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Design of ZnO/ZnS/Au Sandwich Structure Photoanode for Enhanced efficiency of Photoelectrochemical Water Splitting

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We reported a sandwich structure for photoelectrochemical water splitting photoanode enhanced by the introduction of ZnS interlayer and Au nanoparticles.
Design of ZnO/ZnS/Au Sandwich Structure Photoanode for Enhanced Efficiency of Photoelectrochemical Water Splitting

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ABSTRACT

We have demonstrated a ZnO/ZnS/Au composite photoanode with significantly enhanced PEC performance with the ZnS interlayer and Au nanoparticles. The solar-to-hydrogen conversion efficiency of such ZnO/ZnS/Au heterostructure reached 0.21%, which is 3.5 times that of pristine ZnO. The comparison of IPCE and photoresponse in white and visible light region further verified that such enhancement is attributed to the contribution of both UV and visible regions. The modification of Au NPs can improve the PEC performance both in the UV and visible regions due to the effective surface passivation and surface-plasmon-resonance effects. And the ZnS interlayer is favorable for photogenerated electrons under UV light and hot electron under visible light injection into ZnO, simultaneously suppress the recombination at the photoanode-electrolyte interface. The optimizing design of an interlayer between the plasmonic metal/semiconductor composite systems reported here provides a facile and compatible configuration to enhance the utilization efficiency of the incident light for photoelectrochemical application.

1 Introduction

Hydrogen that is formed by the solar splitting of water is clearly considered to be the cleanest energy fuel to meet future demand for energy, and various attempts have been made in order to develop advanced processes to produce hydrogen. Among these different methods[1-3], photoelectrochemical (PEC) water splitting, considered to be one of the most promising hydrogen generation, is a highly-efficient and eco-friendly way. In a PEC system, the selection and design of the photoelectrode materials are critical since the capability of the PEC cell for water splitting is largely determined by the light absorption and carrier transport of the photoelectrode. Light active semiconductors or metal oxides such as titanium
dioxide (TiO₂), Zinc oxide (ZnO), hematite (Fe₂O₃) and cuprous oxide (Cu₂O) have shown great potential for hydrogen generation[4-13]. As a common and inexpensive semiconductor, ZnO nanomaterials have been extensively explored for solar energy conversion because of their excellent electron mobility, electron-transfer efficiency (115-155 cm² V⁻¹ s⁻¹)[14], abundant morphologies and favorable environmental compatibility[15-18]. However, wide bandgap in ZnO limits the photoelectrochemical (PEC) water splitting performance due to poor absorption of visible light. Therefore, it’s urgent to search for a strategy to simultaneously increase the light capture.

Recently, plasmonic nanostructures of noble metal especially gold (Au) have been demonstrated to be promising for photocatalytic and solar energy conversion due to its tunable interactions with light in visible and infrared regions through a strong light scattering and localized surface-plasmon resonance (SPR) [19-22]. Also, Au nanoparticles are stable enough for preventing corrosion during the photoreaction[23]. Many efforts have been attempted to design Au-ZnO based plasmonic nanostructures for solar water splitting. The enhanced photoactivity of Au NPs-decorated ZnO in the UV region is ascribed to effective surface passivation as well as electric-field amplification effect, while the photoactivity enhancement in the visible region is mainly caused by hot electron generation upon SPR excitation[24-28]. Therefore, it is highly desirable to design the ZnO/Au photoanode for improving the efficiency of energy conversion.

A suitable choice of interlayer material not only reduces the recombination losses, but also enhances the electron collection efficiency. The formation of ZnS layer at the ZnO surface has been proved to be a promising platform for photoelectrochemical water splitting, due to fast photogenerated electron-hole separation and enhanced injection efficiency[29-31]. The ZnO/ZnS/Au photoanode offers an optimal configuration for PEC water splitting, as it incorporates the merits of each composition.

In this paper, we demonstrated that the PEC performance of ZnO/ZnS/Au photoanode can be enhanced compared with pristine ZnO and ZnO/Au both in the UV and visible region, which can be explained by EIS measurement and energy band structure.

2 Experimental

The fabrication sequence of ZnO/ZnS/Au nanopods array via hydrothermal process[32], chemical conversion process[33] and photochemical deposition method[34] is shown in Scheme 1.

2.1 Synthesis of ZnO nanorods array. The samples were prepared by the hydrothermal growth method. A colloidal solution of zinc acetate [Zn(CH₃COO)₂·2H₂O] (0.5 M) was spin-coated onto the FTO substrate to form the ZnO seed layer, and subsequently annealed at 350 °C in air for 30 min. In the hydrothermal process, substrates were placed in the aqueous solution containing 50 mM zinc nitrate hexahydrate [Zn(NO₃)₂·6H₂O] and hexamethylenetetramine (HMTA) [(CH₂)₆N₄] at 90 °C for 12 h, with the seeded side facing down. Finally, the substrate with product was repeatedly rinsed with deionized water for several times and annealed in air at 450 °C for 3h to remove residual surface salts.

2.2 Synthesis of ZnS interlayer. A simple chemical conversion approach was adopted to fabricate ZnO/ZnS core/shell nanostructures. The substrate with ZnO nanorods array was immersed in thiacetamide (TAA) aqueous solution (0.2 M) and the sulfidation process was carried out at 95 °C for 12 h, with the seeded side facing down. Finally, the substrate with product was repeatedly rinsed with deionized water for several times and annealed in air at 450 °C for 3h to remove residual surface salts.

2.3 Synthesis of Au nanoparticles. The ZnO/ZnS and ZnO nanorods array were immersed in a 10 ml
chboroauric acid (HAuCl$_4$, 0.01%) solution with a pH=7 adjusted by 0.1M NaOH solution, 1 ml 1% polyvinyl alcohol (PVA, [C$_2$H$_4$O]$_n$) and 0.5 ml methanol (CH$_3$OH, 99.5%). Under UV irradiation for 10 minutes, followed by calcination at 350°C in N$_2$ for 30 minutes, the Au ions (Au$^{3+}$) were reduced to neutral atoms attached to the surfaces.

2.4 Characterization of Materials. The structure and morphology of the electrodes were characterized by X-ray diffraction (XRD) (Rigaku DMAX-RB, CuKα), field emission scanning electron microscopy (FE-SEM) (FEI QUANTA 3D). The formation of ZnS and Au on the ZnO nanorods and the bonding characteristics were determined by X-ray photoelectron spectroscopy (XPS, ESCALAB 250).

2.5 Electrochemical Characterization. The photoanode was fabricated by securing a copper wire on the exposed electric conductive parts of the FTO with a silver conducting paint. The substrate was subsequently sealed on all edge with epoxy resin except the active working area. All electrochemical measurements were performed in a three electrode mode with a photoanode as the working electrode, a coiled Pt wire as counter electrode and a Ag/AgCl reference electrode, and 0.5M Na$_2$SO$_4$ aqueous solution (with pH buffered to ~7.0) as the electrolyte. Electrochemical measurements were performed on an electrochemical workstation (Solartron SI 1287/SI 1260). All photoanodes were illuminated from the front side under AM 1.5G illumination provided by a solar simulator (Oriel, 91159A). Visible light illumination was obtained by passing the AM 1.5 light through a 420 nm long-wave-passfilter. The white and visible light intensity was 50 mW/cm$^2$ and 45 mW/cm$^2$ measured by a Si diode (Newport).

3 Results and discussion

Figure 1(a) and (b) showed a typical SEM image of the as-synthesized ZnO nanorods array with a smooth surface. The side view (Figure 1(a)) clearly showed that ZnO nanorods were aligned with a height of about 5µm. The top view (Figure 1(b)) showed a dense and oriented array of ZnO nanorods with the diameter around 200 nm on the FTO substrate.

After sulfuration and Au-decoration, the morphology changes of the nanorods array are observed in SEM images. Figure 1(c) showed that Au nanoparticles were uniformly distributed on the surface of each ZnO nanorod and the nanorods still maintained their vertically-oriented characteristics. The Au NPs decoration of ZnO nanorods array was achieved by the following reaction under UV illumination:

$$\text{ZnO} \rightarrow \text{ZnO(e+h)}$$

$$\text{ZnO(e+h)} \rightarrow \text{e}^- + \text{h}^+$$

$$\text{AuCl}_4^- + 3\text{e}^- \rightarrow \text{Au} + 4\text{Cl}^-$$

As shown in Figure 1(d), different from the as-synthesized ZnO/Au, the surface morphology after the sulfuration became coarse, while the surface was still hexagonal in shape and the nanorods were still well-ordered, suggesting that sulfuration process did not change the shape and size of the nanorods. During the sulfuration, ZnO on the surface of nanowire was etched and converted into ZnS, resulting in formation of the ZnS shell:

$$\text{CH$_3$CSNH$_2$+H$_2$O=CH$_3$CONH$_2$+H$_2$S}$$

$$\text{H}_2\text{S=2H$^+$+S$_2$}$

$$\text{ZnO+S$_2$-+H$_2$O=ZnS+2OH}^-$$

Figure 1 (a) Cross-sectional-view SEM images of the as-synthesized ZnO nanorods array. Top view of pristine ZnO (b), ZnO/Au(c) and ZnO/ZnS/Au (d) on an FTO substrate. (e) and (f) TEM images of the ZnO/ZnS/Au.

The TEM image shown in Figure 1(e) (f) confirmed the sandwich structure for ZnO/ZnS/Au. As can be seen, the ZnS shell was uniform in width with the thickness
about 4 nm on the surface of ZnO nanorods, and the surface-deposited Au nanoparticles had an average diameter of 10–30 nm distributed on the surface of ZnS. The composition of the as-prepared photoanodes was further examined by energy-dispersive X-ray (EDX) measurement, and the atomic ratios were calculated from the EDX spectrum, as shown in Figure S1 in the ESM.

XRD data of ZnO nanorods (blue curve in Fig. 2) revealed that all diffraction peaks of the pristine photoelectrodes were indexed to the planes of highly crystalline ZnO (JCPDS file no. 36-1451) with no impurities. Moreover, the main phase of all the samples can be identified as the self-supported ZnO nanoarchitectures with wurtzite (002) nanorods array, which is consistent with SEM images. After the decoration of Au nanoparticles, another two new XRD peaks appeared at 20 of 38.1° and 44.4°, which can be identified as the characteristic peaks of (111) and (200) (JCPDS file no. 04-0784). For ZnO/ZnS/Au photoanodes (red curve in Figure 2), a weak peak belonging to ZnS (111) diffraction was detected at 20 ~ 28.5°, resulting from a very thin ZnS layer coating on ZnO (JCPDS file no. 05-0566).

Figure 2 XRD patterns of the ZnO, ZnO/Au and ZnO/ZnS/Au photoanodes on the FTO substrate.

The XPS measurement of ZnO/ZnS/Au sample demonstrated the presence of Zn, O, S and Au without other unexpected elements (Fig. 3(a)). The high resolution scans of Zn2p, S2p and Au peaks were shown in Fig. 3(b), (c) and (d). The XPS data were analyzed by fitting to a Gaussian–Lorentzian function and using a Shirley background subtraction. The Zn2p\(\frac{3}{2}\) peak at 1021.8 eV and Zn2p\(\frac{1}{2}\) peak at 1044.9 eV were shown in Fig. 3(b). In the S2p XPS spectrum of Figure 3(c), the S2p\(\frac{3}{2}\) and S2p\(\frac{1}{2}\) peaks centered at 161.8 eV and 163.0 eV, respectively, are related to Zn–S bondings, indicating that ZnS was successfully synthesized by the chemical conversion process in our experiments. XPS was further employed to identify the chemical states of Au element. For Fig. 3(d), the spectrum can be decomposed into two components, which can be assigned to the peaks of Au\(^{4f_7/2}\) and Au\(^{4f_5/2}\). It can be derived from the XPS results that the Au constituent is in the metallic state.

Figure 3 XPS spectra of ZnO/ZnS/Au composite heterostructure: (a) wide scan, (b) Zn2p, (c) S2p and (d) Au4f.

The PEC performance of various as-synthesized different photoanodes were characterized through photoinduced I-V curves. As can be seen, with the introduction of ZnS interlayer, the ZnO/ZnS/Au photoanode exhibited larger photocurrent density in the whole potential window compared to ZnO/Au and pristine ZnO photoanode. Under illumination as shown in Figure 4(a), the photocurrent densities of the pristine ZnO, ZnO/Au and ZnO/ZnS/Au were 0.18 mA/cm\(^2\), 0.37 mA/cm\(^2\) and 0.58 mA/cm\(^2\) at 1V versus Ag/AgCl. Sweeping the potential anodically, the I-V curve of the ZnO/ZnS/Au exhibited a steeper increase in current with respect to potential and achieved a prompt saturation of the photocurrent density at 0.4 V versus Ag/AgCl. Sweeping the potential anodically, the I-V curve of the ZnO/ZnS/Au exhibited a steeper increase in current with respect to potential and achieved a prompt saturation of the photocurrent density at 0.4 V versus Ag/AgCl. Sweeping the potential anodically, the I-V curve of the ZnO/ZnS/Au exhibited a steeper increase in current with respect to potential and achieved a prompt saturation of the photocurrent density at 0.4 V versus Ag/AgCl, suggesting much more efficient charge separation and collection than in the pristine ZnO and ZnO/Au photoanode.

Furthermore, the photoconversion efficiencies (\(\eta\)) for PEC water splitting of such photoanodes were estimated using the following equation [35]:

\[
\eta = \frac{I(1.23-V_{app})}{P_{light}}
\]
$V_{\text{app}}$ is the applied external potential versus reversible hydrogen electrode (RHE). $I$ is the externally measured current density at $V_{\text{app}}$. $P_{\text{light}}$ is the power density of the incident light. The potentials were measured versus the Ag/AgCl reference electrode and converted to the reversible hydrogen electrode (RHE) scale using the Nernst function:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + E_{\text{Ag/AgCl}}^\circ + 0.059pH$$

(2)

$E_{\text{RHE}}$ is the converted potential versus RHE. $E_{\text{Ag/AgCl}}$ is the external potential measured against the Ag/AgCl reference electrode. $E_{\text{Ag/AgCl}}^\circ$ is the standard electrode potential of Ag/AgCl reference electrode (0.1976 V versus RHE at 25 °C). Figure 4 presented the comparisons of PEC properties of three different photoanodes: pristine ZnO (black), ZnO/Au (blue) and ZnO/ZnS/Au (red): (a) Linear sweep voltammetry measurements under simulated sunlight illumination with a 20 mV/s scan rate. (b) Photoconversion efficiency as a function of applied potential versus RHE.

Figure 4(b) presented the plots of the photoconversion efficiencies vs RHE. The ZnO/ZnS/Au exhibited an optimal photoconversion efficiency of 0.21% at potential of 0.928 V vs RHE, 2 times and 3.5 times higher than that of ZnO/Au and pristine ZnO (0.10% at 0.924 V vs RHE) and pristine ZnO (0.06% at 0.884 V vs RHE) photoelectrode, respectively. The above electrochemical results convincingly concluded that the ZnS interlayer played positive roles in enhancing the PEC water splitting efficiency of ZnO/Au heterostructure.

For better revealing the influence of the ZnS interlayer on the PEC performance of Au-ZnO based plasmonic photoanode, chronoamperometric I-t curves were collected at 0.5V vs Ag/AgCl with repetitive on/off cycles under white light and visible light. As shown in Figure 5(a), the recorded photocurrent densities were consistent with the values obtained from the linear sweep voltammograms, indicating the photocurrents are stable without photoinduced charging effect[36]. From the Diffuse reflectance UV−vis absorption spectra, the absorption edge was extended to the visible-light region due to the modification of Au NPs (Figure S2 in the ESM). For visible light illumination, the photocurrent density of ZnO/Au photoanode was 1.6 μA/cm², while there was barely no photocurrent for pristine ZnO photoanode. The enhanced photocurrent in the visible region is caused by the SPR effect of the modified Au NPs. With the introduction of ZnS interlayer, the photocurrent density reached 3.9 μA/cm², 1.6 times higher that of ZnO/Au photoanode, demonstrating that the adjunction of ZnS layer could enhance the visible-light photoactivity.

Furthermore, incident-photon-to-current-conversion efficiency (IPCE) tests at 0.9 V versus RHE were utilized to investigate the specific PEC active spectra of as-sythesised three different photoanodes. From Figure 5(c), the ZnO/Au showed improved IPCE values both in UV and VIS region due to Au NPs modification. With the introduction of ZnS interlayer, the IPCE values in the UV and VIS region were improved compared to ZnO/Au photoanode, which was consistent with its exclusive photocurrent enhancement observed under white and visible light illumination in Figure 5(a) and (b).
Figure 5 Chronoamperometric I-t curves collected at 0.5V versus Ag/AgCl for three different photoanodes under (a) white-light (50 mW/cm²) and (b) visible-light (45 mW/cm²). (c) IPCE curves for three different photoanodes measured in the wavelength range from 370 to 700 nm at an applied voltage of 0.9 V vs RHE. Electrochemical impedance spectroscopy (EIS) measurements were performed to further explore the influence of the ZnS layer on the charge recombination at an applied bias voltage of 0.1V vs Ag/AgCl under white light and the results were fitted by the equivalent circuit in Figure 6. In the Figure 6, the arch for ZnO/ZnS/Au photoanode was much smaller than that of pristine ZnO and ZnO/Au photoanode, implying that simultaneous introduction of the ZnS and Au significantly reduced the resistance on the movement of charge carriers at the interface. In this work, the obtained results were fitted into the models of a RC circuit inserted in Fig. 6. In this equivalent circuit, $R_s$ is the resistance of the device and $R_{ct}$ is the interfacial charge-transfer resistance of the photoanode-electrolyte interface. According to the fitting data from the EIS results, the $R_{ct}$ were 3.93, 2.30 and 0.97 kΩ cm² coupled for pristine ZnO, ZnO/Au and ZnO/ZnS/Au photoanode, respectively. The $R_{ct}$ of ZnO/Au was smaller than that of pristine ZnO indicated Au NPs enhanced the electron mobility by surface passivation to reduce the recombination of photoexcited electrons and holes[20]. With the introduction of ZnS interlayer, surface traps states such as oxygen vacancies /adsorb oxygen were further reduced, resulting in the highest separation efficiency of photogenerated electron-hole pairs and fastest charge transfer of ZnO/ZnS/Au composite structure[26]. Therefore, such results positively supported the highest acquired water splitting efficiency of ZnO/ZnS/Au in Figure 4(b).

Figure 6 (a) Nyquist plots measured at an applied potential 0.1 V versus Ag/AgCl at white light for ZnO, ZnO/Au and ZnO/ZnS/Au, respectively. The insert is a equivalent circuit employed to fit the Nyquist plots.

For better understanding the electron-transfer mechanism, we displayed the energy level diagram. As illustrated in the Figure 7(b), surface plamons in the Au NPs are photoexcited by visible light
illumination and hot electron-hole pairs are generated. Subsequently, the hot electrons transiently occupying the surface plasmon states (SP states) were transferred to the conduction band of ZnO to improve photocurrent in the visible region[25-26]. With the introduction of ZnS in the Figure 7(c), the higher conduction band position of the ZnS shell than ZnO leads to faster electron transfer to conduction band[29]. And, when ZnO is stacked with ZnS, the lattice strain existed along the interface of ZnO/ZnS heterostructure can lead to an increase in the oscillator strength, where the individual band gap could be smaller than the initial value[37-39]. The band gap of ZnO can be compressed resulting from the interface strain from such a staggered II band alignment for ZnO/ZnS heterostructure. From the point of view of thermodynamic, the free energy change (ΔG) for the plasmon-induced hot-electron transfer from the surface plasmon resonance level to the CB of ZnS-coated ZnO (ΔG_{transfer}) is more positive than that of uncoated ZnO. As a result, the increased ΔG_{transfer} is beneficial for electron transfer from excited Au to ZnO via tunneling effect across a thin layer of ZnS, which finally lead to the improved photocurrent density with the introduction of ZnS layer under visible light.

4 Conclusions

In summary, ZnO/ZnS/Au nanorods array have been successfully fabricated to serve as the photoanode of photoelectrochemical water splitting. The photoconversion efficiency of the ZnO/ZnS/Au photoanode reached to 0.21%, 2 times and 3.5 times higher that of ZnO/Au and pristine ZnO photoanodes, respectively. The ZnO/ZnS/Au sandwich structure possessed superior photocurrent density compared with pristine ZnO nanorods array photoanodes both in the UV and visible region, which can be explained by EIS measurement and energy band structure. The surface passivation and surface-plasmon-resonance effect of Au NPs can enhance the photocurrent under illumination, while the introduction of ZnS interlayer is favorable for electrons injection into ZnO and reduces the recombination at the photoanode/electrolyte interface. The optimizing design confirms a new avenue of preparing efficient photoanode for PEC water splitting.

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