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New evidence for the regulation of photogenerated electron transfer on surface potential energy controlled co-catalyst on TiO_2 – The investigation of hydrogen production over selectively exposed Au facet on Au/TiO_2

Entian Cui^{a,b}, Gongxuan Lu^{a,*}^a State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Science, Lanzhou 730000, China^b University of Chinese Academy of Science, Beijing 10080, China

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ABSTRACT

In this study, Au/TiO_2 samples with different exposed facets ($\{100\}$, $\{100/111\}$, and $\{111\}$) of Au were employed as catalysts for the examination of facet-dependent catalytic activity toward photocatalytic hydrogen evolution from water. By photosensitized using Eosin Y as antenna molecule, Au/TiO_2 series photocatalysts exhibited different photocatalytic hydrogen evolution performances under visible light irradiation. $\text{Au}\{111\}/\text{TiO}_2$ photocatalyst presented the highest photocatalytic hydrogen generation activity among Au/TiO_2 series samples. As evidenced by photoluminescence spectra, photocurrent, electrochemical impedance spectra, and Mott–Schottky characterizations, the difference in photocatalytic activities resulted from the different electron transfer rates from the conduction band of TiO_2 to Au nanoparticles. Au nanoparticles with exposed $\{111\}$ facets were more effective in trapping electrons due to their higher Fermi level. In addition, the apparent activation energy of $\text{Au}\{111\}/\text{TiO}_2$ sample was the lowest, resulted from the biggest uncoordinated numbers of Au atoms on $\text{Au}\{111\}$ nanoparticles, which was favor in forming the hydrogen–metal bond. This study discloses the facet-dependent effect of noble-metal cocatalyst on semiconductor photocatalysts in photocatalytic water reduction, and will give an insight into design and synthesis of high-efficient noble metal/semiconductor hybrid photocatalysts.

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* Corresponding author. Tel.: +86 931 4968178.

E-mail address: gxlu@lzb.ac.cn (G. Lu).

Introduction

One of the main drawbacks of hydrogen production by photocatalytic water splitting is the extremely rapid recombination of the electron–hole pairs on the photocatalyst surface or bulk. Many efforts have been made to improve the photocatalytic activity by preventing the recombination of the electron–hole pairs, such as ion dopant [1–4], semiconductor composite, [5,6] and sacrificial agent addition [7] and so on. Here loading photocatalyst surface with metals has been proven to be an effective way to prevent the rapid recombination of the photogenerated charge carriers [8,9]. When metal nanoparticles are deposited on the photocatalyst surface, the photoinduced electrons migrate preferentially from the conduction band of the semiconductor to the metal, resulting in a decrease in electron–hole pair recombination. Up to date, various metals have been used as cocatalyst including Pt [10], Pd [11], and Au [12]. Recently, Au/semiconductor systems have attracted considerable attention because of the high and stable photocatalytic hydrogen yields [13–15]. But Au is a noble metal, which is too expensive to be used widely. Thus, it is of great importance to utilize Au more efficiently.

Investigations on the optimization the utilization of Au over the conventional Au–TiO₂ catalysts for photo-catalytic hydrogen evolution have been reported. These studies mainly focused on the size and loading amount of Au nanoparticles [13], as well as the interaction between Au nanoparticles and TiO₂ supports [16]. Idriss demonstrated that Au particles in the size range 3–30 nm on TiO₂ were very active in hydrogen production from ethanol and the optimal loading amount of Au was ca. 4 wt%. Further increasing in Au loading amount led to a reduction in the available metal–support sites since both metal and support were all needed for the reaction [13]. Waterhouse found that for Au/TiO₂ photocatalyst, the optimum Au loading was around 1–2 wt%, which afforded a hydrogen production rate of 31–34 mmol g⁻¹ h⁻¹ [17]. Xue reported the similar results [18].

Although great progresses have been made on the optimized utilization of Au/TiO₂ photocatalysts for hydrogen generation, there are few reports on the relation between the Au surface crystallographic structure and the activity of hydrogen evolution reaction (HER). Sluyters studied the reduction of H⁺ from 1 mol L⁻¹ HClO₄ and 1 mol L⁻¹ NaClO₄ solutions at polycrystalline and single crystal faces of very pure gold electrodes. The activities of HER followed in the sequence Au{110} < Au{100} < Au{111}, which resulted from an additional specific double-layer effect, e.g. difference in the electric field strength in the inner layer [19]. However, Weaver also studied the HER on gold single crystals in 0.1 mol L⁻¹ HClO₄ and gave the opposite result. The reason was that the stability of the adsorbed hydrogen intermediate increased as the surface atomic step density increasing from Au{111} to Au{100} since the stronger hydrogen adsorption occurred at gold atoms of lower surface coordination number [20]. Although the order of catalytic activities was contradictory between these two studies, the results all indicated that the hydrogen evolution reaction on Au single-crystal electrodes was structure sensitive. Bai considered that the discrepancies among

reported data mentioned above could be due, at least partially, to the blocking effect of hydrogen bubbles and/or to the influence of the diffusion of dissolved hydrogen away from the interface [21]. Therefore, Villullas studied the HER on Au single crystals in a wider range of over-potentials in HClO₄ solutions by the hanging meniscus rotating disk technique to avoid blocking effects produced by hydrogen bubbles. They found that the reaction proceed through the same mechanism on the Au(111), Au(100), and Au(110) electrodes and the catalytic activities presented the following sequence Au(111) > Au(100) > Au(110), which was associated with atomic density of the surface [22].

Considering the different reported data of facet dependence of Au on electrochemical HER activity, to reveal the facet-dependent effect of Au nanoparticles on photocatalytic HER activity also has important practical significance for optimizing utilization noble metals. In the present work, TiO₂ with high exposed {001} facets was chosen as the support catalyst to reduce the effect of the support and all our further statements of TiO₂ will be about TiO₂ with high exposed {001} unless otherwise noted. Au/TiO₂ photocatalysts with different exposed facets {100}, {100/111}, and {111} of Au fabricated by a combined seed-mediated and wet-absorption method were employed to study the facet effect of Au on the photocatalytic activity of Au/TiO₂ catalyst. To the best of our knowledge, this is the first time to investigate the photocatalytic properties of gold exposed facets supported on TiO₂. Combining the spectroscopic and activity results, we have found that the exposed facets of Au nanoparticles show significant effects on photocatalytic properties of Au/TiO₂.

Experimental

Preparation of Au nanoparticles with different exposed facets

Au nanoparticles with different exposed facets were prepared by a reported seed-mediated method with some modification [23].

Synthesis of Au octahedral seed colloid solution

Firstly, 10 mL of an aqueous solution containing HAuCl₄ (0.25 mmol L⁻¹) and CTAB (75 mmol L⁻¹) was pre-prepared. 0.6 mL ice-cold NaBH₄ (10 mmol L⁻¹) was rapidly injected to the pre-prepared mixture with vigorously stirring in 30 °C. A brown solution was observed a few seconds later. The whole solution was kept stirring slowly for two hours at room temperature to promote the decomposition of the remaining NaBH₄ in the solution. Then, 1 mL of the pre-prepared hydrosol was diluted to 100 mL with water as the seed hydrosol. Secondly, 25 mL of colorless mixture containing HAuCl₄ (0.04 mmol L⁻¹), CTAB (16 mmol L⁻¹) and ascorbic acid (AA, 6 mmol L⁻¹) was prepared. Thirdly, 0.3 mL seed hydrosol was added to the mixture immediately and mixed them by a vortex-mixer. Then the reaction mixture was left undisturbed at 30 °C overnight, and a light purple colloidal solution (containing small Au octahedron) was achieved. The colloidal solution was used as a seed solution for further growth of bigger Au particles without further treatment.

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