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Simple fabrication of thermally stable apertured N-doped TiO_2 microtubes as a highly efficient photocatalyst under visible light irradiation

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Abstract

Apertured N-doped TiO_2 microtubes have been fabricated by simple hydrolysis of titania tetrachloride using ammonia without any external templates. The morphology and microstucture characteristics of apertured N-doped TiO_2 microtubes were characterized by means of the specific surface area (BET), transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Fourier transformed infrared (FT-IR), UV–visible diffuse reflectance spectra (DRS) and X-ray powder diffraction (XRD). The unique morphology of microtubes and mesoporous microstructure were maintained after a heat treatment at 723 K for 3 h, exhibiting significantly thermal stability. The catalysts exhibited high ultraviolet and visible light photocatalytic activity in degrading phenol and methyl orange.

Keywords: Titanium dioxide; Anatase; Titanium tetrachloride; Nitrogen-doped; Photodegradation

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1. Introduction

Semiconductor photocatalysis is an efficient method for the chemical utilization of solar energy. TiO_2, among various photocatalysts, is most frequently employed owing to its cheapness, nontoxicity, and structural stability [1–5]. However, the widespread technological use of TiO_2 is impaired by its wide band gap (ca. 3.2 eV for crystalline anatase phase) which requires the use of UV light during the reaction, thus limiting the possibility of employing solar light in TiO_2 photocatalysis.

Sato et al. reported in 1986 that modification of TiO_2 with the N dopant is a powerful way to extend the adsorption light from UV to visible area, since substitution of the lattice oxygen with nitrogen might narrow the band gap by mixing the N_{1S} and O_{1S} states [6]. Up to now, most N-TiO_2 samples were prepared by treating TiO_2 under NH_3 atmosphere at very high temperature. Besides the energy waste, the treatment at such high temperature usually resulted in the low surface area due to the undesirable sintering of nanocrystallites [7,8]. Hence, the seeking of new facile approaches to the synthesis of N-TiO_2 caught hold of increasingly interesting.

It is also known that hierarchically ordered mesoporous TiO_2 materials may be promising candidates in the field of photocatalysis owing to their large surface area and convenient mass transfer in mesopores in degrading large pollution molecules. However, these TiO_2 materials are traditionally prepared by using surfactant templating in which supramolecular aggregates are considered to direct inorganic deposition across a range of length scales

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[9,10]. The organic templates must then be removed by thermal treatment, resulting in high energy consumption, environmental pollution and most important the agglomeration and collapse of pore structure in many cases [11–13]. So most reported mesoporous titania have a low thermal stability. To the best of our knowledge, no hierarchically ordered mesoporous N-TiO_2 material with highly thermal stability has been reported yet without any templates under mild conditions.

In the present work, we use a simple template-free approach to the synthesis of N-TiO_2 photocatalysts with visible light response via a low-temperature precipitation treatment of $TiCl_4$ by ammonia with the presence of glacial acetic acid. The reaction condition is much milder than that of conventional methods. In addition, it is more interesting to find that the N-TiO_2 sample shows a unique apertured microtube structure which has never been reported yet.

2. Experimental

Titanium tetrachloride ($TiCl_4$, analytical reagent grade) was used as titanium precursor of the preparation of the apertured N-TiO_2 microtubes. Commercially available reagents were obtained from Aldrich and used without further purification. In a typical procedure, 25 mL of dilute aqueous solution of $TiCl_4$ ($3.0\ \mathrm{mol\ L^{-1}}$) was carefully added into 150 mL deionized water with gentle stirring in ice-water bath to avoid a drastic hydrolysis of $TiCl_4$ in water at room temperature. Then the solution was heated to 323 K. After that, 4.5 mL of glacial acetic acid and a 35 wt.% solution of ammonia was added dropwise with vigorous stirring until pH 8, then the mixed solution was quickly cooled down to ambient temperature (about 298 K) by rinsed with running water. After aging in the mother liquor for a few days, the resultant slurry was suction-filtered and washed with distilled water until pH 7 and then washed carefully with absolute ethanol for three times. The N-TiO_2 microtube samples were finally obtained after the as-prepared filter residue being vacuum-dried at 353 K for 12 h, followed by calcination at 723 K in flowing air for 3 h. The yield of these microtubes could reach up to about 35%.

The morphology was analyzed by scanning electron microscopy (SEM, Philips XL 30) and transmission electron microscopy (TEM, JEOL-2011, operated at 200 kV). The samples for TEM were prepared by grinding and subsequent dispersing the powder in acetone and applying a drop of very dilute suspension on carbon-coated grids. The textural structures were measured by N_2 adsorption at 77 K in a Micromeritics TriStar ASAP 3000 system. The X-ray powder diffraction (XRD) patterns, obtained on a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å), were used to identify the phase constitutions in samples and their crystallite size. The accelerating voltage and the applied current were 40 kV and 40 mA, respectively. The crystallite size was calculated from X-ray line broadening analysis by Scherrer equation. Estimation of the content of anatase is based on: $X_A = 1/[1 + 1.265 I_R/I_A] \times 100\%$, where I_A is the (1 0 1) peak intensity of anatase, I_R is the (1 1 0) peak intensity of rutile, and 1.265 is the scattering coefficient. X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI 5000C ESCA System with Mg Kα source at 14.0 kV and 25 mA, respectively. All the binding energies were referenced to the C1s peak at 284.6 eV of the surface adventitious carbon. All samples were calcined under 723 K for 3 h to eliminate removable nitrogen adsorbent. UV–visible diffuse reflectance spectra (UV–visible DRS) were achieved using a UV–visible spectrophotometer (Shimadzu UV-2450) using $BaSO_4$ as the reference sample. Fourier transformed infrared (FT-IR) characterization was performed on a NEXUS 470 system.

The photocatalytic activities of the N-TiO_2 samples were measured by the degradation of phenol and methyl orange in an aqueous solution with concentration at 0.060 and $0.020\ \mathrm{g\ L^{-1}}$, respectively. Flowing air was bubbled into the solution before irradiation for 30 min in order to establish the adsorption equilibrium and throughout the experiment. Four 8 W lamps with various wavelength (254, 365, 420 nm, respectively) were used as ultraviolet and visible light source. 0.050 g of photocatalyst was suspended in a 50 mL aqueous solution of organic reactants. The temperature was controlled at 298 ± 1 K during the overall degradation process. The concentrations of which were measured with a UV–visible spectrophotometer (Shimadzu UV-2450). Millipore discs were used to separate the catalysts before the analysis. The measurements were repeated for each catalyst and the experimental error was found to be within ±3%.

3. Results and discussion

The SEM image displayed in Fig. 1a shows that the unique morphology of the apertured N-TiO_2 microtubes can be preserved well after calcination. The average diameter of each microtube is about 10 μm with the shell thickness about 1 μm. An expanded view in inset (a) gives the array of ventages exhibited regularly on the shell of the microtubes, and the average diameter of each hole is about 1 μm with the interval of ca. 4 μm. TEM analyses were performed to examine the nanocrystallites that make up the microtubes. Fig. 1b presents the nanocrystalline nature of anatase TiO_2. It is found that the size of anatase nanocrystallites is approximately 10 nm. High resolution TEM (top inset of Fig. 1b), confirmed that the sample were comprised of connected crystalline titania nanoparticles (the ovals in the figure), with a lattice spacing consistent with the anatase phase (0.352 nm), giving evidence the polycrystalline nature of N-TiO_2 sample which fit well with the XRD patterns. Besides, we can directly examine the average crystallite size of TiO_2 nanoparticles which is consistent well with that calculated from the XRD data (see Fig. 2), calculate the average pore diameter and compare with the result