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Preparation of Au nanospheres/TiO_2 complexes and their photocatalytic performance of H_2

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ABSTRACT: Au nanospheres/TiO_2 composite was prepared by a sol-gel process. Meanwhile, its photocatslytic activity was investigated for H_2 evolution. The results indicate that it is an efficient photocatalyst with a H_2 evolution rate of approximate 1.18 $mmolg^{-1}h^{-1}$ during first hour under visible irradiation. Additionally, the size of the Au nanospheres plays an importnt role in the hydrogen production. with increasing the size of Au nanospheres, the rate of H_2 evolution gradually increases, reaches a maximum and thereafter begins to decrease. It may be closely related to the change of plasmon resonance absorption induced by the size of Au nanospheres.

1 INTRODUCTION

With the deepening of TiO_2 research, many shortcomings of TiO_2 are exposed. For example, because it only absorbs ultraviolet light, the limitation of its application in photocatalysis is more obvious. Therefore, how to overcome these defects has been a research hotspot in the field of photocatalytic hydrogen production. The researchers have developed many effective methods for TiO_2 modification, such as doping [1], dye sensitization [2,3] and composite with other functional materials [4] etc.

Recently, it has been found that the surface plasmonic resonance absorption effect of gold and silver nanomaterials can make TiO_2 exhibit excellent catalytic performance for H_2 production under visible irradiation [5]. Silva et al. [6] prepared the Au/TiO_2 composite by deposition of gold nanoparticles on P25. The results showed that the composite can exhibite high photocatalytic activity for hydrogen production in both ultraviolet and visible light. The plasma resonance effect of gold nanoparticles is stronger than that of silver nanoparticles [7]. In addition, the higher work function of gold can better promote the charge separation in TiO_2. However, the relationship between the size and morphology of gold nanoparticles and the photocatalytic activity of H_2 production is still not clear. A deep understanding of the structure-effect relationship is of great significance for the utilization of the plasma resonance absorption effect of gold nanoparticles.

Based on the above considerations, we prepared four Au nanospheres with various sizes, and then Au nanospheres/TiO_2 composites were prepared by a simple sol-gel method. On this basis, the relationship between the size of the Au nanospheres and the photocatalytic activity of the composite

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was systematically discussed. Finally, the mechanism of photocatalytic hydrogen production of Au nanospheres/TiO_2 composite was preliminarily studied.

2 EXPERIMENTAL SECTION

2.1 *Materials*

TiO_2 nanoparticles (Degussa P25) were purchased from Shanghai Haiyi trade Co. Other agents were commercially available and used as received. All of reagents were used without further purification. Deionized water was used as the solvent.

2.2 *Characterization*

The powder X-ray diffraction (XRD) analysis was made on a PANalytical Xpert Pro MRD X-ray diffractometer (Netherlands). The UV-vis spectra were recorded with a Hitachi U-3900 (Japan) and a UV1000 (Shanghai Tianmei Science Instrument, China) UV-vis spectrophotometer. The High resolution transmission electron microscopy (HRTEM) pictures were taken on a JEOL JEM-2100F (Japan).

2.3 *Preparation of Au nanospheres*

2.3.1 *Preparation of 12 nm Au nanospheres*

The $HAuCl_4$ solution (50 mL 1 mM) was heated to boiling. Subsequently, 5 mL 1wt% of trisodium citrate solution was quickly added under stirring. Keep the solution boiling for 10 min, then continue to stir for another 15 min. After static and naturally cooled to room temperature, Au nanospheres dispersion was obtained. It is kept in dark at normal temperature.

2.3.2 *Preparation of 30 nm Au nanospheres*

The trisodium citrate solution (150 mL 2.2 mM) was heated to boiling. Under stirring, $HAuCl_4$ solution (1 mL 25 mM) was added. After stirred for 10 min, the Au seed solution was obtained. Next, the solution was naturally cooled to 90°C. Sodium citrate solution (1 mL 60 mM) and $HAuCl_4$ solution (1 mL 25 mM) were added in the solution above in 2 min, and the mixture was kept at 90°C for 30 min. The as-prepared Au nanoparticle dispersion was used as a new Au seed solution, and the above growth steps were repeated 14 times. After cooled to room temperature, the Au nanaspheres diepersion was kept in dark at normal temperature.

2.3.3 *Preparation of 50 nm Au nanospheres*

The $HAuCl_4$ solution (5.4 mL 25 mM) was diluted to 150 mL and heated to boiling. Under vigorous stirring, the trisodium citrate solution (18 mL 1 wt%) was dropped in and kept in boiling for 1 h. After naturally cooled to room temperature, the dispersion above was kept in dark at roon temperature.

2.4 *Preparation of Au nanospheres/ TiO_2 complexes (Au/TiO_2)*

Tetrabutyl titanate (3 mL) and ethanol (10 mL) were mixed at room temperature. The dispersion of Au nanospheres was added drop by drop and then stirred at room temperature for 12 h to form the sol. After the sol was transferred into a Teflon-lined stainless steel autoclave, the autoclave was heated at 120°C for 8 h. Next, the autoclave was cooled to room temperature; the samples were rinsed thoroughly with ethanol and double-distilled water, and dried in air at 50°C for 2 h. The finished product is obtained by grinding. The resulting products are marked as 12-Au/TiO_2, 30-Au/TiO_2 and 50-Au/TiO_2, and the numbers represent the size of the Au nanospheres. In addition, in order to investigate the effect of heat treatment on the properties of the composite, we also heat treatment some products, The Au/TiO_2 composites are calcined at 400° for 2 h in a muffle furnace.

2.5 *Electrochemical measurements*

The AC impedances of the samples were performed with a CHI660D electro-chemical system (Shanghai Chenhua Instruments, China) in a three-electrode system. The working electrode was Au/TiO_2 modified electrode. An Ag/AgCl electrode and a platinum electrode were used as the reference electrode and counter electrode, respectively. The supporting electrolyte solution was a mixture of KNO_3 (0.1mM), $K_3Fe(CN)_5$ (5 mM) and $K_3Fe(CN)_6$ (5 mM).

2.6 *Photocatalytic measurements*

Photocatalytic experiments were carried out with a CEL-SP2N water splitting system (Zhongjiao Jinyuan Instruments, Beijing, China). The photocatalytic reaction is carried out in a sealed quartz reactor. A 300 W xenon lamp with a filter ($\lambda > 420$ nm) was used as the light source. The light source is 1 cm away from the reactor. In a typical experiment, 60 mg Au/TiO_2 was added into 60 mL methanol solution (50 vol.%) under stirring. After dropping 390 μL 10 g L^{-1} chloroplatinic acid solution to the suspension, the system was pumped into vacuum state under stirring. Then, the suspension was reduced under UV light for 30 min to prepare Au/TiO_2 loaded with 1 mol% Pt (Au/TiO_2-Pt) . Finally, the photocatalytic reaction device was vacuumed again, nitrogen was introduced, and the xenon lamp was turned on to start the photocatalytic reaction. The amount of hydrogen produced was measured with a gas chromatography.

3 RESULTS AND DISCUSSION

3.1 *Characterizations*

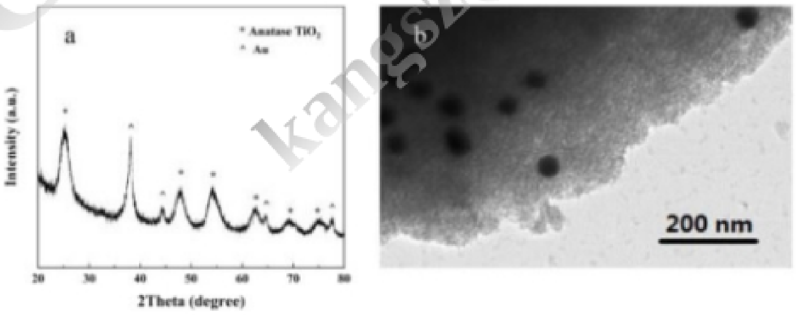

Figure 1. (a) XRD pattern and (b) TEM image of the as-prepared Au nanospheres/TiO_2 composite.

Figure. 1(a) shows the XRD pattern of the as-prepared Au nanospheres/TiO_2 composite. As can be seen from Figure 1(a), the XRD diffraction peak positions of the sample are well coincident with the standard XRD diffraction peaks of anatase TiO_2 (JCPDS No.21–1272) and Au (JCPDS No.04–0784), respectively. Therein, the diffraction peaks at 25.28°, 48.05°, 53.89°, 62.69°, 68.76° and 75.03° should correspond to the (101), (200), (105), (204), (116) and (215) crystal planes of anatase TiO_2, respectively. The peaks at 38.18°, 44.39°, 64.58° and 77.55° could be assigned to the diffraction peaks corresponding to (111), (200), (220) and (311) crystal planes of gold, respectively. This result indicates that the product is composed of Au and TiO_2 complexes.

Figuer 1(b) shows TEM image of as-prepared Au nanospheres/TiO_2 composite. From Figuer. 1(b),we can find that some dark nanoparticles are embedded in a lighter matrix. The lighter part consists of nanoparticles with 5 nm in size. Since Au atoms are heavier than Ti atoms, the contrast of the rich Au region is darker. Therefore, we refer to dark nanoparticles as Au nanospheres, while lighter nanoparticles are TiO_2. The above results further confirm that the sample is a composite composed of Au nanospheres and TiO_2 nanoparticles. And the Au nanospheres are embedded in a matrix composed of the TiO_2 nanoparticles.

3.2 *Optical properties of Au nanosphere/TiO_2 composites*

Figure 2 shows UV-vis spectra of the samples, which are recorded in the range of 250–800 nm. From Figure 2A, we can observe that Au nanospheres have strong absorption capacity in the visible light region, which should be attributed to its surface plasmon resonance effect. Moreover, as the size of the Au nanosphere increases, its absorption band gradually red-shifts from 520 nm to 550 nm. This phenomenon should be caused by the quantum size effect of the Au nanospheres [8]. These results indicate that we can modulate the surface plasmon resonance effect of Au nanospheres by controlling the size of the Au nanospheres.

From Figure 2B we can find that TiO_2 nanoparticles have no absorption in the visible region. In contrast, 30-Au/TiO_2 exhibits a very obvious absorption peak at 565 nm, which might be ascribed to the surface plasmon resonance effect of Au nanoshperes. Compared with the UV-vis spectrum of anatase TiO_2 nanoparticles, it can be observed that the introduction of Au nanospheres does not cause the absorption band of TiO_2 around 400 nm to move. This shows that the band structure of TiO_2 nanoparticles does not change due to the introduction of Au nanospheres. On the other hand, compared with the the UV-vis spectrum of 30 nm Au nanospheres, the plasmon resonance absorption of the Au nanospheres has a significant red shift in the composite. This shows that there exists some strong interaction between Au nanospheres and TiO_2 matrix.

Figure 2C shows the UV-Vis absorption spectra of 12-Au/TiO_2, 30-Au/TiO_2 and 50-Au/TiO_2. It can be seen from Figure 2C that when the size of the Au nanospheres becomes larger, the position of the absorption peak of the samples in the visible light region also undergoes a red shift. However, compared with the results shown in Figure 2A, the degree of red shift of the absorption peak is much smaller. At the same time, it is mentioned in Figure 2B that there is some strong interaction between Au nanospheres and TiO_2 matrix. Under its action, the plasmon resonance absorption of Au nanospheres in the matrix is red-shifted. From these experimental phenomena, we speculate that the interaction between the Au nanospheres and the TiO_2 matrix may be greatly affected by the size of the gold. The interaction between the small-sized Au nanospheres and the TiO_2 matrix is relatively large, so that the change in the position of the sample absorption peak caused by the change in the size of the Au nanospheres becomes weaker. After heat treatment, the absorption peak of the sample has a significant red shift. This may be due to: (1) The size of the Au nanospheres has increased after calcination; (2) The interaction between the Au nanospheres and the TiO_2 matrix has been enhanced due to the calcination.

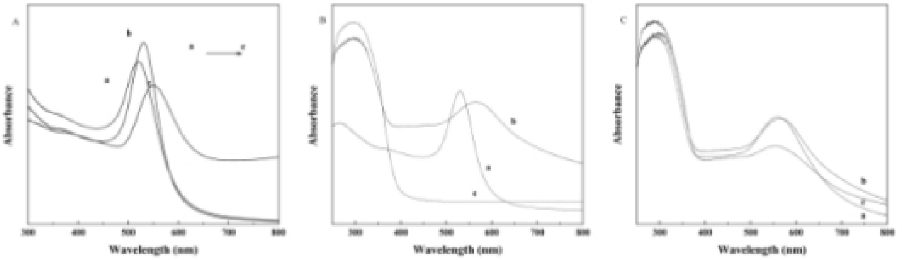

Figure 2. UV-vis spectra of A) Au nanospheres with varius sizes:(a) 12 nm, (b) 30 nm and (c) 50 nm; B) (a) Au nanospheres of 30 nm, (b) 30-Au/TiO_2 and (c) anatase TiO_2; C) Au nanospheres/TiO_2 composites: (a) 12-Au/TiO_2, (b) 30-Au/TiO_2 and (c) 50-Au/TiO_2.

3.3 *Electrochemical properties of Au nanosphere/TiO_2 composite*

Electrochemical impedance spectroscopy is a common method used to study the electron transfer properties of samples. Figure 3 shows the AC impedance diagrams of Au nanospheres/TiO_2 composites modified electrodes. The results show that the charge transfer resistance of the 30-Au/TiO_2 modified electrode is the smallest. The possible explanation is that as the size of the Au nanospheres increases, the effective contact between the Au nanospheres and TiO_2 decreases. On the other hand, as the size of the Au nanospheres decreases, the quantum size effect of the Au nanospheres gradually increases, so that the separation of Au energy levels gradually increases. The size is too large or too small is not favour to the electron transfer. As a result, 30-Au/TiO_2 exhibits the best electron transfer properties, implying that the photocatalystic activity of 30-Au/TiO_2 might be the highest.

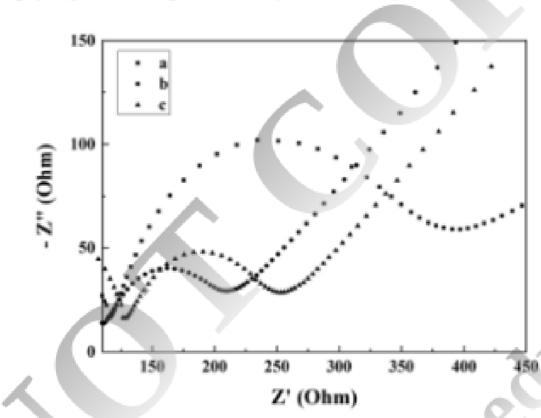

Figure 3. AC impedence of a) 12-Au/TiO_2, b) 30-Au/TiO_2, c) 50-Au/TiO_2.

3.4 *Photocatalytic hydrogen production activity of Au nanosphere/TiO_2 composite*

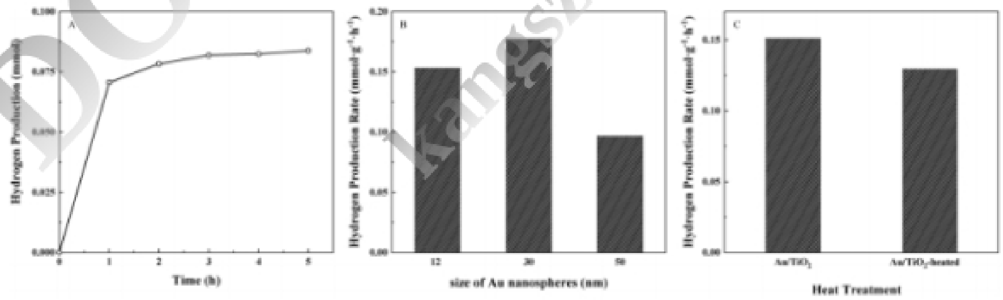

Figure 4. A) Irradiation time dependence of the amount of H_2 evolved from water over 30-Au/TiO_2; B) effect of the size of the Au nanospheres on the photocatalytic activity of Au/TiO_2; C) effect of heat treatment on the hydrogen production rate over 12-Au/TiO_2.

Figure 4A shows the kinetics curves of hydrogen production over 30-Au/TiO_2 loaded with Pt under visible irradiation. It can be clearly observed from Figure 4A that 30-Au/TiO_2 is an efficient visible photocatalyst for hydrogen production from water. Under its catalysis, hydrogen production rate is up to 1.18 $mmol \cdot g^{-1} \cdot h^{-1}$. Here, Au nanospheres play a very important role. Under visible light,the high photocatalytic activity of Au/TiO_2-Pt is attributed to the plasma resonance effect of Au nanospheres. The mechanism may be as follows: Au nanospheres absorb visible light due to plasma resonance effect. Then, the electrons are injected into the conduction band of TiO_2. Next, these excited electrons migrate to Pt under the action of Schottky energy barrier. Finally, the electrons react with water on Pt to produce hydrogen. In the photocatalytic process, Au nanospheres act as visible light capture units. At the same time, Pt acts as a charge separation center and a reactivity center. In addition, due to the interaction between Au nanospheres and TiO_2, the position of TiO_2 conduction band moves towards negative potential [6]. This may be another reason for the high photocatalytic hydrogen production activity of the system. Besides, we can also find that rapid hydrogen production can be achieved by using this catalyst. During the period of the first hours of irradiation, the hydrogen amount can reach 84% of the total hydrogen production. The photocatalytic hydrogen production reaction can reach equilibrium within 2 hours. This shows that the catalyst has a certain application potential in emergency hydrogen production in the future.

Figure 4B shows the effect of the size of Au nanospheres on the photocatalytic activity of Au/TiO_2-Pt. As can be seen from Figure 4B, when the size of Au nanospheres is 30 nm, the photocatalytic activity of Au/TiO_2-Pt is the highest. One possible explanation is that with the increase of the size of Au nanospheres, the interaction between Au nanospheres and TiO_2 tends to decrease, leading to a decrease in hydrogen production activity. Although the interaction between Au nanospheres and TiO_2 will gradually increase with the size of Au nanospheres decreasing, the number of Au nanospheres per unit TiO_2 increases, resulting in more defects in the TiO_2 matrix [9]. Too many defects become the recombination center of electron-hole pairs. Therefore, too small size of Au nanospheres may lead to a decrease in the photocatalytic hydrogen production activity of the system. Therefore, under the action of the above two factors, 30-Au/TiO_2 shows the highest photocatalytic hydrogen production activity.

Figure 4C shows the effect of heat treatment on the efficiency of hydrogen production over Au/TiO_2-Pt. As can be seen from Figure 4C, after heat treatment, the hydrogen production rate of Au/TiO_2-Pt decreased significantly. One possible explanation is that after calcination, the crystallinity of the sample increases and the surface defect concentration decreases, which is very unfavorable to the Pt loadding on Au/TiO_2, which leads to the decrease of photocatalytic hydrogen production. In addition, after calcination, the size of Au nanospheres will increase, which makes the interaction between Au nanospheres and TiO_2 tend to decrease. This will also lead to a decrease in the photocatalytic hydrogen production activity. Therefore, heat treatment will have a negative effect on the photocatalytic activity of Au nanospheres /TiO_2 composite.

4 CONCLUSION

In this paper, Au/TiO_2 composite was successfully prepared using sol-gel method. It is an efficient visible photocatalyst for hydrogen production. In addition, the size of Au nanospheres plays a very important role in the photocatalytic hydrogen production. Only when the size of Au nanospheres is suitable, the composite can show high photocatalytic activity for hydrogen production.

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