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Selective photocatalytic conversion of glycerol to hydroxyacetaldehyde in aqueous solution on facet tuned TiO₂-based catalysts[†]

Ruifeng Chong,^{‡ab} Jun Li,^{‡a} Xin Zhou,^a Yi Ma,^a Jingxiu Yang,^a Lei Huang,^a Hongxian Han,^a Fuxiang Zhang^a and Can Li*^a

Glycerol is selectively converted to hydroxyacetaldehyde (HAA) and H_2 in aqueous solution on TiO₂-based photocatalysts. The product selectivity was verified to be strongly dependent on the facets of TiO₂. Rutile with high percentage of {110} facets results in over 90% superior selectivity of HAA, while anatase with {001} or {101} facets gives only 16% and 49% selectivity for HAA, respectively.

Biomass is an abundant and renewable resource in nature. The utilization of biomass as feedstock to produce fuels and valuable chemicals is promising for the development of sustainable chemical industry.¹ Various kinds of attractive platform chemicals, such as glucose, hydroxymethylfurfural (HMF) and polyols, have been obtained from biomass.² Among these, the biomass-derived polyols are particularly interesting, because they can be further converted into valuable chemicals, such as ethylene glycol and propylene glycol, *etc.*, which are important precursors for producing polymers, resins and fuels.³

Photocatalysis is an attractive methodology for biomass conversion, as it can use solar energy as the energy source. TiO_2 is a frequently employed model semiconductor photocatalyst for exploring new reactions and understanding the fundamental processes of photocatalysis.⁴ And it has been already demonstrated that H₂ can be produced from polyols on TiO_2 -based photocatalysts under anaerobic conditions.⁵ Partial photocatalytic oxidation of glycerol to valuable carbonyl compounds on TiO_2 has also been reported, but the total selectivity was less than 20% at a conversion of 35%.⁶ The low selectivity is mainly due to the existence of different active sites on the catalyst surface for different reactions and the strong reactive oxygen species (•OH) generated during the course of photocatalysis.⁷ Therefore, it is expected that the selectivity of the photocatalytic conversion of glycerol can be further improved by

tailor-designing the surface structure of ${\rm TiO}_2$ to avoid overoxidation of the products. 8

Herein, glycerol was chosen as a model compound of higher polyols. Overall, it was found that aqueous glycerol can be converted to HAA, H₂ and HCOOH through C–C bond cleavage on TiO₂-based photocatalysts under anaerobic conditions. However, the selectivity of HAA production is strongly dependent on the dominant facets of TiO₂. Rutile with a high percentage of {110} facets results in over 90% selectivity of HAA, while anatase with dominant {001} or {101} facets can only give a selectivity of HAA less than 20% and 50%, respectively. More interestingly, EPR results show that a kind of peroxo species was generated on rutile with {110} facets, which is quite different from the reactive oxygen species $^{\circ}$ OH generated on anatase with dominant {001} or {101} facets, implying that different glycerol oxidation mechanisms result in dramatically different product selectivity. Thus, this work provides a new strategy for selective conversion of biomass to valuable chemicals and H₂.

The TiO₂ photocatalysts with different dominant facets,⁹ including anatase with {001} and {101} (denoted as A{001} and A{101}, respectively) and rutile with {110} (denoted as R{110}), were synthesized as shown in the ESI.† TEM and high-resolution TEM images (Fig. 1b–g) show that the morphology of A{001} is sheet-shaped, A{101} is bipyramid-like shaped, and R{110} is rod-like shaped along the [001] direction. The percentage of the exposed {001} facets in A{001} is estimated to be *ca.* 80%, the {101} facets in A{101} is *ca.* 90%, and the {110} facets in R{110} is *ca.* 96%. Their XRD and XPS are provided in the ESI† (Fig. S1 and S2).

The photocatalytic reactions of aqueous glycerol conversion were performed on TiO₂ loaded with some metal nanoparticles by an *in situ* photodeposition method. Preliminary results show that no reaction takes place when light or catalyst is absent (Table S1, ESI†). Fig. 1a shows the selectivity of HAA production (Fig. S3 and S4, ESI†) at a glycerol conversion of *ca.* 20%. The yields of the products from glycerol are listed in Table S2 (ESI†). It can be seen that the selectivity of HAA is remarkably varied with the variation of the dominant facets of TiO₂. With Rh as the reduction metal cocatalyst, R{110} exhibits the highest HAA selectivity of up to 96%, which is 2 times that of A{101} and 6 times that of A{001}. This demonstrates that the

^a State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, 457 Zhongshan Road, Dalian, 116023, China. E-mail: canli@dicp.ac.cn; Web: http://www.canli.dicp.ac.cn; Fax: +86-411-84694447

^b Graduate University of Chinese Academy of Sciences, Beijing, 100049, China

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[‡] These authors contributed equally to this work.



Fig. 1 Photocatalytic performances, TEM and HRTEM images of TiO₂ with different dominant facets. (a) The conversion of glycerol and the selectivities of HAA on different TiO₂-based photocatalysts. And TEM and HRTEM images of A{001} (b and e), A{101} (c and f), R{110} (d and g). The images clearly show the size and morphology of TiO₂. Fourier transform (FFT) patterns show that A{001} and A{101} are in a pure anatase phase and R{110} is in a pure rutile phase. Reaction conditions for (a) catalyst, 0.1 g; co-catalyst, 0.1 wt% Rh; 0.02 mol L⁻¹ aqueous glycerol solution, 100 mL; light source, Xe-lamp (300 W); reaction temperature, 353 K. Reaction time, for A{001} and A {101}, 4 h; R{110}, 2 h.

selectivity of HAA appears to be determined by the exposed facets of TiO₂. To exclude the influence of Rh nanoparticles on the selectivity, other metals (Pt, Pd, Ru, Au, Cu, and Ni) loaded on R{110} were also tested (Table S3, ESI†). In all cases, when a metal cocatalyst is loaded on R{110}, the glycerol conversion efficiency is greatly improved and the yield of H₂ production is also significantly increased. The selectivities of HAA are over 90% for all of the photocatalysts though loaded with different cocatalysts, while the selectivities of glyceraldehyde (GA) are lower than 5%. This suggests that the main roles of the metal cocatalysts are to enhance the photogenerated charge separation, and catalyze H₂ production. In other words, the selectivity of HAA is mainly dependent on the facets of TiO₂, not on the deposited metal cocatalysts.

For R{110} loaded with different metal cocatalysts, the main products are H_2 and HAA, together with some byproducts such as formic acid (FA), CO₂, and GA (Table S3, ESI†). The molar ratio of H_2 /HAA is about 2 and that of CO₂/H₂ is below 0.07 in all cases, indicating that majority of the glycerol is converted into the products of HAA and H_2 . Based on the above results, the possible photocatalytic reaction pathways can be drawn as shown in Scheme 1. Under photoirradiation, the major reaction pathway is the reaction of glycerol with water to produce HAA, FA and H_2 , while the minor reaction is the direct dehydrogenation of glycerol to GA. Once HAA and FA are formed, the consecutive reactions can take place. HAA can be subsequently converted to formaldehyde, FA, and CO₂ (verified by using HAA









Fig. 2 The initial H₂ production rates of glycerol, HAA, FA on TiO₂ catalysts with different dominant exposed facets. Reaction conditions: catalyst, 0.1 g; Co-catalyst, 0.1 wt% Rh; 0.1 mol L⁻¹ aqueous reactant solution, 100 mL; light source, Xe-lamp (300 W); reaction temperature, 353 K; reaction time, 1 h.

as the reagent, Table S4, ESI†). And FA can be further decomposed to CO_2 and $\mathrm{H}_2.$

It is possible to hypothesize that the reactivity of glycerol, HAA and FA on the different facets of TiO2 would be different. To verify this hypothesis, the initial H₂ production rates obtained from aqueous solution of glycerol, HAA and FA were investigated on A{001}, A{101} and R{110}, respectively. As shown in Fig. 2, for the same catalyst, the H₂ production activity is closely dependent on the structure of the reactant. For example, the reactivity of glycerol is more than twice that of FA and HAA on R{110}, which might be due to the distinct difference in interactions between these molecules on the active sites of TiO₂. As for a given reactant, the reactivity is mainly determined by the exposed facets of TiO2. HAA exhibits the highest reactivity compared to glycerol and FA on A{001}, FA shows the highest reactivity on A{101}, and glycerol is the most reactive species on R{110}. These results indicate that the prominent reaction is different on the surface of TiO₂. Therefore, the reaction of glycerol can be promoted and the successive reaction of HAA can be suppressed on R{110}. This is crucial for the high selectivity of HAA production.

In the reaction, water serves not only as a solvent but also as a main reactant. It plays a key role in the reaction of glycerol and the successive reaction of HAA (Scheme 1). The reactive oxygen species are mainly derived from the oxidation of water by a photogenerated hole on the TiO_2 surface. The EPR spin-trap technique



Fig. 3 Typical EPR spectra of DMPO trapped radical species upon photocatalytic oxidation of H_2O on TiO₂-based catalysts with different dominant exposed facets. Concentrations: TiO₂, 0.1 g L⁻¹; DMPO, 0.05 mol L⁻¹, in argon. The characteristic quarter peaks for A{001} and A{101} are ascribed to the DMPO-OH adduct, and the typical seven-line paramagnetic signal for R{110} is assigned to 5,5-dimethyl-1- pyrrolidone-2-oxyl (DMPO-X).

(with DMPO as a trapping reagent) was employed to probe the reactive oxygen species. As shown in Fig. 3, four characteristic peaks of DMPO–OH were obviously observed for A{001} and A{101}.¹⁰ While a typical seven-line paramagnetic signal was detected for R{110}, which is a typical feature of DMPO–X species oxidized by peroxide (the simulated EPR spectra are shown in Fig. S5, ESI[†]).¹¹ It can be concluded that the peroxy species is the most likely reactive oxygen species derived from water oxidation on R{110}, while •OH radical species are the prevailing one on A{001} and A{101}.

To better understand why the different reactive oxygen species can be generated on TiO₂ with different dominant facets, the dissociation pathways of H₂O on anatase {001} facets and rutile {110} facets were studied using theoretical calculations (Fig. S6, ESI†). The calculated results show that the lowest energy state of the dissociated H₂O has hydroxyl bonded to a Ti_{5c} site on anatase {001} facets, while the O adatom is bonded to a Ti_{5c} site on rutile {110} facets. It has been reported that two adjacent Ti–O• radicals on rutile {110} tend to couple with each other to form surface peroxo species, TiOOTi.¹² Thus, the types of reactive oxygen species for dissociation from the surface of TiO₂ and the ability of water oxidation are strongly dependent on the facets of TiO₂.

It is well known that the •OH radical is a highly reactive oxygen species,¹³ which could indiscriminately oxidize glycerol molecules with almost no selectivity. This leads to the poor selectivity of HAA for the anatase-based catalyst. The peroxo species is a known oxidant for selective oxidation of alcohols (or aldehydes), and epoxidation of olefins.¹⁴ Thereby, the peroxo species with mild oxidative behaviors could favorably react with glycerol, which might be the major reason for the high selectivity of HAA for a rutile based catalyst. Although the detailed mechanisms for the C–C cleavage and photocatalytic conversion of polyols require further investigation, the aforementioned experimental results unambiguously suggest that the selectivity of photocatalytic conversion of glycerol is closely related to the surface facets of the M/TiO₂ catalyst due to formation of different oxidative species.

The selectivities at different conversions generated at different reaction times on $Rh/R\{110\}$ were also investigated. As shown in

Fig. S7 (ESI[†]), with the increase of the reaction time, the conversion rate distinctly increases, while the selectivity of HAA slightly decreases. Nevertheless, the selectivity still remains over 90% even when the glycerol conversion reaches 40%. This demonstrates that the photocatalytic conversion strategy is a viable means for converting glycerol into valuable chemicals, such as HAA. The intermediate HAA can be easily hydrogenated at room temperature using a commercial Ru/C catalyst to value-added chemicals, such as ethylene glycol, which is an important chemical currently produced in a large scale mainly from hydration of epoxide.

In conclusion, we found that photocatalytic conversion of glycerol in aqueous solution can selectively produce HAA and H_2 *via* a photocatalytic reaction under anaerobic conditions. The selectivity of HAA can be over 90% for a rutile-based catalyst. The selectivity was verified to be dependent on the facets of TiO₂. The reactive oxygen species derived from H_2O plays a key role in selective conversion of glycerol. The present work provides a new strategy for the conversion of bio-derived platform molecules to highly valuable chemicals.

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