Applied Catalysis A: General 478 (2014) 204–210

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Origin of superior photocatalytic activity in rutile TiO_2 hierarchical microspheres: The dominate role of “microcavity” structure

Tingjiang Yan[a,*], Rusheng Yuan[b], Wenjuan Li[a], Jinmao You[a,*]

[a] *The Key Laboratory of Life-Organic Analysis of Shandong Province, College of Chemistry and Chemical Engineering, Qufu Normal University, Qufu, Shandong 273165, PR China*
[b] *Research Institute of Photocatalysis, State Key Laboratory of Photocatalysis on Energy and Environment, Fuzhou University, Fuzhou 350002, PR China*

ARTICLE INFO

Article history:
Received 8 October 2013
Received in revised form 22 March 2014
Accepted 5 April 2014
Available online 15 April 2014

Keywords:
Hierarchical
Rutile
TiO_2
Microcavity
Photocatalysis

ABSTRACT

This paper aims to investigate the role that hierarchical structure plays in photocatalytic process. Hierarchical rutile TiO_2 microspheres assembled by nanowires bundles were initially synthesized and then treated by thermal annealing or ultrasonic irradiation. Various technologies including SEM, XRD, DRS, and N_2 sorption were employed to investigate the effect of post-treatments on the microstructures of TiO_2 samples. The results revealed that annealing treatment caused obvious growth of particle size, decreased surface area and pore volume, and weakened optical absorbance, while ultrasonic irradiation had little influence on these properties. However, both annealing treatment and ultrasonic irradiation seriously destroyed the microcavity structure which existed in between the roughly parallel nanowires of hierarchical TiO_2 microspheres. The existence of microcavity in these TiO_2 hierarchical microspheres was proved to be crucial to the photoactivity toward degradation of methyl orange (MO). It has been proposed that the microcavities could act as microcapacitors for electronic storage and therefore contribute to a high separation efficiency of photogenerated electron–hole pairs. On the basis of ESR and active species scavenger experiments, h^+ was found to be the primary active species in MO degradation while $^\bullet O_2^-$ slightly promoted the degradation efficiency via the formation of $^\bullet OH$. This finding is of great significance for the design of efficient photocatalytic materials with potential applications in solving worldwide energy crisis and environmental pollution.

1. Introduction

Driven by its wide-ranging potential applications in worldwide energy crisis and environmental pollution, research on semiconductor photocatalysis has attracted great interest over the past four decades [1]. The basic principle of semiconductor photocatalysis has been well documented in the literature and can be simply clarified as follows: after absorbing a photon, semiconductor photocatalyst can produce charge carriers (electrons and holes), which will migrate to the catalyst surface and serve as redox sources that react with adsorbed reactants, leading to the destruction of pollutants. Generally, the photocatalytic activity is largely determined by the separation efficiency of electrons and holes because they are prone to recombine during both the migration and interfacial reaction processes. The current bottleneck in photocatalysis lies in this low overall quantum efficiency, which strongly depends on the ratio of the surface charge carrier transfer rate to the electron hole recombination rate during the photocatalytic reaction.

Among various photocatalytic materials, titania (TiO_2) has been recognized as the most suitable photocatalyst because of its strong oxidizing power, nontoxicity and long-term stability against photo and chemical corrosion. Many studies reported that the photocatalytic activity of TiO_2 is closely related to its structural parameters (e.g., crystal phase, crystallinity, particle size, specific surface area etc.) [2–4]. Generally speaking, anatase is usually considered to be more active than rutile phase, and pure brookite phase has limited photocatalytic activity. However, in some cases, the activity of rutile and brookite TiO_2 has been found to be superior [5,6]. A highly crystalline TiO_2 that contains a small amount of lattice defect can suppress the recombination of photogenerated electrons and holes and thus increases their survival time. Photocatalysts with small particle size correspond to lower electron–hole recombination probability since smaller crystallite size gives rise to shorter carrier migration path from bulk to surface. Large surface area provides significant amounts of active sites for adsorption and/or reaction of reactants, leading to higher photocatalytic efficiency.

---

* Corresponding authors. Tel.: +86 537 4456305; fax: +86 537 4456305.
E-mail addresses: tingjiangn@163.com (T. Yan), jmyou6304@163.com (J. You).

http://dx.doi.org/10.1016/j.apcata.2014.04.013
0926-860X/© 2014 Elsevier B.V. All rights reserved.

Although many previous studies have shown a certain relationship between microstructures and photocatalytic activity of TiO_2 [7,8], the role of a given structural feature in photocatalytic performance is difficult to characterize separately, because simultaneous changes in other structural properties would happen. Thus, it still remains a significant challenge to give new insights into the origin of photocatalytic activity of TiO_2.

Hierarchically structured TiO_2 with collected physics and chemistry properties have appeared to be a promising and important prospect due to the fascinating microstructures and promising photo-electrochemical applications [9,10]. Many efforts have been focused on the fabrication of ordered complex hierarchical architectures or superstructures using TiO_2 nanoparticles, nanorods, nanobelts, and nanosheets as building blocks and applied them in the photocatalytic fields [11,12]. The photocatalytic performance of these hierarchical counterparts was found to be highly improved as compared to the nanostructural building blocks. Many researchers have attributed this activity enhancement to the increased surface area and enhanced light utilization efficiency. However, few attentions are paid to the inner-structure features from nanostructural building blocks among hierarchical assembly [13].

Recently, we reported the preparation of rutile TiO_2 hierarchical microspheres and found that, after Pt deposition, the Pt/TiO_2 microspheres exhibited much higher photocatalytic activity toward the removal of methyl orange (MO) than P25 photocatalyst [14,15]. Such an activity enhancement was ascribed to the Pt-assisted charge separation and the self-assembled microsphere feature. Unfortunately, the synergistic effects complicate us to understand whether the self-assembled feature impacted the photocatalytic activity. In this study, to eliminate the effect of Pt deposition and discover the key factors that governed the photocatalytic properties of TiO_2 hierarchical microspheres, two post-treatments strategies including thermal annealing and ultrasonic irradiation were performed on these TiO_2 microspheres. By comparatively characterizing the microstructures, photoluminescence, photocatalytic and photoelectrochemical properties, experiment evidence about the crucial role of microcavity structure on photocatalytic activity of hierarchically structured materials was observed.

2. Experimental

2.1. Preparation

Rutile TiO_2 microspheres. All reagents employed in the experiments were analytical grade and used without further purification. Rutile TiO_2 microspheres were synthesized as previously described [14]. In a typical experiment, 23.0 mL titanium tetrachloride ($TiCl_4$, Alpha, 99%) was added dropwise into 80 mL of distilled water at 0 °C in an ice-water bath under vigorous magnetic stirring to form a given concentration of aqueous solution. After the solution was stirred for about 1 h, it was transferred into a 100 mL of Teflon-lined stainless steel autoclave and allowed to react at 160 °C for 2 h. After the autoclave was cooled to room temperature, the obtained precipitate was washed with distilled water and dried in air at 80 °C. The final product was labeled as R-as.

Thermal annealing of TiO_2. The as-prepared rutile TiO_2 microspheres were then heated at 300–700 °C in static air for 3 h, followed by naturally cooling to room temperature. The annealed samples were designated R-300, R-400, R-500, R-600, and R-700, respectively.

Ultrasonic irradiation of TiO_2. The as-prepared rutile TiO_2 microspheres were added into a certain amount of distilled water and then the suspension solution was subjected to ultrasonic agitation at a power of 100 W with a 40 kHz working frequency for 48 h. When the irradiated treatment was finished, the separated solids were dried in air at 80 °C. The final product was labeled as R-ultra.

2.2. Characterization

X-ray diffraction patterns (XRD) were collected on a Rigaku MinFlex II equipped with Cu Kα irradiation. Morphologies of the samples were observed by field emission scanning electron microscopy (FE-SEM) (JEOL JSM-6700). The specific surface areas of the samples were determined from the nitrogen adsorption data at liquid nitrogen temperature using the Barrett–Emmett–Teller (BET) technique on a Micromeritics ASAP 2000 surface area and porosity analyzer. A Varian Cary 500 Scan UV/vis system was used to obtain the optical absorption spectra of the sample over a range of 200–800 nm. The photoluminescence spectrum (PL) of the sample was performed on an Edinburgh Analytical Instruments FL/FSTCSPC920 coupled with a time correlated single-photo counting system. Photoelectrochemical measurements were conducted with an epsilon (BAS) electrochemical workstation. A standard three-electrode cell with a working electrode (as-prepared photocatalyst), a platinum wire as counter electrode, and a standard calomel electrode as reference electrode were used in the photoelectric studies. The working electrode was prepared on fluoride tin oxide (FTO) conductor glass. Typically, the as-prepared photocatalyst (10 mg) was ultrasonicated in 0.5 mL of N,N-dimethylflormamide (DMF) to form a slurry solution. The slurry was then spread onto the FTO glass and finally dried overnight under ambient condition. 0.1 M Na_2SO_4 was used as the electrolyte solution. All electrochemical potentials are reported vs. NHE.

2.3. Photocatalytic activity

Photocatalytic degradation of MO was carried out in an aqueous solution at ambient temperature. Briefly, 150 mg of catalyst was loaded into 150 mL of MO solution with concentration of 10 ppm in the reactor surrounded by four UV lamps with a wavelength centered at 365 nm (Philips, TUV 4W/G4 T5). The photoenergy density was 160 $\mu W/cm^2$. Prior to irradiation, the suspensions were magnetically stirred in the dark for 1 h to ensure the equilibrium of the working solution. At given time intervals, 3 mL aliquots were sampled and centrifuged to remove the catalyst. The degraded solutions were analyzed using a PerkinElmer UV WinLab Lambda 35 spectrophotometer, and the absorption peak at 464 nm was monitored. The degradation percentage is reported as C/C_0, where C is the maximum peak of the absorption spectra of MO for each irradiated time interval at wavelength 464 nm and C_0 is the absorption intensity of the starting 10 ppm MO solutions. The total organic carbon (TOC) measurement was performed on a Shimadzu TOC-4100 analyzer. The experiment of the identification of the degraded products during MO degradation process by liquid chromatography–mass spectrometry (LC–MS) was carried out according to our previous report [16].

3. Results and discussion

Degradation of aqueous azo dye (MO) was examined as a model reaction to evaluate the photocatalytic activity of the TiO_2 samples before and after treatments. The MO concentrations vs. the reaction time in all TiO_2 systems are plotted in Fig. 1. The pristine TiO_2 hierarchical microspheres showed high efficiency for MO degradation under 365 nm light irradiation. After 3.5 h of irradiation, nearly 80% MO was degraded. In the case of annealed samples, it is striking to find that regardless of the annealing temperature, no trace of MO degradation was observed, indicating that the highly active TiO_2 became inert after annealing. As for ultrasonicated TiO_2 sample, a decreased activity was obtained. During the same irradiation period, only 40% of MO was degraded by the TiO_2 sample.