepared by multistep etching of silicon substrates [12], but the yield is rather low considering that these nanosheets are based on multi-step etching planar substrates. In an effort to increase the yield of the Janus nanosheets, simultaneous atom transfer radical polymerization (ATRP) grafting from the platelets at a Pickering emulsion interface was proposed as a method to synthesize the corresponding Janus nanoplates [13]. It was, however, necessary to properly modify the platelets to form Pickering emulsions. Recently, we proposed a simple way to fabricate silica Janus nanosheets by crushing the corresponding Janus hollow spheres [8]. The Janus hollow spheres were prepared by materialization of the temporal Janus emulsion interface via a self-organized sol-gel process [14]. One side of the silica Janus nanosheets was terminated with amine groups. Then, starting from this side, other polymers were preferentially grown by ATRP to give polymer-silica composite Janus nanosheets. Additional characteristics, such as thermal or pH responsivity, could also be introduced [15]. However, it was difficult to obtain Janus nanosheets with molecular-scale thickness at the dynamic emulsion interface. A very thin amine/thiol Janus aromatic nanomembrane has been synthesized by electron-irradiation-assisted crosslinking of a monomolecular film on a gold surface or transmission electron microscope (TEM) grid [16]. A Janus graphene monolayer has been synthesized by polymer-mediated transfer-assisted selective grafting of halogen and aryl/oxygen functional groups onto each side of the monolayer [17]. Although they are very thin, these monolayers lack a responsive performance. In addition, the yield is rather low. We have recently developed a method to synthesize flexible Janus nanosheets using a sol-gel process involving a silane self-assembled monolayer (SAM) of (3-butyldianhydride mercaptopropyl)trimethoxysilane (BDMPS) supported on a calcium carbonate (CaCO_3) particle surface [18]. The nanosheets have molecular-level thickness. After selective modification, one side of the exposed surface has alkyl-terminated groups, whereas the acid group is preserved on the other side.

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Herein, we further extend this approach to synthesize an amine/acid composite pH-responsive Janus nanosheet by conjugation of amine groups on the opposite side of the surface (Scheme 1). A self-assembled monolayer of BD-MPS forms with the acid anhydride group attached to the CaCO_3 particle surface by a coordination interaction, with the hydrophobic tail group directed towards the external oil phase. The silica Janus nanomembrane is generated through a sol-gel process supported by the particle surface. The hydrophilic side of the surface is synchronously protected, but the exterior silica surface can be selectively modified with silanes, such as (3-aminopropyl)trimethoxysilane. As a result, the amine group is conjugated on the exterior surface. After acid etching of the CaCO_3 particle under ultrasonication, the Janus nanomembrane is broken into Janus nanosheets. At the same time, the acid anhydride group is hydrolyzed into a carboxyl group and the amine/acid composite Janus nanosheets are formed. These nanosheets are pH responsive and their aggregation/dis-persion in aqueous solution is pH triggered.

EXPERIMENTAL SECTION

Materials

(3-mercaptopropyl)trimethoxysilane and (3-aminopropyl)trimethoxysilane were purchased from Acros. Maleic anhydride and azobisisobutyronitrile (AIBN) were purchased from Sinopharm Chemical Reagent Beijing. BDMPS was synthesized following the previously reported procedure [18]. Toluene was dried by refluxing with sodium and benzophenone, followed by distillation. Dimethylformamide (DMF) was dried and distilled under reduced pressure. CaCO_3 was purchased from Sinopharm Chemical Reagent (Shanghai, China). All reagents were used as received unless otherwise stated.

Characterization

The morphology of the samples was characterized by scanning electron microscopy (SEM) at 15 kV using a Hitachi S-4800 scanning electron microscope equipped with an energy-dispersive X-ray (EDX) analyzer. The samples for SEM observation were prepared by vacuum sputtering with Pt after ambient drying. Fourier transform infrared (FTIR) spectroscopy was performed by scanning KBr pressed pellets of the sample 32 times using a Bruker EQUINOX 55 spectrometer. Atomic force microscopy (AFM) images were recorded under ambient conditions using a Digital Instrument Multimode Nanoscope IIIA operating in a tapping mode. A Zeta Sizer 3000 HS (Malvern Instruments) was used to measure the ζ -potential.

Synthesis of the silica Janus nanosheets

BDMPS (20 mg) in toluene (1 mL) was added to a dispersion of CaCO_3 (1 g) in toluene (12 mL). The mixture was stirred at 400 rpm for 24 h at room temperature. The mixture was centrifuged and washed with toluene three times, then dried under vacuum. A SAM of BDMPS was formed on the particle surface.

CaCO_3 @SAM composite particles (1.0 g) were dispersed in ethanol (15 mL). After 30 min, aqueous ammonia (20 mL) was added. The mixture was stirred at 400 rpm for 24 h at room temperature, and then the system was centrifuged, washed with ethanol three times, and dried under vacuum. A silica Janus monolayer was formed on the particle surface and CaCO_3 @nanomembrane composite particles were obtained. The silica nanosheets were obtained after using 1 M aqueous HCl solution (5 mL) under ultrasonication to etch the CaCO_3 particles.

Synthesis of the amine/acid composite Janus nanosheets

The CaCO_3 @nanomembrane composite particles (1.0 g)

Scheme 1 Synthesis of the amine/acid composite Janus nanosheets. (1) Self-assembled monolayer after preferential adsorption of the amphiphilic silane BDMPS onto the template surface, and Janus silica nanomembrane formed from a surface sol-gel process; the Si-OH groups are positioned at the exterior surface. (2) Janus silica nanomembrane after selective modification of the exterior silica surface with (3-aminopropyl)trimethoxysilane. (3) Amine/acid composite Janus nanosheets after acid etching of the template under ultrasonication.

were dispersed in toluene (15 mL) and (3-aminopropyl)trimethoxysilane (60 μL) was added. The mixture was refluxed at 80°C for 8 h. After cooling to room temperature, the dispersion was centrifuged, washed with toluene three times, and dried under vacuum. CaCO_3 @amine/maleic anhydride nanomembrane composite particles were obtained.

At 50°C, CaCO_3 @nanomembrane composite particles (500 mg) were added to a 1 M aqueous HCl solution (5 mL) under ultrasonication. After cooling to room temperature, the dispersion was centrifuged and washed with water to give the amine/acid composite Janus nanosheets.

Synthesis of the chitosan-capped Fe_3O_4 nanoparticles

The chitosan-capped Fe_3O_4 nanoparticles were synthesized according to a literature procedure [19]. An aqueous solution (44.0 mL) containing $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.70 g) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.30 g) was injected into an aqueous solution of acetic acid [200 mL, 0.25% (v/v)]. Chitosan was added at 2.50 g/L under nitrogen atmosphere. After stirring at 40°C for 1 h, ammonium hydroxide (20.0 mL) was dropped into the solution under vigorous stirring over 30 min. Chitosan-capped Fe_3O_4 nanoparticles were collected using a magnet and washed with water.

Synthesis of the trisodium-citrate-capped Au nanoparticles

Au nanoparticles were prepared by the Frens method [20]. An aqueous solution of HAuCl_4 (100 mL, 0.1 mg mL^{-1}) was refluxed under stirring and an aqueous solution of trisodium citrate (2 mL, 10 mg mL^{-1}) was added. A dispersion of Au nanoparticles with an average diameter of 15 nm was obtained after 40 min.

Labeling the Janus nanosheets with the Au nanoparticles

The Janus nanosheets (1.0 mg) were dispersed in water. A small amount of the trisodium-citrate-capped Au nanoparticles was added to the dispersion. The as-formed mixture was stirred for 12 h to selectively label the nanosheets. The nanosheets were centrifuged and washed with water.

pH responsive dispersion of the Janus nanosheets

After the Janus nanosheets were dispersed in aqueous solution under ultrasonication for 5 min at various pH levels, the dispersions were left to stand for observation.

RESULTS AND DISCUSSION

A silica Janus nanomembrane was formed in a sol-gel process involving the self-assembly of a BDMPS monolayer on the CaCO_3 particle surface (Fig. 1a). The nanomembrane was partially peeled from the particle surface under sonication. After the CaCO_3 particles were etched with acid under ultrasonication, the silica nanomembrane was broken into

Figure 1 (a) Silica Janus nanomembrane after a sol-gel process involving the self-assembly of a BDMPS monolayer on the CaCO_3 particle surface. (b) Silica Janus nanosheets after acid etching of the CaCO_3 particle under ultrasonication. (c) AFM image of the silica Janus nanosheets, which have a thickness of 3.5 ± 0.2 nm. (d) Silica Janus nanosheets after positively charged Fe_3O_4 nanoparticles are preferentially adsorbed onto the carboxyl group terminated side.

small pieces and the silica Janus nanosheets were formed (Fig. 1b). At the same time, the acid anhydride group was hydrolyzed to give a carboxyl group. Both sides of the silica Janus nanosheets are smooth, and the sheets are flexible and easily wrinkled. The average thickness is 3.5 ± 0.2 nm (Fig. 1c), which is close to the calculated value of 3.3 nm [18]. Positively charged chitosan-capped Fe_3O_4 nanoparticles were used to selectively label the carboxyl group terminated side. As a result, this side became coarse, whereas the other side remained smooth (Fig. 1d). In addition, the Janus nanosheets could be manipulated under a magnetic field.

Prior to etching the CaCO_3 , that is, while the anhydride group terminated interior surface is protected, desired groups can be selectively conjugated onto the exterior silica surface of the Janus nanomembrane using silanes. As an example, (3-aminopropyl)trimethoxysilane was used. The corresponding amine/acid composite Janus nanosheets were obtained after etching the CaCO_3 under ultrasonication (Fig. 2a). These nanosheets are 3.9 ± 0.2 nm thick (Fig. 2b), which is slightly thicker than the silica Janus nanosheets. This increase in thickness originates from the conjugation of (3-aminopropyl)trimethoxysilane on one side of the nanosheet. When negatively charged Au nanoparticles were selectively adsorbed onto the amine group terminated side of the amine/acid nanosheet, this side became coarse whereas the acid group terminated side remained smooth (Fig. 2c). In comparison, both sides of the silica Janus nanosheets remained smooth after treatment with Au nanoparticles. No Au nanoparticles were found on

Figure 2 (a) Amine/acid composite Janus nanosheets after etching of the CaCO_3 particles under ultrasonication. (b) AFM image of the Janus nanosheets with a thickness of 3.9 ± 0.2 nm. Negatively-charged-Au-nanoparticle-labeled amine/acid composite Janus nanosheets (c) and silica Janus nanosheets (d). All samples were obtained after drying the dispersion in ethanol. (e) FTIR spectra of silica Janus nanosheets (curve a) and amine/acid composite nanosheets (curve b). (f) ζ -potential of the silica Janus nanosheets (curve a) and the amine/acid composite nanosheets (curve b). All measurements were performed at pH 3.9.

the silica Janus nanosheets (Fig. 2d). In the FTIR spectrum of the silica Janus nanosheets (curve a, Fig. 2e), the peaks at 1024 cm^{-1} and 1098 cm^{-1} are assigned to the $-\text{Si}-\text{O}-\text{Si}-$ of the silica. The peak at 1718 cm^{-1} is assigned to $-\text{COOH}$. The new peak at 1568 cm^{-1} is assigned to the $-\text{NH}_2$ of the amine/acid composite Janus nanosheets (curve b, Fig. 2e). The ζ -potential of the silica Janus nanosheets is -32.2 mV and is attributed to the negatively charged carboxyl groups. After modification, the $\text{Si}-\text{OH}$ group is terminated with an amine group, and this can partially neutralize the carboxyl group. The ζ -potential of the amine/acid composite Janus nanosheets is thus considerably reduced [-7.6 mV (Fig. 2f)].

The composite nanosheets possess two kinds of pH-responsive groups, amine and carboxyl, which are located on opposite sides of the sheet. We were interested in systematically characterizing the dispersion behavior of the composite Janus nanosheets in aqueous solution at various pH levels (Fig. 3a). At low (<4) or high (>10) pH levels, the nanosheets were well dispersed in aqueous solution. At in-

Figure 3 (a) Amine/acid composite Janus nanosheet dispersions in aqueous solution at various pH levels. (b) ζ -potential dependence of the amine/acid composite Janus nanosheet dispersion on pH.

termediate pH levels between pH 5 and 8, the nanosheets precipitated from aqueous solution. The top phase became transparent, which implied that all the nanosheets were present in the bottom phase. On adjusting the pH beyond the pH 5–8 window and after ultrasonication, the aggregates became redispersible in aqueous solution. The ζ -potential dependence of the dispersions on pH was monitored (Fig. 3b). The carboxyl group of the acid anhydride derivative exhibits two dissociations [21]. Between pH 2.5 and 2.8, the ζ -potential changes abruptly but remains at a very high level above 40 mV . This corresponds to the positive charge of the protonated amine group, but the carboxyl group is not significantly dissociated at these pH values. A subtle increase in pH from 3.7 to 4.0 leads to a dramatic decrease in the ζ -potential from $\sim 40\text{ mV}$ to -39.2 mV . The ζ -potential is preserved at this plateau level with any further changes in pH. This change arises from the major dissociation of the carboxyl group. Another abrupt increase in the ζ -potential is observed on subtly increasing the pH from pH 9.8 to 10.0; this corresponds to the dissociation of the amine group on the other side of the nanosheets. At pH values above 4.0, the carboxyl group is dissociated and becomes negatively charged. At pH values below 9.8, the amine group is protonated and becomes positively charged. The composite nanosheets are Janus materials with amphiphilic performance both below pH 4.0 and above pH 9.8. At pH values between pH 4.0 and pH 9.8, both the amine and carboxyl groups are highly charged but have opposite

polarities. The nanosheets can form heavy aggregates because of the strong electrostatic interaction between the two groups.

After ambient drying of the aqueous dispersion at pH 2, the nanosheets were folded and well distinguished (Fig. 4a). At this pH, it is rational that the acid group terminated sides are stacked inwardly face-to-face with the protonated amine group exposed to the aqueous phase. We expected that a bilayered structure would form among the Janus nanosheets [8]. Surprisingly, individual nanosheets were self-folded into a wrinkled structure. This finding is similar to that of our previous study on the encapsulation of paraffin using single alkyl/acid Janus nanosheets [18]. The wrinkling is related to the flexibility of the nanosheets. At pH 6, the carboxyl group is dissociated and becomes negatively charged. Because of the opposite electrostatic interaction between the charged carboxyl and amine groups, the nanosheets should form a face-to-back superstructure and quickly precipitate from aqueous solution (Fig. 4b). To further clarify the structure of these superstructures in aqueous solution, the dispersion was cryo-dried. At pH 6, the nanosheets were stacked to form a multilayered superstructure due to the alternating opposite charge interaction (Fig. 4c). A magnified SEM image reveals local wrinkling of the nanosheets, implying they are rather flexible (Fig. 4d). At pH 12, the morphology of the superstructure is similar to the structure at pH 2 because the nanosheets are Janus materials.

CONCLUSIONS

In summary, we have proposed a facile method to fabricate amphiphilic amine/acid composite Janus nanosheets. Firstly, a silica Janus nanosheet with carboxyl group onto one

side is obtained by sol-gel process of a self-assembly monolayer of an amphiphilic silane BDMPs onto a solid particle template surface by a coordination interaction. The amine group is further terminated onto the other side of the carboxyl group terminated Janus nanosheet. Both the acid and amine groups are distinctly compartmentalized onto the two sides, respectively. Both sides can be pH responsive in a separate way. The nanosheets are dually pH responsive. The nanosheets are well-dispersible at both low and high pH levels. At intermediate pH, a multilayered superstructure is formed by face-to-back stacking due to interaction between the opposite electrostatic charges on the opposite sides of the nanosheets. The method is general to fabricate other functional Janus nanosheets. Thanks to their stimuli-responsive performance, these flexible Janus nanosheets may be potential in controlled loading and release, and heterogeneous catalysis.

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Figure 4 SEM images of the amine/acid composite nanosheets after ambient drying of the aqueous dispersion at pH 2 (a) and pH 6 (b). (c, d) SEM images of the nanosheets after cryo-drying of the aqueous dispersion at pH 6.

- de Gennes PG. Soft matter. Rev Mod Phys, 1992, 64: 645–648
- Hu J, Zhou SX, Sun YY, *et al.* Fabrication, properties and applications of Janus particles. Chem Soc Rev, 2012, 41: 4356–4378
- Jiang S, Granick S, Schneider HJ. Janus Particle Synthesis, Self-Assembly and Applications. London: Royal Society of Chemistry, 2012
- Walther A, Müller AHE. Janus particles: synthesis, self-assembly, physical properties, and applications. Chem Rev, 2013, 113: 5194–5261
- Zhang HB, Hao R, Jackson JK, *et al.* Janus ultrathin film from multi-level self-assembly at air-water interfaces. Chem Commun, 2014, 50: 14843–14846
- Liang FX, Zhang CL, Yang ZZ. Rational design and synthesis of Janus composites. Adv Mater, 2014, 26: 6944–6949
- Nonomura Y, Komura S, Tsujii K. Adsorption of disk-shaped Janus beads at liquid-liquid interfaces. Langmuir, 2004, 20: 11821–11823
- Liang FX, Shen K, Qu XZ, *et al.* Inorganic Janus nanosheets. Angew Chem Int Ed, 2011, 50: 2379–2382
- Walther A, André X, Drechsler M, *et al.* Janus discs. J Am Chem Soc, 2007, 129: 6187–6198
- Wang Y, Zhong WHK, Ji JY, *et al.* Blossoming of nanosheet structures via a disturbed self-assembly. Nano Lett, 2014, 14: 3474–3480
- Qi H, Wang WD, Li CY. Janus polymer single crystal nanosheet via evaporative crystallization. ACS Macro Lett, 2014, 3: 675–678
- Dorvee JR, Derfus AM, Bhatia SN, *et al.* Manipulation of liquid droplets using amphiphilic, magnetic one-dimensional photonic crystal chaperones. Nat Mater, 2004, 3: 896–899
- Kirillova A, Stoychev G, Ionov L, *et al.* Platelet Janus particles with hairy polymer shells for multifunctional materials. ACS Appl Mater Interfaces, 2014, 6: 13106–13114
- Liang FX, Liu JG, Zhang CL, *et al.* Janus hollow spheres by emulsion interfacial self-assembled sol-gel process. Chem Commun, 2011, 47: 1231–1233
- Yang HL, Liang FX, Wang X, *et al.* Responsive Janus composite nanosheets. Macromolecules, 2013, 46: 2754–2759
- Zheng ZK, Nottbohm CT, Turchanin A. Janus nanomembranes: a generic platform for chemistry in two dimensions. Angew Chem Int Ed, 2010, 49: 8493–8497
- Zhang LM, Yu JW, Yang MM, *et al.* Janus graphene from asymmetric two-dimensional chemistry. Nat Commun, 2012, 4: 1443–1149

- 18 Liu YJ, Liang FX, Wang Q, *et al.* Flexible responsive Janus nanosheets. *Chem Commun*, doi: 10.1039/C4CC08420A
- 19 Wang JZ, Zhao GH, Li YF, *et al.* Reversible immobilization of glucoamylase onto magnetic chitosan nanocarriers. *Appl Microbiol Biot*, 2012, 97: 681–692
- 20 Frens, G. Controlled nucleation for the regulation of the particle size in monodisperse gold suspensions. *Nat Phys Sci*, 1973, 241: 20–22
- 21 Tu FQ, Lee D. Shape changing and amphiphilicity reversing Janus particles with pH-responsive surfactant properties. *J Am Chem Soc*, 2014, 136: 9999–10006

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Author Contributions Yang Z proposed the project; Yang Z and Liang F designed the work and wrote the manuscript; Liu Y synthesized the materials and measured the properties. Wang Q and Qu X participated in the analysis of the experimental data and discussion of the results.

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

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中文摘要 含酸酐两亲硅烷偶联剂在颗粒表面吸附形成自组装单分子膜, 可通过溶胶-凝胶法制备二氧化硅Janus纳米片. 本文通过对二氧化硅Janus纳米片选择改性在一侧偶联氨基, 制备了羧基/氨基复合的Janus纳米片. 纳米片两侧的羧基与氨基具有不同的pH值响应性, 表现出相应的荷电性质及润湿性. 二者共同作用, 引起纳米片特殊的分散和聚集行为. 在较低或较高pH值水平, 纳米片表现为Janus特性, 分散良好. 在中间pH值范围, 纳米片两侧羧基、氨基相反电荷相互吸引导致层层组装聚集并沉淀.