ChemComm

ROYAL SOCIETY OF CHEMISTRY

Amphiphilic modification and asymmetric silica encapsulation of hydrophobic Au–Fe₃O₄ dumbbell nanoparticles†

Binghui Wu, Shaoheng Tang, Mei Chen and Nanfeng Zheng*

A facile method is developed for amphiphilic surface modification and asymmetric silica encapsulation of hydrophobic Au–Fe₃O₄ dumbbell nanoparticles. The obtained asymmetric Janus nanocomposites display tunable wettability, enhanced catalysis and better cell internalization as compared to those with complete silica encapsulation.

Janus materials, named after the double-faced Roman god,[1] have recently attracted significant attention due to their novel morphologies and diverse potential applications such as interface stabilizers, catalysts, anisotropic building blocks for complex structures, *etc.*[2] Over the past few years, much research effort has been directed towards the development of effective synthetic strategies and investigations of the unique properties of nanoscale Janus materials with different surface polarity or interior chemistry.[2b–f] Two common strategies have been developed to prepare Janus nanomaterials. One is to decorate single-component nanomaterials (*e.g.*, Au or Fe₃O₄ nanoparticles, SiO₂ nanosheets) with two hydrophilic and hydrophobic ligands.[3] The resulting Janus nanomaterials usually have asymmetric wetting properties at the oil–water interface. The other strategy is to integrate two different internal compositions together in an asymmetric fashion.[2d,e,4] Various nonaqueous/aqueous routes or interfacial reactions have been developed to prepare Janus nanomaterials containing two compositionally distinct components, such as metal–metal,[5] metal–oxide,[2c,4b,6] metal–sulfide,[7] and metal–polymer[4a,8] heterostructures. In contrast to core–shell nanoparticles,[9] typical Janus nanocomposites present their structural moieties asymmetrically on their surfaces. Although many of the reported heterostructures have their both components and interfaces exposed, they are usually of the same surface polarity and hard to be directly dispersed at the oil–water interface. It still remains challenging to transform compositional heterostructures

into functional amphiphilic Janus nanomaterials with opposite polarity on their surfaces for applications.

Herein, we report a facile reverse-micelle strategy that allows the effective conversion of hydrophobic Au–Fe₃O₄ dumbbell nanoparticles at the water–oil interface into amphiphilic Janus nanoparticles. In the as-prepared Janus nanoparticles, while the Fe₃O₄ moieties are fully encapsulated in SiO₂, the Au components are exposed on the surface. The obtained Janus nanoparticles are denoted as Au-(Fe₃O₄@SiO₂) in which the symbol @ is used to represent the encapsulation of the Fe₃O₄ part in SiO₂. The introduction of long-chain alkanethiol and NH₃ solution into the reverse micelle system is critical to the asymmetric encapsulation of Au–Fe₃O₄ in SiO₂. Our studies reveal that NH₃ modifies the surface of Fe₃O₄ nanoparticles into a hydrophilic surface, and the strong binding of alkanethiol on Au stabilizes the hydrophobic surface of Au nanoparticles. Such surface modifications make the overall Au–Fe₃O₄ dumbbell nanoparticles stable at the spherical or the planar oil–water interface for asymmetric silica encapsulation to produce amphiphilic hybrid Au-(Fe₃O₄@SiO₂) nanoparticles or nanofilm. With only Au exposed on the surface, the advantages of the asymmetric encapsulation in catalysis and biological applications are also demonstrated.

The hydrophobic Au–Fe₃O₄ dumbbell nanoparticles (8.1–12.3 nm) were synthesized by microwave heating using 8.1 nm oleylamine (OAm)-capped Au nanoparticles as seeds (see ESI† for more details), and were surface-capped by OAm and oleic acid (OLA).[10] The asymmetric encapsulation of as-prepared hydrophobic dumbbell Au–Fe₃O₄ nanoparticles by SiO₂ was first attempted by employing reverse micelles in the presence of dodecanethiol (RSH) (Fig. 1). Briefly, OAm/OLA-capped Au–Fe₃O₄ nanoparticles were dispersed in a cyclohexane solution of dodecanethiol to form a homogeneous dispersion. The dispersion was then added to a reverse-micelle solution containing Brij C10 and NH₃·H₂O in cyclohexane under vigorous stirring. Tetraethylorthosilicate (TEOS) was added for SiO₂ coating. Interestingly, in the as-obtained asymmetric Au-(Fe₃O₄@SiO₂) nanoparticles, only the oxide moieties were encapsulated by SiO₂, leaving Au uncoated. As clearly revealed by TEM images (Fig. 1d and e), Au-(Fe₃O₄@SiO₂) are nearly-spherical but concave with Au free of silica encapsulation. While the thickness of the silica shell was ∼12 nm,

State Key Laboratory for Physical Chemistry of Solid Surfaces,
Collaborative Innovation Center of Chemistry for Energy Materials,
and Department of Chemistry, College of Chemistry and Chemical Engineering,
Xiamen University, Xiamen 361005, China. E-mail: nfzheng@xmu.edu.cn;
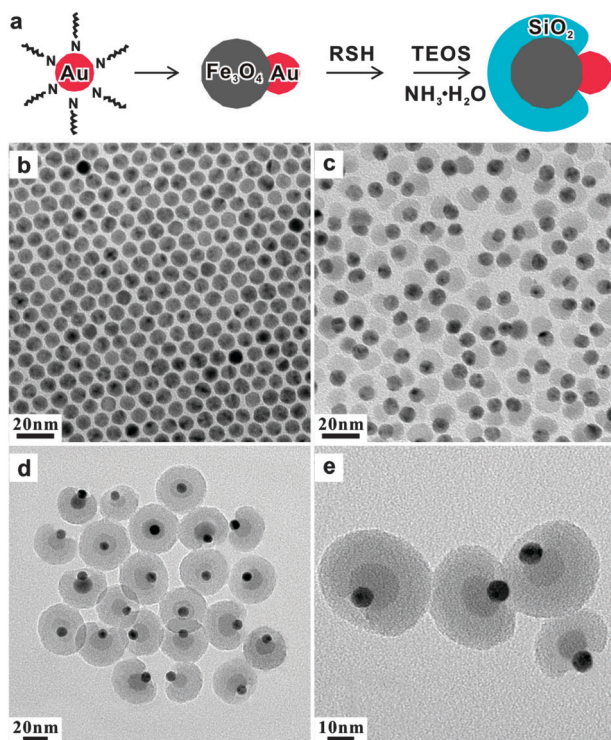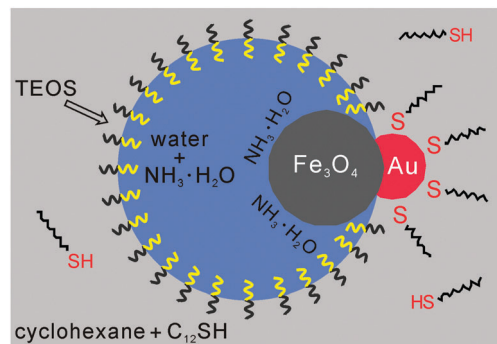*Fax: +86 592 2183047*

Fig. 1   (a) Schematic diagram of the generation of Au-(Fe₃O₄@SiO₂) nano-particles in the presence of alkanethiol and ammonia solution. TEM images of (b) OAm-capped Au nanoparticles, (c) hydrophobic Au–Fe₃O₄ dumbbell nanoparticles and (d and e) Au-(Fe₃O₄@SiO₂) nanoparticles.

Scheme 1   Schematic diagram of the location of Au–Fe₃O₄ nanoparticles and the generation of Au-(Fe₃O₄@SiO₂) nanoparticles in reverse micelles in the presence of alkanethiol and ammonia.

the overall size of Au-(Fe₃O₄@SiO₂) was ∼36 nm. It should be pointed out that the silica shell thickness can be tuned by adjusting the TEOS amount and reaction time. The Au-(Fe₃O₄@SiO₂) nanoparticles reported here can be well dispersed in pure water due to the relatively low coverage of thiol on their surfaces.

The introduction of long-chain alkanethiol into the reverse micelles is critical to the asymmetric silica encapsulation of Au–Fe₃O₄ nanoparticles. Several control experiments were carried out to understand the essential role of alkanethiol. Without the addition of thiol in the reverse micelles, Au–Fe₃O₄ nano-particles that were pre-synthesized using OAm-capped Au nano-particles as seeds were completely wrapped by silica (Fig. S1a, ESI†), similar to our previous report.[11] The resultant nanoparticles with Au–Fe₃O₄ encapsulated in SiO₂ as a whole are denoted as (Au–Fe₃O₄)@SiO₂. In contrast, Au–Fe₃O₄ nanoparticles that were pre-synthesized using thiol-capped Au nanoparticles as seeds were asymmetrically encapsulated by silica, leading to the formation of Au-(Fe₃O₄@SiO₂) as well (Fig. S1b, ESI†). Au-(Fe₃O₄@SiO₂) showed much higher catalytic activity of reduction of 4-nitrophenol by NaBH₄ than (Au–Fe₃O₄)@SiO₂ (Fig. S2 and S3, ESI†).

We consider that the strong affinity of thiol for Au is the main reason why the use of thiol is so important in the asymmetric encapsulation of Au–Fe₃O₄. Under NH₃·H₂O treatment, the surface OAm/OLA ligands on hydrophobic Fe₃O₄ nanoparticles could be exchanged. The ligand exchange results in the change of the hydro-phobic nature and thus easy encapsulation of OAm/OLA-capped Fe₃O₄ nanoparticles in SiO₂ by using reverse-micelle methods.[11,12]

However, due to the better affinity of thiols than amines for Au,[13] the introduction of long-chain alkanethiol helps to stabilize the hydrophobic nature of Au nanoparticles (Scheme 1). That is to say, after treatment by thiol and ammonia solution, Au–Fe₃O₄ nano-particles can locate at the spherical oil–water interface in reverse micelles. Based on this hypothesis, it is expected that in the presence of alkanethiol and ammonia, hydrophobic Au–Fe₃O₄ nanoparticles can be transferred into the oil–water interface without the need to introduce any other surfactants. Indeed, in the presence of dodecanethiol and ammonia only (see ESI† for details), OAm/OLA capped Au–Fe₃O₄ nanoparticles were also completely trans-ferred into the cyclohexane–water interface after stirring, leaving the water phase milk-white and the oil phase transparent (Fig. S4, ESI†). However, under similar treatment without thiol, most nanoparticles were transferred into the aqueous phase and then adsorbed on both ends of the magnet although a small portion of OAm/OLA capped Au–Fe₃O₄ nanoparticles were transferred into the oil–water interface. These results suggest that the hydrophobic surface of Au–Fe₃O₄ was modified under the treatment of ammonia even without thiol (Fig. S5a, ESI†). In contrast, with the treatment in the presence of alkanethiol but in the absence of ammonia, the major portion of Au–Fe₃O₄ nanoparticles remained in the oil phase (Fig. S5b, ESI†). Although thiol can decrease the interfacial tension of the oil–water interface,[14] only thiol and water (without ammonia) cannot transfer hydrophobic Au–Fe₃O₄ nanoparticles into amphiphilic ones. This result reinforces our hypothesis that both thiol and ammonia are necessary to the amphiphilic modification and stabilization of Au–Fe₃O₄ nanoparticles at the oil–water interface.

The amphiphilic Au–Fe₃O₄ nanoparticles obtained with the simple treatment by thiol and ammonia can nicely remain at the cyclohexane–water (Fig. S6 and S7, ESI†), the chloroform–water, or the air–water interface. At the oil–water interfaces, the as-obtained amphiphilic dumbbells should adopt the upright orientation with the long axis of dumbbells perpendicular to the interface. The asym-metric SiO₂ modification of the obtained amphiphilic Au–Fe₃O₄ nanoparticles was also successfully achieved at the macroscopic cyclohexane–water interfaces. When TEOS and ammonia were intro-duced into cyclohexane and water, respectively, a continuous thin nanofilm with all Fe₃O₄ nanoparticles encapsulated and connected by SiO₂ was obtained (Fig. S8–S11, ESI†). Similar to Au-(Fe₃O₄@SiO₂) nanoparticles, Au nanoparticles in the Au–Fe₃O₄/SiO₂ nanofilm were
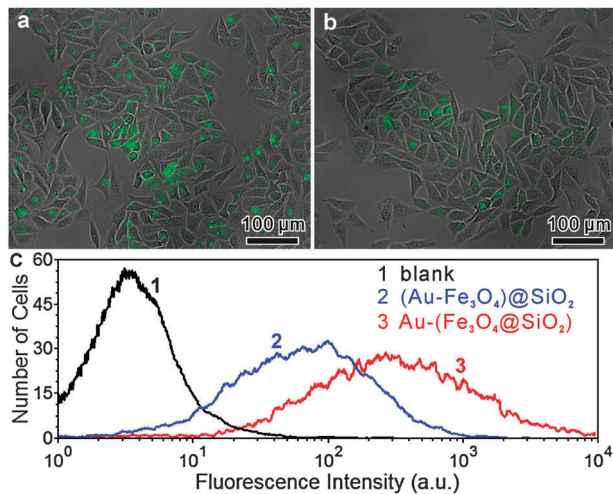
Fig. 2 (a and b) Representative fluorescence microscopic images and (c) flow cytometric profiles of human cervical cancer cells (HeLa) after 8 h incubation with FITC-modified (a) Au-(Fe$_3$O$_4$@SiO$_2$) and (b) (Au–Fe$_3$O$_4$)@SiO$_2$ at 300 μg mL^{-1}, respectively.

also exposed and free of silica encapsulation, confirmed by the wettability test of the nanofilm (Fig. S12 and S13, ESI†).

Both the obtained amphiphilic Au-(Fe$_3$O$_4$@SiO$_2$) nanoparticles and Au–Fe$_3$O$_4$/SiO$_2$ nanofilm nicely behave as inorganic Janus nanostructures that have found various applications in catalysis and nanotechnology.[3e,15] In this work, we demonstrate that the Janus Au-(Fe$_3$O$_4$@SiO$_2$) nanoparticles showed higher cell internalization than (Au–Fe$_3$O$_4$)@SiO$_2$ nanoparticles (Fig. 2). The fluorescent probe, fluorescein isothiocyanate (FITC), was introduced to allow the quantification of nanoparticles entering cells. It should be noted that both Au-(Fe$_3$O$_4$@SiO$_2$) and (Au–Fe$_3$O$_4$)@SiO$_2$ nanoparticles have similar surface charge (Fig. S14, ESI†) and dynamic size (Fig. S15, ESI†). However, both fluorescence microscopic and flow cytometric studies show that the amphiphilic Janus Au-(Fe$_3$O$_4$@SiO$_2$) nanoparticles can be uptaken by cells more effectively than hydrophilic (Au–Fe$_3$O$_4$)@SiO$_2$ nanoparticles, consistent with several recent simulation and experimental studies.[16] It has been predicted that amphiphilic Janus nanoparticles are likely to be engulfed by a membrane and could easily detach from the membrane after they are engulfed by the raft.[16b] This phenomenon is intriguing and will be a subject of further investigations to reveal the physical mechanism behind it. Based on their high cell internalization and material properties, Au-(Fe$_3$O$_4$@SiO$_2$) nanoparticles can be potentially used as a novel drug-delivery system, and contrast agents for dual CT/MRI imaging (Fig. S16 and S17).[13,17]

In conclusion, we have developed a simple wet-chemical approach to amphiphilic modification and asymmetric silica encapsulation of hydrophobic Au–Fe$_3$O$_4$ dumbbell nanoparticles at the spherical or the planar oil–water interface. The combined use of long-chain alkanethiol and NH$_3$ solution was found to be critical to the amphiphilic modification and asymmetric encapsulation of Au–Fe$_3$O$_4$ in SiO$_2$. The obtained asymmetric Janus nanocomposites display tunable wettability, enhanced catalysis and better cell internalization as compared to those with complete silica encapsulation. This work is expected to provide a simple and effective method to convert compositionally asymmetric nanoscale heterostructures into functionally amphiphilic Janus nanomaterials for a wide range of applications such as self-assembly, catalysis, drug delivery, CT/MRI imaging.

Notes and references

1 P. G. de Gennes, *Rev. Mod. Phys.*, 1992, **64**, 645.
2 (*a*) S. Jiang, Q. Chen, M. Tripathy, E. Luijten, K. S. Schweizer and S. Granick, *Adv. Mater.*, 2010, **22**, 1060; (*b*) A. Perro, S. Reculusa, S. Ravaine, E. B. Bourgeat-Lami and E. Duguet, *J. Mater. Chem.*, 2005, **15**, 3745; (*c*) C. Wang, C. J. Xu, H. Zeng and S. H. Sun, *Adv. Mater.*, 2009, **21**, 3045; (*d*) M. Lattuada and T. A. Hatton, *Nano Today*, 2011, **6**, 286; (*e*) J. Hu, S. X. Zhou, Y. Y. Sun, X. S. Fang and L. M. Wu, *Chem. Soc. Rev.*, 2012, **41**, 4356; (*f*) A. Walther and A. H. E. Müller, *Chem. Rev.*, 2013, **113**, 5194.
3 (*a*) M. Lattuada and T. A. Hatton, *J. Am. Chem. Soc.*, 2007, **129**, 12878; (*b*) B. B. Wang, B. Li, B. Zhao and C. Y. Li, *J. Am. Chem. Soc.*, 2008, **130**, 11594; (*c*) J. van Herrikhuyzen, G. Portale, J. C. Gielen, P. C. M. Christianen, N. A. J. M. Sommerdijk, S. C. J. Meskers and A. P. H. J. Schenning, *Chem. Commun.*, 2008, 697; (*d*) L. Cheng, A. P. Liu, S. Peng and H. W. Duan, *ACS Nano*, 2010, **4**, 6098; (*e*) F. X. Liang, K. Shen, X. Z. Qu, C. L. Zhang, Q. A. Wang, J. L. Li, J. G. Liu and Z. Z. Yang, *Angew. Chem., Int. Ed.*, 2011, **50**, 2379; (*f*) X. Liu, M. Yu, H. Kim, M. Mameli and F. Stellacci, *Nat. Commun.*, 2012, **3**, 1; (*g*) H. Kim, R. P. Carney, J. Reguera, Q. K. Ong, X. Liu and F. Stellacci, *Adv. Mater.*, 2012, **24**, 3857; (*h*) D. M. Andala, S. H. R. Shin, H. Y. Lee and K. J. M. Bishop, *ACS Nano*, 2012, **6**, 1044.
4 (*a*) T. Chen, M. X. Yang, X. J. Wang, L. H. Tan and H. Y. Chen, *J. Am. Chem. Soc.*, 2008, **130**, 11858; (*b*) M. R. Buck and R. E. Schaak, *Angew. Chem., Int. Ed.*, 2013, **52**, 6154.
5 (*a*) C. Wang, W. Tian, Y. Ding, Y. Q. Ma, Z. L. Wang, N. M. Markovic, V. R. Stamenkovic, H. Daimon and S. H. Sun, *J. Am. Chem. Soc.*, 2010, **132**, 6524; (*b*) B. H. Wu and N. F. Zheng, *Nano Today*, 2013, **8**, 168.
6 (*a*) H. Yu, M. Chen, P. M. Rice, S. X. Wang, R. L. White and S. H. Sun, *Nano Lett.*, 2005, **5**, 379; (*b*) P. Li, Z. Wei, T. Wu, Q. Peng and Y. D. Li, *J. Am. Chem. Soc.*, 2011, **133**, 5660; (*c*) J. He, M. T. Perez, P. Zhang, Y. J. Liu, T. Babu, J. L. Gong and Z. H. Nie, *J. Am. Chem. Soc.*, 2012, **134**, 3639.
7 (*a*) W. L. Shi, H. Zeng, Y. Sahoo, T. Y. Ohulchanskyy, Y. Ding, Z. L. Wang, M. Swihart and P. N. Prasad, *Nano Lett.*, 2006, **6**, 875; (*b*) J. Yang and J. Y. Ying, *J. Am. Chem. Soc.*, 2010, **132**, 2114.
8 E. Jeong, K. Kim, I. Choi, S. Jeong, Y. Park, H. Lee, S. H. Kim, L. P. Lee, Y. Choi and T. Kang, *Nano Lett.*, 2012, **12**, 2436.
9 (*a*) S. Alayoglu, A. U. Nilekar, M. Mavrikakis and B. Eichhorn, *Nat. Mater.*, 2008, **7**, 333; (*b*) E. V. Shevchenko, M. I. Bodnarchuk, M. V. Kovalenko, D. V. Talapin, R. K. Smith, S. Aloni, W. Heiss and A. P. Alivisatos, *Adv. Mater.*, 2008, **20**, 4323; (*c*) H. Ataee-Esfahani, L. Wang and Y. Yamauchi, *Chem. Commun.*, 2010, **46**, 3684.
10 (*a*) B. H. Wu, H. Y. Yang, H. Q. Huang, G. X. Chen and N. F. Zheng, *Chin. Chem. Lett.*, 2013, **24**, 457; (*b*) B. H. Wu, H. Zhang, C. Chen, S. C. Lin and N. F. Zheng, *Nano Res.*, 2009, **2**, 975.
11 C. Chen, X. L. Fang, B. H. Wu, L. J. Huang and N. F. Zheng, *ChemCatChem*, 2012, **4**, 1578.
12 F. Wang, X. L. Chen, Z. X. Zhao, S. H. Tang, X. Q. Huang, C. H. Lin, C. B. Cai and N. F. Zheng, *J. Mater. Chem.*, 2011, **21**, 11244.
13 (*a*) C. J. Xu, J. Xie, D. Ho, C. Wang, N. Kohler, E. G. Walsh, J. R. Morgan, Y. E. Chin and S. H. Sun, *Angew. Chem., Int. Ed.*, 2008, **47**, 173; (*b*) C. J. Xu, B. D. Wang and S. H. Sun, *J. Am. Chem. Soc.*, 2009, **131**, 4216.
14 N. Glaser, D. J. Adams, A. Boker and G. Krausch, *Langmuir*, 2006, **22**, 5227.
15 Y. Chen, F. X. Liang, H. L. Yang, C. L. Zhang, Q. Wang, X. Z. Qu, J. L. Li, Y. L. Cai, D. Qiu and Z. Z. Yang, *Macromolecules*, 2012, **45**, 1460.
16 (*a*) A. Verma and F. Stellacci, *Small*, 2010, **6**, 12; (*b*) H. M. Ding and Y. Q. Ma, *Nanoscale*, 2012, **4**, 1116; (*c*) S. Pogodin, M. Werner, J. U. Sommer and V. A. Baulin, *ACS Nano*, 2012, **6**, 10555; (*d*) N. Arai, K. Yasuoka and X. C. Zeng, *Nanoscale*, 2013, **5**, 9089.
17 (*a*) C. Barbe, J. Bartlett, L. G. Kong, K. Finnie, H. Q. Lin, M. Larkin, S. Calleja, A. Bush and G. Calleja, *Adv. Mater.*, 2004, **16**, 1959; (*b*) D. Kim, M. K. Yu, T. S. Lee, J. J. Park, Y. Y. Jeong and S. Jon, *Nanotechnology*, 2011, **22**, 155101.