

Magnetic-mesoporous Janus nanoparticles†

Lu Zhang,^a Fan Zhang,^a Wen-Fei Dong,^{*a} Jun-Feng Song,^a Qi-Sheng Huo^b and Hong-Bo Sun^{*ac}

Received 18th September 2010, Accepted 1st November 2010

DOI: 10.1039/c0cc03946b

Novel multifunctional magnetic-mesoporous Janus particles with controlled aspect ratio were developed by a simple one-step synthesis approach. Due to their superior magnetic properties and well-defined pore structures, these particles will be important in drug delivery, molecule targeting, cellular imaging, and as building blocks for the assembly of complex nanostructures.

Janus particles, named by Casagrande and de Gennes after the double-faced Roman mythology god, have emerged as a new division of colloidal structures.¹ These anisotropic/asymmetric particles are currently reported to consist of a type of soft matter with different chemistry, polarity, or other physico-chemical properties on opposite sides.² Although Janus particles combine individual components together,^{3,4} their fingerprint optical, magnetic, and electronic properties are not often altered, interfered or completely lost,⁵ in contrast with other complex nanoparticles.^{6,7} Therefore, these unique particles have a great potential application in drug delivery,⁸ imaging probes,⁹ and electronic devices.¹⁰

Recently, numerous techniques have been developed to produce Janus particles, including direct chemical synthetic routes,^{11,12} indirect chemical modification of particles at biphasic interfaces,^{13,14} and topographically selective modification of particles,^{15,16} *etc.* However, the synthesis of multifunctional Janus particles with spatially separated functionalities, efficient response to stimuli, tunable compositions and uniform size, still remains challenging for a long time.^{17,18}

In this communication, we report a simple and cheap approach for one-step synthesis of novel Janus particles with a magnetic Fe₃O₄ head and mesoporous SiO₂ body. As-formed Janus nanoparticles not only have a uniform size with designable aspect-ratio, but also possess superior magnetic properties and well-defined pore structures.

As illustrated in Fig. 1a, the starting materials of magnetic colloids were prepared by using a high temperature hydrolysis reaction.^{19,20} A stock NaOH solution was prepared by dissolving 2.0 g of NaOH in 20 ml of diethylene glycol (DEG). FeCl₃ (0.8 mmol), poly(acrylic acid) (PAA, 8 mmol, *M_w* = 1800), and DEG (34 ml) were added into a three-necked flask, and the mixed solution was heated to 220 °C for 30 min under

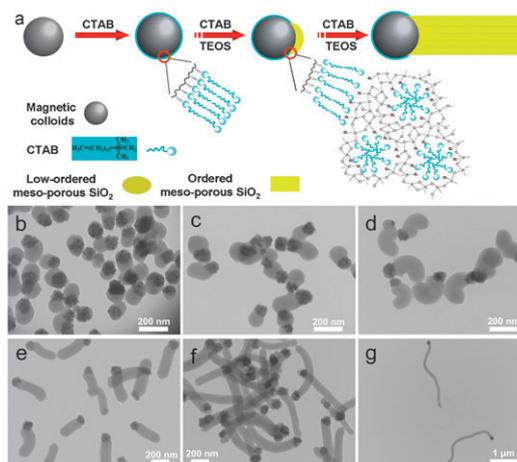


Fig. 1 (a) Strategy used to grow a mesoporous silica stick on Fe₃O₄ nanoparticle. TEM images of Fe₃O₄-SiO₂ Janus particles with different aspect ratios 2 : 1 (b), 3 : 1 (c), 4 : 1 (d) 5 : 1 (e), 7 : 1 (f) and a micrometre-long worm-like Janus particles (g).

nitrogen. The stock NaOH solution was then dropped rapidly into the mixture with vigorous mechanical stirring for an additional one hour. The as-prepared Fe₃O₄ nanoparticles (Fe₃O₄ NP) were cooled to room temperature and, thereafter, washed with deionized water and ethanol three times *via* centrifugation.

In order to obtain Janus particles with controlled aspect ratio, a modified sol-gel process will be developed here, while using tetraethyl orthosilicate (TEOS) as a silica source, hexadecyltrimethylammonium bromide (CTAB) as a template and Fe₃O₄ NP as a substrate, as shown in Fig. 1a. At first, the as-formed magnetic colloidal solution (8.6 mg ml⁻¹) was added into CTAB solution (5 mg ml⁻¹) followed by vigorous ultrasonic treatment for 10 min. Then, the mixture was mechanically stirred at 40 °C in a water bath and 0.5 ml ammonia hydroxide was injected into the solution, followed by a certain amount of TEOS. Finally, the magnetic-mesoporous Janus nanoparticles were obtained in solution, as evidenced by TEM images of Fig. 1b–g. Using this simple approach, the aspect ratio (from 2 : 1 to 7 : 1) of Janus particles can be facilely controlled by the molar ratio of [TEOS]/[Fe₃O₄ NP]. For instance, Fig. 1b shows that nanoparticles were prepared with the lowest molar ratio of [TEOS × 10⁻⁷]/[Fe₃O₄ NP] = 3.8 in the mixture, with an average length of approximately 200 nm. Interestingly, these particles were found to be nearly single mesoporous SiO₂ sticks just linked to every individual Fe₃O₄ NP. However, there are also a few examples of two Fe₃O₄ NPs embedded on a single SiO₂ stick. Obviously, the aspect ratio of Janus nanoparticles will increase when the molar ratio of [TEOS × 10⁻⁷]/[Fe₃O₄ NP] is increasing from

^a State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, 2699, Qianjin Street, Changchun 130012, P.R. China. E-mail: dongwf@jlu.edu.cn, hbsun@jlu.edu.cn

^b State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P.R. China

^c College of Physics, Jilin University, 119 Jiefang Road, Changchun 130023, P.R. China. E-mail: hbsun@jlu.edu.cn

† Electronic supplementary information (ESI) available: Magnetic-mesoporous Janus nanoparticles. See DOI: 10.1039/c0cc03946b

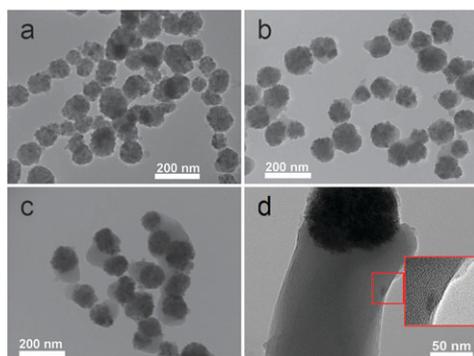


Fig. 2 Time-resolved observation of the growth process of the magnetic-mesoporous nanoparticles. TEM images of the products at the reaction time of 2 min (a), 2.5 min (b), and 3 min (c). (d) HRTEM images of the magnetic-mesoporous Janus nanoparticles. The inset is an enlarged image of a selected region.

4.9, 7.6, to 11.3, respectively, as displayed in Fig. 1b–d. Here, the micrometre-long worm-like asymmetric particles with the highest aspect ratio of 7 : 1 were obtained at a molar ratio of 17.0 in Fig. 1e. Thus, the growth of mesoporous structure from one side of magnetic colloidal nanoparticles can be achieved in a controllable fashion.

In order to understand the growth mechanism of Janus nanoparticles, time-resolved transmission electron microscopy will be used to monitor the growth process. As shown in Fig. 2a, silica aggregates are anchored to the surface of Fe_3O_4 NPs at the beginning of reaction with the help of cooperative assembly between silica species and surfactant molecules. And then continuous growth of silica mesoporous structure takes place until the final SiO_2 stick is formed. Finally, the highly ordered mesoporous structure of Janus particles can be clearly observed along the axis of silica body by high-resolution transmission electron microscopy (HRTEM) image, as shown in Fig. 2d. The inset of micrograph shows the obvious hexagonal array along the axis parallel to the direction of the pore channels, in consistent with the classical MCM-41 structure. In general, the growth of Janus nanoparticles should be governed by two necessary steps: the first is the self-organization of low-ordered aggregates on colloid surface which can be favoured by decreasing solid–liquid interface energy.²¹ The second is the growth of ordered mesoporous architecture starting from those aggregates along both axis and radial (Fig. 2b and c). The growth of aggregates is really so fast (within a second) that it is not detectable by TEM, while the growth reaction rate is relatively slow. As evidenced in Fig. 2, Janus-like particles can be formed within minutes. There are at least two key parameters which play important roles on the morphology of nanoparticles, one is the water-based reaction and the other is Fe_3O_4 NP substrates. Consistent with the recent literature, only a core–shell structure of silica@ Fe_3O_4 can be achieved when the sol-gel reaction takes place in either ethanol solution or water–ethanol mixture.²² However, rod-like mesoporous silica will be obtained when reaction is performed in aqueous solution. On the other hand, without Fe_3O_4 NP substrates, the silica nanorods show a relatively large size-distribution (see ESI†, Fig. S1). In contrast, the monodispersity of Janus nanoparticles is highly improved

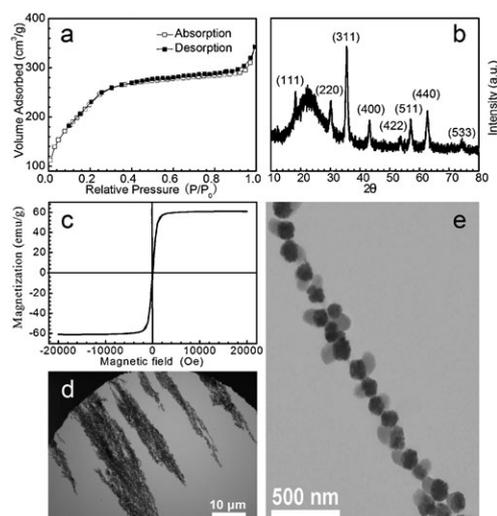


Fig. 3 (a) N_2 adsorption/desorption isotherms and (b) XRD of the magnetic-mesoporous Janus nanoparticles. (c) Hysteresis loops recorded at 300 K of the Fe_3O_4 - SiO_2 Janus nanoparticles. (d) TEM images of the Fe_3O_4 - SiO_2 Janus particles aligned by an external magnetic field. (e) A straight chain of the Fe_3O_4 - SiO_2 Janus particles aligned by an external magnetic field.

with the existence of Fe_3O_4 NP substrates, as evidenced by Fig. 1b–g.

The characterization of the mesoporous structure is evaluated by N_2 adsorption/desorption isotherms and the respective X-ray diffraction (XRD) measurements. N_2 adsorption/desorption isotherms of Janus particles were carried out at 77 K. Fig. 3a exhibits the type IV BET isotherms for the particles, a signature feature of mesoporous materials. Calculated from the absorption branch of the nitrogen isotherm with the BJH method, the predominated pore diameter was evaluated to be 2.8 nm. The uniform mesopores along with the small particle size (< 200 nm) are advantageous for the drug delivery applications compared to commercially available micrometre-sized magnetic polymeric beads. The BET surface area and the cumulative pore volume of the magnetic-mesoporous Janus particles were as high as $838.8 \text{ m}^2 \text{ g}^{-1}$ and $0.5 \text{ cm}^3 \text{ g}^{-1}$, respectively. Fig. 3b shows the XRD patterns of Janus particles. The apparent diffraction peaks are assigned as (111), (220), (311), (400), (422), (511), (440) and (533) planes, which matched exactly with that of inverse spinel-type Fe_3O_4 NP. The results of the magnetic-mesoporous Janus nanoparticles characterized by Raman spectroscopy proved that the magnetic core is Fe_3O_4 (Fig. S2, ESI†). The broad peak at 23° confirmed the existence of amorphous silica.²³

The magnetic property of the particles was examined by a vibrating sample magnetometer (VSM), and the samples show a superparamagnetic behaviour as shown in the hysteresis loops (Fig. 3c). No remanence or coercivity was detected at 300 K due to the fact that the Fe_3O_4 particles made of single-crystalline aggregations retained superparamagnetic behaviour at room temperature and possessed higher saturation magnetization than single nanocrystals. The saturation magnetization of Janus nanoparticles with an aspect ratio of 2 : 1 is 60 emu g^{-1} . As a result of the high magnetic property,

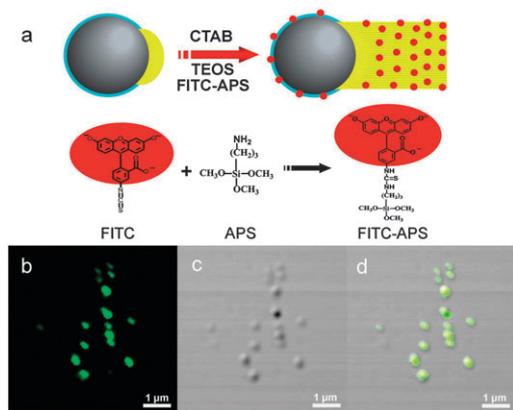


Fig. 4 (a) Schematic illustration of the fluorescent molecular incorporation into silica stick and reactive formulation of FITC and APS. Confocal laser scanning microscopy images of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-FITC}$ Janus particles: (b) fluorescence image; (c) bright-field image; and (d) merged image.

the Janus particles can be readily separated from its dispersion in less than 1 min by simply using a magnet, and redispersed quickly with a slight shaking when the magnetic field was removed. It suggests that the Janus particles possess excellent magnetic responsivity and redispersibility, which is an advantage to their applications for delivery and separation.

Janus nanoparticles with an aspect ratio of 2 : 1 were chosen to further investigate the magnetic-direct assembly property under an external magnetic field (Fig. 3d). The particles were aligned into one-dimensional necklace-like structures under the magnetic field (Fig. 3e), in which dipole-dipole interactions between adjacent magnetic particles couple them together and force the formation of anisotropic structures, revealing high magnetic sensitivity and manipulability under an external magnetic field. A droplet of ethanol dispersion of the Janus particles was carefully placed on a copper TEM grid. Subsequently, a permanent magnet was placed close to the copper grid with the magnetic line of force running parallel to the copper grid plane until ethanol was completely evaporated. Janus particle chains aligned by an external magnetic field, displaying great potential in manipulation and organization of magnetic structures into integrated system.

Besides excellent magnetic and porosity properties, surface modification is another key issue for the utilization of these Janus nanoparticles in the field of biosensor, drug delivery and bio-imaging. Here, fluorescent magnetic-mesoporous particles can be synthesized in order to demonstrate the proof experiment. At first, silane coupling agent 3-aminopropyl-trimethoxysilane (APS) is covalently coupled to an amine-reactive dye fluorescein isothiocyanate (FITC). FITC (0.5 mg) and APS (0.5 ml) were stirred in anhydrous ethanol (10 ml) in the dark at room temperature for 12 h. Next 0.03 ml of as-synthesized FITC-APS in ethanol was added to the reaction mixture after adding TEOS to produce Janus nanoparticles using the same protocol. Fig. 4 shows the confocal laser scanning microscopy images of the fluorescent Janus particles. The incorporation of dye molecules on Fe_3O_4 surface could clearly be seen from the merged image, and the dye molecules were also embedded into the silica matrix *via* the sol-gel method. As-prepared

fluorescent magnetic-mesoporous particles would enable the *in situ* detection and monitoring of the movement of the doped cells under an external magnetic field because of its potential use in bio-separation and related applications.

In conclusion, novel magnetic-mesoporous Janus particles were synthesized by a simple sol-gel method. The aspect ratio of Janus particles can be precisely controlled by varying the molar ratio of $[\text{TEOS}]/[\text{Fe}_3\text{O}_4 \text{ NP}]$. Due to the unique Janus structure, these particles combine individual components together without interfering or sacrificing their magnetic and mesoporous properties. Under an external magnetic field, these Janus particles could be self-aligned and self-assembled, revealing a high magnetic sensitivity and manipulability and displaying a great potential in manipulation and organization of magnetic structures into integrated system. In addition, their facile surface modification strongly indicates their further application in bio/chemo molecule targeting and cellular labelling.

This work is supported by the National Science Foundation of China (Grant Nos. 60977056, 61077066, 60978062 and 90923037).

Notes and references

- P. G. de Gennes, *Rev. Mod. Phys.*, 1992, **64**, 645.
- C. Casagrande, P. Fabre, E. Raphael and M. Veysie, *Europhys. Lett.*, 1989, **9**, 251.
- J. V. 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.
- S. C. Glotzer and M. J. Solomon, *Nat. Mater.*, 2007, **6**, 557.
- Y. D. Jin and X. H. Gao, *Nat. Nanotechnol.*, 2009, **4**, 571.
- C. J. Xu, B. D. Wang and S. H. Sun, *J. Am. Chem. Soc.*, 2009, **131**, 4216.
- T. Mokari, E. Rothenberg, I. Popov, R. Costi and U. Banin, *Science*, 2004, **304**, 1787.
- A. K. Salem, P. C. Searson and K. W. Leong, *Nat. Mater.*, 2003, **2**, 668.
- M. Yoshida, K. H. Roh and J. Lahann, *Biomaterials*, 2007, **28**, 2446.
- D. Graham-Rowe, *Nat. Photonics*, 2007, **1**, 248.
- V. N. Manoharan, M. T. Elsesser and D. J. Pine, *Science*, 2003, **301**, 483.
- A. Perro, E. Duguet, O. Lambert, J. C. Taveau, E. Bourgeat-Lami and S. Ravaine, *Angew. Chem.*, 2009, **121**, 367.
- Y. K. Takahara, S. Ikeda, S. Ishino, K. Tachi, K. Ikeue, T. Sakata, T. Hasegawa, M. Mori, H. Matsumura and B. Ohtani, *J. Am. Chem. Soc.*, 2005, **127**, 6271.
- S. Pradhan, L. P. Xu and S. W. Chen, *Adv. Funct. Mater.*, 2007, **17**, 2385.
- B. Liu, C. L. Zhang, J. G. Liu, X. Z. Qu and Z. Z. Yang, *Chem. Commun.*, 2009, 3871.
- V. N. Paunov and O. J. Cayre, *Adv. Mater.*, 2004, **16**, 788.
- N. Zhao and M. Y. Gao, *Adv. Mater.*, 2009, **21**, 184.
- Z. Nie, W. Li, M. Seo, S. Xu and E. Kumacheva, *J. Am. Chem. Soc.*, 2006, **128**, 9408.
- H. Xia, L. Zhang, Q. D. Chen, L. Guo, H. H. Fang, X. B. Li, J. F. Song, X. R. Huang and H. B. Sun, *J. Phys. Chem. C*, 2009, **113**, 18542.
- J. P. Ge, Y. X. Hu, M. Biasini, W. P. Beyermann and Y. D. Yin, *Angew. Chem., Int. Ed.*, 2007, **46**, 4342.
- J. F. Wang, C. K. Tsung, W. B. Hong, Y. Y. Wu, J. Tang and G. D. Stucky, *Chem. Mater.*, 2004, **16**, 5169.
- Y. H. Deng, D. Qi, C. H. Deng, X. M. Zhang and D. Y. Zhao, *J. Am. Chem. Soc.*, 2008, **130**, 28.
- L. Zhang, S. Z. Qiao, Y. G. Jin, Z. G. Chen, H. C. Gu and G. Q. Lu, *Adv. Mater.*, 2008, **20**, 805.