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ARTICLE

Fabrication of In₂O₃/In₂S₃/Ag nanocubes for efficient photoelectrochemical water splitting Rui Xu^{a,‡}, Haohua Li^{a,‡}, Wenwen Zhang^a, Zepeng Yang^a, Guiwu Liu^{a*}, Ziwei Xu^a,

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In this work, for the first time, three-component $In_2O_3/In_2S_3/Ag$ nanocomposite heterostructured photoanode is prepared on a F-doped SnO₂ (FTO) glass substrate. The threecomponent photoanode exhibits significantly enhanced photoelectrochemical properties compared with the single-component (In_2O_3) and two-component (In_2O_3/In_2S_3 or In_2O_3/Ag) systems. Ag nanoparticles deposited on the surface of In_2O_3/In_2S_3 nanocubes can facilitate the separation of photogenerated charge carriers and enhance the absorption of visible light. In I-V curves, the $In_2O_3/In_2S_3/Ag$ photoanode generates a remarkable photocurrent density of 8.75 mA cm⁻² (at 0 V vs. SCE), which is higher than those of the two-component In_2O_3/In_2S_3 (4.47 mA cm⁻²) and In_2O_3/Ag (3.50 mA cm⁻²). Furthermore, it also gives efficiency as high as 67% around 350 nm in the incident photon to electron conversion efficiency (IPCE) spectrum. These results open a promising avenue for the design and fabrication of novel heterojunction for photoelectrochemical water splitting.

Introduction

Photoelectrochemical (PEC) water splitting using transition semiconductor metal oxides has gained great interest owing to the large-scale production of hydrogen.^{1–7} Among the various transition metal oxides, In_2O_3 stands out as having suitable characteristics for PEC applications, including appropriately positioned conduction and valence bands for water splitting, good conductivity and high stability.^{8–11} However, research on In_2O_3 as a photoanode is progressing at a slow pace due to the limitations presented by its wide band-gap(3.5 eV).^{12–14} Therefore, the modification of highly efficient In_2O_3 nanostructures with good light-harvesting capability is of great importance.

The construction of type-II heterojunction between In_2O_3 and suitable narrow bandgap semiconductors has been demonstrated as a potential solution to address this issue.^{15–19} These heterostructures usually involve two (wide and narrow) bandgap semiconductors to form the type-II staggered band alignment heterostructure, enabling not only the broad absorption of visible light but also the inhibition of charge recombination process. However, the design of In_2O_3 composited with narrow bandgap semiconductor is limited because the conduction band potential for In_2O_3 is too negative.¹⁹ In principle, the band mismatch problem can be solved if the conduction band edge of In_2O_3 is lowered by formation of shallow donor energy levels in the bandgap of In_2O_3 (2.8 eV).^{20–23} To adopt this strategy, we have fabricated In_2O_3/In_2S_3 nanocubes to enhance the PEC properties. Nevertheless, it is still of great challenge to further improve the PEC performance of In_2O_3/In_2S_3 nanocubes.

To achieve highly efficient PEC performance, noble metal nanoparticles such as Ag, Au and Pt *etc.* have been extensively adopted in photoelectrode materials.^{24–28} Because they can act as photosensitizers to strengthen the optical absorption in visible light and enhance the absorption intensity through the localized surface plasma resonance (LSPR) effect.^{29,30} Meanwhile, the junctions formed between the semiconductor and noble metal nanoparticles can facilitate the separation of photogenerated charge carriers, thereby improving the

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In this work, for the first time, we report the synthesis of three-component In₂O₃/In₂S₃/Ag nanocubes by an effective electrodeposition method, which combines the shallow donor energy levels, heterostructure formation and noble metal modification together in order to further improve the PEC performance. The essence of our design is schematically illustrated in Fig. 1. Firstly, type-II In₂O₃/In₂S₃ heterostructured nanocubes by compositing wide-band-gap In2O3 with narrowband-gap In₂S₃ are prepared as schematically illustrated in Fig. 1a.^{32–34} Secondly, as shown in Fig. 1b, Ag nanoparticles are deposited on the surface of the as-prepared In₂O₃/In₂S₃ nanocubes to form three-component $In_2O_3/In_2S_3/Ag$ heterojunction. Here, the Ag nanoparticles play two key roles. Firstly, Ag nanoparticles can facilitate the photoinduced carriers transportation and separation. Secondly, Ag nanoparticles can effectively enhance the visible light absorption intensity through the localized surface plasma resonance (LSPR) effect.^{29,30} It is demonstrated that the threecomponent In2O3/In2S3/Ag heterostructure nanocubes show significantly enhanced PEC performance as compared with the pristine In₂O₃ nanocubes and two-component (In₂O₃/Ag, In₂O₃/In₂S₃) systems.^{35, 36}



Experimental Section

Materials

All chemicals used in this study are analytical reagent and were used without further purification. The used substrates are fluorine-doped SnO₂ (FTO) coated glass purchased from Wuhan lattice solar energy technology Co., LTD.

Preparation precursors of In₂O₃ nanocubes

In our experiment, indium nitrate (In(NO₃)₃•4H₂O), and urea (CO(NH₂)₂) were used to prepare the target product In₂O₃. Electrodeposition of In(OH)₃ nanocubes was performed in a conventional three-electrode cell using a HDV-7C potentiostatic apparatus with a graphite rod counter electrode and a saturated Ag/AgCl reference electrode, and an F-doped SnO₂-coated glass (FTO) substrate (10 mm×20 mm) with a sheet resistance of 14 Ω cm⁻² was used as the working electrode. Prior to electrodeposition, the FTO glass was cleaned ultrasonically with distilled water, ethanol and acetone,

followed by rinsing repeatedly in distilled water for several times. The as-deposited $In(OH)_3$ nanocubes were prepared from a mixed electrolytic solution of 0.012 M $In(NO_3)_3$ and 0.024 M $CO(NH_2)_2$ using a constant potential of -1.2 V at 70 °C for 90 min. After the deposition, the as-prepared $In(OH)_3$ nanocubes film were annealed in air at 350 °C for 180 min, then the faint yellow precursors of In_2O_3 nanocubes were finally obtained.

Synthesis of In₂O₃/Ag and In₂O₃/In₂S₃ nanocubes

Electrodeposition of In_2O_3/Ag nanocubes were performed in twoelectrode cell with a graphite rod counter electrode and the asprepared In_2O_3 nanocubes glass substrate was used as working electrode. The as-deposited In_2O_3 nanocubes were rinsed with deionized water, subsequently, the resulting samples were deposited at a constant current of -0.1 mA in 0.002 M silver nitrate solution for 8 min. Furthermore, the In_2O_3/In_2S_3 core-shell nanocubes were synthesized by an ion-exchange process. The as-prepared In_2O_3 nanocubes on the substrate were immersed into the teflonlined stainless-steel(30 ml)containing 20 ml 0.015 M thioacetamide aqueous solution, then, the autoclave was sealed and heated at 150 °C for 60 min. After the reaction, the autoclave was cooled naturally. Finally, the as-prepared products were washed with distilled water and then with ethanol for three times, then dried under vacuum for 12 h at 30 °C for further characterization.

Synthesis of In₂O₃/In₂S₃/Ag nanocubes

Electrodeposition of $In_2O_3/In_2S_3/Ag$ nanocubes were performed in two-electrode cell with a graphite rod counter electrode and the as-prepared In_2O_3/In_2S_3 nanocubes glass substrate was used as working electrode. The synthetic route to the $In_2O_3/In_2S_3/Ag$ heterostructured nanocubes is as depicted in Fig. 2. The asdeposited In_2O_3/In_2S_3 nanocubes were rinsed with deionized water, subsequently, the samples were deposited at a constant current of -0.1 mA in 0.002 M silver nitrate solution for 8 min. Finally, the as-prepared products were washed with distilled water and then ethanol for three times, then dried under vacuum for 12 h at 30 °C for further characterization.



Characterizations

X-ray diffraction (XRD) was carried out using a Siemens D-500 diffractometer with Cu K- α radiation. The surface morphology and composition of prepared products were analyzed by field emission scanning electron microscopy (FE-SEM, Hitachi, S-4800). The microstructures were observed by transmission electron microscopy (TEM, 200 kV, JEM2010-HR). Furthermore, the UV-vis absorption spectra was recorded using a lambda-750 UV-Vis-NIR spectrophotometer and the photoluminescence spectra was recorded by a combined fluorescence time and steady state spectrometer (PL, Varian Cary Eclipse).

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Photoelectrochemical (PEC) measurements

The PEC measurements were performed using a CHI 760D electrochemical analyzer (ChenHua Instruments, Shanghai, China) with a three-electrode cell using Pt mesh and staurated calomel electrode (SCE) as counter electrode and reference electrode in the 20 ml 0.5 M Na₂SO₃ and 0.43 M Na₂S mixed electrolyte solution. The working electrode were as-prepared nanocubes. The illumination source was a 300 W Xe lamp (PLS-SXE300 (UV), Perfect Light Technology Co., Ltd. Beijing) and a monochromator (Newport) was used to investigate wavelength-dependent photocurrent, and the output intensity of the light source was measured with the same radiometer (Merlin). The distance between the light and solution was fixed to be 25 cm. The PEC measurements were carried out in a three-electrode three-electrode cell with a flat quartz window to facilitate illumination of the photoelectrode surface. A region (size: $1 \text{ cm} \times 1 \text{ cm}$) of the photoelectrode surface was illuminated with light irradiation. The CHI 760D electrochemical workstation was used to record the photocurrent densities by using the difference between the light-off (dark current) and light-on currents acquired consecutively. The photoelectrochemical properties of electrodes were characterized by measuring the photocurrent at zero bias. The linear sweep voltammograms curve was measured from -1.4 V to 0.2 V (vs. SCE) at a sweep rate of 20 mV s⁻¹. The photocurrent density vs. time was measured at a potential of 0 V (vs. SCE). The incident photon to electron conversion efficiency (IPCE) of the samples was calculated as follows:

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

Where I, λ and J_{light} are the photocurrent density (mA cm⁻²), incident light wavelength (nm) and incident light intensity (mW cm⁻²), respectively. Based on the formula "*IPCE* = (1240I)/(λJ_{light})", we know that the IPCE numerical value is up to the I, λ and J_{light} . Therefore, the experiment process was divided into several steps as follows. Firstly, in order to determine the " λ " in the formula, we fixed a monochromatic light wavelength (λ) and it was changed every 20 nm from 300 nm to 700 nm. Secondly, in order to determine the "I" in the formula, under different monochromatic light wavelength (λ) irradiation, the potential was swept from –1.4 V to 0.2 V (vs. SCE) at a sweep rate of 20 mVs⁻¹. And from the I-V curves, we use the photocurrent density at 0 V as a calculated value (I). Thirdly, the "J_{light}" in the formula can be obtained by measuring apparatus automatically. Therefore, according to the λ , I and J_{light}, IPCE can be obtained by the formula above.

Results and Discussions

Phase Formation Characterization

The crystal phases of the as-prepared nanocube were first determined by XRD (Fig. 3). As shown in Fig. 3, it can be seen that the diffraction peaks of In_2O_3 can be perfectly indexed to the body-centered-cubic (bcc) structure of In_2O_3 (JCPDF no. 06-0416). Furthermore, the XRD patterns of In_2O_3/In_2S_3

heterostructure are similar to those of the In_2O_3 nanocubes except additional peaks which are well indexed to the cubic structure of In_2S_3 (JCPDF no. 65-0459). Therefore, it could be concluded that the In_2O_3/In_2S_3 nanocubes are successfully synthesized by anion exchange method. In addition, the ratio of In_2O_3 to In_2S_3 was tested using EDS analysis, and the results are shown in Fig. S1. However, the patterns of the Ag nanoparticles are not detected in the In_2O_3/Ag and $In_2O_3/In_2S_3/Ag$ nanocubes due to the small mass loading, which could be investigated by EDS (Fig. S1) and TEM thereinafter. No other diffraction peaks were detected besides the peaks of SnO₂ that originate from the FTO substrates.



Fig. 3 XRD patterns of as-prepared $In_2O_3,\,In_2O_3/Ag,\,In_2O_3/In_2S_3$ and $In_2O_3/In_2S_3/Ag$ nanocubes.

Morphology and Detailed Structure Observations

To investigate the morphology and detailed structure of the asprepared samples, SEM images were detected as depicted in Fig. 4. Firstly, as shown in Figure. 4a, the In₂O₃ nanocubes are successfully synthesized on the surface of FTO substrates. The more detailed view of In₂O₃ nanocubes is shown in the inset of Fig. 4a. It can be observed that the surface of In₂O₃ nancubes is smooth, the angle between the adjacent edges is close to 90° and the length of the In_2O_3 nanocubes is ~ 300 nm. Fig. 4b is a typical SEM image of In₂O₃/In₂S₃ core-shell nanocubes. The average length of these nanocubes is also ~ 300 nm. This is consistent with the morphology of as-synthesized In₂O₃ being retained and not altered by the anion exchange reaction. Fig. 4c shows the In₂O₃/Ag nanocubes, compared with In₂O₃ nanocubes (Fig. 4a), the surface of In₂O₃/Ag nanocubes is rough since it is covered with a number of Ag nanoparticles. Similarly, in Fig. 4d, the surface of In₂O₃/In₂S₃/Ag is rougher, implying that In2O3/In2S3 system is covered by Ag nanoparticles. Therefore, it can be concluded that the In₂O₃, In₂O₃/Ag, In₂O₃/In₂S₃ and In₂O₃/In₂S₃/Ag nanocubes are grown successfully on the FTO substrates.



Fig. 4 SEM images of as-synthesized (a) $In_2O_3(b)$ In_2O_3/In_2S_3 (c) In_2O_3/Ag and (d) $In_2O_3/In_2S_3/Ag$ nanocubes.

To further examine the detailed microstructure and detect the existence of Ag nanoparticles, the In_2O_3/Ag and $In_2O_3/In_2S_3/Ag$ nanocubes were investigated by TEM and HRTEM (Fig. 5). A representative low-magnification TEM image of In_2O_3/Ag nanocube is illustrated in Fig. 5a. It can be clearly observed that the surface of In_2O_3 nanocubes is rough, which is consistent with the SEM result above. Figure 5b is the HRTEM image of the selected area marked in Fig. 5a, disclosing the lattice fringe spacing of 0.292 nm (see the magnified HRTEM in Fig. 5c), which matches well with the (222) lattice spacing of body-centered-cubic (bcc) In_2O_3 (JCPDF no. 06-0416). In Fig. 5d, the



Fig. 5 TEM images of (a) In_2O_3/Ag and (e) $In_2O_3/In_2S_3/Ag$ nanocubes. HRTEM images of (b) In_2O_3/Ag and (f) $In_2O_3/In_2S_3/Ag$ nanocubes. (c,d) Enlarged images of the selected parts marked in (b). (g, h, i) Enlarged images of the selected parts marked in (f).

lattice fringes with a *d*-spacing of 0.238 nm correspond to the (111) planes of the cubic phase Ag (JCPDF no. 65-8428). This confirms the existence of Ag nanoparticles on the surface of In_2O_3/Ag

nanocubes. Similarly, the TEM image (Fig. 5e) and HRTEM (Fig. 5f, 5h, 5i) of a $In_2O_3/In_2S_3/Ag$ nanocube determine its detailed microstructure. As shown in the Fig. 5g, the lattice fringe spacing of 0.292 nm is also in agreement with that of body-centered-cubic (bcc) In_2O_3 (JCPDF no. 06-0416). In Fig. 5h, the fringe spacing of 0.311 nm matches well with the spacing of the (222) planes of the cubic In_2S_3 crystal structure (JCPDF no. 65-0459). Besides, as shown in Fig. 5i, the lattice fringes with a *d*-spacing of 0.238 nm correspond to the (111) planes of the cubic phase Ag (JCPDF no. 65-8428). Hence, based on the results above, it could be concluded that the In_2O_3 , In_2O_3/Ag , In_2O_3/In_2S_3 and $In_2O_3/In_2S_3/Ag$ nanocubes are successfully grown on the FTO substrates.

Photoelectrochemical (PEC) performance

To further investigate the PEC performance, the deposited films were investigated by the linear sweep voltammograms (Fig. 6a) and time-dependent photocurrent (Fig. 6b). As shown in Fig. 6a, the linear sweep voltammograms of these samples reveal two remarkable differences in PEC performance. Firstly, all the samples exhibit an n-type semiconductor feature PEC response under light illumination. The photocurrent density of the In₂O₃/In₂S₃/Ag is 8.75 mA cm⁻², which is substantially higher than those of In_2O_3/In_2S_3 $(4.47 \text{ mA cm}^{-2})$, $In_2O_3/Ag (3.50 \text{ mA cm}^{-2})$ and $In_2O_3 (2.37 \text{ mA cm}^{-2})$ at the same applied potential (0V vs. SCE). Similarly, the same trend can also be seen in the I-t curve(Fig. 6b), which is clearly shown that the transient photocurrent density of different samples. Obviously, as shown in the Fig.6b, upon irradiation, it is clearly shown that the transient photocurrent density of the In₂O₃/In₂S₃/Ag nanocubes is 8.45 mA cm⁻², which is almost 4 times as high as that of the pristine In_2O_3 nanocube (2.17 mA cm⁻²). Moreover, the photocurrent density of the three-component In₂O₃/In₂S₃/Ag is much larger than that of as-prepared In₂O₃ reported by Tong et al..^{8, 23} In other words, the photocurrent densities follow in this order: $In_2O_3/In_2S_3/Ag > In_2O_3/In_2S_3 > In_2O_3/Ag > In_2O_3$. The higher photocurrent density means that more photoinduced electrons have been transferred from the In2O3/In2S3/Ag nanocubes to the counter electrode via external circuit. Secondly, the onset potential of the $In_2O_3/In_2S_3/Ag$ nanocubes (- 1.09 V) reveals a distinct negative shift compared to other samples, which means the Fermi energy level of the three-component heterostructure has been elevated.37,38 The negative shift of onset potential means that the charge separation and transportation in the samples are more efficient. Accordingly, from the analysis result above, the PEC properties follow this order: $In_2O_3/In_2S_3/Ag > In_2O_3/In_2S_3 > In_2O_3/Ag > In_2O_3$. These results provide explicit evidences that the three-component In₂O₃/In₂S₃/Ag nanocubes are more conducive to providing photoinduced electrons and promoting the separation of charge carriers for enhanced the PEC performance.

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Fig. 6 (a) Linear sweep voltammograms curves for the photocurrent response of the In_2O_3 , In_2O_3/Ag , In_2O_3/In_2S_3 and $In_2O_3/In_2S_3/Ag$ photoelectrodes. (b) The time-dependent photocurrent curves. (c) Chronoamperometric time-dependent photocurrent curves .

Another important performance for the PEC cells application is the chemical stability of the photoelectrode.^{40,41} Fig. 6c presents photocurrent stability (vs. time curve) of the In_2O_3 , In_2O_3/Ag , In_2O_3/In_2S_3 and $In_2O_3/In_2S_3/Ag$ nanocubes at 0 V (vs. SCE). The

photocurrent decays quickly for the uncoated In_2O_3 nanocubes photoanode. In contrast, the In_2O_3/Ag , In_2O_3/In_2S_3 and $In_2O_3/In_2S_3/Ag$ nanocubes show improved photo-stability under continuous illumination for more than 50 min. It clearly demonstrates that the $In_2O_3/In_2S_3/Ag$, In_2O_3/In_2S_3 and In_2O_3/Ag photoelectrode exhibit quite good photostability and chemical stability in electrolyte solution (S²⁻, SO₃²⁻).

Furthermore, IPCE is an important performance for quantitatively investigate the photoactivity in PEC cell. We performed IPCE measurements as a means of studying the photoactive wavelength regime for the deposited films (In₂O₃, In₂O₃/Ag, In₂O₃/In₂S₃ and In₂O₃/In₂S₃/Ag) (Fig. 7).²³ As shown in Fig. 6, the deposited films were assessed at wavelengths ranging from 300 to 650 nm at 0 V (vs. SCE) in 0.5 M Na₂SO₄ electrolyte. Compared with the other films, the In₂O₃/In₂S₃/Ag film gives the highest efficiency. The In₂O₃/In₂S₃/Ag nanocubes achieve an IPCE of 67% at 350 nm, which is 4.46, 2.48, 1.81 times as high as those of In₂O₃, In₂O₃/Ag, In_2O_3/In_2S_3 at the same applied potential of 0 V (vs. SCE), respectively. The results are consistent with the time-dependent photocurrent curves (Fig. 6a). In comparison with previously reported other three-component systems, In2O3/In2S3/Ag system presents higher efficiency.⁴⁰ Accordingly, from the analysis result above, the PEC properties follow this order: In₂O₃/In₂S₃/Ag > $In_2O_3/In_2S_3 > In_2O_3/Ag > In_2O_3$. The three-component In₂O₃/In₂S₃/Ag nanocubes present enhanced PEC performance than single-component system (In2O3) and two-component system (In₂O₃/In₂S₃, In₂O₃/Ag). In a word, the In₂O₃/In₂S₃/Ag threecomponent heterostructured nanocubes exhibit significantly enhanced photoelectrochemical properties compared with the singlecomponent (In₂O₃) and two-component (In₂O₃/In₂S₃ or In₂O₃/Ag) systems.



Fig. 7 IPCE spectra of ln_2O_3 , ln_2O_3/Ag , ln_2O_3/ln_2S_3 and $ln_2O_3/ln_2S_3/Ag$ films, collected at the incident wavelength range from 300 to 650 nm at a potential of 0 V (vs. SCE).

The mechanism of PEC performance

By analyzing the result described above, a schematic diagram is illustrates in Fig. 8 to understand the mechanism of PEC performance with the obtained photoelectrodes. The mechanism of photoelectrode is identified according to the previous reports.^{27,30,31}

It is generally accepted that two aspects are often used to explain the enhanced PEC performance of the photoelectrodes.⁴¹⁻⁴³ One is to enhance the light absorption, and the other is to promote the charge separation and transfer, that is, to inhibit the recombination of the photoinduced electron/hole pairs. Therefore, on the basis of the analysis above, by this strategy, according to four different photoelectrodes, the differences of their PEC performance can be classified into two aspects. Firstly, compared with the In2O3/In2S3 nanocubes, three-component In₂O₃/In₂S₃/Ag nanocubes show better performance in increasing photoelectrons and effective charge separation due to the existence of Ag nanoparticles. Ag nanoparticles play two key roles in the three-component system. On one hand, Ag nanoparticles can facilitate the photoinduced carriers transportation and separation on the interface of metal-semiconductor.³¹ On the other hand, Ag nanoparticles can effectively enhance the visible light absorption intensity through the LSPR effect.^{29,30} Likewise, this mechanism is also suitable for In₂O₃/Ag and In₂O₃, and thus the PEC performance of In₂O₃/Ag nanocubes is distinctively higher than that of In₂O₃ nanocubes. Secondly, in comparison with In₂O₃/Ag, In₂O₃/In₂S₃ nanocubes reveal better PEC properties, which can be attributed to two aspects. On one hand, light absorption capability of narrow band-gap semiconductor shell in type-II heterostructure is substantially higher than the LSPR effect of noble metal nanoparticles of metal-semiconductor composite systems.³⁹ On the other hand, the photoexcited charge separation efficiency of type-II core-shell heterostructure is substantially higher than the interface of metal-semiconductor.^{24,39} As a consequence, the three-component In₂O₃/In₂S₃/Ag heterojunction can emerge optimal PEC performance.



Fig. 8 PEC water splitting mechanism of the $In_2O_3,\ In_2O_3/Ag,\ In_2O_3/In_2S_3$ and $In_2O_3/In_2S_3/Ag$ nanocubes.

through the LSPR effect.^{29,30} Indeed, our experimental observations further confirm this conclusion. As shown in Fig. 9a, in contrast to the In_2O_3/In_2S_3 nanocubes, three-component $In_2O_3/In_2S_3/Ag$ nanostructures exhibit a noticeable increase in light absorption intensity and a remarkable red shift of the bandgap (Fig. S2). Similarly, this trend can also be observed between In_2O_3 and In_2O_3/Ag . Secondly, it is generally believed that the light absorption capability of narrow band-gap semiconductor shell in type-II staggered band alignment is substantially higher than the LSPR effect of noble metal nanoparticles at the interface of metalsemiconductor composite systems.³⁹ This can also be observed in our results. As shown in Fig. 9a, by comparison, the light absorption density of two-component In_2O_3/In_2S_3 heterojunction presents a



Optical properties tests

To further verify our proposed mechanism for the improved PEC performance, the optical properties of the samples were characterized by UV-Vis absorption spectra (Fig. 9a). By analyzing the data, we can draw two conclusions. Firstly, it is widely accepted that the noble metal nanoparticles as photosensitizers can improve the absorption in visible light and enhance the absorption intensity

Fig. 9 (a) UV-Vis absorption spectra of In_2O_3 , In_2O_3/Ag , In_2O_3/In_2S_3 and $In_2O_3/In_2S_3/Ag$ nanocubes. (b) Room-temperature PL spectra of In_2O_3 , In_2O_3/Ag , In_2O_3/In_2S_3 and $In_2O_3/In_2S_3/Ag$ nanocubes collected at the excitation wavelength of 288 nm.

Wavelength (nm)

remarkable red shift of the bandgap than the In_2S_3/Ag . Therefore, $In_2O_3/In_2S_3/Ag$ heterojunction has better performance in light absorption due to its type-II heterostructure and LSPR effect of Ag nanoparticles.

Additionally, the enhanced photoexcited charge separation efficiency could be further verified by photoluminescence (PL)

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spectroscopy (Fig. 9b). By analyzing the data, we can also draw two conclusions. Firstly, it is widely accepted that the noble metal nanoparticles can effectively suppress the recombination of carriers and facilitate the separation and transport of photogenerated carriers, which is in excellent agreement with our experimental observations.²⁴ As shown in the Fig. 9b, it is evident that the PL emission intensity at 428 nm for the In₂O₃/In₂S₃/Ag nanocubes is much lower than the In2O3/In2S3 nanocubes. This trend is also suitable for In₂O₃/Ag and In₂O₃. In comparison with In₂O₃ nanocubes, the In₂O₃/Ag nanocubes have lower emission intensity. Secondly, type-II heterostructures have better performance in separating charge carriers and inhibiting electron and hole recombination.³³ Our experimental observations also further confirm this conclusion. As compared to the In₂O₃/Ag nanocubes, the In₂O₃/In₂S₃ type-II heterostructure nanocubes have the weaker PL intensity. Hence, based on the PL results above, we believe that the drastic quenching of the emission can clearly indicate that the construction of the In₂O₃/In₂S₃/Ag heterostructure is reasonable and can effectively suppress the recombination of charges. In a whole, the enhanced PEC properties of In₂O₃/In₂S₃/Ag heterojunction is direct consequence of the synergetic effects of enhanced visible light absorption and effective carriers separation on the surface of narrow band-gap semiconductor shell heterostructure via the Ag nanoparticles, which is consistent with our original hypothesis (Fig. 1).

Conclusions

In summary, the dramatically enhanced photoelectrochemical performance of three-component $In_2O_3/In_2S_3/Ag$ heterostructured nanocubes are investigated and presented. The remarkable charge separation of the samples is revealed in the significant enhancement of photocurrent generation due to the type-II heterostructure. Furthermore, the Ag nanoparticles deposited on the face of In_2O_3/In_2S_3 nanocubes can effectively promote the separation and transportation of photogenerated carriers and enhance the absorption of visible light. Noble metal loading on type-II heterostructure opens a promising avenue for the rational design and fabrication of high efficiency heterostructured functional materials.

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Notes and references

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