Meaningful comparison of photocatalytic properties of {001} and {101} faceted anatase TiO₂ nanocrystals

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Abstract The facet-dependent photocatalytic performance of TiO₂ 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 TiO₂ 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 TiO₂ nanocrystal photoanodes. The effective surface areas of photoanodes with different facets were measured based on the monolayer adsorption of phthalic acid on TiO₂ 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 TiO₂ nanocrystals exhibited much better photocatalytic activity than that of {101} facets of anatase TiO₂ 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 TiO₂ photoanode are obviously greater than those obtained at {101} faceted anatase TiO₂ photoanode, further verifying the higher photocatalytic activity of {001} facets of anatase TiO₂. 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 TiO₂, 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 (TiO₂) with a variety of crystal facets has been successfully synthesized and extensively investigated for energy and environmental applications [1, 7-13]. Although anatase TiO₂ 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 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 TiO₂ 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 TiO₂ 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 TiO₂ nanocrystals.

2 Materials and methods

2.1 Synthesis of well-defined TiO₂ nanocrystals

Anatase TiO₂ 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 5 times. The obtained product was then dried in an oven at 80 °C for overnight.

{101} facets dominated anatase TiO₂ nanocrystals (denoted as A101) were prepared by a two-step hydrothermal approach [44]. Briefly, 0.3 g commercial TiO₂ 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 TiO₂ photoanodes

To fabricate anatase TiO₂ photoanodes with different exposed crystal facets, aqueous TiO₂ 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 TiO₂ nanocrystals with particle size ranging from 8 to 10 nm. Subsequently, 0.5 g anatase TiO₂ nanocrystals (A001 or A101) were dispersed into 10 mL of deionized water, followed by adding 50 µL of as-prepared TiO₂ colloid to obtain a mixed colloidal solution.

The pre-cleaned ITO glass slides were used as the electrode substrates. First, anatase TiO₂ nanoparticle thin films were fabricated onto ITO glass substrates by a simple dip-coating method in the as-prepared TiO₂ colloidal solution with particle size ranging from 8 to 10 nm. Subsequently, the TiO₂ nanoparticle coated electrodes were thermally treated at 350 °C for 30 min with a heating rate of 10 °C/min in a muffle furnace. 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.

2.3 Characterization

Powder X-ray diffraction (XRD) patterns of the samples were recorded on a Philips X-Pert Pro X-ray diffractometer with Cu K α radiation ($\lambda_{K\alpha1}=1.5418$ Å). Field emission scanning electron microscopy (FESEM) images and energy dispersive X-ray spectra (EDS) of the samples were taken on a FESEM (Hitachi, SU8020) operated at an accelerating voltage of 10.0 kV. Transmission electron microscopy (TEM) images of the samples were obtained by a high resolution TEM (JEOL 2010), operated at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) of the samples were determined by a XPS spectrometer (Thermo ESCALAB 250) with Al K α X-ray as the excitation source and all of the binding energies were calibrated with reference to the C1s peak (284.6 eV). The N₂ adsorption-desorption isotherms of samples were measured with Ommishop 100cx equipment (Coulter, USA).

2.4 Photoelectrochemical measurements

A three-electrode photoelectrochemical cell with a TiO₂ photoanode as working electrode, a Pt mesh auxiliary electrode and a Ag/AgCl (saturated KCl) reference electrode was employed for all photoelectrocatalytic measurements. The cell has a built-in quartz window for illumination. A 0.10 mol/L NaNO₃ aqueous solution was used as the supporting electrolyte. The photoanode was sealed in a homemade special electrode holder with a circular-shaped window (*ca.*0.785 cm²) exposed to the reaction solution to allow photocatalytic reactions under light illumination. A 350 W Xe arc lamp light

source fitted with focusing lenses and 365 band pass filter (CHF-XM-350W, Beijing Trusttech Co. Ltd., China) was used as the irradiation source. The light intensity was regulated and carefully measured at 350 nm by a UV irradiance meter with UV365 detector (UV-A, Instruments of Beijing Normal University, China).

All in situ photoelectrochemical measurements were conducted in 0.10 mol/L NaNO₃ solutions at pH 4.0 with 100 μmol/L organic compound under different light intensities. An ex-situ photoelectrochemical adsorption measurement method was adopted in this work to determine the effective surface area of photoanodes [30, 33]. The quantification of the net charge resulting from the photocatalytic reactions is illustrated in Fig. S1 (online) [30, 33].

3 Results and discussion

3.1 Structure and composition

The crystalline structures of A001 and A101 films are confirmed by XRD technique. Fig. 1a shows the diffraction patterns of all samples, indicating all TiO₂ films with a pure anatase phase (tetragonal, I 41/amd, JCPDS No. 21-1272). Further, it was found that the (004) peak intensity of A001 is obviously higher than that of A101 owing to a preferential growth along [001] orientation of A001. The XRD results indicate that A001 and A101 photoanodes expose with predominant desired {001} and {101} crystal facets, respectively. The morphology of A001 and A101 samples is further investigated by field-emission SEM (FESEM) and transmission electron microscopy (TEM). Fig. 1b and d show the surface and cross-sectional SEM images of A001 and A101 photoanodes, respectively. As shown, the thickness of A001 and A101 films is around 1.0 μm (insets in Fig. 1b and d). Fig. 1c and e show the TEM images of A001 and A101 samples. Their corresponding selected-area electron diffraction (SAED) patterns and high-resolution TEM (HRTEM) images confirm A001 and A101 with predominant {001} and {101} crystal facets, respectively. In detailed, the SAED pattern of A001 (bottom inset in Fig. 1c, indexed as the [001] direction) indicates good single crystal nature. The HRTEM image of A001 (top inset in Fig. 1c) shows the lattice spacing of 0.24 nm, corresponding to the {004} facets of anatase nanocrystal (JCPDS No. 21-1272), revealing that the predominant exposed surface of A001 is (001) surface. The SAED pattern (bottom inset in Fig. 1e) and HRTEM image (top inset in Fig. 1e) of A101 also confirm good single crystal nature of A101 with dominant {101} facets. Based on TEM analysis, the exposed {001} facets of A001 account for *ca.* 85%, while only 5% {001} facets are obtained in A101 (Table 1).

Fig. 1 **a** XRD patterns of A001 and A101 samples. **b** Surface and cross-sectional (inset) SEM images of A001 photoanode. **c** TEM and HRTEM (top inset) images of A001 sample with corresponding SAED pattern (bottom inset). **d** Surface and cross-sectional (inset) SEM images of A101 photoanode. **e** TEM and HRTEM (top inset) images of A101 sample with corresponding SAED pattern (bottom inset).

The element composition of samples was investigated by energy dispersive X-ray spectra (EDS) and X-ray photoelectron spectroscopy (XPS). As shown in Fig. S2a and d (online), the elements of Ti, O, Si and In can be observed for A001 and A101 samples. The elements of Si and In should be from the ITO glass substrate and the atomic ratio of Ti and O is close to 1:2, indicating the formation of stoichiometric TiO_2 for these two samples (Table S1, online). Further, the elemental mapping results indicate that Ti and O are uniformly distributed over A001 and A101 samples (Fig. S2b, c, e, f, online). Fig. S3 (online) shows the XPS analysis results of A001 and A101 samples, suggesting the presence of Ti, O and C elements (Fig. S3a, online). The C element should be from adventitious pollution or reference. The high resolution XPS spectra demonstrate almost identical binding energies of Ti 2p and O 1s in A001 and A101 samples (Fig. S3b, c, online). In this work, hydrofluoric acid (HF) was used as crystal facet controlling agent to form {001} faceted TiO_2 nanocrystals. The fluorine element can be completely removed after thermal treatment (Fig. S3d, online), favourable for improving the photocatalytic activity of photoelectrode. The BET specific surface area (S_{BET}) of A001 and A101 nanocrystals, determined by the nitrogen adsorption-desorption isotherms, is 82 and 38 m^2/g , respectively (Table 1). A higher surface area of A001 means more active site exposure, contributing higher photocatalytic activity [5, 45].

3.2 Determination of effective surface area

It is well known that the {101} faceted anatase TiO_2 possesses the lowest surface energy of 0.44 J/m^2 , while the {001} facets, a typical high energy facet of anatase TiO_2 , possess a surface energy of 0.90 J/m^2 [9, 14]. In this work, the anatase TiO_2 nanocrystals with {001} and {101} facets dominated surfaces are

selected as typical examples to demonstrate the proposed concept. We previously reported a method to quantitatively determine the adsorption constants of organic adsorbents at {001} and {101} faceted TiO₂ photoanodes *via* an ex-situ adsorption process [29, 30, 33]. The method involves two steps: ex-situ adsorbing the targeted adsorbent onto the photoanode, followed by photoelectrocatalytic mineralization of the adsorbed adsorbents to quantify the adsorbed amount and determine the Langmuir adsorption isotherm [33, 40]. The adsorption constant can be calculated by Eq. 1 [33]:

$$\frac{C}{Q} = \frac{1}{Q_{\max}} C + \frac{1}{Q_{\max}} \frac{1}{K} \quad (1)$$

where, K is the adsorption equilibrium constant; C is the bulk concentration of the adsorbent, Q is the measured net charge resulting from the photocatalytic mineralization of the adsorbed adsorbent on the photoanode that represents the surface coverage and $Q_{\max}$ is the maximum charge at the maximum surface coverage.

Considering the $Q_{\max}$ represents the maximum surface coverage, which is directly proportional to the number of active adsorption sites on the photoanode, it can therefore be used to represent the effective surface area. It should be noted that the effect of crystal size and morphology has been accounted when the $Q_{\max}$ is determined in such a fashion. As such, the $Q_{\max}$ could be used to meaningfully represent the intrinsic active surface area of a photoanode regardless of crystal sizes and morphologies.

Table 1 BET specific surface area (S_{BET}), effective surface area ($Q_{\max}$), adsorption equilibrium constant (K) and percentage of exposed {001} facets of A001 and A101 samples.

Sample	Percentage of exposed {001} facets	S_{BET} (m ² /g)	$Q_{\max}$ (mC)	K (10 ⁴ L/mol)
A001	85%	82	1.45	5.78
A101	5%	38	1.86	4.45

In this work, phthalic acid (KHP) is chosen as the adsorbent to determine the effective surface area of photoanodes due to its known strong adsorption to TiO₂ surfaces and readily to be completely mineralized during photocatalysis [30, 33]. Fig. 2 shows the adsorption isotherms obtained from A001 and A101 photoanodes and the corresponding data fittings to Eq. 1. The excellent linear relationships between $C/Q - C$ curves confirm that the measured adsorption isotherms from both photoanodes agree well with the Langmuir adsorption model. According to Eq. 1, the $Q_{\max}$ is inversely proportional to the slope of the $C/Q - C$ curve. The calculated $Q_{\max}$ values from the slopes of the corresponding $C/Q - C$ curves of A001 and A101 photoanodes are 1.45 and 1.86 mC, respectively (Table 1). This means that the $Q_{\max}$ (effective surface area) of A101 photoanode is 1.28 times of that for A001 photoanode. Obviously, the photocurrent density calculated by the illuminated photoanode area will differ significantly from that normalized by $Q_{\max}$.

The adsorption equilibrium constants (K) of KHP at the A001 and A101 photoanodes are also calculated using the previously described method [30, 33]. Noticeably, the K value from A001 photoanode (5.78×10^4 L/mol) is 29.9%

larger than that of A101 photoanode (4.45×10^4 L/mol), suggesting the adsorption of KHP on {001} faceted anatase TiO_2 is stronger than {101} faceted ones. This confirms the previous speculation that the adsorption equilibrium constant is associated with the surface energy of the exposed facets [46]. The superior adsorption property of high energy facets could be a reason for their high photocatalytic activities as the adsorption is an important step of photocatalysis process [16-18, 45, 47].

Fig. 2 a and b Langmuir adsorption isotherm data from A001 and A101 photoanodes fitting to Eq.1. Insets are the corresponding adsorption isotherms of A001 and A101 photoanodes.

3.3 Comparative photocatalytic activities of A001 and A101 photoanodes for water oxidation

Photocatalytic oxidation of water is important not only for energy conversion and storage applications but also for environmental remediation applications that rely heavily on the photocatalytically generated active oxygen species (AOSs) [47]. It is therefore a scientific interest to develop an effective means to meaningfully compare photocatalytic water oxidation activities of nanocrystal photocatalysts with different exposed crystal facets. In this work, the above determined Q_{max} values of A001 and A101 photoanodes by ex-situ adsorption method are used to normalize the obtained photocurrents from different photoanodes, enabling a meaningful comparison of photocatalytic water oxidation activities of anatase TiO_2 nanocrystal photoanodes with {001} and {101} facets dominated surfaces.

Fig. 3 **a** and **b** Photocurrent decay curves (dense-line) and fitting data ($\circ$) of A101 and A001 photoanodes from 0.10 mol/L $NaNO_3$ aqueous solution under different light intensities (ϕ) and an applied potential bias of +0.40 V vs. Ag/AgCl. **c** I_{st} - ϕ relationships derived from **a** and **b**. **d** I_{st}/Q - ϕ relationships derived from **a** and **b**. **e** Q - ϕ relationships derived from **a** and **b**. **f** k - ϕ relationships derived from **a** and **b**.

The A001 and A101 photoanodes with predetermined Q_{max} are employed for photocatalytic water oxidation measurements. Fig. 3a and b show the photocurrent decay curves of A001 and A101 photoanodes obtained from photocatalytic water oxidation. For all cases investigated, a higher initial photocurrent is decayed with time and gradually reaches a steady-state. In order to control the amount of pre-adsorbed water on the photoanode, the measurements were carried out by illuminating the photoanode for 120 s to achieve the steady-status, followed by turning off the illumination for 50 s to allow water adsorption before turning the illumination on again and simultaneously measuring the photocurrent decay with time. The steady photocurrent densities (I_{st} , $\mu A/cm^2$) derived from Fig. 3a and b at $t = 150$ s are plotted against light intensity (ϕ) as shown in Fig. 3c. Linear I_{st} - ϕ relationships can be obtained for both photoanodes with slop values of 9.76 $\mu A/mW$ ($R^2=0.998$) and 3.39 $\mu A/mW$ ($R^2=0.996$) for A001 and A101 photoanodes, respectively. In theory, the slope of an I_{st} - ϕ curve represents the photocatalytic activity of a photoanode [32, 34-36]. As such, the obtained slope ratio of 2.88 suggests that the photocatalytic activity of A001 photoanode toward water oxidation is nearly 3 times of that for A101 photoanode. However, the photocatalytic activity obtained in such a fashion is apparent rather than inherent because the I_{st} values used in Fig. 3c were derived by dividing photocurrents with physical illumination areas of photoanodes for which the crystal size and morphology effects of photocatalysts are not accounted for. As aforementioned, Q_{max} is directly proportional to the intrinsic surface area and can therefore be used to normalize the measured photocurrent into the intrinsic

photocurrent density ($I_{st/Q}=I_{ph}/Q_{max}$) that normalizes the crystal size and morphology effects of photocatalysts, allowing a meaningful comparison of photocatalytic activities of photocatalysts with different crystal sizes and morphologies. The $I_{st/Q}$ values are derived from corresponding photocurrent decay curves shown in Fig. 3a and b at 150 s. The plotting $I_{st/Q}$ against ϕ gives linear relationships for both photoanodes, revealing a slope value of $5.28 \mu A \cdot cm^2/(mC \cdot mW)$ for A001 photoanode, which is 3.69 times of that for A101 photoanode ($1.43 \mu A \cdot cm^2/(mC \cdot mW)$), indicating A001 photoanode indeed possesses higher photocatalytic activity for water oxidation. Although the {001} faceted anatase TiO_2 possesses superior photocatalytic water oxidation activity than that of {101} faceted one can be concluded from the photocurrent densities normalized by both the physical illumination area and Q_{max} of the photoanodes, the extent of photocatalytic superiority of {001} faceted nanocrystals over {101} faceted nanocrystals determined from the slope ratio of the $I_{st/Q}-\phi$ curves (3.69) is almost 30% higher than that determined from the slope ratio of the $I_{st}-\phi$ curves (2.88). Considering the physical meaning of Q_{max} , it is reasonable to believe that the comparative superiority of photocatalytic activity between {001} and {101} facets determined from the slope ratio of the $I_{st/Q}-\phi$ curves better reflects the intrinsic photocatalytic activities of the two crystal facet dominated photoanodes. More importantly, this method allows a meaningful comparison of photocatalysts without comprising by crystal size and morphology of the catalysts.

The superiority of {001} facets over {101} facets could also be confirmed by their instantaneous kinetic rate constants, which can be determined by fitting the photocurrent decay curves into double first-order kinetics expressions as shown in Eq. 2[29, 30]:

$$I_{ph} = I_0 + I_f \exp(-k_f t) + I_s \exp(-k_s t) \quad (2)$$

where I_{ph} is the total photocurrent, I_0 , I_f , I_s are fitting parameters, representing steady and initial photocurrents, and t is the time lapsed from the onset of illumination. k_f and k_s are the instantaneous kinetic constants of fast and slow first-order reactions, respectively. The transferred charges during the fast (Q_f) and slow (Q_s) kinetic processes can be calculated in accordance with Eq. 3 [29]:

$$Q_f = \frac{I_f}{k_f} \quad Q_s = \frac{I_s}{k_s} \quad (3)$$

Considering the percentage contributions of fast and slow kinetic processes to the overall reaction can be represented by Q_f/Q_{Total} and Q_s/Q_{Total} ($Q_{Total} = Q_f + Q_s$), the overall instantaneous kinetic constant can then be expressed by:

$$k = \frac{Q_f}{Q_{Total}} k_f + \frac{Q_s}{Q_{Total}} k_s \quad (4)$$

The kinetic parameters of I_f , k_f , I_s and k_s for photocatalytic water oxidation by A001 and A101 photoanodes (see Table S2, online) are derived from the data fitting of corresponding photocurrent decay curves in Fig. 3a and b in accordance with Eq. 2 and used to calculate Q_f , Q_s and Q_{Total} values of A001 and A101 photoanodes according to Eq. 3. Fig. 3e shows the plots of Q_f , Q_s and Q_{Total} against ϕ . The results reveal that for all cases investigated, the Q_s accounts for a large proportion to the total charge (>80%). The total instantaneous kinetic rate constants (k) are calculated based on Eq. 4 and

plotted against ϕ (Fig. 3f). The results show that k values obtained from A001 photoanode are obviously larger than that obtained from A101 photoanode for all cases investigated, further confirming the superior photocatalytic activity of {001} facets over {101} facets for water oxidation.

Fig. 4 **a** and **b** Photocurrent decay curves (dense-line) and fitting data ($\circ$) of A101 and A001 photoanodes from 0.10 mol/L NaNO_3 aqueous solution containing 100 $\mu\text{mol/L}$ phenol under different light intensities (ϕ) and an applied potential bias of +0.40 V vs. Ag/AgCl. **c** $I_{\text{st}}-\phi$ relationships derived from **a** and **b**. **d** $I_{\text{st/Q}}-\phi$ relationships derived from **a** and **b**. **e** $Q-\phi$ relationships derived from **a** and **b**. **f** $k-\phi$ relationships derived from **a** and **b**.

3.4 Comparative photocatalytic activities of A001 and A101 photoanodes for oxidation of organic compounds

Photocatalytic degradation of organic pollutants is very important for environmental remediation applications [45, 48]. In this regards, a meaningful comparison of the photocatalytic activities of photocatalysts with different exposed crystal facets are useful for objectively evaluating the performance of different photocatalysts. In this work, photocatalytic activities of A001 and A101 photoanodes toward organic compounds containing different functional groups (*e.g.*, $-\text{OH}$, $-\text{CHO}$, $-\text{COOH}$) are compared using the above described methods. Fig. 4a to 4d show the photocurrent decay curves and corresponding $I_{\text{st}}-\phi$ curves as well as $I_{\text{st/Q}}-\phi$ curves from photocatalytic oxidation of phenol by A001 and A101 photoanodes. The linear $I_{\text{st}}-\phi$ and $I_{\text{st/Q}}-\phi$ relationships are obtained for both photoanodes. For A001 photoanode, a slope value of $8.30 \mu\text{A}\cdot\text{cm}^2/(\text{mC}\cdot\text{mW})$ can be obtained from the $I_{\text{st/Q}}-\phi$ curves, which is 2.79 times of that for A101 photoanode ($2.97 \mu\text{A}\cdot\text{cm}^2/(\text{mC}\cdot\text{mW})$). The kinetic parameters (I_{f} , I_{s} , k_{f} , k_{s} , Q_{f} , Q_{s}) for photocatalytic oxidation of phenol by A001 and A101 photoanodes are also obtained (Table S3, online and Fig. 4e). Fig. 4f shows the

k - φ plots of the photoanodes, revealing superior photocatalytic kinetics of A001 photoanode over A101 photoanode under all light intensities investigated.

The results obtained from photocatalytic oxidation of other organics with different functional groups including butyl alcohol, benzyl alcohol, glutaric dialdehyde, benzaldehyde, glutaric acid and benzoic acid by A001 and A101 photoanodes are given in Fig. S4 to S9 (online). The relative photocatalytic activity of A001 and A101 photoanodes towards degradation of different substrates determined by the slope ratios of $I_{st/Q}$ - φ curves are listed in Table 2. The results indicate that for all cases investigated, A001 photoanode exhibits higher photocatalytic activity than that of A101 photoanode [34].

Table 2 The slop ratios of I_{st} - φ and $I_{st/Q}$ - φ curves from A001 and A101 photoanodes.

Compounds	Slop ratios of A001 and A101 Photoanodes	
	I_{st} - φ Curve	$I_{st/Q}$ - φ Curve
water	2.88	3.69
phenol	2.18	2.79
butyl alcohol	2.32	2.97
benzyl alcohol	2.21	2.83
glutaric dialdehyde	2.17	2.78
benzaldehyde	2.22	2.84
glutaric acid	2.04	2.61
benzoic acid	2.13	2.73

4 Conclusions

In summary, the photocatalytic activities of {001} facets and {101} facets dominated anatase TiO₂ photoanodes, which were fabricated with well-defined anatase TiO₂ nanocrystals synthesized by hydrothermal method, were meaningfully compared *via* a simple photoelectrochemical method. The effective surface area of photoanodes was measured by the monolayer adsorption of phthalic acid molecules on TiO₂ film surface. The photocurrent per effective surface area reflects the intrinsic photocatalytic activity of photoanodes toward oxidation of water and organic compounds containing different functional groups (*e.g.*, -OH, -CHO, -COOH). The above results combined with instantaneous kinetic rate constant measurements confirm that the {001} facets of anatase TiO₂ possess higher photocatalytic activity than that of {101} facets dominated anatase TiO₂.

Acknowledgments This work was financially supported by the Natural Science Foundation of China (Grant No. 51372248, 51432009 and 51272255), the CAS/SAFEA International Partnership Program for Creative Research Teams of Chinese Academy of Sciences, China, and the CAS Pioneer Hundred Talents Program.

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