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# Synergistic promotion of solar-driven $H_2$ generation by three-dimensionally ordered macroporous structured $TiO_2$-Au-CdS ternary photocatalyst

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## ABSTRACT

A ternary photocatalyst $TiO_2$-Au-CdS based on three-dimensionally ordered macroporous $TiO_2$ (3DOM $TiO_2$) was successfully prepared to enhance the light absorption, extend the light responsive region, reduce the recombination rate of charge carriers and promote the efficiency of water splitting $H_2$ evolution ultimately. The obtained 3DOM $TiO_2$-Au-CdS powder has a pure anatase phase of $TiO_2$ and greenockite structured CdS according to the XRD results and TEM analysis. Au nanoparticles (AuNPs) and CdS were evenly distributed in the 3DOM structure which enhances $H_2$-generation rate under visible light by improving light harvesting and utilizing its mass transfer facilitation. As a result, the hydrogen generation rate ($1.81\ \mathrm{mmol\ h^{-1}\ g^{-1}}$) using 3DOM $TiO_2$-Au-CdS photocatalyst under visible light irradiation was 13-fold higher than the binary 3DOM $TiO_2$-CdS reference photocatalyst. Under ultraviolet-visible light, the photogenerated electrons in $TiO_2$ would be transferred to recombine with the holes of CdS and under visible light, electrons would move to the conduction band (CB) of $TiO_2$ from CdS via AuNPs. The two different types of internal electron-transfer process in the ternary photocatalyst under ultraviolet and visible light were proposed respectively and both would efficiently reduce the recombination rate of photogenerated electrons and holes thus stimulate $H_2$ evolution rate. The present work demonstrated an excellent example of the synergistic effect of the light absorption enhancement by 3DOM structure, the photosensitizing and electron reservoir effect of AuNPs and the reduction of recombination rate of charge carriers by CdS to highly promote the photocatalytic activity in water splitting reaction.

## 1. Introduction

The global energy crisis and environment problems have become increasingly prominent as the fossil fuel is continuously consumed and hydrogen as a clean, storable and environmentally friendly fuel is recognized as the most promising substitute for fossil fuel. Since Fujishima and Honda firstly reported the photoelectrolysis of water over $TiO_2$, solar driven photocatalytic water splitting over semiconductors to produce hydrogen has been attracting extensively research attention [1–4]. Four facets have been considered to affect the photocatalytic performance of $H_2$ evolution by water splitting: light absorption, photogenerated charge separation and migration, and redox reactions on the surface of semiconductor. For semiconductor photocatalysts, $TiO_2$ is recognized as one of the most popular candidates due to its high chemical stability, nontoxicity and low cost [5,6]. However, two major limitations hamper the application of $TiO_2$: (1) its large bandgap (3.2 eV for anatase phase) restricting its utilization in the visible light zone of the solar spectrum [7] and (2) the high recombination rate of photogenerated electrons and holes leading to a low quantum yield and poor photocatalytic activity [8]. Considerable researches have been conducted to find the solutions to the two problems cited above. Combining $TiO_2$ with narrow band-gap semiconductors such as CdS [9] and $MoS_2$ [10] to form a heterostructure would be an effective method to extend the light absorption of $TiO_2$ to the visible portion

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of the solar spectrum [11]. To improve the life of photogenerated electron-hole pairs, some precise metals as electron reservoirs could be introduced to the surface of $TiO_2$ to gather the photogenerated electrons, thus efficiently reduce the recombination of charge carriers. Serrano et al. deposited Pt on the surface of ordered mesoporous $TiO_2$ and the as-fabricated photocatalyst showed higher $H_2$ evolution under ultraviolet light irradiation [12]. Meanwhile, the surface plasmon resonance (SPR) of noble metal nanoparticles can also improve the photoactivity of $TiO_2$ [13]. Butburee et al. prepared a new type of plasmonic metal@$TiO_2$ (metal = Pd and Au) core–shell structure to utilize the SPR effect to enhance the photocatalytic degradation of phenol. In addition to these compositional modifications, using the slow photon effect, a structure effect in three dimensionally ordered macroporous (3DOM, also called photonic crystals) structure to enhance the light harvesting could also promote the photoreactivity [14–20]. Zhang et al. coupled SPR effect of AuNPs with slow photon effect of $TiO_2$ photonic crystals and proved the synergistic enhancement for photoelectrochemical water splitting activity [21]. The design of ternary photocatalyst $TiO_2$-Au-CdS has been successfully adopted and fabricated by several groups to promote the photocatalytic hydrogen evolution [22–26], in which the structures of $TiO_2$ substrate were designed to be nanorod and nanoparticle. Compared with 3DOM structure, the above nanostructures play a relatively weak role in the light harvesting during the photocatalytic reactions. However, it is almost rare using 3DOM structured ternary photocatalyst for hydrogen evolution. Most recently, Wei et al. fabricated the ternary photocatalyst $TiO_2$-Au-CdS based on 3DOM structure, whereas, the application of the prepared samples was to reduce $CO_2$ to obtain methane [27]. To the best of our knowledge, this ternary photocatalyst is in favor of reducing water for hydrogen compared with $CO_2$ as the hydrogen generation is the dynamically favoured reaction and the hydrogen can't be avoided in the process of reducing $CO_2$ with $H_2O$ under ultraviolet light irradiation.

Hence, it is novel to study a ternary composite photocatalyst $TiO_2$-Au-CdS based on 3DOM $TiO_2$ which could be advantageous to the light absorption enhancement, the light responsive region extension and the recombination rate of charge carrier reduction simultaneously. CdS can be adopted to combine with $TiO_2$ due to its narrow band-gap (2.4 eV), which could extend the light response range to visible region. Meanwhile, the conduction band and valence band (VB) of CdS are capable of completing both the reduction and oxidation of water under visible-light irradiation [28]. To efficiently promote photogenerated electron-hole pairs separation, AuNPs serving as electron reservoirs and photosensitizers as a crucial component can be introduced to this ternary photocatalyst. At the same time, AuNPs could be photosensitized to improve light harvesting due to the presence of surface plasmon resonance (SPR) [13]. 3DOM structure as the skeleton of the ternary photocatalyst could provide the multi-advantages by the periodic structure with large and continuously adjustable pore sizes [29–34]. The slow photon effect, the favorable electron migration to the surface of $TiO_2$ and excellent accessibility of reactants and light to 3DOM structure are expected to enhance the performance of visible light-driven water splitting of some effects.

In this work, the three-component 3DOM $TiO_2$-Au-CdS photocatalyst was successfully fabricated and did exhibit highly improved activity for photocatalytic hydrogen generation rate (1.81 mmol $h^{-1}$ $g^{-1}$) under visible light irradiation, 13-fold higher than the binary structure 3DOM $TiO_2$-CdS as reference sample and as compared to the CdS/$TiO_2$ composite (0.11 mmol $h^{-1}$ $g^{-1}$) fabricated by Jang [35]. This as-fabricated ternary photocatalyst provides a transfer path of the internal electrons from CdS to $TiO_2$ via Au nanoparticles, which significantly enhances the photocatalytic activity for water splitting. In addition, the role of 3DOM structure enhancing $H_2$-genenration rate is also confirmed. The present work tries to shed light on the development of solar-driven photocatalyst by the combination of narrow band-gap semiconductor and metallic nanoparticles with 3DOM $TiO_2$ structure, utilizing the features of enhanced visible light sensitivity and absorption, efficient electron-hole separation and excellent reactant and light accessibility.

## 2. Experimental materials and methods

### 2.1. Materials

Styrene, ethanol, tetraisopropyl titanate (TIPT), sodium sulfide nonahydrate, sodium citrate dihydrate, sodium sulfite, cadmium nitrate tetrahydrate,were purchased from Aldrich. Gold chloride solution was purchased from Alfa Aesar.

### 2.2. Colloidal sphere preparation

Surfactant-free emulsion polymerization method was applied to prepared polystyrene (PS) spheres. Styrene was washed three times by using 2 M NaOH to remove the inhibitors. Prewashed styrene (15 mL) and water (200 mL) were heated to 85 °C in an oil bath under a $N_2$ atmosphere, stirring at a certain speed for 0.5 h. The initiator $K_2S_2O_8$ (0.25 g) was added to activate the polymerization. The reaction was stopped after 3 h by cooling the container and making the air through the system. PS template was obtained directly by using low speed centrifugation of PS spheres.

### 2.3. Preparation of 3DOM $TiO_2$

The method of preparing the 3DOM $TiO_2$ was according to our previous report [32]. The precursor was composed of ethanol (5 mL), hydrochloric acid (1 mL), titanium (IV) isopropoxide (5 mL), and water (2 mL). The mixture was added to a beaker and stirred at room temperature for 5mins. Dried PS template (5 g) was placed on a filter paper in a Buchner funnel, and the precursor was added to the PS templates during suction applied to the Buchner funnel. After air drying the mixture of precursor and template for 48 h, calcination in air was applied to remove the PS template. The sample was stabilized at 300 °C for 2 h, 400 °C for 2 h and 550 °C for 2 h using a heating rate 2 °C/min.

### 2.4. Decoration of Au nanoparticles on the 3DOM $TiO_2$

AuNPs was prepared by using citrate reduction of $HAuCl_4$ in water. ($10^{-2}$ g/L) $HAuCl_4$ aqueous solution was heated to 110 °C and 0.5 g 3DOM $TiO_2$ was immersed into the $HAuCl_4$ aqueous solution rigorous stirring for 0.5 h. Trisodium citrate aqueous solution (1.5 mL 10 g/L) was added to the flask and another 1.5 mL was added after 15 min. The mixture was stirred for 1 h under 110 °C and cooled down to room temperature. The dark purple 3DOM $TiO_2$-Au was obtained after filtering the mixture.

### 2.5. Fabrication of 3DOM $TiO_2$-Au-CdS

3DOM $TiO_2$-Au-CdS sample was prepared by chemical bath deposition (CBD) method. 3DOM $TiO_2$-Au sample was dipped in a 0.05 M $Cd(NO_3)_2$ aqueous solution rigorous stirring for 0.5 h and then 0.05 M $Na_2S$ aqueous solution was added. 3DOM $TiO_2$-Au-CdS was obtained after filtration and washed with DI water.

### 2.6. Characterization

The sample morphology and structure of the 3DOM were observed with a field-emission scanning electron microscope (SEM, Hitachi S-4800) with an energy-dispersive X-ray (EDX) analysis