A Novel Way to Fabrication of Core–Shell-structured Silica–NiO Spheres

Jingdong Feng and Qingwei Wang*
College of Chemistry, Jilin Normal University, Siping 136000, Jilin, P. R. China

(Received February 6, 2007; CL-070142)

Core–shell-structured silica–NiO spheres were prepared by a novel method of adsorbing nickel formate on silica spheres and the subsequent heating process. These obtained core–shell-structured silica–NiO particles are expected to be promising additive materials for Ni–metal hydride battery.

The fabrication of colloidal materials with desired structural, optical, and surface properties has recently been the subject of intense investigations.[1–8] Facile and flexible strategies that afford fine control over the preparation and modification of particles are of paramount importance in building new classes of colloids. Composite particles, often comprised of a solid core surrounded by a well-defined shell layer, are known to exhibit unique, and enhanced characteristics over single component colloids, making them attractive for use in a wide range of applications.[5,8] A commonly employed route to creating composite colloids is the post synthesis modification of core particles, for example, by coating and/or encapsulating them with thin polymer or inorganic shells. Procedures to achieve this have predominantly relied on the in situ fabrication of polymer layers[2,7] or surface reactions (e.g., precipitation and sol–gel condensation) to deposit a range of inorganic layers onto preformed cores.[1,3–6,8,9]

NiO is a very prosperous material, and it has been used in various fields, such as catalysis,[10] battery cathodes,[11] electrochromic films,[12] and fuel cell electrodes.[13] NiO can be conveniently prepared by thermal decomposition of its precursors.[14] As the current research is driving toward nanoscale phenomena and technology, the exploration of new synthesis methods for NiO with different morphologies will find new applications or improve existing performance. In recent years, many reports have concerned the preparation of NiO nanomaterials, including nanosized NiO nanorings,[15] NiO nanosheets,[16] and nanoribbons.[17] However, how to prepare NiO spheres with hierarchical nanostructures is still a big challenge to chemists. Recently, morphology-controlled preparation and the large-scale self-assembly of the nanoscaled building blocks into complex structures have been the focus of significant interests in materials chemistry and device fabrications. Taking all these into account, the aim of this work has been to produce core–shell-structured silica–NiO spheres by using adsorption and thermal decomposition method and then study their morphologies.

Silica spheres were prepared by Stöber method.[18] Typically, 0.5 g of obtained silica spheres was immersed in nickel nitric solution (3.3 M) in a beaker, 24 h later, through centrifugating and washing process, we obtained silica spheres with Ni^{2+} adsorbed on the surface, then we redispersed the obtained silica spheres in the water. While the solution was being stirred, we introduced 0.2 mol/L $NaBH_4$ solution, about several hours later, nickel hydroxide adsorbed on the silica surface was separated from the reaction medium by centrifuging at 4000 rpm and washed twice with water. Next, we dispersed the functionalized silica spheres in concentrated nickel formate solution, heating at 90 °C under stirring for 1 h. The adsorption process was allowed to proceed at room temperature for 10 h under constant stirring, the core–shell-structured materials were obtained, then centrifugated, washed twice with water, and dried in air. Finally, calcination was carried out in air at 600 °C for 12 h. Through this process, we got core–shell-structured silica–NiO spheres.

Figure 1 is the XRD pattern of a typical NiO–silica sample. In addition to the strong silica peak at 23°, which ascribed to silica sphere, several other peaks can be observed, it clearly shows the (111), (200), and (220) reflections of cubic NiO (JCPDS card no. 47-1049). Thus, it can be concluded from XRD pattern that the silica–NiO composites were obtained.

Scanning electron microscope (SEM) images were recorded to reveal the actual structures of the core–shell spheres. As shown in Figure 2, the core–shell spheres are uniform and well dispersed, with diameters of about 400–480 nm. Some of spheres are broken and the NiO shell is left, so the core–shell structure of silica–NiO spheres can be clearly seen from these images.

The morphology of the obtained silica spheres and the core–shell-structured spheres was first characterized using a transmission electron microscope (TEM). Figure 3a shows the morphology of obtained silica spheres prepared with Stöber method. It can be seen that the composite particles are obtained in a monomodal distribution (note the hexagonal packing zones). Addi-

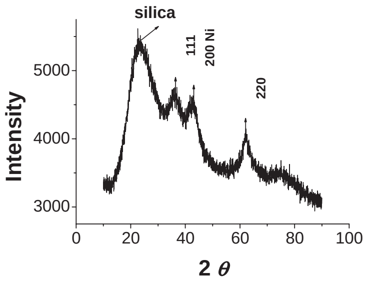

Figure 1. XRD pattern of obtained core–shell-structured silica NiO spheres.

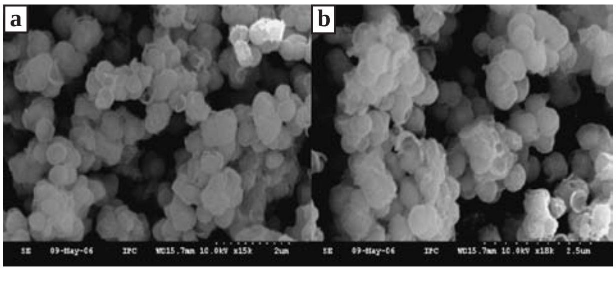

Figure 2. SEM images of silica–NiO core–shell spheres.

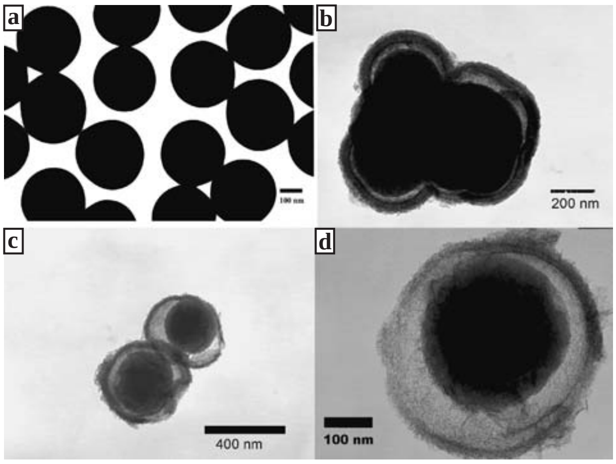

Figure 3. TEM images of (a) silica core, and (b, c, d) NiO–silica sphere.

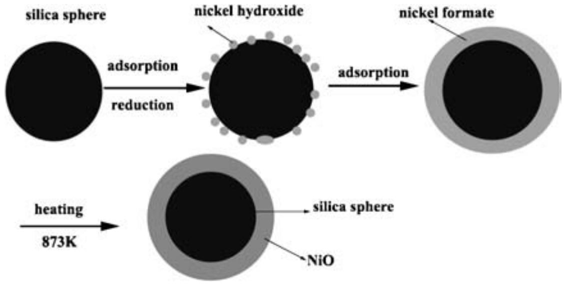

Figure 4. Mechanism of formation of core–shell-structured materials.

tionally, the particles have a smooth surface, they are discrete and not aggregative, and the diameters of silica spheres are about 240–300 nm.

The composite silica–NiO particles were also examined by TEM after calcination at 600 °C for 5 h. The resulting SiO_2–NiO particles have core–shell structure as shown in Figures 3b–3d. The core–shell spheres have a uniform size, the shell is porous NiO, and the core is the SiO_2. The diameters of core–shell spheres are about 400–480 nm, and the diameter of silica is about 240–300 nm. The shell thickness is about 20–60 nm.

Figure 4 illustrates the mechanism of formation of core–shell-structured silica–NiO spheres. First, $Ni(NO_3)_2$ is adsorbed on the silica spheres, after reduction with $NaBH_4$ and then the oxidation process, the silica spheres are covered by a $Ni(OH)_2$ layer. The following process is the adsorption of nickel formate on the silica surface, on which the $Ni(OH)_2$ acts as the nucleus. In this process, as the mixture cooled from 90 °C to room temperature, the nickel formate preferentially deposited on the silica surface. Through heating process, the nickel formate changed to NiO. So from these series process, the core–shell-structured silica–NiO spheres were gained.

In summary, core–shell-structured silica–NiO spheres were successfully prepared via adsorption method. The method is new and facile, needing no expensive raw materials or equipment, it is also easy for mass production and can be extended to prepare other hydroxide or oxide nanocrystals. The obtained core–shell-structured silica–NiO particles are expected to be a promising additive material for Ni–metal hydride battery. Further investigations are currently in progress.

References

1 E. Matijevic, in *Fine Particle Science and Technology*, ed. by E. Pelizetti, Kluwer Academic, Dordrecht, **1996**, p. 1.
2 C. H. M. Hofman-Caris, *New J. Chem.* **1994**, *18*, 1087.
3 R. Davies, G. A. Schurr, P. Meenan, R. D. Nelson, H. E. Bergna, C. A. S. Brevett, R. H. Goldbaum, *Adv. Mater.* **1998**, *10*, 1264.
4 D. V. Goia, E. Matijevic, *New J. Chem.* **1998**, *22*, 1203.
5 L. M. Liz-Marzan, M. Giersig, P. Mulvaney, *Langmuir* **1996**, *12*, 4329.
6 R. Partch, in *Materials Synthesis and Characterization*, ed. by D. Perry, Plenum Press, New York, **1997**, p. 1.
7 S. M. Marinakos, D. A. Shultz, D. L. Feldheim, *Adv. Mater.* **1999**, *11*, 34.
8 S. J. Oldenburg, R. D. Averitt, S. L. Westcott, N. J. Halas, *Chem. Phys. Lett.* **1998**, *288*, 247.
9 T. Toupance, M. Kermarec, C. Louis, *J. Phys. Chem. B* **2000**, *104*, 965.
10 S. Berchmans, H. Gomathi, G. Prabhakara Rao, *J. Electroanal. Chem.* **1995**, *394*, 267.
11 M. Yoshio, Y. Todorov, K. Yamato, H. Noguchi, J. Itoh, M. Okada, T. J. Mouri, *Power Sources* **1998**, *74*, 46.
12 E. L. Miller, R. E. Rocheleau, *J. Electrochem. Soc.* **1997**, *144*, 3072.
13 R. C. Makkus, K. Hemmes, J. H. W. D. Wir, *J. Electrochem. Soc.* **1994**, *141*, 3429.
14 L. Xiang, X. Y. Deng, Y. Jin, *Scr. Mater.* **2002**, *47*, 219.
15 J. H. Liang, Y. D. Li, *Chem. Lett.* **2003**, *32*, 1126.
16 Z. H. Liang, Y. J. Zhu, X. L. Hu, *J. Phys. Chem. B* **2004**, *108*, 3488.
17 D. N. Yang, R. M. Wang, J. Zhang, Z. F. Liu, *J. Phys. Chem. B* **2004**, *108*, 7531.
18 W. Stöber, A. Fink, E. Bohn, *J. Colloid Interface Sci.* **1968**, *26*, 62.

Published on the web (Advance View) April 28, 2007; doi:10.1246/cl.2007.704