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Solvothermal synthesis and photocatalytic properties of NiO ultrathin nanosheets with porous structure

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ABSTRACT

Hierarchical NiO microspheres, composed of ultrathin nanosheets with porous structure, are prepared through a facile solvothermal route followed by a calcination process. First, the precursor $Ni_3(NO_3)_2(OH)_4$ hierarchical architectures assembled by irregular nanosheets were synthesized through urea assisted precipitation. Second, the NiO hierarchical architecture was obtained from the precursor by a simple calcination procedure without changing their morphologies. The resultant products were characterized by XRD, SEM, TEM, TG, FT-IR and BET analysis techniques. The XRD pattern showed that the sample exhibited a rocksalt cubic phase structure after calcined at 500 °C for 2 h. The SEM and TEM images demonstrated that the as-prepared NiO were microspheres composed of ultrathin nanosheets with porous structure. The catalytic efficiency of the NiO nanomaterials is evaluated by the photocatalytic degradation of methylene blue (MB). The obtained NiO displayed the excellent degradable ability and stable cyclability to MB dye, which may be attributed to its unique hierarchical characteristics: ultrathin-porous microstructure.

1. Introduction

With the further exploration of synthetic nanomaterials, a novel paradigm began to emerge which was termed "ultrathin" nanostructures. An ambiguous definition has been conformed for ultrathin: some research teams consider ultrathin nanostructures as further thinning that at least one dimension of usual nanomaterials under 30 nm or even under 10 nm owing to their specific materials and the concerned properties [1,2]. By contrast with the internal atoms' collective effects of traditional materials, surface atoms in ultrathin nanomaterials can implement a more competitive or even dominant role in modifying and regulating the material properties. Meanwhile, it possesses the extremely basic features of nanomaterials, including quantum-confinement effects and unconventional reactivities, which are determined by the significant structure variations from the bulk material [3,4]. Previously, Shi [5] and Wang [6] et al. provided good instances of sample morphology in one-dimensional ultrathin nanosheets. Simultaneously, the products with "porous" structure grabbed extensively attention for their greater surface area than that of the compact ones, which was expected to exhibit new properties in photocatalysis, electrochemistry, gas sensitivity etc. [7,8]. To some extent, the formation of porous structure is always caused by the loss of water molecules and organic matter. For example, Zhu et al. noted that the hierarchical CuO with porous architectures can enhance material sensing properties [9]. Liu and co-workers prepared nest-like γ-Fe_2O_3/ZnO hollow nanostructures via a multi-step process, which showed better visible-light photocatalytic activity [10]. Tailored fabrication of the hierarchically ultrathin porous nanooxide system is therefore a strategic theme of uninterrupted investigations.

As a p-type semiconductor with wide-band gap, NiO is an extremely interesting material because of its extensive practical applications, such as catalysts [11], electrode materials for lithium ion batteries and fuel cells [12,13], electrochemical supercapacitors, gas sensors, adsorbents and magnetic materials [14–17]. Thus far, many NiO structures have been prepared, such as nanoplates, nanorings, nanowires, nanotubes, and hollow microspheres [18–21]. And in general, to synthesize nickel oxide precursor with different morphologies, various methods were adopted involving an addition mediated self-assembly process [22]. For example, biomorphic crystals of NiO were produced using pine as templates [23]. However, the template method suffers from the complication of synthesis process and time-consuming removal of the core particles. In this work, solvothermal was used as a powerful and effective approach for high temperature synthesis of well constructed NiO ultrathin porous nanosheets without any template. To the best of our knowledge, there are few reports

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on NiO, which possess both ultrathin structure and porous architectures.

In this article, NiO ultrathin porous nanosheets were prepared by a simple, low-cost and effective normal approach using urea as the addition agent. Furthermore, the possible mechanism for the formation of NiO hierarchical structures was proposed. The photocatalytic activities of the as-obtained NiO samples were evaluated by the photocatalytic degradations of methylene blue solutions at room temperature.

2. Experimental

2.1. Synthesis

Nickel nitrate hexahydrate was purchased from Sinopharm Chemical Regent Co., Ltd (Shanghai, China); urea was purchased from Beifang Tianyi Chemical Regent Ltd. (Tianjin, China); absolute ethanol was obtained from Tianjin Fuyu Fine Chemical Co. Ltd. All reagents were used without further purification. For the preparation of hierarchical precursor, nickel nitrate hexahydrate, $Ni(NO_3)_2{\cdot}6H_2O$ (0.006 mol) and urea (0.003 mol) were dissolved in absolute ethanol solvent (60 mL) respectively. A light-green solvent was formed under vigorous stirring in this process. The solution was stirred for 0.5 h, and then introduced into a dried Teflon autoclave (100 mL), which was maintained at 180 °C for 12 h. After being cooled to room temperature, the viridescent precipitate was collected, washed with ethanol and distilled water several times, and dried under vacuum at 80 °C overnight. The dried powder was heated to 500 °C with a ramping rate of 5 °C min^{-1}, and then calcined at 500 °C for 2 h to obtain NiO finally.

2.2. Characterization

X-Ray diffraction (XRD) patterns were obtained by using a Bruker D8 advanced X-ray powder diffractometer with Cu-Ka radiation (λ = 1.5418 Å). The morphologies of the precursor and NiO powder were examined by scanning electron microscopy (SEM, Hitachi S-4800 microscope) and high-resolution transmission electron microscopy (HRTEM, JEOL-2100). Furthermore, selected area electron diffraction (SAED) patterns were recorded to determine the growth orientation of the microspheres. Fourier transmission infrared (FTIR) spectra of the powders (as pellets in KBr) were recorded using a FTIR spectrometer in the range of 4000–400 cm^{-1}. Thermogravimetric analysis (TG) was carried out on a SDT Q600 thermal analyzer with a heating rate of 10 °C min^{-1}. The surface areas of the NiO powder were measured by using the Brunauer–Emmett–Teller method with a TriStar II 3020 instrument at liquid nitrogen temperature.

2.3. Photocatalysis

Methylene blue (MB) dye was chosen to evaluate the photocatalytic properties and superior cyclabilities of the hierarchical NiO. 0.1 g of as-prepared samples was dispersed in a pyrex glass reactor containing MB solutions (100 mL) with concentrations of 20 mg L^{-1}. The mixture was stirred magnetically in the dark for 2 h to obtain the equilibrium adsorption state. The optical system for detecting the catalytic reaction consists of a 300 W Xe arc lamp (PLS-SXE300UV, Beijing Perfectlight Co. Ltd), and the degradation of MB dye was monitored by UV/Vis spectroscopy (UV-2600, Shimadzu).

3. Results and discussion

3.1. $Ni_3(NO_3)_2(OH)_4$ precursor synthesis

The $Ni_3(NO_3)_2(OH)_4$ precursor obtained through the solvothermal reaction at 180 °C for 12 h were characterized with XRD, SEM and TG, and the results are shown in Fig. 1. The SEM observations indicate that the products consist of globular like microspheres with the diameters of 3–6 μm. The globular-like architectures are assembled from irregular sheetlike subunits with the thickness of about 10–20 nm (Fig. 1a-c). For clearly viewing the microstructure, TEM observation was then carried out. As shown in Fig. 1d, it is evident that globular like architectures assemble into nanoflakes. This result is consistent with the former SEM observation. The corresponding XRD patterns are displayed in Fig. 1e. All of the diffraction peaks can be indexed to hexagonal structure of $Ni_3(NO_3)_2(OH)_4$ (JCPDS No. 22–0752), revealing that $Ni_3(NO_3)_2(OH)_4$ was phase pure [24].

The thermogravimetry analysis results are shown in Fig. 1f. When the temperature was elevated to 600 °C, the total weight loss was about 32%, owing to the decomposition of $Ni_3(NO_3)_2(OH)_4$ precursor. The weight loss is consistent with the theoretical value within a certain error range. The decomposition process of $Ni_3(NO_3)_2(OH)_4$ can be expressed as follows:

$$2Ni_3(NO_3)_2(OH)_4 \rightarrow 6NiO + 4NO_2 + 4H_2O + O_2$$

The results also indirectly proved that the precursor was $Ni_3(NO_3)_2(OH)_4$ [25]. An exothermic peak in the DSC curve appeared at about 332 °C, which indicated the precursor was easily thermodecomposed. The pyrolysis of the precursor was completely before 500 °C, so the decomposition temperature was chosen at 500 °C to obtain the NiO.

3.2. NiO synthesis

Fig. 2 shows the morphologies of the as-prepared NiO microspheres. From Fig. 2(a–c), we can see the typical SEM images of the as-prepared NiO microspheres, and it can be determined that the microstructure of the sample was composed of irregular ultrathin NiO nanosheets with thickness of about 10 nm. Simultaneously, the ultrathin NiO nanosheets were compounded of tiny nanoparticles with a diameter of around 5–10 nm. It was worth noting that the formation of NiO porous structure was due to non-tightly packed of tiny nanoparticles. Thus, the NiO flower-like microspheres exhibited a hierarchical structure with ultrathin nanosheets as the second grade and tiny nanoparticles as the third grade. SEM micrograph of commercial NiO was presented in Fig. 2d. By comparison, nearly spherical microscale particles are observed. From the SEM image with higher resolution, their unique surface microstructure is shown (Fig. 2e). It clearly demonstrated the lamellar-like morphology of the commercial NiO. The corresponding XRD patterns are shown in Fig. 2f. No impurity peaks from other phases were found in the patterns, suggesting that the precursor product was completely converted to NiO, and the spectra were in agreement with NiO rocksalt symmetry, as shown in the JCPDS file for pure NiO product (JCPDS No. 65-5745). All the diffraction peaks of NiO product are well indexed to the cubic phase structure.

To characterize the crystal face of the NiO nanosheets, the transmission electron microscopy (TEM) measurements were carried out for which the sample was slightly grounded and ultrasonicated in ethanol. A typical TEM image of the dispersed NiO (Fig. 3a and b) confirmed that the NiO nanosheets were composed of nanoparticles with diameter of several nanometers. The high-resolution TEM images of the nanosheets lying on the TEM grid (Fig. 3c and d) revealed the (1 1 1) and (2 0 0) atomic planes with lattice spacing of