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Photocatalytic Performance of Fe_2O_3 Modified TiO_2 Catalyst Towards the Degradation of Rhodamine 6G

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Fe_2O_3-TiO_2 coatings were prepared on glass slide substrates using sol-gel method. The phase structure, thermal microstructure and surface properties of the coatings were respectively characterized by using X-ray diffractometry, scanning electron microscopy (SEM) and UV-Vis diffuse reflectance spectroscopy. The Fe_2O_3-TiO_2 photocatalyst shows obvious red-shift compared with pure TiO_2 by DRS, absorbance in the visible range of the Fe_2O_3-TiO_2 samples increases with the increase of the amount of Fe_2O_3 loaded. The photocatalytic activity had been validated by the photocatalytic degradation of rhodamine 6G. The result showed that 15 wt % Fe_2O_3 modified TiO_2 film is the optimal photocatalyst to degradation. The removal rate of TOC indicated that a lower pH value was beneficial to the mineralization of rhodamine 6G.

Key Words: Titanium dioxide, Photodegradation, Semiconductor, Rhodamine 6G.

INTRODUCTION

TiO_2 has proved to be one of the most promising materials for various applications such as solar energy conversion, fuel cells, paints and photocatalysts, especially in environmental remediation processes. TiO_2 as photocatalyst has come to be the research focus owing to its high efficiency, photochemical ability and non-toxic nature[1]. It has been found to be very effective for photocatalytic degradation of toxic and recalcitrant pollutants such as detergents, dyes, pesticides, herbicides and other pollutants[2].

However, this technique cannot successfully satisfy the practical water treatment due to the rapid recombination of the photoexcited carriers and the limited efficiency in visible light. One critical drawback of TiO_2 is that its band gap is too large to allow efficient absorption of most sunlight. Accordingly, significant efforts have been made to modify and enhance it. As is reported in the literatures, transition metals doping (*e.g.*, Fe, Co)[3,4], non-metallic elements doping (*e.g.*, N, C, S)[5,6] and rare earth ions doping[7,8] (*e.g.*, La, Ce, Nd) have led to noticeable improvement of

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the photocatalytic activity of TiO_2 in the visible region. An efficient way to extend the absorbance of TiO_2 to visible light, to use maximum of sunlight, is the composite of nano-semiconductors[9,10], such as Fe_2O_3/TiO_2, SnO_2/TiO_2, which has been the subject of many researches. Doong *et al.*[11], coupled CdS with TiO_2 for 2-chlorophenol degradation under UV irradiation. In their study, both CdS and TiO_2 could be excited. The combination of the 2 semiconductors showed better photocatalytic activity due to better charge separation. Keller and Garin[12] observed that photocatalytic oxidation of methylethyl ketone (MEK) was increased by coupling TiO_2 with WO_3 and SiC.

Fe_2O_3 has a flat band potential of 0.32 V *versus* NHE (pH 0) and a band gap of 2.2 eV, so it can be considered to be a semiconductor for TiO_2. When the composite film was irradiated with visible light, the electrons in the valence band of Fe_2O_3 layer were excited to the conduction band, leaving holes in the valence band. As a consequence, electrons in the valence bands of TiO_2 were injected into Fe_2O_3 layer (while photogenerated holes moved into the valence band of TiO_2 in an opposite direction) driven by the built-in field in Fe_2O_3-TiO_2 heterojunction.

In this paper, TiO_2 photocatalysts with different loadings of Fe_2O_3 were prepared by Sol-gel method; their phase compositions, crystalline structures and particle sizes were studied. We have focused on the physico-chemical characteristics of different binary oxide catalysts. Their catalytic reactivity was explored by photodegradation performance in treating rhodamine 6G solution. Rh-6G, known as laser dyes, is commonly found in wastewater from industries dyestuffs dealing in paper and pharmaceuticals.

EXPERIMENTAL

Titanium tetra isopropoxide (TTIP) used as TiO_2 precursor and $Fe(CO)_5$ used as Fe_2O_3 precursor were purchased from Chong Qing Chemical Reagents Company, China. All solutions in this experiment were prepared using deionized water (Milipore Alpha Q system, 18.2MO). Other materials used in the test were of analytical grade.

Preparation of nanosize Fe_2O_3-TiO_2 binary oxide photocatalyst: TiO_2 and Fe_2O_3 photocatalysts were synthesized by a sol-gel method in which TTIP and $Fe(CO)_5$ isopropoxide complex were used as precursors for TiO_2 and Fe_2O_3, which was also reported in previous work[13]. The TiO_2 sol was obtained by the following: 20 mL of TTIP and 0.03 g sodium laurylsulfonate [$CH_3(CH_2)_{10}CH_2SO_3Na$] were dissolved in 50 mL of ethyl alcohol forming the solution of precursor. The mixture of 20 mL of ethyl alcohol, 2 mL of acetic acid, a certain amount of NH_4Br, a certain amount of $Fe(CO)_5$ and 6 mL of deionized water were mixed drop-wise into the precursor solution under magnetic stirring at room temperature. The mixture was hydrolyzed at room temperature for 0.5 h under vigorous stirring and the transparent sol was obtained. Glass substrates were dipped into the sol, withdrawn at 5.0 cm/min and dried at air. Then as-coated substrates were preheated at 400 °C for 10 min. The cycle above was repeated three times until the desired thickness was achieved.

Finally, the preheated substrates were heated from 400 to 550 °C at a 5 °C/min and held at 550 °C for 2 h to obtain dense and transparent Fe_2O_3 seed layer on TiO_2/glass catalysts film.

Characterization: The crystalline structure and morphology of the TiO_2 particles was investigated by X-ray diffraction (Bruker D8 Advance X-diffractometer). The UV-Vis reflectance of the catalysts was measured by diffuse reflectance spectroscopy using a Shimadzu UV-3600 instrument. The morphology and size distribution of the photocatalysts were recorded by transmission electron microscopy (Jeol, JEM 2100, Japan). In order to determine the reduction of the dissolved organic carbon, the mineralization of Rh-6G (TOC) was measured by a TOC analyzer (Shimadzu, TOC-V CPH).

Photocatalytic activity measurements: The photocatalytic activity of the samples was evaluated by photodegradation of rhodamine 6G. An annular photocatalytic reactor (PCR) under recycle mode was used to study the degradation of rhodamine 6G. The system consisted of the PCR, a 1 L open reservoir equipped with a stirrer to ensure complete mixing and a peristaltic pump to force the solution from the reservoir to the reactor. The PCR was made of quartz rings to form a reactor height of 25 cm. Each quartz ring had an inner diameter of 30 mm, an outer diameter of 50 mm and a height of 10 mm. Water was divided among the rings and forced to follow a fixed route inside each ring before leaving the reactor, resulting in increased irradiation time. A 250-W metal halide lamp was used as an external source of visible light, housed vertically in the inner reactor center. All experiments were performed at room temperature.

RESULTS AND DISCUSSION

Characterization of Fe_2O_3 modified TiO_2 photocatalysts: Fig. 1 shows the morphologies of 15 wt % Fe_2O_3 modified TiO_2 photocatalysts flim sintered at 550 ºC with magnification of 5000 times, respectively. The magnified images show that 15 wt % Fe_2O_3 modified TiO_2 photocatalysts is much different from pure TiO_2 photocatalysts in that it is more compact and more uniform. In the images with magnification of 5000 times, the mean size of pure TiO_2 crystals is larger than that of the Fe_2O_3/TiO_2 photocatalysts. TiO_2 particles are tightly attached on crystals and cannot be eliminated by rinsing easily. the TiO_2 particles present narrow grain size distribution with a diameter of less than 40 nm, which is consistent with the XRD analysis.

The XRD patterns of all the catalysts are shown in Fig. 2. Peaks appear at 2θ: 25.36, 37.98, 47.94, 55.3, 63.51 and correspond to the diffraction patterns of (101), (112), (200), (211) and (204) planes of anatase. It could be seen that addition of Fe_2O_3 did not reflect on phase transformations from anatase to rutile phase as well as inhibit the formation of well crystalline particles. TiO_2 exists as micro-crystals in an anatase phase in the binary oxide catalysts. But in Fe_2O_3/TiO_2 film photocatalysts,

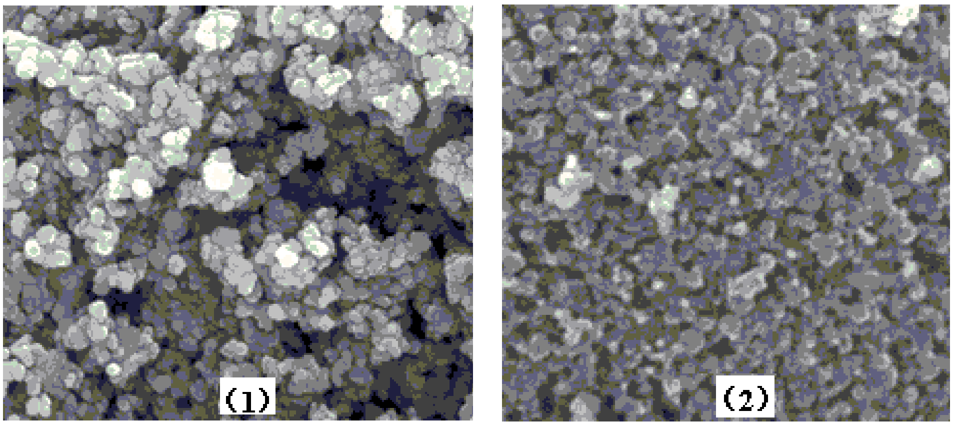

Fig. 1. SEM images of pure TiO_2 film(1) and Fe_2O_3/TiO_2 (2) were magnified 5000 times

some additional peaks were found as well as TiO_2 anatase phase, in spite of the very weak peaks. It is concluded that the peaks were attributed to Fe_2O_3 and $Fe_2Ti_3O_9$. Fe_2O_3 existed in the α-Fe_2O_3 phase, which was directly decomposed from $Fe(CO)_5$. The formation of $Fe_2Ti_3O_9$ phase could be explained by the fact that at high temperature, certain percentage of the Fe^{3+} ions present at the surface of TiO_2, diffused into the bulk TiO_2 producing a substitutional solid solution in which Fe^{3+} is dispersed in the lattice of TiO_2. In fact, as the Fe^{3+} radius is similar to that of Ti^{4+}, the substitution of iron in the matrix of TiO_2 is a favourable process. The major fraction of Fe_2O_3 formed small aggregates of Fe_2O_3 at the surface of the solid solution particles.

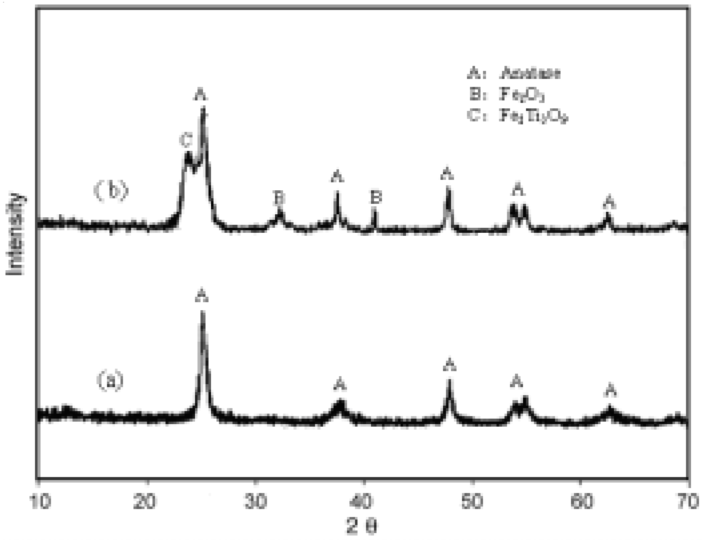

Fig. 2. X-ray diffraction patterns of (a) TiO_2 and (b) 15 % wt, Fe_2O_3/TiO_2 (2)

Diffuse reflectance spectroscopy of Fe_2O_3 modified TiO_2 photocatalysts: Fig. 3 shows the reflectance spectra of pure TiO_2 and different amounts of Fe_2O_3 modified TiO_2 binary oxide catalysts measured by diffuse reflectance spectroscopy. As was expected, pure TiO_2 almost had no absorption above its fundamental absorption sharp edge rising at 400 nm. In contrast, the Fe_2O_3-TiO_2 samples showed a strong absorption in the visible range. The enhanced absorption of TiO_2 in the visible range was obviously attributed to the photosensitization of Fe_2O_3. Moreover, absorbance in the visible range of the Fe_2O_3-TiO_2 samples increases with the increase of the amount of Fe_2O_3 loaded. Obviously, such a red shift might be beneficial for the improvement of the photocatalytic performance of the Fe_2O_3/TiO_2 composite materials. The red shift in the TiO_2 photocatalysts with the Fe_2O_3 loading can be attributed to the size quantization effect due to the formation change of microcrystals of binary oxide and decrase of the band gap, calculated from the formulation of the maximum excited wavelength and band gap: $\lambda = 1240/E_g$

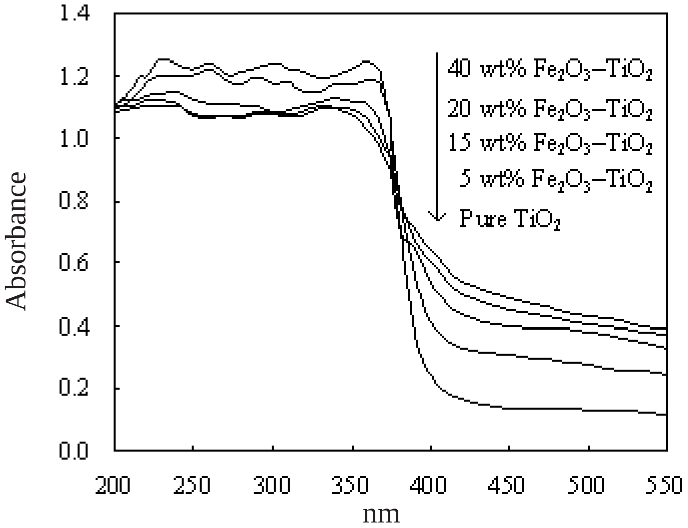

Fig. 3. Diffused reflectance spectra of (a) TiO_2 and (b) Fe_2O_3/TiO_2 (2)

Photocatalytic degradation of rhodamine-6G (Rh-6G): The photocatalytic degradation perfor-mance for these catalysts were tested for the oxidative degradation of Rh-6G and the initial pH values was 3.0. The results are shown in Fig 4. As was expected, the Fe_2O_3-TiO_2 samples showed a higher photodegradation efficiencies of Rh-6G than pure TiO_2. A 65.8 % degradation of Rh-6G was achieved with the pure TiO_2 catalysts for 2 h. The degradation ability for the binary oxide catalysts (Fe_2O_3-TiO_2) increased with an increase in the amount of Fe_2O_3 loadings to TiO_2. The 15 wt % Fe_2O_3 showed the higher percentage of Rh-6G degradation (86.7 %). However, after that weight percentage, there was no noticeable change in the reactivity and the value remained the same with further loadings of Fe_2O_3. In fact, the degradation rate of 40 wt % Fe_2O_3 to TiO_2 was 88.9 %, which was found to be slightly higher than the TiO_2 photocatalyst modified by 15 % wt Fe_2O_3. Therefore, it can be concluded that the 15 wt % Fe_2O_3 coupled with TiO_2 could significantly enhance the photocatalytic activity of Rh-6G.

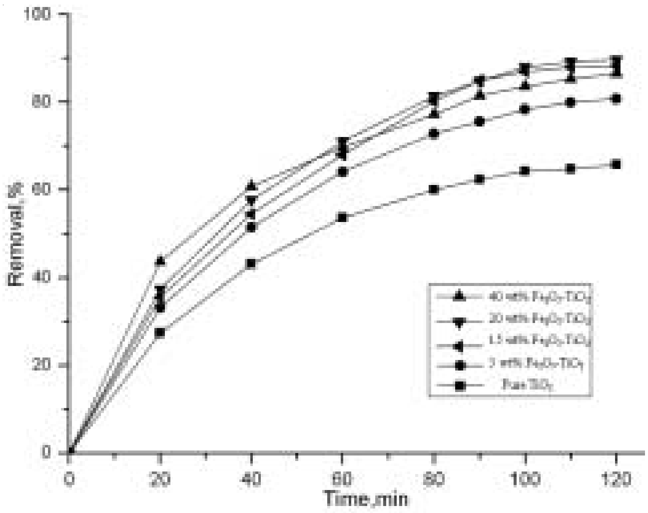

Fig. 4. Effect of Fe_2O_3 amount used in co-deposition solution on photocatalytic degradation performance

The Fe_2O_3 semiconductor has a band gap of 2.2 eV and can utilize visible light with wavelength < 563 nm for photocatalytic reactions. The UV 1ight excites the electron transition from the valence band to the conduction band of Fe_2O_3.The excited electrons then migrate to the condition band of TiO_2, leaving holes in the valence band of Fe_2O_3. By separating the carries. The recombination probability of the electrons and the holes was reduced and the absorbed spectra was extended. The schematic illustration is shown in Fig. 5. These separated electrons and holes can then initiate redox reactions with molecular species adsorbed on the surfaces of the composite catalysts. Thus, response to the wavelength was extended into the visible region and the quantum yield was increased.

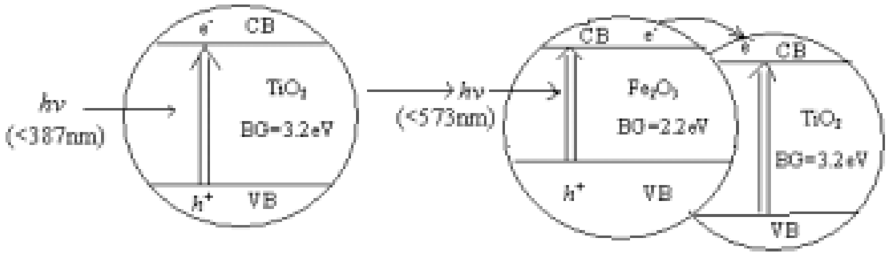

Fig. 5. Schematic illustration of the degradation reaction by the Fe_2O_3/TiO_2 photocatalyst

On the other hand, oxygen vacancies in the TiO_2 crystal lattice were formed by doping with high-valence cations and this could also reduce the recombination probability of the carries. The XRD pattern of the TiO_2-Fe_2O_3 powder suggested that Fe_2O_3 with low loading existed among isolated species The isolated Fe_2O_3 species were bridged to TiO_2 through V-O-Ti bonds, activity sites for photocatalysis.

Effect of initial pH values: In order to observe the influence of initial pH values on the degradation efficiency, we have tested the concentration and TOC removal of photocatalytic degradation in different ranges. The influence of pH in the range of 2-12 on the degradation efficiency of rhodamine-6G is presented in Fig. 6. It showed that both the highest and the lowest pH condition favoured the photocatalytic degradation of rhodamine-6G, especially under acidic condition. However, it was noteworthy that the higher the pH value was, the lower the TOC removal percentage was. It suggested a decrease in the mineralization capacity of the whole solution sample of the catalysts. This indicated that a lower pH value was beneficial to the mineralization of rhodamine-6G.

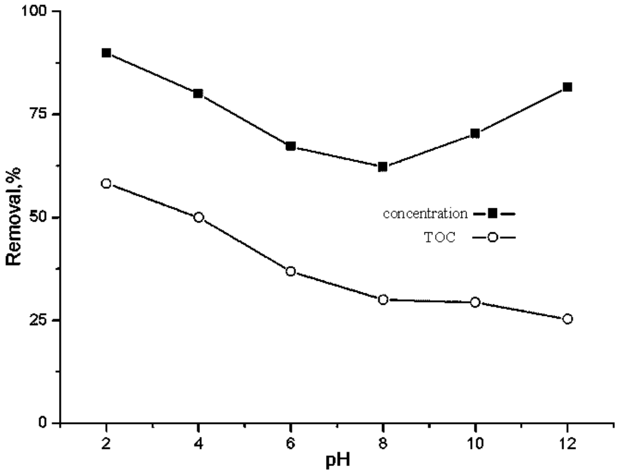

Fig. 6. Effect of the initial pH values on the catalytic performance of Fe_2O_3-TiO_2

Conclusion

This study illustrates the modifications in the physical and photocatalytic properties of doped-titania prepared by sol-gel method. The result shows that a mixed oxide of Fe_2O_3/TiO_2 particles is a more efficient photocatalyst for the photocatalytic degradation of rhodamine-6G than TiO_2 alone in aqueous solution. (1) The SEM and XRD spectroscopies have shown that the TiO_2 particles present narrow grain size distribution with a diameter of less than 40 nm. TiO_2 exists as micro-crystals in an anatase phase in the binary oxide catalysts. (2) The diffuse reflectance spectra of the Fe_2O_3/TiO_2 photocatalyst shows obvious red-shift compared with pure TO_2, which might be beneficial for the improvement of the photocatalytic performance of the Fe_2O_3/TiO_2 composite materials. (3) In this paper, the photocatalytic activity is validated by the photocatalytic degradation of rhodamine-6G and 15 wt % Fe_2O_3 modified TiO_2 film is the optimal photocatalyst. (4) A lower pH value was beneficial to the mineralization of rhodamine-6G.

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