Photocatalysis

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The Surface-Structure Sensitivity of Dioxygen Activation in the Anatase-Photocatalyzed Oxidation Reaction**

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The photocatalytic oxidation reaction in the aqueous TiO_2 system has aroused intensive research interests owing to its significance in the efficient elimination of environmental contaminants and synthesis of fine organic chemicals.[1] During the reaction process, both water and dioxygen will take part in the reaction. Depending on the reaction pathways, the dioxygen molecule will either become the thoroughly reduced product, namely water [Eq. (3a)], or be incorporated into the organic substrate as a functional group [Eqs (3b)–(3d)].[2] Water, acting as both solvent and reactant, is either oxidized by photogenerated holes, producing hydroxyl radicals, or reacts with organic radicals, producing hydroxylation intermediates [Eqs. (2a,b); H−R = substituted aromatic compounds].[3] Consequently, in the anatase-photocatalyzed oxidation reaction, the oxygen atoms introduced in the substrates originate from both water and dioxygen.

$$\mathrm{TiO_2} \xrightarrow{h\nu} \mathrm{e^-} + \mathrm{h^+} \tag{1}$$

$$\mathrm{H{-}R} \xrightarrow{\mathrm{h^+}} \mathrm{H{-}R^{\bullet+}} \xrightarrow{\mathrm{H_2O}} \rightarrow \mathrm{R{-}OH} \tag{2a}$$

$$\mathrm{H_2O} \xrightarrow[\mathrm{-H^+}]{\mathrm{h^+}} {}^{\bullet}\mathrm{OH} \xrightarrow{\mathrm{H{-}R}} \rightarrow \mathrm{R{-}OH} \tag{2b}$$

$$\mathbf{O}_2 \xrightarrow{\mathrm{e^-}} {}^{\bullet}\mathbf{O}_2{}^- \xrightarrow[\mathrm{2H^+}]{\mathrm{e^-}} \mathrm{H_2}\mathbf{O}_2 \xrightarrow{\mathrm{e^-}} \xrightarrow{\mathrm{e^-}} 2\mathrm{H_2}\mathbf{O} \tag{3a}$$

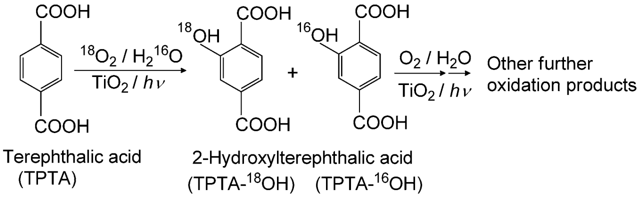
$$\mathbf{O}_2 \xrightarrow{\mathrm{e^-}} {}^{\bullet}\mathbf{O}_2{}^- \xrightarrow[\mathrm{2H^+}]{\mathrm{e^-}} \mathrm{H_2}\mathbf{O}_2 \xrightarrow[\mathrm{-OH^-}]{\mathrm{e^-}} {}^{\bullet}\mathbf{O}\mathrm{H} \xrightarrow{\mathrm{H{-}R}} \rightarrow \mathrm{R{-}}\mathbf{O}\mathrm{H} \tag{3b}$$

$$\mathrm{H{-}R} \xrightarrow{\mathrm{h^+}} \mathrm{H{-}R^{\bullet+}} \xrightarrow{{}^{\bullet}\mathbf{O}_2{}^-} \mathrm{H{-}R}\mathbf{OO} \rightarrow\rightarrow \mathrm{R{-}}\mathbf{O}\mathrm{H} \tag{3c}$$

$$\mathrm{H{-}R} \xrightarrow{\mathrm{h^+}} \mathrm{H{-}R^{\bullet+}} \xrightarrow{\mathbf{O}_2} \mathrm{H{-}R^+}\mathbf{OO} \rightarrow\rightarrow \mathrm{R{-}}\mathbf{O}\mathrm{H} \tag{3d}$$

Theoretical calculations, scanning tunneling microscopy (STM) investigations, and IR spectroscopy studies have suggested that the interaction of dioxygen with titania was closely related to the surface structure.[4] Such an interaction will lead to a surface-structure sensitivity of dioxygen activation and in turn have a direct effect on the performances of the catalyst in the anatase-photocatalyzed oxidation reaction. Most of the previous experimental investigations were conducted under ultrahigh vacuum conditions; in contrast, in aqueous solution, which represents the common reaction conditions, little research has been carried out. Recently, rutile and anatase have been found to perform differently in the photocatalytic oxidation of benzene in an aqueous solution.[5] The experimental findings indicated that the differences in the crystal phase dramatically influence the activation of the reactants and the reaction pathways in the photocatalytic oxidation reaction. It is expected that the distinctions in the surface structure of different crystal facets of the same anatase phase may directly affect their photocatalytic performances. Such a study will more accurately reveal the reaction pathways of photocatalytic oxidation, and provide new insights into this process.

There are two challenges for such a study. First, the anatase crystals with controllable percentages of {001} and {101} facets will be necessary for investigating the effect of crystal facets on the performances of the catalysts. Second, a suitable model reaction has to be chosen to facilitate quantitative determination of the details of the reaction, such as the origin of the oxygen atom of the hydroxy group in the intermediate product, the variance in the concentration of the intermediate product, and the consumption of dioxygen. In the present study, a series of anatase titania crystals were synthesized in which the percentage of exposed {001} facet varied over a wide range.[6] Photocatalytic oxidation of terephthalic acid was chosen as the model reaction (Scheme 1) owing to the following merits: 1) 2-hydroxyterephthalic acid (TPTA-OH) is the only intermediate product of the initial hydroxylation reaction, and it can be produced at a relatively high concentration by photocatalytic oxidation of TPTA in aqueous anatase suspension under UV irradiation;[7] and 2) the functional groups containing oxygen atoms in TPTA-OH do not exchange with water so that it can be determined whether the oxygen atom in the hydroxy group originates from water or dioxygen. ^{18}O-labeled dioxygen and



Scheme 1. Photocatalytic oxidation of terephthalic acid by anatase.

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water, with isotope abundances of 97 % and 98 %, respectively, were used to trace the origins of the hydroxy group of TPTA-OH.[8] We experimentally verified the surface-structure sensitivity of dioxygen activation during photocatalytic oxidation reaction in aqueous anatase suspension. The anatase {101} facet exhibits higher photocatalytic activity than the {001} facet. However, the contribution ratio of dioxygen to water in the hydroxylation reaction is larger on {001} facet than on {101} facet, strongly suggesting that the reaction pathways, by which dioxygen participates in the reactions, are vastly different on {001} and {101} facets.

Anatase titania samples with varying percentages of {001} facet were synthesized using a modified version of a recently reported method.[6] Anatase crystals with {001} facet percentages of 32 %, 49 %, and 63 % are denoted by H32, H49, and H63, respectively (Supporting Information, Figure S1). The scanning electron microscopy (SEM) images in Figure 1 b show the morphologies of the catalysts used in this study. A reference sample of anatase particles, denoted by NP, was synthesized without intentionally controlling the percentage of {001} facet (Figure 1 b5); the percentage of {001} facet was the theoretical value of 6 %.[9] Another reference sample, anatase nanowire, which predominantly has the {101} facet, was also prepared and denoted by NW (Figure 1 b6; Supporting Information, Figure S2).[10] The samples were shown to be fluoride-free anatase crystals by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD; Supporting Information, Figures S3, S4). The BET surface areas of samples H32, H49, and H63 are 2.3, 2.8, and 2.5 $m^2 g^{-1}$, respectively. For reference samples NP and NW, the BET surface areas are 9.5 and 101.3 $m^2 g^{-1}$, respectively (Supporting Information, Table S1).

$H_2{}^{18}O$ was used as the isotope tracer (Figure 1 a), and therefore TPTA-^{16}OH represents TPTA-OH with a hydroxy group originating from dioxygen. The results of the ratios of TPTA-^{16}OH to the total amount of TPTA-OH on each catalyst sample at TPTA conversions of less than 5 % are shown in Figure 1 a. With the increase of the percentage of {001} facet ranging from 32 % to 63 %, the percentage of TPTA-^{16}OH increased from 19.3 % to 25.3 %, suggesting that the contribution ratio of dioxygen to water in the hydroxylation reaction was higher on the {001} facet than on the {101} facet. Compared with the microsized anatase single crystal samples (H32, H49, and H63), the reference catalyst sample NP introduced much less dioxygen-derived oxygen atoms in the substrate, and the percentage of TPTA-^{16}OH was 13.9 %. On anatase NW that had a predominant {101} facet, the content of TPTA-^{16}OH was as low as 11.7 %.

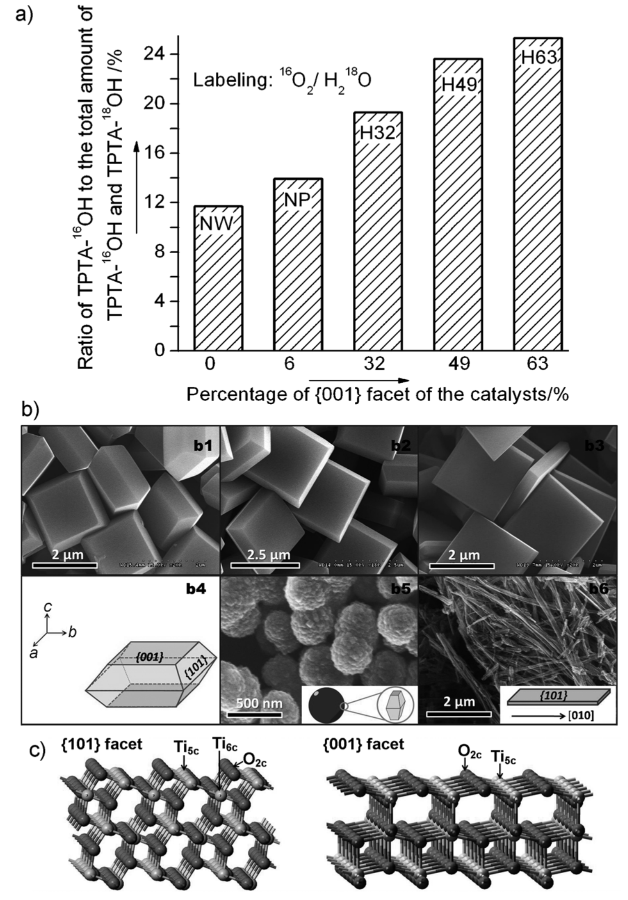

Figure 1. a) The ratio of TPTA-^{16}OH (with hydroxy group originating from dioxygen) to the total amount of TPTA-OH on each catalyst at TPTA conversions of less than 5 %. Catalysts: NW: anatase nanowire with predominant {101} facet; NP: anatase nanoparticle with about 6 % of {001} facet; H32, H49, H63: the microsized anatase single crystals with {001} facet percentages of 32 %, 49 %, and 63 %, respectively. b1)–b3) SEM images of the samples H32, H49 and H63; b4) geometric diagram of the morphology of anatase single crystal; the square shaped facets of the truncated octahedron crystals are {001} facets, and the trapezia shaped crystals are {101} facets. b5) SEM image of sample NP; inset: the nanosphere composed of nanocrystals; b6) SEM image of sample NW; inset: geometric diagram of the morphology of the anatase nanowire. c) The structure of anatase {101} facet and {001} facet; O_{2c} twofold-coordinated oxygen atom; Ti_{5c} fivefold-coordinated titanium atom; Ti_{6c} sixfold-coordinated titanium atom. Reaction conditions: catalyst (10 mg) and aqueous solution (1.0 mL) with TPTA (0.5 mM) and NaOH (2.5 mM) were placed in the pyrex vessel; the reaction was in the $^{16}O_2/H_2{}^{18}O$ system; $P(O_2) = 0.1$ MPa.

To further confirm the effect of anatase facets on the isotope distribution in TPTA-OH intermediate, instead of water, dioxygen was labeled with an ^{18}O isotope. In Table 2, the reactions were carried out in the $^{18}O_2/H_2{}^{16}O$ system. The relationship between the percentage of {001} facet and the ratio of TPTA-^{18}OH to the total amount of TPTA-OH was consistent with that shown in Figure 1 a. As shown in Tables 1 and 2, the ratio of TPTA-*OH (with the hydroxy group originating from dioxygen) to the total amount of TPTA-OH slightly decreased with the increase of TPTA conversion. The catalyst with a higher percentage of {101} facets exhibited a faster reaction rate in converting TPTA. However, in terms of the relationship between the percentage of {001} facet and the ratio of TPTA-*OH (with the hydroxy group originating from dioxygen) to the total amount of TPTA-OH, all experimental data unanimously demonstrated that the contribution ratio of dioxygen to water in the hydroxylation reaction was higher on the {001} facet than on {101} face, suggesting that the processes with dioxygen involved in the hydroxylation reaction are different on {001} and {101} facets.

As shown in Scheme 1, TPTA-OH can be further oxidized. Considering the above-mentioned results, it is

Table 1: The isotope distribution of TPTA-OH in the reaction system of $^{16}O_2/H_2{}^{18}O$.[a]

Catalyst	Reaction time [min]	TPTA conversion [%]	Content of TPTA-^{16}OH [%][b]
NW	3	3.4	11.7
	6	6.1	9.4
NP	5	3.1	13.9
	8	5.5	12.1
H32	10	3.8	19.3
	20	7.6	18.9
H49	15	3.1	23.6
	30	5.4	21.9
H63	30	3.0	25.3
	60	6.0	22.5

[a] For reaction conditions, see Figure 1. [b] Content of TPTA-^{16}OH means the ratio of TPTA-^{16}OH (with hydroxy group originating from dioxygen) to the total amount of TPTA-OH.

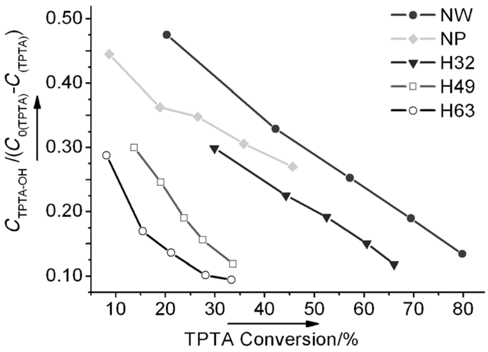

Figure 2. The variance in the concentration of intermediate product TPTA-OH on each catalyst during the reaction. Reaction conditions: catalyst (50 mg) and solution (5 mL) with TPTA (0.5 mM) and NaOH (2.5 mM) were placed in the pyrex vessel; $P(O_2) = 0.1$ MPa.

Table 2: The isotope distribution of TPTA-OH in the reaction system of $^{18}O_2/H_2{}^{16}O$.[a]

Catalyst	Reaction time [min]	TPTA conversion [%]	Content of TPTA-^{18}OH [%][b]
NW	3	7.7	8.4
	6	13.4	7.9
	9	23.0	7.9
NP	2	6.7	10.5
	5	11.5	10.5
	8	18.3	10.3
H32	10	3.2	22.9
	25	7.6	22.5
	40	13.6	22.0
H49	15	3.0	24.1
	55	9.1	23.0
	75	13.0	22.8
H63	32	2.8	25.7
	58	6.0	25.2
	92	8.0	24.7

[a] Reaction conditions: catalyst (15 mg) and aqueous solution (1.5 mL) with TPTA (0.5 mM) and NaOH (2.5 mM) were placed in the Pyrex vessel; $P(^{18}O_2) = 0.1$ MPa. [b] Content of TPTA-^{18}OH means the ratio of TPTA-^{18}OH (with hydroxy group originating from dioxygen) to the total amount of TPTA-OH.

expected that further oxidation on the {001} facet should be different from that on other facets, as more dioxygen-derived oxygen atoms will also be incorporated into the substrate in the following reactions on {001} facet. To verify this deduction, we determined the concentrations of the intermediate product (TPTA-OH) and dioxygen consumptions in the reaction systems with different catalysts.

In Figure 2, the ratio of the concentration of TPTA-OH to the consumed TPTA ($C_{o(TPTA)}-C_{(TPTA)}$) decreased with the increase of TPTA conversion. When the same TPTA conversion was achieved, the concentration of TPTA-OH was lower on the catalyst with a higher percentage of {001} facets. For example, at a TPTA conversion of 30%, the TPTA-OH concentration on catalyst H63 was about one-third that on catalyst H32. This indicates that the reaction pathways, by which the photoinduced electron-activated dioxygen reacts with the substrate, are different on {101} and {001} facets, leading to the difference in the product distribution of the reaction on the catalysts with different ratios of {001} to {101} facets. This statement will be further clarified by the following dioxygen consumption investigation.

As shown in Table 3, when the equal amount of TPTA molecules were converted, more dioxygen molecules were consumed on the catalyst with a higher percentage of {001} facets. Upon converting one TPTA molecule, 2.9 dioxygen molecules were consumed on the sample H32. This increased to 5.4 when sample H63 was used as the photocatalyst. Also, when the reactions were catalyzed by samples NP and NW, which have less {001} facets, the dioxygen consumption per reacted TPTA molecule was as low as 2.4 molecules. Consistent with the experimental facts revealed by Figure 2, dioxygen participates in the reactions via different pathways on the two facets. Upon converting equal amount of substrate, and although the reaction rate is lower on the {001} facet, the {001} facet could incorporate more dioxygen-derived oxygen atoms into the substrate than the {101} facet, leading to the formation of further oxidation products (originating from substrate being incorporated with more than one oxygen atom) and less TPTA-OH (with only one oxygen atom being incorporated into the substrate). These facts also could shed

Table 3: Dioxygen consumption per TPTA molecule converted in the photocatalytic oxidation reaction catalyzed by different catalysts.[a]

Photocatalyst	$M(O_2$ consumed)/ M(TPTA consumed)
NW	2.4
NP	2.4
H32	2.9
H49	3.7
H63	5.4

[a] Reaction conditions: the aqueous suspension contained catalyst (10 mg mL^{-1}), TPTA (0.5 mM), and NaOH (2.5 mM); the dioxygen-saturated suspension (4 mL) was placed in the reactor with a cooling water jacket and irradiated by a 100 W low-pressure mercury lamp; the variance in the concentration of the dissolved dioxygen was determined by a dissolved oxygen analyzer with the sensor sealed in the reaction solution.

light on the enhanced contribution ratio of dioxygen to water in hydroxylation reaction on the catalyst with a larger proportion of {001} facets.

Upon reacting with the conduction-band electrons, dioxygen will be reduced to water or be activated to incorporate into the substrate. In these competitive reactions, the way dioxygen participating in the reaction on different facets would directly influence the origins of the hydroxy group of TPTA-OH. It would also influence the accumulation of the intermediate product (TPTA-OH) during the reaction; the dioxygen consumption, upon conversion of an equal amount of TPTA, could consequently be affected.

There are several distinctions in the physicochemical properties between anatase {101} and {001} facets. The conduction band minimum of the {101} facet is a little more negative (0.04 V) than the {001} facet, while their valance band maxima are equal.[11] According to single-molecule fluorescence investigations, the rate for the emergence of electrons on the {101} facet is about three times faster than on the {001} facet.[12] This should contribute to the high photocatalytic activity of the {101} facet in both activating water and dioxygen. However, the higher efficiency of the {101} facet in producing photoinduced electrons could also facilitate the four-electron transfer to reduce dioxygen into the thoroughly reduced product, namely water [Eq. (3a)]; on the {001} facet, the relatively sparse photoinduced electrons would lead to different reaction pathway and formation of dioxygen-derived active species via partial reduction of dioxygen, by which more dioxygen-derived oxygen atoms can be incorporated into the substrate [see for example Eqs. (3b) and (3c)]. This might be one of the reasons for the distinctions in the catalytic performance of {001} and {101} facets.

On the flat anatase {001} surface, all of the titanium atoms are five-coordinate with a Ti-O-Ti angle of 146°; on the corrugated {101} facet, only half of the titanium atoms are five-coordinate with Ti-O-Ti angles of 102°. The oxygen atoms are more protrudent on the {101} facet than on {001} facet; the titanium atoms on the {001} facet are more exposed than on the {101} facet (Figure 1c).[9] These differences will dramatically influence the behavior of water and dioxygen on {001} and {101} facets. Water molecules are favored to adsorb on anatase {101} facet molecularly, while on the anatase {001} facet, dissociative adsorption and molecular adsorption of water coexist in a 1:1 ratio.[13] Most importantly, it have been experimentally and theoretically shown that water dissociatively adsorbing on the surface could significantly enhance the adsorption of dioxygen molecules. The dissociated water has a long-range effect on dioxygen adsorption, and the adsorbed dioxygen readily diffuses along the Ti_{5c} channel to the reaction sites.[14] As a result, the adsorption of dioxygen on {001} facet is more favorable than on the {101} facet. For the {001} facet, the preferable adsorption of dioxygen together with the low rate in producing photoinduced electrons may result in the formation of dioxygen-derived active spices (rather than water), which leads to more dioxygen-derived oxygen atoms being incorporated into the substrate on the {001} facet. Although the detailed mechanism requires further investigation, the aforementioned experimental results indicate that the process of activating dioxygen to incorporate dioxygen-derived oxygen atoms into substrate is closely related to the surface structure of the catalyst.

In conclusion, although {101} facet exhibits higher photocatalytic activity than {001} facet, the contribution ratio of dioxygen to water in the hydroxylation reaction is higher on the {001} facet than on the {101} facet; during the successive oxidation process, more dioxygen was consumed and incorporated into the substrate on the {001} facet than on the {101} facet upon converting an equal amount of substrate. Based on these experimental facts, it is believed that the pathways, by which dioxygen participates in the reactions, are different on {001} and {101} facets.

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