Synthesis of novel AuPd nanoparticles decorated one-dimensional ZnO nanorod arrays with enhanced photoelectrochemical water splitting activity

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Abstract

The vertically aligned one-dimensional (1D) ZnO nanorod arrays decorated with AuPd alloy nanoparticles have been synthesized with ZnO nanorod arrays as template via a mild hydrothermal method. In this work, the as-prepared AuPd/ZnO nanorod arrays demonstrated high light-harvesting efficiency. The microstructures, morphologies and chemical properties of the obtained AuPd/ZnO composite photocatalysts were investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD), transmission electron microscopy (TEM), UV-vis diffuse reflectance spectra (DRS) and X-ray photoelectron spectroscopy (XPS). The photoelectrochemical (PEC) performances of as-obtained AuPd/ZnO nanorod arrays were examined, and the photocurrent density was up to $0.98 \text{ mA} \cdot \text{cm}^{-2}$ at 0.787 V versus Ag/AgCl, which was about 2.4 times higher than the pure ZnO sample. A possible photocatalytic mechanism of the AuPd/ZnO hybrid nanostructures under the simulated sunlight irradiation was proposed to guide further improvement of other desirable materials. In light of the above experiment results, it can be clearly found that AuPd/ZnO composite nanorod arrays showed excellent PEC performance and have promising applications in the utilization of solar energy.

Keywords: AuPd alloy nanoparticles; ZnO nanorod arrays; photocurrent density; photocatalyst.

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1. Introduction

In response to the emergence of energy crisis and environmental problems, numerous semiconductor materials have attracted considerable attention to solve the energy and environment issues by energy conversion and the degradation of organic pollutants [1-5]. Hydrogen energy is considered as an ideal candidate to replace the traditional fossil energy to solve the above mentioned issues due to its sustainability, renewability and cleanliness [6-7]. Among various technologies of manufacture hydrogen, photoelectrochemical (PEC) water splitting into hydrogen and oxygen via semiconductor photoelectrodes is one of the most promising strategies [8-9]. To date, 1D ZnO nanorod arrays have garnered considerable attention among several semiconductor photocatalysts because of its numerous advantages, such as low cost, nontoxicity, high electron mobility property and larger surface area [10-13]. However, the performances of bare ZnO nanorod arrays are limited due to its large band gap (3.37 eV), quick recombination of photo-generated electron-hole pairs and photocorrosion, which hamper its extensive applications [14-15].

To solve these problems, great efforts have been devoted to improving the photocatalytic performance of 1D ZnO nanorod arrays, such as sensitizing with other semiconductor (for instance ZnS, Ag₂S, CdS/PbS) [16-18], noble metal doping (Au, Ag) [19-21]. It is known from many reports that various bimetallic alloy nanoparticles (such as AgPd, AuPt, PtNi) deposition could improve catalytic performances compared to monometallic nanoparticles due to the size effect and the unique microstructures [22-24]. Nevertheless, as far as we know, there is only a few reports on PEC electrodes of vertically one-dimensional ZnO nanorod arrays decorated with AuPd alloy nanoparticles. Combination of Au and Pd is an interesting possibility to achieve a catalyst with higher activity and to better understand the nature of the outstanding activity of Au containing catalysts [25]. So, it is worth exploring the superiority of bimetallic nanoalloys relative to a single component. Hence, to further

evaluate the synergistic effect between Au and Pd, we report the preparation of AuPd/ZnO nanorod arrays catalyst.

In this work, we have synthesized the AuPd/ZnO nanorod arrays for the first time and applied it in the area of photoelectrochemical water splitting under AM 1.5 G sunlight irradiation. It can be clearly seen from TEM images that AuPd alloy nanoparticles were uniformly dispersed on 1D ZnO nanorods which can enhance the PEC performance. The photocurrent density of AuPd/ZnO photocatalyst is $0.98 \text{ mA} \cdot \text{cm}^{-2}$ at 0.787 V versus Ag/AgCl, which is about 2.4 times higher than pure ZnO nanorod arrays, revealing that bimetallic nanoparticles have greater potential in the utilization of free and inexhaustible solar energy.

2. Experimental

2.1. Synthesis of 1D ZnO nanorod arrays

All chemical reagents which used in our experiment were without any purification. The 1D ZnO nanorod arrays were prepared on the substrate of fluorine doped tin oxide (FTO) glass via a simple hydrothermal method as reported in previous literature with some modifications [26]. The experimental process includes the formation of ZnO seed layer and the hydrothermal growth procedure of ZnO nanorods in a mixing solution. This two-step process can effectively control the nanorod shape, size, density and orientation [27]. Prior to prepare the seed layer of ZnO, FTO glass substrates was ultrasonically cleaned in deionized water, acetone and absolute ethanol two times respectively and each time for 15 min.

The 0.5 ml zinc nitrate solution (0.5M) and a desirable amount of equivalent concentration of hexamethylenetetramine (HMTA) were uniformly added to FTO substrates. A few minutes later, precipitation would be produced after the reaction of mixed solutions and subsequent spin coating, then the modified substrates via the annealing process at 200 °C for 10 min. The above procedure should be

repeated for 4 times in order to obtain an even and high density seed layer. The seeded substrate was put into a Teflon lined stainless-steel autoclave which contained the mixture solution of 0.05 M zinc nitrate and the equal amount of HMTA (0.05 M) to grow 1D ZnO nanorod arrays at 90 °C for 5.5 h. The obtained products were rinsed with deionized water and absolute ethanol three times, and then dried at 60 °C in the air.

2.2 Synthesis of AuPd/ZnO photocatalyst

The AuPd alloy nanoparticles were prepared by using a simple process which employed a reducing agent to reduce Au^{3+} and Pd^{2+} simultaneously as detailed in a previous reported literature [28]. Herein, we prepared AuPd alloy nanoparticles under a mild condition in which NaBH_4 was selected as reductant. In a typical procedure, 0.01 M $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ and PdCl_2 aqueous solution were first prepared. Fresh aqueous solutions of 0.1 M NaBH_4 and 1 wt% PVA were also prepared in advance. The 470 μl PdCl_2 (0.01 M) and 250 μl HAuCl_4 (0.01 M) stock solution were mixed and the required amount (1 wt%) of PVA solution was added ($\text{PVA}/(\text{Au}+\text{Pd})=1.2$, weight ratio), the fresh NaBH_4 solution ($\text{NaBH}_4/(\text{Au}+\text{Pd})=5$, molar ratio) was then added to form a dark-brown solution. The above solution was continuously stirred. Then pre-synthesized 1D ZnO nanorod arrays were immersed in above AuPd alloy solution for 40 min at room temperature. The sample was washed with ethanol then dried at 150 °C for 30 min. Then the AuPd/ZnO composite samples were obtained.

2.3 Characterization

The morphologies of the fabricated samples were analyzed with field emission scanning electron microscopy (SEM, FEI Quanta 200F; accelerating voltage=10 kV). The crystal structure and phase of the pure ZnO were investigated using X-ray diffraction (XRD; Bruker D8 Advance, X-ray diffractometer) with $\text{Cu K}\alpha$ radiation. Transmission electron microscopy (TEM, JEM-2100, accelerating voltage 200 kV) and high-resolution transmission electron microscopy (HRTEM) were performed to

reveal the nanostructure and composition of the as-prepared AuPd/ZnO catalyst. The UV-Vis diffuse reflection spectroscopy (DRS) was performed on a Shimadzu UV-4100 spectrophotometer using BaSO₄ as the reference material. The purpose of DRS was to investigate the optical absorption spectra (solar light harvesting properties) of the photoanodes. X-ray photoelectron spectroscopy (XPS) measurements were undertaken on a PHI 5300 ESCA system to detect the compositions of the as-prepared samples. The binding energies were corrected by the XPS signal of C1s.

2.4. Characterization of photoelectrochemical performances

Photoelectrochemical (PEC) characterization of the samples were performed using an electrochemical workstation (CHI660E), a three-electrode configuration, in which the ZnO nanorods and AuPd/ZnO composite catalysts were employed to be the working photoelectrode, the saturated Ag/AgCl and a platinum foil were used as reference and counter electrode, respectively. The whole photoelectrochemical tests were completed in 0.5 M sodium sulfate electrolyte solution. The solar simulated incident light (AM 1.5 G) with the intensity is 100 mW·cm⁻² was used as the resource of light illumination. Linear sweep voltammograms were measured under a bias voltage between -0.2 V and 1.2 V versus Ag/AgCl with a scanning rate of 10 mV/s under simulated sunlight irradiation.

3. Results and discussion

3.1. Characterization of AuPd/ZnO composite samples

The X-ray diffraction (XRD) pattern of the as-prepared ZnO sample is shown in Fig.1. The pure ZnO sample has a typical hexagonal wurtzite structure and all the diffraction peaks that appear upon nanoarrays match well with the standard ZnO diffraction pattern (JCPDS, No.70-2551). The pure 1D ZnO nanorod arrays have three distinct peaks at 31.8°, 34.5° and 36.3°, which can be attributed to (100), (002) and (101) planes, and the obtained ZnO nanorod arrays are detected to grow preferentially along the (002) direction. This result indicates that the ZnO nanorod arrays are uniform and homogeneous.

The 1D ZnO nanorod arrays were synthesized on conducting glass substrates (FTO) by using a facile and low-cost hydrothermal method as described above. The SEM images of as-prepared pristine ZnO and AuPd/ZnO photocatalysts are shown in Fig.2. It can be seen that the well-aligned ZnO nanorod arrays were vertically grown on the FTO substrates (Fig.2 (a)). The surface of ZnO nanorod arrays is smooth and it appears hexagonal cross section as given in Fig.2 (b). The Fig.2 (c) and (d) presents that the outside surface of the ZnO nanorod arrays is decorated with some nanoparticles randomly and retains the initial nanorod features compared to Fig.2 (b). At the same time, the morphology of AuPd/ZnO is identified with the SEM images. Moreover, the XRD results proved that the AuPd/ZnO composite sample has a good crystallinity.

The morphology and chemical composition of the sample were further analyzed by TEM. Fig.3 displays the TEM (a, b, c) and HRTEM (d and e) images of AuPd/ZnO composite. In Fig.3 (a), we can see that the AuPd/ZnO photocatalysts show 1D microstructure after the embryonic ZnO nanorod arrays were treated in a certain concentration of solution. Fig.3 (b-c) shows that some nanoparticles are distributed on the pristine ZnO sample. Fig.3 (d-e) presents HRTEM patterns with high magnifications for the AuPd/ZnO composite sample. The (111) interplanar distances corresponding to face-centered cubic Au and Pd nanoparticles are about 0.236 nm and 0.227 nm, respectively [29-30]. By calculating from the line profile, the corresponding HRTEM image in Fig.3 (e) expressly depicts the lattice fringes with spacing of $d=0.2603$ nm and $d=0.23$ nm, which can be indexed to the (002) plane of the hexagonal ZnO phase and (111) facet of AuPd alloy nanoparticles, respectively [12, 31]. As a result, HRTEM images demonstrate that the AuPd alloy exists on the surface of ZnO nanorod arrays. Therefore, it is expected to greatly enhance the photoelectrochemical activity of the AuPd/ZnO sample.

The UV-vis diffuse reflectance spectra (DRS) was determined at room temperature to investigate the optical properties of as-prepared ZnO and AuPd/ZnO samples, in which the wavelength range is

300-800 nm as presented in Fig.4. In contrast with natural ZnO nanorod films, the color of the final product obtained from ZnO nanorods have no obvious changes. The pattern displays that pristine ZnO has a strong absorption in the ultraviolet region due to its wide band gap energy (3.37 eV), while that for the target product is at 394 nm. As the results depicted in Fig. 4, we can clearly see that the optical absorption spectra has a redshift in UV range. Referenced to the reported literature, the bulk ZnO sample only shows strong absorption in the ultraviolet region which is centered at 378 nm [32]. Compared with pure 1D ZnO nanorod arrays, the AuPd decorated ZnO has similar absorption edge in shape and slight increase in absorbance intensity. The DRS results prove that the composite sample could improve the light absorption intensity after the introduction of AuPd alloy nanoparticles, which maybe have the potential of enhancing photoactivity.

Furthermore, X-ray photoelectron spectroscopy (XPS) was applied to obtain the chemical compositions and the binding states of AuPd/ZnO nanorod arrays. The XPS spectrum survey illustrates that O, Zn, Au, Pd elements are presented in the AuPd/ZnO photocatalyst as given in Fig.5 (a), and the C 1s is used as a reference to calibrate the peak shifts. As shown in the high resolution XPS spectra of O 1s (Fig.5 (c)), the peak located at 531.2 eV is indexed to O atoms which exists in ZnO lattice [33]. Fig.5 (d) shows the high-resolution XPS spectrum of Zn 2p, the peaks centered at 1022 eV and 1045 eV are corresponding to Zn 2p_{3/2} and Zn 2p_{1/2}, respectively, which implies the existence of Zn element in ZnO [34]. As presented in Fig.5 (e), the peaks located at 82.8 eV and 86.4 eV can be indexed to Au 4f_{7/2} and Au 4f_{5/2}, which display a negative shift compared to that of Au/TiO₂ [35]. There is also a slight downshift in comparison to the peaks in the cross-linked Au/ZnO nanowire arrays, which may be ascribed to the formation of AuPd bimetallic alloy [19, 36]. Moreover, it should be noted that other peaks centered at 88.65 eV and 90.8 eV are ascribed to Zn 3p_{3/2} and Zn 3p_{1/2}, similar to previous literature [19, 37]. Fig.5 (f) gives the XPS spectra of Pd 3d, and shows two peaks centered at 335 eV

and 340.3 eV, which are corresponding to the Pd 3d_{5/2} and Pd 3d_{3/2}, respectively. Consequently, the above XPS analysis together with the XRD and TEM results data have clearly proved that AuPd/ZnO photocatalyst was successfully prepared by using a simple method, as well as in a facile conditions.

3.2 Photoelectrochemical performances of AuPd/ZnO composite samples

To further reveal the effect of AuPd alloy particles, a three-electrodes PEC system was applied to detect the photoelectrochemical performances with as-obtained 1D ZnO nanorod arrays and the AuPd/ZnO samples using Na₂SO₄ as electrolyte (0.5 M) under simulated sunlight illumination. Fig.6 shows the photocurrent density of the two products under the applied potential from -0.2 V to 1.2 V versus Ag/AgCl. In dark condition, the current density of as-obtained two samples can be neglected, while much higher photocurrent density can be achieved under simulated sunlight condition. As it can be seen, the current density of the AuPd/ZnO sample which derives from ZnO nanorod arrays is higher than that of pure ZnO arrays, indicating higher efficiency for PEC water splitting. Fig.6 presents that the photocurrent density of ZnO nanorods array is about 0.41 mA·cm⁻² at 0.787 V versus Ag/AgCl, while the photocurrent density of AuPd/ZnO photocatalyst is 0.98 mA·cm⁻² at 0.787 V versus Ag/AgCl. It is noticed that the photocurrent intensity is about 2.4 times to the pure ZnO nanorod arrays after introducing AuPd, and the result implies the important role of AuPd alloy in enhancing the PEC activity. The calculated efficiencies of hydrogen generation (η) for the AuPd/ZnO photocatalyst and 1D ZnO nanorod nanoarrays were estimated with the following equation [38-42]:

$$\eta = \left[I(1.23 - E_{bias}) / J_{light} \right] \times 100\% \quad (1)$$

Where I is the photocurrent density (mA·cm⁻²), E_{bias} is the applied potential versus RHE, and J_{light} is the intensity of the solar simulated incident light (100 mW·cm⁻²).

The highest efficiency of 0.20% for the pure ZnO nanorod arrays is observed at 0.67 V versus Ag/AgCl (Fig.7). In the same conditions, the supreme calculated hydrogen production efficiency value

for AuPd/ZnO photocatalyst was 0.52% at 0.61 V versus Ag/AgCl, and the highest efficiency is about 160% higher than that of pristine 1D ZnO nanorod arrays which indicating a notable enhancement compared to pure ZnO. In conclusion, the AuPd alloy nanoparticles decorated ZnO nanorod arrays as a PEC electrode is more suitable for water splitting in comparison to ZnO samples.

In addition, to further investigate the stability of AuPd bimetallic nanoparticles decorated ZnO nanorod arrays, linear sweep voltammograms were measured after C-V scanning for 1 and 5 cycles under AM 1.5 G illumination using AuPd decorated ZnO and ZnO nanorod arrays as typical photoelectrode. The current intensity of 5th is about $0.78 \text{ mA} \cdot \text{cm}^{-2}$ at 0.787 V versus Ag/AgCl which was about 20% lower than that of 1cycle (Fig.8). I-V characteristic measurement also verifies an improved efficiency of AuPd/ZnO composite structure (5th) by 91.2% compared to ZnO nanorod arrays electrode. Based on the above results, it can be observed that there is slight decrease in the efficiency of photoelectrochemical water splitting activity.

3.3 Photocatalytic mechanism discussion

It has been proved that the Au-Pd bimetallic nanoparticles can enhance the photocatalytic activity and increase the rate of photodegradation of ZnO nanorods [31]. And it is believed that According to the results analysts above, a possible mechanism for improvement in the PEC performance of the AuPd/ZnO sample was proposed and displayed in Fig.9. It is well known that preventing the quickly recombination of photogenerated electron-hole pairs, enhancing separation efficiency and prolonging the lifetime of charge carriers could significantly improve the photoactivity. Vertically well-aligned 1D ZnO nanorod arrays can reflect unabsorbed lights back to ZnO nanoarrays and AuPd nanoparticles, and enhance the utilization of UV-visible light. In this process, the ZnO nanorods absorb more photons and generate a large number of free electrons and holes in the conduction band (CB) and the valence band (VB), respectively. What's more, vertical ZnO nanorod arrays on the FTO substrate can directly

transport the photo-generated electrons with a high speed, which is beneficial to the carrier transport properties [43]. Simultaneously, the hot electrons generated from surface plasmons photo-excitation of AuPd alloy nanoparticles are injected into the conduction band of ZnO. Finally, the electrons move to the Pt counter electrode through the FTO substrate and participate in the reduction of water to form H₂. The holes in the VB of ZnO are exhausted by water oxidation to generate O₂ under the applied potential [12, 44]. Finally, the significantly enhanced efficiency of PEC water splitting can be attributed to synergistic effect between 1D ZnO nanorod arrays and AuPd alloy nanoparticles. However, deeper investigations for the enhancement mechanism is undergoing in our lab.

4. Conclusions

In conclusion, the AuPd/ZnO composite structure was vertically synthesized on FTO substrate using 1D ZnO nanorod arrays as basement via a facile and efficient hydrothermal method. Among the several bimetallic alloy materials, AuPd alloy nanoparticles are especially attractive owing to their excellent catalytic activity and high stability [45-47]. The optical properties of AuPd/ZnO were investigated by PEC experiment, the photocurrent density was up to 0.98 mA·cm⁻² at 0.787 V vs Ag/AgCl, which exhibited a higher photoactivity than that of the pure ZnO nanorod arrays in PEC water splitting process. The reasons for the enhancement of catalyst activity can be summarized as the following: Firstly, the AuPd bimetallic nanoparticle has higher photocatalytic activity owing to the existence of the plasmonic properties of Au, catalytic behavior of Pd [27] which making the electron on the AuPd alloy with a higher energetic state [48]. Secondly, AuPd alloy nanoparticles on the ZnO nanorod surface can improve the light utilization efficiency by reflect unabsorbed photons back to ZnO nanorod arrays [49-50]. Thirdly, ZnO nanorods grown on the conductive glass substrate can directly transport the excited electrons to outer electrode, which takes full advantage of the excellent charge transport property of ZnO nanorods [51]. As described above, the photoactivity of AuPd/ZnO sample

was significantly enhanced owing to the synergistic effect between 1D ZnO nanorod arrays and AuPd alloy nanoparticles. Further studies to elucidate the mechanism are in progress.

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Figure Captions:

Fig.1 XRD patterns of 1D ZnO nanorod arrays and 70-2551 Zincite, syn.

Fig.2 SEM images of (a), (b) ZnO and (c), (d) AuPd/ZnO photocatalysts.

Fig.3 TEM images (a, b, c) and HRTEM (d and e) images of AuPd/ZnO composite.

Fig.4 UV-vis diffuses reflectance spectra of pure ZnO and AuPd/ZnO composite samples.

Fig.5 (a) Wide XPS spectrum and high resolution XPS spectra of as-prepared AuPd/ZnO sample: (a,b) C 1s; (c) O 1s; (d) Zn 2p; (e) Au 4f and Zn 3p; (f) Pd 3d.

Fig.6 Current Density-Potential curves of the 1D ZnO nanorod arrays and AuPd/ZnO samples under AM 1.5 G illumination (100 mW/cm^2) and dark condition.

Fig.7 Photoconversion efficiency curves of ZnO and AuPd/ZnO.

Fig.8 Linear sweep voltammograms of as-prepared AuPd/ZnO composite with different cycle times.

Fig.9 A proposed mechanism for the improvement of the PEC performance.

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Graphical Abstract