SYNTHESIS AND EFFICIENT PHOTOCATALYTIC ACTIVITY OF Ag-NANOPARTICLES-DECORATED MESOPOROUS TiO₂ SPHERES

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Nano-heterostructures that integrate the advantages of nanomaterials and heterojunctions have attracted wide interest in photocatalysis. Herein, heterostructured Ag-nanoparticles-decorated mesoporous TiO₂ spheres (Ag/m-TiO₂) photocatalyst has been successfully prepared by a facile method. The results show that numerous Ag nanoparticles with diameters less than 5 nm dispersed homogeneously onto the mesoporous TiO₂ spheres and consequently form heterostructures. N₂ adsorption-desorption measurements indicate that the resultant products were porous with highly specific surface area. When used to photodegrade methylene blue (MB), the Ag/m-TiO₂ heteroarchitecture exhibits significantly enhanced photocatalytic performance compared with mesoporous TiO₂ spheres (m-TiO₂). Furthermore, the photocatalytic mechanism also has been discussed.

Keywords: titanium oxide, heterostructure, photocatalytic performance

1 INTRODUCTION

TiO₂ has been applied in the fields of biocompatibility, sunscreen, inorganic pigment, solar cells, sensors and catalysis due to its high physical and chemical stability, non-toxicity, and strong availability, as well as effectiveness.¹–⁵ So far, TiO₂ photocatalytic technology has demonstrated that it is a valid treatment of refractory organic wastewater.⁶–¹⁰ However, the anatase TiO₂ band gap is 3.2 eV, its absorption threshold is 387.5 nm, in the ultraviolet region.¹¹ Expanding the adsorption range to the visible region 400–800 nm is an urgent target. The nano-heterostructure has drawn intense considerations in environmental pollution controlling area, because it can overcome the two obstacles of TiO₂ photocatalyst: the dissatisfactory quantum efficiency and the negligible utilization of visible light. In the last few years, a number of materials have been combined with TiO₂ to form heterostructure to improve the photo-conversion efficiency of TiO₂, such as Ag,¹² Au,¹³ CdS,¹⁴ WO₃.¹⁵

The literature has demonstrated that loading of noble metal nanoparticles is an effective strategy for enhancing the photocatalytic performance. Relative to other noble metals, Ag is attracting enormous research interest due to its low-cost and non-toxicity. As well known, Ag particles can act as electron acceptor centers and separate electron and hole pairs.¹⁶ Simultaneously, its Fermi level is lower than that of the conduction band of TiO₂, which can drastically improve the photocatalytic property of TiO₂ and increase the quantum yield for photocatalytic processes.¹⁷ As we all know, the size of Ag particles has a great effect on the photocatalytic properties. Reducing the particles’ diameter to nano-size is an effective proposal to improve their specific surface area, and consequently the benefits for their performances in lots of surface-related applications. Studies have already confirmed that,⁹,¹⁰,¹⁸,¹⁹ loading silver on the solid carrier to form a composite catalyst is a powerful approach to prevent particles from agglomeration, and enhance the photocatalytic activity.
In previous work we have successfully synthesized mesoporous TiO$_2$ spheres and Ag$_3$PO$_4$/TiO$_2$ heteroarchitecture, and the composite catalysts exhibit excellent photocatalytic performance under visible light. Herein, we demonstrate the synthesis of nano-heterostructured Ag/mesoporous TiO$_2$ spheres (Ag/m-TiO$_2$) photocatalyst via a facile and effective method. Profiting from the unique structure with large pores and the relative high specific surface area of the mesoporous TiO$_2$ spheres, the resultant products were investigated as photocatalysts in the degradation of methylene blue under both the UV light and UV-visible light.

2 EXPERIMENTAL PART

2.1 Synthesis of mesoporous TiO$_2$ spheres

The mesoporous TiO$_2$ spheres (m-TiO$_2$) were obtained by combining the sol-gel method with the solvothermal method, as our previous report.

2.2 Fabrication of Ag/m-TiO$_2$ heterostructured photocatalyst

First, 70 mg m-TiO$_2$ spheres were added into 50 mL 2 × 10$^{-3}$ M silver-ammonia ([Ag(NH$_3$)$_2$]NO$_3$) aqueous solution with ultrasonics for 30 min and then the mixture was kept under a mechanical stir for a while at room temperature to make the [Ag(NH$_3$)$_2$]$^{+}$ ions fully absorbed on the m-TiO$_2$ surfaces via the electrostatic attraction. After that, 15 mL PVP ethanol solution was added and refluxed at 70 °C for 3 h. The final products were centrifuged, washed with ethanol and deionized water, and then dried at 60 °C. The products denoted as Ag-1/m-TiO$_2$.

In addition, the same procedures were performed for the synthesis of sample Ag-2/m-TiO$_2$ and Ag-3/m-TiO$_2$, in which the concentrations of [Ag(NH$_3$)$_2$]NO$_3$ are 2 × 10$^{-2}$ M and 2 × 10$^{-1}$ M, respectively.

2.3 Structural characterizations

X-ray diffractions (XRD) were operated on a D8 Tools X-ray diffractometer using Cu-K$\alpha$ radiation ($\lambda$ = 0.154056 nm). The morphology and microstructure of the as-prepared samples were observed by scanning electron microscope (SEM/EDS, JEOL JSM-6700F) and transmission electron microscope (TEM, JEM 3010 and Tecnai G2 F20). The porosity of the samples was analyzed at 77 K by nitrogen adsorption-desorption using the Barrett–Joyner–Halenda (BJH) method on a Quanochrome Autosorb 1 sorption analyzer. The Brunauer–Emmett–Teller (BET) measurement was used to evaluate the specific surface area. X-Ray photoelectron spectroscopy (XPS) was performed by a VG ESCALAB LKII instrument with Mg KR-ADES (hv = 1253.6 eV) source at a residual gas pressure of below 10$^{-8}$ Pa. A PerkinElmer spectrometer using KBr pellets was adopted to record the Fourier transform infrared (FTIR) spectra.

UV–Vis diffuse reflectance spectroscopy (DRUV-VIS) of the resultant products was characterized by a spectrophotometer Bws003 in the range 190–800 nm and used BaSO$_4$ as a reference standard.

2.4 Photocatalytic property testing of Ag/m-TiO$_2$

A 120 mL of MB solution with different concentrations of 30 mg L$^{-1}$ (ultraviolet light) and 10 mg L$^{-1}$ (visible light) in the presence of a certain amount of solid catalyst (12 mg for ultraviolet light and 60 mg visible light) was put into the photoreactor with light source and coolant system, in which the internal light source was a 50 W high-pressure mercury lamp and a 300 W halogen lamp. In order to make an adsorption-desorption equilibrium, the solution was kept stirring in dark conditions for half an hour. In the test process, aliquots of dispersion with given intervals of illumination were taken out for investigation. UV/Vis spectroscopy (UV-2550PC) was used to monitor the degradation of the MB. In the calculation of the photocatalytic activities, $C$ and $C_0$ stand for the real time concentration of MB and the initial concentration respectively.

3 RESULTS

3.1 Structural features and morphology

XRD was used to determine the crystallographic structures of the m-TiO$_2$ and Ag-1/m-TiO$_2$. All diffraction of m-TiO$_2$ sphere (Figure 1a) peaks at $2\theta$ = 38.2°, 44.3°, 64.4°, and 77.4° can be readily indexed to anatase TiO$_2$, which is consistent with the data JCPDS 21-1272. From the calculation from the Scherrer equation, the crystallite size of TiO$_2$ particles is 8.2±1.6 nm. After loading with Ag, no peaks of Ag are observed (Figure 1b), indicating the Ag is in the nanosize.

Typical SEM images of the m-TiO$_2$ spheres and Ag-1/m-TiO$_2$ hybrid spheres are represented in Figure 2.
The m-TiO$_2$ spheres composed of numerous nanoparticles have good dispersion with uniform diameter of $\phi 750$ nm (Figures 2a and 2b). After loading of Ag nanoparticles (Ag NPs), the diameters and morphologies show no obvious changes (Figures 2c and 2d), indicating the Ag particles are very small and well dispersed.

In order to observe clearly, the Ag-1/m-TiO$_2$ was characterized by TEM as shown in Figure 3. Observed from the low magnification of the TEM (Figure 3a), no Ag particles can be found on the surface of the sphere, attributed to the small size and the good distribution of the Ag particles. Further observations from HRTEM image (Figure 3b) illustrate that there are numerous nanoparticles less than 10 nm attached on the edge of each TiO$_2$ particle. This result reveals the formation of Ag-TiO$_2$ heterostructure, where metallic nano-size Ag and TiO$_2$ layer join. In addition, two sets of lattice fringes of 0.345 nm and 0.238 nm are assigned to the TiO$_2$ and Ag respectively (JCPDS card. 21-1272 and JCPDS card. 04-0783). To further confirm the presence and distribution of Ag NPs on the TiO$_2$ microspheres, electron mapping analysis was shown in Figures 3c to 3f. A variety of color distributions displayed as parts of Figures 3d to 3f, confirm the Ti-, O-, and Ag-enriched areas of the sample, respectively, suggesting Ag has been successfully loaded on the surface of TiO$_2$ and dispersed homogenously. The EDS analysis (Figure 3g) of the Ag-1/m-TiO$_2$ microspheres illustrates the existence of Ti, O and Ag elements and the percent of Ag is 5 %.

Figure 4 shows nitrogen adsorption properties of m-TiO$_2$ and Ag-1/m-TiO$_2$. The m-TiO$_2$ has a type-IV curve with a H1 hysteresis loop, corresponding to the mesoporous characteristic. The feature of the curve shows not much change after Ag loading, indicating the mesoporous structure is maintained after incorporating the Ag. However, the BET specific surface areas and pore volumes all reduce with the inclusion of Ag NPs. Before loading of the Ag, the specific surface areas and
The pore volume values of m-TiO$_2$ are 107.9 m$^2$/g and 0.366 cm$^3$/g. But Ag-1/m-TiO$_2$ has a specific surface area and pore volume of 64.4 m$^2$/g and 0.200 cm$^3$/g. In the pore size distribution curves, samples m-TiO$_2$ microsphere and Ag-1/m-TiO$_2$ present a similar narrow distribution, which are in the range of 0–22 nm (Figure 4b). The average pore sizes of both samples are 12 nm. A previous report demonstrated that loading metal in the mesostructures would result in the remarkable perturbation in the surface area, pore volume, and pore size respects. But the same phenomenon was not observed in this case, suggesting the good dispersion and small size of Ag NPs in the m-TiO$_2$.

XPS has been recognized as a useful measurement for qualitatively determining the surface component and composition for the samples. Figure 5a exhibits the fully scanned spectra from 0 eV to 1200 eV, illustrating that the Ag-1/m-TiO$_2$ sample is comprised of C, Ti, O and Ag. Since the C element is usually ascribed to an adventitious carbon-based contaminant. To harvest further evidences for the a) m-TiO$_2$ and b) Ag-1/m-TiO$_2$ interaction between the Ag nanocrystals and m-TiO$_2$ support, the high-resolution XPS spectra of Ti 2p, O 1s and Ag 3d are shown in the Figures 5b to 5d. Figure 5b is the high-resolution spectrum of Ti 2p, two typical peaks lie in 458.8 eV and 464.5 eV are pointed to the oxidation state of Ti$^{4+}$ in anatase TiO$_2$. As Figure 5c shows, the O 1s curve can be fitted into three peaks located at (530.0, 530.7 and 532.1) eV, which corresponds to the lattice oxygen from the C–O, the OH species resulting from H$_2$O and Ti–O bond in bulk TiO$_2$, respectively. More specially, the peak positions for Ti 2p and O 1s of the Ag-1/m-TiO$_2$ hybrids shift to higher binding energy.
bands than those in pure m-TiO$_2$, which is due to the presence of the oxygen vacancy, resulting in a lower electron density for the Ti and O atoms in Ag-1/m-TiO$_2$ hybrids, and it is beneficial for improving the photocatalytic performance. In order to confirm the chemical status of Ag, the corresponding high-resolution XPS spectrum is shown in Figure 5d. There are two individual peaks centered at 368.1 eV and 374.1 eV could be attributed to Ag 3d5/2 and Ag 3d3/2, and the splitting of 3d doublet is 6.0 eV. This result proves that Ag is certainly present in the form of metallic Ag in the hybrids.

The FT-IR spectra of m-TiO$_2$ and Ag-1/m-TiO$_2$ are displayed in Figure 6. In general, the spectrum of the Ag-1/m-TiO$_2$ resembles that of m-TiO$_2$. The absorption bands located at 3416 cm$^{-1}$ and 1632 cm$^{-1}$ in both spectra are assigned to O-H group in H$_2$O. The IR absorptions appear at 720 cm$^{-1}$ are caused by the Ti-O stretching mode. Although the spectra of m-TiO$_2$ and Ag-1/m-TiO$_2$ are similar, the intensity of the Ti-O in Ag-1/m-TiO$_2$ significantly decreases, indicating that Ag NPs have been successfully loaded in the m-TiO$_2$.

Furthermore, the effects of the [Ag(NH$_3$)$_2$]NO$_3$ concentration on the structure of Ag/m-TiO$_2$ heterostructures were also investigated, as shown in Figure 7. As shown in Figure 7a, increasing concentration of [Ag(NH$_3$)$_2$]$^+$ to $2 \times 10^{-2}$ M, m-TiO$_2$ sphere was nearly completely capped by Ag particles and formed a core-shell structure. Further increasing the concentration to $2 \times 10^{-1}$ M, it is obviously observed that large Ag particles with diameter of 50 nm attach on the m-TiO$_2$ surface (Figure 7b). The corresponding XRD patterns were shown as Figure 7c. Several well-resolved diffraction peaks appeared at 2$\theta$ = 38.0°, 44.2°, 64.3° and 77.2° are readily indexed to metal Ag with face-centered cubic structure (JCPDS card no. 04-0783). The intensity of Ag becomes stronger with the increasing of [Ag(NH$_3$)$_2$]NO$_3$ concentration, suggesting that the content of Ag was increased.

### 3.2 Photocatalytic performance

Ag/m-TiO$_2$ hybrids as photocatalysts were investigated to degrade methylene blue (MB). The $C/C_0$ versus irradiation time is plotted in Figure 8a. In the case of the Ag-1/m-TiO$_2$ catalyst, the MB completely destroyed only takes 25 min. However, with the increasing of Ag, the photocatalytic performance reduces. The reasonable explanation is that Ag particles wrapped on the surface of m-TiO$_2$ reducing the utilization of mesopores, consequently decreasing the contact area between the MB and the catalyst. In other words, only Ag particles play a catalytic role (Ag-2/m-TiO$_2$). Especially, the catalytic activity significantly reduced, even lower than m-TiO$_2$. This may be due to the large particle size of the Ag wrapped on m-TiO$_2$ surface, which reduces the adsorption rate of the light, consequently weakening the photocatalytic performance. Figure 8b shows UV-vis spectra for the degradation of the MB catalyzed by Ag-1/m-TiO$_2$ under UV light. The typical peak of MB at 665 nm disappears fast, suggesting that this sample exhibits excellent photocatalytic activity.

The photocatalytic degradation of MB allows for pseudo first-order kinetics, and the apparent degradation rate constant $k$ could be determined by $\ln \left( \frac{C_0}{C} \right) = kt$. The relationships between $\ln \left( \frac{C_0}{C} \right)$ and the reaction time of all the photocatalysts are linear, as shown in Figure 8c. It can be observed that Ag-1/m-TiO$_2$ possesses the highest apparent reaction rate constant, certifying the high photocatalytic activity, which is attributed...
to its unique structure. First, the large mesopores structure and specific surface area can enlarge the contact between the organics and photocatalyst. Secondly, the heterostructure is beneficial for the separation between photo-generated electron and hole.

Combined with the results of SEM (Figure 2) and photocatalytic activity under UV light (Figure 8), Ag-1/m-TiO₂ was chosen as photocatalyst used under visible light irradiation. Figure 9a exhibits the degradation of MB with times. Compared with m-TiO₂, loading metallic Ag on the surface of m-TiO₂ spheres increases the photocatalytic performance. After 150 min of irradiation, 96% MB was destroyed. It indicates that the Ag-TiO₂ heterojunction could enhance the electron-charge separation efficiency. Figure 9b shows the changes of the absorption spectra of the MB aqueous solution exposed to visible light for various times in the presence of Ag-1/m-TiO₂. Under visible-light illumination, the MB absorption rate rapidly decreases at 665 nm.

4 DISCUSSION

UV-vis diffuse reflectance (DRUV-VIS) was used to further investigate the adsorption of products under visible light and UV light. The DRUV-VIS for Ag/m-TiO₂ and pure m-TiO₂ were compared, as displayed in Figure 10a. The pure m-TiO₂ spheres show the adsorption edges at about 390 nm, which is ascribed to the charge transfer from the valence band (mainly formed by 2p orbitals of the oxide anions) to the conduction band (mainly formed by 3dorbitals of the Ti⁴⁺ cations) and no adsorption can be observed in the visible-light region.²⁷ While for Ag/m-TiO₂, the high absorbance begins from 400 nm to the whole visible region, which is the typical features of the surface plasmon absorption of spatially restricted electrons from Ag NPs and further confirming the presence of the heterostructure between Ag and TiO₂. The absorbance in the range of visible region for the Ag-1/m-TiO₂ system increases and basically stays constant owing to the uniformly distributed Ag NPs on m-TiO₂. While for Ag-2/m-TiO₂, the absorption is even higher than that of Ag-1/m-TiO₂ at the beginning and then decreases gradually from 550 nm to 800 nm, suggesting that Ag NPs on m-TiO₂ are not evenly distributed.²⁸ In particular, the absorption of Ag-3/m-TiO₂ decreases significantly ascribed to large amount of Ag particles wrapped on m-TiO₂ resulting in the high energy surface is covered.

Under UV illumination, TiO₂ is activated and generates electron–hole pairs. Ag NPs have a favorable Fermi level (0.4 V vs. normal hydrogen electrode NHE), which can serve as a good electron acceptor.¹⁄³ Thus, Ag can trap the photogenerated electron in the conduction band of m-TiO₂ for facilitating quick electron transfer and it is energetically favorable.²⁹ Consequently, it lowers the recombination of photo-induced charges, as exhibited in Figure 10b. Furthermore, The Fermi level shifts to more negative and renders Ag more reductive due to the accumulation of trapped electrons in Ag nanoparticles. Both the photogenerated electrons in TiO₂ as well as the trapped electrons in Ag will react with O₂, and yield some highly oxidative species, for example, peroxide.
Conclusions

Ag-1/m-TiO2 manifests its outstanding performance. Photocatalytic measurement results demonstrate that the production of H2O2, which can react with H2O or OH− and also generate OH·, which is a key to affect the photocatalytic performance. For Ag/m-TiO2 composite samples, Ag can trap the photogenerated electrons in the conduction band of m-TiO2 and consequently prolongs the lifetime of holes in the valence band. However, the loading of Ag would also give adverse effects on the photocatalytic performance that Ag can be excited, generating electrons and then transfer back to m-TiO2, which prevents the separation of charges in m-TiO2. Therefore, the amount of Ag is a key to affect the photocatalytic performance.

Under visible light added, an enhancement factor EF, which is defined as $EF = \frac{k_{UV-vis}}{k_{UV}}$, is used as a reference. According to reference no. 8, the EF values of m-TiO2 ad Ag-1/m-TiO2 are 1.81 and 1.79, respectively, which is inversely related to the specific decay rate under visible illumination. It implies the smaller EF, better photocatalytic performance under UV–visible irradiation.

According to the above discussions, it is concluded that the loading Ag composites is indeed improving the photocatalytic performance of m-TiO2.

5 Conclusions

In summary, Ag/m-TiO2 heterostructure photocatalysts have been prepared by a facile method. Ag NPs homogeneously distribute on the m-TiO2 spheres. The [Ag(NH3)2]NO3 concentration is critical for controlling the particle size and the distribution of Ag. Moreover, the hybrids with large pores and a high specific surface area determine Ag/m-TiO2 as a candidate for the catalyst. The photocatalytic measurement results demonstrate that the Ag-1/m-TiO2 manifests its outstanding performance under both UV and visible light, compared with m-TiO2.

Acknowledgements

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6 References

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