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Article

Decorating non-noble metal plasmonic Al on a TiO₂/Cu₂O photoanode to boost performance in photoelectrochemical water splitting

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ARTICLE INFO

Article history:

Received 13 March 2020

Accepted 21 April 2020

Published 5 December 2020

Keywords:

TiO₂

Photoanode

Non-noble metal Al

Surface plasmon resonance

Photoelectrochemical water splitting

ABSTRACT

Designing low-cost and high-performance photoelectrodes with improved light harvesting and charge separation rates is significant in photoelectrochemical water splitting. Here, a novel TiO₂/Cu₂O/Al/Al₂O₃ photoelectrode is manufactured by depositing plasmonic nanoparticles of the non-noble metal Al on the surface of a TiO₂/Cu₂O core/shell heterojunction for the first time. The Al nanoparticles, which exhibit a surface plasmon resonance (SPR) effect and are substantially less expensive than noble metals such as Au and Ag, generate hot electron-hole pairs and amplify the electromagnetic field at the interface under illumination. The as-prepared TiO₂/Cu₂O/Al/Al₂O₃ photoelectrodes have an extended absorption range and enhanced carrier separation and transfer. Their photocurrent density of 4.52 mA·cm⁻² at 1.23 V vs. RHE represents an 1.84-fold improvement over that of TiO₂/Cu₂O. Specifically, the ultrathin Al₂O₃ passivation layer spontaneously generated on the surface of Al in air could act as a protective layer to significantly increase its stability. In this work, the synergistic effect of the heterojunctions and the SPR effect of the non-noble metal Al significantly improve the photoelectrode performance, providing a novel concept for the design of electrodes with good properties and high practicability.

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1. Introduction

Photoelectrochemical (PEC) water splitting can produce oxygen and hydrogen using semiconductor nanomaterials, making it an ideal solution to the energy and environmental crisis. Since TiO₂ was used as a PEC material for splitting water to produce hydrogen by Fujishima et al. [1] in 1972, many materials (such as ZnO [2], Fe₂O₃ [3], WO₃ [4], Cu₂O [5], and CuInS₂ [6]) have been demonstrated to be suitable for PEC water splitting. For decades, seeking and devising suitable semiconductor photoelectrocatalysts with high efficiency light absorption,

charge separation, and utilization to acquire high catalytic efficiency has been the core of the research [7].

Titanium dioxide (TiO₂), an n-type semiconductor, has been investigated extensively due to its appropriate conduction band (CB) and valence band (VB) positions for water splitting, favorable photocorrosion resistance, nontoxicity, and excellent stability. Nevertheless, its wide band gap, narrow spectrum response, high photogenerated carrier recombination rate, and short hole diffusion length have limited the application and development of TiO₂ photoelectrodes in PEC water splitting [8]. To improve the performance of TiO₂, a variety of methods have

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This work was supported by the Science Funds of Tianjin for Distinguished Young Scholar (17JCJQC44800) and Key Research and Development Plan of Tianjin (19YFSLQY00020).

DOI: 10.1016/S1872-2067(20)63637-3 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 41, No. 12, December 2020

been developed, including ion doping [9], heterojunction construction [10], and coupling with a cocatalyst [11]. For example, Liu et al. [12] reported a novel two-dimensional (2D) ZnIn_2S_4 nanosheet/one-dimensional (1D) TiO_2 nanorod heterostructure in which the gradient energy level and built-in electric field led to reduced separation of electron-hole pairs and improved charge separation efficiency, which greatly improved its performance in PEC water splitting. A number of coupled semiconductor structures incorporating TiO_2 , including $\text{TiO}_2/\text{CdS}/\text{Co-Pi}$ [13], TiO_2/CdTe [14], $\text{TiO}_2/\text{BiVO}_4$ [10], and $\text{TiO}_2/\text{TiSi}_2$ [15], have been developed to improve catalytic performance. Cuprous oxide (Cu_2O) is an attractive p-type metal oxide semiconductor material with many desirable characteristics, including nontoxicity and abundant reserves [16,17]. More importantly, owing to its direct narrow band gap and appropriate CB and VB positions, when TiO_2 is coupled with Cu_2O , its absorption range in the visible spectrum is expanded, and a built-in electric field is formed at the interface, which strongly benefits its light absorption and charge separation [18,19]. Ma et al. [20] reported the preparation of a $\text{ZnO}/\text{Cu}_2\text{O}$ photoelectrode for PEC water splitting. Efficient PEC performance was found to be obtained after coupling Cu_2O with ZnO because of the enhanced light absorption and photogenerated carrier separation.

Recently, loading a cocatalyst to accelerate the transfer of carriers and reduce the recombination of photogenerated electron-hole pairs has been attracting increasing attention [21]. Additionally, the SPR character of noble metals such as Au and Ag not only provides excellent light-trapping properties and electromagnetic-field concentrating performance, but also generates hot electrons to directly convert light energy into electrical energy [22]. When such metals are combined with a semiconductor, a metal-semiconductor Schottky junction will be produced [23]. For example, Pu et al. [11] took full advantage of the SPR of Au by depositing various morphologies of Au on a TiO_2 substrate to enhance its PEC water oxidation properties. Due to the effective passivation of the Au nanoparticle surfaces, the photoactivity of the catalyst showed intensification in the UV region. Chaudhary et al. [24] utilized SPR Au nanoparticles as a photosensitizer on the surface of a CNT/TiO_2 photoanode to strongly increase its light absorption and carrier density. Compared to the noble metals Au and Ag, Al not only stimulates an intense SPR effect over most of the visible region, which could amplify the electromagnetic field and generate hot electrons [25], but is also much less expensive, making it an excellent material for enhancing electrode properties. However, until now, few reports regarding the use of Al in PEC water splitting have been published [26,27].

In this work, we synthesize a $\text{TiO}_2/\text{Cu}_2\text{O}$ core/shell heterojunction, and then utilize the non-noble metal Al to decorate the $\text{TiO}_2/\text{Cu}_2\text{O}$ structure for the first time to further improve the PEC properties of TiO_2 . Many hot electrons are generated due to the SPR effect of Al under light excitation, and charge separation is promoted by the heterojunction and amplified electromagnetic field. Remarkably, the Al_2O_3 ultrathin passivation layer spontaneously generated on the surface of Al in air efficiently improves the stability of $\text{TiO}_2/\text{Cu}_2\text{O}$ and retards the

recombination of carriers. Thus, the PEC activity of the TiO_2 photoanode is enhanced. The present study provides a promising approach to develop ideal photoelectrodes by combining the positive effects of a cocatalyst and heterojunctions.

2. Experimental

2.1. Preparation of rutile TiO_2 nanorods (NRs)

Rutile TiO_2 NRs were prepared by a reformative hydrothermal method on the surface of fluorine-doped tin oxide (FTO) glass substrates as reported elsewhere [28]. In this experiment, 5 mL concentrated hydrochloric acid (37 wt%) was diluted with 10 mL deionized (DI) water. 0.15 mL of tetrabutyl orthotitanate was then added to the mixture, which was magnetically stirred constantly for 20 min. The mixture was then poured into a 25 mL Teflon-lined stainless-steel autoclave containing a piece of FTO placed against the inner wall with the conducting surface downward; the system was maintained at 180 °C for 24 h in an oven. The substrate was flushed with DI water, dried in the atmosphere at 60 °C, and annealed at 500 °C under air for 1 h in a muffle.

2.2. Preparation of Cu_2O nanoparticles (NPs)

The Cu_2O NPs were manufactured through an electrodeposition method on FTO/ TiO_2 substrates to form a $\text{TiO}_2/\text{Cu}_2\text{O}$ core-shell nanostructure. First, the chelating agent, lactic acid ($\text{C}_3\text{H}_6\text{O}_3$, 3.00 M), was added to a copper sulfate solution (CuSO_4 , 0.48 M) and stirred well. The temperature of the solution was maintained at 35 °C, and its pH was adjusted to 10 using sodium hydroxide solution (NaOH , 10 M) to avoid generating n-type Cu_2O [29]. The FTO/ TiO_2 substrates were used as the working electrode in a three-electrode system to induce the deposition of Cu_2O at -0.5 V vs. Ag/AgCl under cathodic reduction for 60–120 s.

2.3. Deposition of Al NPs

The Al NPs were prepared by the magnetron sputtering method on the FTO/ $\text{TiO}_2/\text{Cu}_2\text{O}$ substrate with a plasma current I of 2.5 A and a substrate temperature of 33 °C (RT). The thickness of the deposited Al layers was regulated to 10, 20, or 30 nm. Moreover, an ultrathin Al_2O_3 layer is formed on the surface of Al in air.

2.4. Characterization

Scanning electron microscopy (SEM, JEOL JSM-7800F) and transmission electron microscopy (TEM, JEOL JEM-2100) were used to determine the morphology and crystallinity of the samples. X-ray diffraction (XRD, Rigaku-D/max-2500; $\text{Cu } K_\alpha$ radiation; 40 kV; 150 mA) was utilized to further understand the crystalline structures, and energy dispersive spectra (EDS, AZtec from Oxford) were used to obtain the elemental mapping of the samples. UV-vis absorbance was measured using a DU-8B UV-Vis double-beam spectrophotometer, and surface photo-

voltage (SPV) was measured using a surface photovoltage spectrometer (PL-SPS/IPCE1000) system that included a sample chamber, monochromatic light source, and lock-in amplifier (SR830) with a light chopper (SR540). The formation of elements was analyzed by X-ray photoelectron spectroscopy (XPS) using a Thermo ESCALAB 250XI system. The potentials of the VB edges and the work function were estimated using ultraviolet photoelectron spectroscopy (UPS) with a Thermo Fisher ESCALAB 250XI system.

PEC performance was evaluated using a three-electrode system that included the sample, a platinum foil, and Ag/AgCl as the working electrode, counter electrode, and reference electrode, respectively; the electrolyte was 0.1 M Na₂SO₄. The PEC measurements were obtained using a LK2005A workstation. The electrochemical impedance spectra (EIS) and Mott-Schottky (M-S) plots were obtained using a 10 mV AC voltage amplitude. Illumination was provided by a solar simulator with an AM 1.5G filter (CHF-XM500, 100 mW/cm²) during the PEC performance experiments. The potentials were converted to the reversible hydrogen electrode (RHE) scale using the equation [30] $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{ pH} + 0.1976 \text{ V}$ unless otherwise specified. H₂ evolution was measured using a gas chromatograph (GC-7900, TCD detector) with irradiation.

3. Results and discussion

Fig. 1 shows the preparation process of the TiO₂/Cu₂O/Al/Al₂O₃ photoanode. First, TiO₂ NRs were grown on FTO by a hydrothermal method, after which Cu₂O NPs were manufactured on the TiO₂ substrate via an electrodeposition method with a deposition time of 90 s to form the TiO₂/Cu₂O core/shell nanostructure; in this method, the deposition time can be adjusted to control the thickness of the layer. Finally, an Al layer with a thickness of 20 nm was prepared through magnetron sputtering. The SPR effect of Al stimulated by light could improve the PEC performance in water splitting, and the thickness of the Al layers could be adjusted accurately using a film thickness monitoring system. An ultrathin Al₂O₃ layer is naturally formed in air on the surface of the Al layer.

For preliminary observation of the morphological characteristics of the bare TiO₂, TiO₂/Cu₂O, and TiO₂/Cu₂O/Al/Al₂O₃ photoanode, SEM images of samples were obtained and are shown in Fig. 2. The vertically aligned bare TiO₂ NRs have a high density and a smooth surface (Fig. 2(a)), with diameters ranging from 80 to 120 nm and lengths of approximately 1.0 μm (Fig. 2(d)). After the deposition of the Cu₂O NPs, TiO₂/Cu₂O core/shell structure composites (Fig. 2(b)) with a rough surface morphology and highly convergent structures with increased diameters of approximately 30 nm were found. The

Fig. 1. Schematic diagram of the preparation process of TiO₂/Cu₂O/Al/Al₂O₃ photoanode.

Fig. 2. Top-view SEM images of bare TiO₂ (a), TiO₂/Cu₂O (b) and TiO₂/Cu₂O/Al/Al₂O₃ (c) photoanodes; (d) Cross-section SEM image of TiO₂/Cu₂O/Al/Al₂O₃ photoanode.

deposition of Al NPs further increased the diameter, but there was no apparent change at the surface (Fig. 2(c)). The low-magnification TEM and high-resolution TEM (HRTEM) images of the TiO₂/Cu₂O/Al/Al₂O₃ composite clearly indicate that the Cu₂O NPs developed evenly on the TiO₂ NRs to form a core/shell nanostructure with an average thickness of 17 nm (Fig. 3(a) and (b)). In the magnified selected area (Fig. 3(b)), the lattice fringes of 0.248, 0.246, and 0.231 nm correspond to the (101), (111), and (111) planes of TiO₂, Cu₂O, and Al, respectively. The amorphous ultrathin Al₂O₃ layer (approximately 2 nm) that formed naturally in air is demonstrated in Fig. 3(c). This layer not only acted as a passivation layer to prevent the further oxidation of Al, but also retarded the redox reaction of Cu₂O in the electrolyte. In addition, the selected area electron diffraction (SAED) image demonstrated that the TiO₂ NRs had a monoclinic rutile structure. The EDS spectrum and elemental mapping images in Fig. 3(d) and (e) further confirm the existence of the elements Ti, Cu, O, and Al.

The XRD patterns demonstrate the crystalline phase of the TiO₂/Cu₂O/Al/Al₂O₃ composite (Fig. 4) [31]. In addition to the SnO₂ diffraction peaks (JCPDS 77-0452) of the FTO substrate, the obvious diffraction peak of the (101) plane, marked with a “•”, indicates the preferential orientation of tetragonal rutile TiO₂ (JCPDS 03-1122). For TiO₂/Cu₂O, apparent new diffraction peaks corresponding to cubic Cu₂O marked with a “◆” (JCPDS 01-1142) at 2θ values of approximately 36.6° and 42.6° are observed, and the weak intensity (111) plane peak marked with “▼” (JCPDS 03-0932) observed after the deposition of Al demonstrates the low content of Al in the TiO₂/Cu₂O/Al/Al₂O₃ composite. XPS was used to further determine the composition of the composite and the valence states of its constituent elements (Fig. 5(a)–(e)). XPS is a surface analysis method and can only collect data around 3–5 nm from the surface, so only the elements O, Cu, Al, and C can be clearly observed (Fig. 5(a)). Fig. 5(b) shows the O 1s core-level spectrum with a peak at 531.46 eV. In Fig. 5(c), the Al 2p peak is split into two peaks located at binding energies of 74.27 and 72.92 eV, the former of which corresponds to the Al 2p_{3/2} of the ultrathin Al₂O₃ layer formed

Fig. 3. (a) TEM image. Bottom right inset: the SAED image of TiO₂ NRs; HRTEM images of (b) and (c) areas selected in (a). The insets in (b) are magnified images of corresponding selected areas. (d) EDS spectrum of TiO₂/Cu₂O/Al/Al₂O₃ photoanode. (e) SEM image and corresponding elemental mapping images of Ti, O, Cu and Al.

naturally in air, while the latter corresponds to metallic Al. The Cu 2*p* core exhibits two peaks at 952.72 and 932.62 eV (Fig. 5(d)), which are in agreement with the binding energies of Cu 2*p*_{3/2} and 2*p*_{1/2}, respectively, and thus demonstrate that the valence state of copper was Cu⁺. The Cu LMM Auger spectrum in Fig. 5(e) with a peak at 570.05 eV further corroborates that the NPs in sample consisted of Cu₂O rather than CuO or metallic Cu.

The optical characters of TiO₂, TiO₂/Cu₂O, and TiO₂/Cu₂O/Al/Al₂O₃ are reflected by their optical absorption spectra (Fig. 6(a)) [32]. The absorption edge of rutile TiO₂ appears at about 415 nm, which corresponds to a band gap of 3.09 eV (Fig. S1(a)); this value is close to the previously reported band gap width [33]. Due to the presence of the sub-bandgap states in TiO₂ [18], absorption maxima generated by trapped holes and electrons appear at about 430 and 640

nm, respectively. After combining TiO₂ with the narrow band gap ($E_g = 2.10$ eV, Fig. S1(c)) semiconductor Cu₂O, the absorption onset of TiO₂/Cu₂O is located at approximately 500 nm. Notably, compared to that of bare TiO₂, the curve of the TiO₂/Cu₂O core/shell nanostructure exhibits a significant red-shift and improved visible light absorption. After sputtering the plasmonic Al NPs onto TiO₂/Cu₂O, a notable improvement in visible absorption around 550 nm is observed compared to bare TiO₂ and TiO₂/Cu₂O, because the surface plasmas of Al absorbed the energy of the photons to resonate collectively at this visible wavelength, thus improving the PEC properties in water splitting dramatically. In order to prove that the Cu₂O NPs not only extended the spectral absorption range, but also formed heterojunctions when combined with the TiO₂ NRs, Mott-Schottky (M-S) plots were acquired at 1000 Hz with and without irradiation (Fig. 6(b)–(c)). The TiO₂ plots obtained with and without irradiation have positive slopes (Fig. 6(b)), while those of Cu₂O have negative slopes (Fig. S2). These results clearly demonstrate that TiO₂ was an electron-conduction-dominated n-type semiconductor and Cu₂O was a hole-conduction-dominated p-type semiconductor [34–36]. According to the equation $N_A = (2/e\epsilon_0\epsilon)[d(1/c^2)/dV]^{-1}$, where N_A represents the carrier concentration and e , ϵ_0 , and ϵ stand for the electron charge, the permittivity of a vacuum, and the dielectric constant of the material [37,38], the N_A value is inversely proportional to the slope for a given substance. Compared to the N_A value measured in the dark, the N_A of bare TiO₂ under illumination exhibits a slight increase (Fig. 6(b)), which demonstrates the violent recombination of photogenerated electrons and holes in TiO₂. The Mott-Schottky plots of TiO₂/Cu₂O display simultaneous n-type and p-type semiconductor behavior, and correspond to the typical “V-shaped” Mott-Schottky behavior of p–n heterojunctions [39]. Conspicuously, the carrier density of TiO₂/Cu₂O shows a dramatic im-

Fig. 4. XRD patterns of pristine TiO₂, TiO₂/Cu₂O and TiO₂/Cu₂O/Al/Al₂O₃ photoanodes. Bottom lines are standard peaks of TiO₂ (JCPDS 03-1122, blue solid), Cu₂O (JCPDS 01-1142, red solid) and Al (JCPDS 03-0932, magenta solid).

Fig. 5. (a) XPS survey spectrum of $\text{TiO}_2/\text{Cu}_2\text{O}/\text{Al}/\text{Al}_2\text{O}_3$ photoanode; High-resolution XPS spectra of O 1s (b), Al 2p (c) and Cu 2p (d); (e) The Cu LMM Auger spectrum.

Fig. 6. (a) UV-visible absorption spectrum of TiO_2 , $\text{TiO}_2/\text{Cu}_2\text{O}$ and $\text{TiO}_2/\text{Cu}_2\text{O}/\text{Al}/\text{Al}_2\text{O}_3$ photoanodes; Mott-Schottky plots of TiO_2 (b) and $\text{TiO}_2/\text{Cu}_2\text{O}$ (c) photoanodes with and without illumination.

provement under illumination (Fig. 6(c)), demonstrating that the electrons and holes are depleted in the depletion layer without illumination and separate efficiently under light because of the p-n junction. Thus, the Mott-Schottky results clearly demonstrated the presence of a built-in p-n electric field between the uniform, densely arranged TiO_2 NRs and the Cu_2O NPs, which effectively promotes charge separation and reduces the recombination of carriers.

To determine the PEC performance of the as-prepared photoanodes in PEC water splitting, current density-voltage curves were obtained with and without illumination (Fig. 7(a)). In the dark, the current densities of all the photoanodes are negative. The high carrier recombination rate of bare TiO_2 leads to a low photocurrent density ($0.76 \text{ mA}/\text{cm}^2$). Notably, after depositing the Cu_2O NPs to form the built-in electric field, typical anodic photocurrent density begins to be detected at 0.31 V vs. RHE. The photocurrent density of the $\text{TiO}_2/\text{Cu}_2\text{O}$ photoanode reaches $2.46 \text{ mA}/\text{cm}^2$, which is 3.24 times as high as that of bare TiO_2 , at 1.23 V vs. RHE. The photocurrent density-voltage curves of $\text{TiO}_2/\text{Cu}_2\text{O}$ photoanodes with different thicknesses of deposited Cu_2O layers indicate that the photocurrent density increased markedly with increasing deposition time, but began

to attenuate at 120 s (Fig. S3). This decay occurs because the increasing number of Cu_2O NPs begin to cover the majority of the TiO_2 NR surfaces as the coating time is increased, which may block photons from reaching the surface of TiO_2 NRs and thus suppress the production of photogenerated carriers. Additionally, the excessively thick Cu_2O layer leads to a decrease in the surface area of the TiO_2 NRs in direct contact with the electrolyte, thereby preventing water from being oxidized. These results show that an appropriate deposition time is necessary. However, the photocurrent densities of all the $\text{TiO}_2/\text{Cu}_2\text{O}$ samples are higher than that of bare TiO_2 , demonstrating that the p-n heterojunction could promote the separation and transfer of the photon-generated carriers. Dramatically, the current density of $\text{TiO}_2/\text{Cu}_2\text{O}/\text{Al}/\text{Al}_2\text{O}_3$ increases further to $4.52 \text{ mA}/\text{cm}^2$ at 1.23 V vs. RHE, which is 5.95 and 1.84 times greater than the photocurrents of TiO_2 and $\text{TiO}_2/\text{Cu}_2\text{O}$, respectively, thereby confirming the positive effects of the Al NPs on the photoelectric activity. Additionally, the photocurrent density-voltage curves of the photoanodes with different Al layer thicknesses are displayed in Fig. S4, in which the photoanode with a 20 nm Al layer demonstrates the highest current density. The enhanced activity of the $\text{TiO}_2/\text{Cu}_2\text{O}/\text{Al}/\text{Al}_2\text{O}_3$ photoanodes

Fig. 7. Current density-voltage with (solid line) and without (dash line) illumination (a), Applied bias photon-to-current efficiency (b), Photocurrent density-time curves (c), and incident photon-to-current conversion efficiency (d) measured at 1.23 V vs. RHE of TiO_2 , $\text{TiO}_2/\text{Cu}_2\text{O}$ and $\text{TiO}_2/\text{Cu}_2\text{O}/\text{Al}/\text{Al}_2\text{O}_3$ photoanodes. Top right inset: amplifying IPCE plots of samples with the wavelength from 480 to 660 nm.

was due to the photogenerated hot carriers and the intensification of the electromagnetic field caused by the SPR of the Al NPs. The synergistic effect of the p-n heterojunctions and the SPR of the Al NPs efficiently increased the carrier concentration and facilitated the separation of carriers, thus enhancing the photocurrent density.

The applied bias photon-to-current efficiency (ABPE) is used for the quantitative evaluation of PEC water splitting efficiency, and is determined using the following formula [40,41]:

$$\eta(\%) = J(1.23 - V)/P \times 100 \quad (1)$$

where J , V , and P represent the photocurrent density at the measured potential under irradiation, the applied bias versus the RHE, and the intensity of the incident light (100 mW/cm^2 , AM 1.5 G). Fig. 7(b) shows the relationship between the photoelectric conversion efficiency and the potential for the samples. The efficiency of $\text{TiO}_2/\text{Cu}_2\text{O}$ reaches 0.45%, which is 2.05 times that of TiO_2 (0.22%). Notably, the $\text{TiO}_2/\text{Cu}_2\text{O}/\text{Al}/\text{Al}_2\text{O}_3$ photoelectrode shows the highest photoconversion efficiency of 0.96% at 0.88 V vs. RHE, which is 4.36 and 2.13 times greater than that of TiO_2 and $\text{TiO}_2/\text{Cu}_2\text{O}$. The consequences are corresponding to Fig. 7(a).

To observe the light response properties of the samples, the photocurrent density-time curves of the bare TiO_2 , $\text{TiO}_2/\text{Cu}_2\text{O}$, and $\text{TiO}_2/\text{Cu}_2\text{O}/\text{Al}/\text{Al}_2\text{O}_3$ photoanodes were measured at 1.23 V vs. RHE with intermittent illumination and are shown in Fig. 7(c). All the photoanodes had favorable photoresponses during the test. No apparent photocurrent was observed for any of the photoanodes in the dark. Upon irradiation, the photocurrent of bare TiO_2 appears rapidly due to the photogenerated carriers.

The recombination of the photogenerated carriers then gives rise to the rapid decline in the photocurrent. Finally, the current becomes stable upon reaching a dynamic equilibrium between the separation and recombination of the photogenerated carriers [42–45]. Notably, the photocurrent density of the $\text{TiO}_2/\text{Cu}_2\text{O}$ photoanode is relatively more stable during illumination, confirming that the p-n heterojunction formed by the TiO_2 NRs and Cu_2O NPs is greatly beneficial to the separation of the photogenerated carriers. After the deposition of the Al NPs, the enhanced electromagnetic field reduced the carrier recombination, thus leading to a more stable photocurrent under illumination. The photocurrent densities of TiO_2 , $\text{TiO}_2/\text{Cu}_2\text{O}$, and $\text{TiO}_2/\text{Cu}_2\text{O}/\text{Al}/\text{Al}_2\text{O}_3$ are 0.76, 2.46, and 4.52 mA/cm^2 respectively, in agreement with the results in Fig. 7(a). The increased photocurrent density indicates a longer lifetime and a great improvement in the separation of the photogenerated carriers.

To further confirm that the Cu_2O and Al NPs in the photoanode played a positive role in enhancing the PEC water splitting activity, the incident photon-to-current conversion efficiency (IPCE) values of the samples at a potential of 1.23 V vs. RHE are shown in Fig. 7(d). The IPCE values can be calculated using the following equation [46–48]:

$$\text{IPCE} = 1240I/(\lambda J_{\text{light}}) \quad (2)$$

where I , λ , and J_{light} represent the measured photocurrent density (mA/cm^2), incident monochromatic light wavelength (nm), and intensity of the monochromatic light (mW/cm^2), respectively. As shown in Fig. 7(d), due to its wide band gap and narrow absorption range, the photocurrent of bare TiO_2 is mainly

produced by its optical activity in the ultraviolet region. After deposition of the Cu_2O NPs, the photoanode displays strong photoactivity not only in the UV region, but also in the visible-light region. Because of its excellent light absorption properties, the narrow band gap semiconductor Cu_2O increases the absorption range and extends the photoactivity of the photoanode in the visible region, corresponding to the red-shift threshold in the UV-vis spectrum. In addition, the IPCE value of $\text{TiO}_2/\text{Cu}_2\text{O}$ is 23.19%, which is 1.54 times higher than that of bare TiO_2 (15.10%), indicating a higher photoelectric conversion efficiency. Hence, the existence of Cu_2O NPs is beneficial in broadening the visible light absorption and improving the separation and transfer efficiency of the carriers. After deposition of the Al NPs, the photoactivity of the electrode in the ultraviolet and visible regions is further improved. Notably, a typical IPCE peak appears at wavelengths between 500 and 600 nm, which is in agreement with the UV-vis spectrum in Fig. 6(a) and matches well with the SPR region of Al via visible light excitation. The IPCE value of the $\text{TiO}_2/\text{Cu}_2\text{O}/\text{Al}/\text{Al}_2\text{O}_3$ composites clearly increased to 33.79%, which was 2.24 and 1.46 times higher than that of bare TiO_2 and $\text{TiO}_2/\text{Cu}_2\text{O}$. Therefore, the Cu_2O NPs and plasmonic Al NPs strongly improve the visible-light absorption and utilization, markedly increasing the IPCE in the visible light range for the $\text{TiO}_2/\text{Cu}_2\text{O}/\text{Al}/\text{Al}_2\text{O}_3$ photoanode.

The EIS results in Fig. 8(a) measured under illumination clearly indicate the active processes of the carriers in the bare TiO_2 , $\text{TiO}_2/\text{Cu}_2\text{O}$, and $\text{TiO}_2/\text{Cu}_2\text{O}/\text{Al}/\text{Al}_2\text{O}_3$ photoanodes. The results were well fitted by the simplified equivalent circuit (SEC) in the top inset of Fig. 8(a), in which R_s is the series resistance, and R_{ct} and CPE are the mean charge transfer resistance and the capacitance of the space-charge region, including carrier transfer at the FTO/ TiO_2 interface and photoanode/electrolyte interface. W represents the Warburg impedance. CPE_{Pt} and R_{Pt} are the capacitance and the resistance of the Pt counter electrode [12]. According to the simulation results in Table S1, the R_{ct} values of the $\text{TiO}_2/\text{Cu}_2\text{O}$ and $\text{TiO}_2/\text{Cu}_2\text{O}/\text{Al}/\text{Al}_2\text{O}_3$ photoanodes are significantly lower than that of bare TiO_2 , demonstrating that the p-n heterojunction formed by TiO_2 and Cu_2O and the increased electromagnetic field caused by the SPR effect could reduce the carrier recom-

bination and accelerate the movement of carriers [49–51]. The ultrathin Al_2O_3 layer generated in air eliminates the transfer of Forster energy, further reducing the recombination of carriers [27]. The smallest arc radius of the $\text{TiO}_2/\text{Cu}_2\text{O}/\text{Al}/\text{Al}_2\text{O}_3$ composites in the EIS indicates that it has the lowest charge transfer impedance, and thus the lowest potential barrier among the three samples [52–54]. This result clearly demonstrates that the existence of the Cu_2O and Al layers efficiently enhanced the performance of the composite. Additionally, the Bode plots in Fig. 8(b) show that the frequencies of the characteristic peaks for both the $\text{TiO}_2/\text{Cu}_2\text{O}$ and $\text{TiO}_2/\text{Cu}_2\text{O}/\text{Al}/\text{Al}_2\text{O}_3$ photoanodes are lower than for bare TiO_2 , indicating the significantly longer electron lifetime in the $\text{TiO}_2/\text{Cu}_2\text{O}$ and $\text{TiO}_2/\text{Cu}_2\text{O}/\text{Al}/\text{Al}_2\text{O}_3$ composites [55]. This result further confirms that the presence of p-n heterojunctions and the SPR effect of Al significantly improve the properties of the photoanodes.

As shown in Fig. 9(a)–(c), the SPV spectra of the bare TiO_2 , $\text{TiO}_2/\text{Cu}_2\text{O}$, and $\text{TiO}_2/\text{Cu}_2\text{O}/\text{Al}/\text{Al}_2\text{O}_3$ photoanodes indicate a negative response with front illumination, showing that the photogenerated electrons are transferred to the interface of the TiO_2 layer and the FTO substrate. The narrow response range of bare TiO_2 with a wide band gap matches the range of its UV-vis absorption spectrum and IPCE plot. After the deposition of Cu_2O , the response range was broadened; the SPV value of $\text{TiO}_2/\text{Cu}_2\text{O}$ is 2.9 times higher than that of bare TiO_2 because of the concentration of photogenerated electrons provided by Cu_2O at the interface. In addition, the SPV response threshold of $\text{TiO}_2/\text{Cu}_2\text{O}$ is located at about 500 nm, in agreement with the UV-vis absorption spectrum of $\text{TiO}_2/\text{Cu}_2\text{O}$ in Fig. 6(a). The significant enhancement of the SPV signal in Fig. 9(c) shows that the SPR effect of Al is strongly stimulated, with large amounts of hot electrons being transferred and converging on the surface of the FTO substrate. Additionally, to determine the most appropriate thickness for the Al layer, the SPV signals for different Al layer thicknesses are shown in Fig. S5. The positive response of the SPV indicates that the photogenerated holes are transferred to the illumination side. On the other hand, the SPV signal begins to decrease when the thickness reaches 30 nm because the thick Al layer prevents the photons from reaching the surface of Cu_2O and TiO_2 , and the holes are hindered from reaching the surface of the photoanode. Therefore,

Fig. 8. (a) Nyquist plots of bare TiO_2 , $\text{TiO}_2/\text{Cu}_2\text{O}$ and $\text{TiO}_2/\text{Cu}_2\text{O}/\text{Al}/\text{Al}_2\text{O}_3$ photoanodes measured at 1.23 V vs. RHE under illumination. Top inset: the equivalent circuit model used to simulate impedance spectra. (b) Bode plots of bare TiO_2 , $\text{TiO}_2/\text{Cu}_2\text{O}$ and $\text{TiO}_2/\text{Cu}_2\text{O}/\text{Al}/\text{Al}_2\text{O}_3$ photoanodes under illumination.

Fig. 9. Surface photovoltage spectroscopy (SPV) of TiO_2 (a), $\text{TiO}_2/\text{Cu}_2\text{O}$ (b), $\text{TiO}_2/\text{Cu}_2\text{O}/\text{Al}/\text{Al}_2\text{O}_3$ (c) photoanodes under illumination, the right side of the graph is the corresponding SPV measurement configuration schematic.

the combination of the SPR effect of an appropriate thickness layer of Al and the $\text{TiO}_2/\text{Cu}_2\text{O}$ p-n heterojunctions jointly lead to an increased concentration of carriers in $\text{TiO}_2/\text{Cu}_2\text{O}/\text{Al}/\text{Al}_2\text{O}_3$.

Fig. 10 displays the stability of the photoanodes at 1.23 V vs. RHE under illumination. Notably, the photocurrent curve of the $\text{TiO}_2/\text{Cu}_2\text{O}$ photoanode decreases by 53% at 100 min. The common reason is that the Cu^+ at the electrode/electrolyte interface can be oxidized and reduced [56]. However, the outermost Al layer prevents Cu_2O from coming into contact with the electrolyte, retarding the oxidation and reduction of Cu^+ . The stability of the $\text{TiO}_2/\text{Cu}_2\text{O}/\text{Al}/\text{Al}_2\text{O}_3$ composite shows a marked enhancement (Fig. 10), indicating the Al layer is oxidized to form an ultrathin layer of Al_2O_3 that not only prevents further oxidation, but also protects Cu_2O from undergoing redox reaction. Moreover, the H_2 evolution of the $\text{TiO}_2/\text{Cu}_2\text{O}/\text{Al}/\text{Al}_2\text{O}_3$ photoanode over 2 h is 163.3 μmol (Fig. S6) and its faradic efficiency is 96.7%.

Based on the above analysis, a carrier transfer mechanism and energy level graph for the $\text{TiO}_2/\text{Cu}_2\text{O}/\text{Al}/\text{Al}_2\text{O}_3$ photoanode under illumination were proposed and are shown in Fig. 11. The estimated VB and CB positions of the TiO_2 NRs and Cu_2O NPs (Table S2) were determined by combining the UPS spectra (Fig. S7) and band gap energy results. The Fermi energy of Al (4.27 eV) was estimated from the UPS spectra (Fig. S8). In this

Fig. 10. Stability at 1.23 V vs. RHE of bare TiO_2 , $\text{TiO}_2/\text{Cu}_2\text{O}$ and $\text{TiO}_2/\text{Cu}_2\text{O}/\text{Al}/\text{Al}_2\text{O}_3$ photoanodes.

composite photoanode system, Al plays an important role in enhancing the light absorption of the photoanode and amplifying the electromagnetic field produced by the SPR effect; moreover, hot electron-hole pairs are produced when the SPR effect is excited by favorable matching between the photon energy and SPR region. Subsequently, the generated hot electrons are injected into the CB of Cu_2O and then transferred to the CB of TiO_2 along with the photogenerated electrons from Cu_2O due to the more positive CB potential of TiO_2 compared to Cu_2O . The obvious differences in the band energies of TiO_2 and Cu_2O lead to an offset and bending of the energy band, thus promoting charge separation and transfer [40]. Therefore, the synergistic effect of the intense Al SPR effect and the $\text{TiO}_2/\text{Cu}_2\text{O}$ p-n heterojunctions significantly improve the performance of the photoanode in PEC water splitting.

4. Conclusions

In summary, novel $\text{TiO}_2/\text{Cu}_2\text{O}/\text{Al}/\text{Al}_2\text{O}_3$ photoelectrodes were successfully synthesized and showed significantly improved performance in PEC water splitting. The outer non-noble metal surface plasmas Al NPs absorb the photon energy to resonate collectively, amplifying the electrical field at the interface and injecting hot electrons into Cu_2O under illumination. More significantly, the spontaneously oxidized ultrathin Al_2O_3 passivation layer not only acts as a protective layer, but also retards charge recombination, thus enhancing

Fig. 11. Schematic of carriers transfer mechanism and the energy level graph of $\text{TiO}_2/\text{Cu}_2\text{O}/\text{Al}/\text{Al}_2\text{O}_3$ photoanode.

the stability and charge separation of the photoanode. Additionally, the $\text{TiO}_2/\text{Cu}_2\text{O}$ heterojunction core/shell structure further enhanced charge separation and transfer due to its appropriate energy band positions. The above synergistic effect suppressed the recombination of electron-hole pairs and increase the charge separation rate, leading to an enhanced photocurrent density of 4.52 mA/cm^2 at 1.23 V vs. RHE, which is 1.84 times higher than that of $\text{TiO}_2/\text{Cu}_2\text{O}$. Therefore, this work provides a novel strategy for manufacturing photoelectrodes with high performance and practicability through the use of a non-noble metal plasmas cocatalyst.

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Graphical Abstract

Chin. J. Catal., 2020, 41: 1884–1893 doi: 10.1016/S1872-2067(20)63637-3

Decorating non-noble metal plasmonic Al on a $\text{TiO}_2/\text{Cu}_2\text{O}$ photoanode to boost performance in photoelectrochemical water splitting

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Under light stimulation, $\text{TiO}_2/\text{Cu}_2\text{O}$ heterojunctions and the surface plasmon resonance effect of the non-noble metal Al synergistically promote carrier separation and transfer, thus leading to enhanced performance in photoelectrochemical water splitting.

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利用非贵金属等离子体Al修饰TiO₂/Cu₂O异质结以提高光电催化分解水性能

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摘要: 在光电化学(PEC)中, 利用半导体纳米材料分解水产生氧气和氢气成为解决能源和环境危机的有效途径, 而设计具有较高的光子捕获效率和电荷分离率的低成本光电极是研究的重点。近年来, 已有许多半导体材料(例如ZnO, Fe₂O₃, WO₃, Cu₂O, CuInS₂等)被用做光电极参与光电催化分解水。其中, TiO₂作为一种n型半导体, 由于其具有适当的导带(CB)和价带(VB)位置、良好的耐光腐蚀性、无毒性 and 出色的稳定性而引起人们的关注。然而, 光响应范围窄, 光生载流子复合率高等问题限制了TiO₂光电极在PEC水分解中的应用。因此, 选用合适的窄禁带半导体和助催化剂进行复合修饰能够有效地扩大光响应范围, 促进载流子的分离和转移, 从而提升电极的光电催化性能。

本文利用具有表面等离子体共振(SPR)效应的Al对TiO₂/Cu₂O核/壳异质结进行改性, 制备了TiO₂/Cu₂O/Al/Al₂O₃光电阳极。SEM和TEM等结果显示已成功合成核/壳异质结。UV-vis吸收光谱和UPS测试计算表明, Cu₂O不仅可以显著扩展电极的吸光范围, 且计算所得TiO₂和Cu₂O导价带位置验证了p-n异质结的合成。结合光电流、EIS等测试, 证明了异质结能够有效地促进光生载流子的分离和转移。同时, 在光照激发下, UV-vis吸收光谱在550 nm出现明显的特征峰, 表明Al的SPR效应被成功激发。Al纳米颗粒的SPR效应不仅可以产生热电子, 并能够增强与异质结界面处的电场。之后, 通过Mott-Schottk测试和Bode图, 较为直观地说明了异质结和SPR效应的协同作用能够增加载流子的浓度, 抑制电子空穴的复合, 使所制备的TiO₂/Cu₂O/Al/Al₂O₃光电阳极表现出良好的光电性能, 其光电流达到了4.52 mA/cm² (1.23 V vs. RHE), 是TiO₂/Cu₂O异质结的1.84倍。相比于同样具有SPR效应的Au, Ag等贵金属而言, Al不仅价格低廉, 而且在空气中自发形成的超薄Al₂O₃薄膜能够有效地抑制Al的进一步氧化, 并作为保护层能够显著提高电极的稳定性。在对样品稳定性的测试中, 由于Al₂O₃保护层的存在, 电极的稳定性提高了53%。本文对样品的实验测试和原理分析表明了异质结和非贵金属Al的SPR效应的协同作用显著提高了光电极的光电性能, 为设计具有良好性能和高实用性的电极提供了新思路。

关键词: 二氧化钛; 光电阳极; 非贵金属铝; 表面等离子体共振; 光电催化分解水

收稿日期: 2020-03-13. 接受日期: 2020-04-21. 出版日期: 2020-12-05.

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基金来源: 天津市杰出青年基金(17JCJQJC44800); 天津市重点研发计划项目(19YFSLQY00020).

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