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**Role of lanthanum species in improving the
photocatalytic activity of titanium dioxide**

Wai Ruu Siah,^a Hendrik O. Lintang^{ab} and Leny Yuliaty^{ab*}

Series of lanthanum-modified TiO₂ catalysts were prepared by a UV photodeposition method to exclude any heat treatments that may affect the properties and photocatalytic activity of TiO₂. Results showed that the lanthanum modification did not significantly affect the properties of TiO₂, but increased the formation of [•]OH under UV light irradiation; the activity for 2,4-D decomposition rose by a maximum factor of 5.5 when TiO₂ was loaded with 5 mol% La; further increase of La deposition led to a decrease in photocatalytic activity. From the electrochemical impedance and photocurrent results, it was shown that the positive influence of La on TiO₂ photocatalytic activity was caused by the increased charge separation in the TiO₂ photocatalysis, owing to the additional formation of [•]OH states. On the other hand, when tested with the colourless 2,4-D model pollutant under visible and solar simulator irradiation, the presence of lanthanum species did not improve the photocatalytic activity of TiO₂ significantly. Hence, it was shown that lanthanum species only improved the UV photocatalytic activity of TiO₂.

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Introduction

In recent years, photocatalytic degradation has attracted considerable attention as this approach could be used to remove organic pollutants, hence providing a promising solution for wastewater treatment and purification of polluted air. Titanium dioxide (TiO₂) is one of the main photocatalysts used for this purpose due to the strong oxidizing power of its photogenerated holes, its chemical stability, non-toxicity and low cost.¹ However, the photocatalytic performance of TiO₂ was limited by the fast recombination of its photogenerated electrons and holes. Transition metal oxide²⁻⁴ and rare earth metal oxide⁵⁻⁷ co-catalysts supported on TiO₂ have been found to enhance the photocatalytic activity of TiO₂. Among the rare earth elements, lanthanum oxide⁸⁻¹⁰ is considered as a suitable co-catalyst due to its ability to suppress electron-hole recombination of TiO₂ and its relative abundance. To date, there are numerous reports on the effects of lanthanum modifications on the photocatalytic activity of TiO₂, either under UV¹¹⁻¹⁵ visible¹⁶⁻²⁰ or solar²¹⁻²³ irradiation. While all studies reported the enhanced activity under UV light, there are some contradictions on the effect of lanthanum species on the visible light activity of TiO₂. Some studies showed that lanthanum modification of TiO₂ led to the occurrence of visible light ac-

tivity of TiO₂,¹⁴⁻¹⁶ while others reported that the added lanthanum did not contribute to the photocatalytic activity of TiO₂ under visible light irradiation.²⁴⁻²⁷ Taking into account that visible light is the main component of solar light, in contrast all papers reported the beneficial effect of lanthanum species in improving the activity of TiO₂ under solar irradiation.²⁸⁻³⁰

Besides the contradicting activity enhancement between those under visible and solar light, there is also unclear discussion on the role of lanthanum species in improving the activity of TiO₂ photocatalysts. In these reported studies, the La-modified TiO₂ photocatalysts were prepared by sol-gel,^{14,16-18,20,23,25-27} co-precipitation,¹⁷ hydrothermal synthesis,^{19,22} cathodic electrochemical processes,²¹ and impregnation methods,¹⁵ which generally involved calcination of the La-TiO₂ catalysts at high temperatures (200–800 °C). Due to the use of high temperatures, the properties of TiO₂, such as the crystallite size,³¹⁻³³ anatase-rutile ratio^{34,35} and anatase-rutile ratio^{36,37} were affected. Since these properties also contributed to the photocatalytic activity of TiO₂, the role of lanthanum species alone in improving the photocatalytic activity of TiO₂ might not be addressed correctly.

In order to directly investigate the role of the lanthanum species, a synthesis method that does not involve heat treatment shall be employed. One of the promising methods for deposition of lanthanum oxide on the surface of TiO₂ without any heat treatments is UV photodeposition. This method is recognized as an effective and environmentally friendly method as it could be carried out at room temperature under mild experimental conditions. The photodeposition process involves the photodecomposition of metal precursors in the

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presence of TiO₂ and UV irradiation, releasing metal ions that in turn interact with the surface of TiO₂.

In the present study, we deposited the lanthanum oxide on the TiO₂ support *via* a simple UV photodeposition method conducted at room temperature. Such mild synthesis temperature allowed us to investigate the role of lanthanum species while excluding the effects of other factors⁴⁴ aforementioned. The photocatalytic activity of the catalysts was evaluated for the degradation of 2,4-dichlorophenoxyacetic acid (2,4-D), which is a colourless pollutant, under UV, visible, and solar simulator irradiation. The colourless 2,4-D was selected to avoid the possibility that the enhancement in the activity was caused by the effect of pollutant sensitization when the reaction was performed under visible or solar light irradiation. This study demonstrated that under UV irradiation, La-modified TiO₂ showed an excellent photocatalytic activity compared to the unmodified TiO₂³⁷ while such enhancement was not observed for reactions under visible and solar²⁷ light irradiation, suggesting that the lanthanum species did not contribute to the visible light activity.

Experimental

Preparation of La_{ox}/TiO₂ photocatalysts

The series of La oxide-modified TiO₂ catalysts were prepared by a UV photodeposition method. Hombikat UV100 TiO₂ (HK UV100) was used as-received from Sachtleben Chemie. In the first step, the required amount of lanthanum(III) acetylacetonate hydrate (TCl, >98⁷³) was combined with HK UV100 TiO₂ (1 g) and added⁹⁰ to 20 mL of water/ethanol mixture (1:1 v/v) in a beaker (100 mL). The mixture was sonicated for 5 min to obtain a homogeneous suspension, followed by exposure to a UV lamp (200 W, $\phi_1 = 8 \text{ mW cm}^{-2}$) from the top for 5 h under ambient conditions. The irradiated mixture was then centrifuged (3500 rpm, 20 min) to collect the solid³⁶ sample. After rinsing with ethanol and distilled water, the sample was dried in⁶ oven overnight at 80 °C and ground to a fine powder. The samples were denoted as La_{ox}(x)/TiO₂, where x represented the ratio of added La to TiO₂ (0.1–10 mol%).

Characterization of photocatalysts⁸⁹

The diffraction patterns of the samples⁴³ were recorded by X-ray diffraction (XRD; Br²³ker D8 Advance diffractometer) at room temperature, using Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 40 mA. The data were measured in the 2θ range of 20 to 80°. The crystalline phases were matched with the reference patterns from the International⁵ Centre for Diffraction Data (ICDD) database. The mean crystallite sizes of the unmodified TiO₂ and La_{ox}/TiO₂ sample⁷² were calculated by using the Scherrer equation.^{14,19–22,34,38} A Shimadzu UV-2600 spectrophotometer equipped with an integrated sphere³⁵ used to obtain the diffuse reflectance ultraviolet-visible (DR UV-vis) spectra of the samples. The spectra were collected in the range⁷¹ of 220 to 800 nm under ambient conditions, using BaSO₄ as the reference. The absorption spectra were obtained by transformation of the reflectance data on the Kubelka-

Munk function. All spectra were arbitrarily normalized to the²¹ density of 1.0 for comparison. The bandgap energies of the samples were determined from the extrapolation of the linear fit for the Tauc plot onto the photon energy axis.^{14,18,39}

The amount⁵¹ of lanthanum present in the La_{ox}/TiO₂ photocatalysts was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES)⁵⁰ using an Agilent Technologies 700 series spectrometer. Transmission electron microscopy (TEM) was used to²⁰ investigate the morphology of the catalysts. The sample was dispersed in ethanol and a drop of the suspension was deposited on a carbon-coated copper grid and allowed to dry under ambient conditions. The prepared⁴² samples were then viewed using a JEOL JEM-2100 TEM at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) spectra were measured using a Kratos Axis Ultra system with monochromatic Al K α X-rays (1486.6 eV) operated at 10 W and 15 kV with a background pressure of approximately 5.0×10^{-9} Torr. Survey spot size and 20 eV pass energy were used for the measurement. Photoelectrons emitted perpendicularly to the sample surface were recorded.⁷ A charge neutralizer was used and all the binding energies were calibrated with respect to the adventitious contamination hydrocarbon C_{1s} peak at 284.6 eV.

The photocurrent and the electrochemical impedance (EIS) data were measured with an Interface1000 potentiostat/galvanostat (Gamry Instruments Inc.) on the⁸⁸ Gamry Framework software. The catalyst sample (10 mg) was dispersed in 5 mL of deionized water and sonicated for 10 min to form a homogeneous suspension. For the photocurrent measurements, 200 μL of the suspension was pipetted onto an indium tin oxide (ITO) coated glass slide ($1.5 \times 1.5 \text{ cm}$) and allowed to dry under ambient conditions. The photocurrent was recorded by a standard three-electrode configuration *via* the chronoamp¹⁶metry method, with the as-prepared sample⁴¹ coated ITO as the working electrode, Pt wire as the counter electrode and Ag/AgCl (satur⁴⁰: 3 M NaCl) electrode as the reference electrode. The potential of the working electrode against the Pt counter el⁴⁹ectrode was fixed at 0 V. A 60 mL volume of 0.1 M Na₂SO₄ solution was used as the electrolyte. The light source used was a 200 W Xe-Hg UV lamp, and the light intensity on the photoanode was fixed at 8 mW cm^{-2} . All photocurrent measurements were carried out under ambient conditions. For the EIS measurements, 20 μL of the catalyst suspension (10 mg catalyst per 5 mL deionized water) was dropped onto a screen-printed electrode (SPE) and allowed to dry in air before measurements. The EIS measurements were performed in 0.1 M Na₂SO₄ electrolyte (6 mL), along with the presence of 2.5 mM K₃[Fe(CN)₆]²⁶ the redox probe. The impedance spectra were measured under an AC perturbation signal of 10 mV over the frequency range of 1 MHz to 0.1 Hz.

Photocatalytic activity studies¹¹

The photocatalytic activity of the unmodified TiO₂ and La-modified TiO₂ catalysts was evaluated by using photocatalytic

degradation of 2,4-D as a model reaction. The photocatalyst⁸⁷ used was a top-irradiation reactor. Firstly, the catalyst⁵⁰ (mg) was dispersed in 50 mL 2,4-D solution (0.5 mM, Sigma, $\geq 98\%$). The suspension was then stirred under dark conditions for 1 h to reach absorption–desorption equilibrium. While under continuous stirring, the mixture was then exposed for 1 h to a 200 W UV lamp (Hamamatsu, Lightningcure™ LC8, L10852) with a cut off filter that removed emission above 400 nm. The light intensity at 365 nm near the surface of the 2,4-D solution was fixed at 8 mW cm⁻². In order to provide sufficient oxygen for the oxidative degradation of 2,4-D, all reactions were made open to air. The photocatalytic activity of the catalysts was also investigated under solar simulator (Peccell Technologies) irradiation under the same conditions, whereby a 150 W Xenon short arc lamp with an A.M 1.5 G filter was used and the reaction time was 3 h. Photocatalytic activity testing was also performed under visible light conditions, a filter that cuts off wavelengths <400 nm was fitted with the solar simulator. All reaction conditions were kept constant, with the exception of the reaction time, which was set to 6 h for the visible light irradiation reactions. When the reaction⁶³ was completed, about 3 mL of suspension was taken and filtered using a 0.2 μ m nylon membrane filter.⁴⁸ The amount of 2,4-D degraded after UV lamp irradiation was measured by a high performance liquid chromatograph (HPLC, Shimadzu Prominence LC-20A) equipped with a 150 \times 4.6 mm Hypersil GOLD PFP column and the eluent was a mixture of acetonitrile/H₂O 60:40 (v/v), whereby the concentration of 2,4-D was monitored at 283 nm. In order to investigate the long-term photocatalyst activity, La_{ox}(5)/TiO₂ was used to degrade the 2,4-D solution over four cycles. After the first run (UV light irradiation for 6 h)⁶² the solution was centrifuged and the photocatalyst was washed with deionised water and dried at 80 °C overnight. The recovered photocatalyst was subsequently used to degrade a fresh 2,4-D solution under the same reaction conditions for 6 h. The third and fourth cycles were also carried out under the similar process conditions.

Results and discussion

The powder⁶¹ XRD patterns of the unmodified TiO₂ and the La_{ox}/TiO₂ samples with different amounts of lanthanum loadings are shown in Fig. 1. The⁸⁶ UV100 TiO₂ showed the typical diffraction pattern of a pure anatase phase (JCPDS file no.: 21-1272). All the La_{ox}/TiO₂ samples also exhibited⁶⁰ the same diffraction pattern of the anatase phase, indicating that the loading of lanthanum oxide has no appreciable effect on the crystal structure of TiO₂. Characteristic diffraction lines of La₂O₃ were also not detected even in the sample with the highest lanthanum content, further indicating a high degree of dispersion⁵⁹ of lanthanum oxide, which might have formed small clusters on the surface of TiO₂.⁸

The average TiO₂ crystallite size of the samples was estimated based on the Scherrer equation with a line width analysis of the anatase (101) diffraction peak and the values are

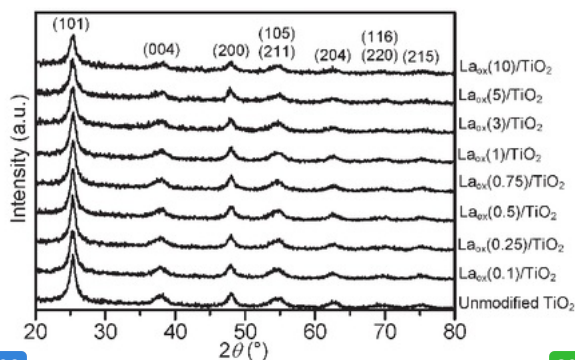


Fig. 1 Powder XRD patterns of the unmodified and La-modified TiO₂ samples.

shown in Table 1. It can be seen from Table 1 that the crystallite size of the unmodified TiO₂ and La_{ox}/TiO₂ samples was in the range of 8 to 10 nm. The unaffected crystal phase and crystallite size clearly³ demonstrated that under the current synthesis conditions, La³⁺ did not enter the TiO₂ crystal lattice to substitute for Ti⁴⁺. This was reasonable since the radius of La³⁺ (1.15 Å) was much larger than that of Ti⁴⁺ (0.64 Å).⁸⁵

Table 1 also displays the lanthanum contents of the unmodified TiO₂ and La_{ox}/TiO₂ samples that were estimated with ICP-OES. For samples with low loadings of La (0.1–5 mol%), the added nominal La loadings were found to be similar to the actual loading measured from ICP-OES. On the other hand, the high loading sample (10 mol%) has a lower measured La content, suggesting that UV lamp exposure might not be sufficiently long to completely deposit all the lanthanum acetylacetonate hydrate precursor.

Shown in Fig. 2(a) are the ultraviolet-visible (UV-vis) absorption spectra of the unmodified TiO₂ and the La_{ox}/TiO₂ samples. The characteristic band edge⁹ for titanium dioxide appeared at about 370 nm, which is associated with the O²⁻(2p) → Ti⁴⁺(3d) charge transfer process and related to electron excitation from the valence band (VB) to the conduction band (CB) of TiO₂.^{41,42} It was obvious that¹⁹ after modifications with lanthanum oxide, TiO₂ did not display extended absorption into the visible region in the range of 400 to 800 nm. The bandgap of the samples was estimated by the Tauc plot, [($\alpha h\nu$)^{1/2} versus $h\nu$, where α is the absorbance]^{14,18,39} whereby the extrapolation of the linear part of² the curve gives direct values of the bandgap. The Tauc Plots are shown in Fig. 2(b) and the estimated bandgap values are listed in Table 1. The unmodified HK UV100 sample has a bandgap of about 3.33 eV. The lanthanum-modified samples showed a similar bandgap value²⁵ to the unmodified TiO₂, in the range of 3.28–3.34 eV. Since there is no significant shift in the bandgap and no absorption in⁷⁰ the visible range, it can be concluded that La³⁺ ions were not incorporated into the crystal lattice of TiO₂. As discussed above, the ionic radius of the La³⁺ species is too large to substitute for⁸⁴ Ti⁴⁺ in the lattice of TiO₂. Thus, they are considered to be dispersed on the surface of the TiO₂ particles.²⁹

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Table 1 Crystallite size, lanthanum content and bandgap energy of the unmodified and La-modified TiO₂ samples

| Samples | Crystallite size ^a (nm) | Amount of loaded La ^b (mol%) | Bandgap ^c (eV) |
|--|------------------------------------|---|---------------------------|
| Unmodified TiO ₂ | 9.3 | 0.00 | 3.33 |
| La _{ox} (0.1)/TiO ₂ | 8.3 | 0.12 | 3.30 |
| La _{ox} (0.25)/TiO ₂ | 9.9 | 0.22 | 3.28 |
| La _{ox} (0.5)/TiO ₂ | 8.8 | 0.46 | 3.28 |
| La _{ox} (0.75)/TiO ₂ | 8.3 | 0.69 | 3.30 |
| La _{ox} (1)/TiO ₂ | 8.8 | 0.91 | 3.30 |
| La _{ox} (3)/TiO ₂ | 8.8 | 2.67 | 3.32 |
| La _{ox} (5)/TiO ₂ | 9.9 | 4.44 | 3.32 |
| La _{ox} (10)/TiO ₂ | 9.9 | 7.82 | 3.34 |

^a Estimated from a full width at half maximum (FWHM) of the XRD anatase (101) reflection by the Scherrer equation. ^b Estimated from ICP-OES. ^c Estimated using the Tauc plot of DR UV-vis data.

TEM studies provided some relevant information on the particle size and morphology of the samples. Fig. 3(a) and (b) show representative images obtained from the unmodified TiO₂ and La_{ox}(5)/TiO₂. In both cases, the samples appeared similar in both size and morphology. No distinct lanthanum oxide particles were observed from the TEM analysis. The La₂O₃ particles were likely to be highly dispersed on the surface of the TiO₂ support. As a result, the La₂O₃ clusters were too small to be observed, which supported the XRD results.

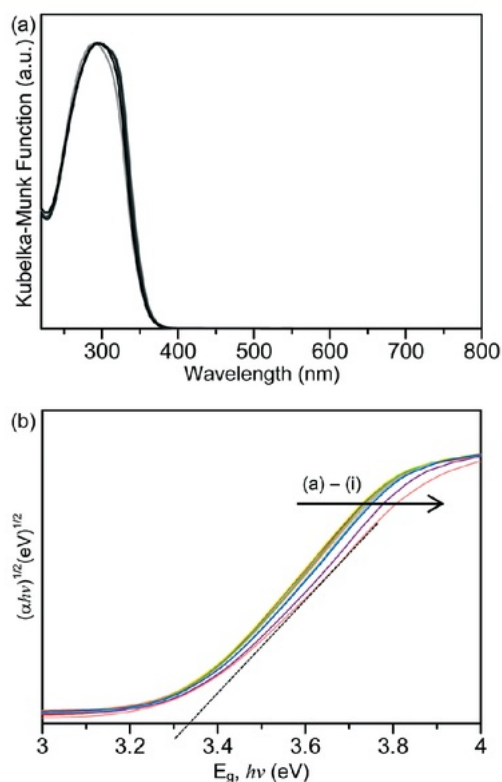


Fig. 2 (a) Absorption spectra and (b) Tauc plot of the unmodified and La-modified TiO₂ samples. Key: (a) La_{ox}(0.5)/TiO₂, (b) La_{ox}(0.25)/TiO₂, (c) La_{ox}(0.1)/TiO₂, (d) La_{ox}(1)/TiO₂, (e) La_{ox}(0.75)/TiO₂, (f) La_{ox}(3)/TiO₂, (g) La_{ox}(5)/TiO₂, (h) La_{ox}(10)/TiO₂ and (i) unmodified TiO₂.

More detailed information regarding the elemental and chemical states of the unmodified TiO₂ and La_{ox}(5)/TiO₂ samples was also ascertained by analyzing the X-ray photoelectron spectroscopy (XPS) data. The full scan survey spectra (Fig. 4(a) and (b)) showed that the Ti, O and C elements were present on the surface of the unmodified TiO₂ sample, while Ti, O, C and La were identified on the surface of the La_{ox}(5)/TiO₂ sample. The C element detected could be ascribed to the adventitious carbon-based compounds, mostly coming from the carbon tape. The high resolution XPS spectra of La 3d, Ti 2p and O 1s are displayed in Fig. 4(c)–(e).

Regarding the La 3d core level spectra (Fig. 4(c)), a splitting of the La 3d_{5/2} and La 3d_{3/2} lines was observed around 834.6 and 851.4 eV, respectively. The peaks at 834.6 and 851.4 eV are identified as the main peaks, and the peaks at 838.8 and 855.6 eV are ascribed to the shake-up satellite peaks of La 3d_{5/2} and La 3d_{3/2}. As reported in previous works, this La XPS profile indicates the presence of lanthanum oxide species, such as La₂O₃.^{15,16,23,24,34,42} In addition to the peak

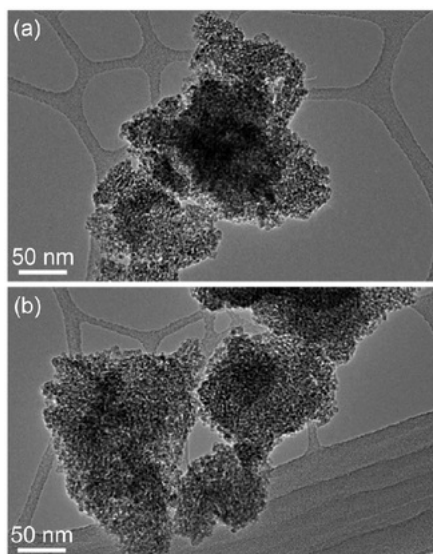


Fig. 3 TEM images of (a) unmodified TiO₂ and (b) La_{ox}(5)/TiO₂ samples.

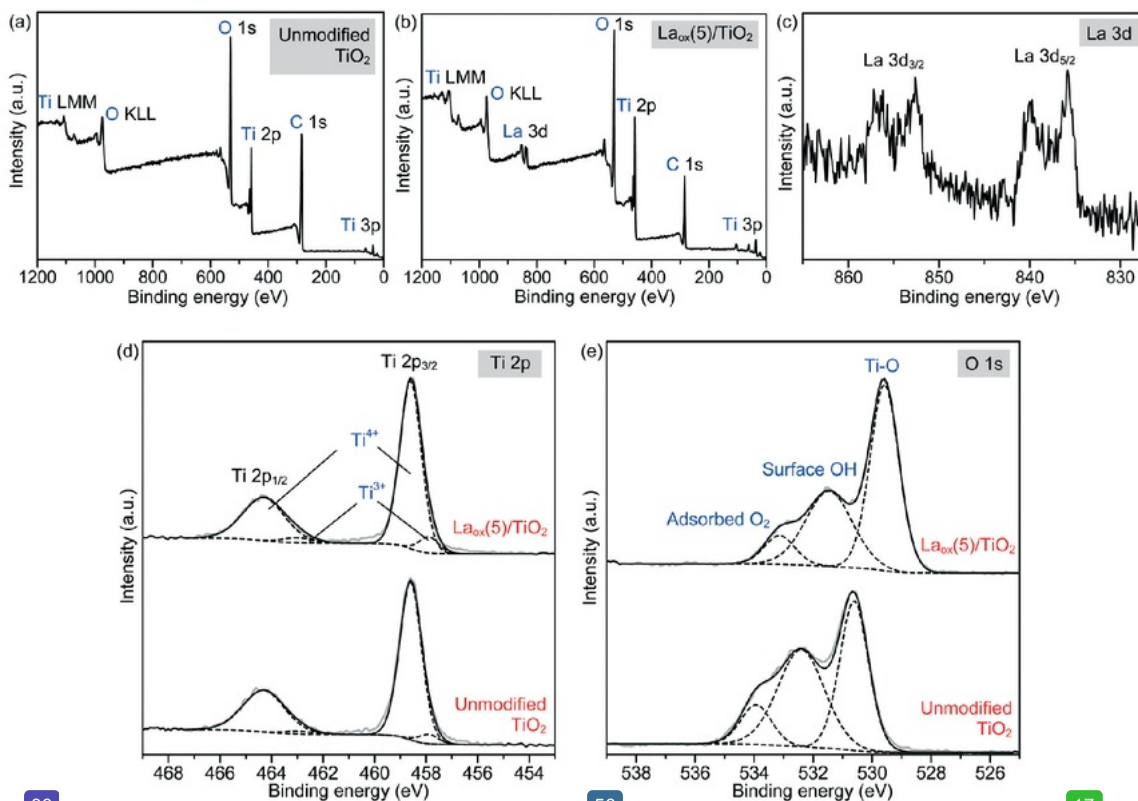


Fig. 4 XPS survey spectra of (a) unmodified and (b) $\text{La}_{\text{ox}}(5)/\text{TiO}_2$ samples. The high resolution XPS spectra of the (c) La 3d region, (d) Ti 2p region and (e) O 1s region of the unmodified and $\text{La}_{\text{ox}}(5)/\text{TiO}_2$ samples. Key for (d) and (e): grey solid line = measured data, black solid line = overall model fit, black dashed line = decomposed components.

position and splitting, the binding energy difference between the main and satellite peaks (ΔE) in the multiplet split can be used to distinguish La_2O_3 from other La^{3+} compounds. It has been reported that the ΔE values for La_2O_3 are in the range of 3.9–4.5 eV for the La 3d_{5/2} spectrum.⁴³ The $\text{La}_{\text{ox}}(5)/\text{TiO}_2$ sample gave a ΔE of 4.2 eV, clearly suggesting that the La species in the sample was La_2O_3 . The photodeposition of La_2O_3 is feasible owing to the oxidative conditions used in this study, as has been also reported to occur in the oxidative photodeposition of Rh_2O_3 ⁴⁴ and CuO .⁴⁰ Since the photodeposition of oxide particles would not occur in the absence of UV light irradiation and oxygen,⁴⁴ the main species to oxidize the lanthanum precursor to form La_2O_3 would be the photogenerated oxygen radicals. The proposed reaction is shown in the following equation.

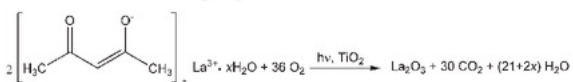


Fig. 4(d) shows the Ti 2p spectrum of the unmodified TiO_2 and $\text{La}_{\text{ox}}(5)/\text{TiO}_2$, each consisting of two obvious peaks at about 458.6 and 464.3 eV, which were assigned to $\text{Ti}_{2p_{3/2}}$ and $\text{Ti}_{2p_{1/2}}$, indicating that titanium predominantly existed in the core level in a Ti^{4+} chemical state. By using the CasaXPS

peak fitting program, the XPS peak for $\text{Ti}_{2p_{3/2}}$ was further resolved into two components at binding energies of 458.6 and 457.6 eV, which were ascribed to Ti^{4+} and Ti^{3+} species, respectively.^{9,46} It was obvious that the Ti^{4+} was the dominant surface state, with a small quantity of Ti^{3+} states.⁴⁷ Upon modification with 5 mol% La, the Ti^{3+} increased by approximately 62% from 4.75 to 7.69%. This result suggests that the presence of La might have led to the additional formation of Ti^{3+} valence states, in good agreement with previously reported studies.^{9,16,42}

The high resolution XPS O 1s spectra of the unmodified TiO_2 and $\text{La}_{\text{ox}}(5)/\text{TiO}_2$ are shown in Fig. 4(e). The wide and asymmetric O 1s spectra indicate that there was more than one component and they could be further decomposed into three peaks, which are the crystal lattice oxygen ($\text{O}_{\text{Ti-O}}$ at 529.6–530.6 eV), surface hydroxyl groups ($\text{O}_{\text{O-H}}$ at 531.5–532.4 eV) and adsorbed O_2 (at 533.2–533.9 eV). The binding energies of these three peaks agree well with reported values in the literatures.^{9,23,24,46} As shown in Table 2, the surface hydroxyl groups accounted for 45.7% of the total oxygen species on the surface of the unmodified TiO_2 . After La modification, the proportion of surface hydroxyl groups increased to 36.0%, which may be due to La being trapped on the surface of TiO_2 .^{9,16} Additionally, the O 1s core level peak positions of

Table 2 The O 1s XPS fitting data of the unmodified and La_{ox}(5)/TiO₂ samples. Key: BE = binding energy, O_{Ti-O} = lattice oxygen, O_{O-H} = surface OH

| Catalysts | O _{Ti-O} | | O _{O-H} | | Adsorbed O ₂ | |
|---------------------------------------|-------------------|----------|------------------|----------|-------------------------|----------|
| | BE (eV) | Area (%) | BE (eV) | Area (%) | BE (eV) | Area (%) |
| Unmodified TiO ₂ | 530.6 | 43.6 | 532.4 | 45.7 | 533.9 | 10.7 |
| La _{ox} (5)/TiO ₂ | 529.6 | 55.0 | 531.5 | 36.0 | 533.2 | 9.0 |

the La-modified TiO₂ was slightly shifted to lower binding energy, indicating the presence of interaction between the La species and TiO₂.³⁷

32 Photocatalytic activity

The photocatalytic activities of the La_{ox}/TiO₂ samples were evaluated for 2,4-D-degradation under UV light irradiation as shown in Fig. 5(a). It was confirmed that under the same conditions 2,4-D could not be degraded under UV irradiation in the absence of TiO₂ photocatalysts. In the presence of the unmodified TiO₂ catalyst, 5.3% of 2,4-D was removed after 1 h UV irradiation. Upon lanthanum modification, all of the TiO₂ samples showed improved activity when compared with the unmodified TiO₂ catalyst. In particular, the La_{ox}(5)/TiO₂ catalyst showed the highest photocatalytic activity, approximately 5.5 times more active than the unmodified TiO₂ catalyst. The results indicated that the photocatalytic performance of TiO₂ could be significantly enhanced by the presence of lanthanum oxide species. With a La loading above 5 mol%, the decrease of photocatalytic activity might be due to excessive La₂O₃ covering the surface, which blocked the TiO₂ active sites from UV irradiation. This result agreed well with previously reported works^{7-10,12,13} and similar to the masking effect reported on copper oxide modified TiO₂.⁴⁰

As shown in Fig. 2, the lack of optical absorption of the La-modified TiO₂ photocatalysts in the visible region suggested that La would not assist in improving the visible light absorption of TiO₂. The activity of the La-modified samples was further evaluated by conducting visible light activity testing. The results are shown in Fig. 5(b). The unmodified TiO₂ led to a 1.2% degradation of 2,4-D after 6 h of irradiation. The low activity observed on the unmodified TiO₂ might be originated from defect states that allow for limited visible light activity.^{40,45} The La-modified samples displayed a very similar activity to the unmodified TiO₂, obviously indicating that lanthanum species did not contribute to the visible light activity of TiO₂.

The photocatalytic activity of the catalysts was also evaluated under solar simulator irradiation and the results are shown in Fig. 5(c). The solar simulator consists of mostly visible light, with the presence of a small fraction of UV irradiation. Therefore, the activity trend between visible and solar activity shall be similar to each other. As expected, upon modification with various loadings of La, the activity of the La_{ox}/TiO₂ remained nearly unchanged as compared with the unmodified TiO₂. Further increase of lanthanum loading beyond 1 mol% led to a decrease in photocatalytic activity.

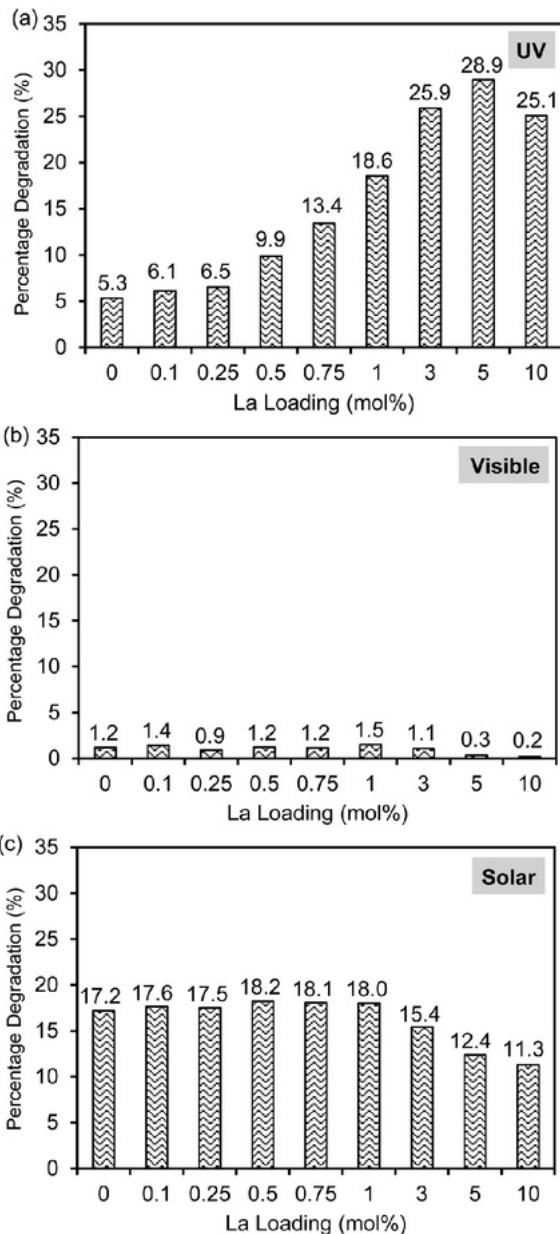


Fig. 5 Photocatalytic activities of unmodified and lanthanum-modified TiO₂ photocatalysts under (a) UV, (b) visible, and (c) solar simulator light irradiation for 1, 6, and 3 h, respectively.

These results supported that La modification did not give rise to the enhancement of TiO₂ visible light activity. In

comparison with previous works that reported the occurrence of visible light activity of La-TiO₂ catalysts, the visible light activity was most likely caused by the photosensitization effect, when organic dyes were used as the model pollutants.^{14,15,19–27}

Four recycle runs of the best photocatalyst, the La_{0.05}(5)/TiO₂ sample, were carried out to investigate the stability of the photocatalyst. The reactions were each carried out under UV light for 6 h. As shown in Fig. 6, the regenerated photocatalyst exhibited good performance and stability. Over all four cycles, the degradation rate of 2,4-D remained almost unchanged compared to the fresh photocatalyst. The consistent photocatalytic performance indicated that the photocatalyst has an excellent long-term stability and good potential for wastewater treatment applications.

The charge separation and transportation characteristics of the unmodified TiO₂ and the best photocatalyst were investigated with EIS. The typical EIS spectra of the unmodified TiO₂ and the La_{0.05}(5)/TiO₂ were presented as Nyquist plots and simulated with the equivalent circuit. As shown in Fig. 7(a), each sample exhibited a partial semicircle at the high-frequency region of the EIS measurement. Upon the introduction of lanthanum species, the diameter of the semicircle in the plot became smaller, which indicated a decrease in the charge transfer resistance on the TiO₂ surface.²³ Furthermore, model fitting (with the constant phase element (CPE) with a diffusion model) revealed a lower charge transfer resistance value of the La_{0.05}(5)/TiO₂ sample (2.65 kΩ) as compared to the unmodified TiO₂ sample (3.66 kΩ). The significant decrease in the electron-transfer resistance in the presence of lanthanum species resulted in an effective charge transfer and separation of TiO₂, leading to an enhanced photocatalytic degradation of the 2,4-D pollutant.

In order to investigate the effect of lanthanum modification on the photo-electrochemical properties of the resulting La-TiO₂ composites, measurements of the time-dependent photocurrent response were performed. As shown in Fig. 7(b), anodic (positive) photocurrent responses indicate that the samples exhibited n-type semiconductor characteristics under UV light illumination. The photocurrent traces of

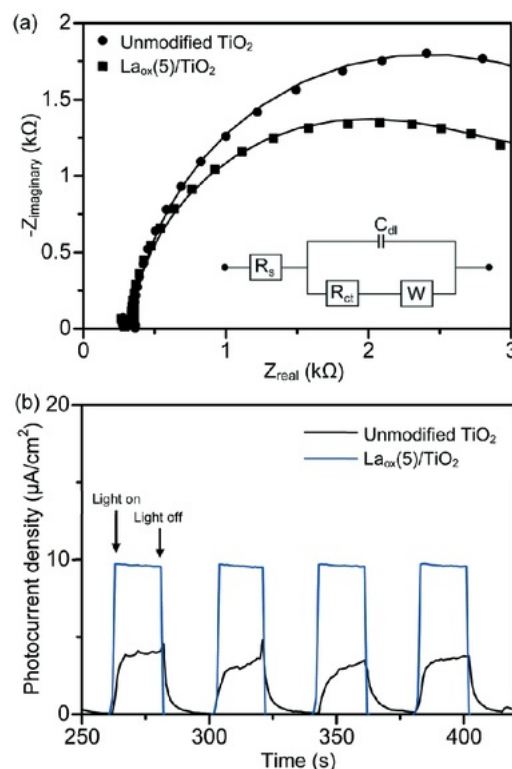


Fig. 7 (a) Nyquist plots (solid circles and squares) of the EIS changes of the unmodified TiO₂ and La_{0.05}(5)/TiO₂ samples, with the corresponding circuit model fits (line). The EIS measurements were performed in the presence of 2.5 mM K₃[Fe(CN)₆] in 0.1 M Na₂SO₄ aqueous solution. Inset: Equivalent circuit for fitting the charge transfer impedance of the photocatalysts, where C_{dl} = double layer capacitance, R_s = solution resistance, R_{ct} = charge transfer resistance and W = Warburg impedance. (b) Photocurrent vs. time response of the unmodified TiO₂ and La_{0.05}(5)/TiO₂ samples measured under pulsed UV light illumination in Na₂SO₄ (0.1 M) electrolyte vs. Ag/AgCl reference electrode at an applied potential of 0 V.

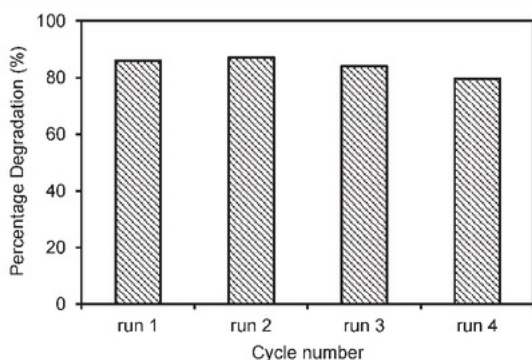


Fig. 6 Recycling tests on the La_{0.05}(5)/TiO₂ sample for photocatalytic degradation of 2,4-D under UV light for 6 h.

the unmodified TiO₂ and La_{0.05}(5)/TiO₂ showed a rapid response and good reproducibility at each of the turn-on and turn-off instances. In the absence of applied biased potential, the photoelectrodes of the La_{0.05}(5)/TiO₂ photocatalyst generated a significantly higher photocurrent density than the photocurrent of the unmodified TiO₂ photoelectrode. These results further confirm the ability of the La species to improve the separation of photogenerated electron-hole pairs.^{37,48}

Proposed mechanism

Based on the results shown above, a mechanism for the role of lanthanum species in enhancing the activity of TiO₂ under UV irradiation is proposed and depicted in Fig. 8. As shown in Fig. 8, there are three possible pathways of electron transfer in the photocatalytic system, denoted as P1, P2 and P3, respectively. The first pathway (P1) involves the conventional

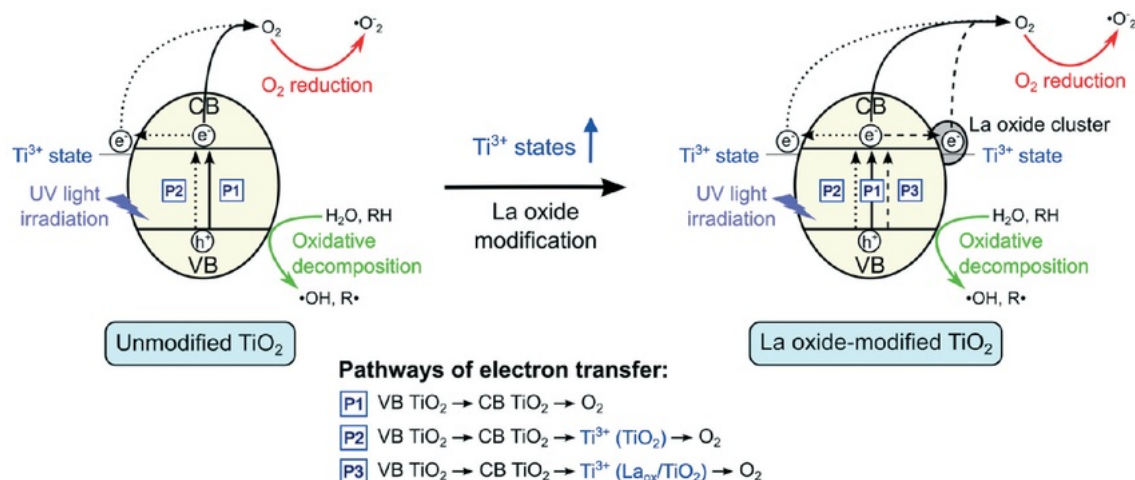


Fig. 8 Proposed mechanisms on the lanthanum-modified TiO₂ under UV light irradiation.

bandgap transition of 4.6 eV. When illuminated, the electrons in the VB of TiO₂ were excited to the CB, leaving holes in the VB. The excited electrons could then react with adsorbed oxygen to form superoxide radicals. Due to the short lifetime of the photogenerated electron-hole pairs, they normally tend to recombine quickly.

As shown by the XPS results, in addition to the dominant Ti⁴⁺ states, there is also a small proportion of Ti³⁺ species present in the unmodified TiO₂. When the TiO₂ is excited, the electrons in the VB could be transferred to the 3d states of Ti³⁺. The Ti³⁺ species that have accepted the electrons could then transfer the electrons to form other active species, such as superoxide anions (O₂^{•-}) and hydroxyl radicals (•OH),^{10–12,26,34} which could further degrade the 2,4-D molecules. Hence, in the absence of lanthanum modifications, this pathway (P2) and the conventional excitation of electrons from VB TiO₂ to CB TiO₂ (P1) were expected to contribute to the photocatalytic activity of the unmodified TiO₂.

The EIS and photocurrent results shown above suggested that in the presence of lanthanum species on the surface of TiO₂, the recombination of the electron-hole pairs was reduced, resulting in the improved photocatalytic activity. However, previous reports proposed that the CB edge of La₂O₃ is located at a far more negative position (~–1.8 to –3.5 V vs. standard hydrogen electrode (SHE)) than that of anatase TiO₂ (~–0.3 V vs. SHE). Since La₂O₃ does not possess the suitable potential, electron transfer from the CB edge of TiO₂ to La₂O₃ is not possible.^{7,9,10} Hence, there might be another species that led to the improved charge separation of TiO₂.

From the XRD and DR UV-vis results, it was shown that the crystal structure, crystallite size and bandgap of TiO₂ were not significantly affected by the La modification. These suggested that only surface modification took place. At the La₂O₃ and TiO₂ interface, a charge imbalance of TiO₂ might be created in the presence of La³⁺ species. In order to overcome this charge imbalance, Ti⁴⁺ is thus reduced to

Ti³⁺.^{7,9,10,12,14,16,17,33,34,37} In this study, as indicated by the XPS Ti_{2p} analysis, the increase of Ti³⁺ species on the surface of the TiO₂ photocatalysts was attributed to the lanthanum modification. The incorporation of La³⁺ species led to the formation of additional impurity Ti³⁺ states that resulted in the increased charge transfer and separation. Therefore, upon modification with lanthanum species, there is an additional pathway (P3) where electrons could be captured. As such, lanthanum modified TiO₂ photocatalysts showed decreased charge recombination, leading to the increased photocatalytic activity. However, if the amount of Ti³⁺ was too high, it might act to promote electron-hole recombination.^{7,9,10,12} Therefore, the optimum amount of La₂O₃ that gave the optimum photocatalytic performance under UV light irradiation could be also related to the optimum amount of Ti³⁺.

Conclusions

Lanthanum oxide was successfully loaded onto the surface of HK UV100 TiO₂ by a photodeposition method, which did not require any heat treatment processes. This method resulted in the formation of highly dispersed La(III) oxide species on the TiO₂ surface, and it did not alter the crystallite size and the phase structure of TiO₂. The photocatalytic activity testing under UV irradiation showed a notable improvement of La-modified TiO₂ photocatalytic activity over the unmodified TiO₂ up to 5.5 times at 5 mol% La loading. The added lanthanum species was proposed to create additional Ti³⁺ states that improved the charge separation of TiO₂. Recycling tests confirmed that the La_{ox}(5)/TiO₂ catalyst showed good stability. On the other hand, when under visible or solar simulator irradiation, there was no significant improvement of photocatalytic activity of the La_{ox}/TiO₂ catalysts as compared to the unmodified TiO₂. This observation confirmed that the lanthanum species did not contribute to the visible light activity of TiO₂ under visible or solar irradiation conditions.

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