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Controllable synthesis of Au-TiO₂ nanodumbbell photocatalysts with spatial redox region

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ABSTRACT

Photocatalytic water splitting has increasingly attracted attention as one of the most useful methods of converting solar energy into chemical fuel. However, the undesirable reverse reaction significantly limits the enhancement of efficiency. Herein, we fabricated an Au nanorods/TiO₂ nanodumbbells structure photocatalyst (Au NRs/TiO₂ NDs) via a facile synthetic strategy, which has spatially separated oxidation and reduction reaction zones. Owing to the unique structure, the charge separation of these photocatalysts can be significantly improved and the reverse reaction can be efficiently inhibited. The photogenerated electrons were injected from the TiO₂ to the Au NRs, and a positively charged TiO₂ region and negatively charged Au region were formed under UV irradiation. An enhanced hydrogen production performance was obtained compared with that seen in normal Au-TiO₂ heterostructure. Under optimized conditions, the H₂-production rate can reach up to 60,264 μmol/g/h, about six times higher than previously reported Au/TiO₂ photocatalysts. Besides this, our work also demonstrates the key factors of precise synthesis of the Au NRs/TiO₂ NDs structure, which provides a new perspective and experience for the design of similar catalysts.

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1. Introduction

Solar energy is considered one of the most ideal energy resources as it is clean and abundant [1–3]. Among the various solar energy collection technologies, photocatalysis water splitting is a widely used strategy to convert solar energy to chemical energy [4]. Unfortunately, most single photocatalysts exhibit low H₂-evolution activity, which severely limits their practical applications [5]. In this regard, many reports have used a simple and effective strategy of loading the cocatalyst to improve

catalytic efficiency [6–11]. However, the undesirable reverse reaction of H₂ and O₂ in the photocatalytic water splitting process significantly reduces efficiency and requires rigorous high-cost gas separation in practical applications [12,13]. Therefore, it is of significance to find a way to suppress the reverse reaction while effectively catalyzing the splitting of water [14].

Previous studies have made considerable efforts to solve the aforementioned problems. For example, in GaN nanowires with Rh/Cr₂O₃ core-shell nanostructures the Cr₂O₃ shell prevents

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the O_2 from reaching the hydrogen production site, thus preventing the reverse reaction [15]. Interestingly, a GaN:ZnO photocatalyst with pre-chemisorbed CO on metal co-catalysts (Rh, Pt, Pd) can enhance H_2 production by hindering the reverse reaction [16]. A Pt-TiO₂ photocatalyst with pre-adsorbed halogen atoms can suppress the reverse reaction by hindering the adsorption and activation of H_2 and O_2 molecules [14]. At present, one-dimensional (1D) hybrid nanostructure photocatalysts are considered one of the most effective strategies to suppress the reverse reaction because of their directional separation of photogenerated charges instead of random flow of photogenerated electron-hole pairs [17–19]. Recently, dumbbell-like nanostructures such as Au-SiO₂ [20,21], Au-Fe₃O₄ [22], Cu_{1.94}S-CuS [23], Au-PbS (PbSe) [24], Cu-Ag [25], and Ag-Fe₃O₄ [26] have been synthesized by different methods [27]. However, the above studies on synthesis conditions of dumbbell-like nanostructure materials are relatively complicated, and the growth mechanism is not clear.

In this study, we develop a wet-chemistry method for the fabrication of Au nanorods/TiO₂ nanodumbbells (Au NRs/TiO₂ NDs) structure photocatalysts. The TiO₂ nanoparticles (NPs) are anchored at two ends of the Au NRs. This structure can achieve directional separation of electron-hole pairs and reduce their recombination under light irradiation. Simultaneously, the spatially separated areas of oxidation and reduction reaction are formed and the reverse reaction is efficiently inhibited. More importantly, a mechanism of precious synthesis of Au NRs/TiO₂ NDs structure photocatalysts is successfully obtained.

2. Experimental

2.1. Reagents

In the experiment, all chemical reagents were of analytical grade. Hexadecyltrimethylammoniumbromide (C₁₆TAB) was ordered from AMERCO. Methanol (CH₃OH), chloroauric acid (HAuCl₄·3H₂O), and titanium (III) chloride solution (TiCl₃) were purchased from Beijing Sinopharm Chemical Reagent Co., Ltd. Sodium borohydride (NaBH₄) and L-ascorbic acid (AA) were purchased from Alfa Aesar. Sodium bicarbonate (NaHCO₃) was ordered from Beijing Chemical Works.

2.2. Preparation of gold seeds

Au NRs were prepared via a seed-mediated method. C₁₆TAB capped Au seeds were synthesized through chemical reduction of HAuCl₄ with NaBH₄. First, 100 μ L of Haulm (24 mM) was mixed with 7.5 mL of C₁₆TAB (0.1 M) aqueous solution. Next, 0.6 mL of ice-cold Nash (0.01 M) was added with magnetic stirring. After 3 min, the stirring was stopped and the seed solution was kept undisturbed at 30 °C for the next step. The seeds were effective within 2–5 h after the experiment.

2.3. Preparation of Au NRs with localized surface plasmon resonance (LSPR) at 720 nm

The growth solution of the Au NRs was made up of C₁₆TAB (0.1 M, 100 mL), HAuCl₄ (25.5 M, 1.96 mL), AgNO₃ (0.01 M, 1.1 mL) and AA (0.1 M, 0.55 mL). To encourage growth of the Au NRs, 120 μ L of seed solution was added to the above growth solution. After 12 h, the Au NRs with LSPR at 720 nm were synthesized by adding 55 μ L of 0.1 M AA. The AA was added twice every 30 min. Silver nitrate and AA were used to regulate the diameter and length of the Au nanorod by adjusting the surface properties of the Au NRs and removed by centrifugation after the reaction. Next, 30 mL of Au NRs solution was extracted and separated by centrifuging at 9700 rpm for 7 min. Finally, it was dispersed into 5 mL of deionized water as the stock solution.

2.4. Preparation of Au NRs/TiO₂ NDs structure photocatalysts

First, 200 μ L stock solution was extracted from a centrifuge tube and added to 3.8 mL of H₂O. These were separated by centrifugation at 12,000 rpm for 10 min. Then, 3.8 mL of the supernatant was extracted and the precipitated Au NRs was added with 1 mL of H₂O. Next, 100 μ L of 15%–20% TiCl₃ was diluted with 4 mL of H₂O. To control the hydrolysis degree of TiCl₃ and obtain different amounts of TiO₂, a different volume of NaHCO₃ solution (1 M) was added into the reaction solution dropwise with stirring. Then, the Au NRs solution was immediately injected. The mixed solution was stirred at room temperature for 30 min and a series of Au NRs/TiO₂ NDs with different TiO₂ weights were obtained. As the concentration of NaHCO₃ increases, the catalysts can be changed from nanodumbbell structure to core-shell structure. Finally, the prepared Au NRs/TiO₂ NDs structure photocatalysts were washed twice with ethanol. The prepared Au NRs/TiO₂ NDs structure photocatalysts were re-dispersed in ethanol for the next step.

2.5. Photocatalytic H₂ production activity measurements

The Au NRs/TiO₂ NDs structure photocatalysts kept in ethanol were washed twice with deionized water, and then dispersed in water. In a representative photocatalytic H₂-production test, a moderate solution was extracted separately from five centrifuge tubes containing different structure catalyst solutions. The weights of Au NRs in the obtained samples were measured by inductively coupled plasma mass spectrometry (ICP-MS) and UV-visible spectroscopy (UV-vis) (see the Supporting Information, Table S1). As the weight of TiO₂ increases, the five obtained samples with different structures are named (a)–(e) correspondingly, and their morphologies are shown in Figs. 4(a)–4(e). To evaluate their photocatalytic efficiencies, samples with the same Au weight (30 μ g) are used. Quantitative Au NRs/TiO₂ NDs photocatalyst solution was placed in the reactor and diluted to 10 mL by water. Next, a volume fraction of 20% methanol was added, sealed with a rubber stopper and deaerated with argon gas for 30 min. An Hg lamp (500 W) was used as the irradiation source, and the H₂ production efficiencies were measured after 5 h of light irradiation. The amount of hydrogen produced was determined by Tianmei gas chromatography (7900) with a thermal conductiv-

ity detector (TCD), 5Å molecular sieve columns, and an Ar carrier.

3. Results and discussion

3.1. Precious control of morphology of the Au NRs/TiO₂ NDs photocatalysts

The Au NRs with aspect ratio 3 were used as matrix (Fig. S1). The morphologies of the Au NRs/TiO₂ NDs photocatalysts were confirmed by scanning electron microscopy (SEM) (Fig. S2) and transmission electron microscopy (TEM) images (Fig. 1(a)). The TiO₂ nanoparticles were loaded selectively on the ends of the Au NRs by finely controlling the coating dynamics, and all the nanoparticles were in a good monodisperse state (Fig. 1(a) and Fig. S2). The high-resolution TEM (HRTEM) image demonstrates the close surface contact between the Au and TiO₂ nanoparticles (Fig. 1(b)). The lattice spacings of 0.20 nm correspond to the (200) plane of metallic Au, and the absence of lattice spacings of TiO₂ indicates its amorphous structure. The X-ray powder diffraction (XRD) results show five sharp diffraction peaks belonging to the crystallographic Au NRs, and no apparent TiO₂ diffraction peak is observed, which further confirms the amorphous structure of the TiO₂ nanoparticles (Fig. S3). The uniform distribution of each element (Au, Ti, O) can be distinctly seen from the energy-dispersive X-ray spectroscopy HRTEM (EDS-HRTEM) image (Figs. 1(c)–1(g)). The UV–vis extinction spectrum of bare Au NRs displayed two LSPR bands at 728 and 512 nm, corresponding to their longitudinal and transverse modes, respectively (Fig. 1(h)) [28]. After the coating of TiO₂ at the ends of the Au NRs, the longitudinal surface plasmon resonance (SPR) band of Au NRs/TiO₂ NDs photocatalysts was found to increase to 785 nm, demonstrating the effect of the TiO₂ coating with a higher refractive index on the longitudinal modes of the Au NRs [17]. However, the transverse SPR band barely changed. Simultaneously, it was shown that the absorbance of the Au NRs/TiO₂ NDs photocatalysts in the

UV region had been enhanced. To elucidate the valence states of each element, X-ray photoelectron spectroscopy (XPS) was introduced and the presence of Au, Ti and O could be clearly confirmed (Fig. S4). The spectra show two peaks located at 83.2 and 86.8 eV, indicating the Au element in the Au NRs/TiO₂ NDs photocatalysts was in metallic nature. The binding energies of the 2p orbital of the Ti component are at 458.5 and 464.2 eV, respectively, which indicates that the Ti component is positive and tetravalent. The 1s orbital of asymmetric O was fitted to two characteristic peaks with binding energies of 530.0 and 531.5 eV. The characteristic peak at 530.0 eV belongs to the Ti–O bond, and the other characteristic peak at 531.5 eV belongs to the hydroxyl oxygen formed after adsorbing water molecules on the surface of TiO₂. Moreover, compared with the XPS results of pure Au rods and pure amorphous TiO₂ NPs, the valence states of Au, Ti and O in Au NRs/TiO₂ NDs photocatalysts did not change. It is speculated that there is not a strong chemical force at the interface between Au and TiO₂ [29].

It is well known that the optical, electronic, and catalytic properties of photocatalysts are strongly dependent on their morphologies [30]. In this case, we first explored the controllable synthesis processes of Au NRs/TiO₂ NDs structure photocatalysts.

The SEM images of Au NRs/TiO₂ NDs photocatalysts obtained at different reaction times are shown in Figs. 2(a)–2(c). We can see that the sizes of the TiO₂ NPs at the ends of the Au NRs remain unchanged with increasing reaction time. Correspondingly, the UV–vis absorption spectra of the Au NRs/TiO₂ NDs photocatalysts obtained at 60 and 90 min did not red-shift, compared with the sample obtained at 30 min. It is shown that the nucleation growth rate of TiO₂ NPs on the surface of Au NRs is faster. The entire growth process of the Au NRs/TiO₂ NDs photocatalysts can be completed within 30 min [31].

Similarly, we have also investigated other multiple-reaction conditions and obtained two key factors which can precisely control the growth process of TiO₂ on the ends of Au NRs.

The temperature has a very important effect on the mor-

Fig. 1. Transmission electron microscopy (TEM) images (a), high-resolution TEM (HRTEM) images (b), and energy-dispersive X-ray spectroscopy HRTEM (EDS-HRTEM) elemental maps (c–g) of Au NRs/TiO₂ NDs photocatalysts; (h) UV–vis extinction spectra of bare Au NRs (red line) and Au NRs/TiO₂ NDs photocatalysts (purple line).

Fig. 2. SEM images of Au NRs/TiO₂ NDs photocatalysts with increasing reaction times. (a) 30 min; (b) 60 min; (c) 90 min. (d) UV-vis extinction spectra of Au NRs (red line) and Au NRs/TiO₂ NDs photocatalysts (from 30 to 90 min) in water.

phologies of Au NRs/TiO₂ NDs photocatalysts. As shown in Figs. 3(a)–3(d), the coating thickness of TiO₂ on the Au NRs gradually increased as a result of the temperature increase. The Au NRs were almost completely covered with TiO₂ at 50 °C, and a core-shell structure was formed. Similarly, the absorption

Fig. 3. SEM images (a–d) and UV-vis extinction spectra (e) of Au NRs/TiO₂ NDs photocatalysts with different reaction temperatures in water. (a) 25 °C; (b) 30 °C; (c) 40 °C; (d) 50 °C.

peaks of Au NRs/TiO₂ NDs photocatalysts regularly red-shifted as the reaction temperature increased. The influence is indirectly realized through its influence on C₁₆TAB. The C₁₆TAB state is significantly affected by temperature [32]. The adsorption of C₁₆TAB on Au NRs is an example of Langmuir isotherm adsorption [33]. The C₁₆TAB molecules are in dynamic equilibrium of adsorption and desorption at a specific temperature. They can easily desorb from the Au NRs at a higher or lower temperature [34]. Therefore, the surfaces of Au NRs tend to be covered by more TiO₂ NPs to form the core-shell structure.

Another key factor affecting the morphology of Au NRs/TiO₂ NDs structure photocatalysts is acidity in the system. The TiCl₃ hydrolyzes to form an acidic environment during the formation of TiO₂ ($\text{Ti}^{3+} + 2\text{H}_2\text{O} = 0.5\text{H}_2 + 3\text{H}^+ + \text{TiO}_2$). When the acidity reaches a certain limit, it will inhibit the hydrolysis of TiCl₃. The degree of hydrolysis of TiCl₃ can be regulated by adding NaHCO₃. The OH⁻ ions from the NaHCO₃ aqueous solution react with the H⁺ from the hydrolysis process of TiCl₃. Thus, the addition of NaHCO₃ promotes the hydrolysis of TiCl₃. Thereby, we obtained a series of dumbbell-like structure photocatalysts with different TiO₂ amounts by changing the amount of NaHCO₃ (shown in Figs. 4(a)–4(e)). As the concentration of NaHCO₃ increases, the deposition of TiO₂ NPs on the ends of the Au NRs gradually increases until the core-shell structure is formed. As shown in the UV-vis absorption spectrum in Fig. 4(f), the red shift of the absorption peak of Au NRs/TiO₂ NDs structure photocatalysts (in Fig. (5)) increases with the in-

Fig. 4. SEM images of Au NRs/TiO₂ NDs photocatalysts with increasing amount of NaHCO₃. (a) 450 μL; (b) 480 μL; (c) 510 μL; (d) 540 μL; (e) 570 μL. (f) UV-vis extinction spectra of Au NRs (red line) and Au NRs/TiO₂ NDs photocatalysts from a–e in water.

Fig. 5. Key factors of morphological control of the Au NRs/TiO₂ NDs photocatalysts.

crease in TiO₂ head sizes. Therefore, a series of Au NRs/TiO₂ NDs structure photocatalysts with different spectral response ranges were synthesized, which can extend this structure in other application fields. In addition, XRD did not change for different Au NRs/TiO₂ NDs photocatalysts obtained under various conditions (Fig. S5), which further confirms that the TiO₂ in the photocatalysts is amorphous.

We propose a fundamental mechanism for the growth of Au NRs/TiO₂ NDs structure photocatalysts (Fig. (5)). The C₁₆TAB molecules are adsorbed less on the heads of Au NRs than on the sides, when the concentration of C₁₆TAB is controlled within a suitable range [35]. Due to the larger curvature and the weaker molecular resistance of the heads of Au NRs, Ti³⁺ ions make easier contact with the heads. Then, the Ti³⁺ ions are oxidized by water to amorphous TiO₂ NPs [36]. Meanwhile, the TiO₂ NPs exhibit a porous morphology due to the H₂ bubbles generated during the reaction [37]. The key factors controlling the head sizes of the Au NRs/TiO₂ NDs photocatalysts are reaction temperature and acidity, according to the above experimental results. When the reaction temperature or the acidity of the system are at the optimum conditions, Au NRs/TiO₂ NDs structure photocatalysts are formed.

3.2. Water-splitting reactivity of the Au NRs/TiO₂ NDs photocatalysts

We have evaluated the hydrogen production performance of the Au NRs/TiO₂ NDs photocatalysts by using methanol as the sacrificial agent. Under UV irradiation, TiO₂ is stimulated into generating charge carriers. The electrons in the conduction band of TiO₂ are transferred to the Au NRs due to the lower Fermi level of Au NRs. As a result, the individual positively charged TiO₂ region and negatively charged Au NRs region are formed. Thus, the oxidation and reduction reactions are produced on the sides of Au NRs and tips of coated TiO₂ NPs, respectively, and the reverse reaction of water splitting can be inhibited significantly. Therefore, the Au NRs/TiO₂ NDs structure photocatalysts have excellent hydrogen production per-

formance. From Fig. 6(a), it can be seen that sample d demonstrates the best hydrogen production rate of 60,264.2 μmol/g/h (AQY 0.63% at 315 nm), which is about six times higher than that for previously reported Au/TiO₂ photocatalysts [38].

It is widely accepted that the oxidation half-reaction of water splitting is the rate-limiting step. In this work, the oxidation reaction takes place on the TiO₂ part under UV light irradiation. Therefore, the larger the size of the TiO₂ attached to the heads of the Au NRs, the more favorably the oxidation reaction will proceed. However, the core-shell structure is unfavorable for hydrogen diffusion and charge-carrier separation. As a result, the activity of sample e is the lowest of the samples. The photogenerated charge separation and transfer properties are further explored by transient photocurrent responses [39]. As shown in Fig. 6(b), sample d exhibited the highest photocurrent compared with the other four structures. Therefore, it is speculated that its structure may achieve the most efficient charge separation, which is consistent with the photocatalytic activity measurement [40,41]. Nyquist plots of electrochemical impedance spectra further confirm that the charge transfer resistance of sample d was lower than those of the other four samples (Fig. S6) [42]. Thus, it can be concluded that the structure of sample d favors charge separation and transfer, leading to a much higher H₂-production efficiency. The photocatalytic mechanism is shown in Fig. 6(c). Our previous work has confirmed that under full-spectrum light irradiation, the photogenerated electrons transferred from TiO₂ to Au. Therefore, the Au NRs acted as a H₂-production reaction site and the SPR effect of Au does not work in such a case [17]. Under Hg lamp light irradiation, TiO₂ NPs were stimulated into generating electrons and holes. Then, the photogenerated electrons were transferred to Au NRs due to the lower Fermi level of Au, and so a positively charged TiO₂ region and negatively charged Au region were formed, which correspond to the oxidation and reduction region, respectively.

To demonstrate the potential practical application value, a photocatalytic stability experiment was carried out. As depicted

Fig. 6. (a) Hydrogen production activity of the Au NRs/TiO₂ NDs photocatalysts for different samples (the used samples a–e correspond to samples a–e in Figs. 4a–4e; all the photocatalysts contain the same Au NRs weight of 30 μg); (b) photocurrent responses of the Au NRs/TiO₂ NDs photocatalysts with different TiO₂ contents; (c) schematic of the mechanism for photocatalytic water splitting; (d) stability evaluation of Au NRs/TiO₂ NDs photocatalysts for H₂ production.

ed in Fig. 6(d), the photocatalytic hydrogen evolution activity can be sustained for more than 20 h. XRD and TEM results indicate the catalysts do not obviously change after the stability test, and confirm that the obtained catalyst is durable under the photocatalytic reaction conditions (Fig. S7).

4. Conclusions

In summary, we synthesized a series of one-dimensional Au NRs/TiO₂ NDs structure photocatalysts with spatially separated oxidation and reduction reaction areas, and we studied the key factors that affect the morphology of this structure. The reaction temperature and acidity significantly affect the anchored amount of TiO₂ on the ends of Au NRs. By accurately adjusting the amount of TiO₂, we gradually improved the hydrogen production reactivity of the Au NRs/TiO₂ NDs photocatalysts.

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Graphical Abstract

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Controllable synthesis of Au-TiO₂ nanodumbbell photocatalysts with spatial redox region

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We report the key factors of precise synthesis of Au NRs/TiO₂ NDs structure photocatalysts, which have spatially separated oxidation and reduction reaction zones, and we synthesized a series of one-dimensional Au NRs/TiO₂ NDs structure photocatalysts.

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可控合成具有氧化还原分区的Au-TiO₂纳米哑铃光催化剂

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摘要: 太阳能因其环保清洁和来源丰富的特性被认为是最理想的资源之一。而光催化水分解是将太阳能转化为化学能的众多转换技术中, 使用最广泛的策略之一。但H₂和O₂的逆反应显著降低了光催化水分解的效率, 并且在实际应用中需要高昂的气体分离成本。因此, 找到一种既可实现光催化有效水分解, 同时抑制逆反应的策略具有十分重要的意义。

到目前为止, 为了实现光生电荷的有效分离, 构建一维(1D)异质纳米结构光催化剂, 被认为是抑制逆反应最有效的策略之一。其中哑铃状纳米结构, 如Au-SiO₂, Au-Fe₃O₄, Cu_{1.94}S-CuS, Au-PbS(PbSe), Cu-Ag, Ag-Fe₃O₄, 在促进光生电荷有效分离方面具有很大优势。但关于上述哑铃状纳米结构材料合成条件相对复杂, 生长机理尚不清楚。对此, 我们通过一种简便的合成策略制备了Au纳米棒/TiO₂纳米哑铃结构光催化剂(Au NRs/TiO₂ NDs)。TiO₂纳米颗粒(NP)仅包裹在Au NRs的两端。由于其独特的结构, 可以实现电子空穴的定向分离, 并减少它们在光照射下的复合, 从而显著地提高电荷分离效率。同时,

形成了氧化和还原反应的空间分离区域,从而有效地抑制了逆反应.

通过SEM, XRD, 和UV-Vis研究了可控合成哑铃状结构形态的关键因素. 发现反应温度和酸度对Au NRs末端TiO₂的包裹量有显著影响. 基于此, 我们提出了Au NRs/TiO₂ NDs结构光催化剂的合成机理. 并且通过改变加入的NaHCO₃含量精准调节TiO₂在Au NRs两端的包裹量, 从而逐步提高Au NRs/TiO₂ NDs光催化剂的产氢活性. 在不断优化条件下, H₂产率可达60264 μmol/g/h, 大约是报道的Au/TiO₂光催化剂6倍. 而电化学测试结果显示, 在UV光照射下, Au NRs末端TiO₂的包裹量越大, 光电流相应越大. 进一步证明光生电子定向从TiO₂注入到Au NRs中, 发生还原反应, 而空穴留在TiO₂上, 发生氧化反应, 从而实现氧化还原反应的分区.

关键词: Au纳米棒; 哑铃结构; 光催化水分解; 可控合成

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