## Fabrication of Magnetic Yolk–Shell Nanocatalysts with Spatially Resolved Functionalities and High Activity for Nitrobenzene Hydrogenation

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Recent advancements in the design and fabrication of controlled nanostructures offer numerous opportunities to achieve the ultimate goal of catalysis. Nanocatalysts are considered to be a bridge between homogeneous and heterogeneous catalysts,<sup>[1,2]</sup> which in general show high catalytic activity and selectivity, but have issues with separation and recovery.<sup>[3]</sup> To overcome this problem, fabrication of nanocatalysts with a magnetic response property would allow for easy recovery with an external magnet. To date, various magnetic nanocatalysts have been synthesized by entrapment or grafting of noble metals and ligands on the surface of magnetic supports,<sup>[4,5]</sup> or by embedding active components into magnetic composites.<sup>[6]</sup> To warrant successful application of magnetic nanocatalysts, their magnetic property, high activity and selectivity, and long-term stability must all be retained.<sup>[7]</sup>

Hollow carbon spheres are extremely promising candidates as catalyst supports due to the large fraction of void space in the hollow structures, low effective density and high specific surface area.<sup>[8]</sup> In particular, the carbon shells are an ideal matrix for isolating the entrapped species from the external environment by introducing them into the interior hollow space.<sup>[7]</sup> As known, multiple small nanometersized magnetic particles inside the shell are more advantageous than one relatively big nanometer-sized one; in this way the magnetic intensity of the sample can be easily tuned by varying the amount of magnetic cores.<sup>[2c]</sup> To date, the encapsulation of multiple cores into hollow structures is still a great challenge.<sup>[2d]</sup> Inspired by the recent synthesis of hollow spheres through weak acid-base interaction-induced assembly with the use of oleic acid as soft template and functional dihydroxybenzoic acid (DA) as precursor,<sup>[8d]</sup> we

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D-45470 Mülheim an der Ruhr (Germany) Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201300307. have developed a new and facile method for the fabrication of bifunctional magnetic yolk-shell type nanocatalysts, by direct encapsulation of magnetic  $Fe_3O_4$  nanoparticles within the hollow core, and inlaying Pt nanoparticles (other noble metals, Pd and Ag, are also possible) in the carbon shell (Figure 1 a). The obtained nanocomposites show high cata-



Figure 1. a) Schematic illustration of the synthetic procedure for  $Fe_3O_4@h$ -C/noble metal. TEM images of: b)  $Fe_3O_4$  nanoparticles prepared by thermal decomposition method, c) hollow polymer nanospheres. d) HAADF-STEM image, and e) photographs of  $Fe_3O_4@h$ -C/noble metal dispersed in H<sub>2</sub>O before (left) and after (right) adding a magnet.

lytic activity, reusability, and good magnetic separation property in the hydrogenation of nitrobenzene.

Typically, Fe<sub>3</sub>O<sub>4</sub> nanoparticles prepared by using a thermal decomposition method<sup>[9a]</sup> were transferred into H<sub>2</sub>O with sodium oleate as surfactant, to form a Fe<sub>3</sub>O<sub>4</sub> colloidal solution. As shown in Figure 1b, the TEM image of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles exhibited a 2D assembly of uniform 16 nm nanocrystals. Then, to this solution, a DA/hexamethylene tetramine (HMT) solution with a pH value of about 2.98 was added, to form an emulsion in which the  $Fe_3O_4$ nanoparticles were stabilized. HMT was used as a precursor, and could decompose into formaldehyde and ammonia under hydrothermal condition. Subsequently, polymerization occurs around the emulsion droplets, generating Fe<sub>3</sub>O<sub>4</sub>@h-P nanospheres (Figure 1c). Due to the presence of carboxylate in the polymer shell of as-obtained Fe<sub>3</sub>O<sub>4</sub>@h-P, various noble metal cations can be introduced into the shell through an ion-exchange process. Noble metal cations can be converted into nanocrystals with small size and high dispersion in the carbon shells after pyrolysis, yielding the final products of Fe<sub>3</sub>O<sub>4</sub>@h-C/noble metal (Figure 1d and Figure S1 in the Supporting Information). In this unique configuration,



 $Fe_3O_4$  nanoparticles act as magnetic carriers, which allow the hollow carbon composites to be manipulated by an external magnet and the carbon shells to be used as noble metal catalyst support. This synthesis concept can produce novel functional nanostructures with properties that are different from those expected from the simple sum of the individual blocks.

Here,  $Pt^{2+}$  was chosen as candidate to fabricate a bifunctional catalyst, resulting in  $Fe_3O_4@h$ -C/Pt nanospheres. The content of Pt in  $Fe_3O_4@h$ -C/Pt composite was determined to be 1.59 wt. % by inductively coupled plasma atomic emission spectrometry (ICP-AES). The TEM image of sample  $Fe_3O_4@h$ -C/Pt shows that the  $Fe_3O_4$  nanoparticles are trapped inside the hollow structures (Figure 2a). High angular



Figure 2. a) TEM, and b) HAADF-STEM images of Fe<sub>3</sub>O<sub>4</sub>@h-C/Pt, and c) SEM image of Fe<sub>3</sub>O<sub>4</sub>@h-C/Pt after cutting the hollow carbon spheres into hemispheres.

annular dark-field scanning transmission electron microscopy (HAADF-STEM; Figure 2b) revealed the characteristics of individual nanospheres. Interestingly, self-assembly periodic arrays of Fe<sub>3</sub>O<sub>4</sub> nanoparticles were observed. This interesting phenomenon shows that the emulsion of sodium oleate can encapsulate water dispersible Fe<sub>3</sub>O<sub>4</sub> nanoparticles by balancing the attractive depletion forces and the repulsive electrostatic forces. During the drying process, solvent evaporation would lead to organization of the nanostructure rather than random aggregation; this is similar to the principle of the well-know solvent evaporation induced self-assembly for the preparation of ordered mesoporous film.<sup>[10]</sup> The relatively high contrast of the nanoparticles in the Zcontrast image indicates that the Pt nanoparticles were highly dispersed without aggregation in the carbon shells with small diameters of 2-3 nm. To obtain an insight on the spatial configuration of the multicomponents of the yolkshell nanospheres, samples as cut hemispheres were characterized by using high resolution SEM. The SEM image in Figure 2c shows the configuration of the cut hemispheres corresponding to sample Fe<sub>3</sub>O<sub>4</sub>@h-C/Pt. It can clearly be seen that the Fe<sub>3</sub>O<sub>4</sub> nanoparticles are, in all cases, nicely encapsulated within the hollow structures, whereas Pt nanoparticles are embedded on the outer surface of Fe<sub>3</sub>O<sub>4</sub>@h-C/Pt. This allows reactants easy access to the surface-located Pt active site. We also effectively applied the ion-exchange scheme of Pt<sup>2+</sup> to other transition-metal ions, such as Pd<sup>2+</sup> and Ag<sup>+</sup>, to obtain bifunctional yolk-shell nanospheres (Figure S2 in the Supporting Information).

The crystalline phases of the as-obtained samples were characterized by XRD (Figure S3 a in the Supporting Information). The XRD pattern of  $Fe_3O_4@h$ -C displays the reflections of  $Fe_3O_4$  (JCPDS No.: 11-0614) and  $Fe_xC_y$  (JCPDS No.: 23-0298), indicating that part of the encapsulated  $Fe_3O_4$  nanoparticles react with carbon to form  $Fe_xC_y$  during pyrolysis. In the sample containing noble metals,  $Fe_3O_4@h$ -C/Pt, the XRD pattern also shows the reflection of the individual metal. Interestingly, all the diffraction peaks are broad in width and weak in intensity, implying the smaller sizes of the in situ formed crystals.

The porosities of the obtained Fe<sub>3</sub>O<sub>4</sub>@h-C and Fe<sub>3</sub>O<sub>4</sub>@h-C/Pt were analyzed by  $N_2$  adsorption technique at 77.4 K. As can be seen in Figure S3b (in the Supporting Information), the two samples possess similar N<sub>2</sub> adsorption isotherms without any hysteresis, indicating that the carbon shells of all the products are essentially microporous. However, it is worth mentioning that with increasing relative pressure, there is a further increase in the amount of adsorbed nitrogen, reflecting a certain proportion of small mesoporosity present in the samples. The surface areas and pore volumes of samples Fe<sub>3</sub>O<sub>4</sub>@h-C and Fe<sub>3</sub>O<sub>4</sub>@h-C/Pt are in the range of 400–440 and 0.24– $0.25 \text{ cm}^3 \text{g}^{-1}$ , respectively (Table S1 in the Supporting Information). These results demonstrate that there is minimal effect on the textural property of the carbon shell after introduction of the noble metal.

To evaluate the thermal stability of the nanospheres, thermogravimetric (TG) experiments were conducted by heating samples to up to 800 °C under air. Based on the TG curves (Figure S3 c in the Supporting Information), the calculated magnetite nanoparticle content in sample Fe<sub>3</sub>O<sub>4</sub>@*h*-C is approximately 3.4 wt.% (assuming that the residues consist of completely oxidized  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>). As for Fe<sub>3</sub>O<sub>4</sub>@*h*-C/Pt, its residue is greater (14.2 wt.%), which may be caused by the loading of noble metal nanoparticles. Besides, the TG result shows a good thermal stability of Fe<sub>3</sub>O<sub>4</sub>@*h*-C/Pt at temperatures below 300 °C in air.

Magnetic properties were studied by using a vibrating sample magnetometer. The magnetic hysteresis curves of Fe<sub>3</sub>O<sub>4</sub>@*h*-C and Fe<sub>3</sub>O<sub>4</sub>@*h*-C/Pt recorded at room temperature show no remanence or coercivity at room temperature, indicating a superparamagnetic property (Figure S3 d in the Supporting Information). This proves that the encapsulated Fe<sub>3</sub>O<sub>4</sub> nanoparticles retain their small size without sintering after pyrolysis. In addition, their saturation magnetization values are in the range of 0.20–0.25 emug<sup>-1</sup>, indicating a magnetic separation capability.<sup>[9b]</sup> It is believed that the saturation magnetization value of Fe<sub>3</sub>O<sub>4</sub>@*h*-C/Pt can be adjusted by varying the amount of Fe<sub>3</sub>O<sub>4</sub> nanoparticles used in the synthesis system.

In order to demonstrate the performance of the nanocatalysts, we used  $Fe_3O_4@h$ -C/Pt for the hydrogenation of nitrobenzene. The catalytic reactions were carried out under moderate reaction conditions: propan-2-ol as solvent, 30 °C and 1 atm of H<sub>2</sub>, and 2 h reaction period. Unexpectedly, the catalyst only gave an aniline conversion of 9%, which only consumed 0.162 mmol hydrogen (see the Supporting Information for details) whereas about 84 mmol H<sub>2</sub> was supplied in the reaction vial. The low catalytic activity may be due to the covered species on the surfaces of the Pt nanoparticles. However, the used catalyst after calcination at 250 °C under air for 1 h, showed excellent results in the second run, that is, a high conversion of >99% (Figure 3). The magnetic



Figure 3. Conversion of the recycled  $Fe_3O_4@h-C/Pt$  catalyst for hydrogenation of nitrobenzene.

nanocatalyst was collected by a magnet for reuse, which gave again 99% yield of aniline over seven consecutive runs without any deactivation. Judging from the activity per Pt site, we carried out a catalytic reaction using the calcined catalyst in which the molar ratio of nitrobenzene to Pt used was 1500. After 2 h reaction period, the catalyst gave 38% yield of aniline, with a higher turnover frequency (TOF, calculated on the basis of the total Pt weight according to the ICP-AES data) of 285 h<sup>-1</sup> (see Table S2 in the Supporting Information for details of comparison). This catalyst still showed excellent results in a total of four cycles (aniline conversions are accordingly 38.0, 37.4, 38.2, and 37.5%), and an average TOF of approximately 280 h<sup>-1</sup>. These results confirm the high catalytic activity, great reusability, and good magnetic separation property of the as-synthesized nanocatalyst.

In conclusion, we have developed a novel and facile synthesis for highly engineered bifunctional yolk-shell nanocomposites with tailored structural configuration and spatially resolved functionalities, that is, hollow carbon spheres as the matrix, entrapped magnetite nanoparticles in the hollow core as the magnetic carrier, and in situ formed and highly dispersed noble metal nanoparticles in the carbon shells as the active catalyst sites. As demonstrated, the nanocomposites showed a high catalytic activity, were reusable and had magnetic separation capabilities in liquid phase reactions. It should be noted that in this synthesis, oleate emulsions act not only as soft-templates to fabricate the hollow structure but also as containers to carry magnetite nanoparticles, stabilized by sodium oleate, into the hollow cores. In principle, the hollow structure would allow higher exposing efficiency of the supported catalyst to the reactants than the solid one. Moving forward, one can envisage that besides magnetic nanoparticles, other inorganic nanoparticles (e.g., Au,<sup>[11a]</sup> Ag,<sup>[11b]</sup> Pt,<sup>[11c]</sup> etc., which are commonly stabilized by oleic acid or oleate) can in principle be introduced into the hollow structures. Furthermore, using the properties of the functionalizable hollow carbon shells, we rationally believe that multifunctional nanocatalysts can be fabricated at will, using the current proposed synthesis principle. This method has the advantage of producing materials with tailored properties because it allows a better control on the size and the morphology of the building blocks. This may have a great impact on the development of recyclable nanocatalysts for green and sustainable chemistry.

## **Experimental Section**

**Chemicals**: FeCl<sub>3</sub>·6 H<sub>2</sub>O, 1-octadecene, 2,4-dihydroxybenzoic acid (DA), Pd(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub> and Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> were obtained from Aldrich. Oleic acid, sodium oleate, hexane and hexamethylene tetramine (HMT) were obtained from Sinopharm Chemical Reagent Company. All chemicals were used as received without any further purification.

Synthesis of  $Fe_3O_4$  nanoparticles: The  $Fe_3O_4$  nanoparticles were synthesized by the thermal decomposition method reported previously.<sup>[9a]</sup> Then, the as-obtained  $Fe_3O_4$  nanoparticles, redispersed in hexane, were transferred into deionized water by using sodium oleate. Typically, hexane (500 µL) containing approximately 15 mg  $Fe_3O_4$  nanoparticles was poured into deionized water (5 mL) containing sodium oleate (110 mg), and was then treated by ultrasonification for 10 min to yield the oil-in-water emulsion. Subsequently, the oil-in-water emulsion was treated under vacuum (200 mbar) at 50 °C for 15 min in order to evaporate the hexane. Finally, the transparent black  $Fe_3O_4$ /sodium oleate solution was obtained.

**Synthesis of Fe<sub>3</sub>O<sub>4</sub>@***h***-P: Typically, DA (2.5 mmol) and HMT (0.625 mmol) were dissolved in deionized water (95 mL). The Fe<sub>3</sub>O<sub>4</sub>/ sodium oleate solution was added into the DA/HMT solution, to form an oleate emulsion containing magnetic nanoparticles. The stable emulsion solution was then transferred into a Teflon-lined stainless steel autoclave of 150 mL capacity, sealed and maintained at 160 °C for 4 h. The products of Fe<sub>3</sub>O<sub>4</sub>@***h***-P were collected by centrifugation at 8000 rpm (reactive centrifugal force: 6700 g) for 10 min, washed three times with deionized water and once with ethanol, and finally dried in an oven at 50 °C for 8 h.** 

**Synthesis of Fe<sub>3</sub>O<sub>4</sub>@h-C/noble metal and Fe<sub>3</sub>O<sub>4</sub>@h-C**: Briefly, Fe<sub>3</sub>O<sub>4</sub>@h-P (150 mg) was immersed in aqueous solution (10 mL) containing a certain amount of precious metal compound (13.6 mg Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>, 8.6 mg Pd(NH<sub>3</sub>)Cl<sub>2</sub> or 0.143 g AgNO<sub>3</sub>). The suspension was transferred into a vial, sealed and magnetically stirred at 50 °C for 12 h. Subsequently, the product was washed three times with deionized water, dried under vacuum at 50 °C for 6 h, and then pyrolyzed at 500 °C for 2 h under H<sub>2</sub>/Ar (5%/95%) flow. In this way, bifunctional magnetic nanocatalyts were obtained. In addition, Fe<sub>3</sub>O<sub>4</sub>@h-C was prepared by pyrolysis of Fe<sub>3</sub>O<sub>4</sub>@h-P at 500 °C for 2 h in H<sub>2</sub>/Ar (5%/95%) atmosphere.

**Catalytic tests**: The catalytic test was carried out in a vial reactor. For hydrogenation of nitrobenzene, nitrobenzene (0.6 mmol) was treated in propan-2-ol (6 mL) over 25 mg of Fe<sub>3</sub>O<sub>4</sub>@-C/Pt (0.002 mmol Pt, determined by ICP-AES analysis) under 30 °C and 1 atm of H<sub>2</sub> by using a balloon for 2 h (about 84 mmol H<sub>2</sub> was supplied in the reaction vial). The molar ratio of the nitrobenzene to Pt was 300 according to calculations. The product was filtered with a 200 nm pore filter, and analyzed by GC (Agilent 7890A). Fe<sub>3</sub>O<sub>4</sub>@h-C/Pt catalyst was collected by a magnet, and washed with ethanol before its reuse in the next run.

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## Acknowledgements

This work was supported by the NSFC (No. 21073026), National Natural Science Funds for Distinguished Young Scholar (No. 21225312), and the Program for New Century Excellent Talents in University of China (NCET-09-0254).

**Keywords:** hollow carbon spheres • hydrogenation • nanocatalysts • nanoparticles • yolk-shell particles

- a) M. Poliakoff, J. M. Fitzpatrick, T. R. Farren, P. T. Anastas, *Science* 2002, 297, 807–810; b) V. Polshettiwar, R. Luque, A. Fihri, H. Zhu, M. Bouhrara, J.-M. Basset, *Chem. Rev.* 2011, 111, 3036–3075; c) D. J. Cole-Hamilton, *Science* 2003, 299, 1702–1706; d) J. Liu, H. Q. Yang, F. Kleitz, Z. G. Chen, T. Yang, E. Strounina, G. Q. Lu, S. Z. Qiao, *Adv. Funct. Mater.* 2012, 22, 591–599.
- [2] a) D. Astruc, F. Lu, J. R. Aranzaes, Angew. Chem. 2005, 117, 8062–8083; Angew. Chem. Int. Ed. 2005, 44, 7852–7872; b) C.-J. Jia, F. Schüth, Phys. Chem. Chem. Phys. 2011, 13, 2457–2487; c) X. W. Lou, C. Yuan, E. Rhoades, Q. Zhang, L. A. Archer, Adv. Funct. Mater. 2006, 16, 1679–1684; d) J. Liu, S. Z. Qiao, J. S. Chen, X. W. Lou, X. Xing, G. Q. Lu, Chem. Commun. 2011, 47, 12578–12591.
- [3] R. A. Sheldon, H. Van Bekkum, Fine Chemicals through Heterogeneous Catalysis, Wiley-VCH, Weinheim, 2001.
- [4] a) S. C. Tsang, V. Caps, I. Paraskevas, D. Chadwick, D. Thompsett, Angew. Chem. 2004, 116, 5763-5767; Angew. Chem. Int. Ed. 2004, 43, 5645-5649; b) C.-H. Jun, Y. J. Park, Y.-R. Yeon, J.-R. Choi, W.-R. Lee, S.-J. Ko, J. Cheon, Chem. Commun. 2006, 1619-1621; c) J. Kim, J. E. Lee, J. Lee, Y. Jang, S.-W. Kim, K. An, J. H. Yu, T. Hyeon, Angew. Chem. 2006, 118, 4907-4911; Angew. Chem. Int. Ed. 2006, 45, 4789-4793; d) L. M. Rossi, F. P. Silva, L. L. R. Vono, P. K. Kiyohara, E. L. Duarte, R. Itri, R. Landers, G. Machado, Green Chem. 2007, 9, 379-385.

- [5] a) M. J. Jacinto, O. H. C. F. Santos, R. F. Jardim, R. Landers, L. M. Rossi, *Appl. Catal. A* 2009, *360*, 177–182; b) K. Mori, N. Yoshioka, Y. Kondo, T. Takeuchi, H. Yamashita, *Green Chem.* 2009, *11*, 1337–1342; c) B. Panella, A. Vargas, A. Baiker, *J. Catal.* 2009, *261*, 88–93; d) R. L. Oliveira, P. K. Kiyohara, L. M. Rossi, *Green Chem.* 2010, *12*, 144–149.
- [6] a) A.-H. Lu, W. Schmidt, N. Matoussevitch, H. Bönnemann, B. Spliethoff, B. Tesche, E. Bill, W. Kiefer, F. Schüth, Angew. Chem. 2004, 116, 4403-4406; Angew. Chem. Int. Ed. 2004, 43, 4303-4306; b) H. Yoon, S. Ko, J. Jang, Chem. Commun. 2007, 1468-1470; c) J. Ge, Q. Zhang, T. Zhang, Y. Yin, Angew. Chem. 2008, 120, 9056-9060; Angew. Chem. Int. Ed. 2008, 47, 8924-8928; d) Y. Deng, Y. Cai, Z. Sun, J. Liu, C. Liu, J. Wei, W. Li, C. Liu, Y. Wang, D. Zhao, J. Am. Chem. Soc. 2010, 132, 8466-8473.
- [7] a) A.-H. Lu, E. L. Salabas, F. Schüth, Angew. Chem. 2007, 119, 1242–1266; Angew. Chem. Int. Ed. 2007, 46, 1222–1244; b) J. Gao, H. Gu, B. Xu, Acc. Chem. Res. 2009, 42, 1097–1107; c) J. Liu, S. Z. Qiao, Q. H. Hu, G. Q. Lu, Small 2011, 7, 425–443.
- [8] a) G. S. Chai, S. B. Yoon, J. H. Kim, J.-S. Yu, *Chem. Commun.* 2004, 2766–2767; b) B. Fang, M. Kim, J.-S. Yu, *Appl. Catal. B* 2008, 84, 100–105; c) X. W. Lou, L. A. Archer, Z. Yang, *Adv. Mater.* 2008, 20, 3987–4019; d) G.-H. Wang, Q. Sun, R. Zhang, W.-C. Li, X.-Q. Zhang, A.-H. Lu, *Chem. Mater.* 2011, 23, 4537–4543.
- [9] a) J. Park, K. An, Y. Hwang, J.-G. Park, H.-J. Noh, J.-Y. Kim, J.-H. Park, N.-M. Hwang, T. Hyeon, *Nat. Mater.* 2004, *3*, 891–895; b) J. Kim, H. S. Kim, N. Lee, T. Kim, H. Kim, T. Yu, I. C. Song, W. K. Moon, T. Hyeon, *Angew. Chem.* 2008, *120*, 8566–8569; *Angew. Chem. Int. Ed.* 2008, *47*, 8438–8441.
- [10] Y. Wan, Y. Shi, D. Zhao, Chem. Commun. 2007, 897-926.
- [11] a) C. Wang, Y. Hu, C. M. Lieber, S. Sun, J. Am. Chem. Soc. 2008, 130, 8902–8903; b) X. Z. Lin, X. Teng, H. Yang, Langmuir 2003, 19, 10081–10085; c) C. Wang, H. Daimon, Y. Lee, J. Kim, S. Sun, J. Am. Chem. Soc. 2007, 129, 6974–6975.

Received: January 27, 2013 Published online: March 27, 2013

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