

Facile Fabrication of Nickel Oxide Hollow Spheres and Amorphous Carbon/Nickel Nanoparticles Composites Using Colloidal Carbonaceous Microspheres as Template

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Core/shell structure with colloidal carbonaceous microspheres as core and nanowhisker-like $\text{Ni}(\text{OH})_2$ as shell was synthesized by a facile precipitation method. NiO hollow spheres with hierarchical nanostructure and amorphous carbon/nickel nanoparticles composites were obtained by heat treatment in air and nitrogen, respectively. Nitrogen adsorption and desorption analysis indicated that these two novel products are both nanoporous materials with high specific surface area and large pore volume.

NiO and Ni have attracted increasing attention because of their extensive applications, especially in electrodes,^{1–3} catalysis,⁴ and magnetic materials.⁵ As the current research is driving towards nanoscale phenomena and technology, the exploration of new synthesis methods for NiO and Ni with novel nanostructure will find new applications or improve their performance. Therefore, many reports have concerned the synthesis of NiO and Ni nanomaterials, including NiO nanosheets,^{6a} NiO nanoribbons,^{6b} NiO hollow spheres,^{6c} porous NiO ,^{6d,6e} nanoporous metallic nickel colloids,⁷ and nickel nanoparticles/carbon nanowall composites.⁵

Recently, colloidal carbonaceous microspheres as a novel template have been reported.^{8,9} In comparison with polymer or silica spheres, carbonaceous microspheres have two apparent advantages: 1) they are green template; 2) surface modification is unnecessary.

In this letter, a novel core/shell structure with colloidal carbonaceous microspheres as a core and nanowhisker-like $\text{Ni}(\text{OH})_2$ as a shell was successfully prepared. NiO hollow spheres with hierarchical nanostructure and amorphous carbon/nickel nanoparticles composites were obtained by heat treatment in air and nitrogen, respectively.

The colloidal carbonaceous microspheres were fabricated according to the method reported previously.⁸ The preparation procedure of NiO hollow spheres and amorphous carbon/nickel nanoparticles composites is described as follows: 0.001 mol of nickel acetate was dissolved in 40 mL of distilled water to form a clear solution. 100 mg of carbonaceous microspheres was added to the above solution. The mixture was ultrasonicated for 0.5 h and stirred for 1 h. Then the pH of the mixture was slowly adjusted to 9 by addition of 5 wt % NH_4OH dropwise. The resulting suspension was stirred for an additional 3 h. Then the solid was centrifuged, washed, and redispersed in distilled water, and this cycle was repeated five times. The solid was then oven-dried at 100 °C for 5 h, resulting in the $\text{Ni}(\text{OH})_2$ /carbonaceous microspheres composites. The composites were heat-treated under 450 °C for 4 h in air and heat-treated under 600 °C for 4 h in nitrogen, respectively. The crystal structures of the samples were characterized by X-ray diffraction (XRD) (Bruker

D8 advance). The size and morphology of the samples were examined by transmission electron microscopy (TEM) (FEI, TECNAI-20) and scanning electron microscopy (SEM) (LEO1530). The N_2 adsorption/desorption analyses were performed on a Micromeritics ASAP 2010 instrument.

Figures 1a, 1b, and 1c show the XRD patterns of the sample before calcinations, the sample calcined in air and the sample calcined in nitrogen, respectively. The pattern of Figure 1a corresponds to the layered $\alpha\text{-Ni}(\text{OH})_2$ structure (JCPDS code: 38-0715). The main peaks in Figures 1b and 1c can be indexed to the (111), (200), (220) planes of cubic-phased NiO (JCPDS code: 47-1049), and (111), (200), (220) planes of cubic-phased metallic nickel (JCPDS code: 04-0850), respectively.

Figure 2a displays the TEM image of colloidal carbonaceous microspheres. From this image, it can be seen that they

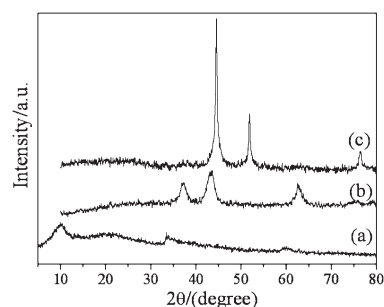


Figure 1. XRD patterns of the samples. (a) before calcination; (b) calcined in air; (c) calcined in nitrogen.

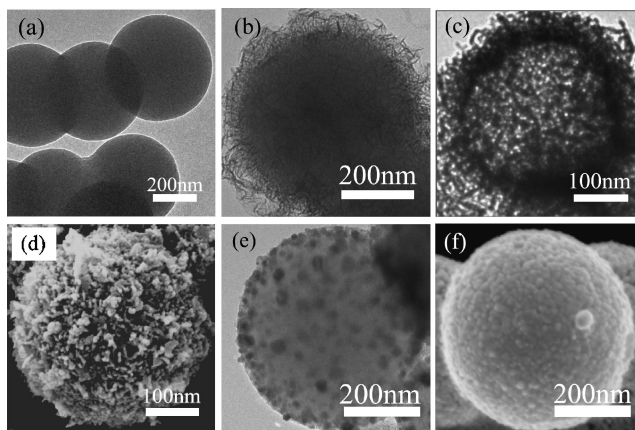


Figure 2. (a) TEM image of colloidal carbonaceous microspheres; (b) TEM image of composites of $\text{Ni}(\text{OH})_2$ and carbonaceous microspheres; (c) TEM, and (d) SEM images of NiO hollow spheres; (e) TEM, and (f) SEM images of amorphous carbon/nickel nanoparticles composites.

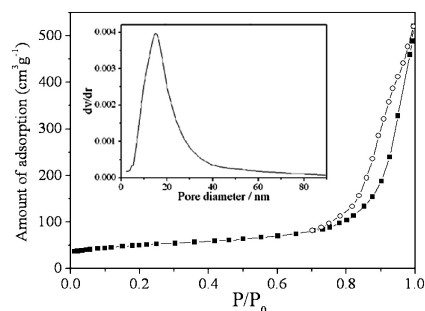


Figure 3. BET nitrogen adsorption and desorption isotherm and pore size distribution plot (inset) for NiO hollow spheres.

have smooth surface. Figure 2b shows the typical TEM image of the as-prepared sample. Nanowhiskers of $\text{Ni}(\text{OH})_2$ covered the exterior of carbonaceous microspheres. It reveals a novel core/shell structure with carbonaceous microspheres as the core and nanowhisker-like $\text{Ni}(\text{OH})_2$ as the shell. Figures 2c and 2d present the TEM and SEM images of the sample calcined in air, respectively. One can see that the sample has hierarchical structure. The shell of the hollow spheres is composed of loosely packed nanowhiskers and nanoparticles. Besides, the sample underwent some shrinkage during the calcinations. The TEM image (Figure 2e) and SEM image (Figure 2f) of the sample calcined in nitrogen show the emergence of nickel nanoparticles. Most of the particles in the products were found to be less than 25 nm in dimension. According to Wang's report,¹⁰ the template transforms into amorphous carbon after calcination.

Figure 3 presents N_2 adsorption/desorption analysis of NiO hollow spheres. It exhibits a type IV isotherm with H_3 -type hysteric loop attributed to an interconnected mesoporous system with a broad pore-size distribution.¹¹ The inset of Figure 3 shows the pore-size distribution plot calculated by the BJH (Barrett–Joyner–Halenda) equation. It can be observed that the pore sizes of the sample are mainly in a range of 5–40 nm. The Brunauer–Emmett–Teller (BET) surface area and pore volume are $169.8 \text{ m}^2 \text{ g}^{-1}$ and $0.81 \text{ cm}^3 \text{ g}^{-1}$, respectively. The unique nanoporous system and high BET surface area of NiO hollow spheres may facilitate electrochemical reaction. To evaluate the electrochemical property, we use NiO hollow spheres to fabricate the electrode of electrochemical capacitors.² Cyclic voltammograms (CV) measurements were carried out in 2 M KOH in a half-cell setup configuration at room temperature. According to Srinivasan's formula,¹² the specific capacitance of NiO hollow spheres is calculated to be about 369 F g^{-1} at a scan rate of 5 mV s^{-1} . The high value is probably attributed to the novel structure of NiO hollow spheres. The unique nanoporous system and large pore volume of NiO sample can facilitate OH^- transfer to the NiO surface, thus allowing for fast faradaic reactions. The loosely packed and nanometer-sized NiO provides a very high surface area for charge storage. Extensive electrochemical studies are under way in our lab.

N_2 adsorption/desorption analysis of amorphous carbon/nickel nanoparticles composites (not present) indicates that it is also a nanoporous material. The pore sizes of the sample are mainly in a range of 2–20 nm. The BET surface area and pore volume are $326 \text{ m}^2 \text{ g}^{-1}$ and $0.24 \text{ cm}^3 \text{ g}^{-1}$, respectively. These properties indicate that the composites have potential applications in catalysis and electrode materials.

The polysaccharide-like surface of colloidal carbonaceous microspheres is hydrophilic and has a distribution of $-\text{OH}$ and $-\text{C}=\text{O}$ groups.⁸ When the carbonaceous microspheres were dispersed in the solution of nickel acetate, the Ni^{2+} ions could be adsorbed on the surface of the microspheres, which led to the high local supersaturation of Ni^{2+} , thus provide potential nucleation sites for the crystallization of the $\text{Ni}(\text{OH})_2$. With the increasing pH by ammonia titration, $\text{Ni}(\text{OH})_2$ would firstly heterogeneously nucleate on the surface of the carbonaceous microspheres. As the reaction time increased, Ni^{2+} and OH^- diffuse continuously to the surface of the microspheres, and $\text{Ni}(\text{OH})_2$ nuclei would grow and develop into $\text{Ni}(\text{OH})_2$ nanowhiskers. During the calcination at 450°C in air, the template may transform into CO_2 ,¹³ which would escape effectively without breaking the shell wall, and $\text{Ni}(\text{OH})_2$ would decompose into NiO. When the composite was calcined at 600°C in nitrogen, the template would be carbonized into amorphous carbon. Meanwhile, the NiO particles, which were prepared by thermal decomposition of $\text{Ni}(\text{OH})_2$ on the surface of the template, would be reduced to metallic Ni in the reductive atmosphere resulted from the thermal decomposition of carbonaceous microspheres.⁷

In summary, NiO hollow spheres with hierarchical nanostructures and amorphous carbon/nickel nanoparticles composites have been successfully prepared using carbonaceous microspheres as template. N_2 adsorption/desorption analysis indicated that these two novel products are nanoporous materials with high specific surface area and large pore volume. It is anticipated that these novel materials will have potential applications in electrode materials, catalysis and other fields.

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