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Photocatalytic removal of Famotidine with TiO_2 from water in the presence of dye under visible light irradiation

Md. Ashraful Islam Molla[a,*], Ikki Tateishi[a], Mai Furukawa[a], Hideyuki Katsumata[a], Tohru Suzuki[b], Satoshi Kaneco[a,b]

[a] *Department of Chemistry for Materials, Graduate School of Engineering, Mie University, Japan, email: professoraislam@gmail.com (Md.A.I. Molla), 417d002@m.mie-u.ac.jp (I. Tateishi), maif@chem.mie-u.ac.jp (M. Furukawa), hidek@chem.mie-u.ac.jp (H. Katsumata)*
[b] *Mie Global Environment Center for Education and Research, Mie University, Japan, email: suzuki@chem.mie-u.ac.jp (T. Suzuki), kaneco@chem.mie-u.ac.jp (S. Kaneco)*

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ABSTRACT

Photocatalytic degradation of Famotidine (FMT) by dye-sensitized TiO_2 was investigated under visible light ($\lambda > 400$ nm). The photodegradation experiments were carried out at different time periods using dye-sensitized 20 mg of TiO_2 and 30 mL of initial concentration of FMT (2 and 5 mg/L) at room temperature and at natural pH value of the solution. Dye-sensitization of 5 mg/L orange II (OII), bromophenol blue (BPB), acid red 88 (AR88) and rhodamine B (RhB) for TiO_2 enhanced the photoactivity in FMT degradation. Investigation of the photocatalytic mechanism showed it that the TiO_2 dye-sensitized degradation of Famotidine under visible light irradiation was mainly attributed to the oxidization by $\cdot O_2^-$ and h^+ radicals, while the $\cdot OH$ radicals played only a relatively minor role in the oxidization process. The kinetics of FMT photodegradation were found to follow the pseudo-first order rate law, and could be described in terms of Langmuir–Hinshelwood model.

Keywords: Dyesensitization; Famotidine; Photocatalytic degradation; TiO_2; Visible light

1. Introduction

In recent years, the presence of pharmaceuticals in the environment has become a serious cause for concern, and the problem is continuing to grow with the on-going development of more potent and more metabolically resistant drugs [1]. Numerous studies have documented it that both metabolized and non-metabolized pharmaceutical residues are speculated to have adverse effects on human health and the safety of ecosystems [2–4].

Famotidine (FMT, Fig. 1) is chemically 3-[({2-[(diaminomethylidene)amino]-1,3-thiazol-4-yl}methyl)sulfanyl]-*N′*-sulfamoylpropanimidamide. It is a histamine H2-receptor antagonist used to treat peptic ulcers, gastroesophageal reflux and conditions, where the stomach produces an excess of acid [5,6]. FMT is also used for treatment of Alzheimer's [7] and Parkinson's diseases [8]. It has been documented that 65~70% of the parent compound is found unchanged in the urine, when patients used the FMT [9]. The fact indicates that the drug is one of the many compounds released into the environment on a day-to-day basis. FMT demonstrates excellent complicated properties, due to the presence of amine, thiazole and thioether groups in its structure [10]. It creates stable complexes with palladium, copper, cobalt and nickel. Previous research reports have proved the stability of FMT in the environment and water bodies [11]. Taking the above-mentioned issues into account, one can argue that FMT should be considered as persistent contaminants in an aqueous environment which are frequently found in wastewater at various detectable concentrations. The frequent presence of these pharmaceuticals in wastewater underscores the necessity of removal of them from water matrices before they are discharged into the environment.

Titanium dioxide (TiO_2) has drawn great attention since they are one group of the most promising photocatalysts in water splitting and the mineralization of toxic organic substances, owing its virtue of non-toxicity, highly chemical

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*Corresponding author.

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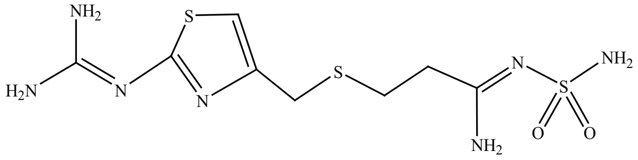

Fig. 1. Chemical structure of Famotidine.

stability and low cost [12,13]. However, TiO_2 can only be excited by the irradiation of UV light, which merely occupies about 4% of total solar energy [14]. This problem can be solved only by extending the light absorption capacity of those catalysts. Semiconductor photocatalysts can be modified to expand their photoresponse to the visible region for the degradation in several ways, including the doping with cations/anions or the coupling with another small band gap semiconductor. Most of these methods, however, are quite expensive and time-consuming. Dye-sensitization, on the other hand, is a simpler method that can extend catalysts activation to wavelengths longer than those corresponding to its band gap.

The dye-sensitization technique has been reported as an innovative technology that can play an important role in development of efficient and cost-effective semiconductor photocatalyst in the near future [15]. Dye-sensitization begins with electron injection from the excited dye into the conduction band (CB) of TiO_2, followed by interfacial electron transfer [16–20]. Chatterjee et al. [21] investigated the visible light assisted photodegradation of halocarbons on the dye modified TiO_2 surface using visible light with Xe lamp and UV filter. Chowdhury et al. [22] reported the visible solar light driven photocatalytic degradation of phenol with dye sensitized TiO_2 using solar simulator. Xing et al. [23] studied the enhanced self-sensitized degradation of colored pollutants under visible light with mercury lamp and filter. According to our knowledge, there is little information on the photocatalytic removal of Famotidine-contaminated solution in the presence of dye with dye-sensitized photocatalysts under visible-light irradiation.

The present study is intended to investigate the photocatalytic degradation of Famotidine contaminated solution in the presence of dye with dye-sensitized TiO_2 under visible light irradiation ($\lambda > 400$ nm).

2. Materials and methods

2.1. Materials

All reagents were of analytical grade and were used without further purification. Famotidine, orange II, bromophenol blue, acid red 88 and rhodamine B used in this study were purchased from Nacalai Tesque. Ascorbic acid (AA), ammonium oxalate (AO) and *tert*-butyl alcohol (TBA) were obtained from Wako Pure Chemicals. P-25 TiO_2 was purchased from Degussa. Ultrapure water (18 MΩ cm) was prepared by an ultrapure water system (Advantec MFS Inc.).

2.2. Characterization

The UV–visible diffuse reflectance spectra of the photocatalysts (TiO_2 and dye-adsorbed TiO_2 after the photocatalytic treatment) were recorded using a Shimadzu UV-2450 spectrophotometer equipped with an integral sphere assembly. The analysis range was 200–800 nm, and $BaSO_4$ was used as a reflectance standard.

2.3. Photocatalytic activity and detection of reactive oxygen species

The photocatalytic activities of dye (Orange II, Bromophenol blue, Acid red 88 and Rhodamine B) sensitized TiO_2 (label as: TiO_2-OII, TiO_2-BPB, TiO_2-AR88 and TiO_2-RhB) were evaluated by the degradation of Famotidine under visible light irradiation ($\lambda > 400$ nm) at ambient temperature. Typically, 30 mL of Famotidine solution, 20 mg of photocatalyst and sensitizer (5 mg/L) were added to a 35 mL Pyrex glass cell. The initial concentration of Famotidine in all experiments was 2 and 5 mg/L, and the Famotidine solution containing the appropriate quantity of the photocatalyst powder was magnetically stirred before and during irradiation. Before irradiation, the photocatalyst suspension containing Famotidine was allowed to equilibrate for 30 min in the dark. The sample solution was irradiated with a LED lamp (TOSHIBA LDA14L-G/100 W) in conjunction with a UV cut filter (Y-44, HOYA), which was positioned on the side of the reaction cell. The luminous intensity was measured by a UV radio meter (UD-400, TOPCON TECHNOHOUSE Co., Japan). The light intensity of the LED lamp after the filter was 5.3 mW/cm^2. After the desired irradiation time, the photocatalyst was separated by the centrifugation. The amount of the remnant Famotidine in the aqueous solution was measured using a high-performance liquid chromatograph (HPLC, GL-7400), equipped with a HITACHI L-3000 optical detector and an Inertsil ODS-3 column (GL Science, Japan). The elution was monitored at 276 nm. The mobile phase was a mixture of acetonitrile and water (1/1, v/v), and was pumped at a flow rate of 1.0 mL/min. The concentration of dye was measured by UV-vis spectrophotometer. Radical scavenger studies were carried out to investigate the active species in the photodegradation of FMT. Three scavengers were selected, namely, *tert*-butyl alcohol (·OH radical scavenger), *di*-ammonium oxalate monohydrate (hole scavenger) and ascorbic acid ($\cdot O_2^-$ radical scavenger). Different quantity of *tert*-butyl alcohol, *di*-ammonium oxalate monohydrate [24] and ascorbic acid [25] were added into the dye solution prior to addition of catalysts.

2.4. Calculation of photocatalytic efficiency

The degradation efficiency of FMT in the reaction process was calculated using the following formula:

$$\text{Degradation rate} = \frac{C}{C_0} \tag{1}$$

where C is the concentration of Famotidine at time t, and C_0 is the initial concentration of Famotidine (2 and 5 mg/L) at the start of the reaction.

3. Results and discussion

3.1. UV-Vis DRS analysis

Fig. 2 shows the diffuse reflectance spectra of the dye-adsorbed TiO_2 materials after the treatment in the 200–800 nm range, as %R.

The semiconductor photocatalysis with dyes is known largely to occur through dye adsorption on the surface of the photocatalyst, followed by e^-–h^+ generation on photoexcitation and oxidative breakdown of the dye molecule on action of reactive species generated [27]. It is cleared from UV-vis DRS (Fig. 2) that the dye molecules adsorbed onto TiO_2 semiconductors were excited under visible light irradiation and then injected electrons into the conduction band (CB) of TiO_2 particle. However the significant adsorption of dye onto the TiO_2 surface decreased with increasing time due to degradation of dye by self-sensitization. The UV-vis DRS for all four dyes adsorbed TiO_2 showed it that absorption edges were not changed.

3.2. Photocatalytic efficiency of dye-sensitized TiO_2 in Famotidine degradation

Photocatalytic activity of dye-sensitized TiO_2 photocatalysts was evaluated through photocatalytic degradation of Famotidine (2 and 5 mg/L) under visible light irradiation (λ > 400 nm) for 8 and 24 h, respectively. Fig. 3 shows the degradation efficiency of Famotidine (2 mg/L) with reaction time using only bare TiO_2 and TiO_2 in the presence of OII, BPB, AR88 and RhB. The degradation of Famotidine rapidly increased with increasing irradiation

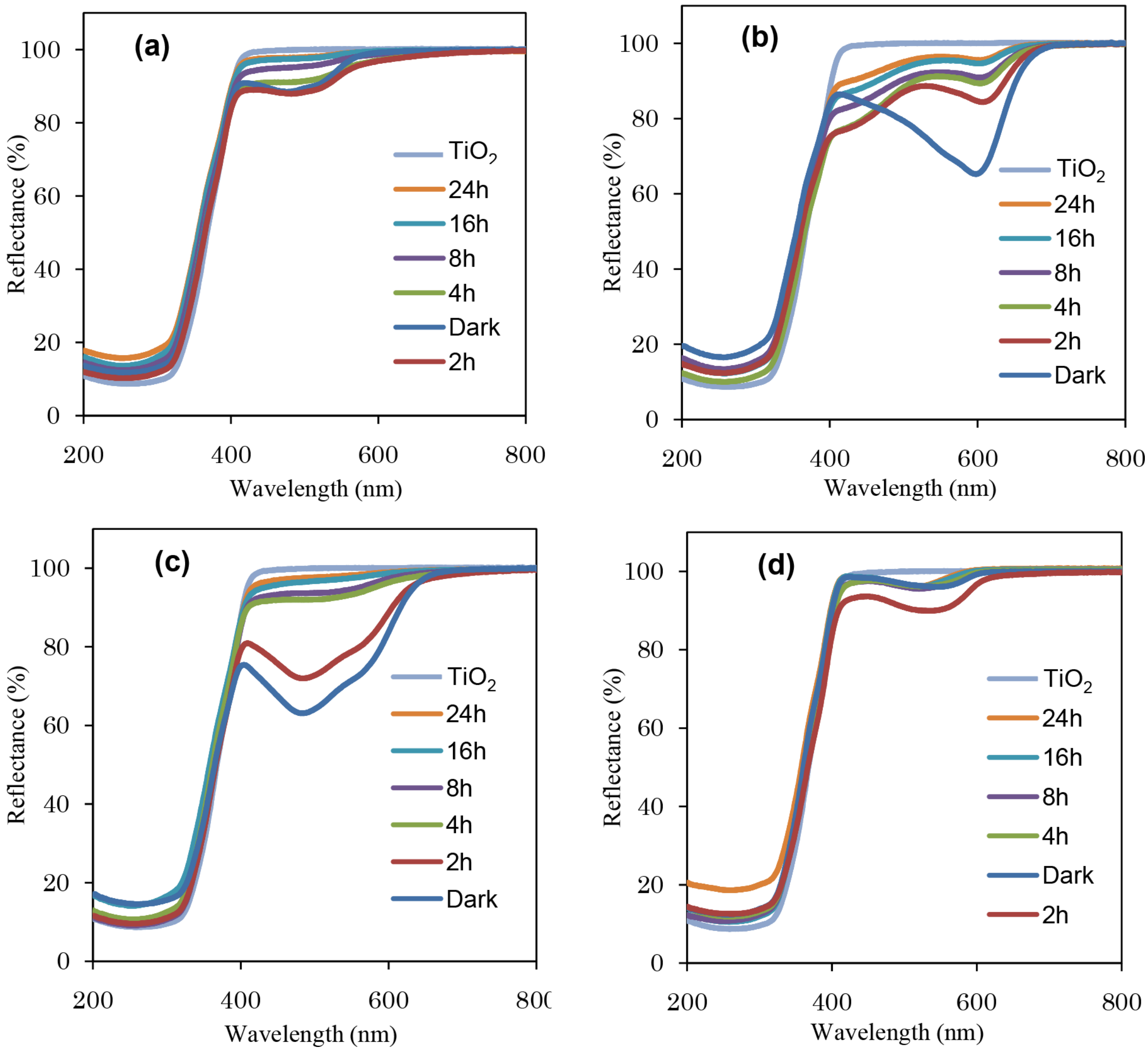

Fig. 2. UV-Vis DRS patterns of TiO_2 and dye adsorbed TiO_2 at different time irradiations. (a) TiO_2-OII, (b) TiO_2-BPB, (c) TiO_2-AR88, (d) TiO_2-RhB.

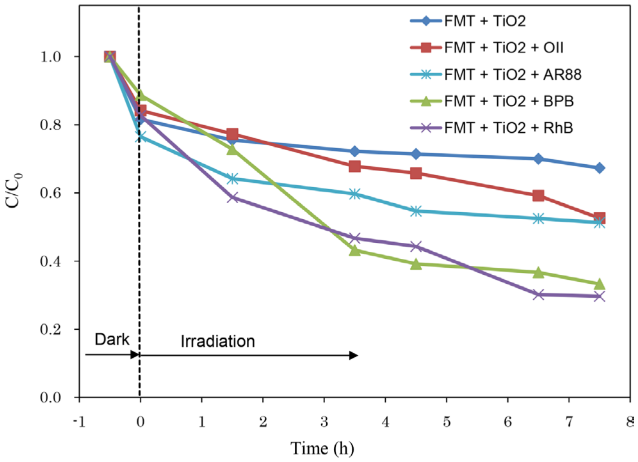

Fig. 3. Time courses of Famotidine concentration (2 mg/L) in the dispersions containing dye (OII, BPB, AR88 and RhB) sensitized TiO_2 under λ > 400 nm irradiation.

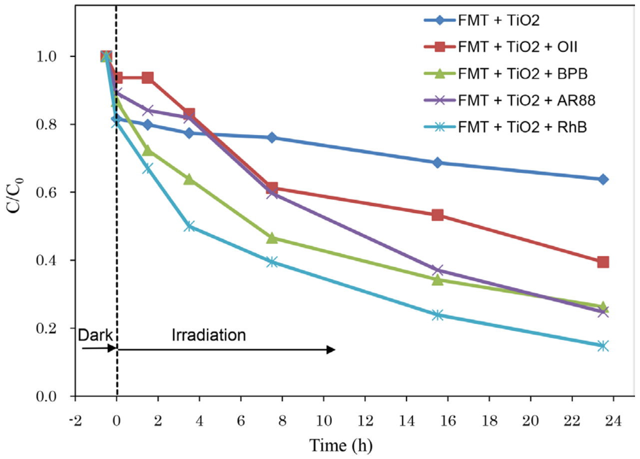

Fig. 4. Time courses of Famotidine concentration (5 mg/L) in the dispersions containing dye (OII, BPB, AR88 and RhB) sensitized TiO_2 under λ > 400 nm irradiation.

times, reaching almost 48%, 67%, 49% and 70% degradation after 8 h in the presence of OII, BPB, AR88 and RhB, respectively. Under the same conditions, the percentage of Famotidine degradation with TiO_2 catalysts was only 33%. This clearly showed it that under visible light the dye-sensitized TiO_2 exhibited higher catalytic activity in the degradation of Famotidine compared with those obtained with P25-TiO_2.

In order to compare the photodegradation performance of different concentrations of Famotidine, the TiO_2 in the presence of OII, BPB, AR88 and RhB were applied into 5 mg/L of Famotidine under visible light irradiation (λ > 400 nm) in 24 h. Fig. 4 shows the photocatalytic degradation of Famotidine (5 mg/L) as a function of irradiation time for the different systems investigated. The photodegradation of FMT with TiO_2 in the presence of OII, BPB, AR88 and RhB catalysts were about 60%, 74%, 75% and 85% after 24 h irradiation under visible light, respectively. The case of only TiO_2 achieved about 36% adsorption of Famotidine after 24 h under the same conditions. Hence, the results for all of dye sensitized TiO_2 samples are significantly better than that observed with TiO_2. The improvement of the catalytic activities may be due to the sensitized TiO_2 in the presence of dye. TiO_2 with RhB exhibited the highest activity of FMT elimination from water.

The adsorption of Famotidine with TiO_2 in the presence of OII, BPB, AR88 and RhB was carried out (Fig. S1). The adsorption (removal) percentage of FMT on TiO_2 particles was found to increase up to 30 min for four dyes, and after the time the appreciable change was not observed until 4.5 h. Photolysis experiment of FMT in absence of photocatalyst under visible light was performed. As shown in Fig. S2, the FMT degradation efficiency by photolysis was approximately 5% after 24 h under visible light irradiation. The adsorption of FMT in the presence of bare TiO_2 was carried out under dark (Fig. S2). The efficiency increased up to 30 min, and then adsorption increased slowly with increasing time.

The degradation efficiency of sensitizer (OII, BPB, AR88 and RhB) was also evaluated under visible light irradiation. The concentration of sensitizer in the treatment decreased with increasing time shown in Figs. S3–S6. Thus, the dye may be firstly excited by absorbing visible light, and then degraded through a self-sensitized mechanism.

3.3. Kinetic analysis

The photocatalytic oxidation kinetics of many organic compounds has often been modeled with the Langmuir-Hinshelwood (L-H) equation, which also covers the adsorption properties of the substrate on the photocatalyst surface. This model was developed by Turchi and Ollis [28] and expressed as Eq. (3):

$$r_0 = -\frac{dC}{dt} = \frac{kKC_0}{1+KC_0} \tag{2}$$

where r_0 is the degradation rate of the reactant, k is the reaction rate constant and K and C_0 are the adsorption equilibrium constant and concentration for the reactant, respectively. If the concentration of substrate is very low, i.e., $KC_0 << 1$, the L-H equation (Eq. (3)) simplifies to a pseudo-first-order kinetic law (Eq. (4)) where k_{obs} is being the apparent pseudo-first-order rate constant.

$$-\frac{dC}{dt} = kKC = k_{obs}C \tag{3}$$

Integration of the above equation with the limit of $C = C_0$ at $t = 0$ with C being the equilibrium concentration of the bulk solution gives the following equation:

$$-Ln\frac{C}{C_0} = k_{obs}t \tag{4}$$

The primary degradation reaction is estimated to follow a pseudo first-order kinetic law, according to Eq. (5). In order to confirm the speculation, Ln(C/C_0) was plotted as a function of illumination time for Famotidine 2 and 5 mg/L shown in Fig. 5a and 5b, respectively. Since the linear plots were observed as expected, the kinetics of Famotidine in the

TiO_2 suspension with dye solution followed the first-order degradation curve which was consistent to the L-H model resulting from the low coverage in the experimental concentration range (2 and 5 mg/L).

The photocatalytic degradation kinetic parameters such as pseudo-first-order rate constant, correlation coefficient and substrate half-live are shown in Table 1. The values of rate constants have been determined from the slope and intercept of these plots. As shown in Table 1, the rate constant values k_{obs} (h^{-1}) of FMT (2 and 5 mg/L) were better for dye-sensitized TiO_2 than that observed with bare TiO_2.

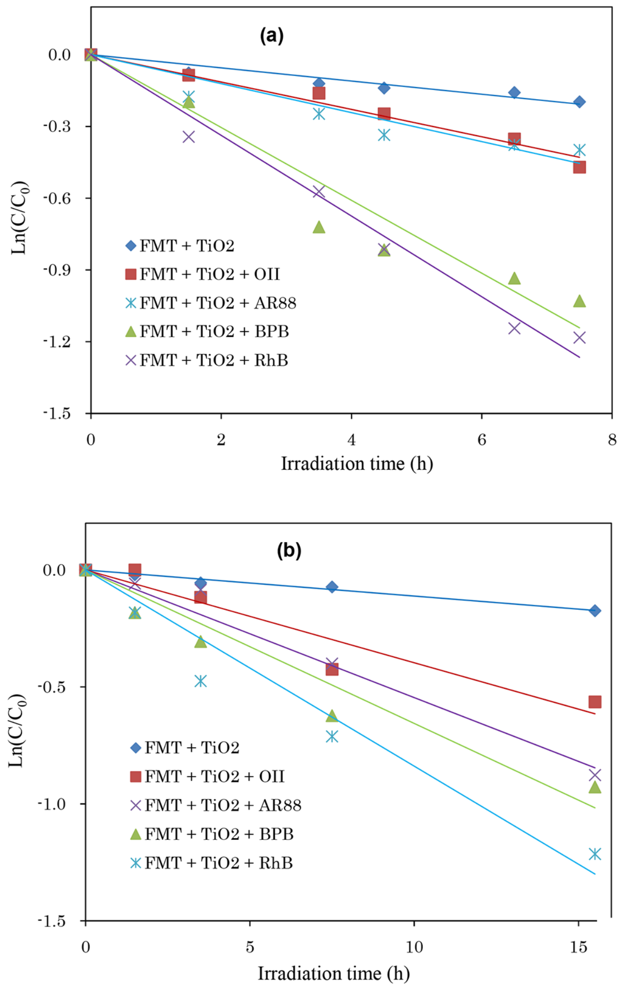

Fig. 5. Kinetic plot of $\mathrm{Ln}(C/C_0)$ versus irradiation time for Famotidine (a) (2 mg/L) and (b) (5 mg/L).

3.4. Detection of reactive species

The radical and holes trapping experiments (scavenger tests) with different scavenger molecules were performed so as to elucidate the photocatalytic degradation mechanism of FMT under visible light irradiation over dye-sensitized TiO_2. Generally, the reactive species such as, hydroxyl radicals (·OH), superoxide radical anions ($\cdot O_2^-$) and holes (h^+) are expected to be involved in the photocatalytic dye degradation processes [29]. In this study, *tert*-butyl alcohol (TBA), *di*-ammonium oxalate monohydrate (AO) and ascorbic acid (AA) were adopted to be the scavengers of hydroxyl radicals (·OH), superoxide radical ($\cdot O_2^-$) and holes (h^+), respectively. As shown in Fig. 6a, the photocatalytic degradation of FMT over the RhB sensitized TiO_2 was affected slightly by the addition of TBA, demonstrating that ·OH active species played a small role in the photocatalytic degradation of FMT. However, the photocatalytic degradation efficiency of FMT decreased significantly in the presence of AO. Moreover, the photocatalytic activity of the RhB sensitized TiO_2 was completely suppressed by AA additions. This indicates that h^+ and $\cdot O_2^-$ play a dominant role in the photocatalytic degradation of FMT over RhB sensitized TiO_2 under visible light.

In order to investigate the active species involved in photodegrading FMT, scavenger studies were also carried out on dye-sensitized TiO_2 at 24 h, as shown in Fig. 6b. The photocatalytic degradation of FMT over TiO_2 was retarded with the presence of AA and AO. The results strongly indicated that h^+ and $\cdot O_2^-$ were the active species in the photodegradation of FMT. However, $h^+$was more dominant in the photodegrading of FMT as the most important active species. The presence of TBA had little effect on the decolorization rate, indicating that FMT was almost not degraded by ·OH.

3.5. Reaction mechanism

TiO_2 cannot absorb visible-light directly due to the band gap 3.2 eV [30,31], but when a colored organic compound is present, a sensitized photocatalytic process is able to operate. In dye sensitized photocatalysis, a dye absorbing visible light excites an electron from the HOMO (highest occupied molecular orbital) of a dye to the LUMO (lowest unoccupied molecular orbital). The HOMO and LUMO

Table 1
Rate constants, R^2 and half-life values of Famotidine (2 and 5 mg/L) using TiO_2 and dye-sensitized TiO_2

Catalysts	k_{obs} (h^{-1})		R^2		$t_{1/2}$ (h)	
	FMT (2 mg/L)	FMT (5 mg/L)	FMT (2 mg/L)	FMT (5 mg/L)	FMT (2 mg/L)	FMT (5 mg/L)
TiO_2	0.0275	0.0112	0.89	0.98	25.2	61.9
TiO_2-OII	0.0572	0.0397	0.98	0.91	12.1	17.5
TiO_2-AR88	0.0606	0.0546	0.86	0.98	11.4	12.7
TiO_2-BPB	0.1522	0.0656	0.92	0.93	4.5	10.6
TiO_2-RhB	0.1687	0.0839	0.98	0.94	4.1	8.3

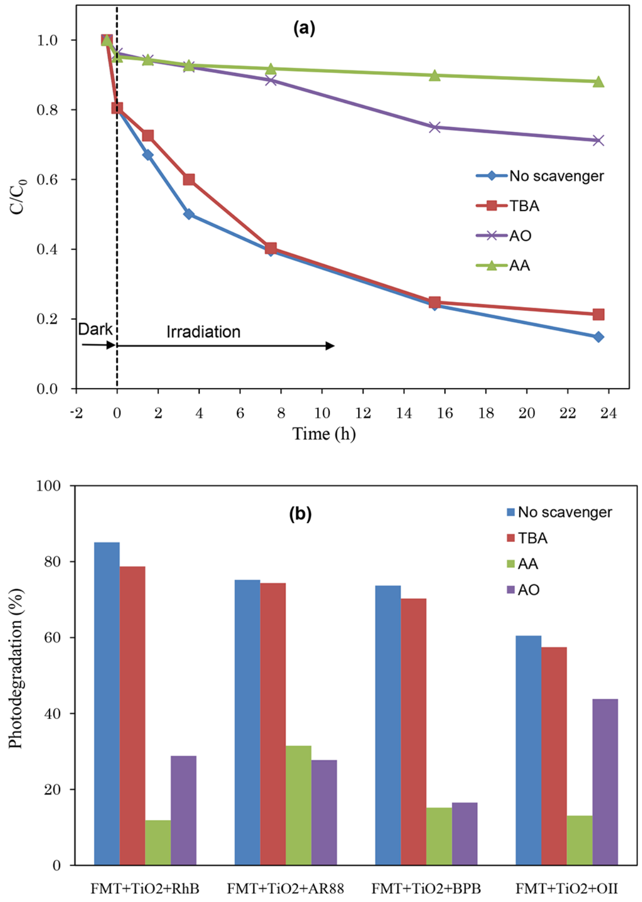

Fig. 6. Effects of different scavengers on the degradation of Famotidine (5 mg/L) with TiO_2 in the presence of (a) RhB and (b) various dyes at 24 h under visible-light irradiation.

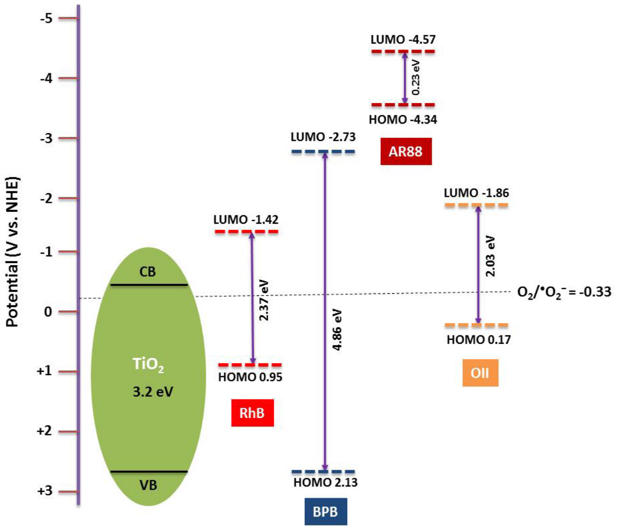

Fig. 7. Schematic energy level diagram of TiO_2 with respect to potential of $O_2/\cdot O_2^-$ and the HOMO–LUMO levels of dye.

Table 2
HOMO and LUMO levels and energy gaps (eV) of dye molecules and λ_{max}

Molecules	HOMO	LUMO	Energy gaps	λ_{max} (nm)	Ref.
OII	0.17	–1.86	2.03	485	[34]
BPB	2.13	–2.73	4.86	590	[35]
AR88	–4.34	–4.57	0.23	506	[36]
RhB	0.95	–1.42	2.37	553	[30]

levels and band gap energy of OII, BPB, AR88 and RhB were obtained from literatures and the values are presented in Table 2 [27,32–34]. Fig. 7 demonstrates the valence band (VB) and conduction band (CB) levels and the band gap energy of TiO_2 vs NHE reference electrodes. It is observed that the LUMO levels of OII, BPB, AR88 and RhB are more negative than the conduction band edge potential of TiO_2. Otherwise, as the more negative potential of dye of lowest unoccupied molecular orbital (LUMO) level than the conduction band (CB) of TiO_2 [35,36], the electron transfer from the LUMO of dyes to the CB of TiO_2 is feasible. It is reported the redox potential of $O_2/\cdot O_2^-$ is –0.33 V vs NHE [37], which is less negative than conduction band potential of TiO_2 (–0.5 V vs NHE) [38].

Under visible-light irradiation, a dye sensitized mechanism has been depicted in Fig. 8. Upon Irradiation of visible-light, a dye absorbs the light to create an electron and hole in the conduction and valence bands (LUMO and HOMO) of the dye [39]. The electron in the LUMO then transfers to the CB of TiO_2. The adsorbed molecular oxygen on the catalyst captures electron from the CB of TiO_2 to form $\cdot O_2^-$. Thus the FMT could be efficiently degraded by the aid of high oxidizing-power of the $\cdot O_2^-$ for the formation of S-oxide of Famotidine [40]. The oxidant ($\cdot O_2^-$) radical also

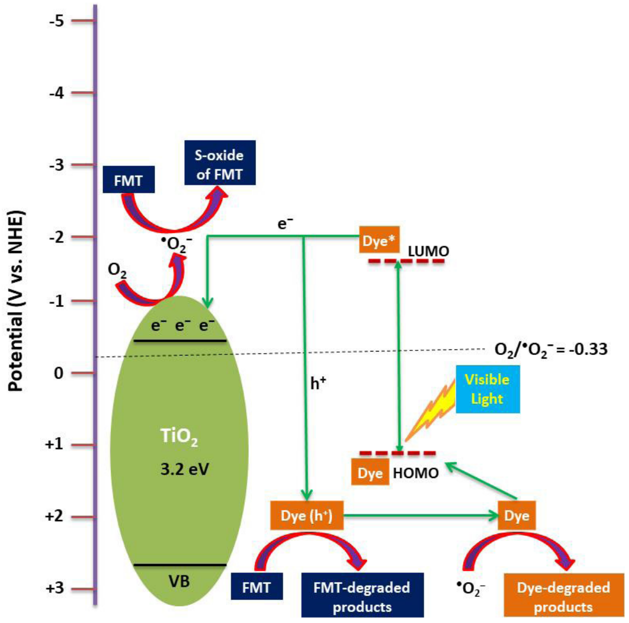

Fig. 8. Schematic of dye-sensitization directed photogradation of Famotidine with TiO_2 under visible-light irradiation.

reacts with adsorbed dye to degrade it. The holes in the dye (HOMO) react with adsorbed OH^- species to form ·OH radical. However, the formation channel to OH is minor under visible right [39], which is similar with the result shown in Fig. 6a and 6b. The holes of dye react with adsorbed FMT to form the degraded products and to regenerate of dye molecules for the next dye-sensitization process [22,39]. According to the results of the radical scavengers, FMT was attacked easily by the holes for the degradation of FMT in aqueous solution. Therefore, the TiO_2-dye-sensitized degradation of FMT under visible light irradiation could be mainly attributed to the oxidization by h^+ and $\cdot O_2^-$ radicals,while the ·OH radicals played only a relatively minor role in the oxidization process.

On the basis of the photodegradation results with a scavenger, a possible degradation reaction mechanism is described below.

$$\text{Dye + visible light} \rightarrow \text{dye}\ (e_{CB}^{-} + h_{VB}^{+}) \tag{6}$$

$$\text{Adsorbed dye}\ (e_{CB}^{-} + h_{VB}^{+}) + TiO_2 \rightarrow TiO_2\,(e_{CB}^{-}) + \text{dye}\ (h_{VB}^{+}) \tag{7}$$

$$TiO_2\,(e_{CB}^{-}) + O_2 \rightarrow TiO_2 + \cdot O_2^{-} \tag{8}$$

$$\cdot O_2^{-} + \text{FMT} \rightarrow \text{S-oxide of FMT} \tag{9}$$

$$\text{Dye}\ (h_{VB}^{+}) + \text{FMT} \rightarrow \text{FMT degraded products + dye} \tag{10}$$

$$\cdot O_2^{-} + \text{dye} \rightarrow \text{dyedegraded products} \tag{11}$$

4. Conclusions

In summary, the photocatalytic activity of dye-sensitized TiO_2 in the degradation of Famotidine under visible light irradiation (λ > 400 nm) was investigated. TheTiO_2 in the presence of RhB exhibited excellent photocatalytic performance for Famotidine degradation, displaying a considerably higher photocatalytic activity compared with that of TiO_2. According to the investigation of the photocatalytic mechanism, the TiO_2 dye-sensitized degradation of Famotidine under visible light irradiation could be mainly attributed to the oxidization by h^+ and $\cdot O_2^-$ radicals, while the ·OH radicals played only a relatively minor role in the oxidization process. The kinetics of FMT photodegradation was found to follow the pseudo-first order rate law and could be described in terms of Langmuir-Hinshelwood model. The present work may provide deep insight into the photosensitization induced photocatalytic mechanism, and also offer new opportunities for their industrial application in the elimination of Famotidine and dye pollutants from wastewater.

Acknowledgments

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Supplemental Information

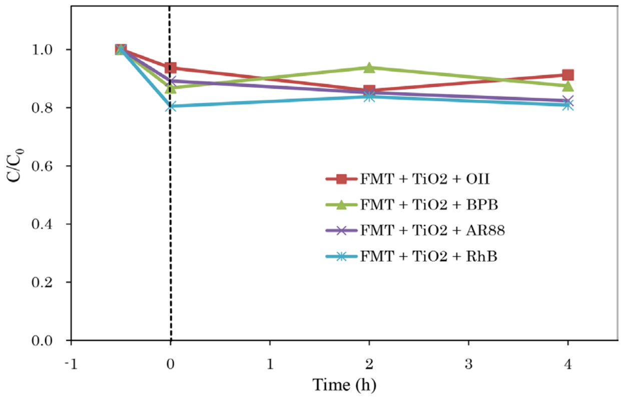
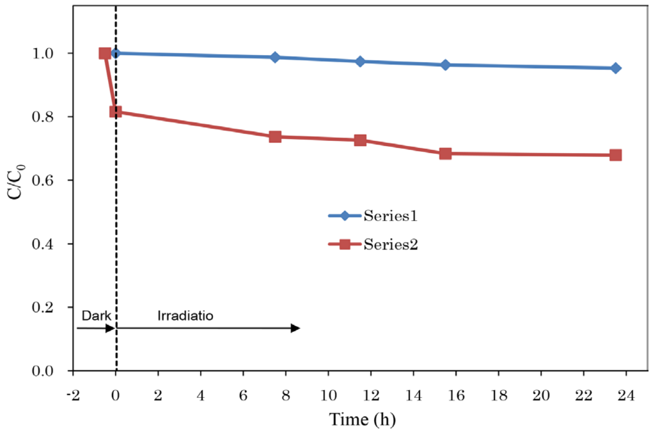


Fig. S1. Time courses of Famotidine concentration (5 mg/L) in the dispersions containing TiO_2 and dye (OII, BPB, AR88 and RhB) under dark.



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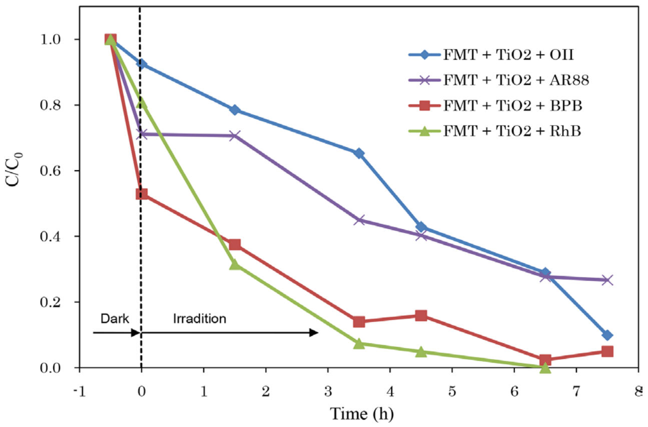

Fig. S3. Time courses of dye (OII, BPB, AR88 and RhB) concentration in the dispersions containing Famotidine (2 mg/L) with TiO_2 under λ > 400 nm irradiation.

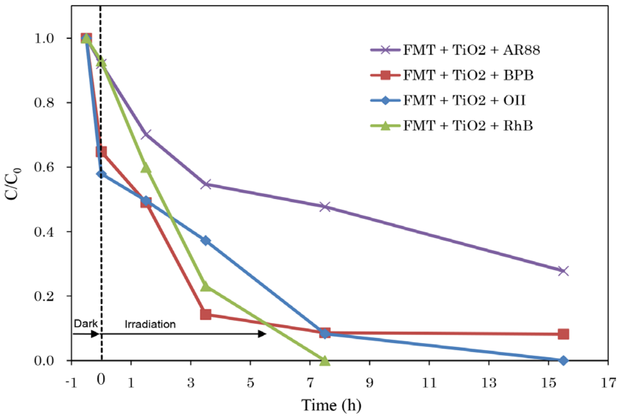

Fig. S4. Time courses of dye (OII, BPB, AR88 and RhB) concentration in the dispersions containing Famotidine (5 mg/L) with TiO_2 under λ > 400 nm irradiation.

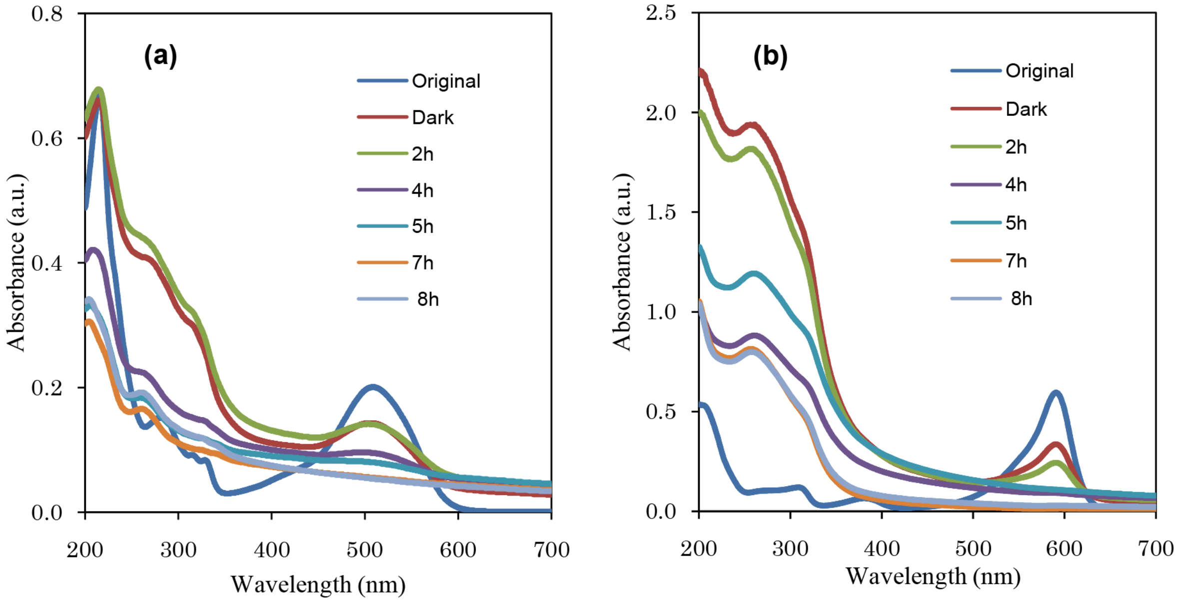

Fig. S5.Absorption spectra of Famotidine (2 mg/L) in the presence of dye (5 mg/L) of the photocatalytic degradation with TiO_2 under λ > 400 nm irradiation.(a) AR88 and (b) BPB.

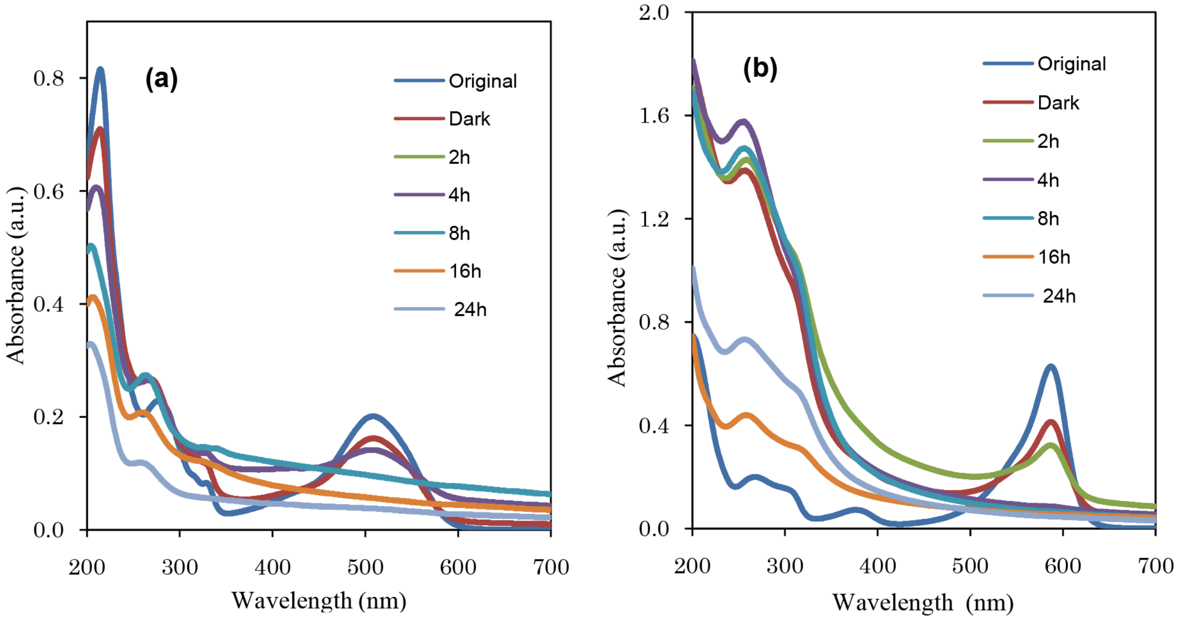

Fig. S6.Absorption spectra of Famotidine (5 mg/L) in the presence of dye (5 mg/L) of the photocatalytic degradation with TiO_2 under λ > 400 nm irradiation.(a) AR88 and (b) BPB.