



Morphology-dependent defect structures and photocatalytic performance of hydrogenated anatase TiO₂ nanocrystals



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ABSTRACT

Effects of hydrogenation treatments on the structure and the photocatalytic performance in water reduction of anatase TiO₂ nanocrystals with various morphologies were studied and strong morphology/facet-dependent effects were demonstrated. F¹⁺ color centers and Ti³⁺ species are created by hydrogenation treatments of TiO₂ nanocrystals predominantly enclosed with the {001} facets (TiO₂-{001}) and are mainly located in the subsurface/bulk region; O₂ species, F¹⁺ color centers, Ti³⁺ species, and Ti⁴⁺-O[•] radical species are created in TiO₂ nanocrystals predominantly enclosed by the {100} facets (TiO₂-{100}) and located from the surface to the subsurface/bulk region; and O₂ species, F¹⁺ color centers, and Ti³⁺ species are created in TiO₂ nanocrystals predominantly enclosed by the {101} facets (TiO₂-{101}) and located from the surface to the subsurface/bulk region. The created defects enhance the light absorption/charge creation of TiO₂ nanocrystals but also the charge recombination probabilities, and hydrogenated TiO₂-{100} and TiO₂-{101} nanocrystals exhibit photocatalytic activity similar to that of the corresponding TiO₂ nanocrystals. However, an electric field was found to form between the stoichiometric surface and the defective subsurface for hydrogenated TiO₂-{001} nanocrystals. This facilitates charge separation and leads to much higher photocatalytic activity of hydrogenated TiO₂-{001} nanocrystals than of TiO₂-{001} nanocrystals. These results not only shed light on the fundamental understanding of hydrogenated TiO₂ photocatalysts but also demonstrate hydrogenated TiO₂-{001} nanocrystals as highly active photocatalysts, nicely exemplifying the concept of morphology engineering as an effective approach to both fundamental studies of oxide catalysis and optimizations of oxide catalysis.

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1. Introduction

TiO₂ has been extensively studied as a stable, low-cost, and nontoxic photoactive material for photocatalysis, solar cells, and so on [1–3]. However, photocatalytic applications of TiO₂ are substantially restricted by the wide band gap (3.2 eV) and the relatively fast electron–hole recombination [3–5]. Thus great effort has been devoted to improving the photocatalytic performance of TiO₂.

Since the first report of black hydrogenated TiO₂ photocatalysts with significantly improved solar-driven photocatalytic performance [6], hydrogenation treatment of TiO₂ photocatalysts has received much attention as a novel strategy for enhancing the photocatalytic performance. Various structural changes of TiO₂ induced by hydrogenation treatments with different extents have

been observed and proposed to be responsible for enhanced photocatalytic performance [5], including the formation of a black disordered surface layer surrounding a crystalline TiO₂ core [7–9], the blueshifts of the valence band maximum and formation of lower-energy midgap states [6,7,9–12], the formation of Ti–H species [13–15], and the formation of surface Ti³⁺ species and oxygen vacancies [14,16–18]. However, serious hydrogenation treatment of TiO₂ was found to create not only surface Ti³⁺ species and oxygen vacancies but also bulk defects, which act as charge recombination color centers and subsequently decrease the photocatalytic performance [18–20]. Among these reported structural changes of TiO₂ induced by hydrogenation treatment, defects are of particular interest because they are one of the key parameters affecting the surface chemistry and catalysis of TiO₂. Thus hydrogenation treatment seems likely to be developed as an effective strategy to control the defect structures of TiO₂ and thus it is of importance to establish the relation between hydrogenation treatment and the defect structures of TiO₂.

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Recently, uniform oxide nanocrystals that selectively expose one or two types of crystal planes have been reported to exhibit morphology-dependent surface chemistry and catalysis that exemplify the concept of morphology engineering as an effective approach to both fundamental studies of oxide catalysis and optimizations of oxide catalysts [21–25]. Uniform anatase TiO₂ nanocrystals preferentially exposing {001} facets (denoted as TiO₂-{001}), {100} facets (denoted as TiO₂-{100}), and {101} facets (denoted as TiO₂-{101}) were successfully synthesized [26–30] and exhibited strong morphology-dependent catalytic/photocatalytic performance [14,20,26,28,29,31–33]. A hydrogenation treatment of TiO₂-{001} nanosheets at 400 °C for 2 h under 10 bar pressure was reported to enhance the activity in photodegradation of methylene blue under UV-visible light irradiation, which was attributed to the produced Ti³⁺ ions and oxygen vacancies and the subsequent improved light absorption [14]. Later, a hydrogenation treatment of TiO₂-{001} nanosheets at 600 °C for longer than 10 h at atmospheric pressure was also reported to enhance the activity in photodegradation of methylene blue under a UV illumination by 10 times, which, however, was attributed to the formation of hydrogenated TiO₂-{001} nanosheets with a high surface-to-bulk defect ratio and a nonuniform distribution of defects between the bulk and surface due to preferential diffusion of bulk defects to the surface [20].

Although hydrogenation treatments of TiO₂-{001} nanosheets were studied, the photocatalytic reaction was limited to photodegradation of methylene blue and arguments existed for the structural factors leading to the improved photocatalytic performance; meanwhile, systematic studies of hydrogenation treatments of TiO₂ nanocrystals with various morphologies have not been reported. In this paper, we comparatively studied the defect structures and photocatalytic performances in photocatalytic water reduction of TiO₂-{001}, TiO₂-{100}, and TiO₂-{101} nanocrystals subjected to different hydrogenation treatments. Defect structures of various TiO₂ nanocrystals induced by hydrogenation treatments depended on the morphology and exerted different effects on the photocatalytic activity of hydrogenated TiO₂ nanocrystals in photocatalytic water reduction. The enhancement effects of hydrogenation treatments were observed profoundly on TiO₂-{001} nanocrystals but not on TiO₂-{100} or TiO₂-{101} nanocrystals.

2. Experimental

All chemical reagents were of analytical grade and were purchased from Sinopharm Chemical Reagent Co.

Anatase TiO₂-{001} nanocrystals were prepared by a hydrothermal procedure [28]. Typically, 25 mL Ti(OBu)₄ and 3 mL HF aqueous solution (40 wt.%) were mixed under stirring at RT. (*Caution:* Hydrofluoric acid (HF) is extremely corrosive and a contact poison, and it should be handled with extreme care! Hydrofluoric acid solution is stored in Teflon containers in use.) The solution was then transferred into a 50 mL Teflon-lined stainless steel autoclave and kept at 180 °C for 24 h. The resulted white precipitate was collected by centrifugation, washed repeatedly with ethanol and water, and dried at 70 °C for 12 h. The acquired powder was dispersed in 700 mL NaOH aqueous solution (0.1 mol/L), stirred for 24 h at RT, centrifuged, and washed repeatedly with water until the pH value of aqueous solution was 7–8.

Anatase TiO₂-{100} and TiO₂-{101} nanocrystals were prepared following Liu et al.'s procedure [30]. Typically, 6.6 mL TiCl₄ was added dropwise into 20 mL HCl aqueous solution (0.43 mol/L) at 0 °C. After being stirred for an additional 0.5 h, the solution was added dropwise into 50 mL NH₃ aqueous solution (5.5 wt.%) under stirring at RT. Then the pH value of the solution was adjusted

to between 6 and 7 using 4 wt.% NH₃ aqueous solution, after which the system was stirred at RT for 2 h. The resulted precipitate was filtered, washed repeatedly with water until no residual Cl⁻ could be detected, and then dried at 70 °C for 12 h to acquire Ti(OH)₄ precursor. To prepare anatase TiO₂-{100} nanocrystals, 2.0 g Ti(OH)₄ and 0.5 g (NH₄)₂SO₄ were dispersed in a mixture of 15 mL H₂O and 15 mL isopropanol under stirring at RT; then the mixture was transferred into a 50 mL Teflon-lined stainless steel autoclave and kept at 180 °C for 24 h. The obtained white precipitate was collected and washed repeatedly with water. To prepare anatase TiO₂-{101} nanocrystals, 2.0 g Ti(OH)₄ and 0.2 g NH₄Cl were dispersed in a mixture of 15 mL H₂O and 15 mL isopropanol under stirring at RT; then the mixture was transferred into a 50 mL Teflon-lined stainless steel autoclave and kept at 180 °C for 24 h. The obtained white precipitate was collected and washed repeatedly with water.

Hydrogenation treatments of anatase TiO₂ nanocrystals were carried out by heating the TiO₂ nanocrystals in a quartz tube to the desired temperature at a rate of 10 °C/min under a H₂/Ar (5%) gas flow (30 mL/min) at atmospheric pressure and then continuing the reduction process for 1 h.

Powder X-ray diffraction (XRD) patterns were recorded on a Philips X'Pert Pro Super diffractometer with CuK α radiation ($k = 0.15406$ nm) operating at 40 kV and 50 mA. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were acquired with a JEOL JEM-2100F with electron acceleration energy of 200 kV. UV-vis diffuse reflectance spectra (UV-vis DRS) were obtained on a Shimadzu DUV-3700 spectrophotometer equipped with an integrating sphere attachment. Raman spectra were recorded at RT with a HORIBA LabRAM HR confocal microscope spectrograph with a spectral resolution of 0.6 cm⁻¹ and an excitation line at 514 nm. Photoluminescence (PL) spectra were measured on a HORIBA LabRAM HR spectrograph with a continuous wave laser (325 nm) as the exciting source, and the signal was collected by passing through a filter with cutoff wavelength below 380 nm. BET specific surface areas were measured using a Micromeritics Tristar II 3020M system and the sample was degassed at 180 °C under nitrogen before the measurement. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 high-performance electron spectrometer using monochromatized AlK α ($h = 1486.7$ eV) as the excitation source, and the likely charging of samples was corrected by setting the C1s binding energy of the adventitious carbon to 284.8 eV. Electron paramagnetic resonance (EPR) spectra were recorded on a JEOL JES-FA200 EPR spectrometer (9.063 GHz, X-band) at 130 K with employed microwave power, modulation frequency, and modulation amplitude of 0.998 mW, 100 kHz, and 0.35 mT, respectively. Temperature-programmed reduction (TPR) experiments were performed on a conventional system equipped with a thermal conductivity detector (TCD). A 100 mg sample was first pretreated under Ar at 120 °C for 60 min and cooled to room temperature, and then was heated from room temperature to 800 °C at a linear heating rate of 10 °C min⁻¹ and kept at 800 °C for 30 min in a flow of 5% H₂-Ar mixture at a rate of 30 mL min⁻¹.

Experiments in photocatalytic water reduction to produce hydrogen were performed in a top-irradiation Pyrex flask. Simulated solar light (PLS-SXE300, Beijing Trusttech Co., Ltd.) was used as the light source. Typically, 50 mg photocatalysts were dispersed in 120 mL 20% volume methanol aqueous solution under magnetic stirring. Prior to the irradiation, the reaction mixture was deaerated repeatedly with Ar gas for 50 min to thoroughly remove air and dissolved oxygen. A cooling-water jacket was used to keep the photocatalytic reaction temperature at 25 °C. To evaluate the photocatalytic hydrogen production, the gas-phase composition of the photocatalytic reactor was analyzed every hour by extract-

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