



Critical roles of co-catalysts for molecular hydrogen formation in photocatalysis



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ABSTRACT

Surface atomic structure can play a critical role in the reactivity of materials, because many physicochemical processes occur at surfaces. As an important semiconductor material, titanium dioxide (TiO₂) crystals with tailored facets have opened up intensive research in surface chemistry, such as photocatalytic hydrogen generation. However, the convincing measurement and explanation of the crystal facets effect for molecular hydrogen formation in photocatalysis has remained elusive. One longstanding controversy is between the exposed {001} and {101} facets. Here we demonstrate, through a combination of state-of-the-art electron microscopy and quantum chemical calculations, that the crystal facets of TiO₂ do not play the critical role in photoreactivity; the bare TiO₂ semiconductors without co-catalysts are catalytically inactive, whereas the location and species of the co-catalysts essentially determine the capacity for the hydrogen evolution reaction. Our results provide a unified explanation for the disparate results in the previous literature and highlight a feasible route to fabricating efficient photocatalysts.

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1. Introduction

Identifying the relationship between surface structures and physicochemical properties of materials is of great importance for various reactions that occur on the surface [1–3]. The discovery of the Fujishima–Honda effect has stimulated continuous attention to the photocatalytic hydrogen evolution reaction (HER) on semiconductor materials, because hydrogen (H₂) has been widely considered as a promising alternative for traditional fossil fuels in the future [4–7]. Benefiting from its unique atomic structure, anatase titanium dioxide (TiO₂) has been commonly regarded as a benchmark material for photolysis of water and the role of its facets has been studied substantially for decades [8–11]. Since theoretical studies suggest that the {001} face of TiO₂ is much more reactive for water decomposition than the thermodynamically more stable {101} face [12–19], numerous attempts have been made to maximize the exposure of the {001} facets for higher efficiency in HER than with the octahedral ones [20–25]. Alternatively, recent results have claimed that {101} facets are indeed more active than {001} facets in HER [26,27]. Thus, it is critical to identify the real role of crystal facets of TiO₂ in molecular H₂ formation.

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It should be noted that bare TiO₂ is rarely seen in photocatalytic HER [5], although the photogenerated electrons and holes can migrate to the surface spontaneously, as illustrated in Fig. 1a. Thus, the additional active sites (so-called co-catalysts), such as metallic platinum (Pt) co-catalyst, have generally been loaded onto TiO₂ in most previous studies [20–27]. Interestingly, metallic Pt is more favorable to deposits on the TiO₂(101) face than on the (001) face (Fig. 1b), because the {101} face contains surplus electrons, causing the Pt precursor to be readily reduced compared to the {001} face [28–31]. Unfortunately, the location of the Pt co-catalyst has largely been neglected over past years, which would undoubtedly affect the photoreactivity order of HER between the {001} and {101} facets. Recently, our group has developed a new Pt-based co-catalyst [32], ultrafine PtO clusters, which can be stabilized on both the {001} and {101} faces of TiO₂ (Fig. 1c). Therefore, by means of PtO clusters and metallic Pt co-catalysts, we can systematically investigate the true photoreactivity order of the {001} and {101} facets.

Here we find that the TiO₂ crystal facets are not the decisive factor in photoreactivity in HER, whereas the location and valence state of the co-catalysts crucially determine the performance of HER (Fig. 1d). The findings in this work may pave the way to eliminating the conflict of opinions on TiO₂-involved H₂ formation

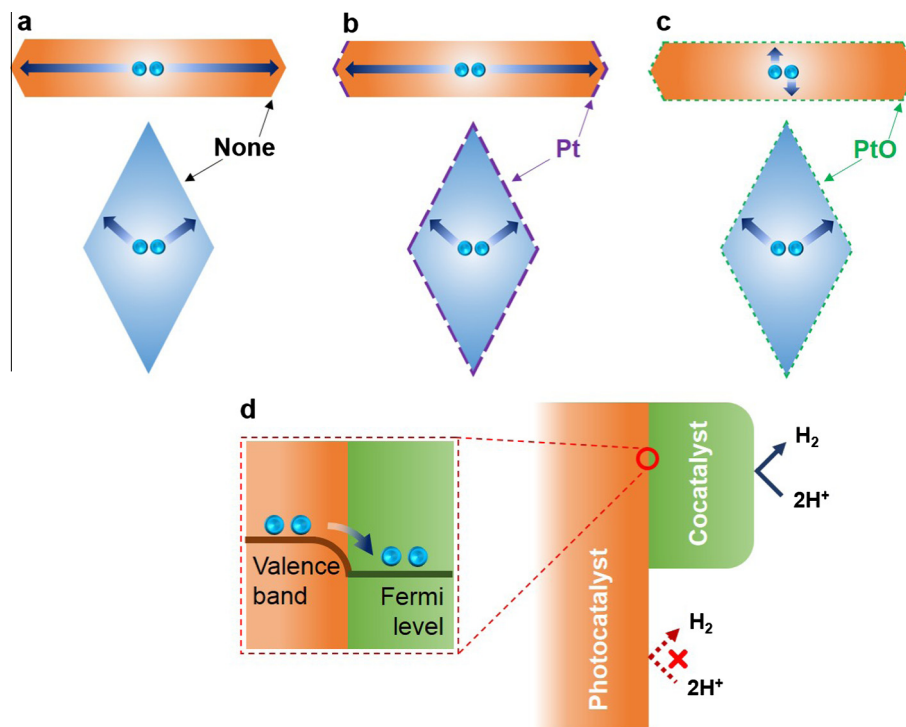


Fig. 1. Schematic photogenerated electron transfer in photocatalysts. The migration of the photogenerated electrons in anatase titanium dioxide without co-catalyst (a), with metallic Pt co-catalyst (b), and with PtO clusters co-catalyst (c). Both PtO clusters and metallic Pt co-catalysts can trap the photogenerated electrons from the host TiO₂, and the migration distances of both electrons and holes affect recombination of electrons and holes. (d) Schematic model of electron transfer between the co-catalyst and the host photocatalyst. The active sites for H₂ evolution are not the Ti atoms of the TiO₂ surface but should be the Pt atoms of the loaded co-catalyst. Green, purple, and blue dots represent PtO clusters, metallic Pt, and electrons, respectively. Orange hexagons and blue rhombi indicate the vertical sections of the TiO₂{001} nanosheets and TiO₂{101} octahedra, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

reactions and cause rethinking of the real decisive factor in other model catalytic systems.

2. Experimental methods

2.1. Sample synthesis

T-001 and T-101 were synthesized by a hydrothermal process according to our previous studies [24,33]. For T-001, 5 mL of tetrabutyl titanate (Sinopharm, 98%) and 0.8 mL of hydrofluoric acid (Sigma–Aldrich, 48%) were added dropwise into a dried Teflon-lined stainless steel autoclave with a capacity of 50 mL under agitation. Then the autoclave was sealed and heated at 180 °C for 24 h. After the autoclave cooled to room temperature, the sample was first washed with dilute sodium hydroxide solution (0.1 M NaOH) and then collected by washing the precipitate thoroughly with absolute ethanol and deionized water several times to remove the residual contamination. After being dried overnight at 60 °C under vacuum, anatase TiO₂ nanosheets dominated by {001} facets were finally harvested and then kept carefully for the experiments. For T-101, commercial titanium chloride (Sigma–Aldrich, 99.9%) was dissolved in ice water with stirring to prepare a 0.0072 wt.% TiCl₄ aqueous solution. The titanium hydrate was precipitated by adding 3.2 wt.% NH₄OH aqueous solution dropwise into TiCl₄ solution below 4 °C. Subsequently the precipitate was washed repeatedly with deionized water to remove the Cl[−] and NH₄⁺ ions. Then the titanium hydrate was mixed with 30 mL H₂O₂ solution (30 wt.%, Sinopharm) to obtain a 10 mM solution, followed by hydrothermal treatment in an electric oven at 180 °C for 24 h. Under ambient conditions, as-prepared TiO₂{101} were separated by centrifugation and washed several

times with deionized water and absolute ethanol, and then dried overnight at 60 °C under vacuum. To ensure that the two samples attached similar numbers of hydroxyl groups, the samples were added into glass beakers contained 0.1 M NaOH solution. The beakers were heated at 80 °C for 2 h under agitation, and the samples were separated by centrifugation and washed several times with deionized water and absolute ethanol, and then dried overnight at 60 °C under vacuum.

2.2. Co-catalyst deposition

The PtO clusters co-catalyst was loaded on T-001 and T-101 through a ligand-assisted chemical reduction process [32]. Portions of 50 mg of TiO₂ and 24.6 mg of polymer ligands were added into a screw-neck glass bottle containing chloroplatinic acid solution (5 mL, 0.2 mg/mL). After the suspension became uniform by sonication, 0.5 mL of freshly prepared sodium borohydride (NaBH₄) aqueous solution (2 mg/mL) was injected to reduce chloroplatinic acid under vigorous stirring, and another 0.5 mL of freshly prepared NaBH₄ solution was injected after 2–3 h. The solution was stirred overnight. The precipitate was separated by a centrifuge and washed several times with deionized water and ethanol. After it was dried at room temperature, PtO-loaded photocatalysts with clean surfaces were harvested. The metallic Pt co-catalyst loading process was similar without adding the polymer ligands.

2.3. Materials characterization

The crystal structure was determined using X-ray diffraction (XRD; D/MAX 2550 VB/PC). The detailed surface hydroxyl groups

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