Novel Synthesis of Nanoporous Nickel Oxide and Nickel Nanoparticles/Amorphous Carbon Composites Using Soluble Starch as the Template

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A simple and green synthetic route based on the use of soluble starch as the template has been utilized to prepare novel $Ni(OH)_2$/starch precursors. Nanoporous nickel oxide (NiO) and nickel nanoparticles/amorphous carbon (Ni/C) composites have been successfully prepared by thermal decomposition of the novel $Ni(OH)_2$/starch precursors in air and in nitrogen, respectively. N_2 adsorption–desorption measurements show the two final products having nanoporous structures. The electrochemical measurements indicate that the nanoporous NiO sample has a favorable faradaic pseudocapacitance behavior.

In the last decade, NiO has been found to play an increasingly important role in gas sensors[1] and electrochemical capacitors for power source applications.[2] The Ni/C composites have potential applications in information-storage media and catalysts in medicinal chemistry.[3] As the current research is driving towards nanoscale science and technology, many reports have investigated the synthesis of nanosized NiO[4] and metallic nanoparticles/C composites[5–7] materials by different methods.

Recently, it has been shown that water-soluble polysaccharides are powerful tools for controlling the particle shapes and sizes of inorganic materials.[8] Soluble starch, a kind of water-soluble polysaccharide, is low cost, renewable, and environmentally friendly. Lately, it has been reported that macroporous materials have been prepared using starch gel as the template.[9]

Herein, we demonstrate a novel and environmentally friendly synthetic route to prepare nanoporous NiO and Ni/C composites with large surface areas based on the use of soluble starch as the template. The two products can be directly obtained by heat treatment of the same novel precursors in different atmospheres.

The typical procedure for the preparations of nanoporous NiO and Ni/C composites is described as follows: Soluble starch (1.0 g) was dissolved in 20.0 mL of distilled water with vigorous magnetic stirring for 2 h. Then, it was mixed with a 10 mL of aqueous solution of nickel acetate (0.2 M). This slurry was stirred for an additional 5 h to complete the immobilization of metal ions to starch skeletons. Then, the pH of the mixture was slowly adjusted to 9 by dropwise addition of NH_4OH (5 wt %). The mixture was maintained at 100 °C for 3 h with vigorous magnetic stirring, and a green gel was obtained. The gel was then dried in a drying oven at 100 °C for 10 h to obtain light green $Ni(OH)_2$/starch precursors. The precursors were ground, then calcined at 380 °C for 2 h in the presence of air or calcined at 550 °C for 3 h in the presence of nitrogen.

The thermal decomposition of the $Ni(OH)_2$/starch precursors in the presence of air was studied using simultaneous thermal analysis (STA) on an SDT Q600 thermal analysis device. The final products were characterized by X-ray diffraction (XRD) (Bruker D8-Advance), transmission electron microscope (TEM) (FEI TECNAI-20) and N_2 adsorption–desorption measurements (Micromeritics ASAP 2010 system). The NiO powders were used to fabricate the electrode of electrochemical capacitors according to the previous report.[4c] The performance of the as-prepared electrode was measured with a CHI660 electrochemical working station.

Simultaneous thermal analysis data for the $Ni(OH)_2$/starch precursors reveals that the starch template is completely removed at about 380 °C in air (Figure S1). (S refers to Supporting Information)

The XRD patterns (Figure S2) of the sample which was obtained by thermal decomposition of $Ni(OH)_2$/starch precursors at 380 °C for 2 h in air reveal that the diffraction peaks can be perfectly indexed to the crystalline NiO (JCPDS code: 47-1049). The average size of the crystals, which was calculated with Scherrer's formula, was found to be 10.8 nm.

The TEM images of the NiO sample are shown in Figure 1. Nanosized NiO crystals can be observed. The magnified view of the crystalline NiO (Figure 1b) presents that most of the NiO crystals are fine and uniform. The average size of the crystals is approximately 11 nm, which is basically consistent with that calculated from the XRD data. Inset in Figure 1b presents the corresponding selected area electron diffraction (SAED) patterns of the sample. The diffraction rings account for the polycrystalline characteristic of the NiO sample.

Figure S3a presents the N_2 adsorption–desorption isotherms of the NiO sample. It shows a typical IV isotherm with an H3-type hysteretic loop attributed to an interconnected nanoporous system with a broad pore-size distribution.[10] The specific surface areas and the pore volume of the sample are 76 $m^2\,g^{-1}$ and 0.16 $cm^3\,g^{-1}$, respectively. Figure S3b illustrates the pore-size distribution plot calculated by the BJH (Barrett–Joyner–Halenda) equation. The pore sizes are mainly in a range of 2–30 nm, confirming that the NiO sample has a nanoporous structure. It is inferred that the nanopores formed mainly as a result of the

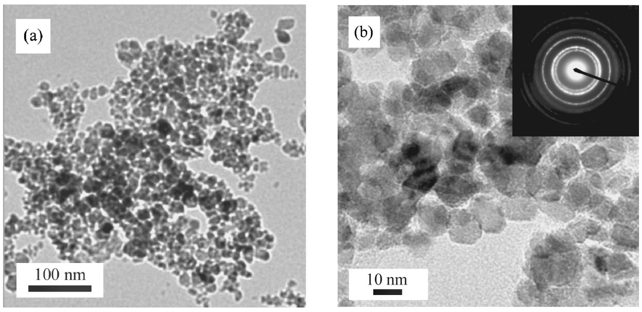

Figure 1. TEM images of the NiO sample: (a) low-magnification image; (b) high-magnification image and the corresponding SAED patterns (inset).

removal of the starch template in the process of calcinations in air. These pores existing in the sample may facilitate the electrochemical reactions during the electrochemical property measurements. The cyclic voltammograms of the NiO electrode exhibits two current peaks (a and b) that relate to the faradaic reaction at the surface of NiO (Figure S4). The electrode has a large specific capacitance of $329\,\mathrm{F\,g^{-1}}$ at a sweep rate of $10\,\mathrm{mV\,s^{-1}}$, which was calculated according to the formula reported in the literature.[11] The high specific capacitance of the NiO sample can probably be attributed to the nanoporous structure and large pore volume, both of which can facilitate OH^- in the electrolyte transferring to the NiO surfaces, thus allowing for the high efficient faradaic reaction.

Polysaccharides can form complexes with divalent metal ions in solution, which is due to their high number of coordinating functional groups.[8a] Hence, it is likely that the majority of the Ni^{2+} ions are closely incorporated with the starch molecules in solution. Because of the strong interactions between Ni^{2+} and –OH, –C=O groups of starch macromolecules, Ni^{2+} are uniformly and tightly anchored. Such interactions would lead to the high local supersaturation of Ni^{2+} at the binding sites, thus providing potential nucleation sites for the crystallization of the $Ni(OH)_2$. With the increasing pH by NH_4OH titration, $Ni(OH)_2$ would homogeneously nucleate and develop into nanoparticles at the binding sites. During the process of calcinations in air, $Ni(OH)_2$ nanoparticles decomposed into NiO nanoparticles and H_2O. In addition, the starch template decomposed into CO_2 and H_2O, which may result in high numbers of pores between the NiO crystals.

The XRD patterns (Figure S5) of the sample which was obtained by heat treatment of $Ni(OH)_2$/starch precursors at 550 °C for 2 h in nitrogen reveal that the diffraction peaks can be perfectly indexed to the cubic-phased metallic nickel (JCPDS code: 04-0850).

The typical TEM image of Ni/C composites is shown in Figure 2a. Figure 2b exhibits that fine and uniform Ni nanoparticles (the black dots) are well dispersed in the amorphous carbon (the gray matrix) and few Ni particles aggregated. Most of the Ni particles in the product were found to be approximately 8 nm in size. The corresponding SAED patterns show that the product contains the metallic Ni. N_2 adsorption–desorption analysis (Figure S6) of Ni/C composites indicates that it has a nanoporous structure. The pore sizes of the sample are mainly in a range of 2–8 nm. The BET surface areas and pore volume are $263\,\mathrm{m^2\,g^{-1}}$ and $0.15\,\mathrm{cm^3\,g^{-1}}$, respectively. This high value is mainly attributed to a large number of nanopores in amorphous carbon which were formed in the process of carbonization.[6]

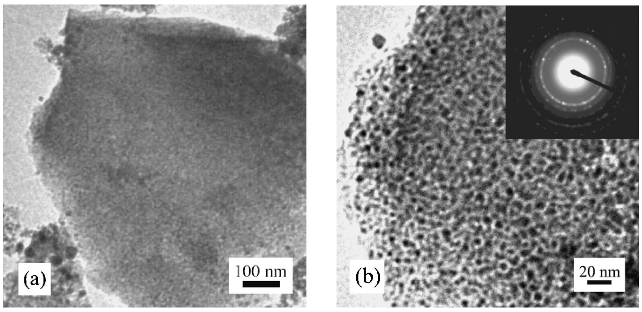

Figure 2. TEM images of the sample calcined in N_2: (a) low-magnification image; (b) high-magnification image and the SAED patterns (inset).

When the $Ni(OH)_2$/starch precursors were calcined at 550 °C in nitrogen, the organic component carbonized into amorphous carbon.[6] Meanwhile, the NiO particles, which were prepared by thermal decomposition of $Ni(OH)_2$, were reduced to metallic Ni in the reductive atmosphere resulting from the thermal decomposition of the organic component.[7] Amorphous carbon plays an important role in the prevention of the metallic Ni nanoparticles from aggregation and oxidation, because surface-active sites for oxidation of the metallic Ni particles are terminated by carbon atoms.[5]

In summary, a novel and environmentally friendly synthetic route based on the use of soluble starch as template for the preparations of uniform NiO and Ni/C composites through thermal decomposition of $Ni(OH)_2$/starch precursors in air and in nitrogen, respectively, has been presented. N_2 adsorption–desorption measurements reveal that both products have nanoporous structures with high BET surface areas and large pore volumes. The electrochemical measurements of the NiO sample indicate that it has a favorable faradaic pseudo-capacitance behavior. This method offers a new synthetic route to exploit nanoporous metal oxides and metal nanoparticles/C composites for potential industrial applications.

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