Hierarchical porous hollow nickel microspheres with nickel nanoparticles as the in situ formed building units have been fabricated via a novel precursor hydrothermal redox method in alkaline solution of KBH₄. The microspheres exhibit enhanced coercivity and remanent magnetization as compared with hollow nickel submicrometer spheres, hollow nickel nanoparticles, bulk nickel, and free Ni nanoparticles. Investigations have demonstrated that the enhancement is attributed to the hierarchical porous hollow structure, while the hierarchical structure has little influence on saturation magnetization.

Over the past few years, nanoscale materials with special morphologies have attracted intensive interest, because the intrinsic properties of nanoscale materials are mainly determined by their composition, crystallinity, size, and morphology. As we know, nanoparticles often demonstrate novel properties different from those of bulk materials, and they can be used as fundamental building blocks for nanoscale science and technology. Recently, several reports have shown that metal nanoparticles, such as Pt, Ru, Rh and Ni, can be assembled to form porous hierarchical spheres over multiple length scales with enhanced properties compared with both discrete nanoparticles and bulk powders. Moreover, the hollow spheres constructed by nanostructured materials also exhibit distinctive properties different from those of the nanoparticles, thus they have potential applications in a variety of fields, such as catalysts, magnetic materials, drug delivery, low-density structural materials, etc. Therefore, the creation of the hierarchical porous hollow structure with the above three kinds of structure combined is of great significance. In the past decade, various structural and morphological forms of Ni nano- and micromaterials were synthesized, for example, nanoparticles, nanowires, thin film, hollow nickel submicrometer spheres, hollow nickel nanospheres, and so on. However, to the best of our knowledge, the fabrication of hierarchical porous hollow nickel spheres has not been reported. Therefore, it is a big challenge to fabricate hierarchical hollow nickel spheres with nanostructured building blocks.

In this communication, a hierarchical and porous structure of nickel hollow microspheres with nickel nanoparticles as the in situ formed building units was successfully fabricated by a novel, hydrothermal redox method with Ni(OH)₂ as the precursor. Preliminary results of magnetic properties of the hierarchical porous hollow nickel microspheres were also reported. Moreover, the influence of the hollow and hierarchical structure on the magnetic properties was investigated by means of a comparison between the magnetic properties of the hollow microspheres and those of their building units—nanoparticles.

All the reagents were analytical grade, and used without further purification. As described in our previous study, Ni(OH)₂ hollow microspheres used as the precursors were fabricated via a hydrothermal approach in strong alkaline solution of glycine (see the ESI). In a typical experiment, 20.0 mmol of KBH₄ and 1.0 g of NaOH were dissolved in 30 mL of deionized water to form a solution, then 0.35 g of the Ni(OH)₂ spheres were added into the solution. The resulting suspension was then sealed into a 50 ml Teflon-lined autoclave, followed by hydrothermal treatment at 160 °C for 48 h in an electric oven. After the treatment, black nickel products were collected by filtration, washed three times with deionized water, and dried at room temperature for 24 h. The chemical reaction involved in the nickel synthesis could be formulated as follows:

$$4\text{Ni(OH)}_2 + \text{BH}_4^- \rightarrow \text{BO}_2^- + 4\text{Ni} + 6\text{H}_2\text{O}$$

Fig. 1 displays the X-ray diffraction (XRD, X'Pert PRO MPD, Panalytical, Cu Kα radiation, λ = 0.154178 nm) pattern of the as-prepared nickel powder. The as-prepared nickel is identified as the single phase nickel with face-centered cubic (fcc) structure (a = 0.35238 nm, JCPDS file No. 04-0850). No peaks from other phases are found, indicating that β-Ni(OH)₂ is completely converted to Ni after being reduced for 48 h.

The morphology and structure of the as-synthesized nickel powder were further investigated by field emission scanning electron microscopy (FESEM, JEOL JSM-6700F). Fig. 2a–b
indicate that the sample consists of microscopic spheres with diameters of 2–3 μm. Interestingly, the nickel microspheres are in fact built from nanoparticles with diameters of 40–60 nm, and the nanoparticles spontaneously align with one another to form a porous spongelike sphere with an interior cavity (Fig. 2c–d).

The hollow and hierarchical structure of the as-prepared nickel microspheres was further confirmed by transmission electron microscopy (TEM, Hitachi H-700, 200KV) equipped with electron diffraction (ED) (Fig. 3a–e). As shown in Fig. 3a–e, the pale center together with the dark edge is the evidence for the hollow structure of the microsphere, and the spongelike porous shell wall built from nanoparticles is the evidence for the hierarchical structure. The thickness of the shell wall is one quarter to one third of the sphere diameter. Fig. 3e–f show the typical TEM image of the nickel microsphere and its corresponding ED pattern. As shown in Fig. 3f, the corresponding ED pattern suggests the nickel microspheres are polycrystalline. In addition, the ED pattern shows principally four rings with d spacing 0.203, 0.176, 0.124 and 0.106 nm, which correspond to the (111), (200), (220), and (311) planes of the standard fcc nickel pattern.

Magnetic properties of the as-prepared nickel microspheres were recorded using a vibrating sample magnetometer (MagLab-12, Oxford), and the hysteresis loop of the hierarchical porous hollow nickel microspheres at 300 K is shown in Fig. 4. The typical coercivity (Hc), saturation magnetization (Ms), and remanent magnetization (Mr) at 300 K are 216.3 Oe, 45.2 emu g⁻¹ and 13.0 emu g⁻¹, respectively. Compared with Hc and Mr values reported in the literature on hollow nickel submicrometer spheres,13 hollow nickel nanoparticles,14 bulk nickel,18 and free Ni nanoparticles,9 the nickel microspheres we prepared exhibit much enhanced coercivity and remanent magnetization (Table 1). In addition, the Mr value (45.2 emu g⁻¹) of the nickel microspheres we prepared is lower than that of bulk nickel (55 emu g⁻¹), but higher than those of other nickel structures listed in Table 1.9,13,14 Because the magnetic properties of nanoscale materials were closely associated with their size, crystallinity and structure, we deduced that suitable size, good crystallinity and novel morphology of the product contributed to the enhanced coercivity. However, compared with that of the bulk nickel (55 emu g⁻¹), the Mr value (45.2 emu g⁻¹) was a little reduced, which was possibly originated from the inevitable surface oxidation which decreased the effective magnetic moment.

In order to investigate the influence of hollow and hierarchical structure on the magnetic properties, the individual nanoparticles that formed the hierarchical porous hollow nickel microspheres were obtained by sonication (1 h in an ultrasonic water bath; refer
to the ESI) and subjected to the magnetic property characterization. The hysteresis loop of the nanoparticles at 300 K is presented in Fig. 5, which shows that the typical coercivity ($H_c$), saturation magnetization ($M_s$), and remanent magnetization ($M_r$) are 171.9 Oe, 46.1 emu g$^{-1}$ and 9.6 emu g$^{-1}$, respectively. Compared with that of the hierarchical porous hollow nickel microspheres (45.2 emu g$^{-1}$), $M_s$ of the corresponding nanoparticles has a comparable value, indicating that the hollow and hierarchical structure has little effect on their magnetic properties. In addition, such hollow microspheres have some promising applications in the fields of magnetic materials and catalysis. We also expect that this precursor hydrothermal redox method can be extended to synthesize hollow spheres of other kinds of metal by using hollow spheres of corresponding metal hydroxides or metal oxides as precursors.

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### Table 1  Coercivity ($H_c$), saturation magnetization ($M_s$), and remanent magnetization ($M_r$) of the hierarchical hollow nickel microspheres we prepared, nanoparticles as the building units of the microspheres and comparison to other nickel structures

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_s$/emu g$^{-1}$</th>
<th>$M_r$/emu g$^{-1}$</th>
<th>$H_c$/Oe</th>
<th>Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hierarchical hollow nickel microspheres$^a$</td>
<td>45.2</td>
<td>9.6</td>
<td>216.3</td>
<td>2–3 µm</td>
</tr>
<tr>
<td>Nanoparticles as the building units$^b$</td>
<td>46.1</td>
<td>9.6</td>
<td>171.9</td>
<td>40–60 nm</td>
</tr>
<tr>
<td>Hollow nickel submicrometer spheres$^c$</td>
<td>21.1</td>
<td>0.69</td>
<td>32.3</td>
<td>300–450 nm</td>
</tr>
<tr>
<td>Hollow nickel nanospheres$^d$</td>
<td>13.6</td>
<td>2.67</td>
<td>102</td>
<td>50–60 nm</td>
</tr>
<tr>
<td>Bulk nickel$^e$</td>
<td>55</td>
<td>2.7</td>
<td>100</td>
<td>2–3 µm</td>
</tr>
<tr>
<td>Free Ni nanoparticles$^f$</td>
<td>32</td>
<td>5.0</td>
<td>40</td>
<td>ca. 12 nm</td>
</tr>
</tbody>
</table>

$^a$ This work. $^b$ This work. $^c$ From Ref. 13. $^d$ From Ref. 14. $^e$ From Ref. 18. $^f$ From Ref. 9.

### References