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# Short Communication

# Photocatalytic oxidation of toluene to benzaldehyde over anatase $TiO_2$ hollow spheres with exposed {001} facets

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# A R T I C L E I N F O

# ABSTRACT

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#### 1. Introduction

Catalyst morphological and structural (both surface and bulk) studies have attracted great interest since they are key to catalyst design and performances [1–3]. Initiated by Lu group [4,5], many recent investigations have been devoted to controlled synthesis and potential applications of TiO<sub>2</sub>-based photocatalysts with exposed {001} crystal facets. Such TiO<sub>2</sub> catalysts with dominant {001} facets can be divided into two major categories: micrometer single crystals [6–11], and nanometer TiO<sub>2</sub> crystals [12–14] that can only be obtained under rigorous conditions. Both bulk crystals and nano crystals are not ideal for heterogeneous catalysis since micro crystals have relatively small surface area, while nano crystals are difficult to handle. Microstructured particles consist of nanostructured units have been expected to be a better model in this sense.

The  $TiO_2$  with dominant {001} facets exhibited superior photoactivities in many reaction systems, such as water splitting and pollutant removal [6,9,10]. Their intrinsic activity was mainly focused on photocatalytic degradation of organic dyes [8,11,15]. Selective photocatalysis has developed into a promising area for 21st century organic chemistry[16] to synthesize organic compounds by photocatalytic process, such as from ethylbenzene to acetophenone, toluene to benzaldehyde, and cyclohexane to cyclohexanol [13,16–19]. However, the performance of  $TiO_2$  with

A new series of anatase  $TiO_2$  hollow structures were prepared by a facile hydrothermal process. When the hydrothermal time was increased from 20 min to 72 h, the resulting TiO<sub>2</sub> solid spheres gradually transformed into TiO<sub>2</sub> hollow spheres with higher surface crystallinity and exposed {001} facets. The as-prepared TiO<sub>2</sub>-72 h sample exhibited the highest activity comparing to other TiO<sub>2</sub>-based samples and commercial product Degussa P-25 towards the selective photocatalytic oxidation of toluene to benzaldehyde. Such great photocatalytic performance was mainly attributed to enhanced UV-adsorption and better charge separation efficiency due to higher surface crystallinity of TiO<sub>2</sub>-72 h.

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dominant {001} facets in selective photocatalysis was not investigated so far.

In this work, we described a facile process to synthesize anatase  $TiO_2$  hollow spheres based on a hydrothermal reaction between  $TiF_4$  and  $H_2O$ . Structural characterizations showed that shells of such hollow spheres were made of  $TiO_2$  nanocrystals with exposed {001} facets. The catalytic performance of such  $TiO_2$  hollow spheres was evaluated by using the selective photocatalytic oxidation of toluene to benzaldehyde as a model reaction. The as-prepared  $TiO_2$  hollow spheres exhibited higher photo-efficiency than commercial  $TiO_2$  Degussa P-25. Such high catalyst performance towards conversion of toluene to benzaldehyde was attributed to higher UV absorbance and lower recombination of free carriers of these hollow  $TiO_2$  spheres with exposed {001} facets due to their unique high surface crystallinity.

#### 2. Experimental

#### 2.1. Catalysts preparations

In a typical run, 0.20 g of TiF<sub>4</sub> was dissolved in 40 mL of distilled water. After stirring for 10 min, a clear solution was obtained. The solution was then transferred into a 50 mL of Teflon-lined stainless steel autoclave. The autoclave was heated to 250 °C for a hydrothermal time ranging from 20 min to 72 h, then cooled to room temperature. The samples were collected by centrifugation and washed three times with alcohol. After being dried at 80 °C in air for 6 h, the resulting catalysts were labelled as TiO<sub>2</sub>-t where t denotes different hydrothermal time.

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Fig. 1. XRD patterns of  $TiO_2$  samples with different hydrothermal time: (a) 20 min; (b) 40 min; (c) 6 h; (d) 12 h; and (e) 72 h.

#### 2.2. Catalysts characterizations

X-ray diffractions of the catalysts were determined using XRD (D/MAX-2000 with Cu K $\alpha$  radiation). The crystal sizes were calculated by applying the Scherrer equation. The morphologies were observed by field emission scanning electron microscopy (FESEM, HITACHI S4800), transmission electron microscopy (TEM), and selected area electron diffraction (SAED) on a JEM-2100. Nitrogen adsorption-desorption isotherms were measured at 77 K (Quantachrome NOVA 4000e), and the surface area (S<sub>BET</sub>) were calculated using the BET method. The light absorption and photoluminescence spectra were recorded by photoluminescence spectrum (PLS, Varian Cary-Eclipse 500) and UV-visible diffuse reflectance spectrum (DRS, MC-2530). The Raman spectra were conducted on a Dilor Super LabRam II (Light source, 650 nm). The diffuse reflectance FTIR spectroscopy (DRIFTS) was performed on MAGNA IR 760.

#### 2.3. Catalysts evaluations

Selective photocatalytic oxidations of toluene to benzaldehyde were carried out in self-designed quartz tube-like reactor with length, diameter and volume of 200 mm, 31 mm and 150 mL. The initial solution contained 0.10 g of  $TiO_2$ , 10 mL of deionized  $H_2O$ , and 0.010 mL of toluene. The concentration of toluene was 9.4 mmol/L and the total volume of the reaction solution was 10 mL. Six 6 W UV lamps (310 nm) were used as light source. The distance between light and reactor was 60 mm. After reacting for 2 h at 20 °C, the mixtures were extracted with diethyl ether, then analysed on a gas chromatograph (Shimadzu, GC-17A) equipped with a TC-1 column and a flame

Table 1Physicochemical characteristics of various TiO2 samples.

Samples	$S_{\rm BET}~(m^2/g)$	$V_P (cm^3/g)$	Crystal size (nm)	Relative intensity <sup>a</sup> (%)	
				XRD	Raman
TiO <sub>2</sub> -20 min	19	0.061	31	29	6
TiO <sub>2</sub> -40 min	17	0.054	38	50	7
TiO <sub>2</sub> -6 h	7.3	0.037	50	60	62
TiO <sub>2</sub> -12 h	6.8	0.033	52	71	81
TiO <sub>2</sub> -72 h	6.6	0.032	56	100	100

<sup>a</sup> Relative intensity of the main peak in XRD and Raman spectra was calculated by comparing different samples with TiO<sub>2</sub>-72 h.



**Fig. 2.** Raman spectra of  $TiO_2$  samples with different hydrothermal time: (a) 20 min; (b) 40 min; (c) 6 h; (d) 12 h; and (e) 72 h.

ionization detector (FID). The GC-MAS (Agilent 6890 N/5973) was used to confirm the products. Only benzyl alcohol and benzaldehyde have been detected. The saturated  $Ca(OH)_2$  solution was used as absorbance to collect carbon dioxide. NO precipitates were found after reaction. The selectivity was calculated from the yield of benzyl alcohol and benzaldehyde. Control experiments showed no measurable amounts of oxidation of toluene. Reproducibility of the experiments was checked by repeating the runs at least three times and was found to be within acceptable limits ( $\pm$ 3%).

## 3. Results and discussion

#### 3.1. Catalyst characterization

Fig. 1 showed XRD patterns of various  $TiO_2$  samples with different hydrothermal time. All  $TiO_2$  samples displayed well-defined characteristic diffraction peaks of anatase phase corresponding to  $2\theta$  of 25.3° (101), 37.8° (004), and 48.0° (200) [20]. Anatase crystals were easily obtained after hydrothermal treatment at 250 °C for 20 min. With increased hydrothermal time, the intensities of the diffraction peaks were gradually enhanced, indicating better crystallinity of anatase phase. As summarized in Table 1 [21,22], there was a clear trend between crystal size and crystallinity.

The qualities of crystals were also investigated by Raman spectra. As shown in Fig. 2, all TiO<sub>2</sub> samples exhibited peak around  $144 \text{ cm}^{-1}$ , which was ascribed to the Eg mode of anatase. This result was consistent with the XRD data. Increasing the hydrothermal time from 20 min to 6 h resulted in a negative shift toward the lower wave number, which indicated a decrease of surface O to Ti atoms ratio possibly due to the decreased surface oxygen vacancies [23]. Meanwhile, extending the time from 6 h to 72 h showed no obvious shifts. To describe the relative crystallinity of different samples, the Raman adsorption intensities around 144 cm<sup>-1</sup> were semi-qualitatively calculated as shown in Table 1. The relative intensity of Raman showed similar trend to that of the XRD data. However, small differences were noticed between TiO<sub>2</sub>-20 min and TiO<sub>2</sub>-40 min samples. As observed in the XRD patterns, the relative intensity of TiO<sub>2</sub>-40 min (50%) was much higher than that of TiO<sub>2</sub>-20 min (29%). However, both samples had a similar Raman intensity (6% and 7% for TiO<sub>2</sub>-20 min and TiO<sub>2</sub>-40 min, respectively). It should be noted that Raman spectrum is surface sensitive, while XRD is a representation of bulk material. Such discrepancy between the XRD and



Fig. 3. FESEM and TEM images of TiO<sub>2</sub> samples with different hydrothermal time: (a) 20 min; (b) 40 min; (c) 6 h; (d) 12 h; and (e, f) 72 h. The inset of (f) is the texture of a shell fragment and the corresponding top and side view of SAED patterns.

Raman data may imply an intrinsic crystallization process from the core to the outside. Similar results related to the transformation from anatase to rutile have been reported by Li group [24].

Fig. 3 showed the morphology evolution of TiO<sub>2</sub> samples over time. Uniform and smooth solid spherical particles (a) were obtained after 20 min. Partial quadrate pieces and (b) were formed on the external surfaces after 40 min. With prolonged reaction time, the whole external surfaces were covered by quadrate pieces, which then gradually crystallized into decahedron blocks with enhanced degree of crystallinity. Meanwhile, solid spheres transformed into hollow structures(c-f). Interestingly, the size of these particles increased very little during the transformation (from 1.1  $\mu$ m to 1.3  $\mu$ m when the reaction time was extended from 20 min to 72 h). The SEM images (Fig. 3b) also showed the crystalline pieces, the Ostwald reopening process will drive the dissolution of inner TiO<sub>2</sub> with low crystallinity and formation of high crystalline TiO<sub>2</sub> on outside. Similar Ostwald ripening process has been reported previously by Zeng group [25].

The exposed crystal facets of shell fragments were also investigated. As shown in the inset of Fig. 3f, a square shape, which is indicative of  $\{001\}$  facet, was found from the top view. The atomic planes of (200) or (020) crystal faces with the *d*-spacing around 0.189 nm were marked in SAED pattern, which was in good agreement with reported data [13]. The side view TEM image showed that the individual elongated fragments were single-crystalline with the long axes parallel to the [001] face of the crystal, further confirming the existence of exposed  $\{001\}$  facets on the external surfaces.

Such a structure evolution was also supported by the nitrogen sorption experiment (Fig. S1). The N<sub>2</sub> adsorption/desorption isothermals of TiO<sub>2</sub>-20 min and TiO<sub>2</sub>-40 min ascribed to type IV indicated a mesoporous structure, which was also clearly seen by TEM. With extended growth time, the hysteresis loop (type H1) gradually shrunk due to the loss of mesopores, which resulted in a sharp decrease of the specific surface area ( $S_{\text{BET}}$ ). As shown in Table 1, the  $S_{\text{BET}}$  decreased from 17 to 7.3 m<sup>2</sup>/g when the reaction time was increased from 40 min to 6 h. The significant decrease in  $S_{\text{BET}}$  and pore



Fig. 4. UV–Vis DRS (a) and PL (b) spectra of  $\text{TiO}_2$  samples with different hydrothermal time.

volume was most likely due to the destruction of porous structure initiated by the crystallization of small crystals.

UV–Vis DRS spectra (Fig. 4a) demonstrated that all TiO<sub>2</sub> samples were inactive in the visible range. While significant differences were found in the UV region (<400 nm). The UV absorbance increased significantly when the hydrothermal time was prolonged from 20 min to 72 h. Considering the similar  $S_{\text{BET}}$  and morphology of TiO<sub>2</sub>-6 h, TiO<sub>2</sub>-12 h and TiO<sub>2</sub>-72 h, the difference was mainly attributed to different degrees of anatase crystallinity. The low absorbance of TiO<sub>2</sub>-20 min and TiO<sub>2</sub>-40 min further confirmed that surface crystallinity was possibly more important than bulk crystallinity in determining UV absorbance, which was in agreement with the above XRD and Raman analysis.

PL spectra of various TiO<sub>2</sub> samples were also examined to investigate the efficiencies of charge carrier trapping, migration and transfer (Fig. 4b). As TiO<sub>2</sub> crystals evolved over time, PL intensity gradually decreased. TiO<sub>2</sub>-72 h sample displayed much weaker PL than that of the others, suggesting a lower recombination rate between photoelectrons and holes. Taking into account the fact that TiO<sub>2</sub>-72 h has the highest surface and bulk crystallinity, we concluded that the increased quantum efficiency of TiO<sub>2</sub>-72 h was due to a high crystalline single-crystal structure on external surfaces with exposed {001} facets. Similar results have shown that high crystallinity of anatase accelerates the transfer of free carriers and limits the recombination of free carriers [22,26].

#### 3.2. Efficiency evaluation

The selective oxidation of toluene to benzaldehyde was selected as a model reaction to examine the photocatalytic performances of  $TiO_2$  samples. The diffuse reflectance FTIR spectroscopy (DRIFTS) showed obvious IR absorption in the spectral range of 1660–1760 cm<sup>-1</sup>, which can be assigned to the C=O bonds, confirming the existence of benzaldehyde on the surface of photocatalyst after reaction. As shown in Fig. 5, the conversion of toluene gradually increased from 9.0% to 21% when the hydrothermal time was increased from 20 min to 6 h. And all samples showed 90+% selectivity for benzaldehyde. With the increase of surface crystallinity, the obtained TiO<sub>2</sub> samples showed activities in the order of TiO<sub>2</sub>-20 min<TiO<sub>2</sub>-40 min<TiO<sub>2</sub>-6 h<TiO<sub>2</sub>-12 h<TiO<sub>2</sub>-72 h. From XRD and Raman spectra, it seemed that the crystallinity of catalyst have been increased by extending solvothermal time. In addition, crystal piece with exposed {001} facet were gradually formed on the surface of



Fig. 5. Photocatalytic performances of TiO<sub>2</sub> samples with different hydrothermal time.

catalyst. The tendency of surface crystallinity was well consistent with the change of activity. By comparing with commercial sample, the TiO<sub>2</sub>-72 h showed activity two times higher than P-25. Because that P-25 has higher surface area ( $45 \text{ m}^2/\text{g}$ ) and crystallinity of {101} facets than TiO<sub>2</sub>-72 h, the higher activity of TiO<sub>2</sub>-72 h may be induced by higher crystallinity of {001} facets. We proposed that the crystallinity, especially the surface crystallinity of TiO<sub>2</sub>, was more important than surface area in determining its final activity in photocatalysis. To our best knowledge, this was the first time that surface crystallinity of anatase crystals with exposed {001} facets showed a profound influence on its photocatalytic activities. It is also mentioned that TiO<sub>2</sub>-72 h can easily precipitate out of solution under gravity in 10 min providing easier separation than other reported nanocrystals.

## 4. Conclusion

In conclusion, a simple hydrothermal method has been developed for the synthesis of  $TiO_2$  hollow spheres with exposed {001} facets. The resulting  $TiO_2$ -72 h was more active than other  $TiO_2$  samples and commercial P-25 in photocatalytic conversion of toluene to benzaldehyde, which could be attributed to enhanced UV-adsorption and charge separation efficiency due to its higher surface crystallinity of anatase with exposed {001} facets.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.catcom.2011.03.007.

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