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Influence of Metal (Au, Ag) Micro-Grid on the Photocatalytic Activity of TiO_2 Film

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Abstract In this paper, we prepared TiO_2 thin film with the surface modified by a connected Au micro-grid via a microsphere lithography strategy, and the modified films show higher photocatalytic activity than the pure TiO_2 film. The photocatalytic activity improved as Au loading increased, obtaining the best performance at a certain loading amount, and then decreased at higher loading amount. This behavior, not observed in TiO_2 films modified with Ag micro-grid, can be attributed to the relationship between the energetic positions and the metal clusters size.

Keywords Photocatalyst · Metal micro-grid · Microsphere lithography strategy

1 Introduction

TiO_2 under anatase form is usually considered as an efficient photocatalyst. Several attempts, for example, ion doping [1], noble metal deposition [2] and adding a coadsorbent [3] are mostly used to enhance the activity. Ion doping and noble metal deposition can separate photogenerated electrons and the holes; while the function of coadsorbent is to improve the absorption of the catalyst. The approach of establishing a semiconductor-metal composite system is usually considered as an effective way to reduce the recombination of charge carriers and improve quantum efficiency of the photocatalytic process [4]. Some studies have shown that, when a gold nanoparticle contacts a photoexcited semiconductor, the semiconductor-metal composite system undergoes charge equilibration [5–7]. Small metal clusters, with diameter of only several nanometers, deposited on surfaces of semiconductors, can enhance photocatalytic activity of catalysts in comparison with larger-sized metal particles, due to the small metal clusters's ability of trapping photoelectrons generated in the semiconductor [2, 8, 9]. The metal deposition on the surface of semiconductor can improve the efficiency of the photocatalytic redox, while high surface loading will cause electrons accumulation on the metal particles due to the fact that holes can react with many species in redox process, while only oxygen is the acceptor of electrons, which results in the unbalanced utilization of holes and electrons and low quantum efficiency. In our previous research, connected Ag micro-grid was deposited on the TiO_2 film [10], where electrons was removed to the metal micro-grid, transferred throughout the whole sample and finally consumed by the adsorbed oxygen on the surface. If the TiO_2 particles are not connected with Ag micro-grid, electrons will accumulate on those metal particles without adsorbed oxygen, causing charge recombination and lower quantum efficiency. The Ag micro-grid suppresses recombination of the photogenerated electrons and holes in the semiconductor, and hence improves the photocatalytic activity. In order to investigate whether this phenomenon occurs in other metal-semiconductor composite systems, we studied TiO_2/Au system in this paper and found that Au micro-grid also benefits the photocatalytic activity of TiO_2 thin film and there existed an optimum loading amount of Au on TiO_2 to obtain the best activity, which is unlike TiO_2/Ag system reported in our previous work.

This micro-grid modified TiO_2 film is endowed with acceptable transparency in the visible region and low infrared emissivity, so it can be used on the window glass

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as low-e films, which can purify the indoor air as well. Further more, this metal micro-grid may be used as transparent and conductive electrode in some devices.

2 Experimental

TiO_2 film was deposited on the quartz substrate using a dip-coating method with TiO_2 sol as the precursor and then was annealed in the air for 2 h at 723 and 1173 K, respectively, to obtain an anatase form. Then, well-ordered latex spheres template of polystyrene were prepared on the surface of the TiO_2 film by a vortical surface method [11]. Briefly, deionized water was poured in a glass beaker, with a cleansed hollow Teflon ring floating on the water surface. By stirring the water with a magnetic stirrer at 120 rpm, a stable volution was obtained in the vessel. Monodispersed latex spheres were dropped at the rolling surface in the ring and spread around quickly. When enough monodispersed latex spheres were droped on the water surface, the magnetic stirrer was stopped, and compact PS thin film then formed. The quartz substrate coated with TiO_2 film was vertically inserted and lifted up at a speed of 2 mm/min and then close-packed crystal PS template was created on the TiO_2 thin film. Au was deposited in the template surface with a working pressure of 1.5 Pa and a deposition rate of about 1–2 nm/s. Finally, the sample was supersonically vibrated and washed in a tetrahydrofuran (THF) solution to obtain the expected structure of Au micro-grid. By changing the sputtering time, we prepared samples with different loadings amount of metal Au. Au micro-grid with two kinds of size was prepared on the TiO_2 film by using

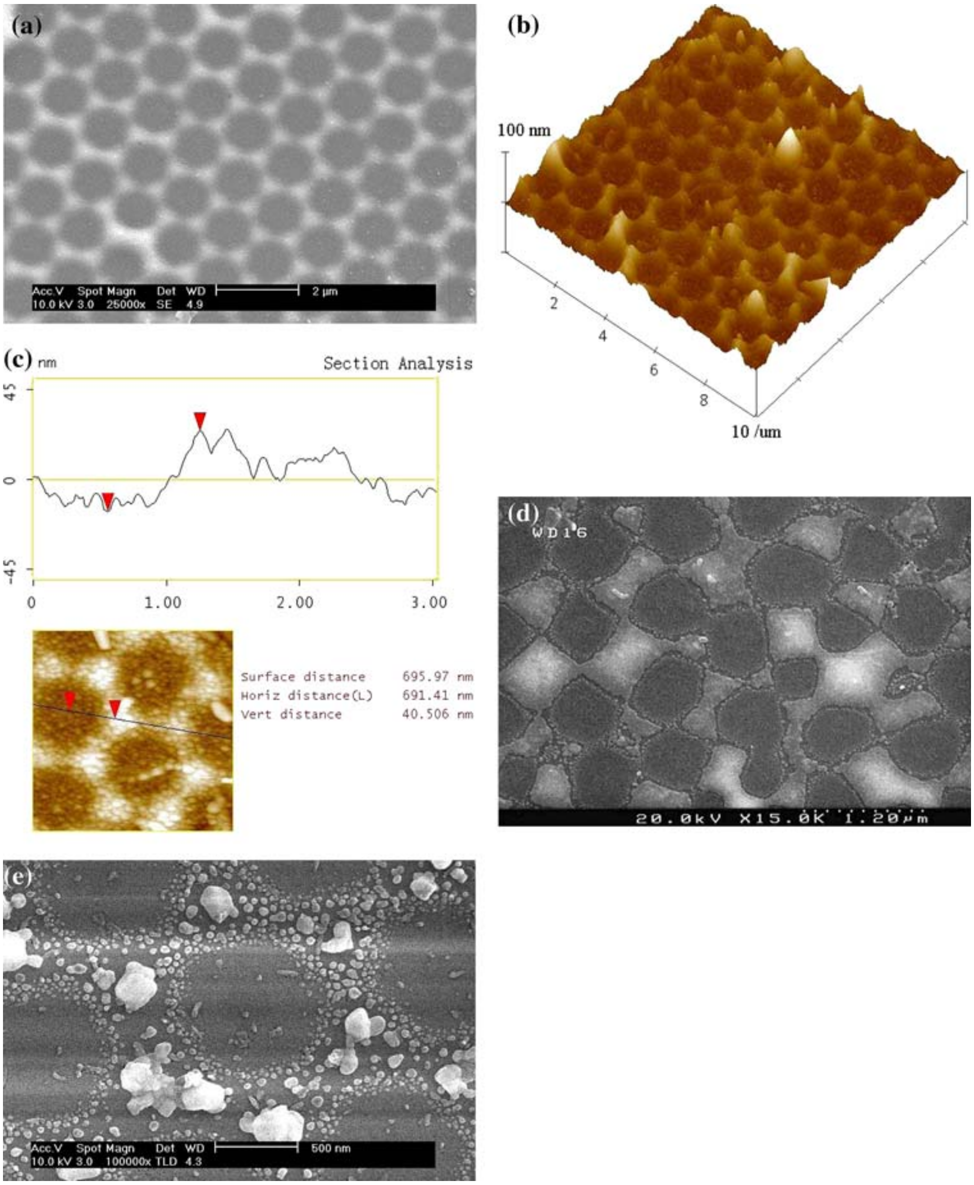

Fig. 1 Morphology of Au deposited on the TiO_2 film investigated by SEM and AFM. (**a**) Morphology of connected Au micro-grid on TiO_2 film when the sputtering time of Au is 210 s, and the cell size is 1.3 um, (**b**) AFM image of the connected Au micro-grid, (**c**) A specially magnified cell of connected Au micro-grid, (**d**) The sample shown in Fig. 1a was annealed at 473 K for 30 min and some parts of the micro-grid turn into isolated particles, (**e**) The sample with the Au sputtering time of 30 s was annealed at 473 K for 30 min, and most of the micro-grid turn into isolated particles

polystyrene spheres with diameter of 1.4 and 3 um, respectively.

The morphology of the sample was investigated by scanning electric microscopy (SEM) and atomic force microscopy (AFM). The photocatalytic activity of the samples was evaluated by measuring the degradation rates of methylene blue (MB) under ultraviolet (UV) irradiation. The transmittance spectra of the films were recorded on a UV-3010 spectrophotometer.

3 Results and Discussion

Figure 1 exhibits the ordered Au grid on the TiO_2 particle films. We observe that the vertical thickness of the Au grid increases with increasing the sputtering time. For instance, when the sputtering times for the Au metal are 30, 210 and 240 s, the vertical thicknesses of the Au micro-grid are 9.4, 40.5 and 55.2 nm, respectively. So we use the vertical thickness to denote the loading amount of metal deposited on semiconductor surface. There exists obvious relationship among the electroconductibility, transmission spectrum and the vertical thickness of the metal micro-grid, which is shown in Figs. 2 and 3. The sheet resistances of the samples change from 3 GΩ/γ to 16.7 Ω/γ with increasing the vertical thickness, and the transmission also decreases continually.

Under UV-irradiation, the pure TiO_2 film can decompose 55% of MB after 1-h irradiation, and the TiO_2/Au system obtained higher photocatalytic activity than the pure TiO_2 film as shown in Fig. 3. With the vertical thickness changing from 9.4 nm to 40.5 nm, the performances of the samples improve and the TiO_2/Au film decomposes 66% MB when the vertical thickness is 40.5 nm. However, when the vertical thickness of the Au grid reaches 55.2 nm, there is an obvious degrading of the photocatalytic activity. We change the size of the Au cell and the annealing temperature of the TiO_2 film to verify whether the similar results can be gained. In Fig. 3b, all

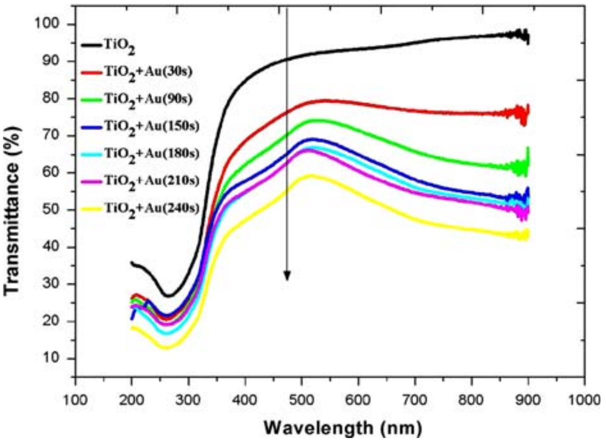

Fig. 2 Transmission spectra of the samples when the sputtering time of Au varies

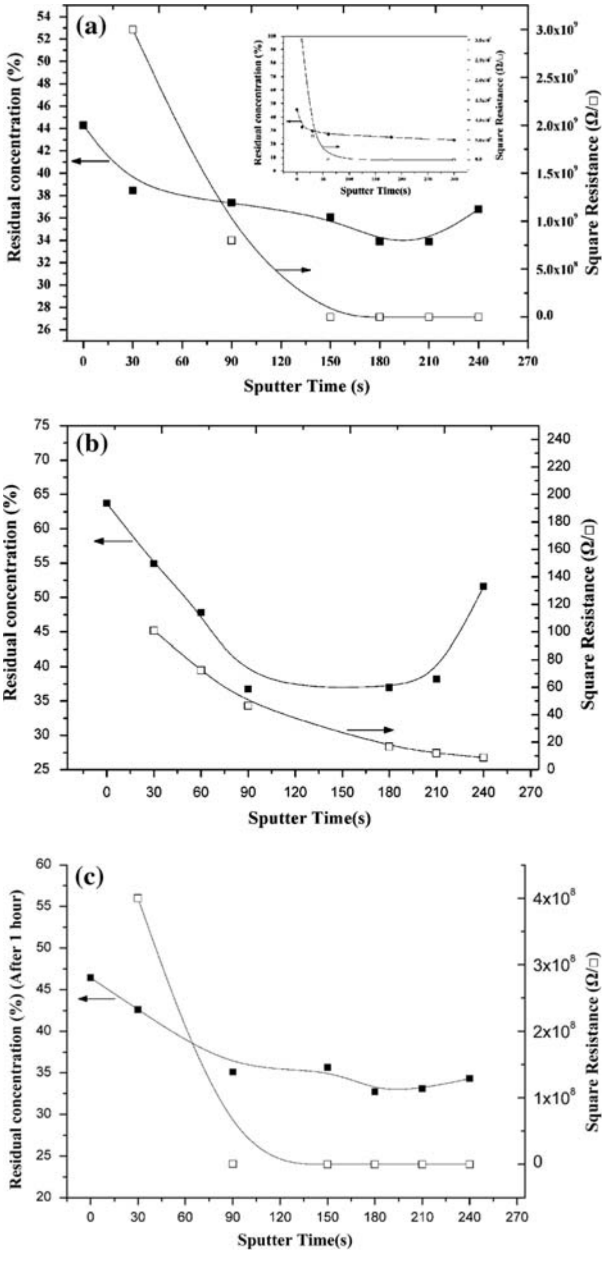

Fig. 3 Electroconductibility and photocatalytic activity of the TiO_2/Au system with different sputtering time of Au. Photocatalytic activity is represented by the residual concentration of MB solution after irradiation using UV light for 1 h. When sputtering time equals to zero, the sample is the pure TiO_2. (**a**) The TiO_2 films were annealed at 723 K before depositing Au and the size of a cell Au micro-grid is about 1.3 um. Inserted is the performance of TiO_2/Ag system, (**b**) The TiO_2 films were annealed at 1173 K before depositing Au and the size of a cell Au micro-grid is about 3 um, (**c**) The TiO_2 films were annealed at 723 K before depositing Au and the size of a cell Au micro-grid is about 3 um

TiO_2 films were annealed at 1173 K before sputtering and the size of a cell Au micro-grid is about 3 um; In Fig. 3c, TiO_2 films were annealed at 723 K before sputtering and the size of a cell Au micro-grid is about 3 um. Similarly with the result in Fig. 3a, we observed the enhanced photocatalytic activity when appropriate amount of Au micro-grid was deposited on the surface of the TiO_2 films, which confirms the universality of this experimental result. In order to compare the connected Au micro-grid modified TiO_2 film with the isolated Au particles modified film, the samples with Au sputtering times of 210 and 30 s respectively, were annealed at 473 K for 30 min. After annealing, it can be clearly seen that some parts of the connected grid became isolated particles because of the low melting point of the nano-sized Au as indicated in Fig. 1d, e. The TiO_2/Au composite films shown in Fig. 1d, e are similar to the samples prepared with conventional metal-semiconductor composite technology reported previously. What is more important is that the sample in Fig. 1a can decompose 66% MB after 1-h irradiation, while the samples indicated in Fig. 1d can only decompose 48% of MB, dramatically deactivated in comparison with sample shown in Fig. 1a. This result can confirm that Au connected micro-grid can benefit photocatalytic activity.

The influence of Au micro-grid on the photocatalytic activity of TiO_2 film is different from our previous research of TiO_2/Ag composite system, in which the photocatalytic activity of the TiO_2/Ag films continually improves with increasing the Ag content (Fig. 3a, inserted picture) [10]. Considering the metal bulk effect, the activity of this composite system can not be improved infinitely with increasing the Au content but there exists optimum content, and in the TiO_2/Au system, the optimum content is represented by the vertical thickness of 40.5 nm. We show energetic positions of TiO_2 and metal clusters in Fig. 4 so as to explain the fact that the TiO_2/Au system needs an optimum loading amount of Au in order to get the best photo catalytic performance [2]. To M_n ($M = Ag$, Au), increasing n to a large value yields cluster sizes of properties approaching that of the bulk metal. For Ag_n, clusters occupy energetic positions below the vacuum level that ranges from -1.302 eV for $n = 1$ to that of the bulk Ag work function of -4.26 eV; while for Au, it changes from -2.309 eV to -5.2 eV [12]. If n reaches a suitable number so as to make the energy band of the metal clusters locate between the bottom of the conduction band of semiconductor and the energetic position of O_2 adsorbed on the semiconductor, the metal clusters can accept the photogenerated electrons from the conduction band of TiO_2 and transfer the electrons to the O_2 adsorbed so as to benefit the formation of super oxide $O_2^{\bullet -}$. Thus, this composite system can efficiently suppress the recombination of photogenerated carriers and enhance the photocatalytic activity. The electron accepting energy level of the M_n cluster must lie close to, or lower than -4.4 eV below the vacuum level [2]. If n rises to a large number, the energy position of the metal clusters will locate below the energetic position of O_2 adsorbed and the metal can only store the electrons from the semiconductor, and can not release them to oxygen because of high value of electron affinity. In this situation, large metal clusters on TiO_2 are usually considered as recombination sites based on their ability of capturing photogenerated carriers. In our experiment, limited by our preparation method [10, 11], n can not increase infinitely. In our previous experiment of TiO_2/Ag composite system, we observed the enhanced photocatalytic activity (in Fig. 3b) without detecting the degradation of the photocatalytic activity in these series of samples because of the content limitation of Ag deposited on the semiconductor and its lower work function (4.26 eV). Due to high work function (5.2 eV) of Au in comparison with Ag, Au_n will exhibit stronger bulk effect than that of Ag_n even with the same n. So in the TiO_2/Au system, when the thickness of Au is 55.2 nm, we can observe degeneration of photocatalytic activity. However, in TiO_2/Ag composite system,

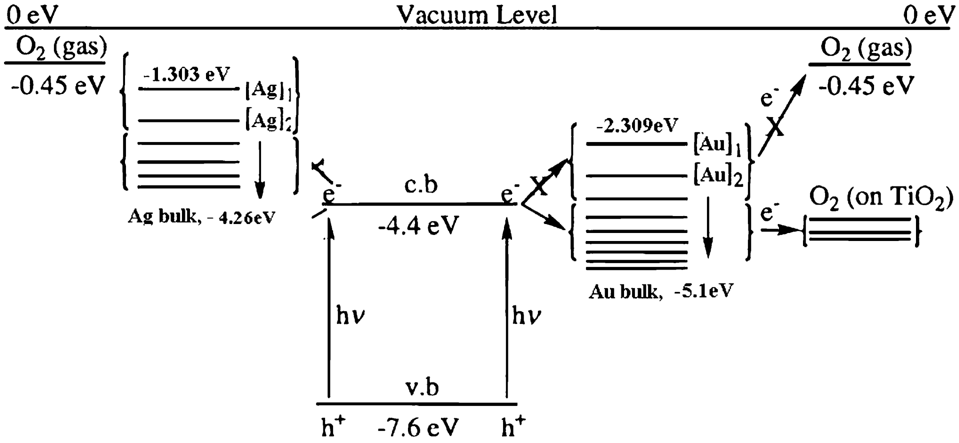

Fig. 4 Energetic position of TiO_2 and relative positions of the metal clusters (Au and Ag) [2]

with the limitation of the preparation method, there is no enough content of Ag deposited on surface of TiO_2 thin film to obtain the optimum loading amount of Ag.

4 Conclusions

In conclusion, colloidal monolayer TiO_2 films modified by connected metal grid (Au and Ag) show higher photocatalytic activity than the pure TiO_2 film. It is attributed to the result of the carrier separation and electron transfer by the conducting metal grid, and there exists an optimum loading amount of Au on TiO_2 to obtain the best photocatalytic activity due to the bulk effect. To TiO_2/Au composite system, the best vertical thickness for photocatalytic activity is about 40.5 nm.

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