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Short communication

Nickel titanate microtubes constructed by nearly spherical nanoparticles: Preparation, characterization and properties

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ABSTRACT

In this paper, we report the successful synthesis of NiTiO₃ microtubes constructed by nearly spherical nanoparticles via a simple solution-combusting method employing a mixture of ethanol and ethyleneglycol (V/V = 60/40) as the solvent, nickel acetate as the nickel source, tetra-n-butyl titanate as the titanium source and oxygen gas in the atmosphere as the oxygen source. The as-obtained product was characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and energy dispersive X-ray spectrometry (EDS). The UV-vis absorption spectrum of the product showed two absorption peaks centered at 258.6 and 350.1 nm, respectively. The Brunauer–Emmett–Teller (BET) surface area of the product was 14.06 m²/g and the pore size distribution mainly located from 20 to 30 nm. The photocatalytic degradation property of the product for organic dyes showed that the as-obtained porous NiTiO₃ microtubes could strongly promote the degradation of organic dyes including Pyronine B, Safranine T and Fluorescein.

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1. Introduction

Trinary oxides containing titanium and transition metals, such as MTiO₃ (M = Ni, Pb, Fe, Co, Cu and Zn), are universally known as chemical and electrical materials due to their weak magnetism and semiconductivity with wide applications in semiconductor industry, nuclear waste technology, refractory systems, metal-air barrier, high performance catalysts, color mixtures of surface coating, gas sensing devices, and solid-oxide fuel cells [1-7]. Nickel titanate (NiTiO₃) belongs to the ilmenite structure. Both Ni and Ti atoms prefer octahedral coordination with alternating cation layers occupied by Ni and Ti alone [8]. Powder neutron diffraction studies [9] and susceptibility measurements [10] have shown that NiTiO₃ has an antiferromagnetic structure with M²⁺ spin parallel within each layer perpendicular to the rhombohedral axis, and antiparallel between adjacent layers; also, the spins are directed in the layers and the Neel temperature is 23 K. Magnetization measurements between 4.2 and 300 K suggested that NiTiO₃ has weak anisotropy in the lower range of temperatures [11,12]. Furthermore, as a solid lubricant, NiTiO₃ has been investigated as a tribological coating to reduce friction and abrasion in hightemperature applications [13,14] and it is found that titanium oxide coatings containing nickel can provide lubricious surfaces without the need of liquid lubricants [15,16]. Solid lubricants that can minimize friction and abrasion over a wide operating range are essential to minimizing the replacement cost and logistical support costs of advanced engines [17,18]. Many methods, such as sol–gel technique [17,19], the flux method [20], co-precipitations [21], solid state reactions [22], electrospinning [23] and the Pechini process [24,16], have been reported for synthesis of crystalline NiTiO₃ powders. However, NiTiO₃ fabricated by the above methods usually require complex equipment and complicated operation. At the same time, the traditional preparation methods can produce large NiTiO₃ particles with uncontrolled morphologies due to their inherent problems such as high reaction temperature and heterogeneous solid phase reaction. So, it is still a great challenge to search for a simple and cost-effective route to prepare NiTiO₃ with a high yield.

In 2007, our group designed a simple solution-combusting route for preparation of binary metal oxide nanoparticles such as ZnO and cobalt oxides [25]. In this paper, we further developed this method and successfully prepared NiTiO₃ microtubes constructed by nearly spherical nanoparticles in one step, employing a mixture of ethanol and ethyleneglycol as the solvent, nickel acetate (NiAc₂) and tetra-n-butyl titanate as the nickel and titanium sources. The combustion reaction was carried out in air. Compared with the above-mentioned methods, this method has the following advantages: (1) it is very cost-effective and convenient because of not requiring any sophisticated experimental setups and complicated operations; (2) different from the high-temperature

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treatment over 1273 K in conventional solid state reactions, the present method does not need any high-temperature annealing; (3) the reaction is safe, quick and environmentally friendly since the byproducts are CO_2 and H_2O ; (4) the experiments can be easily repeated and the yield is high (>95%). Furthermore, to our best knowledge, this is the first report on the synthesis of NiTiO₃ microtubes constructed by nearly spherical nanoparticles in the literature.

2. Experimental

2.1. Synthesis of NiTiO₃ microtubes

All chemicals and reagents were purchased from Shanghai Chemical Corp. Ltd. and used without further purification. In a typical experiment, 0.01 mol of nickel acetate (NiAc₂·4H₂O) was dissolved in 100 mL mixed solvents of ethanol and ethyleneglycol with the volume ratio of 60/40. Then, 0.01 mol of $Ti(OC_4H_9)_4$ was added under magnetic stirring. After the solution was transferred into a spirit lamp with an absorbent cotton lampwick, the spirit lamp was fired with a match. For a moment, some yellow products appeared. After the reaction finished, the yellow products were collected and repeatedly washed with distilled water to remove the impurities, and finally, dried at 323 K in air for 5 h.

2.2. Characterization of the samples

X-ray powder diffraction (XRD) of the product was carried out on a Shimadzu XRD-6000 X-ray diffractometer equipped with Cu K α radiation ($\lambda = 0.154060$ nm), employing a scanning rate of 0.02° s⁻¹ and 2θ ranges from 10° to 80°. Transmission electron microscopy (TEM) images of the product were carried out on a JEOL JEM-200CX transmission electron microscope, employing an accelerating voltage of 200 kV. Field-emission scanning electron microscopy (FESEM) images and energy dispersive spectrometry (EDS) analysis of the product were obtained on a Hitachi S-4800 field-emission scanning electron microananlyser, employing the accelerating voltage of 5 or 15 kV. The UV-vis absorption spectra were obtained on a Hitachi U-4100 spectrophotometer (Tokyo, Japan). The Brunauer–Emmett–Teller (BET) surface area and pore size distribution of the product was measured with an accelerated surface area and porosimetry system (ASAP 2020).

2.3. Photocatalytic activity measurements

In order to investigate the photocatalytic property of NiTiO₃ microtubes for the degradation of organic dyes, 15 mg of NiTiO₃ was dispersed into 40 mL aqueous solutions containing Pyronine B, Safranine T, or Fluorescein with a concentration of 10 mg L⁻¹ and irradiated by the 254 nm UV light for the given time, respectively. The suspension was dispersed by ultrasonic wave for 15 min and then stirred in the dark for 30 min to ensure an adsorption/ desorption equilibrium prior to UV irradiation. The suspension was then irradiated using the 254 nm UV light under continuous stirring for given time. Finally, the suspensions after irradiating various time were centrifuged at 10,000 rpm for 5 min to remove the NiTiO₃ catalysts and the UV–vis absorption spectra of the asobtained solutions were measured.

3. Results and discussion

Fig. 1a shows the XRD pattern of the product prepared under the present conditions. All of the diffraction peaks can be indexed as hexagonal NiTiO₃ form with measured lattices parameters a = 5.033 Å and c = 13.82 Å, which is in good agreement with the literature values (JCPDS Card files No. 89-3743, a = 5.031 Å and



Fig. 1. (a) The XRD pattern and (b) EDS analysis of the product prepared under the present conditions.

c = 13.78 Å, space group: R3[148]). No characteristic peaks of other impurities such as TiO₂ and NiO are detected, indicating that the product is rather pure. The strong and narrow diffraction peaks reveal the highly crystalline nature of the as-prepared product. Further evidence of the formation of NiTiO₃ came from energy dispersive X-ray spectrum (EDS) analysis of the product (see Fig. 1b). The peaks of Ti, Ni and O can be easily found. Based on the calculation of the peak areas, the atomic ratio of Ni/Ti/O equals 1:1:3.1, which is very close to the stoichiometry of NiTiO₃. The weak C and Cu peaks should be attributed to CO₂ adsorbed by the sample and the support, respectively.

The morphology of the product was characterized by FESEM and TEM. Fig. 2a gives a representative FESEM image of the product. Abundant tubular products with outer diameters of 500–600 nm, inner diameters of 400–500 nm and lengths ranging from 2 to 4 μ m can be found. A magnified FESEM image shown in Fig. 2b clearly showed that all tubes was composed of many nearly spherical nanoparticles with a mean diameter of ~50 nm. There are many pores among the nanoparticles. The NiTiO₃ nanoparticles are significantly faceted in the SEM and TEM images. Fig. 2c depicts a typical TEM image, from which the tube constructed by nearly spherical nanoparticles can be clearly seen. This further confirmed the result of FESEM observations.

Fig. 3a is the UV–vis absorption spectrum of the as-prepared NiTiO₃ microtubes, which was obtained on a Hitachi U-4100



Fig. 2. (a) A low magnification SEM image, (b) a magnified SEM image and (c) a typical TEM image of the as-prepared NiTiO₃ particles.

spectrophotometer by dispersing NiTiO₃ powders in distilled water and using distilled water as the reference. One shoulder peak centered at 258.6 nm and one strong peak centered at 350.9 nm can be found. Since no report is found on the optical property study of NiTiO₃ in the literature, the application of its optical property needs further studying. Fig. 3b shows the N₂ adsorption/desorption isotherm and the corresponding pore size distribution of NiTiO₃ microtubes constructed by nanoparticles. The measurement showed that the BET surface area was 14.06 m²/g and the pore size distribution mainly located from 20 to 30 nm (inset in Fig. 3b). According to the SEM observations, the product should have a bigger BET surface area. The present low BET value should be caused by the sintering/coalescence of NiTiO₃ nanoparticles during the measurement.

As for various materials, one of the challenging and intriguing problems is to investigate their potential properties and thus to achieve application in life-relating fields. At present, water pollution control and rapid detection of biomolecules are considered to be two of the most troublesome embarrassments. Applications of nano/micromaterials in these fields may be a direction of materials research. Generally, catalytic process is mainly related to the adsorption and desorption of molecules on the surface of the catalyst. Porous micro/nanostructures usually possess the higher specific surface area and more unsaturated surface coordination sites, which are favorable to the adsorption of molecules. As a result, the catalytic performance will be enhanced. In order to investigate the photocatalytic degradation property of the as-obtained porous NiTiO₃ microtubes, we studied the optical property changes of several organic dyes such as

Pyronine B, Safranine T, and Fluorescein in the absence/presence of porous NiTiO₃ microtubes under the irradiation of 254 nm UV light. Fig. 4 depicts the UV-vis absorption spectra of three dyes irradiated by the UV light of 254 nm for 0–90 min in the presence/ absence of porous NiTiO₃ microtubes, respectively. A similar change trend can also be found: under the absence of porous NiTiO₃ microtubes, the intensities of all absorption peaks slightly reduced after irradiation for 60 min; while the peak intensities obviously decreased when the systems contained porous NiTiO₃ microtubes and were irradiated only for 30 min. After 90 min, the absorption peaks nearly disappeared in all spectra. The above facts clearly imply that the as-prepared porous NiTiO₃ microtubes possess good photocatalytic property for the degradation of Pyronine B, Safranine T and Fluorescein, which has potential application in wastewater treatment and environmental protection. In general, the solution containing organic dyes can produce hydroxide radicals (*OH) under UV irradiation, which cause the degradation of dyes. However, when no catalyst is used, the above photochemical reaction is slow due to the production of a small amount of •OH. Since NiTiO₃ is a semiconductor [1], it can generate electron-hole pairs under UV irradiation, which rapidly combine with water molecules in the presence of oxygen to fabricate a great deal of •OH. As a result, organic dyes can be rapidly degraded.

Usually, the flame of a spirit lamp contains flame-heart, innerflame and outer-flame; and the flame temperature ranges from 673 to 773 K, the highest to 1073 K. This provides necessary temperature condition for synthesis of NiTiO₃. In order to ascertain the formation process of NiTiO₃, we employed NiAc₂ or Ti(OC₄H₉)₄



Fig. 3. (a) The UV-vis absorption spectrum and (b) N_2 adsorption/desorption isotherm and the corresponding pore size distribution (inset) of the as-prepared NiTiO_3 microtubes constructed by nanoparticles.

as the initial reagent and successfully obtained NiO and TiO_2 nanoparticles, respectively. Thus, a possible formation process of NiTiO₃ nanoparticles can be suggested below: when the solution containing equal molar ratio of NiAc₂ and Ti(OC₄H₉)₄ was ignited, the mixed solvents of ethanol and ethyleneglycol firstly combusted to produce CO₂, H₂O and to released lots of heat; then, NiAc₂ and Ti(OC₄H₉)₄ reacted with O₂ in air to form NiO and TiO₂ nanoparticles, respectively. The fresh-prepared NiO and TiO₂ nanoparticles rapidly reacted to produce composite trinary metal oxide NiTiO₃ nanoparticles. All byproducts are CO₂ and H₂O, so the present approach is environment-friendly. The relative reactions can be described as follows:

$$C_2H_5OH(C_2H_6O_2) + 3O_2(2.5O_2) \rightarrow 2CO_2 + 3H_2O \tag{1}$$

$$Ni^{2+} + 2CH_3COO^- + 4O_2 \rightarrow NiO + 4CO_2 + 3H_2O$$
(2)

$$Ti(OC_4H_9)_4 + 24O_2 \rightarrow TiO_2 + 16CO_2 + 18H_2O \tag{3}$$

$$NiO + TiO_2 \rightarrow NiTiO_3$$
 (4)

However, it is still unclear why the as-prepared NiTiO₃ nanoparticles can self-assemble into porous microtubes and needs to be further studied.



Fig. 4. UV-vis spectra of various dyes under the irradiation of 254 nm UV light for various time in the absence/presence of $NiTiO_3$ microtubes: (a) Pyronine B, (b) Safranine T, and (c) Fluorescein.

4. Conclusion

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In summary, porous NiTiO₃ microtubes constructed by abundant nearly spherical nanoparticles with the mean size of \sim 50 nm have been successfully prepared via a simple solution-combusting

method without any requirement of calcination step under a mild condition. The as-prepared product possessed good UV-vis absorption property and strong photocatalytic degradation property for some organic dyes such as Pyronine B, Safranine T and Fluorescein. This implies the porous NiTiO₃ microtubes prepared via the present method have potential applications in wastewater treatment and environmental protection. The present synthesis strategy provides a simple, mild and practical method for the synthesis of highly crystalline NiTiO₃ microstructures on a large scale and can also be further developed for syntheses of other trinary metallic oxides.

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