LETTER

NJC
www.rsc.org/njc

Amorphous Ni-B hollow spheres synthesized by controlled organization of Ni-B nanoparticles over PS beads *via* surface seeding/electroless plating

Xueying Chen,[a] Wuli Yang,[b] Shuai Wang,[a] Minghua Qiao,*[a] Shirun Yan,[a] Kangnian Fan[a] and Heyong He*[a]

[a] *Department of Chemistry and Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai, 200433 P.R. China. E-mail: mhqiao@fudan.edu.cn, heyonghe@fudan.edu.cn; Fax: +86 21 65642978; Tel: +86 21 65643916*

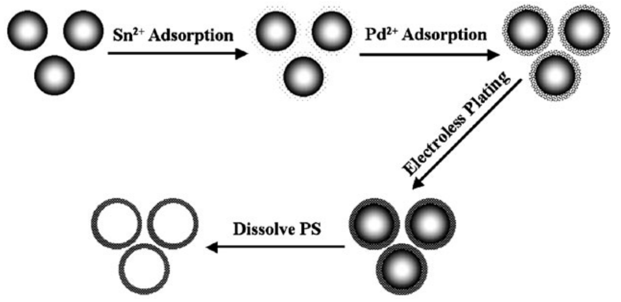
[b] *Department of Macromolecular Science and Key Laboratory of Molecular Engineering of Polymers, Ministry of Education, Fudan University, Shanghai, 200433 P.R. China*

Received (in Montpellier, France) 22nd July 2004, Accepted 15th October 2004
First published as an Advance Article on the web 13th December 2004

The synthesis of amorphous Ni-B hollow spheres, exhibiting superior catalytic properties in acetophenone hydrogenation compared to their nanoparticle form, has been achieved by a combination of polystyrene microsphere templating and electroless plating.

Due to their unique short-range ordering and long-range disordering, associated with special characteristics such as easy magnetization, corrosion resistance and interesting electronic properties, amorphous metal-metalloid alloys have attracted much attention from metallurgists, physicists and chemists.[1–5] Recently, hollow spheres have provoked increased interest because of their great potential in pharmaceutics, catalysis, photonics, contaminated waste removal and materials science, to name only a few.[6–10] Hollow spheres of a variety of materials, including polymers, metals, oxides, carbons and semiconductors, have been prepared by templating a removable spherical material, such as polystyrene (PS) or silica microspheres.[11–13] However, to the best of our knowledge, hollow spheres made of an amorphous alloy have never been prepared, although the controlled organization of amorphous alloys into ordered structures is anticipated to result in functional materials with physical and chemical characteristics distinct from their crystalline counterparts.

In this paper, we report the synthesis of amorphous Ni-B hollow spheres with a uniform shape and size by the so-called surface seeding/electroless plating strategy: Pd-modified PS microspheres are prepared from Sn^{2+}-preadsorbed beads and coated with amorphous Ni-B nanoparticles (Scheme 1). Ni-B hollow spheres are obtained after PS dissolution by tetrahydrofuran (THF). Application of these Ni-B hollow spheres to acetophenone hydrogenation is also discussed.



Scheme 1 Schematic representation of the different steps involved in the fabrication of amorphous Ni-B hollow spheres *via* the surface seeding/electroless plating strategy.

DOI: 10.1039/b411261j

In Fig. 1(a) and 1(b) scanning electron (SEM, Philips XL30) and transmission electron (TEM, JEM2011) micrographs of the pristine PS microspheres are presented. PS microspheres are smooth and monodisperse, with an average particle diameter of ~2 μm. Once coated with an Ni-B overlayer, the core-shell Ni-B/PS composites preserve the uniformity of the PS beads [Fig. 1(c) and 1(d)], which is indicative of an isotropic growth of the Ni-B alloy on the PS microspheres. Energy dispersive X-ray (EDX) analysis of the coated particles

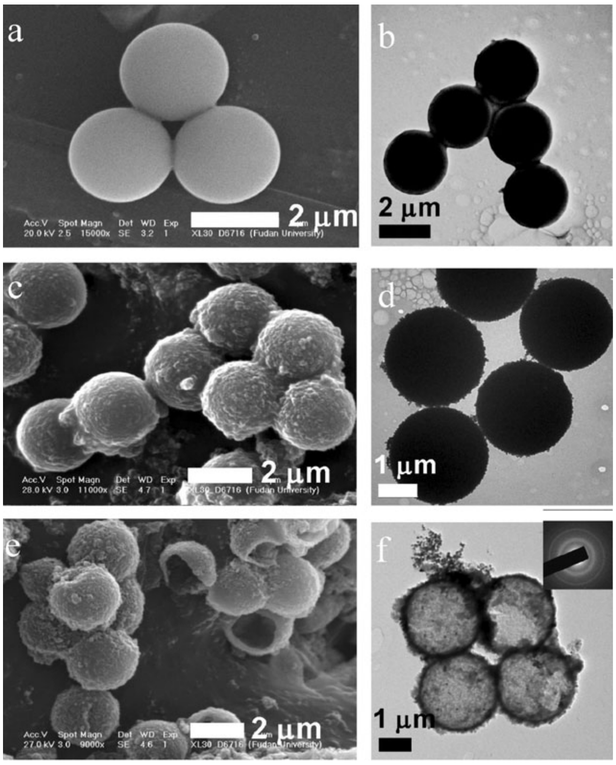


Fig. 1 SEM (a, c and e) and TEM (b, d and f) micrographs of the PS microspheres before and after Ni-B deposition: (a; b) pristine PS microspheres; (c; d) core-shell Ni-B/PS composites; (e; f) Ni-B hollow spheres. Inset shows the SAED pattern of the Ni-B hollow spheres.

revealed the presence of nickel, confirming the deposition of Ni-B. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES, IRIS Intrepid) analysis determined the molar composition of the overlayer to be $Ni_{97.2}B_{2.8}$. It was found that the thickness of the Ni-B overlayer can be adjusted either by changing the concentration of the plating solution or by varying the plating time, which shows the versatility of the method. The proper choice of $NaBH_4$ concentration and plating time can provide a homogeneous and complete coverage of PS spheres with Ni-B shells of the desired thickness in the range of 50–300 nm, as confirmed by TEM. The higher the concentration of $NaBH_4$ in the electroless plating bath, the thicker the Ni-B shell for a given plating time. For example, when the weight ratio between $NaBH_4$ and Ni^{2+} is changed from 0.106 to 0.15, the thickness of the Ni-B shell at a plating time of 2 h increases from 50 nm to 120 nm. Also, when plating times are increased, so does the thickness of the Ni-B overlayer (Ni-B wall thickness *of ca.*120, 200 and 300 nm at plating times of 2, 2.5, and 3 h, respectively).

Fig. 1(e) and 1(f) show micrographs of the hollow Ni-B spheres after THF etching of the Ni-B/PS core-shell composites. It is worth noting that the hollow structure and the shape of the PS spheres are essentially preserved. The TEM micrograph in Fig. 1(f) shows a reduced electron density of the spheres compared to the corresponding unetched samples, which can be assigned to the formation of a hollow structure. A wall thickness of *ca.* 120 nm for the Ni-B coating was estimated from Fig. 1(f) by measuring the dark ring on the perimeter of the hollow spheres. EDX revealed that no carbon was left in these hollow spheres, in support of the complete dissolution of the PS template by THF. A selected-area electron diffraction [SAED, inset in Fig. 1(f)] pattern of a hollow sphere exhibited only diffractive halos rather than distinct dots, unambiguously confirming the amorphous nature of the Ni-B walls.[14]

To our knowledge, there has been no work to date on the catalytic performance of core-shell or hollow materials. Here, the catalytic behaviour of the synthesized Ni-B/PS core-shells and their corresponding Ni-B hollow spheres was explored using acetophenone hydrogenation as a probe. Ni-B nanoparticles prepared from the same electroless plating bath, but without the addition of templating Pd-modified PS spheres, were also tested for comparison.

The hydrogenation results showed that the yields of 1-phenylethanol over Ni-B/PS core-shell microspheres and Ni-B hollow spheres were 13.8 and 28.1 mol %, respectively, being much higher than that over Ni-B nanoparticles (1.9 mol %). Table 1 summarizes the calculated active surface areas (S_H) and turnover frequency (TOF) values of the three tested Ni-B catalysts. TOF is expressed here as the number of H_2 molecules consumed per active surface nickel atom and per hour, by differentiating the H_2 uptake curve and extrapolating to a reaction time of zero. It is observed from Table 1 that the difference in the yields of 1-phenylethanol over Ni-B/PS and Ni-B hollow spheres is due to their discrepancy in active surface area, while their TOF values are essentially the same (~ 5.2 h^{-1}), suggesting that THF etching did not affect the nature of the Ni-B alloy. On the contrary, the Ni-B nanoparticles only exhibit a TOF value of ~ 0.4 h^{-1}, demonstrating that the controlled organization of the Ni-B nanoparticles on the PS spheres surface is beneficial to superior catalytic properties when compared to their unsupported counterpart, although the underlying mechanism responsible for this remains unsolved at this time.

Table 1 Intrinsic catalytic activity of Ni-B samples in the hydrogenation of acetophenone to 1-phenylethanol

Sample	S_H/m^2 g$_{Ni}$$^{-1}$	TOF/h^{-1}
Ni-B/PS	2.6	5.2
Ni-B hollow spheres	6.5	5.2
Ni-B nanoparticles	7.4	0.4

In brief, we have developed a simple but effective way to prepare amorphous Ni-B hollow spheres, which show superior catalytic properties compared to their nanoparticle counterparts. We suggest that this method can be extended to the preparation of other amorphous metal-metalloid hollow materials. Moreover, the method may open a new avenue to the preparation of crystalline metal-metalloid hollow spheres, which are difficult to achieve by other synthetic routes.

Experimental

The preparation procedure of amorphous Ni-B hollow spheres follows the surface seeding/electroless plating strategy. The method starts by activating the surface of neutral PS microspheres with colloidal Pd particles at room temperature, which was achieved by immersing the PS microspheres in a 1.0 M $SnCl_2$ aqueous solution for 2 min, followed by immersing the centrifuged Sn^{2+}-preadsorbed PS beads in a 0.1 M $PdCl_2$ aqueous solution for another 2 min. Although inspection of electron microscopy micrographs or EDX analysis did not reveal the presence of any Pd on the PS microspheres, ICP-AES showed that ~ 0.02 wt % Pd was left on the PS microspheres after treatment, inferring the low loading capability and extremely small size of the Pd particles. This seeding step is still crucial for subsequent Ni-B deposition, as no amorphous Ni-B alloy is plated onto the surface of the particles if this step is omitted. Electroless plating of amorphous Ni-B alloy constituting the next step was performed as follows. In a typical synthesis, the Pd-modified PS microspheres, after repeated centrifugation and water-wash cycles, were added to a Ni complex electroless plating bath having a weight distribution of $5.0\,Ni^{2+} : 0.75\,NaBH_4 : 65\,C_4H_4O_6KNa$ (sodium potassium tartrate) : 40 NaOH. The mixture was mechanically stirred for 2 h at 90 °C to allow the growth of the Ni-B overlayer. The resulting Ni-B/PS core-shell composites were then subjected to THF etching to remove the PS core, and hollow Ni-B amorphous alloy spheres were obtained.

In a typical hydrogenation experiment, 59 mg of catalyst and 0.2 ml of acetophenone were dissolved in 20 ml of ethanol and introduced into a 75 ml teflon-lined stainless steel autoclave equipped with a magnetic stirrer. The reaction was carried out at 343 K with an H_2 pressure maintained at 2.0 MPa for 20 h. The products were analyzed by gas chromatography (GC122) with a CP-Chirasil-Dex CB capillary column and an FID detector.

Acknowledgements

This work was supported by the State Key Basic Research Development Program (G2000048009), the NSF of China (20203004, 20005310), the Shanghai Science and Technology Committee (02ZA14006, 03QB14004) and Cyrus Tang Science and Technology Innovation Fund.

References

1 I. Bakonyi, A. Burgstaller, W. Socher, J. Voitlander, E. Tothkadar, A. Lovas, H. Ebert, E. Wachtel, N. Willmann and H. H. Liebermann, *Phys. Rev. B*, 1993, **47**, 14961.
2 T. Saito, M. Igarashi and M. Kobayashi, *J. Appl. Phys.*, 2000, **88**, 7209.
3 C. A. Brown and H. C. Brown, *J. Am. Chem. Soc.*, 1963, **85**, 1003.
4 B. Liu, M. H. Qiao, J. Q. Wang and K. N. Fan, *Chem. Commun.*, 2002, 1236.
5 H. X. Li, W. J. Wang, H. Li and J. F. Deng, *J. Catal.*, 2000, **194**, 211.
6 (*a*) *Hollow and Solid Spheres and Microspheres: Science and Technology Associated with their Fabrication and Application*,

eds. D. L. Wilcox, M. Berg, T. Bernat, D. Kellerman and J. K. Cochran, MRS Symposium Proceedings, vol. **372**, Materials Research Society, Pittsburgh, PA, 1995; (*b*) E. Mathlowitz, J. S. Jacob, Y. S. Jong, G. P. Carino, D. E. Chickering, P. Chaturvedl, C. A. Santos, K. Vijayaraghavan, S. Montgomery, M. Bassett and C. Morrell, *Nature (London)*, 1997, **386**, 410; (*c*) H. Huang and E. E. Remsen, *J. Am. Chem. Soc.*, 1999, **121**, 3805.

7 C. A. Morris, M. L. Anderson, R. M. Stroud, C. I. Merzbacher and D. R. Rolison, *Science*, 1999, **284**, 622.

8 R. Langer, *Science*, 1990, **249**, 1527.

9 C. P. Pathak, A. S. Sawhney and J. A. Hubbell, *J. Am. Chem. Soc.*, 1992, **114**, 8311.

10 M. Freemantle, *Chem. Eng. News*, 1999, **77**, 32.

11 J. Lee, K. Sohn and T. Hyeon, *J. Am. Chem. Soc.*, 2001, **123**, 5146.

12 E. Donath, G. B. Sukhorukov, F. Caruso, S. A. Davis and H. Möhwald, *Angew. Chem., Int. Ed.*, 1998, **37**, 2202.

13 G. L. Egan, J. S. Yu, C. H. Kim, S. J. Lee, R. E. Schaak and T. E. Mallouk, *Adv. Mater.*, 2000, **12**, 1040.

14 J. Wonterghem, S. Mϕrup, S. W. Charles and S. Wells, *Nature (London)*, 1986, **322**, 622.