Research Article

AgBr-Coupled TiO_2: A Visible Heterostructured Photocatalyst for Degrading Dye Pollutants

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A series of AgBr/TiO_2 visible photocatalysts with heterojunction structure was synthesized using Ti(OC_4H_9)_4, KBr, and AgNO_3 as precursors. The phase composition, particle morphology and size, microstructures, and absorbance of these photocatalysts were characterized by X-ray diffraction, transmission electron microscope (TEM), high-resolution TEM, and UV-vis spectra. It was found that the coupled AgBr/TiO_2 was an effective photocatalyst to degrade the methylene blue under visible light irradiation, compared with the other noncoupled photocatalysts of AgBr, AgBr/P25, and P25. The photocatalytic activities of AgBr/TiO_2 increase first and then decrease with increasing the mass ratio of \( m_{\text{AgNO}_3}/m_{\text{TiO}_2} \) and the photocatalyst with the mass ratio of 3.35 has the highest photocatalytic activity. The results showed that the coupled photocatalyst has the particle size of about 15 nm with homogeneous dispersion and has the strongest absorption in whole UV-vis light region (250–800 nm) originated from the synergetic effect of heterostructured AgBr/TiO_2. The coupled AgBr/TiO_2 photocatalyst can keep stable photocatalytic activity after five-circle runs.

1. Introduction

In recent years, the photocatalysis technology for the purification of contaminated water and the remediation of polluted air has attracted significant attention due to its advantages of low cost, being environment-friendly, and high efficiency [1, 2]. Among many photocatalysts, titania has been widely studied for its wide application in photocatalysis, solar cells, and hydrogen production because of its nontoxicity, stability in aqueous solution, and no photocorrosion [3]. However, most applications so far are limited to UV light irradiation because the light absorption edge of pure titania is less than 380 nm. Moreover, using UV light is expensive, and its content in sunlight accounts for less than 5% [4, 5]. Therefore, attempts have been made to increase the TiO_2 efficiency by doping with transition metal ions and nonmetal elements, by modification with other semiconductors or by covering the surface with photosensitizers such as organic dyes and inorganic light absorbers to enhance the optical absorption in the visible range. The dye molecules as sensitizer can be easily desorbed, resulting in the deterioration of photocatalytic activity during the reaction process, and even degradation of themselves by titania photocatalyst under illumination [6, 7].

It is well known that silver bromide with a band gap of 2.6 eV is an inorganic photosensitive semiconductor material [8], which has high photographic sensitivity in the visible light region and can be used to modify titania to have visible light activity. Hu et al. [9, 10] reported that AgBr/TiO_2 visible light photocatalysts prepared by deposition-precipitation method can efficiently destruct azodyes and bacteria. Zang et al. [11] synthesized an AgBr/TiO_2 catalyst and studied its photocatalytic activity under simulated sunlight irradiation. In their study, the influence of AgBr content in catalyst and the incident light intensity on the degradation of methyl orange (MO) was also investigated. Li et al. [12] synthesized an AgI/TiO_2 composite photocatalyst with core/shell nanostructures that exhibited higher photocatalytic activity in the visible region due to its strong light absorption and low recombination rate of the electron-hole pairs. Recently, it has drawn much attention to form heterojunction photocatalyst to enhance the photoactivity of semiconductor catalyst. The construction of heterostructured photocatalysts can promote the separation of photoexcited electron-hole pairs through...
various carrier-transfer pathways and extend the light-response range by coupling suitable electronic structures in two or multicomponent semiconductors [13]. Robert [14] reviewed the TiO₂ heterostructured photocatalysts modified by MnO₂ and MgO nanoparticles. Zhang et al. [15] synthesized AgBr-Ag-Bi₂WO₆ nanojunction photocatalysts with multi-visible-light active components. Ag can improve the separation of electron-hole pairs when it was used as electron-transfer system. The catalyst AgBr-Ag-Bi₂WO₆ showed high photocatalytic activity for the degradation of Procion Red MX-5B and pentachlorophenol.

In this study, a nanosized AgBr/TiO₂ heterojunction-coupled photocatalyst was synthesized by double-reaction route using Ti(OCl₂)₄ as the precursor. AgBr/TiO₂ was investigated in terms of its structure and activity compared to AgBr/P25 which was synthesized by simply depositing AgBr on P25 TiO₂ through single-reaction route. The influence of AgBr content on AgBr/TiO₂ photoactivity and the cycling life of the photocatalyst were also studied.

2. Experimental

Tetraethyl titanate Ti(OC₄H₉)₄ (Beijing Xingjin Chemical Co., >98.5%) was used as a titanium precursor in the sol-gel process. Other chemicals and solvents were of analytical grade and were used without further purification.

2.1. Preparation of Photocatalysts

2.1.1. Synthesis of AgBr/TiO₂ by Double-Reaction Route. AgBr and TiO₂ sol precursors were prepared as follows: AgBr sol was obtained by adding 1.0192 g polyvinyl pyrrolidone (PVP) to 0.03 mol/L KBr (200 mL) solution under magnetic stirring. Then 200 mL AgNO₃ with the same molar concentration was added slowly to the solution above, and a light yellow AgBr sol was obtained. A titania sol was prepared by hydrolyzing tetrabutyl titanate (Ti-(OBu)₄) in anhydrous ethanol. The mixture of Ti-(OBu)₄ and acetylacetone (volume ratio was 5:2) [16] was added into an appropriate amount of ethanol and stirred for half an hour to obtain a bright yellow titania sol. Then the titania sol was added into the AgBr sol under vigorous stirring, refluxing at 80°C for 15 hours, during which TiO₂ sol precursor was hydrolyzed slowly and deposited on the surface of AgBr nanoparticles. The formed precipitate was separated by centrifugation followed by washing with distilled water and ethanol for several times. Finally, the as-prepared powder was dried at 70°C and calcined in air at 500°C for 3 hours to get the AgBr/TiO₂ compound photocatalyst. A series of AgBr/TiO₂ photocatalysts were prepared by changing the mass ratio of AgBr to TiO₂ (mAgBr/mTiO₂ = 1, 2, 3, 3.35, 4).

2.1.2. Synthesis of AgBr/P25 by Single-Reaction Route. For the purpose of comparison, AgBr/P25 composite photocatalyst was also prepared according to the procedure in the previous study [9]. A certain amount of P25 TiO₂ (Germany’s Degussa Corporation) was dispersed in 200 mL distilled water and stirred for 30 min, then an appropriate amount of KBr and PVP was added into it, followed by stirring for another 30 min to dissolve all the chemicals adequately. After that, 0.03 mol/L AgNO₃(200 mL) was added into the mixture solution. The next step was the same as the synthesis of AgBr/TiO₂. At last, AgBr/P25 photocatalyst with mass ratio of mAgBr/mP25 = 3.35 was obtained.

2.2. Characterization of Photocatalysts. X-ray powder diffraction (XRD) patterns were recorded on Rigaku D/MAX-2500 VB2 diffractometer, operated at 40 kV, 200 mA with a Cu target (λ = 1.5406 Å). Particle morphology and size were observed by a transmission electron microscope (TEM) (Hitachi 800) at an accelerating voltage of 200 kV. Microstructures were observed by a high-resolution transmission electron microscope (HRTEM) (JEOL-3010) at an accelerating voltage of 300 kV. The UV-visible absorption spectra were carried out on a TU-1901(Beijing Purkinje General Instrument Co., Ltd.) double-beam UV-Vis spectrophotometer. X-ray photoelectron spectroscopy (XPS) spectra were acquired by a Thermo ESCALAB 250 X-ray photoelectron spectrometer. Mg Kα radiation was selected as the X-ray source.

2.3. Evaluation of Photocatalytic Activity. A 500 W Xe lamp was used as the visible light source, and the visible wavelength was controlled through a 420 nm cut filter (LF420, China), which was hanged in a dark box and kept at about 15 cm above the liquid surface. Aqueous suspensions of methyl blue (MB) dye (100 mL, with an initial concentration of 10 mg/L) and photocatalyst powder (1.5 g/L) were placed in a beaker. Before irradiation, the suspensions were magnetically stirred for 30 min under dark condition to establish an adsorption/desorption equilibrium between the dye
solutions and the surface of photocatalysts. Under stirring, a small amount of suspension (about 5 mL) was taken out every 10 min under irradiation and then centrifuged and analyzed using a 752 spectrophotometer (made in China). The photocatalytic activity of the synthesized photocatalysts was evaluated by plotting the absorbance-time curve and calculating the specific absorbance of $C/C_0$.

3. Results and Discussion

3.1. XRD Characterization. The XRD patterns of AgBr, TiO$_2$, and AgBr/TiO$_2$ synthesized with different mass ratios were shown in Figure 1. The as-synthesized TiO$_2$ is a mixed crystal phases of anatase and rutile. The contents of the two phases were calculated according to the XRD data [17] and given in Table 1. The phase composition of as-synthesized TiO$_2$ is denoted as $W_A$ (70.8%) and $W_R$ (29.2%) as shown in Table 1 (Sample b). But in the AgBr/TiO$_2$ system, the content of anatase increases initially and then decreases with increasing AgBr content which indicates that the excess Br ions may stabilize the metastable anatase phase [18] and be beneficial to the increase of anatase phase up to $m_{AgNO_3}/m_{TiO_2} = 3.35$, where the anatase phase reaches its maximum content. Besides, there are no any diffraction peaks of metallic Ag in all the AgBr/TiO$_2$ systems indicating that the fresh catalysts are stable after calcinations and other procedures.

3.2. TEM Characterization. The microstructures of AgBr/TiO$_2$ composite photocatalyst synthesized with different mass ratios were characterized by TEM and HRTEM as shown in Figure 2. It can be seen that AgBr/P25 shows an agglomerated mixture of AgBr with black color and P25 with light color (Figure 2(a)). The similar agglomerated mixture can also be found in Figure 2(b) which shows that the black AgBr crystallite is about 30 ~ 50 nm, and the light TiO$_2$ crystallites agglomerate obviously and are even smaller than several nanometers when the mass ratio is $m_{AgNO_3}/m_{TiO_2} = 1$ (Figure 2(b)). Consequently, while $m_{AgNO_3}/m_{TiO_2} = 2$, a coupled structure of AgBr/TiO$_2$ is formed where it shows a one-to-one corresponding relation of the deep and light colored particles in homogeneous dispersion. However, there are a few lonely TiO$_2$ particles because some AgBr particles cannot be matched with their counterpart of TiO$_2$. In Figure 2(d), the coupled structure of AgBr/TiO$_2$ with smaller size of about 15 nm is formed homogeneously and dispersed very well as shown by the composite particles of deep AgBr and light TiO$_2$ in color. The HRTEM image (Figure 2(e)) of the sample further demonstrates that the lattice spacing of the two fixed
Table 1: Synthesis condition, phase composition, and crystalline size of AgBr/TiO₂ photocatalysts.

<table>
<thead>
<tr>
<th>Sample No</th>
<th>AgNO₃/TiO₂ (wt)</th>
<th>Phase composition of TiO₂</th>
<th>Crystalline size/nm</th>
<th>C/C₀</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anatase/%</td>
<td>Crystalline size/nm</td>
<td>Rutile/%</td>
<td>Crystalline size/nm</td>
</tr>
<tr>
<td>a</td>
<td>AgBr</td>
<td>——</td>
<td>——</td>
<td>——</td>
</tr>
<tr>
<td>b</td>
<td>TiO₂</td>
<td>70.8</td>
<td>20</td>
<td>29.2</td>
</tr>
<tr>
<td>c</td>
<td>1</td>
<td>13.9</td>
<td>28</td>
<td>86.1</td>
</tr>
<tr>
<td>d</td>
<td>2</td>
<td>66.7</td>
<td>23</td>
<td>33.3</td>
</tr>
<tr>
<td>e</td>
<td>3</td>
<td>86.9</td>
<td>15</td>
<td>13.1</td>
</tr>
<tr>
<td>f</td>
<td>3.35</td>
<td>97.1</td>
<td>18</td>
<td>2.9</td>
</tr>
<tr>
<td>g</td>
<td>3.5</td>
<td>75</td>
<td>17</td>
<td>25</td>
</tr>
<tr>
<td>h</td>
<td>4</td>
<td>87.4</td>
<td>18</td>
<td>12.6</td>
</tr>
</tbody>
</table>

3.3. UV-Vis Characterization. Figure 3 shows the UV-vis spectra of different samples. It is seen that P25 (Figure 3(a)) and TiO₂ (Figure 3(b)) have little or no absorption in the visible light region (>400 nm), which accords with its intrinsic absorption properties. However, AgBr has strong absorption both in UV and visible light that should be assigned to surface plasmon resonance absorption of silver produced by the photoreduction of AgBr [19]. The composite photocatalysts of AgBr/P25 (Figure 3(d)) and AgBr/TiO₂ (Figure 3(e)) have strong visible light absorption, and the absorbance of AgBr/P25 composite photocatalyst is similar to the pure AgBr (Figure 3(c)), indicating that the visible light absorption of AgBr/P25 is only due to the AgBr without forming the coupled structures between them. This was confirmed by the TEM photo of AgBr/P25 in Figure 2(a). AgBr/TiO₂ (Figure 3(e)) exhibits much higher visible light absorbance than AgBr/P25 (Figure 3(d)). It is reasonable that the formed heterojunction microstructure between AgBr and TiO₂ can construct a channel that is beneficial for the electron transfer and ion diffusion, and this can promote the possible doping of Ag⁺ in TiO₂ lattice, leading to the strong visible light absorption [15, 20].

As shown in Figure 4, AgBr/TiO₂ with different mass ratios of m₃NO₃/m₃TiO₂ was characterized by the UV-vis spectra. It can be clearly seen that the AgBr/TiO₂ has the strongest absorption in the visible region when m₃NO₃/m₃TiO₂ = 3.35. This result was also related to the formation of special microstructures of this sample including smaller particle size, homogeneous dispersion, and interface matching semiconductor heterojunction microstructure demonstrated by TEM and HRTEM (Figure 2).
3.4. Evaluation of Photocatalytic Activity

3.4.1. Evaluation before and after Combination. Figure 5 shows the photodegradation curves of methylene blue (MB) for different samples. The order of visible light activity is as follows: AgBr/TiO$_2$ > AgBr > AgBr/P25 > P25 > TiO$_2$. Generally, TiO$_2$ has almost no visible light activity, and it can only be activated under UV light irradiation because of its large band gap of 3.0–3.2 eV. The samples of P25 and as-synthesized TiO$_2$ show only little degradation originated from the photolysis of MB. AgBr can be excited by visible light and generate electron-hole pairs to exhibit some photocatalytic activity for degrading MB [8, 19]. However, AgBr/P25 is only the simple mixture of active AgBr and inactive TiO$_2$ which shows poorer photocatalytic activity than single AgBr. The photocatalytic activity of AgBr/TiO$_2$ with homogeneous coupled structure leading to the strongest visible light absorption is higher than AgBr/P25 in the form of the agglomerated mixture. These results suggest that there is a synergetic effect between the components of AgBr and TiO$_2$ in the coupled AgBr/TiO$_2$ compared to the simple mixture of them [12]. The photogenerated electron excited by narrow band gap semiconductor of AgBr under visible light irradiation could be directly injected to the TiO$_2$ via the coupled structure, resulting in effective separation of photogenerated electron and hole and enhancing the photocatalytic activity.

3.4.2. Effect of AgBr Content in AgBr/TiO$_2$ Photocatalyst. In order to determine the optimal AgBr content in catalyst, a series of AgBr/TiO$_2$ photocatalysts with different mass ratios ($m_{AgNO_3}/m_{TiO_2}$) were prepared, and their photocatalytic activities on degradation of MB were compared. It is found that the photocatalytic activity of AgBr/TiO$_2$ increases gradually to maximum with increasing the mass ratio of $m_{AgNO_3}/m_{TiO_2}$ up to 3.35 and then decreases as shown in Figure 6. The sequence is consistent with the content of anatase in AgBr/TiO$_2$ as showed in Table I implying that the higher content of anatase contributes to the better photocatalytic activity, which is in accordance with a previous study [21]. Moreover, the homogeneously dispersed coupled heterostructure microstructures were formed while $m_{AgNO_3}/m_{TiO_2} = 3.35$ which have stronger absorption in the whole visible region and are beneficial to the further improvement of photocatalytic activity. The decrease of photocatalytic activity with further increasing the content of AgBr in AgBr/TiO$_2$ may result from the fact that the excessive AgBr particles shorten the average distance between the trapping centers of photogenerated electrons and holes so as to increase the probability of recombination rate of electron-hole pairs [9]. More studies are needed to further understand the interaction mechanism of AgBr content in AgBr/TiO$_2$ photocatalyst.
3.5. Catalyst Stability. The stability of AgBr/TiO₂ catalyst with coupled structure is shown in Figure 7 for the degradation of MB under visible light irradiation. AgBr/TiO₂ was easily recycled by simple filtration without any further treatment in these experiments. The photocatalytic activity did not decrease significantly in the degradation MB after five successive cycles under visible irradiation. The high-resolution XPS spectra of the Ag3d and Br3d regions for fresh AgBr/TiO₂ photocatalyst and AgBr/TiO₂ after the 5th run are shown in Figure 8. The Ag 3d₅/₂ and Ag 3d₃/₂ peaks are identified at 367.7 and 373.6 eV before reaction which are attributed to Ag⁺ in AgBr, and they slightly shifted to low-energy side at 367.4 and 373.3 eV, respectively, after reaction. Probably the Ag⁺ is interacting with some electronegative elements of MB dye or intermediate molecules adsorbed on the surface of photocatalyst after reaction, resulting in a small distortion of electron density of Ag⁺, leading to its small shift toward lower values [22, 23]. Moreover, the peak of Br 3d at 68.3 eV is due to the crystal lattice of Br in AgBr [24]. These results confirm that the heterostructure between AgBr and TiO₂ might inhibit silver atoms from forming larger clusters and prevent AgBr decomposition.

Generally speaking, AgBr with high photosensitivity is unstable under light irradiation and can be photodecomposed into a metal cluster of Ag through the photografting process. However, once the heterojunction structure between AgBr and TiO₂ formed, most of the photoexcited electrons can be transferred from the conduction band of AgBr to that of TiO₂ that inhibits the reduction of AgBr and promotes the stabilization of AgBr under light irradiation [11]. The stable photocatalytic performance of the coupled AgBr-TiO₂ heterostructures indicates that the AgBr/TiO₂ photocatalyst has a better application potential in wastewater treatment using solar energy. However, further work is required to elucidate the mechanism for AgBr stability.

4. Conclusions

Using AgBr as the inorganic photosensitive material, a series of AgBr/TiO₂ composite photocatalysts and AgBr/P25 were synthesized by double- and single-reaction procedure. The photocatalytic activity of AgBr/TiO₂ synthesized using double-reaction procedure is higher than that of AgBr/P25 prepared by the single-reaction procedure. The order of photocatalytic activity of the above photocatalysts under visible light irradiation is as follows: AgBr/TiO₂ > AgBr > AgBr/P25 > P25 > TiO₂, which is consistent with the order of the absorbance in UV-vis spectra. While increasing AgBr content in the AgBr/TiO₂ photocatalyst, the phase contents of anatase increase initially and then decrease, which is in accordance with the sequence of photocatalytic activity. When the mass ratio $m_{\text{AgNO}_3}/m_{\text{TiO}_2}$ equals 3.35, the good-matching semiconductor heterojunction microstructures are formed between the interfaces of AgBr and TiO₂, which obviously enhances the absorption of visible light and contributes to the best photocatalytic activity.

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References


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