Facet-Dependent Diol-Induced Density of States of Anatase TiO₂ Crystal Surface

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ABSTRACT: Owing to their fundamental importance and practical applications, anatase TiO₂ crystals with well-defined {001} and {101} facets attracted intensive research interests. In this study, we systematically investigated solvent dependence of the photoreaction of the different coexposed crystal facets during noble metal photodeposition. By examining the deposition position in each solvent, we revealed that solvents play a pivotal role on the facet selectivity. On the basis of density functional theory calculations, the solvent molecules were found to modify both the crystal facet electronic structure and the {001}−{001} heterojunction. These modifications are not only the origin of diverse charge-carrier pathways but are also responsible for carrier accumulation at specific facets that increase their reductive power. These findings are vital for a better understanding of photocatalytic materials and an improved design for the next-generation materials.

INTRODUCTION

Photocatalytic processes occurring at a semiconductor surface, such as TiO₂, are key factors for the development of renewable energy and green chemistry. Recently, anatase TiO₂ crystals with well-defined {001} and {101} facets have attracted tremendous attention. Their special shape-dependent physicochemical properties and lower electron/hole (e⁻/h⁺) recombination rate compared to conventional TiO₂ particles gave an insight on the higher photoactivity of predominant {001} facets for the degradation of organic pollutants and H₂ production. Contradictory results, however, revealed that the low-energy facets {101} exhibit higher photocatalytic activities. This indicates that a comprehensive understanding of the reactivity of the crystal facets still remains urgent. Despite the efforts focusing on the structural properties, less attention has been paid to the molecular adsorption of crystals on each facet with the solvents used and their resulting photochemical behavior. For this purpose, photocatalytic reactions, such as metal photodeposition, can be used to explore both reduction and oxidation sites of the photocatalyst including BiVO₄, Cu₂O, and BiOCl. However, the solvent effect on this facet dependency still remains unclear, although it plays a substantial role during the metal photodeposition.

In this study, the role of solvent adsorption on coexposed anatase crystal facets {001} and {101} is systematically investigated through noble metal photodeposition. Particularly, comparing methanol, water, and ethylene glycol (EG), we found that metal nanoparticles (NPs) can be photodeposited selectively on different facets of the TiO₂ single crystal. Complementary first-principles density functional theory (DFT) calculations were performed to assess the impact of different solvent adsorptions on the crystal facet electronic structures and to suggest a change in photogenerated charge (e⁻/h⁺) pathways upon solvent adsorption. The theoretical study implies that these pathways induce the diol selectivity of metal photodeposition. However, their role during the metal photodeposition.

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well-defined anatase TiO₂ crystals, which could be useful for a better engineering of advanced titanium-based photocatalysts.

### RESULTS AND DISCUSSION

Synthesis of a well-defined anatase TiO₂ single crystal was carried out under hydrothermal condition according to the previous report. Briefly, an aqueous titanium tetrafluoride (TiF₄) precursor containing hydrofluoric acid (HF) and 2-propanol was used to prepare TiO₂ crystal. HF was added to control the morphology of the crystals. More specifically, HF reduces the surface energy and retards the growth of the {101} facets to facilitate the growth of the thermodynamically less stable {001} surfaces. Furthermore, 2-propanol was also added as a protecting agent to enhance the stabilization effect associated with fluorine adsorption over the {001} surface, thus promoting the growth of {001}. The crystals washed three times with ethanol were drop-cast on a cover glass and annealed at 475 °C for 2 h before the photodeposition experiment in order to remove excess F ions that could inhibit metal photodeposition and ensure to obtain clean facet surfaces.

Figure 1. (Top) Scanning electron microscopy (SEM) images of the synthesized anatase TiO₂ crystals: (a) top-view crystal and (b) side-view crystal. A and B (inset) denote, respectively, the long side and the short side of the crystal. (Bottom) Statistical data for the (c) size of the long side of the crystals and (d) degree of truncation (B/A) of anatase TiO₂ single crystals.

Figure 2. SEM images of metal NPs photodeposited on well-defined TiO₂ anatase crystals using Pt NPs in a (a) methanol/H₂O solvent mixture and an (b) EG/H₂O solvent mixture. Au NPs in (c) H₂O and an (d) EG/H₂O solvent mixture. (e–h) Histograms of the size distribution of the respective photodeposited metal NPs based on the SEM images of 10 crystals.
Figure 1 shows SEM images of the synthesized anatase TiO₂ single crystals. Both top- and side-view images of the crystal display the truncated tetragonal bipyramidal structure in which two square surfaces and eight isosceles trapezoidal surfaces were identified as {001} and {101} facets, respectively, as confirmed by the interfacial angle (68.3°) corresponding to the theoretical value between the two facet planes (Figure 1a,b). The average length of the long side of the crystal marked with “A” is ~3.5 μm and that of the short side (B) is ~3.1 μm (Figure 1b). Although some agglomerated particles were occasionally seen, most of them are well-defined crystals. Darker spots on the {001} facets are most likely due to surface defects. The uniformity of the anatase crystals was estimated by statistically analyzing 20 crystals; the length A is 3.5 ± 0.5 μm (Figure 1c) and the degree of truncation (B/A) is 0.87 for over 40% crystals (Figure 1d), corresponding to 53% of {001} facets from the total exposed facet surface. As a result, our crystals exhibit almost equally coexposed facets, which allow us for the fair assessment of the role of different facets because they would contribute equally to the metal particle photodeposition.

During the photodeposition of noble metal NPs under UV light irradiation, photogenerated electrons from the TiO₂ valence band (VB) are excited into conduction band (CB) while leaving holes (h⁺) in the VB. The photogenerated electrons are transferred to the facet surface and will react with the used metal precursor (either H₂PtCl₆ or HAuCl₄), promoting the photoreduction of metal ion Au⁺ or Pt⁴⁺ on the TiO₂ surface. This is generally accompanied by the elimination of photogenerated holes by water oxidation.

The photodeposition of Pt or Au NPs on TiO₂ crystals is rarely possible to be realized using pure water as a solvent owing to the difficulty of photoreduction of the metal ions. In particular, for Pt, almost no metal deposition was observed even after 5 min of UV radiation (Figure S1). To increase the photodeposition efficiency, organic solvents, such as methanol or EG, are often added as a sacrificial hole scavenger. These alcohol molecules have a lower oxidation potential than water, leading to a faster oxidation. Furthermore, alcohols are better hole scavengers because the oxidation of alcohols is more efficient per molecule; three h⁺ are consumed for the full oxidation of a monoalcohol (methanol), whereas five are needed for a diol, such as EG. Indeed, by adding 20 vol % of methanol or EG to the aqueous solution, the NP photodeposition efficiency was enhanced (Figure 2a,b).

A striking feature, clearly seen in the SEM images (Figures 2a–d and S2), is the position of photodeposited metal NPs depending on solvents used for the reaction. When Pt photodeposition is conducted in a methanol/H₂O mixture, 96% of the grafted Pt NPs were selectively deposited on the {101} facets rather than on the {001} facets (Figure 2a). The Pt NPs are relatively polydisperse with an average size of around 350 nm (Figure 2e). By contrast, when photodeposition is performed using an EG/H₂O mixture, around 93% of the NPs are found on the {001} facet (Figure 2b). In this case, the NPs are relatively monodispersed with the size of less than 100 nm (Figure 2f). Therefore, higher yield and better quality of photodeposition are possible in the presence of EG in terms of uniformity and reproducibility.

Similar results were found for the photodeposition of Au NPs. The Au photodeposition tends to be more efficient than the Pt photodeposition because while four electrons are necessary to reduce one Pt⁴⁺ ion atom, Au³⁺ only needs three electrons, leading to faster deposition. Au NPs are deposited mostly on the {101} facet (78%) in water with an average size over all facets of 110 nm (Figure 2c,g). Adding monoalcohols does not significantly induce facet preferences of Au photodeposition: particles are deposited on both facets, but still a strong preference of deposition on or close to the {101} facet remains. The particle size is relatively large, and their size and shape are highly polydispersed under this condition (Figure S4b,c). Remarkably, adding a low amount of EG into water altered the facet preference. Most particles are now found on the {001} facet (98%) with a size less than 200 nm (Figure 2d,h). Interestingly, using pure anhydrous EG as a solvent, the facet preference completely disappears. Instead, the particles were well-spread over the crystal with more uniform size (~50 nm) (Figures S4d and S5).

Facet dependence of the metal photodeposition is obviously affected by the organic solvent added to the aqueous solution. When water or monoalcohols are adsorbed onto the anatase crystals, the {101} facets provide more reduction sites, resulting in the selective reduction of the metal. The complementary water/methanol oxidation will occur more at the {001} facet. The same tendency of selective Pt loading on the {101} facet has previously been observed by adding small amounts of 2-propanol to the water. In contrast to this conventional behavior, when diol solvents, such as EG, are adsorbed onto the TiO₂ crystal surface, the reduction sites are mainly located on the {001} facet.

Because monoalcohols are good hole scavengers, they reduce the e⁻/h⁺ recombination. Therefore, once a metal NP is created, it acts as an electron trap, through Schottky barrier formation, prohibiting other electrons from reducing Pt or Au at other positions. This may explain the larger Pt or Au NPs photodeposited on the anatase TiO₂ crystal in the presence of monoalcohol. According to our previous research, the EG molecules, by contrast, block the TiO₂ surface with both hydroxyl groups. Therefore, EG controls the positions where the electrons and holes reach the surface, explaining the creation of monodispersed small NPs.

Recent theoretical studies pointed out that different anatase crystal facets possess different surface energy levels of the CB and VB owing to the difference in their atomic arrangements. Because of this energy difference between {001} and {101} facets and the fact that they are in contact, a new concept has been studied, and it suggested that {001} and {101} facets can form a surface heterojunction, that is, realignment of the energy bands at the {001}–{101} interface, which promote the transfer of photogenerated electrons and holes between the crystal facets. However, these previous calculations were performed on clean crystal facets, that is, without any consideration of the adsorbed molecules including solvents. In order to unravel the mechanism governing the facet dependence observed in this study, we theoretically evaluated the effect of solvent adsorption on the electronic structures of both anatase crystal facets ({001} and {101}) by performing DFT calculations.

DFT calculations were performed within the generalized gradient approximation as implemented in the SIESTA computational code within the Perdew–Burke–Emzerhof form. A double-ζ basis set of localized atomic orbitals was used for the valence electrons, and the core electrons were replaced by Troullier–Martins pseudopotentials. Sampling of the Brillouin zone was restricted to the Γ point during geometric relaxation, and a (10 × 10 × 1) Monkhorst–Pack grid was used for the density of state (DOS) calculations.
while a mesh cutoff energy of 300 Ry has been imposed for real-space integration. All structures were relaxed until forces were less than 0.05 eV/Å. In the calculations, a vacuum interval of more than 10 Å was used to avoid the interaction between the periodic slabs. A two-layer TiO2 slab is used to model the adsorption of methanol and EG on the {001} and {101} facets.18 The advantage of this simple model is that it is not time-consuming, and Martsinovich et al.27 have shown that a two-layer slab is sufficient to describe the adsorption of molecules on anatase TiO2. The surface areas are 7.57 Å × 7.57 Å and 10.24 Å × 11.35 Å for anatase TiO2 {001} and {101} facets, respectively.

After geometric relaxation, both methanol and EG dissociate upon adsorption on the {001} facet (Figure S6). An O−Ti bond is broken in both cases; methanol forms a methoxy group (CH3O−Ti) on the TiO2 surface, whereas EG forms a hydroxyl−ethanolate group (HO−CH2−CH2−O−Ti). On the {101} facets, molecular adsorption through hydrogen bonding between the OH groups of the solvent molecules and oxygen atoms of TiO2 was found in our calculation. These simulations are consistent with the previous reports.27 The calculation in this study has been limited on the first molecular layer because it has been already shown that the first layers give the highest impact on the electronic properties of TiO2 and that the results with single layer28 and multilayers29 are qualitatively similar.

The DOS of both facets clearly shows a typical electronic band gap of about 3 eV.30 It is noteworthy that the DOS of the two facets was aligned by the position of the O 2s core levels and to avoid confusion in the energy scale, the highest occupied state of the {001} facet is chosen as the Fermi level and is set to zero. In the presence of a methanol molecule, the band gap position on the {101} facet shifts toward lower energies with respect to that of the {001} facets without changing the band gap width (Figure 3a). Similar behavior has been found for clean {001} and {101} facets and upon adsorption of water molecules on both TiO2 facets (Figure S7).17c,20 A striking difference was found in the presence of EG molecules: the dissociative adsorption of EG on the {001} facet induces the formation of an extralocalized electron state within the TiO2 band gap at ~2 eV below the CB minimum, whereas the band gaps of both facets are relocated within the same energy range (Figure 3b). This localized state may facilitate the electron excitation formation by acting as a stepping stone between the VB and CB. Thus, less energy is required for the electron excitation from the extra DOS to the CB, which could result in enhancement of the electron transfer between TiO2 and the acceptor species.

When the {001} and {101} facets are in contact, their Fermi level should be located at the same energy level.21 Therefore, the energy difference between the facets adsorbed with methanol inevitably drives a migration of photogenerated electrons from the higher surface energy facet to the lower surface energy facet (Figure 3c). Subsequently, the holes tend to accumulate on the {001} facet to reach the most stable energy configuration. This is the origin of the selective metal reduction on the {101} facets in the presence of water or methanol. This charge-carrier-transfer scenario changes upon adsorption of EG molecules on the surface (Figure 3d).

When EG molecules are adsorbed, a lower energy difference between the crystal facets is found, suggesting that electron migration between {001} and {101} is mostly suppressed. In this case, photogenerated e−/h+ could be found simultaneously on both crystal surfaces. The photocatalytic oxidation and reduction can take place synchronously on both {001} and {101} facets. However, owing to the extralocalized state

Figure 3. (Top) DOS plots of {001} and {101} facets upon adsorption of (a) methanol and (b) EG. Extralocalized state is induced by the adsorption of EG within the band gap of TiO2. (Bottom) Energy band diagrams illustrating the {001} and {101} surface heterojunction affected by the adsorption of (c) methanol and (d) EG and their different photogenerated e−/h+ trajectories over the anatase TiO2 crystal.
inducing more electrons, the lack of electron transfer to the \{101\} facet, and the larger facet surface, the excited electrons are located more at the \{001\} facet. Hence, metal ions will be reduced more efficiently at this facet (Figure 3d). EG adsorption leads not only to a favorable selectivity of the \{001\} facet but also to a more controlled photodeposition of noble metal NPs on both facet surfaces. Because more electrons are produced on the \{001\} facet owing to the extralocalized state, holes are also produced in the same facet, which are localized at the \{001\} facet. The generated holes on the \{001\} facet could induce a slightly higher oxidation power of the \{001\} facet. In our experiments, EG molecules were likely oxidized as they are very efficient hole scavengers. Although the enhanced oxidation power could be used for selective photodeposition of a metal oxide as performed in ref 29, it is out of scope in this study.

\section*{CONCLUSIONS}

In summary, the pivotal role of solvents on the facet-dependent photocatalytic property on highly uniform anatase TiO$_2$ crystals with equally coexposed \{001\} and \{101\} facets was revealed. On the basis of the agreement between the experimental and DFT results, the selectivity and reactivity of different facets are found to be highly affected by the adsorption of reactant molecules. This behavior is confirmed to be related to the different electron pathways over TiO$_2$ crystals. Interestingly, we found that EG adsorption not only lowers the energy difference between the anatase crystal facets but also induces a new localized state, resulting in a more efficient NP photodeposition on the \{001\} facet and a higher quality and uniformity of metal NPs. Thus, using the appropriate solvent is a key factor to tune the selectivity of facets and to control the quality of metal NP photodeposition (size and position) on the anatase TiO$_2$ crystals. These findings provide new insights for a more effective and comprehensive assessment on the role of TiO$_2$ crystal facets in photocatalytic processes. The latter is a necessity to design advanced photocatalytic materials for large-scale applications.

\section*{EXPERIMENTAL SECTION}

\textbf{Materials.} TiF$_4$, HCl (10 M), iso-propylalcohol, HF (48%), and EG (99%, spectrograde) were purchased from Sigma-Aldrich and used without further purification. H$_2$PtCl$_6$ (99.999% trace metal basis) was purchased from Acros Chemicals and used without further purification. Methanol was purchased from Merck and used without further purification. All solutions were prepared in Milli-Q water (18 MΩ, Millipore).

\textbf{Synthesis of Anatase TiO$_2$ Single Crystals.} TiO$_2$ crystals with controlled \{101\} and \{001\} facets were synthesized under hydrothermal conditions, following literature procedures. In detail, 49.5 mg of TiF$_4$ was dissolved in 10 mL of a 0.01 M HCl solution. This solution (1 mL) was mixed with 13.5 mL of iso-propylalcohol, 13.9 mL of H$_2$O, and 0.104 mL of 48% HF. \textbf{Caution:} Hydrofluoric acid is extremely corrosive and a contact poison. Addition of HF was carried out in a specially assigned room wearing protective clothes, with calcium gluconate in close vicinity. An autoclave with total volume of 12 mL was filled with 9 mL of the latter solution and heated in an oven at 180 °C for 24 h. The crystals were centrifuged and washed three times with ethanol. The cleaned crystal solution (5 µL) is drop-casted on a clean glass cover slide. During the preselected synthesis, an excess amount of F ions usually covers the TiO$_2$ facets. These F ions lower the surface energy of both crystal facets, influencing their adsorption, specificity, and reactivity.\textsuperscript{31} In order to remove them, the crystals were annealed for 2 h at 475 °C prior to the metal photodeposition experiments.

\textbf{Photodeposition of Metal NPs.} For Pt photodeposition experiments, the crystals were submerged in a 5 mM H$_2$PtCl$_6$ solution, with the solvent either a methanol/water mixture or an EG/water mixture (alcohol concentration, 20 vol %). The prepared samples were then irradiated with UV light for 3 min. For Au photodeposition, the crystals were submerged in a 20 mM HAuCl$_4$ solution with the solvent either water or 10 vol % EG aqueous solution. The prepared samples were then irradiated with UV light for 1 min and thoroughly washed and dried afterward. Irradiation was conducted using a 300 W xenon light source (Asahi-Max 303) with a 300 nm short-pass filter. After radiation, the samples were rinsed with Milli-Q water (18 MΩ) and gently dried with Ar. SEM measurements were performed on a JEOL JSM-6010 InTouchScope.

\section*{ASSOCIATED CONTENT}

\textbf{Supporting Information}

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.6b00473.

\begin{itemize}
  \item SEM images of Pt and Au NPs photodeposited on well-defined TiO$_2$ and surface atomic structure of anatase crystal facets using different solvent adsorptions (PDF)
\end{itemize}

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\textbf{Author Contributions}

All authors contributed in writing this manuscript and approved its final version as well.

\textbf{Notes}

The authors declare no competing financial interest.

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