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Article

ZnO nanorod decorated by Au-Ag alloy with greatly increased activity for photocatalytic ethylene oxidation

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ABSTRACT

In recent years, the preservation of fruits and vegetables in cold storage has become an issue of increasing concern, ethylene plays a leading role among them. We found ZnO has the effect of degrading gaseous ethylene, however its effect is not particularly satisfactory. Therefore, we used simple photo-deposition procedure and low-temperature calcination method to synthesize Au, Ag, and AuAg alloy supported ZnO to improve the photocatalytic efficiency. Satisfactorily, after ZnO loaded with sole Au or Ag particles, the efficiency of ethylene degradation was 17.5 and 26.8 times than that of pure ZnO, showing a large increase in photocatalytic activity. However, the photocatalytic stability of Ag/ZnO was very poor, because Ag can be easily photooxidized to Ag₂O. Surprisingly, when ZnO was successfully loaded with the AuAg alloy, not only the photocatalytic activity was further improved to 94.8 times than that of pure ZnO, but also the photocatalytic stability was very good after 10 times of cycles. Characterization results explained that the Au-Ag alloy NPs modified ZnO showed great visible-light absorption because of the surface plasmon resonance (SPR) effect. Meanwhile, the higher photocurrent density showed the effective carrier separation ability in AuAg/ZnO. Therefore, the cooperative action of plasmonic AuAg bimetallic alloy NPs and efficient carrier separation capability result in the outstanding photoactivity of ethylene oxidation. At the same time, the formation of the alloy produced a new crystal structure different from Au and Ag, which overcomes the problem of poor stability of Ag/ZnO, and finally obtains AuAg/ZnO photocatalyst with high activity and high stability. This work proposes a new concept of using metal alloys to remove ethylene in actual production.

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1. Introduction

In recent years, the noble metals have attracted great attention because of their outstanding physical, chemical and optical performances, which made them suitable as co-catalysts on some photocatalysts [1–8]. Most of them can be used as the electron-transfer active sites in photodegradation of dye [9],

photocatalytic H₂ production [10,11], CO₂ reduction [12], transformation of green organic [13], thermocatalytic reduction of nitroaromatics in water [14] and so on. In particular, Au and Ag as common noble metals in our life are also widely investigated in photocatalytic academic research due to their unique surface plasmon resonance (SPR) [15–19]. The Au, Ag NPs under SPR-excitation have strong visible-light absorption,

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thus they can be applied to solve the challenges in photocatalytic reactions such as narrow spectral response [15–19]. Furthermore, just like a semiconductor heterojunction can promote carrier separation [20–23], Au or Ag NPs can act as the active sites for capturing electrons, improving the separation of electron and hole pairs in photocatalytic system as well. Therefore, the Au or Ag supported materials have been also investigated in solving the problem of low quantum efficiency [24].

Bimetallic alloy is composed of two metals by a certain method. Recently, some studies have found that the semiconductors loaded with bimetallic alloy have many superior properties compared to that loaded with sole metal [25–29]. More importantly, they can complement each other to achieve a win-win situation. For example, Au-Cu alloy supported on TiO_2 is effective on photocatalytic CO_2 reduction [30]. Among them, the selectivity in CH_4 conformation owned to the Cu bonding to CO_2 on TiO_2 , while the visible light photoresponse would be due to the surface plasmon band of Au, illustrating Au and Cu in the Au-Cu alloy have been put to the best utilization from each other [30]. In addition, Au-Pt alloy loaded on WO_3 was used to strengthen hydrogen and oxygen generation owing to the mutual promotion of plasmonic function in Au and catalytic characteristic in Pt [15]. As we all know, Ag has similar plasmonic property as Au. Therefore the Au and Ag in Au-Ag alloy exhibit outstanding photocatalytic performances and synergistic effects which are superior to the pure metals under visible-light irradiation [31]. Au-Ag alloy loaded semiconductors have been applied to restore CO_2 to fuels [32], heighten the photoelectrocatalytic properties [33], oxide of methanol selectively [34], and so on. In particular, we have found Au-Ag alloy played an important role in the degradation of the harmful gas ethylene recently.

Ethylene is produced in natural sources, plants and plant products. It has some harm on the storage life, development and growth of many ornamental crops, fruits and vegetables at extremely low concentration [35,36]. Some researchers have already realized the dangers of ethylene and looked for some ways to degrade it to keep fresh of fruits and vegetables. In the field of photocatalysis, many studies were focus on traditional TiO_2 and TiO_2 -based photocatalysts [37–40], while new materials were rarely exploited on ethylene degradation. Actually there were only few new semiconductors had ethylene-oxidation function and their photocatalytic activity were very poor, such as BiVO_4 and In_2O_3 -Ag- Ag_3PO_4 [41,42]. Recently, we reported that Fe-doped WO_3 has the property of degrading ethylene [43], and the activity was greatly improved compared with previous studies. However, the ethylene cannot be completely mineralized to CO_2 . Therefore, it is urgent to find a highly active substance to deal with the ethylene. In this paper, we interestingly found ZnO had capability to oxide ethylene, but the activity was not so satisfactory. To improve the photocatalytic reaction rate greatly, Au-Ag bimetallic alloy NPs were loaded on the ZnO. We systematically investigated the performance of single Au, Ag, and Au-Ag alloy decorated on ZnO, and we found the photocatalytic ethylene-oxidation activity of ZnO decorated by 0.8 wt% of Au-Ag alloy was 94.8 times higher

than that of pure ZnO, while loaded by single 0.8 wt% of Au or Ag was only 17.5 or 26.8 times higher than that of ZnO. These results confirm the Au-Ag alloy is superior to the single metal Au or Ag in ethylene-oxidation process. Therefore, the Au-Ag alloy is the promising cocatalyst for ethylene oxidation to freshen fruits and vegetables in refrigeration storage.

2. Experimental

2.1. Materials synthesis

2.1.1. ZnO nanorods

The ZnO nanorods were prepared referring to the simple hydrothermal method [44]. Particularly, 0.4 g NaOH was added to 60 mL ethanol under ultrasonic treatment until forming homogeneous 0.17 mol/L NaOH/ethanol solution. Then the solution was put into a Teflon tank of 100 mL capacity containing 2 mmol $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and stirred for 30 min. The tank was transferred into a stainless-steel autoclave and heated at 160 °C for 24 h, the white powder was obtained after suction filtration with water and dried at 60 °C. Then the ZnO powder was calcined at 400 °C for 1 h to remove the adsorbed ethanol.

2.1.2. Au or Ag NPs loaded on ZnO nanorods

The deposition of single Au NPs on the ZnO nanorods was synthesized via a photo-reduction method. Briefly, 0.15 g ZnO was dispersed in 100 mL H_2O in a beaker. Then different volumes of 0.1 mol/L HAuCl_4 were dripped into the system and stirred for 5 min in order to form a homogeneous mixture. Before irradiation, 1 mL methyl alcohol was added as the sacrificial agent. Then the mixture was irradiated for 30 min under the Xe lamp of 300 W. Finally, the solid was filtered, dried at 60 °C and calcined at 400 °C for 1 h to make the Au NPs have a tightly integrated with the surface of ZnO and remove the adsorbed ethanol. The deposition of single Ag NPs on the ZnO nanorods was similar with these processes. The only difference was that 0.1 mol/L HAuCl_4 was replaced with 0.1 mol/L AgNO_3 .

2.1.3. Au-Ag bimetallic alloy NPs loaded on ZnO nanorods

The Au-Ag bimetallic alloy NPs supported on ZnO nanorods were conducted with a co-photodeposition method. That is, a certain volume of HAuCl_4 (0.5 wt% Au) and AgNO_3 (0.3 wt% Ag) were put together into the ZnO suspension under continuous stirring, and other reaction conditions were same as single Au/ZnO. The optimal Au-Ag proportion on ZnO was 0.8 wt%. Therefore, 0.8 wt% Au/ZnO and 0.8 wt% Ag/ZnO were also obtained as comparison by using the similar procedure.

2.2. Characterization

Morphologies were investigated by SEM (Hitachi S-4800) equipped with an EDS. XRD patterns were conducted on a Bruker AXS D8 diffractometer equipped with $\text{Cu K}\alpha$ radiation to reveal the crystal structure. The UV-vis DRS analyzes were recorded by Shimadzu UV-2550 spectrophotometer using BaSO_4 as reflectance standard to explore the optical absorption. The TEM and HRTEM tests were performed with a JEOL JEM-2100F

microscope to analyze the nanostructure and composition of the as-prepared AuAg/ZnO photocatalyst. XPS measurements were obtained using a Thermo ESCALAB 250XI, and the peak positions of various elements were calibrated by C 1s (284.8 eV). Photoelectrochemical tests were measured by CHI-660C electrochemical workstation using a three-electrode system. The FTO glass coated catalyst was served as working electrode, Pt sheet as counter electrode and Ag/AgCl as reference electrode. 0.2 mol/L Na₂SO₄ solution was used as the electrolyte. A 300 W Xe-arc lamp (CEL-HXF300, Beijing CEAU Light, China) was used for a light illuminant. The gas mixture was researched by means of the Shimadzu GC-2014C.

2.3. Photocatalytic evaluation

Photocatalytic oxidation of ethylene was measured in a quartz-covered reactor with 400 mL volume irradiated by a 300 W Xe lamp. 0.12 g photocatalyst was dispersed uniformly in the bottom of the container with a rotor. The reactor was then sealed by the quartz cover and injected into 0.5 mL ethylene under stirring. Before turning on the lights, the container was stirred in the dark for 2 h to make ethylene and air in the container mix evenly and attain the adsorption and desorption balance. When the balance was achieved, the reactor was illuminated on top of quartz cover and 50 μ L of gas mixture was sampled at regular intervals and tested by a gas chromatography. C/C_0 indicates the degradation percentage of ethylene, where C is ethylene concentration at a specific time and C_0 is the initial concentration of ethylene. Stability of AuAg/ZnO product was also investigated as follows: after each ethylene oxidation reaction, opened the cover and set aside 30 minutes to allow excess CO₂ and C₂H₄ in the container to diffuse out. Then the reactor was sealed again to degrade a new 0.5 mL ethylene for another test under the same irradiation.

3. Results and discussion

3.1. X-ray diffraction research of as-prepared nanocomposites

The XRD spectra of obtained products are shown in Fig. 1. As can be seen from the left figure, the peaks of pure ZnO match well with the standard ZnO card (JCPDS, No. 70-2551). All of the diffraction peaks of the as-prepared samples after incorporation of noble metals are very identical to that of pristine ZnO, with only small peak displacement in the part of the dotted line. From the magnified figure on the right and the Table 1 below, it can be seen that the Ag/ZnO has two peaks at 37.99° and 44.21° while the peaks of Au/ZnO at 38.30° and 44.66°, which are in line with the Ag and Au standard cards (Fig. S1). It should be pointed out, however, the AuAg/ZnO has peak locations (38.22° and 44.39°) different from any one of single Au and Ag, which are located between the peaks of Au and Ag. Similar consequence of Au-Ag alloy peak-displacement was also found in Fig. S1. This interesting phenomenon concludes that Au-Ag alloy might come into being when Au and Ag are co-loaded on the ZnO and calcined at 400 °C. Certainly, this conclusion needs to be proved further by the following results.

Fig. 1. The XRD patterns of the pure ZnO and Au, Ag, Au-Ag alloy nanoparticles decorated on ZnO samples.

3.2. EDS and elemental maps of nanocomposites

Fig. 2a reveals the distribution and content of C, O, Zn, Au and Ag. Among them, the source of C might be conductive plastic or the adsorbed CO₂. As can be seen from Fig. 2b, the weight percentages of Au and Ag are, respectively, 0.55% and 0.21%, which are close to the actual loading amount of 0.5% and 0.3%. From Fig. 2c, we can see the overall distribution of Au and Ag elements are strongly uniform, illustrating that Au and Ag are evenly loaded on the surface of ZnO.

3.3. UV-vis diffuse spectroscopy

To understand the different absorption of Au, Ag and AuAg loaded ZnO, the UV-vis diffuse reflectance spectra of 0.8 wt% Au/ZnO, 0.8 wt% Ag/ZnO and 0.5 wt% Au@0.3 wt% Ag/ZnO samples, together with that of pure ZnO nanorods, are investigated and exhibited in Fig. 3.

As can be observed in Fig. 3, pure ZnO has no absorption in the visible range, in agree with the reported band gap of ~3.1 eV. However, the Au or Ag loaded ZnO displays increased visible light absorption owned to the surface plasmon resonance (SPR) effect of the metallic Au and Ag particles. Especially, there is a characteristic peak at around 550 nm of Au/ZnO while Ag/ZnO is approximately at 470 nm, which is in accordance with the previous article [31,45,46]. Interestingly, when Au or Ag is replaced by the same amount of Au-Ag, it shows a broader and stronger peak at about 510 nm lying between the characteristic peaks of single Au and Ag. These data further illustrate that when Au and Ag were co-loaded on ZnO, they might form the Au-Ag alloy with the synergistic SPR effect, which can enhance the light absorption at 400–800 nm [32,33]. And it is worth putting forward that the promoted light absorption generally along with the increased photocatalytic property.

Table 1

The two XRD peaks in the range of 37°–45° of Ag/ZnO, AuAg/ZnO and Au/ZnO samples.

Sample	$2\theta_1$ (°)	$2\theta_2$ (°)
Ag/ZnO	37.99	44.21
AuAg/ZnO	38.22	44.39
Au/ZnO	38.30	44.66

Fig. 2. (a, b) EDS spectra and (c) EDS elemental mapping analysis of O, Zn, Au, and Ag in the AuAg/ZnO sample.

3.4. SEM and TEM

Fig. 4a and b are typical SEM images of the as-prepared ZnO and AuAg/ZnO. As can be seen, ZnO are nanorods with an average thickness of around 20 nm. After loaded by Au-Ag alloy NPs, we can see from Fig. 4c that there are some small particles deposited on the surfaces and edges of nanorods. The key is that these nanoparticles have uneven size, some are big and some are small, with an average of ~6 nm by calculating (see Supporting Information Fig. S2), and they are closely attached to the ZnO surfaces to have a better contact. Fig. 4d, e and f are the corresponding HRTEM images of AuAg/ZnO. The detected lattice fringes of ZnO are matching well with the (002) plane of

Fig. 3. UV-vis diffuse reflectance spectra of ZnO, Au/ZnO, Ag/ZnO and AuAg/ZnO samples.

Fig. 4. (a) SEM of pure ZnO, (b) SEM of AuAg/ZnO, (c) TEM of AuAg/ZnO, and (d, e, f) HRTEM images of AuAg/ZnO.

0.26 nm (JCPDS, No. 70-2551). After a lot of detection, the *d*-spacing values of these small metal NPs (3–7 nm) are 0.235 nm (Au(111) JCPDS 01-1172) and 0.237 nm (Ag(111) JCPDS 01-1164), one of the pictures is presented in Fig. 4d. However, the *d*-spacing values of these big metal NPs (10–15 nm) are all 0.236 nm (AgAu(111) JCPDS 65-8424), presented in Fig. 4e and 4f. The size of AuAg NPs coated on ZnO is larger than Au or Ag NPs due to Au-Ag alloy formation [32].

Besides, the information crisply exhibits that the AuAg/ZnO photocatalyst possesses not only a distribution of the Au-Ag alloy NPs but also the coexistence of unalloyed Au and Ag NPs. Similar phenomenon is also appeared in Au-Cu alloy loaded on TiO₂, that is, AuCu/TiO₂ sample consists of Au-Cu alloy NPs together with independent Au and Cu NPs, which is difficult to avoid [30]. Anyway, this result further proves the formation of Au-Ag alloy NPs in AuAg/ZnO and its photocatalytic activity and stability are both satisfactory in the following tests.

3.5. X-ray photoelectron spectroscopy study

To obtain the surface chemical status of AuAg/ZnO before and after irradiation, X-ray photoelectron spectroscopy was carried out. Fig. 5a is the full spectra of AuAg/ZnO sample before and after degradation, where the peaks for Zn 2p and O 1s can be seen clearly. In Fig. 5b, the two peaks centered at 1021 eV and 1044 eV are corresponding to the Zn 2p_{3/2} and Zn 2p_{1/2}. There is no displacement of the peak position before and after the reaction, indicating that the chemical state of the Zn element has not changed. Similarly, as seen from Fig. 5c, the peaks of AuAg/ZnO before degradation located at 529.5 eV and 531.4 eV are indexed to lattice oxide and adsorbed oxygen [32]. After degradation, the peak of lattice oxide has no change, indicating ZnO did not change before and after reaction. However, the

Fig. 5. (a) XPS survey spectra and (b–e) high-resolution XPS spectra of Zn 2p, O 1s, Au 4f and Ag 3d for AuAg/ZnO before and after degradation.

peak of adsorbed oxygen exhibits a slightly negative shift, suggesting the chemical reactions of adsorbed O_2 might be involved. In Fig. 5d, the diffraction peak located at 83.3 eV and 88.1 eV are corresponded to Au 4f_{7/2} and Au 4f_{5/2}. It can be seen that the valence state does not change significantly before and after illumination, indicating the alloyed Au and unalloyed Au are very stable. But Fig. 5e shows that before the illumination, the peak positions are located at 367.1 eV and 373.2 eV, respectively, which are features of Ag⁰. After the illumination, the peak position shifts slightly to the high binding energy at 367.4 eV and 373.5 eV and exists a mixed state. This is because the Ag particles are unstable and easily lose electrons under long-time illumination. The unalloyed Ag particles lose electrons and become Ag⁺ and thus the peaks exhibited a positive shift [47]. However, the most Ag elements in AuAg alloy are still Ag⁰, which proves the superiority of the AuAg alloy. This result also corresponds to the test results of photocatalytic stability.

3.6. Photocatalytic C_2H_4 oxidation and stability test of as-obtained samples

Ethylene is used as an objective organic pollutant to measure the photocatalytic activity of the as-prepared products at 15 °C. The total experimental results are shown in Fig. S3 and Fig. 6. Firstly, the blank test of ethylene without photocatalyst is performed and we find that the pure ethylene can hardly be decomposed in the absence of photocatalyst. Therefore, all the following degradation of ethylene is due to the presence of the photocatalyst. Fig. S3a illustrates the degradation curves over pure ZnO and Au decorated ZnO. Fig. S3b and c are the corresponding kinetics curves and reaction rate constants. It is obvious that pure ZnO has a poor reaction rate constant of 0.004 g⁻¹min⁻¹. After loading with a small amount of Au, the activity

has been significantly improved and the reaction rate of 0.5% Au/ZnO even reaches up to 0.162 g⁻¹min⁻¹, which is 40 times that of pure ZnO. It can be seen the existence of noble metal Au has a great role in promoting the activity due to its extended light absorption, which confirms our speculation exactly. Then we study the effect of Au-Ag alloy and the optimal loading amount of Ag (Fig. S3 d–f). We find that when the precursor of Au (0.5%) and Ag (0.1%–0.7%) are simultaneously added into the ZnO suspension and reduced to Au, Ag and Au-Ag alloy, the activity has been further upgraded. When the ratios of Au and Ag are 0.5% and 0.3% (total amount of noble metal is 0.8%), the reaction rate reaches the highest. Then we also make a comparative experiment of 0.8% Au and 0.8% Ag in Fig. 6, both are less active than AuAg/ZnO. The reaction rate of 0.8% AuAg/ZnO is approximately 5.41 and 3.54 times more than the 0.8% Au/ZnO and 0.8% Ag/ZnO. Hence, it is clear that the synergistic effect of Au and Ag has unmatched superiority.

In order to compare the photocatalytic effects of our synthesized photocatalysts with other photocatalysts, the photocatalytic degradation activity of AuAg/ZnO sample was compared with that of other photocatalysts such as Pt-TiO₂, Pt@Fe-WO₃, Ag/AgCl/TiO₂, Ag-ZnO, BiVO₄/P25, P25/Bi₂WO₆ and In₂O₃-Ag-Ag₃PO₄, the detailed results are shown in Table S1. It can be seen from the roughly calculated reaction rate (ppm g⁻¹ min⁻¹) that the AuAg/ZnO has the highest activity among many photocatalysts, which proves that AuAg/ZnO sample has a good application prospect. In addition, we have done similar experiments using nanoflower-like ZnO and found that the morphology of ZnO did not affect the experimental rules. That is, the regularity in C_2H_4 degradation of nanoflower-like ZnO was similar to that of the nanorod-like ZnO, indicating that the regularity of AuAg/ZnO in degradation of ethylene is universal. The related comparison experiment results

Fig. 6. (a) Comparative photodegradation activities of C_2H_4 , (b) the corresponding kinetics curves, (c) the reaction rate constants of the total contrast activities of pure ZnO, 0.8% AuAg/ZnO, 0.8% Au/ZnO and 0.8% Ag/ZnO under (UV-vis) light illumination, (d) the recyclability for the photocatalytic degradation of C_2H_4 in the presence of 0.8% AuAg/ZnO composite.

are presented in Fig. S4.

Besides the photocatalytic behavior, the stability of the photocatalyst is another vital character in practical application. To investigate the stability of 0.8% AuAg/ZnO, ten-test cycles were conducted under the same condition. In detail, Fig. 6d is photodegradation kinetic constant of C_2H_4 of these ten-time tests. As can be seen, the photocatalytic C_2H_4 oxidation over 0.5%Au@0.3%Ag/ZnO shows a slight downward trend after one cycle and the rate constant drops from $0.379\text{ g}^{-1}\text{min}^{-1}$ to $0.343\text{ g}^{-1}\text{min}^{-1}$. However, there is no significant decrease of activity from the second to the tenth cycle of photocatalytic measurements, that is, the corresponding k constant is 0.343, 0.324, 0.335 and $0.325\text{ g}^{-1}\text{min}^{-1}$, separately. The reason for this phenomenon, in our opinion, may be due to that part of the separate Ag is oxidized to Ag_2O . After one-time irradiation, the all or most isolated Ag is become Ag_2O because of its unstable chemical properties. But the Au-Ag alloy and separate Au have no change because they are quite stable. Thus, after the first little decline, the succeeding photocatalytic activities show little

changes.

In order to verify this conjecture, the stability of single Au/ZnO and Ag/ZnO has also been studied (Fig. 7a and b). It can be seen that the Au/ZnO has very great stable activity. After ten times of circulations, the reaction rates are almost unchanged. However, it is interesting to see that the Ag/ZnO has a relatively poor stability. The reaction rate drops to almost half after the first cycle and attenuates in the following tests. When going to the tenth cycle, the reaction rate is close to one tenth of the first. This result just verifies our conjecture that isolated Ag is not stable while Ag in the Au-Ag alloy is quite stable. These results demonstrate the Au-Ag alloy exhibits good stability compared to the separate Ag and exhibits great activity compared to the separate Au. Above all, the Au-Ag alloy supported on the ZnO nanorods has unparalleled excellence.

To examine the mineralization ratio of ethylene oxidation, the photocatalytic measurement over the AuAg/ZnO product is further conducted in Fig. 8. At beginning, the concentration of C_2H_4 and CO_2 is 1250 ppm and 0 ppm (the 0 ppm is after de-

Fig. 7. The recyclability for the photocatalytic degradation of C_2H_4 in the presence of (a) single Au and (b) single Ag under (UV-visible) light illumination.

Fig. 8. Photocatalytic C₂H₄ degradation and CO₂ generation of AuAg/ZnO.

ducting the CO₂ content in the air), respectively. When the light is turned on, the concentration of C₂H₄ rapidly decreases to zero in 1 h, meanwhile, the concentration of CO₂ increases with two times of C₂H₄ reducing. Finally, the concentration of CO₂ is 2467 ppm (about 2500 ppm). The result confirms that ethylene oxidation is truly driven by a photocatalytic process, and C=C bond in C₂H₄ is almost broken into two times of O=C=O bond. The mineralization ratio of ethylene is about 100% in this reaction.

3.7. Photoelectrochemical measurements

The strong capacity of charge migration can be certified by the enlarged photocurrent [49,50]. Just like the results of photocatalytic activities, the photocurrents of these products have the same discipline. As shown in Fig. 9, pure ZnO has a very poor photoelectric response, which means that the electrons and holes in ZnO are easily recombined under light irradiation. Surprisingly, Au/ZnO and Ag/ZnO all have the enhanced photocurrent as expected, which signifies that Au and Ag acting as electronic capture centers are beneficial to effective charge-transfer process. On the other hand, by combining Au and Ag NPs with ZnO, the plasmon-excited electrons can be injected into ZnO and make it visible light active, resulting in stronger photocurrent. Then just as we thought, the photocurrent intensity of AuAg/ZnO is further increased compared with that of single Au or Ag deposited on ZnO, indicating the synergy effect of Au-Ag alloy can excite more electrons and they have

Fig. 9. Transient photocurrent response of pure ZnO, Au/ZnO, Ag/ZnO and the AuAg/ZnO composites under (UV-visible) light illumination.

the function to accelerate the separation of charge carriers further more. The above results show that the Au-Ag alloy has good synergy effect to have a prolonged recombination time and enhanced photocurrent density.

3.8. Mechanism study

Based on the above results, a feasible reaction mechanism is proposed in Fig. 10. As we know, ZnO is a semiconductor with a wide band gap of 3.1 eV, which can only absorb the UV light. Thus, the ZnO cannot be excited by visible light. Nevertheless, Au and Ag have good absorption in the visible light area due to their special surface plasmon resonance (SPR) [15–19]. Because the conduction band position of ZnO (−0.31 eV vs NHE) is more negative than $E_0(\text{O}_2/\bullet\text{O}_2^-)$ (−0.046 eV vs NHE), the process of the single-electron reduction of oxygen can proceed and generate $\bullet\text{O}_2^-$ [50]. Hence, the plasmon-induced electrons in the Au, Ag and Au-Ag alloy NPs can migrate to the CB of ZnO through the metals-ZnO interface. These electrons can produce $\bullet\text{O}_2^-$ and be used for the degradation of C₂H₄. Details of the mineralization process of ethylene and the reactions are given in Fig. 10. It is worth mentioning that the reaction efficiency under visible light is very low because the number of plasmon-induced electrons is very small compared to those photo-excited electrons in ZnO. The corresponding irradiations were performed with filtered visible light ($\lambda > 420$ nm) in Fig. S5. We find that there is no capacity of pure ZnO to degrade C₂H₄ under the visible light while the AuAg/ZnO has a certain performance that can degrade half of the ethylene in 24 h. When the light source is UV-visible light, the AuAg/ZnO can absorb both visible and UV light. On the one hand, Au, Ag and Au-Ag can absorb the visible light and induce the plasmon-excited electrons e^-_{AuAg} . On the other hand, the ZnO body can be excited by ultraviolet light to produce photogenerated electrons e^-_{CB} . More importantly, the Au, Ag and Au-Ag NPs serve as electronic capture center, which can receive electrons from the conduction band of ZnO and prolong the life of electrons. These two types of electrons work together so that the reaction rate at full arc light is much greater than that under visible light. In addition, the synergy of Au and Ag is another important reason of

Fig. 10. Pictographic representation and the possible mechanisms of the excitation of surface plasmon and electron transfer process during the irradiation of UV-visible light.

good activity. In a word, the overall high photocatalytic activity of Au-Ag NPs loaded ZnO in gaseous pollutants oxidation can be ascribed to efficient visible light absorption by Au-Ag alloy NPs, synergistic effects of SPR excitation and electronic captures of Au-Ag NPs.

4. Conclusions

The phenomenon presented here shows that Au and Ag co-loaded ZnO sample in the suitable Au/Ag ratio is an outstanding product for the solar-light oxidation of C_2H_4 to CO_2 . Among them, the photocatalytic ethylene oxidation of 0.8% AuAg/ZnO is approximately 94.75, 5.41 and 3.54 times more than that of pure ZnO, 0.8% Au/ZnO and 0.8% Ag/ZnO. These data also appear that highly efficient photocatalytic activity is related to the synergistic effects of Au-Ag based on their special SPR excitation. Therefore, the co-deposition of plasmonic Au-Ag bimetallic alloy on semiconductor provides a new route on better utilizing a wide range of solar spectrum.

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Graphical Abstract

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ZnO nanorod decorated by Au-Ag alloy with greatly increased activity for photocatalytic ethylene oxidation

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Au-Ag alloy NPs were loaded on ZnO by photo-deposition procedure with high photocatalytic activity and stability, which can be ascribed to efficient visible light absorption by AuAg alloy NPs and synergistic effects of LSPR excitation.

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贵金属Au-Ag合金修饰ZnO用于光催化高效降解乙烯

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摘要: 乙烯是一种植物激素, 可以促进水果和蔬菜在生长过程中成熟, 然而在水果和蔬菜成熟之后, 源源不断产生的乙烯会加速它们的衰老和腐烂, 不利于水果和蔬菜的贮存和保鲜. 考虑到现实因素, 直接在储存环境中去除乙烯很有必要, 而光催化技术操作简单易行, 在降解乙烯方面具有应用前景. 我们发现ZnO具有降解乙烯的作用, 但纯ZnO由于光吸收范围窄及载流子分离效率低, 使得其降解乙烯的效果不佳. 而金、银纳米颗粒由于其表面的等离子体共振效应, 可以增强半导体的光吸收, 同时贵金属颗粒还可以充当捕获电子的活性位点, 加快电子和空穴分离, 提高光催化效率. 因此, 将金或银作为ZnO的助催化剂可能是提高ZnO催化性能的有效途径. 一些研究还发现, 使用双金属合金作为助催化剂可以达到比单一金属更优越的效果. 因此在本论文中, 我们采用简单的光沉积工艺和低温煅烧方法合成了Au, Ag和Au-Ag合金负载的ZnO, 研究了它们对ZnO光催化效率的促进作用.

活性测试表明, 在ZnO负载了单独的Au或Ag颗粒后, 乙烯降解效率分别是纯ZnO的17.5和26.8倍, 光催化活性大幅增加. 而当ZnO成功负载Au-Ag合金后, 光催化活性进一步提高到纯ZnO的94.8倍. 紫外-可见光谱结果表明, 由于表面等离子体共振(SPR)效应, Au-Ag合金改性后的ZnO显示出很强的可见光吸收. 同时, 较高的光电流密度表明AuAg/ZnO具有有效的载流子分离能力. 因此, 等离子体Au-Ag双金属合金纳米粒子的协同作用和有效的载流子分离能力共同带来了乙烯氧化的优异光催化活性. 催化剂稳定性测试表明, Ag/ZnO的光催化稳定性非常差, 在10次循环后活性下降很多, 而Au/ZnO和AuAg/ZnO在10次循环后光催化稳定性非常好. 结合XPS分析可知, Ag单质颗粒可以容易地光氧化成为Ag₂O, 造成活性降低, 而Au-Ag由于形成了合金结构, 不易被氧化, 因而变得异常稳定. 最终我们得到了高活性、高稳定性的AuAg/ZnO光催化剂. 这项工作提出了在实际生产中使用金属合金作为助催化剂去除乙烯的新思路, 具有良好的应用前景.

关键词: 等离子体共振效应; Au-Ag合金; 协同效应; 高效载流子分离

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