Sci. Bull. (2016) 61(13):1003–1012
DOI 10.1007/s11434-016-1109-8

www.scibull.com
www.springer.com/scp

Article

Chemistry

Meaningful comparison of photocatalytic properties of {001} and {101} faceted anatase TiO_2 nanocrystals

Yang Lu · Yipeng Zang · Haimin Zhang ·
Yunxia Zhang · Guozhong Wang · Huijun Zhao

Received: 6 April 2016 / Revised: 27 April 2016 / Accepted: 29 April 2016 / Published online: 30 May 2016

Abstract The facet-dependent photocatalytic performance of TiO_2 nanocrystals has been extensively investigated due to their promising applications in renewable energy and environmental fields. However, the intrinsic distinction in the photocatalytic oxidation activities between the {001} and {101} facets of anatase TiO_2 nanocrystals is still unclear and under debate. In this work, a simple photoelectrochemical method was employed to meaningfully quantify the intrinsic photocatalytic activities of {001} and {101} faceted TiO_2 nanocrystal photoanodes. The effective surface areas of photoanodes with different facets were measured based on the monolayer adsorption of phthalic acid on TiO_2 photoanode surface by an ex situ photoelectrochemical method, which were used to normalize the photocurrents obtained from different faceted photoanodes for meaningful comparison of their photocatalytic activities. The results demonstrated that the {001} facets of anatase TiO_2 nanocrystals exhibited much better photocatalytic activity than that of {101} facets of anatase TiO_2 nanocrystals toward photocatalytic oxidation of water and organic compounds with different functional groups (e.g., –OH, –CHO, –COOH). Furthermore, the instantaneous kinetic constants of photocatalytic oxidation of pre-adsorbates on {001} faceted anatase TiO_2 photoanode are obviously greater than those obtained at {101} faceted anatase TiO_2 photoanode, further verifying the higher photocatalytic activity of {001} facets of anatase TiO_2. This work provided a facile photoelectrochemical method to quantitatively determine the photocatalytic oxidation activity of specific exposed crystal facets of a photocatalyst, which would be helpful to uncover and meaningfully compare the intrinsic photocatalytic activities of different exposed crystal facets of a photocatalyst.

Keywords Anatase TiO_2 · Crystal facet · Photocatalysis · Structure–activity relationships

1 Introduction

It has been widely recognised that the photocatalytic performance of crystalline materials can be altered by their crystal facets [1–6]. As an important class of photocatalyst, titanium dioxide (TiO_2) with a variety of crystal facets has been successfully synthesized and extensively investigated for energy and environmental applications [1, 7–13]. Although anatase TiO_2 crystals with high energy surfaces made of {001}, {100}, {103}, {105} and {107} facets have been theoretically predicted to possess superior photocatalytic oxidation activity compared to {101} faceted low energy surfaces [14–18], the obtained experimental data for

---

Electronic supplementary material The online version of this article (doi:10.1007/s11434-016-1109-8) contains supplementary material, which is available to authorized users.

Y. Lu · Y. Zang · H. Zhang (✉) · Y. Zhang · G. Wang ·
H. Zhao (✉)
Key Laboratory of Materials Physics, Centre for Environmental and Energy Nanomaterials, Anhui Key Laboratory of Nanomaterials and Nanotechnology, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, China
e-mail: zhanghm@issp.ac.cn

H. Zhao
e-mail: h.zhao@griffith.edu.au

Y. Zang
University of Science and Technology of China, Hefei 230026, China

H. Zhao
Centre for Clean Environment and Energy, Griffith University, Gold Coast Campus, Gold Coast, QLD 4222, Australia

quantifying the extent of such superiority are unclear and sometimes controversial [19–26]. This is due primarily to the lack of effective characterization method capable of meaningfully quantifying the intrinsic photocatalytic activity under comparable conditions [25, 27, 28].

To date, the majority of reported photocatalytic studies determine the apparent reaction kinetics rather than the intrinsic reaction kinetics [29–31]. To resolve the issue, we have developed a simple and rapid photoelectrocatalytic (PEC) method to quantitatively characterize important photocatalytic properties of {001} and {101} faceted anatase TiO_2 photocatalysts [32–37]. This method employs a catalyst coated conducting substrate as the photoanode in a photoelectrochemical cell. As a photocatalysis process is essentially an electron transfer process, the measured photocurrent under controlled conditions represents the incident rate of electron transfer resulting from photocatalytic process, which can therefore be used to determine the intrinsic kinetics of photocatalytic reactions and other important photocatalysis processes such as electron transport resistance inside the catalyst film and reactant adsorption on the catalyst surface [31, 32, 35–38]. Nevertheless, the photocurrent per illuminating area rather than per effective area was employed in these studies [35–37, 39], which could potentially compromise the effectiveness of certain measurements because the photocurrent per illuminating area cannot be used to precisely reflect the intrinsic photocatalytic activities of photoanodes that are made of photocatalysts with different sizes and morphologies. In this regard, the photocurrent per effective surface area is ideal to represent the intrinsic photocatalytic activity. However, the determination of effective catalyst surface area, especially under the working environment, remains as a great challenge.

Herein, we report a simple approach to determine the effective surface area of nanocrystalline TiO_2 film photoanodes with predominant {001} and {101} facets via an ex situ adsorption technique [33, 40]. The measured effective surface area is then used to normalize the photocurrents obtained from different photoanodes for meaningful comparison of their photocatalytic activities. The instantaneous kinetic constant can be determined by an in situ photoelectrochemical method [30, 41], which also confirms the relative photocatalytic activities of {001} and {101} facets of anatase TiO_2 nanocrystals.

2 Materials and methods

2.1 Synthesis of well-defined TiO_2 nanocrystals

Anatase TiO_2 nanocrystals with predominant {001} facets (denoted as A001) were synthesized via a facile one-pot hydrothermal method [42, 43]. In a typical synthesis, 10 mL of $Ti(OBu)_4$ (99 %) was added to a 100 mL of Teflon vessel followed by dropwise adding 2.2 mL of HF solution (40 %) under magnetic stirring. The Teflon vessel was subsequently sealed in a stainless steel autoclave and heated up to 200 °C for 24 h. After the hydrothermal reaction, the autoclave was naturally cooled to the room temperature and the precipitates were centrifuged to collect and washed with deionized water and ethanol for five times. The obtained product was then dried in an oven at 80 °C for overnight.

{101} facets dominated anatase TiO_2 nanocrystals (denoted as A101) were prepared by a two-step hydrothermal approach [44]. Briefly, 0.3 g commercial TiO_2 powder (99 %, 25 nm) was dispersed into 35 mL of KOH aqueous solution (10 mol/L) in a 100 mL of Teflon vessel under magnetic stirring for 5 min. Then, Teflon vessel was sealed in a stainless steel autoclave and heated up to 200 °C for 24 h. The collected precipitates were centrifuged and washed with diluted HCl and deionized water until the washing solution reached pH of 7.0. The obtained white powder was dried at 80 °C for overnight. 100 mg of the dried white powder was then dispersed ultrasonically into 60 mL of deionized water in a 100 mL of Teflon vessel and subsequently sealed in a stainless steel autoclave, subjecting to a thermal treatment process at 200 °C for 24 h. The obtained product was dried at 80 °C for overnight.

2.2 Fabrication of anatase TiO_2 photoanodes

To fabricate anatase TiO_2 photoanodes with different exposed crystal facets, aqueous TiO_2 colloid was first prepared by hydrolysis of $Ti(OBu)_4$ (99 %) according to the previous reported method [32]. The resulting colloidal solution contains 50 g/L anatase TiO_2 nanocrystals with particle size ranging from 8 to 10 nm. Subsequently, 0.5 g anatase TiO_2 nanocrystals (A001 or A101) were dispersed into 10 mL of deionized water, followed by adding 50 µL of as-prepared TiO_2 colloid to obtain a mixed colloidal solution.

The pre-cleaned indium tin oxides (ITO) glass slides were used as the electrode substrates. First, anatase TiO_2 nanoparticle thin films were fabricated onto ITO glass substrates by a simple dip-coating method in the as-prepared TiO_2 colloidal solution with particle size ranging from 8 to 10 nm. Subsequently, the TiO_2 nanoparticle coated electrodes were thermally treated at 350 °C for 30 min with a heating rate of 10 °C/min in a muffle furnance. The above obtained electrodes were used as the substrates for fabrication of the A001 and A101 photoelectrodes via a dip-coating method in their corresponding colloidal solutions. Finally, the as-synthesized A001 and A101 electrodes were calcined at 550 °C for 90 min in air in a muffle furnace to obtain A001 and A101 photoelectrodes for photoelectrochemical measurements.