

A Visible Light-Driven Titanium Dioxide Photocatalyst Codoped with Lanthanum and Iodine: An Application in the Degradation of Oxalic Acid

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A series of photocatalysts was synthesized by codoping TiO₂ with lanthanum and iodine (La–I–TiO₂). The structure and properties of the catalysts were studied by X-ray diffraction (XRD), the Brunauer–Emmett–Teller (BET) method, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and UV–vis diffuse reflectance spectra. The prepared anatase-phase La–I–TiO₂ (molar ratio 20:20:100) calcined at 400 °C had a BET surface area of 92.9 m² g^{−1}, and the crystallite size calculated from XRD data was ~3.57 nm, and it had a remarkable absorption in the visible light range of 400–550 nm. The catalytic efficiency was tested by monitoring the photocatalytic degradation of oxalic acid under visible light irradiation. An optimum molar ratio of 20:100 La/TiO₂ was determined for the most efficient inhibition of the recombination of electron–hole pairs and the photocatalytic activity of La–I–TiO₂ calcined at 400 °C was significantly higher than that calcined at 500 or 600 °C in aqueous oxalic acid solution. The probable process of oxalic acid degradation was that it was first adsorbed onto the surface of the catalysts, where it reacted with valence band holes (h_{vb}^+) and the surface-bound or adsorbed ·OH radicals (·OH_{ads}) as well as reactive oxygen species (ROS) derived from oxygen reduction by photogenerated electrons, and finally converted into CO₂ and H₂O without any stable intermediate.

Introduction

Since titanium dioxide (TiO₂) was reported by Fujishima et al. in 1972 as an efficient photocatalyst,¹ it has received much attention due to its advantages of being inexpensive, nontoxic, and a good photostable semiconductor. However, its wide energy band gap (3.2 eV) for the anatase form means that only UV light is able to create electron–hole pairs to initiate photocatalytic processes, and thus only ~5% of the solar spectrum can be utilized.²

To efficiently utilize solar energy, recent research has concentrated on lowering the threshold energy of TiO₂ to extend its optical response to the visible region. One efficient approach of these contributions is doping TiO₂ with various metals or nonmetals. This method creates intra-band-gap states close to the conduction or valence band edges that induce visible light absorption at the sub-band-gap energies.³ There have been reports of TiO₂ doped with rare earth elements such as lanthanum and cerium.^{4,5} The number of surface oxygen vacancies and defects increased after doping La into TiO₂. The oxygen vacancies and defects could become centers for the capture of photoinduced electrons during photocatalytic reactions, and thus the recombination of photoinduced electrons and holes could be effectively inhibited.⁶ However, excess dopant may serve as an electron–hole recombination center.

Also, TiO₂ doped with nonmetal atoms, such as N, S, I, and C, all showed high levels of photocatalytic activity under visible

light.^{7–11} Furthermore, there have been reports of doped TiO₂ with both nonmetal elements and metal oxides. The results reported by Zhao et al. suggest that, by modification with two dopants, nonmetal and a metal oxide, the goals both of shifting TiO₂ response to visible light and of improving its catalytic activity are realized.¹² However, to the best of our knowledge, there are few reports of La/I codoped titania.

In this study, we have synthesized and characterized a new type of photocatalyst — lanthanum and iodine atom codoped titania (denoted as La–I–TiO₂). We have investigated in detail its catalytic efficiency of oxalic acid degradation under visible light irradiation, and we propose a tentative degradation process. Oxalic acid was chosen as a model target pollutant in our study because: (1) oxalic acid is widely used in a variety of industries, including textiles, plastics, chemicals, powders, catalysts, photography, and wood bleaching; (2) it is corrosive, toxic, and hazardous to human health; (3) it is a relatively stable intermediate product in the photocatalytic degradation of many larger organic compounds.^{13,14}

Experimental Section

Materials. Tetrabutyl titanate, iodic acid, lanthanum nitrate, and *n*-butanol (purity ≥98%) were purchased from Huadong Medicine Co., Ltd., China. Oxalic acid (purity 99.5%) was purchased from Shanghai Meixing Co., Ltd., China. Sodium nitrite (NaNO₂) was supplied by Lanxi Zhongxing Co., Ltd., China. Nitrogen (purity 99.99%) was provided by Zhejiang Jingong Co., Ltd., China. Sodium fluoride (NaF), potassium iodide (KI), tert-butyl alcohol (*t*-BuOH), and potassium peroxydisulfate (K₂S₂O₈) were purchased from Huadong Medicine Co., Ltd., China. All chemicals were of analytical grade or

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higher and were used as received. Deionized and doubly distilled water was used for all synthesis and treatment processes.

Synthesis of the Photocatalyst. All samples were prepared by a standard procedure. Typically, 30 mmol of lanthanum nitrate was dissolved in 35 mL of *n*-butanol, and then 51 mL of tetrabutyl titanate was added. After that, the solution was added dropwise into 200 mL of 30 mM aqueous iodic acid with vigorous stirring. Different samples were prepared by varying the quantity of lanthanum nitrate dissolved (1.5, 15, and 45 mmol).

The solution changed from colorless to white upon addition of the alkoxide because of hydrolysis of tetrabutyl titanate in reaction with water. The mixture was dried at 80 °C in a temperature-controlled bath, and the precursors were formed. We calcined the precursors in an oven (CWF 1100, CARBO-LITE) as follows: the temperature was raised to 400 °C at a heating rate of 5 °C/min (NB 5 °C is a temperature, 5 °C is an increment) and kept at that temperature for 2 h before cooling to room temperature. Further samples were calcined at 500 and 600 °C by the same method. Finally, the samples were washed and again dried at 80 °C in a temperature-controlled bath.

Characterization. The crystalline phase that evolved after calcination of the powders was examined by X-ray diffraction (XRD) with a Thermo ARL SCINTAG X'TRA diffractometer at room temperature using Cu K α irradiation at 45 kV and 40 mA. Crystal sizes were estimated by applying the Scherrer equation.¹⁵ The Brunauer–Emmett–Teller (BET) surface area was determined by nitrogen adsorption–desorption isotherm measurements at 77 K with a Micromeritics ASAP 2010 Analyzer. The morphology and the particle size distribution of the samples were studied by transmission electron microscopy (TEM) using a JEOL–2010 microscope operating at an accelerating voltage of 200 kV with 0.19 nm point resolution. X-ray photoelectron spectroscopy (XPS) experiments were done with an RBD upgraded PHI-5000C ESCA system (Perkin-Elmer) with Mg K α radiation (1253.6 eV). The binding energies of Ti, I, La, and O were calibrated by using the containment carbon (C 1s = 284.6 eV). The data analysis was carried out by using the XPSPEAK4.1 software provided by Raymund W. M. Kwok (The Chinese University of Hongkong, China). In addition, UV–vis diffuse reflectance spectra were measured at room temperature with a UV–vis spectrometer (UV-2500, Shimadzu).

Photocatalytic Activity Measurement. Photocatalytic experiments were done in a cylindrical Pyrex photoreactor (diameter 16 cm; height 20 cm; total capacity 3000 mL) containing 1.5 g of La–I–TiO₂ particles and 1.5 L of 1.5 mM aqueous oxalic acid with an initial pH of 2.9 and total organic carbon (TOC) content of 44 mg L^{−1}. The stable aqueous solution was irradiated with a 500-W dysprosium lamp (Beijing Electric Light Sources Research Institute, Beijing, China), which has a spectrum very close to solar light, through 1000 mL of 2 M sodium nitrite as a filter for visible light, with continuous stirring.¹⁶ A port at the top of the photoreactor was used for measuring temperature and for withdrawing samples. During operation, the water-jacketed reactor was used to maintain the temperature of the oxalic acid solution at 22(±1) °C and of the filter solution at 55(±1) °C, controlled by a thermostat (THD-2015, Tianheng Instrument Factory, Ningbo, China).

For the experiments with purging by nitrogen gas, we used a cylindrical nitrogen gas diffuser with coarse porosity, placed at the bottom of the reactor. The flow rate was 0.06 m³ h^{−1}, which was controlled by a rotameter. Nitrogen gas was supplied for 30 min in order to reduce the dissolved oxygen level before

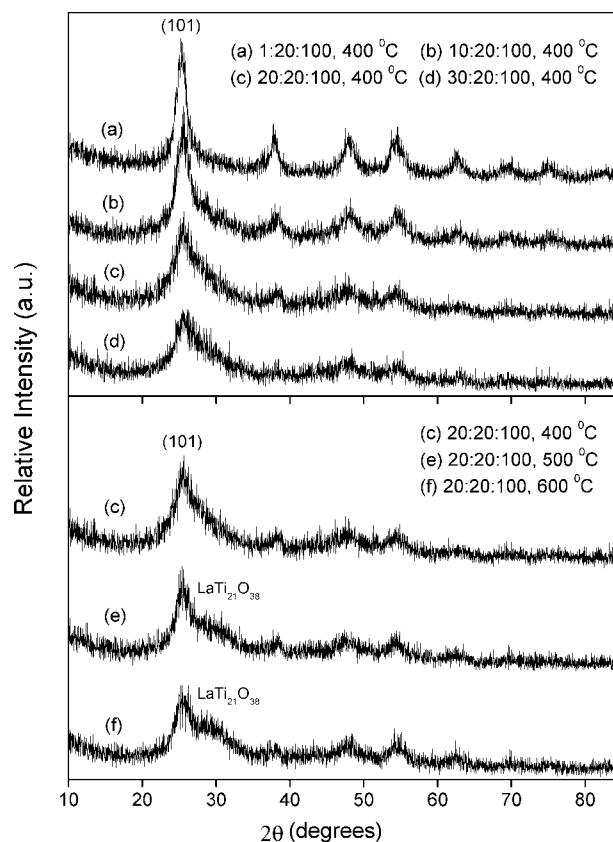


Figure 1. The XRD patterns of La–I–TiO₂ (molar ratios 1:20:100, 10:20:100, 20:20:100, and 30:20:100) calcined at 400 °C and La–I–TiO₂ (molar ratio 20:20:100) calcined at 400, 500, and 600 °C.

the experiments. In experiments requiring scavengers, these were added to the oxalic acid solution before introduction of the catalyst. Samples were withdrawn at predetermined time-points and then centrifuged and filtered through a 0.45 μ m pore size membrane filter to remove the catalyst particles. The concentration of oxalic acid was monitored by a Dionex model ICS 2000 ion chromatograph, and the decrease of TOC, which confirmed the mineralization of oxalic acid, was determined using a TOC-V_{CPH} total organic carbon analyzer (Shimadzu, Kyoto, Japan).

Results and Discussion

Catalyst Characterization. Figure 1 shows the XRD patterns in the 2 θ region from 10 to 85° for samples with various doping contents calcined at different temperatures. The patterns show that all samples contained a little rutile structure but were dominated by anatase. The TiO₂ rutile phase is usually observed in impurity-free TiO₂ samples calcined at temperatures of 600 °C and above, and iodine-doped TiO₂ calcined at 600 °C contains only the rutile structure.⁹ In this study, the analytical results showed that the relative intensity of 101 peaks decreased significantly with increased La doping (Figure 1) suggesting that the addition of La to I–TiO₂ retarded the thermodynamically feasible anatase to rutile phase transformation and stabilized the anatase phase.¹⁷

The ionic radius of La³⁺ (0.1016 nm) is much larger than those of Ti⁴⁺ (0.068 nm) and I⁵⁺ (0.062 nm). Therefore, it is difficult for the La³⁺ ion to enter into the lattice of TiO₂ to replace the Ti⁴⁺ ion, but it may be present in the surface layer of TiO₂; at the same time it is possible for I⁵⁺ to substitute for Ti⁴⁺ in the titania matrix.^{9,11} The XRD peaks of the crystal plane

TABLE 1: Surface Areas and Crystallite Sizes Calculated from XRD Data of La-I-TiO₂

mole ratio of La:I:Ti	calcination temperature (°C)	surface area (m ² g ⁻¹)	crystallite size (nm)
1:20:100	400	158.0	4.42
10:20:100	400		4.11
20:20:100	400	92.9	3.57
30:20:100	400	62.6	1.64
20:20:100	500	105.0	

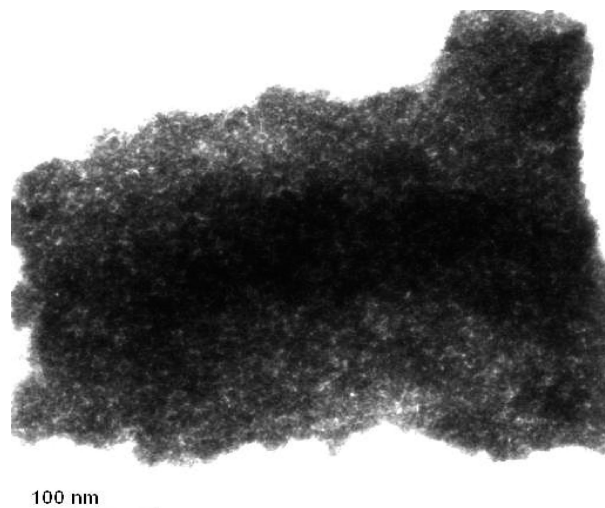
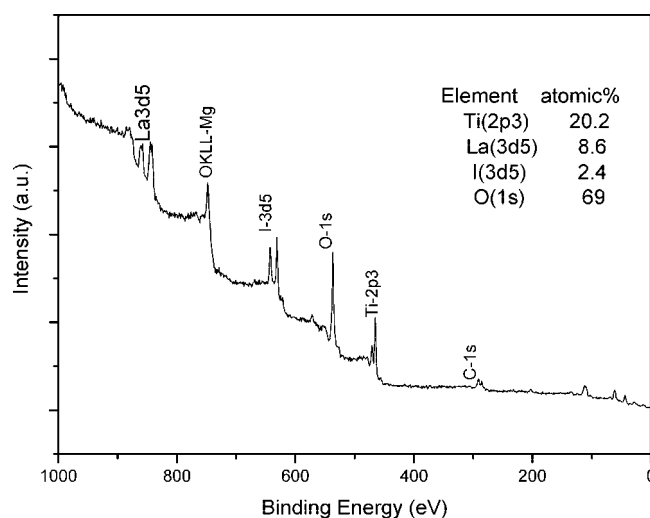
101 in anatase were selected to determine the cell parameters *a* and *c* of the samples before and after doping with La. The results showed that *a* and *c* of La-I-TiO₂ (molar ratio 20:20:100, 400 °C) are 3.782 and 9.502 Å, respectively, while those of I-TiO₂ (molar ratio 20:100, 400 °C) are 3.785 and 9.514 Å, respectively. The slight difference in the cell parameters before and after La doping might be due to the substitution of La³⁺ with Ti⁴⁺ ions at the interface in the lattice of La₂O₃,¹⁷ and the evidence from XPS (see below) adds support to this suggestion. Furthermore, there is a possibility of forming a Ti-O-La bond when the calcination temperature is elevated. The XRD profiles of samples calcined at 500 and at 600 °C (parts e and f of Figure 1) reveal a peak due to the compound LaTi₂O₃₈ (JCPDS File No. 13-0505), and the intensity of this peak increased with increasing temperature of calcination.

The crystallite sizes calculated from the XRD data of samples doped with various La doping contents calcined at 400 °C are given in Table 1. With the increase of lanthanum content, the crystallite size decreased from 4.42 to 1.64 nm. This reduction in crystallite size can be attributed to segregation of the dopant cations at the grain boundary, which inhibits grain growth by restricting the coalescence of some smaller neighboring grains.¹⁸ It is well-known that, in general, catalysts with smaller crystallites exhibit better catalytic properties.¹⁹

The BET surface areas of various samples are given in Table 1, where it can be seen that the specific surface areas of samples changed considerably, depending on the calcination temperature and the La content doped into I-TiO₂. Reddy et al. reported the relation between specific surface area and calcination temperature. In their work, the specific surface area decreased with increased calcination temperature, which was suggested to be due to sintering of the samples at higher temperatures.²⁰ However, our study showed that the BET surface area of La-I-TiO₂ (400 °C) is 92.9 m² g⁻¹, while that of La-I-TiO₂ (500 °C) is 105.0 m² g⁻¹. The greater surface area of La-I-TiO₂ (500 °C) may be due to the formation of LaTi₂O₃₈. The decrease in specific surface area with increased La doping may be attributed to blocking the pores of the support by lanthanum on the surface.

Figure 2 shows the TEM image of La-I-TiO₂ (molar ratio 20:20:100) calcined at 400 °C. During the calcination, lanthanum nitrate was converted into La₂O₃ and deposited onto the surface of I-TiO₂, which is in accord with the XPS findings (see below). However, this is difficult to see in the typical image of La doping into I-TiO₂ shown in Figure 2. La₂O₃ coated onto the surface of I-TiO₂ may favor separating charge carriers efficiently, prolonging the carrier lifetime, and eventually inhibiting the recombination of photogenerated electron-hole pairs, which enhances the reactivity.²¹

The XPS spectra (Figure 3) for La-I-TiO₂ (molar ratio 20:20:100) calcined at 400 °C show the peaks of binding energy (BE) for Ti 2p3, I 3d5, La 3d5, O 1s, and C 1s, and the high-resolution XPS spectra of I 3d5, La 3d5, and Ti 2p3 are shown in Figure 4. The spectra in the core level of I and La were

**Figure 2.** TEM picture for La-I-TiO₂ (molar ratio 20:20:100) calcined at 400 °C.**Figure 3.** XPS spectra of La-I-TiO₂ (molar ratio 20:20:100) calcined at 400 °C.

consistent with I⁵⁺ and La³⁺, respectively. The Ti 2p3 peak of La-I-TiO₂ showed a slight deformation in the lower side of the BE (see the Supporting Information), corresponding to Ti³⁺. The Ti³⁺ surface states have been generated to maintain the electroneutrality by I⁵⁺ substituting Ti⁴⁺; meanwhile, the reduction of titanium to a lower valence state may be induced by a charge imbalance when Ti⁴⁺ enters the lattice of La₂O₃ during the heat treatment.²² The existence of the Ti³⁺ surface state can retard the recombination of the electron-hole pairs.⁹ The BE of I 3d5 observed at 623.8 eV cannot pertain to I 3d5 of HIO₃ (623 eV) because HIO₃ decomposes at 300 °C, and it also cannot pertain to I3d5 of TiI₄, which does not exist above 400 °C because its boiling point is 377 °C. The shift of the BE of I 3d5 is caused by I⁵⁺ doped into the titania matrix.⁹

The molar ratio of La/Ti on the surface of La-I-TiO₂ (molar ratio 20:20:100, 400 °C) was about 43:100, which is larger than the doping ratio of La/Ti (molar ratio 20:100). This could be because part of the doped La was coated onto the surface of I-TiO₂, since the XPS analysis is surface sensitive. In the XPS spectra in the core level of O 1s (see the Supporting Information), the O 1s region of I-TiO₂ (molar ratio 20:100, 400 °C), and La-I-TiO₂ (molar ratio 20:20:100, 400 °C) were composed of three peaks (the fitting data are given in table 2). The dominant peaks at ~530 eV agree with the O 1s electron BE

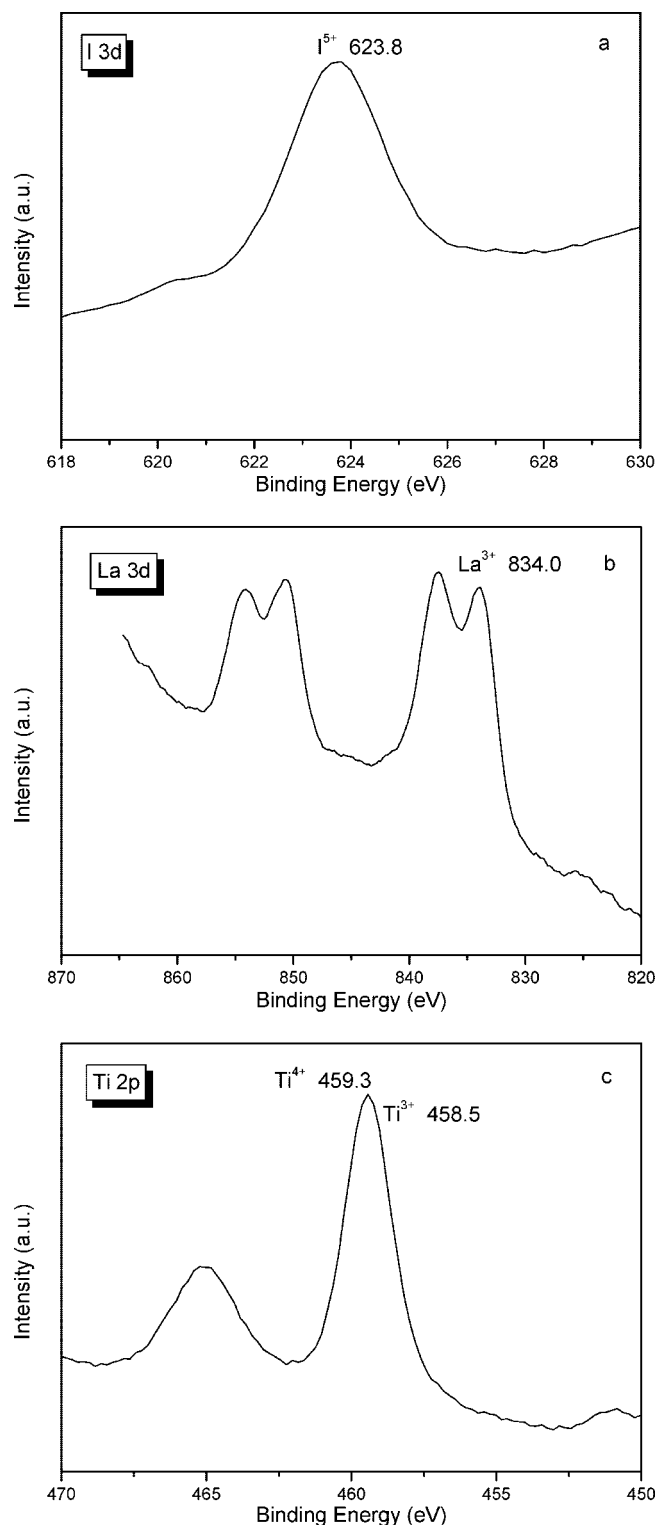


Figure 4. XPS spectra in the I 3d (a), La 3d (b), and Ti 2p (c) core levels for La-I-TiO₂ (molar ratio 20:20:100) calcined at 400 °C.

for TiO₂ and La₂O₃, and the fitting data at 531.5 eV $\pm$ 0.5 eV (O 1s_{2/3}) might be attributed to the surface hydroxyl groups. The peak at $\sim$ 528 eV (O 1s_{3/3}) might represent Ti₂O₃.¹⁷ According to Table 2, the surface hydroxyl groups accounted for 20.9% of the total oxygen on the surface of I-TiO₂ (molar ratio 20:20:100, 400 °C). After doping La, the proportion of surface hydroxyl groups decreased to 14.4%, which may be due to La trapped on the surface of I-TiO₂. Table 2 gives the ratio of O/Ti on the surface of I-TiO₂ (molar ratio 20:100, 400 °C)

TABLE 2: XPS Fitting Data of O 1s of I-TiO₂ (Molar Ratio 20:100, 400 °C) and La-I-TiO₂ (Molar Ratio 20:20:100, 400 °C)

catalysts	O/Ti	O 1s _{1/3}		O 1s _{2/3}		O 1s _{3/3}	
		BE (eV)	area (%)	BE (eV)	area (%)	BE (eV)	area (%)
I-TiO ₂	2.79	529.8	49.8	531.1	20.9	528.6	29.3
La-I-TiO ₂	3.42	530.3	72.2	532.2	14.4	528.7	13.4

and La-I-TiO₂ (molar ratio 20:20:100, 400 °C). The greater total oxygen content of La-I-TiO₂ might be caused by the presence of La₂O₃ on the surface of the photocatalyst after La doping. Moreover, in contrast to the literature,^{22,23} splitting of La 3d_{5/2} and La 3d_{3/2} was observed in our sample. The interpretation of this splitting in the oxide is now widely accepted to be due to configuration effects in the final state of La.²⁴ Therefore, La does exist in the resulting photocatalyst as the oxide La₂O₃.

Figure 5 shows the UV-vis diffuse reflectance spectra for powder samples with various doping contents calcined at different temperatures. The two La-I-TiO₂ samples (molar ratios 20:20:100 and 30:20:100) calcined at 400 °C have obvious absorption in the visible light range of 400–550 nm, and the steep shape of the spectrum indicates that the visible light absorption is not due to the transition from the impurity level but to the band gap transition.²⁵ The shifts of absorption edges to the visible region result from doping I to TiO₂.⁹ With increased La doping into I-TiO₂, the absorption edge shifted to a shorter wavelength region because of the white color of La₂O₃ deposited on the surface of I-TiO₂. The band gap of 2.64 eV for La-I-TiO₂ (molar ratio 20:20:100; 400 °C) was estimated according to the absorption edge.²⁶ The calcination temperature also affected the light absorption in the visible region (Figure 5).

Photocatalytic Activity. We compared the photocatalytic activities of La-I-TiO₂ and I-TiO₂ (400 °C) under visible light, and the results are shown in parts a and b of Figure 6. It seems clear that the photocatalytic degradation of oxalic acid is improved significantly when La is doped in I-TiO₂. As reported, I-TiO₂ is a visible light-activated photocatalyst, and according to the catalyst characterization, La₂O₃ was deposited on the surface of the I-TiO₂ in La-I-TiO₂. So, we consider that the increased photocatalytic degradation of oxalic acid

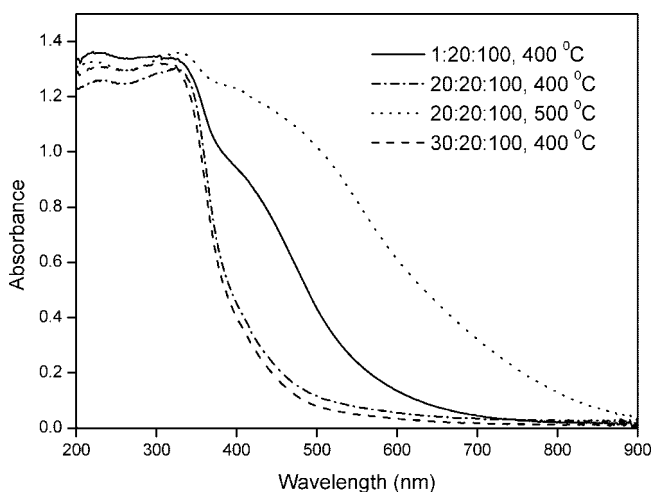


Figure 5. UV-vis diffuse reflectance spectra of La-I-TiO₂ (molar ratios 1:20:100, 20:20:100, and 30:20:100) calcined at 400 °C and La-I-TiO₂ (molar ratio 20:20:100) calcined at 400 and 500 °C.

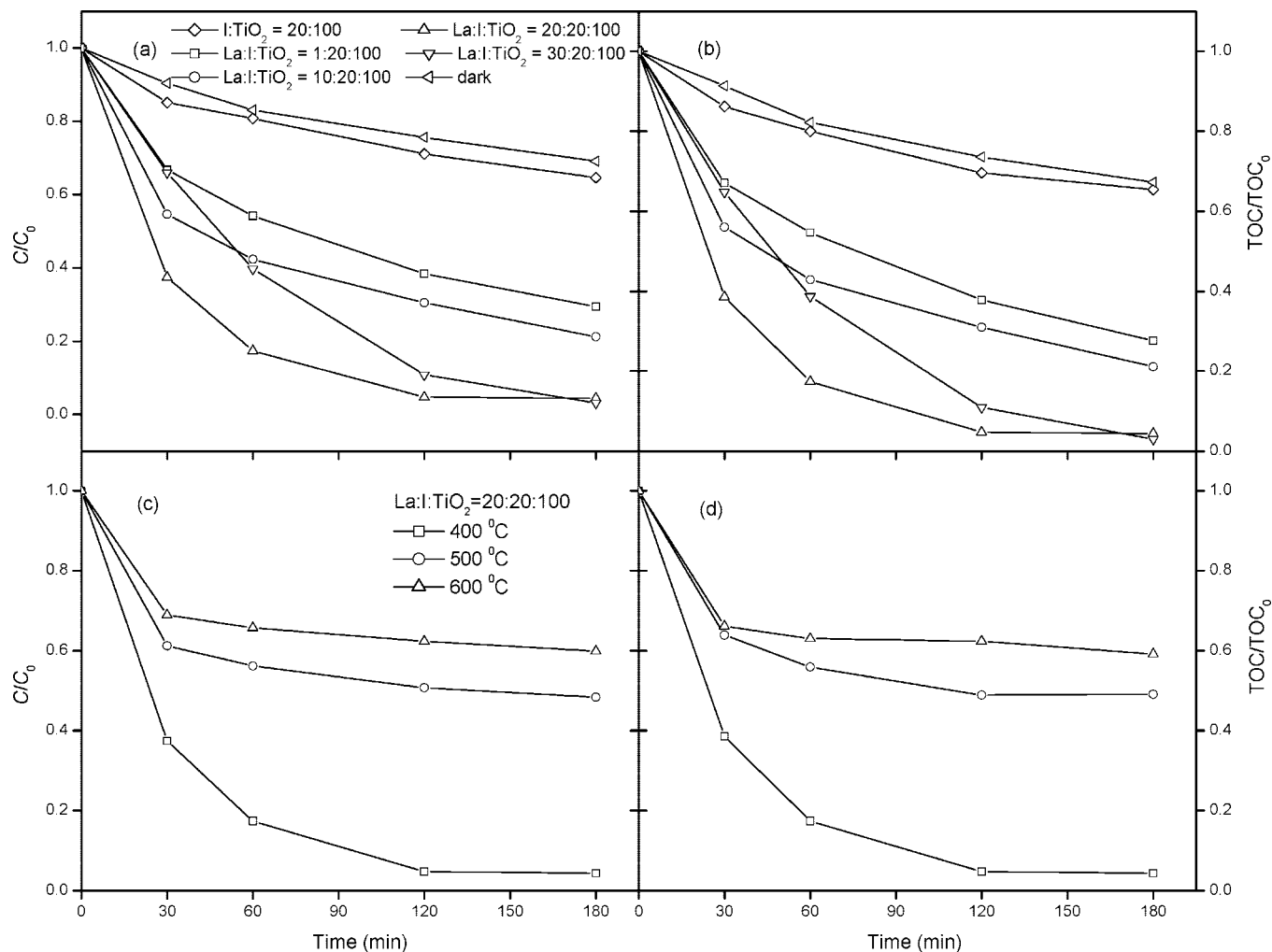


Figure 6. Comparison of the change of concentration and the TOC removal of oxalic acid in the presence of I-TiO₂, La-I-TiO₂ (a, b), La-I-TiO₂ (400 °C) with different La/Ti molar ratios (a, b), La-I-TiO₂ (molar ratio 20:20:100) calcined at 400, 500, and 600 °C (c, d) and without photocatalyst under visible light irradiation or in the presence of La-I-TiO₂ (molar ratio 20:20:100, 400 °C) in the dark (a, b).

activity by La-I-TiO₂ may be due to the dopant La acting as barrier and thus facilitating charge carrier separation,²¹ which is in accordance with the XPS explanation.

To evaluate the effects of La content on photocatalytic activity, we carried out a set of tests to degrade oxalic acid in water by using La-I-TiO₂ (400 °C) with different molar ratios of La/Ti. Parts a and b of Figure 6 show the efficiency of the photocatalytic degradation of oxalic acid during 180 min of illumination under visible light. The degradation efficiency increased with La/Ti content from a molar ratio of 1:100 to 20:100 and then remained almost constant, and the molar ratio was 30:100 after reaction for 180 min. Meanwhile, the TOC removal rate, which was used to prove the total mineralization of oxalic acid, displayed a similar trend.

The superior photocatalytic activity of La-I-TiO₂ (molar ratio 20:20:100) calcined at 400 °C indicates that there is an optimum doping content of La in TiO₂ for the most efficient inhibition of the recombination of electron-hole pairs. Both negative and positive effects on the separation of electron-hole pairs occur with respect to the doping content of La. As the doped La content increases, the surface barrier becomes higher, and hence the space charge region becomes narrower, and the electron-hole pairs within the region are separated efficiently by the large electric field before recombination. However, when the doped La content is too high, the space charge region becomes very narrow and the depth of penetration of light into

TiO₂ greatly exceeds the space charge layer, and recombination of the photoinduced electron-hole pairs becomes easier.²¹ Consequently, there is an optimum concentration of dopant La to make the thickness of the space charge layer substantially equal to the depth of light penetration.

The calcination temperature is a crucial factor in determining the photocatalytic activity (parts c and d of Figure 6). La-I-TiO₂ (molar ratio 20:20:100) calcined at 400 °C had a significantly higher level of photocatalytic activity than La-I-TiO₂ (molar ratio 20:20:100) calcined at 500 °C and La-I-TiO₂ (molar ratio 20:20:100) calcined at 600 °C. After reaction for 180 min under visible light with La-I-TiO₂ (molar ratio 20:20:100, 500 °C) and La-I-TiO₂ (molar ratio 20:20:100, 600 °C) the concentration of oxalic acid was decreased by ~52 and 40%, respectively, while the TOC removal rate was decreased by ~51 and 41%, respectively. Other catalysts doped with different La content and calcined at 500 and at 600 °C had similar photocatalytic rates of oxalic acid degradation, which were not higher than 52% (data not shown). The anatase structure is predominant in our sample, and when the calcination temperature is increased the samples have larger surface area, which allows exposure of more active sites to the targeted reactants.²⁷ This suggests that the LaTi₂O₃₈ formed during calcination at 500 and 600 °C may be responsible for the inferior photocatalytic activity.

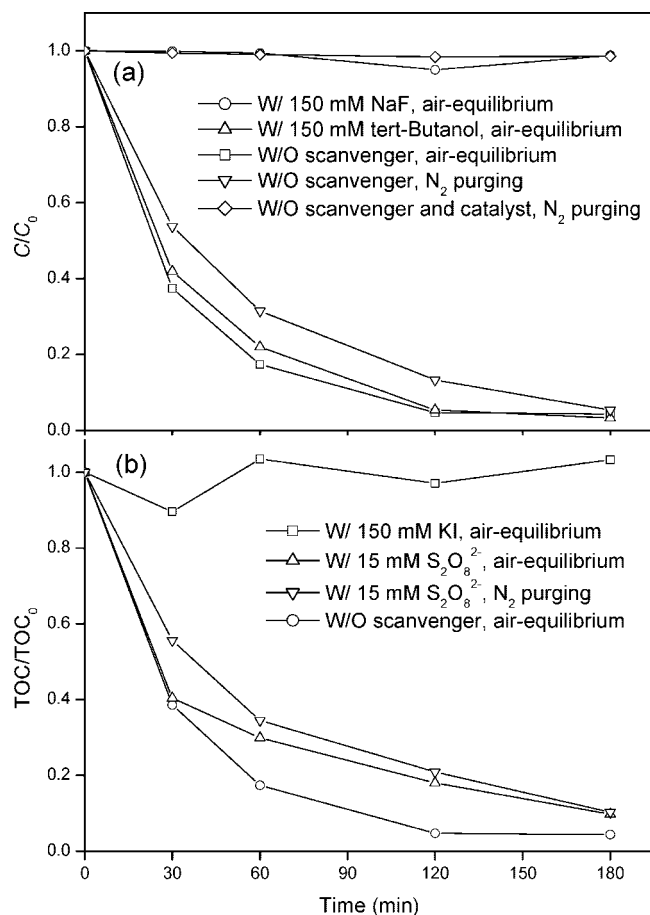
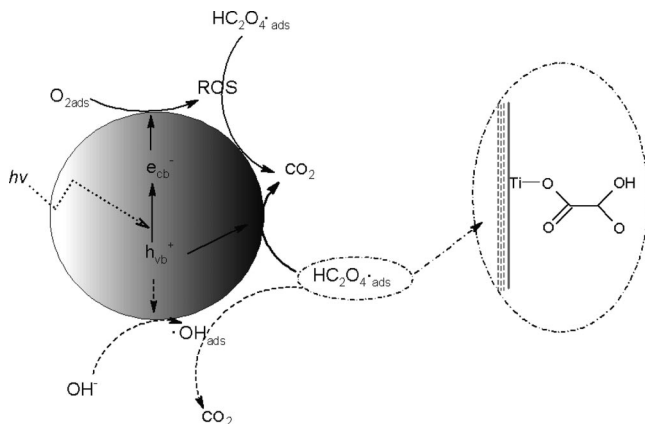


Figure 7. The change of concentration of oxalic acid in the absence of photocatalysts with N₂ purging and in the presence of La–I–TiO₂ (molar ratio 20:20:100, 400 °C) under visible light irradiation with scavengers in air equilibrium systems, without scavengers in air equilibrium systems, with S₂O₈²⁻ in N₂ purging systems, and without scavengers in N₂ purging systems.

SCHEME 1: Illustration of the Simplified Pathways for Oxalic Acid Degradation on Catalyst Under Photocatalytic Condition and Surface Complex Formed by the Chemisorption of Oxalate onto Catalyst



Possible Reaction Process. Information regarding the pathway of photocatalytic reaction may be provided by determining the influence of different scavengers and N₂ purging on the rate of degradation of oxalic acid as shown in parts a and b of Figure 7. Oxalic acid is mainly in the HC₂O₄⁻ form at the pH used in our experiment (~2.9). Fluoride has strong adsorption on the surface of TiO₂ catalysts. Thus, the surface-bound or adsorbed

•OH radicals (•OH_{ads}) and adsorbed oxalic acid (HC₂O₄⁻_{ads}) on the surface of TiO₂ were almost replaced by F⁻.^{28,29} The rate of degradation of oxalic acid was inhibited strongly by the presence of 150 mM NaF, which can be explained by the fact that oxalic acid has preferential adsorption on the surface of catalysts before degradation.

The photocatalytic degradation of oxalic acid was inhibited greatly by the addition of 150 mM KI, which is a scavenger and reacts with valence band holes (h⁺_{vb}) and •OH_{ads},^{30,31} indicating that the h⁺_{vb} and •OH_{ads} pathways may have important roles in the mechanism of oxalic acid oxidation. Whether the •OH in the bulk solution that was the dominant oxidant in most TiO₂ photocatalytic reactions was involved in the degradation of oxalic acid was tested by comparing the photocatalytic oxidation of oxalic acid in the presence and in the absence of tert-butanol (an •OH scavenger in the bulk solution).³² As shown in Figure 7a, adding tert-butanol to a final concentration of 150 mM did not change the degradation rate, implying that •OH in the bulk solution was not involved in the photocatalytic oxidation of oxalic acid.

A blank control was done using purging with N₂ without photocatalyst, and the result shows that the concentration of oxalic acid was not decreased. The solution with photocatalysts purged with N₂, which decreased the dissolved oxygen level from 0.15 mM to 0.01 mM, had a slower rate of oxalic acid removal than that in the air-equilibrated solution. This indicates that the effects of oxygen cannot be discounted. Experiments were done using the conduction band electron (e_{cb}⁻) scavenger S₂O₈²⁻, which is a more efficient e_{cb}⁻ acceptor than molecular oxygen.^{33,34} As shown in Figure 7b, 15 mM K₂S₂O₈ had a non-negligible effect on the degradation of oxalic acid either in air equilibrium or in N₂ purging systems, suggesting that the e_{cb}⁻ mechanism is effective for the degradation of oxalic acid. The presence of oxygen prevents the electron–hole recombination by trapping electrons through the formation of reactive oxygen species (ROS) to finally degrade oxalic acid.^{35,36} Furthermore, by use of gas chromatography/mass spectrometry we identified intermediate compounds during the photocatalytic degradation of oxalic acid, and no stable intermediate was detected, indicating that oxalic acid was oxidized directly into carbon dioxide and water. Scheme 1 illustrates the process of photocatalysis over La–I–TiO₂.

Conclusions

The present study demonstrated that titanium dioxide codoped with lanthanum and iodine shows a high level of visible-light-catalyzed activity in aqueous oxalic acid solution. I⁵⁺ substituted for Ti⁴⁺ in a titania matrix has an important role in determining the photocatalytic activity in the visible light range, and the dopant La in the form of La₂O₃ deposits on the surface further suppresses the recombination of electron hole. We believe that with further investigation and improvement this photocatalyst will be worthy of further application in the degradation of other organic contaminants in wastewater utilizing solar energy efficiently.

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Supporting Information Available: The XPS spectra in the core level of Ti 2p_{3/2} and O 1s of I–TiO₂ (molar ratio 20:100, 400 °C) and La–I–TiO₂ (molar ratio 20:20:100, 400 °C). This

information is available free of charge via the Internet at <http://pubs.acs.org>.

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