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Thermally Stable Hematite Hollow Nanowires

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Thermally stable hematite (α-Fe_2O_3) hollow nanowires were synthesized by a vacuum-pyrolysis route from β-FeOOH nanowires for the first time. The products can catalyze the oxidation of almost 100% carbon monoxide at 320 °C, exhibiting excellent catalytic performances despite their small BET surface area.

Hematite (α-Fe_2O_3) is traditionally used as a red pigment in art paints and anticorrosion protective paints, in gas sensors, and as a raw material for the synthesis of magnetic oxide ceramics.[1] There is great scientific interest in the synthesis of α-Fe_2O_3 particles and the modification of their size, morphology, and porosity. Recently, it was reported that Fe_2O_3 nanoparticles can be applied as catalysts for the removal of carbon monoxide by catalytic oxidation,[2] which has attracted much interest because of its important applications in gas purification, carbon dioxide lasers, carbon monoxide gas sensors, and pollution control devices.[3−8] In this communication, we describe the first synthesis of thermally stable hematite (α-Fe_2O_3) hollow nanowires by a vacuum-pyrolysis route from β-FeOOH nanowires. Their catalytic performance for the oxidation of carbon monoxide was found excellent.

Our group's recent research revealed that β-FeOOH nanowires could be prepared by stirring aqueous solutions containing $FeCl_2$ and 1,10-phenanthroline at room temperature.[9] In this work, we studied the thermal stability of β-FeOOH nanowires by the thermal analysis (TGA) on a Shimadzu TA-50 thermal analyzer, in which the sample was heated from room temperature to 600 °C at a rate of 5 °C/min in a steady flow of dry N_2 gas. The sample after TGA measurement was characterized by X-ray diffraction (XRD) with a Mac Science MXPAHF rotating anode X-ray diffractometer with Cu Kα radiation (λ = 1.54178 Å). It was found that the β-FeOOH sample would decompose to α-Fe_2O_3 with 12% weight loss by dehydration above 520 °C. The morphological transformations of the β-FeOOH nanowires under vacuum pyrolysis at 530 °C for different times were observed with a Hitachi H-800 transmission electron microscope (TEM, Figure 1) using an accelerating voltage of 200 kV. It revealed that the β-FeOOH nanowires transformed to α-Fe_2O_3 hollow nanowires via a dehydration−melting−recrystallization process upon pyrolysis for 12 h. Thus, we developed a vacuum-pyrolysis route with β-FeOOH nanowires as precursors and chose the pyrolysis condition as 530 °C for 12 h.

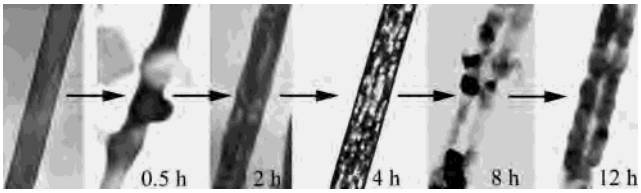

Figure 1. Transformation from β-FeOOH nanowires to α-Fe_2O_3 hollow nanowires at stages for different pyrolysis time at 530 °C.

In a typical synthetic process, the precursors of β-FeOOH nanowires were placed in a porcelain boat, which was placed in the hot zone inside the quartz tube and then pyrolyzed in a vacuum with a pressure range of 10^{-2}−10^{-3} atm at 530 °C for 12 h. The as-obtained solid products were washed with ethanol and distilled water several times and then dried in a vacuum at 60 °C for 4 h.

The phase and purity of the as-prepared products were determined from the XRD pattern. All of the diffraction peaks can be indexed to pure hexagonal α-Fe_2O_3 (JCPDS card 33-664, a = 5.035 Å and c = 13.74 Å). No characteristic peak was observed for other impurities such as β-FeOOH, Fe_3O_4, and γ-Fe_2O_3.

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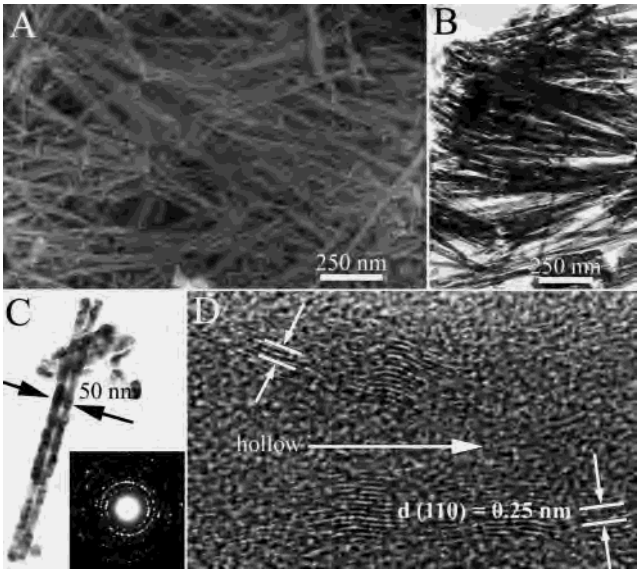

Figure 2. (A) FE-SEM image, (B,C) TEM images, and (D) HRTEM image of the as-obtained α-Fe_2O_3 hollow nanowires. The inset of C is the ED pattern of an α-Fe_2O_3 hollow nanowire.

Figure 2A shows a typical field emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F SEM) image of the α-Fe_2O_3 products without any dispersion treatment and with an outer layer of gold. From the image, one can see that the product consists of nanowires with a high yield of above 90%. The average outer diameter and length of the nanowires are ca. 50 nm and 1−2 μm, respectively. Because of the existence of covering gold layer, their hollow characteristics cannot be observed. More careful observation was provided by TEM image (Figure 2B and C), revealing the hollow nature of nanowires and the inner diameter of about 15 nm. The hollow core continues through the entire length of the nanowire. The hollow nanowires look like tubular nanostructures with rough walls composed of some nanoparticles. The Energy-dispersive X-ray analysis (EDXA) on the hollow nanowires shows their composition to be iron and oxygen. The inset of Figure 2C is the electron diffraction (ED) pattern of a hollow nanowire. The diffraction rings composed of dots can be indexed to (104), (110), (113), (202), (024), and (116) of α-Fe_2O_3. A further investigation by high-resolution transmission electron microscopy (HR-TEM, JEOL-2010 TEM, Figure 2D) revealed that the nanowires actually had hollow pores and were polycrystalline and oriented along (110) plane. It is noteworthy that it was difficult to obtain clear rounded lattice images of nanowires with pore sizes of 8−22 nm; thus, this HRTEM image was taken on the thinnest nanowires with pore sizes of 4−5 nm.

The hollow nature of the products was further confirmed by the measurement of the pore size distribution, which was obtained by the nitrogen adsorption−desorption isotherm and Barrett−Joyner−Halenda (BJH) methods on a Micromeritics ASAP 2010 accelerated surface area and porosimetry system. The isotherm can be categorized as type IV, with a distinct hysteresis loop observed in the range of 0.6−1.0 P/P_0 (Figure 3). The measurement shows that these nanowires have pores with diameters of ca. 15 nm (Figure 3, inset) and that the Brunauer−Emmett−Teller (BET) surface area is 19.06 m^2/g. The measured pore diameter is in good agreement with the value determined by TEM and shows that the α-Fe_2O_3 nanowires obtained here are a kind of porous material.

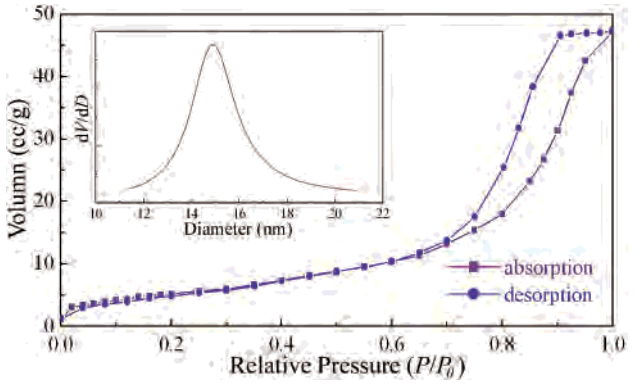

Figure 3. N_2 adsorption−desorption isotherm of the as-obtained α-Fe_2O_3 hollow nanowires; inset, pore-size distribution curve obtained from the desorption data.

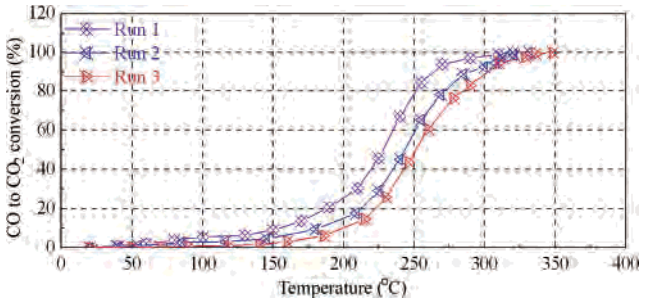

Figure 4. Carbon monoxide conversion efficiencies of three runs with the as-obtained α-Fe_2O_3 hollow nanowires as catalysts.

The excellent effectiveness of the as-obtained hollow α-Fe_2O_3 nanowires as catalysts for carbon monoxide oxidation is shown in Figure 4. The sample was contained in a stainless steel tube with diameter of 0.25 cm, and the outlet gas mixture was separated on a gas chromatography column and then detected with an FULI9750 thermoconductor cell. A 100-mg sample of the nanowires can catalyze the oxidization of almost 100% of the carbon monoxide to carbon dioxide at 320 °C, in an inlet gas mixture of 3.11% carbon monoxide, 8.03% oxygen, and 88.86% nitrogen at 360 mL/min. To test the recycling performance of the sample, two additional runs were performed after the reactor had completely cooled to room temperature each time. It was found that the sample catalyzed the oxidization of almost 100% carbon monoxide at 332 and 348 °C in the second run and the third runs, respectively, revealing its excellent thermal stability and recycling performance. It was reported that Fe_2O_3 nanoparticles with diameters of ca. 3 nm and a BET surface area of 250 m^2/g could catalyze the oxidization of almost 100% carbon monoxide at over 350 °C for the first run; the corresponding temperatures shifted to over 450 °C in the second run and the third runs.[2] The catalytic efficiency decreased slightly in the fourth catalytic cycle. After five catalytic cycles, the catalytic efficiency kept constant. Using helium or hydrogen as the carrier gas, the analogous data were obtained. One can see that the conversion temperatures of our products were lower, and their recycling performance was better, despite their smaller BET

surface area. The high surface area of nanoparticles, corresponding to more unsaturated surface coordination sites, is usually thought to be a crucial parameter for their catalytic performance. The detailed reason for the phenomenon that the sample with fewer unsaturated surface coordination sites exhibited better catalytic performance is not yet clear. However, because the sample was prepared at 530 °C, the hollow characteristics of nanowires should be thermally stable. Most probably, the unique catalytic performance can be ascribed to the stable porosity. More gas molecules can be stored in the hollow pores of sample and have many chances to participate in reactions, greatly improving the catalytic efficiency of the nanowires. The excellent catalytic recycling performance of the sample was also attributed to its excellent thermal stability. We carefully observed the morphologies of the nanowires after one-, two-, and three-run catalytic cycles, and no obvious changes in the morphologies of the nanowires were found, revealing their thermally stability. These interesting experimental results deserve further research. The prepared α-Fe_2O_3 pore nanowires with unique catalytic performances can most probably be applied to remove carbon monoxide emitted from automobiles.

Undoubtedly, the selection of the pyrolysis temperature and time was crucial to the preparation of hollow α-Fe_2O_3 nanowires in the present work. More careful study showed that the hollow nanowires would collapse into nanoparticles if the pyrolysis temperatures were too high (>550 °C) or the pyrolysis process was carried out in air, nitrogen, or argon atmosphere.

In summary, thermally stable hematite (α-Fe_2O_3) hollow nanowires were synthesized by a vacuum-pyrolysis route from β-FeOOH nanowires for the first time. The products exhibit excellent catalytic performances, despite their small BET surface area. The present work shows that the nanostructures of catalysts are important to their catalytic performances. Further research will be performed on more novel nanostructures of catalysts exhibiting different catalytic performances, in which more excellent catalysts might be found.[10] On the other hand, because 1,10-phenanthroline can be used repeatedly without any wastage, the whole synthetic process consumes only $FeCl_2$ and H_2O. The low cost, convenient process, good reproducibility, high yield, and clean reactions of the present synthetic method make it possible to scale it up to industrial production.

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Supporting Information Available: FE-SEM, TEM, and HRTEM images; TGA curve; and preparation details of precursors of β-FeOOH nanowires. XRD pattern and EDXA spectrum of as-obtained α-Fe_2O_3 hollow nanowires. This material is available free of charge via the Internet at http://pubs.acs.org.

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