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Synergistic effects of doped Fe^{3+} and deposited Au on improving the photocatalytic activity of TiO_2

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Fe^{3+} doped together with Au deposited TiO_2 (Au/Fe^{3+}–TiO_2) was successfully prepared, which shows excellent photocatalytic activity for degradation of methyl orange (MO) under both UV and visible light ($\lambda > 420$ nm) illumination. Fe^{3+} has been confirmed by EPR to substitute for Ti^{4+} in the TiO_2 lattice, and Au exists as Au^0 on the surface of the photocatalyst indicated by the results of XRD. Fe^{3+} and Au have synergistic effects on improving the photocatalytic activity of TiO_2. A proposed mechanism concerning the synergistic effects is discussed to explain the improvement of the photocatalytic activities.

KEY WORDS: Fe^{3+} doped; Au deposited; TiO_2 photocatalyst; synergistic effects.

1. Introduction

TiO_2 is one of the most promising photocatalysts because of its chemical stability, nontoxicity, low cost, and excellent degradation for organic pollutants [1–5]. However, the large band gap and low quantum yields of TiO_2 prevent it from practical application. To solve these problems, many groups have been involved in doping titania with transition metal ions to extend the absorption into the visible region, among which Fe^{3+} has been the most extensively examined [6–9]. Also numerous attention has been devoted to depositing noble metals such as Pt, Ag, Au onto the surface of titania to improve the separation of electrons and holes [10–12].

Although doping titania with transition metal ions can extend its photoresponse into the visible region, the photocatalytic performance in the UV region usually decreases significantly [13]. Noble metals deposited on titania can effectively hinder the recombination of electron-hole pairs, but they have little effects on extending the light absorption into visible region, thus the photoactivity can be improved under UV light illumination instead of visible light. So it is a challenging issue to develop the photocatalysts which show excellent photocatalytic activities both under visible and UV light illumination. Enlightened by the respective advantages of doping and deposition, we try to combine doping Fe^{3+} with depositing Au in order to improve the visible and UV light activity of titania through the synergistic effects of Fe^{3+} and Au. To the best of our knowledge, researches concerning this area have not been reported until recently.

2. Experimental

2.1. Preparation of Photocatalysts

The preparation procedure of Fe^{3+} doped TiO_2 deposited with Au (Au/Fe^{3+}–TiO_2) consists of two steps. Firstly, a series of Fe^{3+} doped TiO_2 was prepared by combining sol-gel method with hydrothermal treatment. 6 mL tetrabutyl titanate was dissolved into absolute ethanol (solution A), solution B consisted of absolute ethanol, nitric acid, water and $Fe(NO_3)_3$ in the required stoichiometry. Then solution A was added drop-wise to solution B under electromagnetic stirring. The resultant mixture was stirred at room temperature for about 2 h for hydrolysis until the transparent sol was obtained. The sol was then aged for 2 days until the formation of gel, which was then transferred into a 100 mL Teflon-inner-liner stainless steel autoclave. The autoclave was kept for 10 h under 180 °C for crystallization. After this hydrothermal treatment, the precipitate grains were washed, dried and ground to obtain Fe^{3+} doped TiO_2 nanoparticles. Pure TiO_2 was also prepared in this way without the addition of $Fe(NO_3)_3$. In our work, 0.57 atom % Fe^{3+} doped TiO_2, referred to as 0.57Fe–TiO_2, shows the highest activity under visible light illumination. Secondly, in order to enhance the photocatalytic activity of TiO_2 to the maximum limit, we deposited Au onto 0.57Fe–TiO_2 using the deposition–precipitation method, described by Catherine Louis [14]. The content of Au deposited on 0.57Fe–TiO_2 is

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0.0, 1.0, 1.5, 2.0, 3.0 and 4.0 wt%, designated as 0.57Fe–TiO_2, 1.0Au/0.57Fe–TiO_2, 1.5Au/0.57Fe–TiO_2, 2.0Au/0.57Fe–TiO_2, 3.0Au/0.57Fe–TiO_2, 4.0Au/0.57Fe–TiO_2, respectively. Pure TiO_2 deposited with 2.0, 3.0 wt% Au are designated as 3.0Au/TiO_2, 4.0Au/TiO_2, respectively. All chemicals are of analytical grade and used without further purification.

2.2. *Characterization of photocatalysts*

XRD analysis of the prepared photocatalysts was carried out at room temperature with a Rigaku D/max 2550 VB/PC apparatus using Cu $K\alpha_1$ radiation (λ = 1.5406 Å) and a graphite monchromator, operated at 40 kV and 30 mA. The X-band EPR spectra were recorded at room temperature (Varian E-112). To analyze the light absorption of the photocatalysts, UV–vis diffuse reflectance spectra (DRS) were obtained using a scan UV–vis spectrophotometer (Varian Cary 500) equipped with an integrating sphere assembly, while $BaSO_4$ was used as a reference.

2.3. *Measurements of photocatalytic activities*

The photocatalytic acticity of each sample was evaluated in terms of the degradation of methyl orange (MO). MO was selected as a model pollutant because it is a common contaminant in industrial wastewater and good resistance to light degradation. Photocatalyst (0.6 g) was added into an 80 mL quartz photoreactor containing 60 mL of a 20 mg L^{-1} MO solution. The mixture was sonicated for 10 min and stirred for 30 min in the dark in order to reach the adsorption–desorption equilibrium. A 1000 W tungsten halogen lamp equipped with a UV cut-off filters (λ > 420 nm) was used as a visible light source and a 300 W high-pressure Hg lamp for which the strongest emission wavelength is 365 nm was used as a UV light source. The lamp was cooled with flowing water in a quartz cylindrical jacket around the lamp, and ambient temperature is maintained during the photocatalytic reaction. At the given time intervals, the analytical samples were taken from the mixture and immediately centrifuged, then filtered through a 0.22 μm Millipore filter to remove the particles. The concentration of the filtrate was analyzed by checking the absorbance at 464 nm with a UV–vis spectrophotometer (Varian Cary 100).

3. Result and discussion

3.1. *Catalysts characterization*

The XRD patterns of the samples are shown in figure 1. Within the detection limits of this technique, all samples consist of anatase as the unique phase. No characteristic peak of iron oxide can be observed implying iron ions are incorporated into the crystalline of TiO_2 [15]. Sample c, d, e, f show reflections at 38.2, 44.4, and 64.6° 2θ values which are characteristic of Au^0, demonstrating the deposited Au mainly exists as Au^0 on the surface of the samples [16]. The intensities of the diffraction lines attributed to Au increase with the content of Au. Crystalline sizes corresponding to TiO_2 are estimated using the Scherrer equation to be 10–11 nm, and the intensities of the peaks assigned to anatase are almost the same among all the samples. So it can be concluded that doped Fe^{3+} as well as deposited Au exert no significant influence on the crystalline phase, crystalline size, and crystallinity of TiO_2.

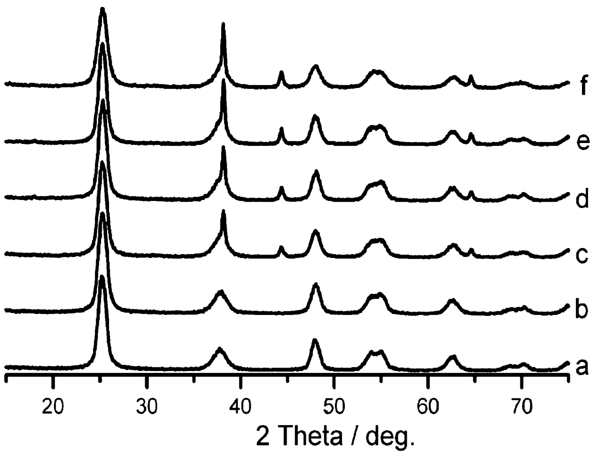


Figure 1. XRD patterns of different samples: (a) TiO_2, (b) 0.57Fe–TiO_2, (c) 2.0Au/0.57Fe–TiO_2, (d) 2.0Au/TiO_2, (e) 3.0Au/0.57Fe–TiO_2, (f) 3.0Au/TiO_2.

The EPR spectra of 0.57Fe–TiO_2 and 2.0Au/0.57Fe–TiO_2 are shown in figure 2. The two samples both show intense signal at g = 1.99 and very weak signal at g = 4.22. These two signals can be attributed to Fe^{3+} substituted for Ti^{4+} in the TiO_2 lattice (g = 1.99) and to Fe^{3+} substituted in the lattice adjacent to a charge-compensating oxide anion vacancy (g = 4.22), similar to those described by other investigators [9,17]. The

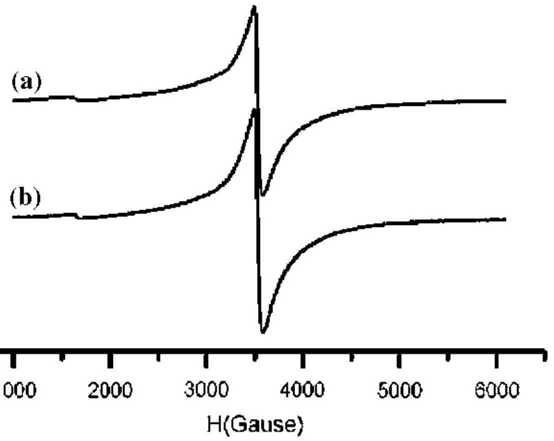


Figure 2. EPR spectra of different samples: (a) 0.57Fe–TiO_2, (b) 2.0Au/0.57Fe–TiO_2.

analysis of EPR results prove that iron ions are successfully incorporated into the anatase crystal lattice of 0.57Fe–TiO_2 and 2.0Au/0.57Fe–TiO_2.

The UV–vis DRS of samples are presented in figure 3. The spectrum of 0.57Fe–TiO_2 shows a significant enhancement of light absorption at a wavelength of 400–600 nm compared with pure TiO_2. The origin of this visible light absorption is due to the formation of a dopant energy level within the band gap of TiO_2. The electron-transition from the dopant energy level to the conduction band effectively red shifts the band edge absorption threshold [9]. 2.0Au/0.57Fe–TiO_2 and 2.0Au/TiO_2 show a strong absorption peak at 500–600 nm due to the plasmon resonance of Au. Since only the material on the surface of nanoparticles is responsible for the surface plasmon resonance, the absorption of 2.0Au/0.57Fe–TiO_2 and 2.0Au/TiO_2 centered at 537, 563 nm indicates Au has been successfully deposited on the surface of TiO_2 [12,18].

3.2. Evaluation of photocatalytic activity

Figure 4a shows the photodegradation rate of MO over several samples under visible light illumination (2.5 h). It can be found that the degradation rate of MO is increased gradually with an increase in the content of Au. 2.0 wt% is found to be the optimal content of Au to achieve the highest photocatalytic activity, and any higher content could result in lower photocatalytic activity. This may due to the fact that on one hand, Au deposited on 0.57Fe–TiO_2 plays a positive role in reducing electron-hole recombination; on the other hand, excess amount of Au loaded not only influences the penetration of light but also becomes the recombination center and results in low photoactivity [19]. The photodegradation rates of MO over these samples under UV light illumination (75 min) are shown in figure 4b. Up until now, it has been pointed out by many groups that inclusion of metal ions descreases photocatalytic activity of TiO_2 under UV light illumination despite enhanced light absorption in the visible region [13,20]. However, it can be seen from figure 4b these highly visible light active

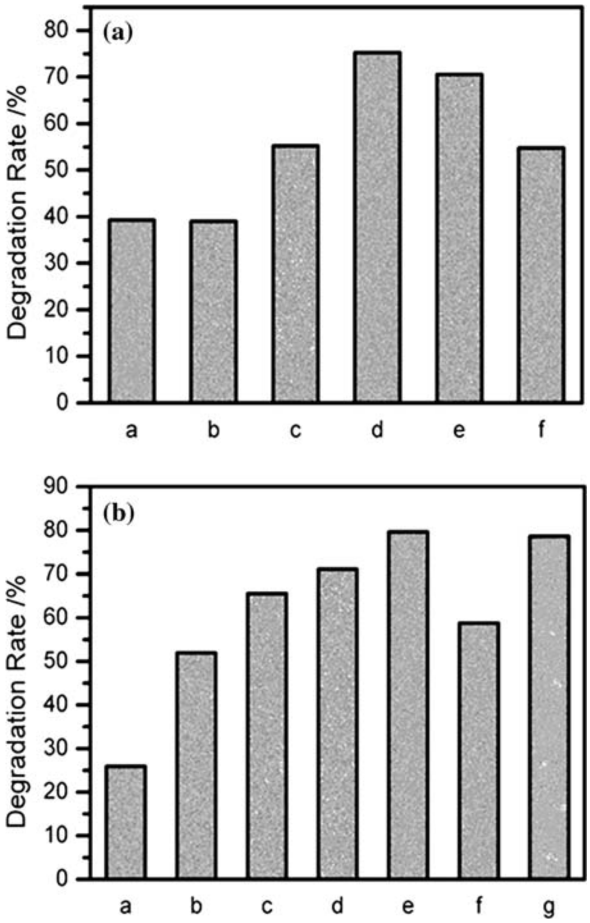


Figure 4. Photocatalytic degradation rate of MO under (a) visible light (λ > 420 nm) and (b) UV light illumination over (a) 0.57Fe–TiO_2, (b) 1.0Au/0.57Fe–TiO_2, (c) 1.5Au/0.57Fe–TiO_2, (d) 2.0Au/0.57Fe–TiO_2, (e) 3.0Au/0.57Fe–TiO_2, (f) 4.0Au/0.57Fe–TiO_2, (g) P25.

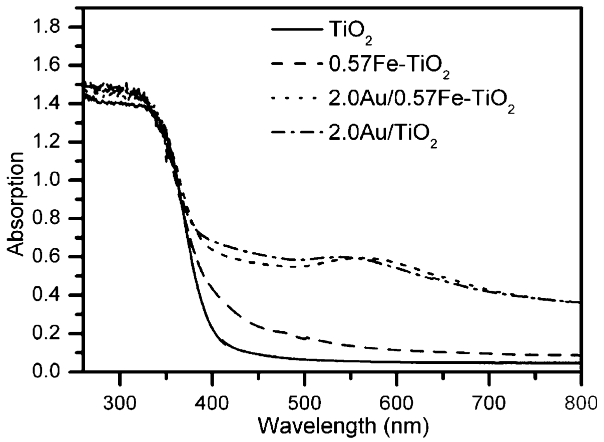


Figure 3. UV–vis diffuse reflectance spectra of various samples.

samples also exhibit excellent UV light activities. Different from visible light illumination, the optimal content of Au is 3.0% for the degradation of MO under UV light illumination, in which case the photocatalytic activity is even a little higher than that of P25, a well-known commercial photocatalyst of high photoactivity.

To test and verify the respective role played by Fe^{3+} and Au as well as their synergistic effects on photocatalytic activity of TiO_2, several typical samples are chosen for further analysis. The photocatalytic degradation data of the selected samples are converted to a linear pattern using the first-order kinetics model and the results are shown in figure 5. The observed rate constants are also calculated and listed in table 1. The comparison of visible light activities of the four samples show activity in following order: 2.0Au/0.57Fe–TiO_2 > 2.0Au/TiO_2 > 0.57 Fe–TiO_2 > TiO_2. The observed rate constant of 0.57Fe–TiO_2 is nearly two times higher than that of pure TiO_2, which may due to the enhanced absorption in the visible region of the former. The rate constant of pure TiO_2 is observed to be just one half of 2.0Au/TiO_2, explanations are that Au deposited on 2.0Au/TiO_2 can capture electrons and efficiently inhibit the electron-hole recombination. It is very clear the rate constant of 2.0Au/0.57Fe–TiO_2 is fairly higher than that of the remaining samples, this may be owing to the synergistic effects of doped Fe^{3+} and deposited Au on the enhancement of visible light photocatalytic activity which will be illustrated in details later. Figure 5b shows the photocatalytic activities of the selected samples under UV light illumination. The photocatalytic activity of them which is different from visible light illumination decreases in the following sequence: 2.0Au/0.57Fe–TiO_2 > 2.0Au/TiO_2 > TiO_2 > 0.57Fe–TiO_2. The rate constant of 0.57Fe–TiO_2 is lower than that of TiO_2, which is in agreement with other groups [13]. This may attribute to the detrimental effect of Fe^{3+} under UV light illumination: without Au, electrons in 0.57Fe–TiO_2 cannot be efficiently transferred to the surface but deeply trapped by Fe^{3+}, and then recombine with holes, thus Fe^{3+} acts as recombination centers instead of suppressing electron-hole recombination. The rate constant of 3.0Au/TiO_2 is higher than that of TiO_2 owing to the same positive role plays by Au as under visible light illumination. Compared with the other three samples, 3.0Au/0.57Fe–TiO_2 exhibits a very obvious increase in the photocatalytic activity, confirming the synergistic effects of doped Fe^{3+} and deposited Au on UV light photocatalytic activity.

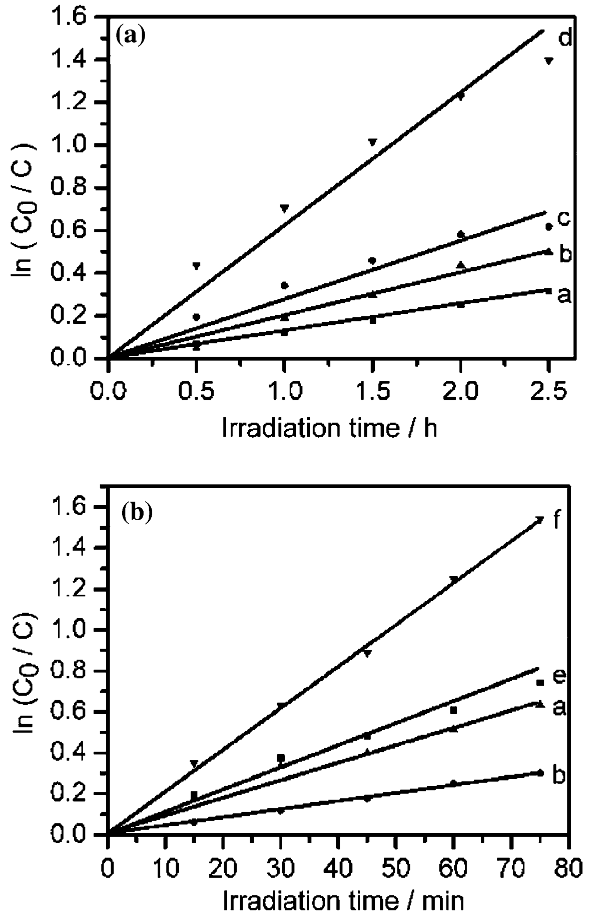


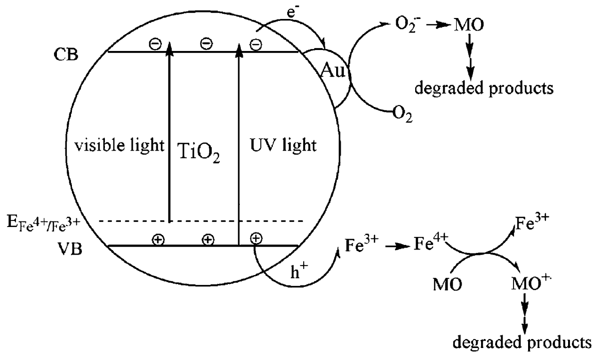
Figure 5. Fit of (a) visible light ($\lambda > 420$ nm) and (b) UV light photodegradation data to a first-order kinetic model: (a) TiO_2, (b) 0.57Fe–TiO_2, (c) 2.0Au/TiO_2, (d) 2.0Au/0.57Fe–TiO_2, (e) 3.0Au/TiO_2, (f) 3.0Au/0.57Fe–TiO_2.

3.3. Synergistic effects of Fe^{3+} and Au

On the basis of the comparison in the photocatalytic activities of the selected samples above, the mechanism for the synergistic effects of Fe^{3+} and Au on the photocatalytic activity of TiO_2 is proposed in scheme 1. It has been confirmed by EPR that Fe^{3+} presents in the substitutional position in the TiO_2 lattice, which can

Table 1
The first-order kinetic constant of MO photodegradation using various photocatalysts

Photocatalysts (visible light)	Kinetics constants, (h^{-1})	Correlation coefficient, R^2	Photocatalysts (UV light)	Kinetics constants, (h^{-1})	Correlation coefficient, R^2
TiO_2	0.1255	0.9992	TiO_2	0.4848	0.9911
0.57Fe–TiO_2	0.2151	0.9929	0.57Fe–TiO_2	0.2418	0.9993
2.0Au/TiO_2	0.2499	0.9823	2.0Au/TiO_2	0.5772	0.9939
2.0Au/0.57Fe–TiO_2	0.5529	0.9884	2.0Au/0.57Fe–TiO_2	1.2174	0.9991



Scheme 1. Proposed mechanism for the synergistic effects of Fe^{3+} and Au.

introduce a dopant energy level into the band gap of TiO_2, so the light absorption of TiO_2 can be extended into the visible region [20,21]. Under visible light illumination, the electrons can be excited from the dopant level to the conduction band [6], and then they are transferred to Au^0 deposited on the surface of TiO_2, which can enhance the electron-hole separation and the subsequent transfer of the trapped electrons to the adsorbed O_2 molecules [12], consequently increase the efficiency of the photocatalytic reactions. Under UV light illumination, a large number of excited electrons can be rapidly trapped by Au, meanwhile the remaining holes are shallowly trapped by Fe^{3+} and then transferred to the surface to initiate the photocatalytic processes [19]. During this procedure, elctron-hole recombination is largely suppressed leading to high photocatalytic activities. In brief, Au and Fe^{3+} also have synergistic effects on both visible light and UV light photocatalytic activity.

4. Conclusion

Fe^{3+} doped together with Au deposited TiO_2 (Au/Fe^{3+}–TiO_2) has been successfully obtained. The series of Au/Fe^{3+}–TiO_2 show excellent photocatalytic activity both under visible and UV light illumination. The synergistic effects of Fe^{3+} and Au are presumed to be responsible for the high photocatalytic activity of TiO_2.

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