Non-basic solution eco-routes to nano-scale NiO with different shapes: Synthesis and application

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The assembly of NiO nanodiscs (namely nanoflowers) as well as the dispersed NiO nanodiscs have been successfully synthesized via the thermal decomposition of Ni(OH)2 obtained from different Ni sources in non-basic solution. The route is environment-friendly. The materials were characterized by X-ray diffraction (XRD), field-emission scanning electron microscope (FE-SEM), transmission electron microscope (TEM) and N2 adsorption–desorption. The porous structures with pore size around 6 nm can be observed on the single NiO disc. The nanoflowers exhibit better performance than nanodiscs in the electrochemical test and water treatment experiments, due to much more available surface areas and spaces formed in the NiO nanoflowers.

1. Introduction

Nickel oxide (NiO) has been attracting more and more interests due to its practical and potential application as catalysts [1], gas sensors [2], water treatment adsorbents [3,4], electrochromic devices [5], electrode materials for electrochemical capacitor [6], lithium ion batteries [7,8], fuel cells [9], solar cells [10,11], and so forth. In recent years, along with the development of synthetic techniques of nano-materials, NiO in three-dimensional (3D) nanostructures [12,13] as well as in low-dimensional nanostructures such as nanoparticles [14] (0D), nanotubes [15] (1D), nanorolls [16] and nanosheets [17] (2D) have been reported. It is well known that the microstructures of materials have significant influence on their properties. Considering the wide applications of NiO, it is important to synthesize their controllable micro/nanostructures which can improve the transportation of electrons or can enhance the effective contact of active sites with liquid and gas molecules.

The general route to NiO consists of a two-step reaction: (1) the formation of the precursors such as α-Ni(OH)2, β-Ni(OH)2, Ni2CO3(OH)2 and (2) the thermal decomposition of the precursors to NiO. The first step is very important, which concerns whether the whole process is simple and environment-friendly. However, to the best of our knowledge, most methods involve the use of an alkaline reagent such as NH3·H2O [12], NaOH [18] and N2H4·H2O [19], or structure-directing agent including PVP [20], SDS [21], glucose [22], and biomolecules [23], which bring about many troubles for subsequent disposal and the environment. Therefore it motivates us to seek a facile synthesis route. In this work, we prepared the assembly of NiO nanodiscs (namely nanoflowers) as well as the NiO dispersed nanodiscs in neutral solutions free of any alkaline reagent and structure-directing agent, and comparatively evaluated the performance of NiO nanodiscs and nanoflowers using electrochemical properties and wastewater treatment ability as probes. The whole synthesis is “green”, as we just use C2H5OH and water as blend solvent.

2. Experimental

2.1. Synthesis

β-Ni(OH)2 nanodiscs and nanoflowers were obtained by means of hydrothermal synthesis in non-basic solution. All chemicals were used as received without further purification. In a typical synthesis, 0.2 mmol Ni(CH3COO)2 or Ni(NO3)2, 5 mL H2O and 5 mL C2H5OH were mixed to form a clear green liquid at room temperature, then...
the mixture was transferred in a 25 mL Teflon-lined stainless steel autoclave, kept in an oven at 200 °C for 8 h. After cooling to room temperature naturally, the resultant jade-green precipitate was collected, washed several times with distilled water, and finally dried in the air. For the time-dependent experiments, samples were collected at different intervals such as 2 h, 4 h, 6 h and other conditions were kept the same.

For synthesis of the NiO nanodiscs and nanoflowers, the β-Ni(OH)₂ nanodiscs and nanoflowers precursors were calcined in the air from room temperature to 450 °C with a heating rate of 10 °C min⁻¹ and maintained for 30 min.

2.2. Characterization

The phase composition of the samples was investigated by a Rigaku Ultima III X-ray diffractometer using Cu Kα radiation. The morphologies of the samples were observed by a LEO 1530VP field-emission scanning electron microscope (FE-SEM) and a JEM 200CX transmission electron microscope (TEM). The nitrogen adsorption–desorption isotherms were collected on a Micromeritics Tristar-3000 surface area and porosity analyzer at 77 K after the sample had been degassed in the flows of N₂ at 150 °C for 4 h. The specific surface area was calculated using the Brunauer–Emmett–Teller ( BET) method and the pore size distribution was calculated from nitrogen desorption data using the Barrett–Joyner–Halenda (BJH) method.

All the electrochemical measurements were performed on a CHI 660B (Shanghai Chenhua Apparatus, China) and PGSTAT30 (Autolab, EkoChemie, Netherlands) electrochemical workstation using a standard three-electrode configuration coupled with the sample film (working electrode), a saturated calomel electrode (reference electrode) and platinum wire electrode (counter electrode). A 3 wt% KOH aqueous solution was used as electrolyte. The working electrodes were prepared by coating a paste onto a nickel foam substrate (1 cm × 1 cm), which consists of 80 wt% NiO, 15 wt% acetylene black and 5 wt% polytetrafluoroethylene (PTFE) binder.

Water Treatment Experiments: K₂Cr₂O₇ was dissolved in distilled water to form a solution containing 15 mg L⁻¹ Cr (VI). Then, 0.1 g NiO sample was added to 25 mL of the above solution under magnetic stirring. At given time intervals, the suspension was taken out and centrifugally separated. The supernatant was analyzed by the Hitachi 180-80 atomic absorption spectrophotometer.

3. Result and discussion

X-ray diffraction (XRD) patterns shown in Fig. 1, indicate that all samples possess good crystallinity. Fig. 1A displays XRD patterns of the as-synthesized precursors with Ni(CH₃COO)₂ and Ni(NO₃)₂ as the nickel sources, respectively. In spite of nickel sources, all peaks of the precursors can be assigned to layered metal hydroxide β-Ni(OH)₂ in hexagonal system with lattice constants of a = 3.127 Å and c = 4.606 Å, referring to Joint Committee on Powder Diffraction Standards (JCPDS, PDF #14-0117), and no obvious peaks of α-Ni(OH)₂ have been observed. β-Ni(OH)₂ has brucite-type structure by stacking of the Ni(OH)₂ layers along the c axis in an interlayer distance of 4.606 Å. Unlike α-Ni(OH)₂, its layers do not be intercalated with any species [24]. Whereas the main peaks in Fig. 1B for the as-calcined samples can be indexed to cubic-phased NiO (PDF #47-1049), suggesting the formation of cubic-phased NiO completely after heat treatment at 450 °C in air. The main reaction is as follows:

\[
\text{Ni(OH)}_2 \rightarrow \text{NiO} + \text{H}_2\text{O}
\]  

(1)

The morphology of the obtained Ni(OH)₂ and NiO was characterized using a scanning electron microscope (SEM). As can be seen from Fig. 2, the Ni(OH)₂ obtained from Ni(CH₃COO)₂ shows disc-like morphology with diameters of 400–600 nm (Fig. 2a). However, use of Ni(NO₃)₂ as nickel source produces the flower-like Ni(OH)₂ with diameters of 3–6 μm and assembly of several nanodiscs as the building blocks (Fig. 2b). The time-dependent experiments were performed to explore the morphology evolution. Fig. 3a–c is the time-line based SEM images of Ni(OH)₂ nanodiscs from Ni(CH₃COO)₂ to Ni(OH)₂. When the reaction time is as short as 2 h, thin nanodiscs are obtained, which connect with each other in two dimension direction. With the time reaction extended, the edges of nanodiscs become more and more clear. Coarse circular discs, round-angle hexagonal discs, and hexagonal discs are the main morphologies for the 4 h, 6 h, 8 h samples, respectively. Fig. 3d–f shows the SEM images of the samples collected at 2 h, 4 h and 6 h during the reaction from Ni(NO₃)₂ to Ni(OH)₂. At the initial stage (2 h), many individual Ni(OH)₂ sheets with irregular profile are observed (Fig. 3d). When the reaction time is prolonged to 4 h, the sheets grow into slight regular nanodiscs and intercross with each other (Fig. 3e). As the reaction proceeds (6 h), more and more nanodiscs assemble together, leading to flower-like structures, as shown in Fig. 3f. It can also be observed there are some flowers with sparse petals, suggesting an incomplete growth. As mentioned above, further increasing the time to 8 h, the sparse flowers become dense and the whole evolution process is finished. About the growth mechanism, layered metal hydroxide is generally limited to grow along two-dimensions, thus sheet-like morphology is preferred. Moreover, several researchers reveal that anions play an important role in controlling the shape of as-synthesized nanostructures [25,26]. In our case, it can be deduced that the final morphologies of Ni(OH)₂ are closely related to the anions, because all experimental parameters were kept unchanged except nickel source. In a control experiment, when the nickel source was replaced by NiCl₂, no product was obtained, suggesting anion is a crucial factor. As for the as-calcined samples, from Fig. 4, it can be found that the morphology of all the precursors is well retained during the heat treatment process. Even for nanoflower-like sample, the hierarchical structures could also be retained perfectly. There are some nanodiscs over-
lapped each other as coins. It might be due to the ferromagnetic behavior of NiO nanocrystals [27,28], which can magnetize each other.

Fig. 5 represents the TEM image to reveal the actual feature of the NiO morphology. It can be clearly found that every disc consists of many pores and the nanoflowers are also assembled from discs with rich porosity. As shown in Fig. 5a, high-resolution transmission electron microscopy (HRTEM) image of the nanodisc clearly displays lattice fringes and pores indicated by the circles. Interestingly, the lattice fringes around the pores are uniformly directed. The selected area electron diffraction (SAED) pattern from the nanodisc presents hexagonal diffraction pattern, revealing its single crystal nature. This phenomenon of obtaining single-crystal NiO nanosheets from Ni(OH)₂ nanosheets has been observed previously [12]. Although the crystal structures of NiO and Ni(OH)₂ are different, the (1 1 1) planes of cubic NiO have the same symmetry of the lattice array as the (0 0 1) planes of hexagonal Ni(OH)₂, and the d-spacing value of the (2 2 0) plane (0.147 nm) in NiO is quite close to that of the (2 0 0) plane (0.136 nm) in Ni(OH)₂. Hence the transformation is possible under a mild condition.

In Fig. 5b, SAED pattern taken from a petal of NiO nanoflowers shows the same hexagonal diffraction pattern as that of the nanodiscs, implying the NiO nanoflowers consist of single-crystal discs.

As for the formation of pores, from the above mentioned reaction (1), it can be deduced that during the decomposition of Ni(OH)₂, the release of gaseous water molecules induces the porous structure. The similar phenomena have been reported by many groups, for example, the porous ZnO [29,30] and MgO [31] could be obtained by decomposition of precursor. To further describe the porous properties, the N₂ adsorption–desorption isotherms are plotted in Fig. 6, and the inserts are the pore size distributions. Both nanodiscs and nanoflowers present similar adsorption–desorption isotherms profile. Compared to type II isotherms of the Ni(OH)₂ precursors, type IV isotherms with H1-type hysteresis loops were observed for both NiO materials, confirming the presence of porosity structure. Moreover, narrow pore size distributions are shown with a sharp peak centered at 5.39 nm for NiO nanodiscs and 6.06 nm for nanoflowers. Brunauer–Emmett–Teller (BET) surface areas calculated from nitrogen adsorption isotherms, show that
the specific surface area of the NiO nanodiscs is 70.0 m² g⁻¹, which has a slight increase over that of the NiO nanoflowers (62.3 m² g⁻¹).

In order to investigate the effect of the morphology on the capacitive behavior of the NiO samples, the performance of the materials were examined by cyclic voltammetry (CV) and chronopotentiometry (CP). The CV curves shown in Fig. 7 are for the NiO materials with different morphology in the potential range from 0 to 0.55 V (vs. SCE) at a scan rate of 10 mV s⁻¹. Clearly, different from a rectangular mirror image for electrical double-layer capacitance, a couple of redox peaks reveal its pseudocapacitive character based on the reversible redox reactions between Ni²⁺ and NiOOH. It can be also clearly seen that compared to the nanodiscs, the NiO nanoflower has a larger current density, indicating a higher energy density. Fig. 8 shows the charge/discharge curves of the NiO nanodiscs and nanoflowers within potential range of 0–0.55 V at a current density of 0.5 A g⁻¹. The specific capacitance can be calculated according to the following formula:

\[ C_s = \frac{I \cdot t}{m \Delta \overline{E}} \]

where \( \Delta \overline{E} \) represents the potential difference, \( I \) is the discharge current, \( t \) is the time of discharge and \( m \) is the mass of electrochemical active material. The specific capacitance values for the nanodiscs and nanoflowers calculated from the whole discharge curves are 82 and 120 F g⁻¹, respectively. Such results indicate that the nanoflower NiO can provide higher power and maintain a more promising energy density than the NiO
nanodiscs. The better performance can be ascribed to the special morphology. It is well known that Faradaic reaction occurs on the surface of electro-active material. Although the NiO nanodiscs possess more BET surface area for N₂ molecules, the NiO nanoflowers can offer more accessible areas for the electrolyte solution owing to improved geometrical configuration.

NiO could also be used to remove heavy metal ion from aqueous solution by ion exchange sorption at the liquid/solid interface [3,4]. Herein, we chose Cr (VI) ions as the probe. Fig. 9 shows that NiO nanoflowers exhibit not only faster adsorption rate, but also better removal capacity than the nanodiscs, when 0.1 g NiO sample was added to 25 mL chromium solution with an initial concentration of 15 mg L⁻¹. The adsorption capacities were measured as 4.6 mg Cr g⁻¹ for nanoflowers and 4.2 mg Cr g⁻¹ for nanodiscs. In general, high surface area is beneficial for adsorption. Similar to above discussion in electrochemical performance, the poor adsorption rate curve for the nanodiscs means poor mass transportation, and poor adsorption capacities means that not all surface area can be available. In the case of the nanoflowers, the spaces between the nanodisc units result in easy access by the solution containing Cr (VI) ions, so each nanodisc can be fully immersed in the electrolyte.

**Fig. 6.** N₂ adsorption–desorption isotherms and pore size distributions (inset) of the nanodiscs (a: Ni(OH)₂ and b: NiO) and nanoflowers (c: Ni(OH)₂ and d: NiO).

**Fig. 7.** Cyclic voltammograms of the NiO in 3 wt% KOH solution at a scan rate of 10 mV s⁻¹.

**Fig. 8.** Charge/discharge curves in the potential range from 0 to 0.55 V at a current density of 0.3 A g⁻¹.
4. Conclusions

In conclusion, NiO nanodiscs and nanoflowers have been controllably fabricated via the thermal decomposition of Ni(OH)$_2$ by using different Ni sources in non-basic solution for anion-assisted effect. When applied in electrochemical test and water treatment, the nanoflowers exhibit better performance than the nanodiscs, due to their much more available surface areas and spaces.

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References


Fig. 9. Adsorption rate curves of Cr (VI) on the NiO samples.