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Highly Efficient Synthesis of Environmentally Friendly Ag-modified TiO_2 Nanoflowers to Enhance Photocatalytic Performance

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Abstract: Ag-modified TiO_2 nanoflowers were prepared using a two-step process. The experimental process is green and free from contamination and can be synthesized directly at room temperature. Compared with pure TiO_2, Ag-modified TiO_2 enhances the absorption of visible light and effectively promotes the detachment of photoelectron pairs, Ag-TiO_2 has a significantly enhanced visible light response activity to photodecomposition of methyl orange (MO). It is shown that the strong interaction between Ag nanoparticles and TiO_2 enhances the photocatalytic activity of TiO_2 nanoflowers. The self-made open-air reactor was used to test the photocatalytic performance of different samples. The results showed that Ag-modified TiO_2 nanoflowers had excellent photodegradation ability. After repeated photodegradation of MO, Ag-modified TiO_2 nanoflowers showed good stability.

Key words: hydrolysis; Ag-TiO_2 ; photocatalytic activity

1 Introduction

In recent years, semiconductor photocatalysis has been extensively studied from the viewpoint of environmental accountability and energy conversion[1-3]. Titanium dioxide (TiO_2) has been shown to be promising due to effective oxidized powder, good durability and low cost[4-10]. However, pure TiO_2 has a wide band gap and exhibits photocatalytic activity only in the UV range[11-13]. Therefore, it is very desirable to develop photocatalysts with high catalytic activity in the visible light range[1,14-16].

Due to the localized surface plasmon resonance (LSPR) effect, silver nanoparticles show great potential in the field of photochemistry due to their highly tunable absorption[17-19]. LSPR is a collective free-charge oscillation in photo-excited metal nanoparticles[20,21]. It has been reported that slight silver deposition on the TiO_2 surface can extend the light absorption spectrum to the visible region[22]. In addition, due to the Schottky barrier formed at the interface of the metal TiO_2, the deposited silver particles can effectively retard the recombination of e^--h^+[22-24]. Moreover, some studies have shown that photoelectrons in silver particles can be directly captured by O_2 of reactive superoxide ions[20,21,25-27]. While these achievements are gratifying, it is worthwhile to prepare high performance, low cost, environmentally friendly and recyclable photocatalysts.

Herein, silver-modified 3D single-crystal anatase titanium dioxide nanoflowers have been successfully prepared by simple hydrolysis and subsequent Ag loading methods. Among them, silver nitrate was used in a mixed solution of sodium hydroxide and hydrogen peroxide to control the hydrolysis of Ti as a source of silver at room temperature. The amount of silver particles is controlled by the stirring time. The prepared Ag-TiO_2 nanoflowers extended the light absorption spectrum to the visible light region, and the methyl orange had a higher photocatalytic activity than the pure TiO_2 nanoflowers. In addition, the prepared Ag-TiO_2 nanoflower composite exhibits excellent contaminant degradation recyclability.

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2 Experimental

2.1 Synthesis of 3D nanowires-assembled anatase TiO_2 nanoflowers

All the chemicals in the study were analytically pure and did not require further purification. The anatase titanium dioxide nanoflowers assembled by three-dimensional nanowires were synthesized by a simple hydrolysis method. First, 24 g of sodium hydroxide was dissolved in 40 mL of deionized water. 60 mg of Ti was then added to the above solution with magnetic stirring. After the mixture was stirred for 10 minutes, 0.5 mL of hydrogen peroxide was added to the above solution under magnetic stirring. After sufficient reaction, the pH of the mixture was adjusted to 7 with hydrochloric acid solution. A precipitate was then obtained by centrifugation and washed several times with distilled water and anhydrous ethanol. After drying at 60 ℃ overnight, the resulting powder was annealed at 350 ℃ for 3 hours.

2.2 Synthesis of silver-modified 3D nanowires-assembled anatase TiO_2 nanoflowers

In a typical synthesis, 100 mg of prepared 3D TiO_2 nanoflowers (labeled as S_0) and 17 mg of $AgNO_3$ were dispersed in 100 mL of anhydrous ethanol and sonicated for 10 minutes. After sonication, the solution was magnetically stirred for 10 hours. The powder was then centrifuged, washed three to five times with water and absolute ethanol, and dried at room temperature, designated S_1. Other parameters are kept constant, only the agitation time is varied, and a similar experimental procedure is performed to produce samples S_2 and S_3. The detailed parameters are shown in Table 1.

Table 1 Different stirring time of Ag coupled with TiO_2 nanoflowers

Sample	The stirring time/h
S_1	6
S_2	12
S_3	24

For comparison purpose, schematic synthesis processes and diagram of Ag loaded TiO_2 nanoflowers are prepared as schematically illustrated in Fig.1.

2.3 Photocatalytic experiments

The photocatalytic degradation experiments of the prepared samples based on methyl orange were carried out in a room where the temperature and humidity were relatively stable. During degradation, the sample was immersed in an 80 mL beaker containing 50 mL of an aqueous solution of anaerobic bubbles in MO (15 mg/L). The solution was first darkened in a dark environment using a magnetic stirrer for half an hour to ensure that the catalyst surface molecules of the catalyst and the dye molecules in the solution reached an adsorption equilibrium, and then the 350 W xenon lamp was used to simulate the irradiation solution. The straight distance between the solution level and the horizontal plane of the light source is kept at 10 cm. At intervals of 10 minutes, 3 mL of the solution was taken from the reaction apparatus. Absorbance of the solution at a wavelength of 464 nm as measured by a UV-Vis spectrophotometer (UV-3200S, MAPADA analytic apparatus Ltd., Inc., Shanghai, China). A 420 nm cut-

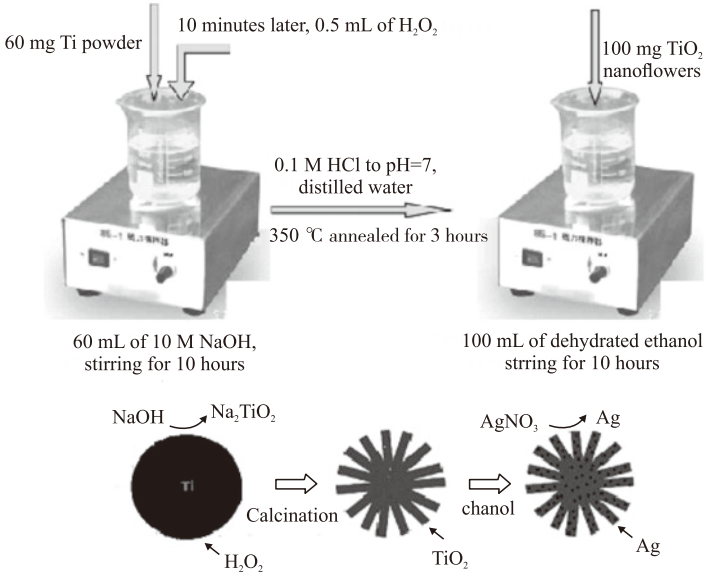

Fig.1 Schematic illustration of the synthesis processes and diagram of TiO_2 nanoflowers and Ag loaded TiO_2 nanoflowers

off filter was used in the experiment to obtain a visible light source.

3 Results and discussion

Fig.2 shows an XRD pattern of TiO_2 nanoflowers in which sample S_0 is unmodified and samples S_1, S_2, and S_3 are silver modified. It can be seen from the curve corresponding to sample S_0 that all diffraction peaks are only related to titanium (JCPDS 44-1294) and anatase TiO_2 (JCPDS 44-1294); Compared with the sample S_0, the diffraction peaks of the samples S_1, S_2, and S_3 not only include titanium and anatase TiO_2, but also face centered cubic (fcc) silver (JCPDS 4-0783), which is inferred. Silver nanoparticles have been successfully attached to the surface of TiO_2 nanoflowers. With increasing stirring time, the relative peak strength of Ag to TiO_2 increased, indicating that the amount of modified Ag increased with increasing mixing time. Based on the Scherrer equation, the crystal size of the Ag nanoparticles of the sample S_3 was estimated to be 20 nm using the (200) reflection, which is substantially consistent with the TEM pattern (Fig.4), showing that the prepared silver particles are single crystals.

Fig.3 shows the SEM images of S_0, S_1, S_2, and S_3, respectively. It is clear that the Ag/TiO_2 heterostructure maintains the prepared TiO_2. Moreover, TiO_2 nanoflowers have a smooth surface (Fig.3(a)). After stirring in the $AgNO_3$ solution, the size and overall shape of the sample did not change except for the silver nanoparticles deposited on the surface of the TiO_2 nanoflowers. When the stirring time was performed for 6 hours, the silver nanoparticles were sparsely attached to the surface layer of the TiO_2 nanoflower of the prepared sample S_1 (Fig.3(b)). When the stirring time was continuously performed for 12 hours, lots of silver nanoparticles were uniformly supported on the surface of the TiO_2 nanoflower of the prepared sample S_2 (Fig.3(c)). In addition, the silver nanoparticles attached to the edge of the TiO_2 nanoflowers are much larger than the dimensions on the plane (Fig.3(c)). As the stirring time increased to 24 hours, there was no significant change except for the number and size of silver nanoparticles of sample S_3 (Fig.3(d)).

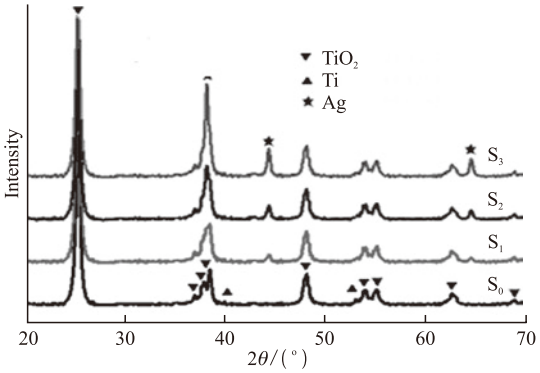

Fig.2 XRD patterns of sample S_0 and sample S_1, S_2, and S_3

To further investigate the microstructure of the composite, Fig.4 shows the TEM and HRTEM measurements of the resulting products. Fig.4(a) shows a TEM image of a sample S_0 with a radius of about 500 nm. In addition, TiO_2 nanoflowers have a smooth surface. Fig.4(b) shows a TEM image of sample S_1 with a radius of about 500 nm. According to XRD results, Ag atoms are clustered together. Therefore,

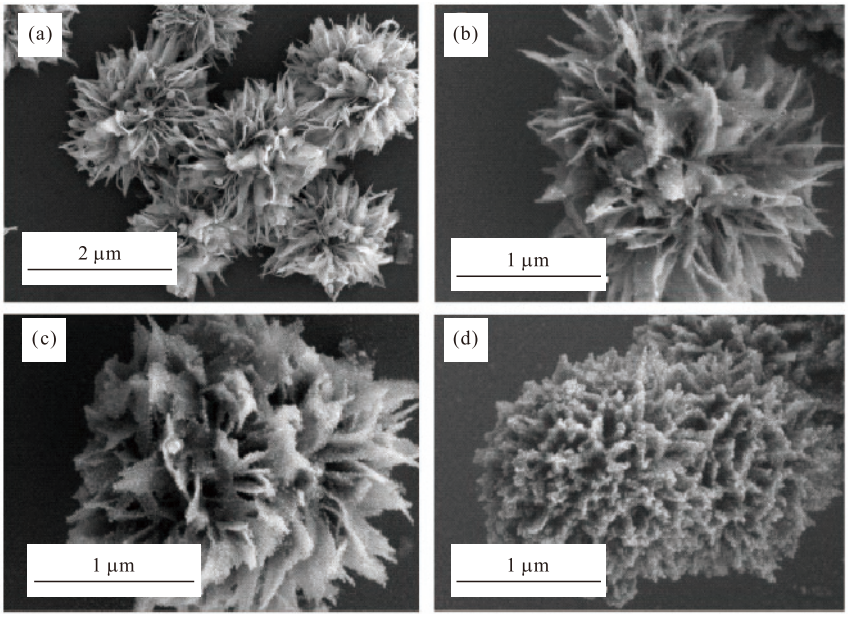

Fig.3 SEM images of (a) sample S_0, (b) sample S_1, (c) sample S_2, and (d) sample S_3

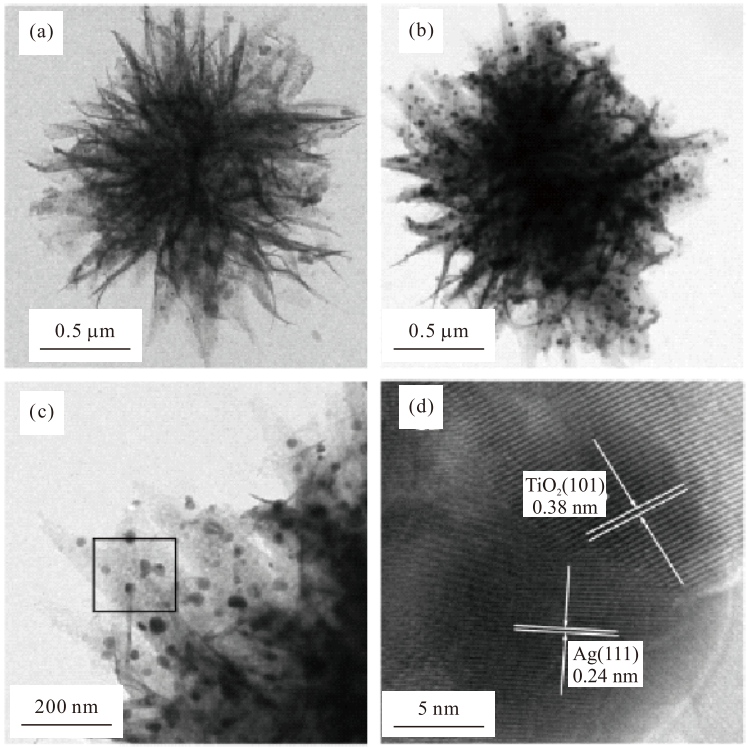

Fig.4 TEM and HRTEM images of sample S_0 (a) and sample S_1 (b-d)

the observed large particles should be aggregated Ag. The HRTEM image of sample S_1 is shown in Fig 4(c). It is apparent that silver nanoparticles having a radius of about 5 nm are attached to the surface layer of the TiO_2 nanoflower. Fig.4(d) shows the lattice fluctuations of the spheroidal particles in the rectangular region identified in Fig.4(c). In Fig.4(d), a lattice fringe of d=0.35 nm is observed, corresponding to anatase TiO_2 (101). Small particles were found in the anatase (101) facets. The atomic plane with a lattice spacing of 0.24 nm can be easily observed, which corresponds to the Ag(111) crystal plane (JCPDS, 04-0783). Therefore, Ag particles can be deposited on the anatase (101) surface[8,20].

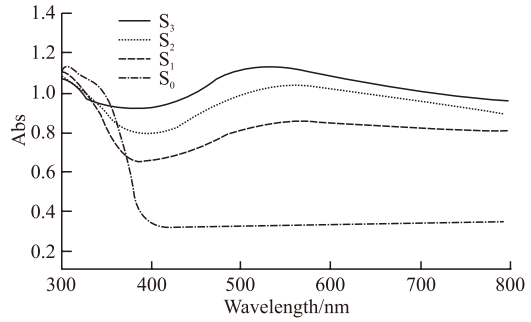

Fig.5 UV-Vis absorption curves of sample S_0 and sample S_1, S_2, and S_3

Fig.5 shows the UV-Vis diffuse reflection absorption spectra of the prepared samples S_0 and samples S_1, S_2, and S_3. Ag nanoparticles adhere to the surface layer of TiO_2 nanoflowers and produce localized surface plasmon resonance, thus enhancing the absorption values of all samples (S_1, S_2, and S_3) from 400 nm to 550 nm. The Ag-modified TiO_2 nanoflower surface layer expands its absorption spectrum region, which increases the absorption of visible light. It is worth noting that by increasing the amount of Ag modification, the absorption of TiO_2 nanoflowers in the visible region is greatly enhanced.

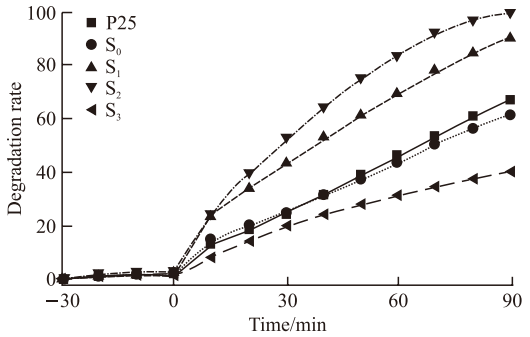

Fig.6 Photocatalytic degradation efficiency and illumination time curves of different preparation samples S_0, S_1, S_2, and S_3 and sample P25 on methyl orange solution

Fig.6 shows a graph of photocatalytic degradation rate as a function of time. The results showed that with the increase of irradiation time, the degradation rate of methyl orange increased rapidly. The duration of the entire experiment was 90 minutes, and the degradation rates of the five samples of methyl orange were 68%,

60%, 90%, 99%, and 38%, respectively. Obviously, under the irradiation of xenon lamp, the photocatalytic performance of the Ag modified sample is much better than that of the unmodified sample S_0, indicating that the surface modified silver of TiO_2 can enhance the photocatalytic activity, but this case does not imply that the silver particles have a higher load. It is beneficial to the improvement of photodegradation to increase the photodegradation efficiency. The appropriate proportion of Ag modified samples is superior to the photocatalytic activity of commercial photocatalysts (P25). However, too many silver nanoparticles may cover more TiO_2 surface area, which will reduce the utilization of incident light and cause the amount of photon absorption of TiO_2 to decrease, thereby suppressing the generation of free electrons and holes[28,29]. In addition, excess Ag nanoparticles cause it to occupy the recombination center of electron-hole pairs and is not conducive to the absorption of organic dyes by the surface layer of the composite, which may lead to reduced photocatalytic activity in excess of Ag loading[30,31].

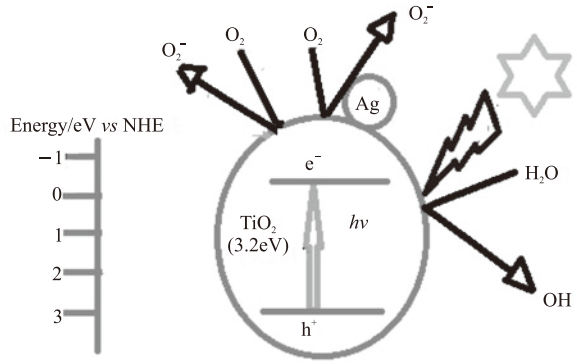

Fig.7 Photoexcitation charge separation diagram of Ag/TiO_2

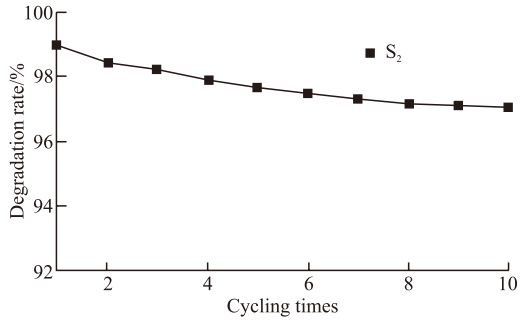

Fig.8 The cyclic degradation test of methyl orange solution was carried out on the prepared sample S_2

Fig.7 shows the photocatalytic activity enhancement of TiO_2 nanoflowers modified with Ag nanoparticles. The photocatalytic performance of silver-modified TiO_2 nanoflowers can be improved, which can be attributed to the following points. First, the fermi level of Ag is lower than that of TiO_2, and when silver nanoparticles are attached to the surface layer of TiO_2, photogenerated electrofns in TiO_2 can migrate therein. The silver nanoparticles then capture the migrated photogenerated electrons, causing the photoelectrons and hole pairs to be effectively separated and their recombination suppressed. Thus, more photogenerated electrons and hole pairs can generate and participate in the photocatalytic degradation reaction. The photocatalytic activity of Ag/TiO_2 composites is significantly improved.

In practical applications, the stability of the catalyst is often an important factor for scientific research workers to consider. Fig.8 shows a cycle experiment of photocatalytic degradation of methyl orange using the prepared sample S_2. For the degradation of methyl orange, the degradation efficiency remained at 96.7% after 10 cycles. Evidently, the activity of the photocatalyst was only slightly reduced after each cycle test. Therefore, it can be demonstrated that the prepared Ag-modified TiO_2 nanoflowers have excellent cycle stability.

4 Conclusions

The Ag-TiO_2 nanoflowers photocatalysts with high-performance are successfully synthetized by a simple two-step process and the Ag nanoparticles were well modified in the system. As the stirring time increases, more (101) faces of the anatase TiO_2 are exposed. The catalyst showed high photodegradation activity to MO under UV and visible light irradiation. In addition, Ag-TiO_2 nanoflower photocatalysts also exhibit excellent long-term recyclability for organic pollutant degradation.

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