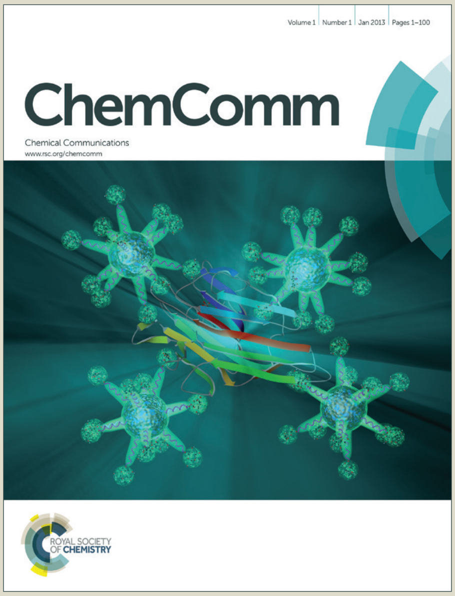
ChemComm

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Journal Name RSCPublishing

COMMUNICATION

Flexible Responsive Janus Nanosheets

Cite this: DOI: 10.1039/x0xx00000x

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

Received 00th January 2012,
Accepted 00th January 2012

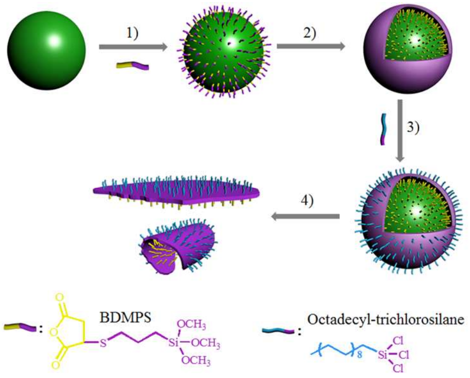
DOI: 10.1039/x0xx00000x

www.rsc.org/

Flexible Janus nanosheets of molecular scale thickness (3.5 nm) are massively fabricated by sol-gel process of self-assembled monolayer of an amphiphilic silane onto a template. Groups of both sides are tuneable thus performance of the nanosheets for example pH responsive. As a flexible solid emulsifier, desired species can be wrapped with an individual nanosheet, which is pH triggered.

Janus materials with two different compositions compartmentalized onto one object, [1] have shown diversify potential applications. It is interesting for them to serve as solid emulsifiers [2] due to their amphiphilic characteristics. Shape control is important to determine their performances. Among those shapes including particles, rods and cages, [3] nanosheets (or discs) should deserve more attention due to their highly anisotropic shape besides chemistry. Since rotation of Janus nanosheets at an interface is restricted, [4] the nanosheets appear mosaic onto the emulsion interface. The emulsion becomes more stable than using the spherical counterparts.

Polymeric Janus nanosheets have been synthesized by delamination of the alternatively layered supramolecular structures from block copolymers. [5] Narrow molecular weight distribution is required to attain uniformity of the layered structure. Although the Janus nanosheets are flexible to encapsulate desired species, they are easily swollen with solvents to lose their original shape. [6] Inorganic Janus nanosheets can tolerate organic solvents. Recently, inorganic Janus nanosheets are achieved by multiple-lithography etching silicon. [7] However, this approach is difficult for massive production. We have proposed a simple way to fabricate silica based Janus nanosheets by crushing the corresponding Janus hollow spheres. [8] The spheres are formed by materialization of an emulsion interface via self-organized sol-gel process of silane precursors. [9] It is required to use an amine- group terminated silane together with other silanes in order to form a self-organized interfacial layer by specific interaction with acid moiety of the emulsifier. One side the Janus silica nanosheets should be terminated with the amino- group. This provides a platform for atomic transfer radical polymerization (ATRP) towards polymer-silica composite Janus nanosheets. Additional performances such as thermal, pH and ionic responsive are introduced. [10] However, it is difficult to achieve molecular scale thick Janus nanosheets at the dynamic emulsion interface. Besides, the nanosheets are too rigid to adapt the interface curvature deformation. It is urgently required to develop a method to large scale synthesize flexible Janus nanosheets. Extremely decrease thickness is a straightforward way. Very thin Janus aromatic nanomembrane has been synthesized by electron irradiation assisted crosslinking of the monomolecular film of 4’-nitro-1,1’-biphenyl-4-thiol supported on a gold surface or TEM grid. Amino- and thio- groups are terminated onto both sides, respectively. [11] The crosslinking requires either electron or UV irradiation. [12] During the irradiation, carbon-hydrogen bonds are initially cleaved, followed by a crosslinking between carbon-carbon of the aromatic units. The approach is restricted within aromatic monolayers. Janus graphene monolayer has been synthesized by PMMA-mediated transfer assisted selective grafting of halogen and aryl/oxygen-functional groups onto each side, respectively. [13] Although they are very thin and flexible, they lack of responsive performance. It remains challenging to develop a facial approach to large scale synthesize a flexible and responsive Janus nanosheets.



Scheme 1. Synthesis of the flexible responsive Janus nanosheets. 1) A self-assembled monolayer (SAM) forms after a preferential absorption of the amphiphilic silane BDMPS onto the template surface; 2) silica based Janus monolayer formed by a surface sol-gel process; 3) silica composite Janus monolayer formed by a selective modification of exterior silica surface with octadecyltrichlorosilane to introduce hydrophobic group; 4) Janus nanosheets are derived after acid etching the template under ultrasonication.

Herein, we report a facile approach towards Janus nanosheets of molecular scale thickness by a surface sol-gel process of the self-assembled monolayer (SAM) of an amphiphilic silane onto the template particle, as illustrated in Scheme 1. The example amphiphilic silane of 3-butyldianhydride mercaptopropyltrimethoxysilane (BDMPS) is synthesized (Figs. S1 and S2). A SAM of BDMPS forms onto $CaCO_3$ particle surface by coordination interaction. The acid anhydride group faces the particle surface, while the tail group faces the external oil phase. Silica based Janus monolayer is derived by the surface sol-gel process. The hydrophilic side is automatically protected via binding onto the particle surface. This allows a selective modification of the exterior silica surface by other silanes for instance octadecyltrichlorosilane. As a result, other groups such as hydrophobic alkyl- group are easily terminated thereby. After acid etching $CaCO_3$ particle under ultrasonication, Janus nanosheets are obtained. Meanwhile, the acid anhydride group is converted into carboxyl- group by hydrolysis. The Janus nanosheets can serve as solid surfactants to emulsify immiscible solvents forming stable emulsions. Moreover, the Janus nanosheets are flexible sufficiently to adapt the interfacial curvature. Eventually, organic compounds can be encapsulated with a single Janus nanosheet. The emulsion stability can be pH triggered when the carboxyl- group terminated Janus nanosheets are employed.

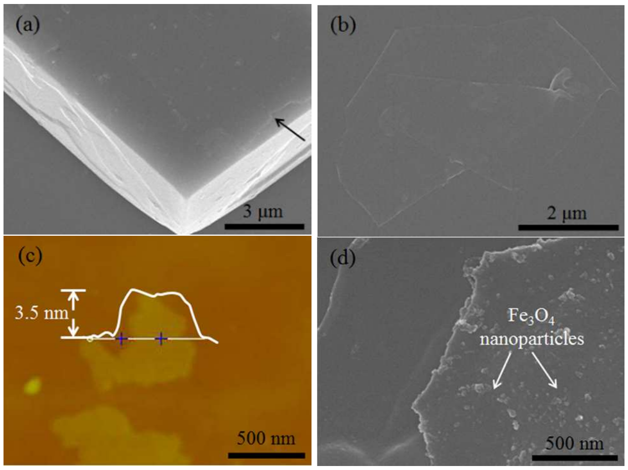


Fig. 1 (a) Janus silica monolayer of molecular scale thickness by surface sol-gel process of BDMPS self-assembled monolayer onto $CaCO_3$ particle; (b) Janus silica nanosheets after etching the $CaCO_3$ particle under ultrasonication; (c) AFM image of the Janus silica nanosheets, 3.5±0.2 nm thick; (d) Janus silica nanosheets after positively charged Fe_3O_4 nanoparticles are preferentially absorbed onto the carboxyl- group terminated side.

Onto $CaCO_3$ particle surface (Fig. S3a), BDMPS can form a SAM by coordination interaction. Morphology of $CaCO_3$ particle is not influenced by the formation of SAM (Fig. S3b). At room temperature, the SAM of BDMPS experiences an alkaline catalyzed sol-gel process, forming a silica based Janus monolayer. As a result, the $CaCO_3$ particle surface becomes slightly coarsening. The silica nanomembrane is clearly distinguished from the particle surface in the broken $CaCO_3$@silica particle (Fig. 1a). After acid etching $CaCO_3$ under ultrasonication, the Janus silica monolayer is broken into pieces deriving Janus silica nanosheets (Fig. 1b). The nanosheets are only dispersible in water rather than in oil. After drying from their ethanol dispersion, individual nanosheet is distinguished. Both sides are smooth. They are rather flexible and easily wrinkled. Presence of the carboxyl- group is confirmed by FT-IR spectrum (Fig. S4). The Janus nanosheets are uniform in thickness of 3.5±0.2 nm measured by AFM (Fig. 1c), which is rather close to the calculated one 3.3 nm. [14] This reveals the Janus nanosheets are thick at a molecular level. Positively charged chitosan-capped Fe_3O_4 nanoparticles (about 10 nm in diameter) are used to selectively label the carboxyl- group terminated side. As a result, the side becomes coarsened, while the other side remains smooth (Fig. 1d).

BDMPS concentration is significant to control morphology of the Janus nanosheets. At low BDMPS concentration for instance 0.2 wt.-%, individual Janus nanodiscs of 3.5±0.2 nm thick are obtained (Fig. 2a). This can be explained that BDMPS is insufficient to form a complete monolayer covering the whole particle surface. When BDMPS concentration is increased to 1.0 wt.-%, porous Janus nanosheets are achieved (Fig. 2b). The thickness is about 3.7±0.2 nm. At 2.0 wt.-% of BDMPS, no pores is found and Janus nanosheets are obtained. With further increase in BDMPS concentration for example 4.0 wt.-%, morphology of the Janus nanosheets preserves the same as 2.0 wt.-% (Fig. 2c). The thickness remains 3.6±0.2 nm. Therefore, the excess BDMPS can't participate in the formation of SAM.

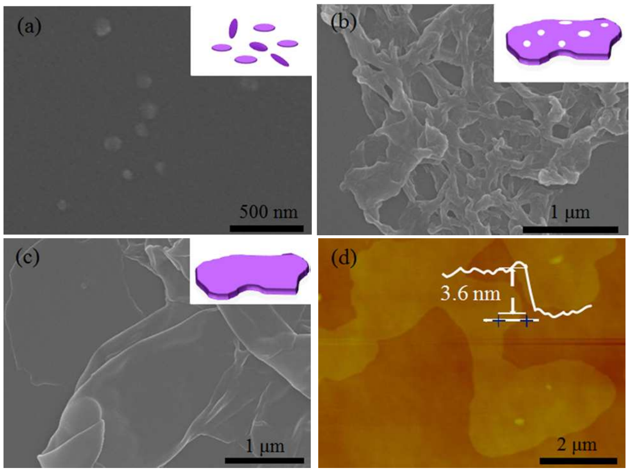


Fig. 2 Some representative Janus silica synthesized at varied BDMPS concentration (wt.-%): (a) 0.2; (b) 1.0; (c) 4.0; (d) AFM image of the nanosheets synthesized at 4.0 wt.-% of BDMPS, 3.6±0.2 nm thick.

Prior to etching $CaCO_3$, a selective modification of the exterior silica surface is allowed to easily introduce other groups while the carboxyl- group terminated interior surface is protected. As an example, octadecyltrichlorosilane is employed to modify the exterior silica surface to introduce the corresponding hydrophobic alkyl-group. Accordingly, the carboxyl/alkyl composite Janus nanosheets are derived after etching $CaCO_3$ under ultrasonication (Fig. 3a). The nanosheets become slightly thicker about 4.5±0.2 nm (Fig. S5). Presence of the alkyl- group is confirmed by FT-IR spectrum (Fig. S4). After the positively charged Fe_3O_4 nanoparticles are selectively absorbed onto the carboxyl- group terminated side, the side becomes coarsening while the other side remains smooth (Fig. S6a). The carboxyl/alkyl composite Janus nanosheets are well dispersible both in water at high pH level for example 8 and oil. They are well distinguished after drying the aqueous dispersion (Fig. 3b). Due to their amphiphilic property, in water the Janus nanosheets are stacked into a face-to-face bi-layered superstructure with the carboxyl- group terminated side exposed to the aqueous phase. Similarly, in toluene a back-to-back stacking bi-layered superstructure forms with the hydrophobic alkyl- group facing the toluene phase (Fig. S7). At low pH for example 3, the nanosheets aggregate and precipitate from the aqueous dispersion (Fig. 3c). This implies that the nanosheets are pH responsive. Zeta potential of the carboxyl/alkyl composite Janus nanosheets aqueous dispersion increases dramatically along the negative direction with pH, which levels off a plateau at pH~4 (Fig. 3d). It is known that pKa~4 of the carboxyl- group. Above pKa, carboxyl- group thus the terminated side becomes highly polarity after ionization. On the other hand, the side becomes less polarity below pKa.

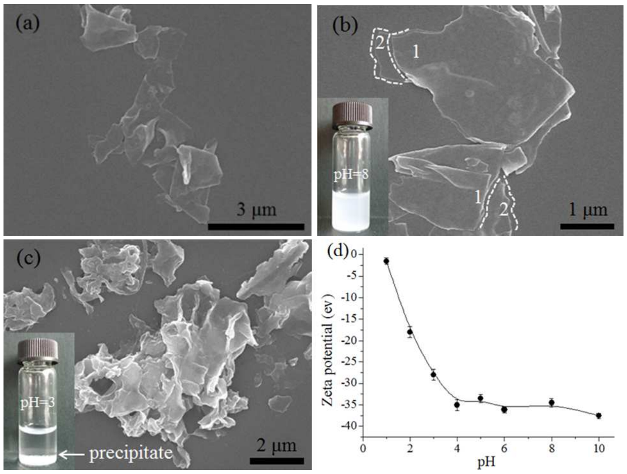


Fig. 3 SEM images of (a) the carboxyl/alkyl composite Janus nanosheets after drying the ethanol dispersion; (b) SEM image the Janus nanosheets after drying the aqueous dispersion at pH=8, 1 and 2 mean two hydrophobic surfaces of two Janus nanosheets are face-to-face stacked, inset photograph of the dispersion; (c) at pH=3; (d) Zeta potential dependence on pH of the aqueous dispersion.

The carboxyl/alkyl composite Janus nanosheets can serve as a pH responsive solid emulsifier. As proof of the concept, a paraffin-in-water emulsion forms at pH=8 (inset Fig. 4a) when paraffin is a minor phase. At low temperature, the paraffin spheres become crystalline (Fig. 4a). Diameter of the spheres is in the range of 2-3 µm (Fig. S8a). The paraffin sphere surface is covered with a single layer of the Janus nanosheets. All the nanosheets are lying parallel onto the surface (Fig. 4b). The nanosheets are curved along the spherical surface. This is explained by easy deformation of the flexible Janus nanosheets adaptive to the oil/water interface. Upon absorbing the positively charged Fe_3O_4 nanoparticles, all the exterior surface of the nanosheets becomes coarsened (Fig. S8b). This indicates that the carboxyl- group terminated side faces exclusively towards the external aqueous phase. At higher Janus nanosheets content, the paraffin spheres become smaller (Fig. S8c). The Janus nanosheets become more curved at the surface (Fig. 4c). A further increase in the Janus nanosheet content leads much smaller paraffin spheres (Fig. S8d). Especially, if the Janus nanosheets are sufficient, paraffin can be wrapped with a single Janus nanosheet (Fig. 4d). When acid is added to the emulsion to lower pH to 3, the emulsion starts to de-emulsify and separate into two layers (inset Fig. S8e). Paraffin is released forming aggregates (Fig. S8e). In another experiment, although paraffin and water can be emulsified at pH=3, the emulsion becomes less stable. The paraffin spheres become larger (Fig. S9a, S9b). The nanosheets are staked into multiple layers onto the sphere surface (Fig. S9c). Not all the exterior surface can absorb the positively charged Fe_3O_4 nanoparticles (Fig. S9d). Especially, it is found that some nanosheets stand perpendicularly to the sphere surface. The poor orientation of the nanosheets at interface is understandable by their Pickering effect at pH=3.

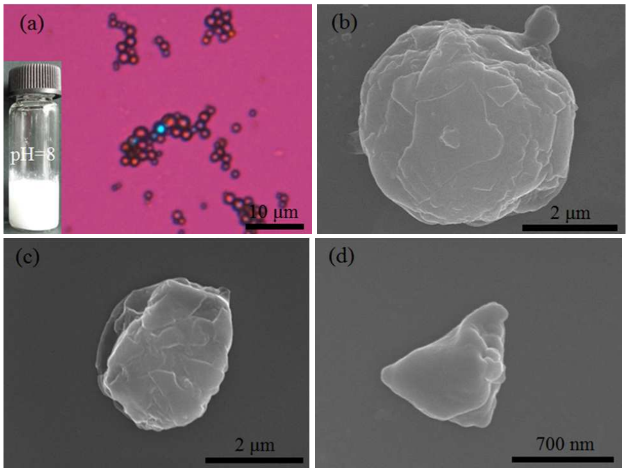


Fig. 4 Janus performance of the carboxyl/alkyl composite Janus nanosheets. (a) Optical microscopy image of the paraffin-in-water emulsion at pH=8, and inset photograph of the emulsion; SEM images of the paraffin spheres stabilized with the nanosheets at varied weight ratio of nanosheet/paraffin: (b) 1:100; (c) 1:50; (d) 1:10. Water is fixed at 500.

Conclusion

In summary, we propose a facile method to large scale synthesize Janus nanosheets by surface sol-gel process of a silane SAM onto a particle template. The Janus nanosheets are molecular scale thickness and rather flexible. Desired groups can be easily introduced by selective modification of the silica exterior side using silanes to derive Janus composite nanosheets. The composite nanosheets are flexible thus adaptive to the oil/water interfacial curvature. This made it feasible to wrap species with a single Janus nanosheet. The emulsion stability can be pH triggered to release the encapsulated species. The method can be extended to other crosslinkable SAM to derive a huge family of Janus nanosheets.

Acknowledgement
This work was supported by MOST (2012CB933200), and NSFC (51233007, 51173191)

Notes and references

State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. E-mail: liangfuxin@iccas.ac.cn, yangzz@iccas.ac.cn;
Fax: +86-10-62559373; Tel: +86-10-82619206

1 P. G. de Gennes, Rev. Mod. Phys. 1992, **64**, 645.
2 (a) A. Walther, K. Matussek, A. H. E. Müller, ACS Nano 2008, **2**, 1167; (b) A. Walther, M. Drechsler, A. H. E. Müller, Soft Matter 2009, **5**, 385; (c) A. Walther, M. Hoffmann, A. H. E. Müller, Angew. Chem. Int. Ed. 2008, **120**, 723.
3 (a) A. Walther, A. H. E. Müller, Chem. Rev. 2013, **113**, 5194; (b) J. Hu, S. X. Zhou, Y. Y. Sun, X. S. Fang, L. M. Wu, Chem. Soc. Rev. 2012, **41**, 4356; (c) S. Jiang, Q. Chen, M. Tripathy, E. Luijten, K. S. Schweizer, S. Granick, Adv. Mater. 2010, **22**, 1060; (d) S. Jiang, S. Granick, Janus Particles Synthesis, Self-assembly and Applications, RSC, London, England, 2012; (e) F. X. Liang, C. L. Zhang, Z. Z. Yang, Adv. Mater. 2014, **26**, 6944; (f) J. Z. Du, R. K. O'Reilly, Chem. Soc. Rev. 2011, **40**, 2402.
4 (a) Y. Nonomura, S. Komura, K. Tsujii, J. Phys. Chem. B 2006, **110**, 13124; (b) Y. Nonomura, S. Komura, K. Tsujii, Langmuir 2004, **20**, 11821.
5 A. Walther, X. Andre, M. Drechsler, V. Abetz, A. H. E. Müller, J. Am. Chem. Soc. 2007, **129**, 6187.
6 L. Gao, K. Zhang, Y. M. Chen, ACS Macro Lett. 2012, **1**, 1143.
7 J. R. Dorvee1, A. M. Derfus, S. N. Bhatia, M. J. Sailor, Nat. Mater. 2004, **3**, 896.
8 F. X. Liang, K. Shen, X. Z. Qu, C. L. Zhang, Q. Wang, J. L. Li, J. G. Liu, Z. Z. Yang, Angew. Chem. Int. Ed. 2011, **50**, 2379.
9 F. X. Liang, J. G. Liu, C. L. Zhang, X. Z. Qu, J. L. Li, Z. Z. Yang, Chem. Commun. 2011, **47**, 1231.
10 (a) H. L. Yang, F. X. Liang, X. Wang, Y. Chen, C. L. Zhang, Q. Wang, X. Z. Qu, J. L. Li, D. C. Wu, Z. Z. Yang, Macromolecules 2013, **46**, 2754; (b) X. Y. Ji, Q. Zhang, F. X. Liang, Q. Chen, Z. X. Qu, C. L. Zhang, Q. Wang, J. L. Li, X. M. Song, Z. Z. Yang, Chem. Commun. 2014, **50**, 5706.
11 Z. K. Zheng, C. T. Nottbohm, A. Turchanin, H. Muzik, A. Beyer, M. Heilemann, M. Sauer, A. Gölzhäuser, Angew. Chem. Int. Ed. 2010, **49**, 8493.
12 (a) W. Geyer, V. Stadler, W. Eck, M. Zharnikov, A. Gölzhäuser, M. Grunze, Appl. Phys. Lett. 1999, **75**, 2401; (b) W. Eck, A. Küller, M. Grunze, B. Völkel, A. Gölzhäuser, Adv. Mater. 2005, **17**, 2583; (c) A. Turchanin, D. Käfer, M. El-Desawy, C. Wöll, G. Witte, A. Gölzhäuser, Langmuir 2009, **25**, 7342.
13 L. M. Zhang, J. W. Yu, M. M. Yang, Q. Xie, H. L. Peng, Z. F. Liu, Nat. Commun. 2012, **4**, 1443.
14 The single molecular length of hydrolyzed BDMPS is estimated ~3.3 nm according to Materials Studio-4.0 Compass model. Length summary of all bonds at full extension states is ca. 1.7 nm; size summary of all atoms is ca. 1.6 nm (1.09 (6C)+0.29(2O)+0.23(Si)).