Preparation and photocatalytic properties of a novel kind of loaded photocatalyst of $TiO_2/SiO_2/\gamma\text{-}Fe_2O_3$

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A novel kind of loaded photocatalyst of $TiO_2/SiO_2/\gamma\text{-}Fe_2O_3$ (TSF) that can photodegrade effectively organic pollutants in the dispersion system and can be recycled easily by a magnetic field is reported in this paper. The $\gamma\text{-}Fe_2O_3$ cores in $TiO_2/\gamma\text{-}Fe_2O_3$ are found to reduce the activity of the TiO_2 photocatalyst in the photodegradation of dyes under either UV or visible light irradiation. Addition of a SiO_2 membrane between the $\gamma\text{-}Fe_2O_3$ core and the TiO_2 shell weakens efficiently the influence of the $\gamma\text{-}Fe_2O_3$ cores on the TiO_2 photocatalytic activity and leads to a highly active and magnetically separable photocatalyst on TSF. Comparison of the photodegradation processes of dyes under UV and visible irradiation is also carried out.

Keywords: loaded photocatalyst, magnetically separable photocatalyst, TiO_2

Irradiated TiO_2 shows an enormous potential for the destruction of organic pollutants under either UV [1–4] or visible light [5–8] irradiation. Many studies have been carried out on the application and modification of this semiconductor. TiO_2-coated hollow glass beads [9], TiO_2/TCO membranes [10,11], and fiberglass loaded with titania [12] have been prepared and used in fixed beds. However, the activity of the photocatalyst in the fixed-bed system is significantly reduced due to the immobility of titania.

In the present paper, a novel kind of loaded photocatalyst $TiO_2/SiO_2/\gamma\text{-}Fe_2O_3$ (TSF), which can photodegrade effectively organic pollutants in the dispersion system and can be recycled easily by a magnetic field, is reported. The photocatalyst is made up of a $\gamma\text{-}Fe_2O_3$ core, a SiO_2 membrane, and a TiO_2 shell. In this photocatalyst, the TiO_2 shell is the photocatalyst, the $\gamma\text{-}Fe_2O_3$ core is for separation by the magnetic field and the SiO_2 membrane between titania shell and $\gamma\text{-}Fe_2O_3$ core is used to weaken the bad influence of the $\gamma\text{-}Fe_2O_3$ core on the photocatalysis of the TiO_2 shell. The photodegradation of dyes on TSF under UV irradiation is also examined compared with that under visible irradiation.

$\gamma\text{-}Fe_2O_3$ (F, particle size ~200 nm) was supplied by Tianjin Ferric Oxide Pigment Factory of China. Titania was obtain from Degussa Co. (P25, ca. 80% anatase, 20% rutile, particle size ~35 nm). Titania-coated $\gamma\text{-}Fe_2O_3$ (TF) was prepared by the following method: $\gamma\text{-}Fe_2O_3$ was mixed with titania at a mass ratio of 1 : 1, abraded, then after addition of a small quantity of water sonificated, and at last, dried and annealed at 500 °C for 30 min. Silica-coated $\gamma\text{-}Fe_2O_3$ core with a titania shell (TSF) was prepared by the same way as TF prepared, except that $\gamma\text{-}Fe_2O_3$ was replaced by silica-coated $\gamma\text{-}Fe_2O_3$. The silica membrane around the $\gamma\text{-}Fe_2O_3$ core was prepared by stirring $\gamma\text{-}Fe_2O_3$ cores in a sodium silicate solution (Fenghuangshan Chemical Plant of China) at a fitting pH value for 48 h under sonification, the pH value of the solution was controlled by adding ion exchange resin (732 type, particle size ~1 mm, Shanghai Chemical Reagent Stock-Supply Station) to the stirred solution, the $SiO_2/\gamma\text{-}Fe_2O_3$ powder formed was washed with water, then dried and finally annealed at 450 °C for 30 min. The photocatalyzed degradation of a dye Fluorescein under UV and visible light irradiation was done to examine the activity of the photocatalyst. The photodegradation of Fluorescein under UV irradiation with a Hg lamp ($\lambda > 330$ nm, Toshiba SHLS-1002A, 100 W) is presented in figure 1. As a control experiment, a mixture catalyst (T + F, equal mass

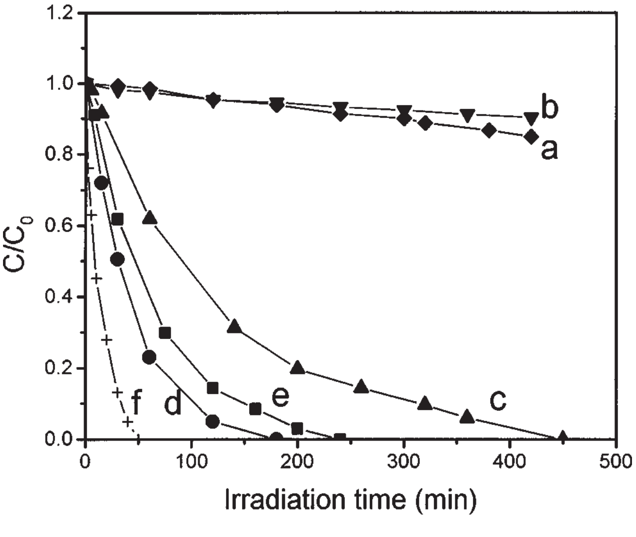

Figure 1. Degradation of Fluorescein (0.39 mmol dm^{-3}) with different photocatalysts under UV irradiation: (a) blank, (b) F (1 g dm^{-3}), (c) TF (2 g dm^{-3}), (d) TSF (2 g dm^{-3}), (f) P25 (1 g dm^{-3}), (e) T+F (2 g dm^{-1}).

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mixture of γ-Fe_2O_3 and TiO_2) was also used in our experiments. Curve (a) shows that γ-Fe_2O_3 has no photocatalytic activity under UV irradiation. Among the curves (b)–(e) the same amount of titania was used, but great differences in the degradation of the Fluorescein were observed. Comparing with P25, the photocatalytic activity of TF is markedly depressed. The apparent first-order photodegradation rate constant of P25 is 4.9×10^{-2} min^{-1} while that of TF is 7.4×10^{-3} min^{-1}. The photodegradation rate by the mixture catalyst T + F is a litle lower than that of P25, the apparent first-order photodegradation rate constant is 1.1×10^{-2} min^{-1}. On the other hand, addition of a SiO_2 membrane between the γ-Fe_2O_3 core and the titania shell can effectively increase the photocatalytic activity of the loaded photocatalyst. The apparent first-order photodegradation rate constant of TSF is 1.65×10^{-2} min^{-1}, markedly higher than that of TF and a little higher than that of T + F. TSF can be well separated by a magnetic field from the degraded solution and the recycled photocatalyst shows a mostly uncharged photocatalytic activity.

Photodegradation rates of Fluorescein under visible light irradiation are illustrated in figure 2. Visible irradiation experiments were carried out using a halogen lamp (Institute of Electric Light Source of Beijing, 500 W) as a visible light source and a light filter was used to cut completely light below 450 nm to guarantee irradiation with visible light. The photodegradation rates of these photocatalysts obey the following order: P25 > T + F > TSF > TF > F. The bad influence of the γ-Fe_2O_3 cores and the function of the silica partition under visible light irradiation are similar to those under UV irradiation.

In order to explain the above phenomena, especially to explain the difference in the photodegradation characteristics on TSF under UV and visible irradiation, a model of TSF is established (scheme 1).

Strong light absorption of the γ-Fe_2O_3 cores under either UV or visible irradiation is one of the important reasons for the lower photocatalytic activity of the loaded catalyst. Because of the strong absorption of the γ-Fe_2O_3 cores, the self-photosensitization of the dye was markedly weakened, and the discoloration of the dye under visible irradiation by F (curve (b)) was much slower than that in the blank reaction (curve (a)). Another important reason is related to the photocatalytic mechanism by UV and visible irradiation. Under visible illumination (note that the TiO_2 particles cannot be excited by visible light), the photodegradation of Fluorescein proceeds by two concurrent routes: (i) a route implicating $^1O_2$ [13], which was generated by energy transfer from excited dye to ground state oxygen; and (ii) a route involving electron transfer from an excited state of Fluorescein to photocatalyst particles [5,14,15]. The excited dyes inject electrons to the conduction band (CB) of the titania, then the injected electrons react with the preadsorbed oxygen to form oxidizing species ($O_2^{\bullet -}$, $\cdot$OOH, and then $\cdot$OH radicals) that can bring about the photooxidiation of dyes. After well-knitting of the titania nanoparticles with the γ-Fe_2O_3 cores (photocatalyst TF), a competitive process happens in which the generated CB electrons not only react with the oxygen but also inject into the conduction band of the γ-Fe_2O_3, because the CB energy of γ-Fe_2O_3 is lower than that of titania ($E_{CB}(TiO_2) = -0.5$ V vs. NHE at pH 7, $E_{CB}(\gamma\text{-}Fe_2O_3) = 0.1$ V vs. NHE at pH 7). Because of little activity of γ-Fe_2O_3, the photocatalytic activity of TiO_2/γ-Fe_2O_3 is depressed. Under UV illumination, titania absorbs photons with energy larger than the band gap of the titania to produce electron–hole couples. The produced CB electrons can also inject rapidly into the CB of the γ-Fe_2O_3 cores; and the produced valence band (VB) holes not only inject into the VB of the γ-Fe_2O_3 cores since the VB energy of the γ-Fe_2O_3 is higher than that of the titania ($E_{CB}(\text{titania}) = 2.7$ V vs. NHE at pH 7, $E_{CB}(\gamma\text{-}Fe_2O_3) = 2.3$ V vs. NHE at pH 7), but also cause photocatalytic reaction of the substrate. As a good electron–hole recombination center [16,17], γ-Fe_2O_3, which has little photocatalytic activity (as shown by curve (b) in figure 1), greatly depressed the photocatalytic activity of the loaded photocatalyst.

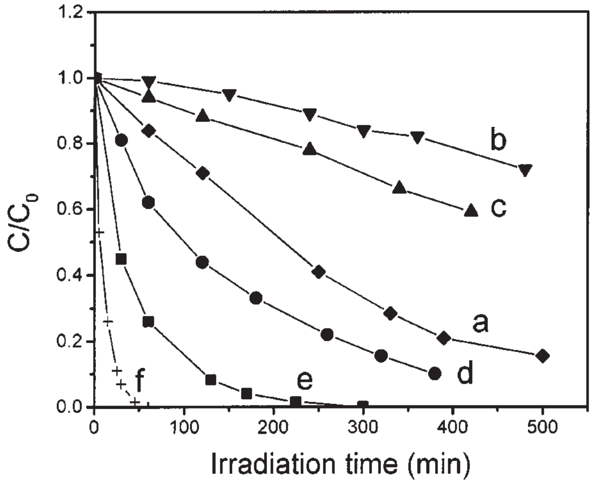
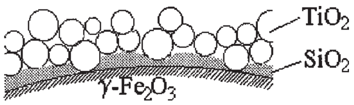


Figure 2. Degradation of Fluorescein (0.39 mmol dm^{-3}) with different photocatalysts under visible irradiation: (a) blank, (b) F (1 g dm^{-3}), (c) TF (2 g dm^{-3}), (d) TSF (2 g dm^{-3}), (f) P25 (1 g dm^{-3}), (e) T+F (2 g dm^{-1}).



Scheme 1.

Some initial processes for the photocatalytic reaction on TiO_2 have been established, and characteristic times for the various steps in the mechanism under UV and visible irradiation are given as follows:

Under UV irradiation [4,18,19]:

$$TiO_2 + h\nu \rightarrow h_{vb}^+ + e_{cb}^- \quad (fs) \tag{1}$$

$$e_{cb}^- + O_2 \rightarrow {>}Ti^{IV}OH + O_2^{\bullet -} \quad (ms) \tag{2}$$

$$h_{vb}^+ + {>}Ti^{IV}OH \leftrightarrow \{{>}Ti^{IV}OH^\bullet\}^+ \quad (10\ ns) \tag{3}$$

$$\{{>}Ti^{IV}OH^\bullet\}^+ + Red \rightarrow {>}Ti^{IV}OH + Red^{\bullet +} \quad (100\ ns) \tag{4}$$

Under visible irradiation [4,20–22]:

$$\mathrm{Dye} + h\nu \rightarrow \mathrm{Dye}^* \quad \text{(fs)} \tag{5}$$

$$\mathrm{Dye}^* + \mathrm{TiO_2} \rightarrow \mathrm{e}^-_{\mathrm{cb}} + \mathrm{Dye}^{\bullet +} \quad \text{(10 ps)} \tag{6}$$

$$\mathrm{e}^-_{\mathrm{cb}} + \mathrm{O_2} \rightarrow {>}\mathrm{Ti^{IV}OH} + \mathrm{O_2^{\bullet -}} \quad \text{(ms)} \tag{2}$$

The time of the e^-_{cb} and h^+_{vb} transit to the surface in a nanometer TiO_2 particle is about 1 ps [23,24], the characteristic time of the injection of the e^-_{cb} and h^+_{vb} from TiO_2 to γ-Fe_2O_3 is shorter than 10 ns [25,26].

For the photocatalyst TF, the mechanism hereinbefore leads to the following relationship:

(1) Under UV irradiation:

$$k_{ei} \gg k_{er}, \qquad k_{hi} \approx k_{hr}.$$

k_{ei} and k_{hi} are the rate constants of injecting processes of an electron and hole from TiO_2 to γ-Fe_2O_3, respectively; k_{er} and k_{hr} are the rate constant of the reacting process of an electron with preadsorbed oxygen and of a hole with OH^- and H_2O, etc.

Because of the injection of charge carriers and the great light absorption of the γ-Fe_2O_3 core, the rate of photodegradation under UV irradiation is depressed greatly.

(2) Under visible irradiation:

$$k_{ei} > k_{er}.$$

The CB electron in the TiO_2 particle formed by an electron transfer process from the excited dyes can inject to the CB of the γ-Fe_2O_3, which ceases the reaction of the CB electron with oxygen and slows down the photodegradation of dyes. The photocatalytic activity of TF under visible irradiation is strongly depressed due to the prominent advantage of k_{ei} in the competition over k_{er} and the great light absorption of the γ-Fe_2O_3 core. Because the reaction of an electron with oxygen is three orders of magnitude lower than the reaction of a hole with OH^- and H_2O, the bad influence of γ-Fe_2O_3 under visible irradiation is expected and found to be much more notable than that under UV light irradiation.

For the photocatalyst TSF, because of the obstruction of the SiO_2 membrane, the values of the k_{ei} and k_{hi} are greatly reduced, the competition between the injecting process and the reacting process of h^+_{vb} and e^-_{cb} is more favorable to the latter one. Compared with TF, TSF has a much higher photocatalytic activity under either UV or visible irradiation.

It is found that the photocatalytic activity of TSF was a little higher under UV irradiation and lower under visible irradiation than that of $T + F$. We think this relates to the different mechanism of generation and subsequent reaction of electron and the hole.

In summary, the loaded photocatalyst $TiO_2/SiO_2/\gamma$-Fe_2O_3 which can be separated easily from the dispersion system by a magnetic field has a high photocatalytic activity. The partition of SiO_2 effectively weakens the bad influence of the γ-Fe_2O_3 cores on the photocatalysis TiO_2 shell. Differences in photocatalytic mechanisms under UV and visible irradiation lead to the differences in photodegradation characteristics of dyes on TSF.

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