Yellow–colored mesoporous pure titania and its high stability in visible light photocatalysis ☆

Yanlong Tian, Binbin Chang, Jie Fu, Fengna Xi, Xiaoping Dong *

Department of Chemistry, School of Sciences, Zhejiang Sci-Tech University, 928 Second Avenue, Xiasha Higher Education Zone, Hangzhou, China

ARTICLE INFO

ABSTRACT

Yellow–colored pure titania with a mesoporous structure was prepared by the aggregate of titania nanocrystals, which were stabilized by exfoliated titanate nanosheets via an electrostatic interaction. X–ray diffraction patterns and images of transmission electron microscope confirm that titanate sheets are randomly dispersed into the assembled titania nanocrystals without forming any self–restacked phase. This nanocrystals–nanosheets composite exhibits a mesoporous structure with pore size of ~6.5 nm and surface area of 236.3 m^2 g^{-1}. Greatly different from the UV–responded properties of titania nanocrystals and titanate nanosheets, the absorption edge of nanocomposite red–shifts to visible light region. The visible light photocatalytic tests demonstrate that this nanocomposited titania shows excellent activity for the degradation of organic dyes, as well as a colorless organic pollutant of 2, 4–dichlorophenol. The possible photocatalytic mechanism that photogenerated holes as the mainly oxidant species in photocatalysis is proposed based on the trapping experiments of hydroxyl radicals or photogenerated holes. Moreover, as the nanocomposite depicts an extreme stability, no obvious deactivation occurs after five cycles.

1. Introduction

In recent years, semiconductor photocatalysis has received considerable attention since it holds promising potential in both energy and environmental fields [1–3]. Among various semiconductors, titania is most widely used because of its nontoxicity, chemical stability, water insolubility, low price, and favorable photochemical property [4,5]. However, titania can only be excited by ultraviolet (UV) light due to its large band gap of 3.2 eV. Given that UV light only accounts for a small fraction (<5%) of the solar spectrum, thus, its overall efficiency remains too low under natural light irradiation. Moreover, its quantum efficiency is further limited owning to the high recombination rate of photogenerated electron–hole pairs [6,7]. Therefore, designing, fabricating, and tailoring the optical and physicochemical properties of titania are necessary to enhance its absorption in visible region thus to realize the purpose of solar energy derived applications of titania.

Over the last few decades, enormous efforts have been devoted to realize visible light harvesting capability of titania [8–11,14–19]. Doping with metal or nonmetal elements is the most used method that has successfully extended its absorption to visible light range

[8–11]. However, impurity elements may act as charge carrier recombination centers, which would reduce the photocatalytic efficiency of material [12]. For example, Wang et al. have confirmed that titania doped with nitrogen can efficiently improve its activity under visible light irradiation, but remarkably lowers its UV light activity [13]. Dye–sensitization is another effective approach to enhance the visible light absorption of titania [14–16]. Unfortunately, it is a fact that appropriate sensitizing dyes are extremely rare, and meanwhile as organic species, they are unstable with respect to chemical and photochemical attacks, which would affect the photocatalytic performance of photocatalyst. Coupling with narrow band gap semiconductors has been reported to effectively improve the visible light catalytic activity of titania [17–19]. Such a combination not only enhances the visible light absorption, but also promotes the separation of photogenerated electron–hole pairs. However, these narrow band gap semiconductors, such as sulfides, are very unstable toward photocorrosion that is not propitious for their long–term use. In addition, both dyes and narrow band gap semiconductors would detach from the surface of titania, which reduces the activity of photocatalyst and meanwhile brings a secondary pollution to the environment. Therefore, great efforts remain to be drawn on the exploitation of "pure" titania materials that respond to visible light [12,20–22]. Most recently, Ye's group developed a novel titania photocatalyst by the bonding assembly of titania nanocrystals (TNCs), which exhibits a narrowed band gap and greatly enhanced visible and solar photocatalysis in comparison with individual TNCs [23]. Nevertheless, the main drawback of this doping–free material is that its visible light response disappears rapidly when it is dispersed into aqueous solution or crushed into a powder. Moreover, the long–term

exposure in air at room temperature would also make this material slowly fade to whiteness. Therefore, improving the stability of assembled TNCs is very important for its practical application.

Electrostatic aggregate of exfoliated titanate nanosheets (TNSs) bearing negative charges with positively charged nanoparticles has been widely studied, which always forms porous structures [24–30]. The structure of assembled system of TNSs and nanoparticles is strongly dependent on the ratio of nanoparticles to TNSs, from nanoparticles–pillared layered structure to disordered mesoporous structure with the increase of ratio [31,32]. The electrostatic assembly of TNSs and titania nanoparticles has been deeply investigated, including structural properties and UV–responsed photocatalytic performance [33,34]. However, in these reports attentions were focused on the interaction of nanoparticles and TNSs, and the aggregate of incorporated nanoparticles was omitted.

Herein, we reported a yellow–colored pure titania material with a high stability. The titania nanocomposite was prepared via incorporating TNCs into TNSs by the electrostatic interaction, and the followed aggregate of incorporated TNCs by ethanol treating. The resulting TNCs–TNSs nanocomposite possesses a mesoporous structure and enhanced visible light response, which make it show an excellent photocatalytic activity for degrading organic pollutants under visible light irradiation. Moreover, because the assembled TNCs are stabilized by TNSs, the TNCs–TNSs photocatalyst exhibits a high stability and durability during five successive cycles. In addition, the possible photocatalytic mechanism of this material was also discussed.

2. Experimental section

2.1. Synthesis

All reagents were analytical grade and used as received. TNSs were synthesized by delaminating layered protonic titanate (LPT) using ethylamine (EA) aqueous solution as an intercalant, which was described in our previous report [35]. A monodispersed TNCs colloid was prepared by hydrolysis of tetrabutyl titanate using glacial acetic as an inhibitor. In a typical procedure, 10.2 mL of tetrabutyl titanate was slowly added to a mixed solution of glacial acetic acid (12 mL) and distilled water (15 mL) drop by drop under violent stirring. After stirred for 15 min, 30 mL of distilled water was slowly added and then stirred for another 3 h.

The TNCs–TNSs photocatalyst was obtained by the incorporation of TNCs into TNSs. Typically, the TNCs colloid was slowly added to the suspension of TNSs in the molar ratio of $[Ti]_{TNCs}/[Ti]_{TNSs}$ being 3:1. After the mixture was continuously stirred for 12 h, the white precipitate (WP) was collected by centrifugation, washed with absolute ethanol thoroughly, and finally dried at 100 °C overnight. The resulting yellow product was ground for further use.

2.2. Characterization

X–ray diffraction (XRD) patterns were monitored by a DX–2700 diffractometer (Dandong Haoyuan Instrument Co. Ltd., China) using Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm). A scanning electron microscope (SEM, Hitachi S–4800) was used to characterize the morphology of samples. Transmission electron microscope (TEM) images were obtained on a JEOL JEM–2100 electron microscope with an accelerating voltage of 200 kV. Thermogravimetric (TG) data was performed from ambient temperature to 800 °C in flowing N_2 at a rate of 10 °C min^{-1} on a PE Instruments Pyris Diamond 1 thermalanalyzer. Diffuse reflectance spectra were recorded on a Shimadzu 2450 UV–vis spectrometer with an integrating sphere using $BaSO_4$ as the reference. The adsorption/desorption isotherms of nitrogen at 77 K were measured using a Micromeritics ASAP 2020 accelerated surface area and porosimetry analyzer.

2.3. Photocatalytic tests

Visible light photocatalytic activities of photocatalysts were examined by the degradation of methyl orange (MO) in aqueous solution. In each test, 50 mg of catalyst was suspended in an aqueous solution (5 mg L^{-1}, 100 mL) of MO in a quartz glass reactor, which was cooled by recycled water to prevent the thermal catalytic effect. Prior to illumination, the suspension was stirred in the dark for 1 h to ensure the establishment of adsorption–desorption equilibrium of MO on the surface of photocatalyst. A 300 W xenon lamp (HSX–F300, Beijing NBet) equipped with a combination of two glass filters to obtain a wavelength range of 420–780 nm was used as the light source. At given irradiation time intervals, 4 mL of the suspension was extracted and subsequently centrifuged to remove the catalyst particles. The concentration of MO solution was analyzed by measuring the maximum absorbance at 464 nm using a Shimadzu UV–2450 spectrophotometer.

3. Results and discussions

3.1. Characterization of NCs–TNSs

Fig. 1 shows the powder XRD patterns of LPT, EA–intercalated titanate, TNCs, and TNCs–TNSs. The pristine LPT is well crystalline and all of these diffraction peaks can be indexed as the lepidocrocite–like layered structure, in accordance with the literature [36]. Before the reaction with TNCs colloid, the LPT was first intercalated with EA and subsequent exfoliated into TNSs via an osmotic swelling process [37]. Drying the TNSs suspension without adding TNCs colloid results in the formation of EA–intercalated form. The well–developed (0k0) peaks indicate that EA is intercalated between the TNSs to form a turbostatic lamellar structure with the interlayer space of 1.03 nm. Upon reacting TNSs with TNCs colloid, these peaks corresponding to the protonic phase and EA–intercalated phase disappear and give place to three broad peaks at 25.6°, 37.9° and 48.1°, which can be indexed as the anatase (JCPDS 21-1272). This indicates that TNSs are randomly dispersed into assembled TNCs without forming any layered phases. The average particle size of TNCs in the nanocomposite estimated by the Scherrer equation is ~4.6 nm, in accordance with that of the precursor TNCs, as shown in Fig. 1d, which suggests that the aggregate process would not influence the crystal size and phase of the stabilized TNCs.

The morphology and microstructure of the samples were investigated by SEM and TEM. The LPT (Fig. 2a) exhibits a plate–like morphology with well–ordered layered structure. After exfoliation and subsequent restacking with TNCs colloid, a disorganized microtexture can be observed (Fig. 2b). This should be attributed to the random hybridization of TNSs with TNCs, which also brings a porous structure. This structure is favorable for the adsorption and transfer of guest
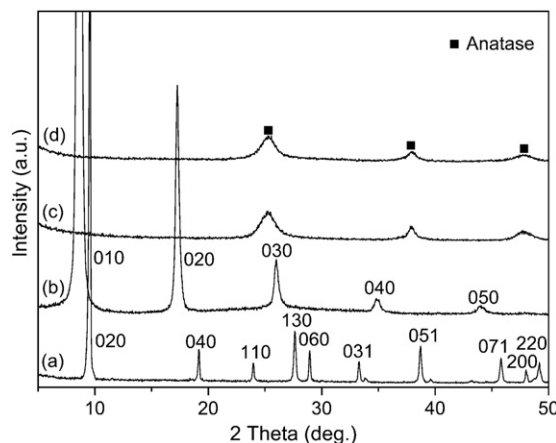

Fig. 1. XRD patterns of (a) LPT, (b) self–restacked form (EA–intercalated titanate), (c) TNCs–TNSs, and (d) TNCs.