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Synthesis and photocatalytic activities of $H_2Ti_6O_{13}$ nanofibers and anatase TiO_2 nanofibers with high-density nanocavities

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ABSTRACT

Single-crystalline $H_2Ti_6O_{13}$ nanofibers have been prepared from $Li_2Ti_6O_{13}$ nanobelts as precursor templates via hydrogen/lithium ion-exchange under hydrothermal condition. Then, $H_2Ti_6O_{13}$ nanofibers are successfully converted into anatase TiO_2 nanofibers with high-density nanocavities after calcination at 700 °C for 10 h in air. Both $H_2Ti_6O_{13}$ and anatase TiO_2 nanofibers are characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and high-resolution transmission electron microscopy. When evaluated for photocatalytic properties for the degradation of Rhodamine B under ultraviolet light irradiation, anatase TiO_2 nanofibers exhibit higher photocatalytic behavior than $H_2Ti_6O_{13}$ nanofibers. Furthermore, the photocatalytic efficiency of anatase TiO_2 nanofibers with high-density nanocavities is higher than that of anatase TiO_2 nanoparticles with an average diameter of 40 nm, which may be attributed to its one-dimensional morphology and high-density nanocavities.

1. Introduction

One-dimensional (1D) nanostructures of metal oxide compounds, such as tungstates, molybdates, niobates, tantalates, and titanates, have attracted extraordinary attention as photocatalysts due to their large specific surface area and structural anisotropy. Among these, alkali-metal hexatitanates ($A_2Ti_6O_{13}$, A is alkali-metal) with a tunnel structure have been indicated to be good photocatalysts. Studies have shown that $Na_2Ti_6O_{13}$ whiskers, nanorods, and nanobelts exhibit enhanced photocatalytic performance for the degradation of methyl orange (MO) or Rhodamine B (RhB) under ultraviolet light (UV) irradiation [1–5]. Furthermore, the photocatalytic behavior of $K_2Ti_6O_{13}$ nanowires has been investigated [6,7]. In a recent work, we have synthesized $Li_2Ti_6O_{13}$ nanobelts and explored their photocatalytic efficiency for the degradation of RhB [8]. In addition, Wang et al. reported the synthesis of $H_2Ti_6O_{13}$ nanowires through a facile hydrothermal method followed with an acid treatment, and then investigated their Li-storage behavior in non-aqueous electrolyte [9]. However, to the best of our knowledge, there is no report on photocatalytic activity of 1D $H_2Ti_6O_{13}$ nanostructures till now.

It is well known that TiO_2 exists mainly in four polymorphs in nature: anatase, rutile, brookite, and TiO_2 (B). Among these, anatase is the most photoactive. Anatase TiO_2, being one of the most important photocatalysts, has been extensively investigated due to its increasing applications in hydrogen generation, solar energy utilization, and environmental remediation [10–13]. For improving the photoreactivity of TiO_2, different approaches, including doping [14–19] (in order to extend its absorption wavelength into the visible region) and metal loading [20–24] (for increasing effective electron-hole pairs separation), have been proposed. Furthermore, studies have indicated that shape and surface structure (surface atomic arrangement and coordination) of TiO_2 have also significant influences on its photoelectric properties [25–31]. For example, it is suggested that charge carriers are less localized in 1D nanostructured single crystals where the photogenerated electrons and holes are free to transport throughout the whole length dimension of the crystal due to a high degree of crystallinity [28]. In addition, mixed-phase photocatalysts consisting of anatase and TiO_2(B) have also been designed to improve the photocatalytic activity of TiO_2 based on

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the increase of charge separation efficiency resulting from interfacial electrons transfer [32–35].

Recently, novel nanostructures with dense nanocavities inside 1D morphology of TiO_2 have been prepared, which present good photocatalytic or electrochemical properties. Han and coauthors reported the preparation of anatase TiO_2 nanorods with dense regular polyhedral nanocavities by heating $H_2Ti_3O_7$ nanorods in air and found that these dense nanocavities significantly enhance the optical absorption coefficient of TiO_2 in the near-ultraviolet region [36]. Li et al. have also indicated that the TiO_2 (B) nanoribbons with dense nanocavities show higher discharge specific capacity than those of TiO_2 (B) nanotubes and nanowires [37]. Tang et al. found that anatase TiO_2 nanowire array (TNWA) with dense nanocavities exhibited higher electrochemical performance than that of TNWA-D prepared by the same hydrothermal route using Ti substrate directly for Li-ion batteries [38]. Furthermore, theoretical calculations have predicted that a significant enhancement of the effective optical absorption coefficient (by a factor of about two to more than four) in a thin Si layer can be achieved by optimizing the dimensions and distribution of nanovoids [39].

In this paper, we have successfully synthesized single-crystalline anatase TiO_2 nanofibers with high-density nanocavities by heating $H_2Ti_6O_{13}$ nanofibers at 700 °C for 10 h in air for the first time. The $H_2Ti_6O_{13}$ nanofibers were prepared from $Li_2Ti_6O_{13}$ nanobelts as precursor templates via a hydrothermal procedure. The photocatalytic activities of $H_2Ti_6O_{13}$ and anatase TiO_2 nanofibers are investigated and compared with that of anatase TiO_2 nanoparticles (40 nm in diameter) for the photo-degradation of RhB under UV light irradiation. Although the size of anatase TiO_2 nanofibers with high-density nanocavities is larger than that of anatase TiO_2 nanoparticles, the photocatalytic efficiency of the TiO_2 nanofibers is higher than that of anatase TiO_2 nanoparticles. The increased photocatalytic behavior of anatase TiO_2 nanofibers with nanocavities is attributed to its 1D morphology and high-density nanocavities. This also opens a new way to improve the photoreactivity of TiO_2 nanostructures for use in applications related to absorbing photons.

2. Experimental details

Synthesis of $H_2Ti_6O_{13}$ nanofibers was performed by a hydrothermal process. In a typical procedure, 0.25 g of $Li_2Ti_6O_{13}$ nanobelts prepared by a molten salt synthesis method [8], were dispersed in a 160 mL, 10 M HCl aqueous solution. After stirring for 30 min, the resulting suspension was transferred into a 200 mL Teflon-lined stainless steel autoclave. The autoclave was maintained at 60 °C for 120 h and then cooled to room temperature naturally. The resulting precipitate was washed with distilled water, and then dried at 80 °C for 24 h in air. Finally, anatase TiO_2 nanofibers with high-density nanocavities were obtained upon heating $H_2Ti_6O_{13}$ nanofibers at 700 °C for 10 h in air.

The crystallinity of as-synthesized samples was examined by X-ray diffractometer (XRD, Rigaku, D/Max-RA) with Cu Ka radiation ($\lambda = 1.54$ Å). The morphology and microstructure were observed on a field emission scanning electron microscope (FE-SEM, JEOL JXA-8200) and transmission electron microscope (TEM, JEM-4000EX). The photocatalytic activities of $H_2Ti_6O_{13}$ and TiO_2 nanofibers were investigated by measuring the photodegradation rate of RhB aqueous solution (2.0×10^{-5} M) under exposure to UV light. In the photocatalytic reaction, 20 mg sample was immersed into a RhB solution of 20 mL, and then the suspension was irradiated by a 500 W xenon lamp (CHF XM 500W) attached with a cutoff filter to eliminate visible and infrared light under continuous stirring. The remaining amount of RhB in solution was determined by measuring the absorption intensity of the main peak at 554 nm by a visible spectrophotometer (KD723PC).

3. Results and discussion

Fig. 1a shows the XRD pattern after hydrogen/lithium ion-exchange between HCl and $Li_2Ti_6O_{13}$, which can be identified to a single phase of $H_2Ti_6O_{13}$, similar to the report of Akimoto et al. [40]. Moreover, Pérez-Flores et al. has investigated the crystal structure of $H_2Ti_6O_{13}$ in details via Rietveld analysis of synchrotron and neutron powder diffraction data combined with IR spectroscopy [41]. The morphology of as-synthesized $H_2Ti_6O_{13}$ is showed in Fig. 1b. It can be seen that a large quantity of nanofibers with an average diameter of about 200 nm and length of several microns have been obtained. More detailed views of the morphology and microstructure of $H_2Ti_6O_{13}$ nanofibers were disclosed by means of TEM combined with selected area electron diffraction (SAED). Fig. 1c shows a typical TEM image of a single $H_2Ti_6O_{13}$ nanofiber with a diameter of 150 nm. The presence of sharp diffraction spots (see the inset of Fig. 1c) reveals the formation of well-developed, single-crystalline $H_2Ti_6O_{13}$ nanofibers. Furthermore, the measured interfacial angles of 62.5° between (400) and (210) diffraction planes, and 27.5° between (020) and (210) diffraction planes, are in good consistent with the calculated interfacial angles of 62.7° and 27.3°, respectively. Fig. 1d presents a two-dimensional (2D) lattice image, which further demonstrates that the nanofiber is single-crystalline in nature. The lattice spacings of 0.37 and 0.33 nm correspond to the (400) and (210) interplanar distance of monoclinic $H_2Ti_6O_{13}$, respectively. The measured interfacial angle of between (400) and (210) crystal planes is about 63°, which coincides well with the calculated interfacial angle of 62.7°. On the basis of the SAED and HRTEM patterns, the growth direction of the $H_2Ti_6O_{13}$ nanofiber is determined to its [010] crystallographic orientation, which is consistent with that of $H_2Ti_6O_{13}$ nanowires [9].

The XRD pattern of the product obtained by calcining $H_2Ti_6O_{13}$ nanofibers at 700 °C is shown in Fig. 2a, which can be indexed to single-phase anatase TiO_2. A SEM image revealing morphology of as-synthesized anatase TiO_2 is showed in Fig. 2b. It is evident that TiO_2 retained the 1D nanostructure of the precursors, but the average length of TiO_2 nanofibers is shorter than that of the precursor $H_2Ti_6O_{13}$ nanofibers. The crystal structure of the anatase TiO_2 nanofibers was further examined using TEM and HRTEM techniques. Fig. 2c is the TEM image of a typical anatase TiO_2 nanofiber. Interestingly, however, unlike the precursor $H_2Ti_6O_{13}$ nanofibers, we can see numerous nanocavities inside the TiO_2 nanofiber. The typical size of the nanocavities is about 10 nm. Moreover, the nanocavities are rarely presented near the edge of TiO_2 nanofiber, which is similar to a previous report [36]. Fig. 2d presents the corresponding HRTEM image of the TiO_2 nanofiber. The lattice spacings of 0.37 and 0.35 nm in the image correspond to the interplanar space of the (010) and (101) planes of anatase TiO_2, respectively. The inset of Fig. 2d is the fast Fourier transform (FFT) from the whole area, which further shows the TiO_2 nanofiber is single-crystalline in nature. It should be noted that the presence the forbidden reflection of (010) is probably due to double-diffraction phenomenon. The growth direction of TiO_2 nanofiber is determined to its [010] crystallographic orientation, which is consistent with that of TiO_2 nanobelts [28].