

Fabrication of AgAu alloy-TiO₂ core-shell nanoparticles and their photocatalytic properties*

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In this paper, for improving the photocatalytic efficiency of titania (TiO₂) nanoparticles (NPs), AgAu alloy-TiO₂ core-shell NPs are fabricated via a sol-gel (SG) process in the presence of AgAu alloy NPs with block copolymer shells as templates. The photocatalytic activities of the AgAu-TiO₂ NPs on the photodecomposition of methylene blue (MB) are investigated. The AgAu-TiO₂ composite NPs coated with 5.0% titania related to block copolymers show higher photocatalytic activity than the other samples in which the titania contents are larger than 5.0%. The results indicate that the increase of the thickness of the TiO₂ shell leads to the decrease of the photocatalytic activity.

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Titania (TiO₂) is of a great interest as an effective photo-degradation catalyst with unique properties, such as biocompatibility, high oxidative power, ease of production and inexpensive commercial availability^[1]. However, the photocatalytic efficiency of TiO₂ alone is rather poor because of its wide band gap. TiO₂ can be excited only under ultraviolet (UV) irradiation with wavelengths shorter than 400 nm^[2]. Numerous attempts have been carried out to optimize its photocatalytic efficiency for the practical application, and these studies include doping with noble metal and non-metal ions and semiconductor coupling^[3].

One strategy is to couple TiO₂-based materials with noble metal nanoparticles (NPs). Many reports have demonstrated that noble metals, like Pt, Fe, Ag, Au and Pd, can enhance the photocatalytic activity of TiO₂ catalysts^[4-6]. For example, Ag/TiO₂ composites show higher activity compared with bare titania, which have become better candidate materials primarily in practical applications^[7]. Au@TiO₂ nanoreactors with movable Au cores and nanochannels in the TiO₂ shell nanoparticles were also presented^[8]. Recently, bimetallic Au-M (M: Pd, Cu, Ag) nanocrystals have attracted considerable interest because of their high specific surface, low density and fascinating catalytic activities different from their solid counterparts^[9-11]. In recent years, novel nanostructured bimetallic sphere-semiconductor oxides have become one of the most attractive candidate materials because bimetallic NPs, such as AuAg, have been prepared^[12,13]. So the preparation of composite NPs containing a TiO₂ outer shell and an inner AuAg alloy NPs will be of inter-

est.

In this paper, AgAu alloy NPs are prepared and used to generate AgAu-TiO₂ composite NPs. To this end, poly(2-vinyl pyridine)-b-poly(ethylene oxide) (P2VP-b-PEO) block copolymers are used as a template. Ag NPs with core-shell structures are first synthesized by UV irradiating the solution of P2VP-b-PEO/AgNO₃ complexes, then AgAu alloy NPs are obtained through a galvanic replacement reaction, and finally the composite NPs containing a TiO₂ outer shell and an inner AuAg alloy NPs with block copolymer shell structures are prepared by using AgAu NPs as templates and combining with the sol-gel (SG) process. After the removal of block copolymers, the composite TiO₂ NPs containing an inner AgAu alloy NPs are generated. The photocatalytic activities of the AgAu-TiO₂ NPs on the photodecomposition of methylene blue (MB) are investigated. It is found that TiO₂ decorated with AuAg alloy NPs can improve the photocatalytic degradation efficiency of MB.

P2VP-b-PEO was purchased from Polymer Source Inc., Canada. The molecular weight of the P2VP block was 3 000 g/mol, and that of the PEO block was 10 000 g/mol. Hydrogen tetrachloroaurate tetrahydrate, 4-dihydroxybenzophenone (BPH) and silver nitrate were purchased from Alfa Aesar. Titanium (IV) tetraisopropoxide (TTIP) was purchased from Aladdin. Tetrahydrofuran (THF), MB, 2-propanol, toluene and hydrochloric acid were purchased from Sinopharm Chemical Reagent Co., Ltd.. All of the chemicals were reagent grade and used without further purification.

Ag NPs with block copolymer shells were synthesized

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by UV irradiating the solution of P2VP-b-PEO/AgNO₃ complexes in THF^[14]. Typically, P2VP-b-PEO diblock copolymer (5.0 mg), silver nitrate (1.2 mg) and BPH (0.1 mg) were dissolved in THF (10 g) under stirring at ambient temperature for 48 h until a clear solution silver nitrate was obtained, in which the polymer weight concentration was 0.05%. The molar ratio (MR) of AgNO₃/VP is 0.6. Silver NPs about 10 nm in diameter with block copolymer shells were synthesized by UV irradiating the above solution in a quartz volumetric flask for 16 h.

The as-prepared AgNPs were used as sacrificial templates to prepare AgAu alloy NPs^[15]. The Ag NPs solution (2 mL) was mixed with different amounts of HAuCl₄ solution to generate AgAu alloy nanostructures. The MR of HAuCl₄/Ag was changed from 0.04 to 0.12.

The preparation process of the sol-gel (SG) precursor solutions was reported previously^[15]. The desired amount of sol-gel precursor solution was added to the AgAu alloy NPs solution drop by drop and stirred for 50 min. The volume ratio of the precursor (V_{titania}) to the copolymer was changed from 5.0% to 20.0%.

UV-vis spectra of the prepared nanoparticle solutions were recorded on a TU1810 spectrometer (Beijing Purkinje General Instrument Co., China). Electron micrographs of the particles were taken with an H-800 transmission electron microscope (Hitachi, Japan) operating at 100 kV. High resolution transmission electron microscopy (HRTEM) image measurements were performed on a JEM-2100 electron microscopy (JEOL Ltd., Japan) operating at 200 kV. The samples were prepared by mounting a drop of the solutions on a carbon-coated Cu grid and allowing it to dry in air. X-ray diffraction (XRD) was performed using a D8 FOCUS diffractometer (Bruker-AXS, Germany) with Cu K α radiation ($\lambda=0.15418$ nm).

The photocatalytic activities of the AgAu-TiO₂ NPs on the photodecomposition of MB were investigated. The AgAu-TiO₂ films were produced by casting the TiO₂ solution (10 μ L) coated AgAu alloy NPs on a piece of Si substrate and then removing the block copolymer template by deep UV irradiation (254 nm) in air for 2 days. The AgAu-TiO₂ film was immersed in the 5.0 mL MB aqueous solution with a concentration of 5.0 mg/L, and the solution was irradiated by UV light at 254 nm. The change of absorption at 664 nm was applied to identify the concentration of MB using a UV-Vis spectrophotometer with a time interval of 30 min for the total irradiation time of 270 min.

Fig.1(a) shows a typical TEM image of Ag NPs with diameter of about 10 nm. The XRD result shown in Fig.1(b) reveals that the Ag NPs are crystalline. The diffraction peaks at 2θ of 38.1°, 44.09°, 64.36° and 77.29° are corresponding to the (111), (200), (220) and (311) planes of Ag, respectively. The surface plasmon resonance (SPR) energy of the Ag NPs is 414 nm as shown in Fig.2(a).

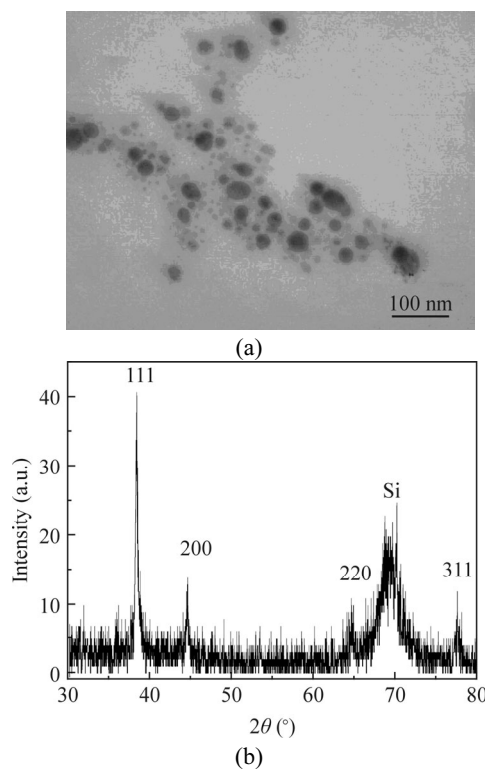
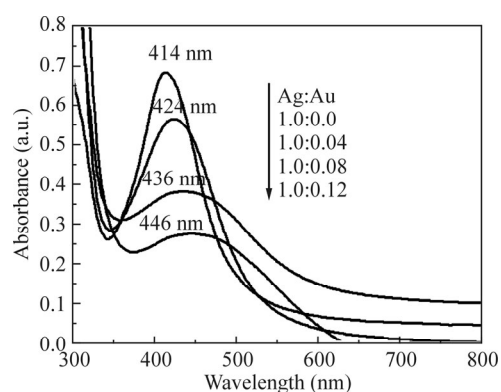


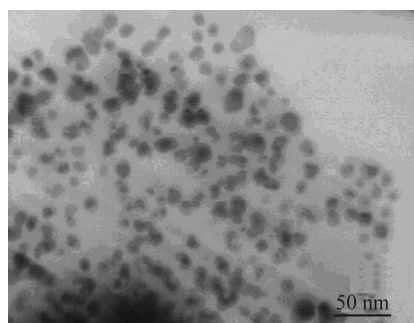
Fig.1 (a) TEM image and (b) XRD result of Ag NPs

Using the Ag NPs stabilized with P2VP-b-PEO block copolymers as sacrificial templates, AgAu alloy NPs were prepared by carrying out a galvanic replacement reaction between Ag NPs and HAuCl₄ solution. The MR of HAuCl₄ to Ag is adjusted by controlling the concentration of the HAuCl₄ solution. When the MR is changed from 0.04 to 0.12, AgAu alloy NPs are obtained^[14]. As shown in Fig.2(a), there is only one SPR peak in the UV-vis absorption spectra of AgAu alloy NPs, which is red-shifted from 414 nm for pure Ag NPs to 446 nm for AgAu alloy NPs with Au/Ag MR of 0.12. Fig.2(b) shows a TEM image of AgAu alloy NPs with Au/Ag MR of 0.12. From Fig.2(b), it can be seen that there is no significant change occurring in the internal part and edge of the NPs. It can be seen from the HRTEM image shown in Fig.2(c) that the particle size of AgAu alloy NPs is changed from ~10 nm to ~20 nm compared with the Ag NPs shown in Fig.1(a). These results prove that the AgAu alloy NPs are formed.

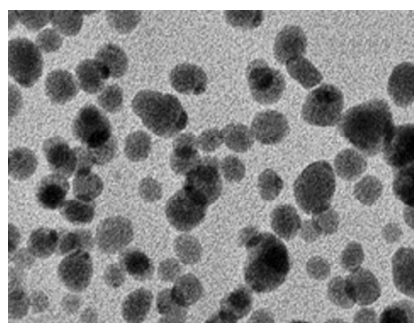
Subsequently, the AgAu alloy NPs were coated with the TiO₂ shell to make the photocatalyst. The PEO blocks on the surfaces of AgAu alloy NPs are used as anchoring sites for the growth of titania, leading to the formation of a AgAu core and titania shell composite NPs. Fig.3(a) presents a TEM image of AgAu-TiO₂ composite NPs prepared by addition of sol-gel of titania to the AgAu NPs (MR of 0.12) solution. Grey area in the images surrounding the black AgAu alloy NPs indicates the titania. After the removal of block copolymers, composite titania NPs containing an inner AgAu alloy NPs are generated as shown in Fig.3(b).



(a)



(b)

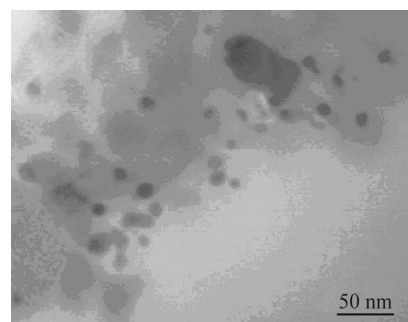


(c)

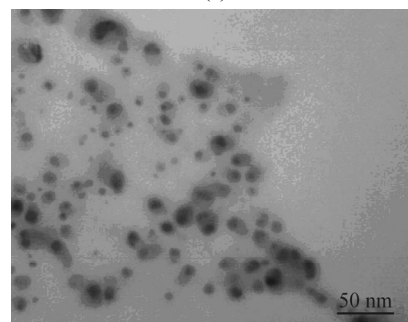
Fig.2 (a) UV-vis spectra of Ag and AgAu alloy NPs with different MPs of Ag/Au; (b) TEM image of AgAu alloy NPs with MR of 0.12; (c) HRTEM image of (b) with amplified factor of 150 000

The photocatalytic properties of AgAu-TiO₂ composite NPs are evaluated by measuring the time-dependent degradation of MB under UV irradiation at 254 nm. In the process of photocatalytic degradation of MB solution, the absorbance of MB at 664 nm decreases in intensity with time as shown in Fig.4(a). The influence of the content of TiO₂ in AgAu-TiO₂ composite NPs on the photocatalytic activities is considered. As shown in Fig.4(b), the AgAu-TiO₂ composite NPs coated with 5.0% titania show higher photocatalytic activity than the other samples. The results indicate that the increase of the thickness of the titania shell leads to a decrease of the photocatalytic activity^[16]. It may be due to the fact that AgAu NPs inside the TiO₂ shells can act as a sink for electrons, which contributes to the interfacial charge transfer between the metal and semiconductor and the

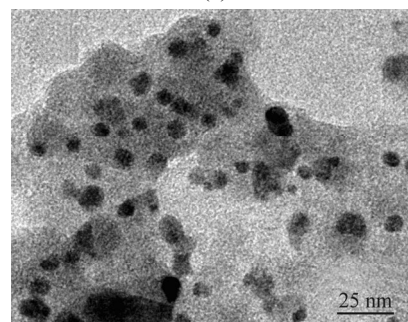
separation of photogenerated electron-hole pairs, thereby enhancing the photocatalytic activity^[17].



(a)



(b)



(c)

Fig.3 TEM images of AgAu-TiO₂ composite NPs with MR of 0.08 and V_{titania} = 5.0% (a) before and (b) after the removal of block copolymers; (c) HRTEM image of (b)

The degradations of MB using TiO₂ and Ag-TiO₂ NPs prepared by using P2VP-b-PEO and Ag NPs stabilized by P2VP-b-PEO block copolymers are also performed. As shown in Fig.5, the photocatalytic properties of TiO₂ are improved when AgAu alloy NPs are used as dopants. The phenomenon can be interpreted as follows. When AgAu alloy NPs contact with TiO₂ particles, migration patterns of electrons on their surface change, and the final result is that the excessive negative charges are on the metal surface and the excessive holes are on the TiO₂ surface, so electrons and holes are in different phases for inhibiting the photogenerated electrons and holes in the compound, improving the utilization of electronic transition. On the other side, AgAu alloy NPs can cut the energy band of TiO₂, so its efficiency of absorption can be improved.

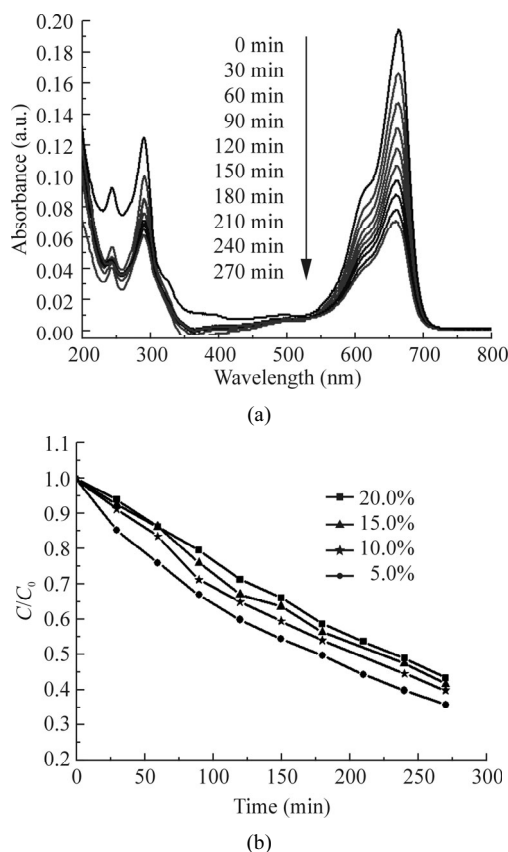


Fig.4 (a) UV-vis spectra of MB under UV irradiation for different times using AgAu-titania NPs ($V_{\text{titania}} = 5.0\%$) as photocatalyst; (b) The concentration of MB with Au/Ag MR of 0.12 as a function of irradiation time for different V_{titania} values

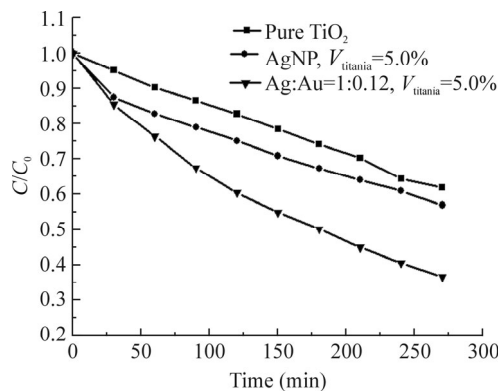


Fig.5 The concentration of MB as a function of irradiation time at different V_{titania} values

In this paper, AgAu alloy- TiO_2 NPs are fabricated, and their photocatalytic activities are investigated. The photocatalytic properties of TiO_2 are improved when AgAu alloy NPs are used as dopants. It is also found that the AgAu- TiO_2 composite NPs coated with 5.0% TiO_2

show higher photocatalytic activity than the other samples in which TiO_2 contents are larger than 5.0%. The results indicate that the increase of the thickness of the TiO_2 shell leads to a decrease of the photocatalytic activity. The novel architectures are expected to prevent the aggregation of the AgAu NPs, and have potential applications in the areas of environmental cleanup.

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