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## Article (Special Issue of Photocatalysis for Solar Fuels)

# Steering plasmonic hot electrons to realize enhanced full-spectrum photocatalytic hydrogen evolution



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## ABSTRACT

Integration of surface plasmons into photocatalysis is an intriguing approach to extend the light absorption range over the full solar spectrum. However, the low migration rates and uncertain diffusion directions of plasmonic hot electrons make their photocatalytic efficiency fail to meet expectations. It remains a challenging task to steer the migration of hot electrons and take full advantage of the plasmonic effect to achieve the desired high photocatalytic efficiency. Herein, we have developed an efficient strategy to steer the migration of plasmonic hot electrons through a well-designed hybrid structure that synergizes a “surface heterojunction” with a Schottky junction. The hybrid structure was synthesized by modifying titanium dioxide (TiO<sub>2</sub>) nanosheets (NSs) with gold (Au) nanoparticles (NPs) as a plasmonic metal and platinum (Pt) NPs as a co-catalyst. The “surface heterojunction” formed between two different crystal facets in the TiO<sub>2</sub> NSs can induce the injection of plasmonic hot electrons from Au NPs excited by visible light to TiO<sub>2</sub>. Meanwhile, the Schottky junction formed between the Pt NPs and TiO<sub>2</sub> NSs can force the migration of electrons from TiO<sub>2</sub> to Pt NPs instead of flowing to Au NPs, attaining the efficient unidirectional transfer of carriers in the Au–TiO<sub>2</sub> system. Plasmonic photocatalysts with this design achieved dramatically enhanced activity in full-spectrum photocatalytic hydrogen production. This work opens a new window to rationally design hybrid structures for full-spectrum photocatalysis.

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## 1. Introduction

Photocatalytic hydrogen evolution is a promising approach to address current energy and environmental demands. Ideal

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solar-to-fuel photocatalysts should harvest the broad spectrum of solar light to maximize the formation of photoinduced electron-hole pairs. It remains an important challenge to develop photocatalysts that can harvest the full solar spectrum to achieve efficient solar energy conversion. Titanium dioxide ( $\text{TiO}_2$ ) has attracted much attention because of its great potential in photocatalysis and solar cells [1–5]. However, because  $\text{TiO}_2$  has a wide bandgap ( $\sim 3.2$  eV), it can only absorb ultraviolet (UV) light, which accounts for just ca. 5% of the solar spectrum [6]. Given this situation, great effort has been made to extend the light absorption of  $\text{TiO}_2$  to the visible spectral region, typically by combining it with narrow-bandgap semiconductors [7–9] or dye molecules [10,11]. In particular, plasmon-mediated photocatalysis has attracted considerable attention from researchers interested in semiconductor photocatalyst systems [12–16]. Recently, the development of plasmonic gold (Au) [17,18] and silver (Ag) [19,20] has offered  $\text{TiO}_2$  a new opportunity to achieve visible-light photoactivity via the plasmonic effect.

Taking plasmonic Au as a model system, it demonstrates plasmon-enhanced photoactivity when directly contacting a semiconductor. When irradiated by visible light, the electrons in the  $d$ -band of Au nanoparticles (NPs) can be excited to empty bands above the Fermi level ( $E_F$ ) to form “hot electrons”, leaving equilibrated  $d$ -band “hot holes” below  $E_F$  [21]. These hot electrons can inject into the conduction band (CB) of  $n$ -type semiconductors and initiate reduction reactions [22]. Recently, several Au– $\text{TiO}_2$  hybrid systems that display plasmon-enhanced photoactivity in the visible-light region because of the plasmonic absorption of Au NPs have been reported [23–25]. However, the plasmon-enhanced photoactivity of these Au– $\text{TiO}_2$  hybrid systems has been primarily restricted to the visible region. In these cases,  $\text{TiO}_2$  cannot be excited by visible light, and only plays roles in separating and transferring the injected electrons from Au NPs. When irradiated under the full solar light spectrum,  $\text{TiO}_2$  and plasmonic Au NPs are simultaneously excited. In this case, the injection of plasmonic hot electrons from Au NPs to  $\text{TiO}_2$  is counteracted by the opposite flow of photogenerated electrons from  $\text{TiO}_2$  to Au NPs determined by the Schottky junction, weakening the plasmonic effect. To make full use of plasmonic hot electrons and achieve full-spectrum photocatalysis, it is necessary to steer the migration of plasmonic hot electrons from Au NPs and photogenerated electrons from  $\text{TiO}_2$  in the desired directions.

Herein, we develop a hybrid structure to steer the migration of electrons in the desired direction, which enables the full use of plasmonic hot electrons to realize full-spectrum photocatalysis. In this design, a “surface heterojunction” is synergized with a Schottky junction. The “surface heterojunction” consists of a semiconductor with two or more different exposed crystal facets, in which electrons can be transferred from the facet with higher  $E_F$  to the facet with lower  $E_F$  by the internal electric field because of their different electronic states [26,27]. When plasmonic Au NPs are deposited onto the facet with higher  $E_F$ , hot electrons can be efficiently steered towards the facet with lower  $E_F$ . Meanwhile, a Schottky junction can be formed through the intimate contact between the noble metal NPs and  $n$ -type

semiconductor when the work function of the noble metal is higher than that of the  $n$ -type semiconductor [22]. Driven by the Schottky junction, the photogenerated carriers on the semiconductor can be separated more efficiently, thereby enhancing the photocatalytic activity of the structure [28–31]. Platinum (Pt) is a widely used co-catalyst that possesses a high work function to form the Schottky junction and thus can efficiently separate the photogenerated electrons from the semiconductor [32].

In this work, we use  $\text{TiO}_2$  nanosheets (NSs) covered with {001} and {101} facets as a model “surface heterojunction”. Au NPs as the plasmonic metal are anchored on the {001} surface of  $\text{TiO}_2$  by the intermediate ligand 3-mercaptopropionic acid (MPA). This structure can achieve facile injection of hot electrons because of the internal electric field of the “surface heterojunction” in the  $\text{TiO}_2$  NSs. To prevent the backflow of electrons from  $\text{TiO}_2$  NSs to Au NPs under full-spectrum irradiation, we integrate co-catalyst Pt NPs with the designed Au– $\text{TiO}_2$ {001} sample to form a Schottky junction. This Schottky junction can force the migration of electrons from  $\text{TiO}_2$  to Pt NPs instead of flowing back to Au NPs to realize the efficient unidirectional transfer of electrons in the Au– $\text{TiO}_2$  system. This hybrid structure is a highly efficient catalyst for full-spectrum photocatalytic hydrogen production. This work provides fresh insights into the rational design of photocatalyst structures that steer plasmonic hot electrons, representing a step towards full-spectrum photocatalysis.

## 2. Experimental

### 2.1. Synthesis

$\text{TiO}_2$  NSs were synthesized by the solvothermal method as reported previously [33]. Typically, hydrofluoric acid (HF) aqueous solution (4.5 mL, 40 wt%) was added to tetrabutyl titanate (25 mL) and stirred for 30 min. Subsequently, the mixture was transferred into a 50-mL Teflon-lined autoclave and kept at 180 °C for 24 h. After the solvothermal reaction, the obtained white precipitate was collected, washed with deionized water and ethanol several times, and then calcined at 550 °C for 2 h in a furnace to remove surface fluoride ions.

In a standard process, sodium citrate dihydrate (107.04 mg) and  $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$  (4.79 mL, 0.1 mol/L) were mixed in deionized water (93 mL). The stirred mixture was heated at 80 °C for 2 h in a 250-mL round-bottom flask. The as-synthesized Au NPs were dispersed in the solution by sonication and stored for further use. The concentration of Au NPs was measured by inductively coupled plasma mass spectrometry (ICP-MS).

The Au– $\text{TiO}_2$ {001} hybrid structure was obtained using MPA as an intermediate ligand [34]. In brief,  $\text{TiO}_2$  NSs (20 mg) were added to a 50-mL quartz tube containing deionized water (20 mL), and then sonicated to form a uniform suspension. Then, MPA (50  $\mu\text{L}$ ) was dispersed in the suspension by stirring for 6 h. After the reaction, the sample was collected and washed with deionized water by centrifugation to remove the dissociated MPA. The obtained MPA-modified  $\text{TiO}_2$  NSs were dispersed in deionized water (20 mL) by sonication in a 50-mL

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