

Fabrication of β -Ni(OH)₂ and NiO hollow spheres by a facile template-free process†

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Ni(OH)₂ hollow microspheres with β -Ni(OH)₂ nanosheets as the *in situ* formed building units were fabricated *via* a novel template-free approach in a strong alkaline solution of glycine, and can be converted into NiO hollow microspheres by a thermal decomposition process.

Over the past few years, micro- and nanostructures with hollow interiors have attracted significant interest owing to their potential in a variety of fields, such as catalysts, drug delivery, photonic materials, and battery materials.^{1–4} Nickel hydroxide (Ni(OH)₂), as an important material, has aroused increasing attention with its applications in alkaline rechargeable batteries.⁵ Currently, Ni(OH)₂ electrodes are made from dense spherical Ni(OH)₂ powder, whose electrochemical performance is unsatisfactory for high-rate and high-temperature charge/discharge applications due to the inactiveness of the material in the core region.⁶ It has also been demonstrated that the electrochemical performance of Ni(OH)₂ electrodes could be significantly enhanced when nano-phase Ni(OH)₂ was added to micrometer-size spherical Ni(OH)₂.⁷ Therefore, fabrication of Ni(OH)₂ hollow spheres with nanostructured building blocks is of great significance in high-energy-density batteries. Recently, Ni(OH)₂ hollow spheres have been synthesized by a template-assisted process using poly(styrene-methyl acrylic acid) (PSA) particles as the templates. However, the as-prepared hollow spheres were poorly crystallized and lacking in structure stability.⁸ Moreover, template-assisted processes fall short of practical significance due to the high cost as well as being time-consuming.⁹ For high-performance battery applications, it is still a big challenge to fabricate nickel hydroxide hollow spheres with good crystallinity, homogeneity and stability by a facile process.

In this communication, we report a novel, template-free approach to fabricating a hierarchical structure of Ni(OH)₂ hollow microspheres with β -Ni(OH)₂ nanosheets as the *in situ* formed building units. It is noted that the Ni(OH)₂ hollow microspheres were fabricated *via* a single-step process without using any templates or surfactants, which could avoid subsequent complicated procedures of removing the templates or surfactants. In addition, NiO hollow spheres were successfully synthesized by thermal

decomposition of the as-synthesized Ni(OH)₂ hollow spheres at 600 °C for 2 h.

In a typical experiment, 5.0 mmol of Ni(NO₃)₂·6H₂O and 2.0 g of glycine as well as 2.0 g of Na₂SO₄ salt were dissolved in 25 mL of deionized water, then 10 mL of NaOH solution (5 M) was added dropwise into the above solution under magnetic stirring to form a clear blue solution. The solution was then sealed into a Teflon-lined autoclave, followed by hydrothermal treatment at 100–180 °C for 24 h in an electric oven. After the treatment, green Ni(OH)₂ products were collected by filtration, washed three times with deionized water, and dried at room temperature for 24 h. NiO hollow spheres could be obtained by thermal decomposition of the as-synthesized Ni(OH)₂ powder at 600 °C for 2 h.

Fig. 1 displays the X-ray diffraction (XRD, X'Pert PRO MPD, Panalytical, Cu K α radiation, $\lambda = 0.154178$ nm) patterns of the as-prepared Ni(OH)₂ and NiO. In Fig. 1a, the as-prepared Ni(OH)₂ is identified as the single phase β -Ni(OH)₂ with a suitably crystalline hexagonal structure ($a = 0.3126$ nm, $c = 0.4605$ nm, JCPDS file No. 14-0117). No peaks from other phases are found, suggesting high purity of the as-synthesized β -Ni(OH)₂. In Fig. 1b, all the diffraction peaks can be indexed to the face-centered cubic (fcc) NiO phase ($a = 0.41780$ nm, JCPDS file No. 71-1179). No peaks due to β -Ni(OH)₂ are observed by XRD, indicating that β -Ni(OH)₂ is completely converted to NiO after being heated at 600 °C for 2 h, which is also confirmed by TG and DSC studies (see ESI†).

The morphology and structure of the as-synthesized Ni(OH)₂ powder were further investigated by field emission scanning electron microscopy (FESEM, JEOL JSM-6700F). As shown in Fig. 2, the typical morphology of the as-prepared Ni(OH)₂ is spherical in shape with diameters of 2 to 3 μ m. Interestingly, the Ni(OH)₂ microspheres are in fact built from two-dimensional

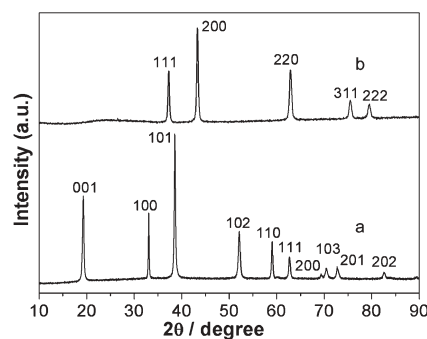


Fig. 1 XRD patterns of (a) the as-prepared β -Ni(OH)₂ powder (140 °C, 24 h) and (b) NiO prepared by thermal decomposition of the β -Ni(OH)₂ at 600 °C for 2 h.

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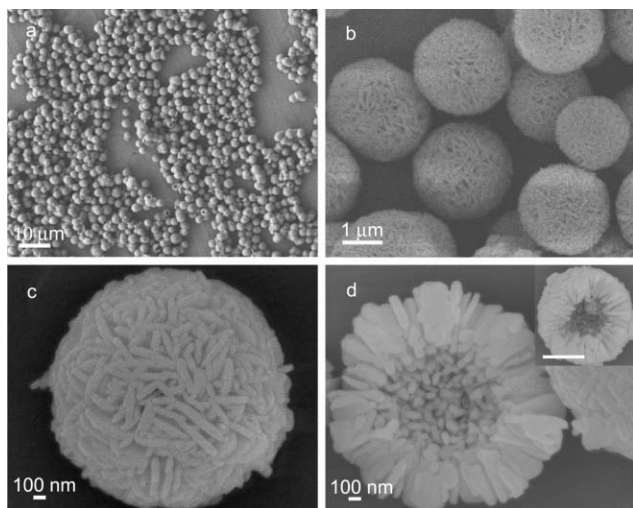


Fig. 2 Morphologies of Ni(OH)₂ hollow microspheres (prepared at 140 °C, 24h): (a)–(c) SEM images of Ni(OH)₂ hollow spheres observed under different magnifications; (d) SEM images of two broken Ni(OH)₂ microspheres. The scale bar of inset in (d) is 1 μm.

nanosheets, and the nanosheets align with one another to form a sphere with an interior cavity (Fig. 2c–d). The thickness of the shell wall is about one-quarter to one-third of the sphere diameter.

The hollow structure of as-prepared Ni(OH)₂ microspheres is further confirmed by transmission electron microscopy (TEM, Hitachi H-700, 200KV) equipped with electron diffraction (ED) (Fig. 3a). Individual crystal sheets from Ni(OH)₂ hollow microspheres can be obtained by sonication (1 h in an ultrasonic water bath). Fig. 3b and c show a typical TEM image of a Ni(OH)₂ nanosheet and its corresponding ED pattern. The ED pattern of the nanosheet can be indexed to the hexagonal β-Ni(OH)₂, consistent with the XRD investigations. The individual Ni(OH)₂ nanosheets are actually single crystals with a size of 100–500 nm and thickness of 50–100 nm, as revealed in the diffraction pattern of the [101] zone spots. The suitably crystalline nature of the nanosheets is also revealed by clear lattice fringes of 0.27 nm between two adjacent (010) planes and 0.23 nm between two adjacent (−111) planes as shown in the high-resolution TEM (HRTEM, JEOL JSM-2010) image in Fig. 3d.

The influence of synthesis conditions on morphology development was experimentally investigated and it was found that the presence of glycine, together with strong alkaline conditions, was

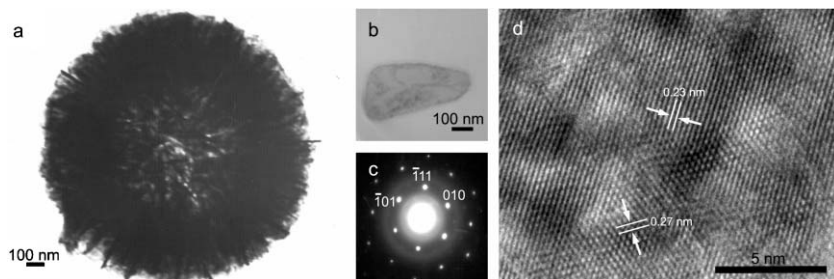


Fig. 3 (a) TEM image of an individual sphere; (b) TEM image of Ni(OH)₂ nanosheets as the formed building units of hollow microspheres; (c) ED pattern of the nanosheet shown in (b); (d) HRTEM image of a single Ni(OH)₂ nanosheet.

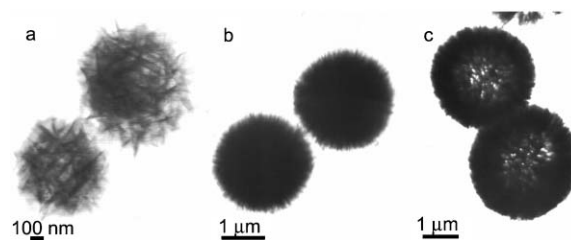


Fig. 4 Typical TEM images of Ni(OH)₂ prepared at 100 °C with different experimental time: (a) 30 min; (b) 1 h; (c) 24 h.

essential for the hollow structure development. Without glycine, Ni(OH)₂ particles rather than hollow Ni(OH)₂ microspheres are obtained, while no precipitate can be obtained if the pH is less than 14. With the combination of the above-mentioned synthesis conditions, hollow sphere morphology can be easily obtained in this work. Experiments also revealed that synthesis temperature has a minor effect on the hollow morphology development. With the synthesis temperatures varying from 100 to 180 °C, hollow microspheres of similar size can always be obtained if sufficient reaction time is provided. Hollow Ni(OH)₂ spheres can even be obtained at temperatures below 100 °C (see ESI†).

To understand the formation mechanism of the hollow structure, time-dependent experiments were carried out and the resultant products were analyzed by TEM investigations. As shown in Fig. 4, three obvious evolution stages could be clearly identified. In the first stage (≤ 30 min), the precipitated Ni(OH)₂ crystals assemble together to form loosely attached aggregates with diameters of 800–900 nm (Fig. 4a). With increasing reaction time, the aggregate continuously grows in size and density to form a sphere with a solid core (Fig. 4b), which is the typical character of the second stage. The second stage lasts for several hours. In the third stage, an interior cavity is gradually formed *via* a core evacuation process, possibly through a mechanism similar to Ostwald ripening. The crystallinity of the as-prepared Ni(OH)₂ increases with reaction time (see ESI†), which confirms that Ostwald ripening (crystallites grow at the expense of the smaller ones) is the underlying mechanism in this hollowing process. Such a core evacuation process was also observed in the synthesis of titania hollow spheres.¹⁰ Investigations also revealed that 24 h would be sufficient for the Ni(OH)₂ hollow spheres to reach their equilibrium size. Due to this hollow forming mechanism, the shell of the microsphere has communicable intercrystallite channels that could serve as the gateway for material/solution exchange between the interior cavity and the exterior space.

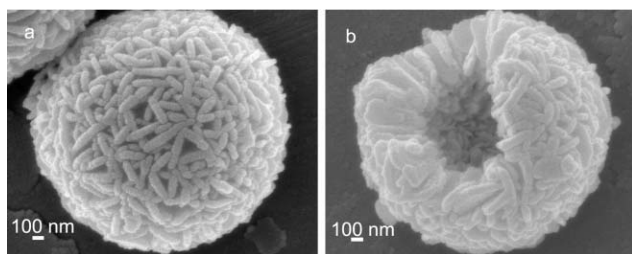


Fig. 5 SEM images of (a) an individual NiO microsphere and (b) a broken NiO microsphere obtained by thermal decomposition of Ni(OH)₂ microspheres at 600 °C for 2 h.

NiO hollow spheres can be easily obtained by heating the as-synthesized Ni(OH)₂ hollow spheres at 600 °C for 2 h. Investigations demonstrated that the hollow spherical structure can be suitably preserved during the calcination process at 600 °C as illustrated in Fig. 5.

In summary, a novel single-step, template-free process has been developed to fabricate the hierarchical structure of Ni(OH)₂ hollow microspheres with β-Ni(OH)₂ nanosheets as the *in situ* formed building units. The characterization, synthetic parameters and possible formation mechanism of the hierarchical structure have been investigated. Furthermore, NiO hollow spheres have

also been successfully synthesized by thermal decomposition of the as-synthesized Ni(OH)₂ hollow spheres. The hollow microspheres of Ni(OH)₂ and NiO have potential applications in alkaline rechargeable Ni-based batteries, micro-rechargeable lithium batteries and catalysts.

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