

# Enhanced photo-catalytic activity of TiO<sub>2</sub> films with doped La prepared by micro-plasma oxidation method

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## Abstract

Mesoporous thin titanium dioxide films have been prepared on titanium plates through micro-plasma oxidation. To increase the films' photo-catalytic activity, La ions with different concentrations (0, 0.025, 0.005, 0.075, 0.1 g/L) were added into the H<sub>2</sub>SO<sub>4</sub> electrolyte solution. X-ray diffraction, X-ray photoelectron spectroscopy, atomic force microscopy, and scanning electron microscopy techniques were applied to characterize the modified films. A kind of typical textile industry pollutant (Rhodamine B) was used to evaluate the photo-catalytic activity of the films. The results showed that this activity of the films had been improved by adding La ions into the electrolyte solution. The enhanced photo-catalytic activities might be resulted from the increase of mesopores' number, producing more reactive sites to absorb and oxidize pollutants. Also, the improvement was related to the forming of titanium dioxide lattice distortion, which could accept more photoexcited holes and produce more strong surface free radicals to oxidate adsorptive molecules.

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**Keywords:** Micro-plasma oxidation; Ion doping; Titanium dioxide; Photo-catalysis

## 1. Introduction

The world faces a number of environmental problems. Accordingly, a mass of research activities have been carried out in search of advanced chemical, biochemical, and physicochemical methods, to eliminate hazardous chemical compounds in the air and water [1–3]. Photo-catalytic treatments with various semiconductors have been widely studied to eliminate environmental pollutants. Among semiconductor photo-catalysts (i.e. ZnO, ZnS, CdS, Fe<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub>, etc.), titanium dioxide (TiO<sub>2</sub>) has been proved to be the most active, due to its photo-stability, strong oxidizing power, non-toxicity, chemical and biological inertness, stability, as well as its low cost. Due to the above advantages, TiO<sub>2</sub> which can be used as a kind of photo-catalyst has attracted considerable attention in various processes, such as the purification of drinking water, the degradation of oil spills in water systems, and the decomposition of harmful

organic contaminants (e.g. herbicides, pesticides, and refractive dyes).

To improve photo-catalytic efficiency, many efforts have been made in recent years, which include both the synthesis of composite photo-catalysts [4–7] and the change of the TiO<sub>2</sub> films' character. TiO<sub>2</sub> mixed with certain kinds of the transition metals have been widely studied, since these transition metal clusters can elongate the electron–hole pairs' separation [8,9]. TiO<sub>2</sub> films have been prepared by a number of deposition techniques such as the sol–gel process, colloid baking, chemical vapor deposition, evaporation and various reactive sputtering depositions [10–14]. But these approaches are very complicated, expensive and not environmentally friendly. Besides, coatings produced by these methods present weak adherence to the substrates and not uniform. Fortunately, a novel coating technology, the micro-plasma oxidation (MPO), has been developed [15]. This method is based on the anodic oxidation, which occurs at a potential above the breakdown voltage of the oxide films growing on the anode surface [16]. In a certain sort of electrolyte solution, MPO occurs only under a high cell voltage. The process consists of numerous simultaneous and uniform plasma discharges over the metal surface. Uniform films have been synthesized in the

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plasma discharge process and the films have good adherence to the substrates [17].

In this paper, MPO was applied to prepare TiO<sub>2</sub> films on titanium substrates. La(NO<sub>3</sub>)<sub>3</sub> of different concentrations were doped into the H<sub>2</sub>SO<sub>4</sub> electrolyte solution during the process of MPO. Rhodamine B dye, a typical kind of compound, was used to test the photo-oxidation efficiency of the films under ultraviolet (UV) irradiation (365 nm). The objective of the research was to investigate the effects of La(NO<sub>3</sub>)<sub>3</sub> of different concentrations, which were doped into the H<sub>2</sub>SO<sub>4</sub> electrolyte solution in the MPO process, on the structural property, the surface morphology and the photo-catalytic activity of the modified films.

## 2. Experimental

### 2.1. Catalyst preparation

A titanium sheet (99.9% in purity) was selected as an anode, with a reaction area of 25 mm × 10 mm × 0.5 mm and a copper sheet was introduced as a cathode. The set-up scheme of the oxidation equipment is shown in Fig. 1. The anode was located in the centre of the electrolyte cell. The MPO process with a homemade 3 kW dc power supply was conducted in two stages; the galvanostatic anodization with a constant current density was first performed until a designated anode-to-cathode voltage was reached, and then the voltage was maintained until the end of oxidation, with a gradual decrease in the current. The temperature was controlled in the range (20 ± 0.2 °C) by a cold water jacket. The electrolyte solution consisted of 0.5 M analytical-grade H<sub>2</sub>SO<sub>4</sub> (supplied by Beijing Chemical Reagent Plant) and different concentrations of analytical-grade La(NO<sub>3</sub>)<sub>3</sub> (0 g/L, 0.025 g/L, 0.050 g/L, 0.075 g/L, 0.100 g/L) solutions (supplied by Shanghai Chemical Product Plant). All the aqueous solutions were prepared with distilled water. The produced films were then rinsed in distilled water and dried in a current of hot air. The films generated by this method were marked as TiO<sub>2</sub> and La/TiO<sub>2</sub>, respectively. According to the previous work [18], TiO<sub>2</sub> thin films had higher photo-catalytic activity when the current density was 80 mA/cm<sup>2</sup>, the voltage was 160 V and the oxidation time was 10 min. The above process parameters kept constant in this research.

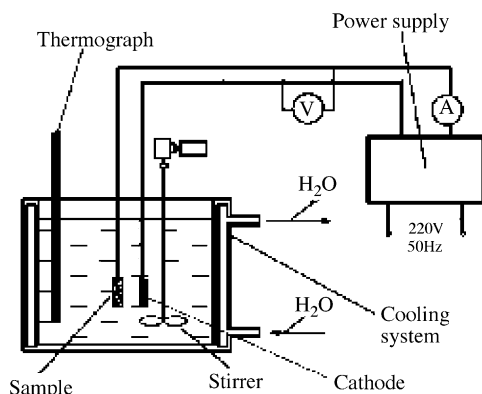


Fig. 1. Schematic view of the micro-plasma oxidation set-up.

### 2.2. Characterizations of synthesized catalyst

Scanning electronic microscopy (SEM) (D/max-rB) was used to study the surface morphology and pore distribution of the produced films. Surface morphology, roughness and the maximum height of projections of the modified TiO<sub>2</sub> films were examined with a digital Instruments Nanoscope III atomic force microscope (AFM), operating in the tapping mode (TM).

The crystalline structure of the films was examined by X-ray diffraction (XRD) with a Cu K $\alpha$  source. The accelerating voltage and applied current were 40 kV and 30 mA, respectively. The compositions of TiO<sub>2</sub> films were analyzed through X-ray photoelectron spectroscopy (XPS) with the Mg K $\alpha$  source generated by a VG Scientific ESCALAB Mark II spectrometer, equipped with two ultrahigh-vacuum (UHV) chamber. The pressure in the chamber during the experiments was approximately  $2.4 \times 10^{-6}$  Pa. X-ray photoelectron spectra were referenced to the C 1s peak ( $E_b = 284.6$  eV) resulting from the adventitious hydrocarbon (i.e. from the XPS instrument itself) present on the films' surfaces.

### 2.3. Photo-degradation experiment

The bench-scale photoreactor system consisted of a cylindrical quartz cell with the size of 25 mm in diameter and 50 mm in height, a 20 W UV lamp with a maximum UV irradiation peak of 365 nm. The schematic diagram of photoreactor was presented in previous papers [19]. The photo-catalytic activity of each films produced by MPO was examined by measuring the degradation of Rhodamine B dye solution. Samples of 2.5 cm<sup>2</sup> were immersed into 10 ml aqueous Rhodamine B solution (10 mg/L). The solution was stirred continuously and supplied with air during the reaction process. The UV light was irradiated for 2 h perpendicularly to the surface of the samples through the side-wall of the cylindrical quartz cell. The distance between the UV source and the films was 2 cm. The change of Rhodamine B concentration with the irradiation time was measured by UV spectrophotometry.

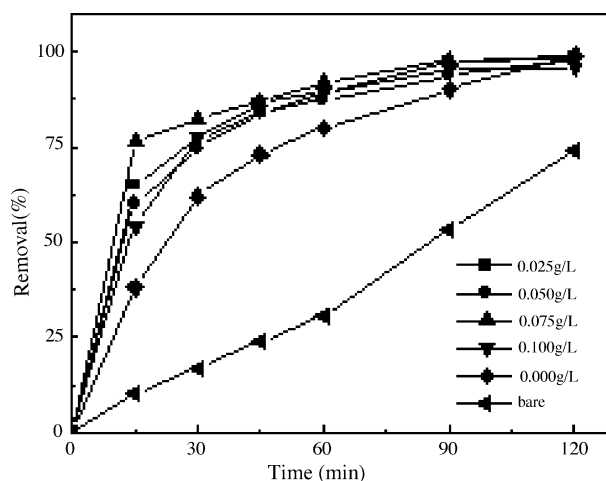


Fig. 2. Effect of the La(NO<sub>3</sub>)<sub>3</sub> doping on the removal of Rh B.

### 3. Results and discussion

#### 3.1. Photo-degradation of Rhodamine B

Firstly, the pollutant solution was photolyzed in the absence of the photo-catalyst to examine its stability. The experiments demonstrate that the removed speed of Rhodamine B is very low in the absence of the  $\text{TiO}_2$  films under UV-illumination. The degradation efficiency of Rhodamine B over the produced films

and without film irradiated by UV light is shown in Fig. 2. It can be seen that the doped films enhance the efficiency of degradation and the speed of Rhodamine B' photo-catalytic degradation increases gradually with the concentration of  $\text{La}(\text{NO}_3)_3$ . When the dopant concentration is 0.075 g/L, the produced film achieves the faster photo-degradation of Rhodamine B. The removal of Rhodamine B using the film with UV irradiation of 15 min reaches 76%, which is 38% higher than the film produced with pure electrolyte.

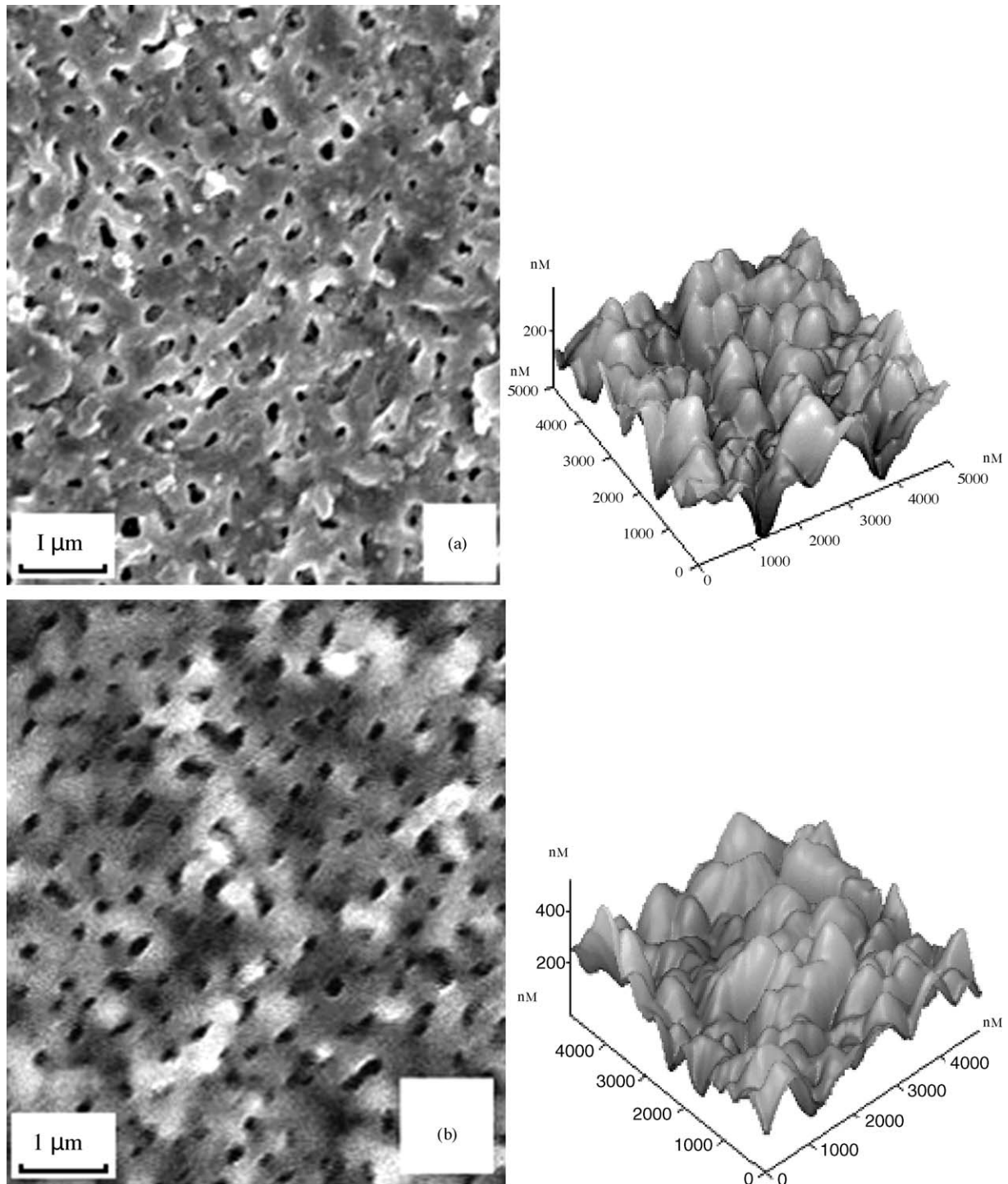


Fig. 3. SEM (left) and AFM (right) images under different condition: (a)  $\text{TiO}_2$ ; (b)  $\text{La}/\text{TiO}_2$ .

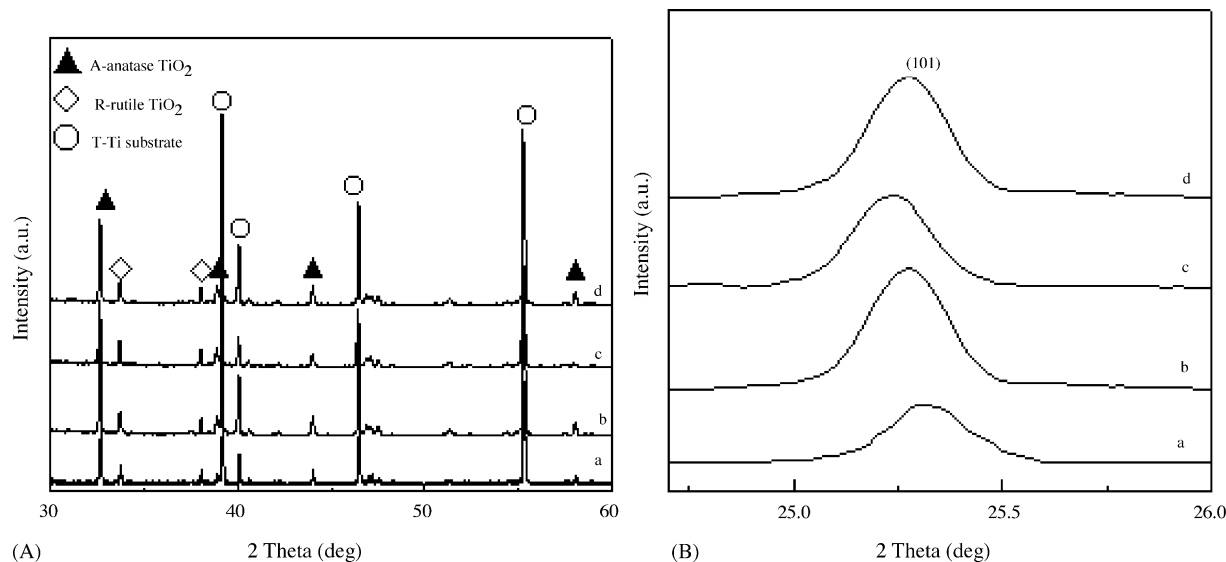


Fig. 4. The XRD patterns under different condition: (A) absolute patterns; (B) partial patterns. (a) Pure  $\text{TiO}_2$ ; (b)  $\text{La/TiO}_2$  0.50 g/L; (c)  $\text{La/TiO}_2$  0.75 g/L; (d)  $\text{La/TiO}_2$  0.10 g/L.

### 3.2. Characterizations

Fig. 3 depicts the SEM photographs and AFM images of the films ( $\text{TiO}_2$ ,  $\text{La/TiO}_2$ ). It can be seen from SEM photographs magnified by 3000 times that the surfaces of the micro-plasma films are mesoporous. Compared with pure  $\text{TiO}_2$ , the surface grain size and the density of  $\text{La/TiO}_2$  pores increase, which could improve the photo-catalytic activity of the films because more mesopores can produce more reactive sites to absorb and oxide pollutants.

In parallel to the SEM photographs, AFM images for the above two kinds of films are shown in Fig. 3 as well. These images verify that the  $\text{La/TiO}_2$  film is more uniform, which is consistent with the SEM results. The value of the mean roughness and the maximum height of projections can be obtained directly from these AFM images. The roughness of the  $\text{TiO}_2$  films is 42.893 nm and that of the  $\text{La/TiO}_2$  films is 60.46 nm, while maximum heights of projections on the films are 200 and 510 nm, respectively. The above results indicate that the roughness of the films increase when La ions were doped into the electrolyte solution, which enable the film surfaces to better absorb and decompose organic compounds.

The films prepared under different conditions were examined by XRD. The XRD spectra are shown in Fig. 4, in which the peaks of the substrate Ti, the anatase and rutile forms of  $\text{TiO}_2$  are labeled as T, A, and R, respectively.

From Fig. 4(A), it can be noticed that the produced films consist of much anatase phase and less rutile phase, and no new crystal phases are produced by doping. Fig. 4(B) displays the enlarged XRD peaks of anatase  $\text{TiO}_2$  plane A (101) in the  $2\theta$  region of  $24.5\text{--}26^\circ$ . It can be found from Fig. 4(B) that the X-ray diffraction peaks of crystal plane A (101) shift to lower diffraction angle with increasing concentration of La ions. However, the diffraction angle is minimized when the concentration of  $\text{La}(\text{NO}_3)_3$  is 0.075 g/L. The X-ray diffraction peaks of crystal plane (101) and (200) in anatase are selected to determine the

Table 1  
Effect of  $\text{La}(\text{NO}_3)_3$  doped concentration on crystal structure of anatase  $\text{TiO}_2$

$\text{La}^{3+}$ ion addition concentration (g/L)	$a = b$ (nm)	$c$ (nm)	Cell volume ( $\text{nm}^3$ )
0.000	0.3783	0.9499	0.1359
0.050	0.3783	0.9508	0.1361
0.075	0.3792	0.9627	0.1384
0.100	0.3785	0.9582	0.1373

lattice parameter of the produced  $\text{TiO}_2$  films. The calculated results of the doped film parameters are shown in Table 1. It can be seen from this table that the cell volume and lattice parameters ( $a$ ,  $b$  and  $c$ ) generally increase with increase of  $\text{La}(\text{NO}_3)_3$  concentration in the electrolyte, and the increase reaches the maximum at the  $\text{La}(\text{NO}_3)_3$  concentration of 0.075 g/L.

The chemical composition of the  $\text{TiO}_2$  and  $\text{TiO}_2/\text{La}$  (0.075 g/L) films was determined by XPS. The survey spectra are presented in Fig. 5. It can be seen from Fig. 5 that the peaks

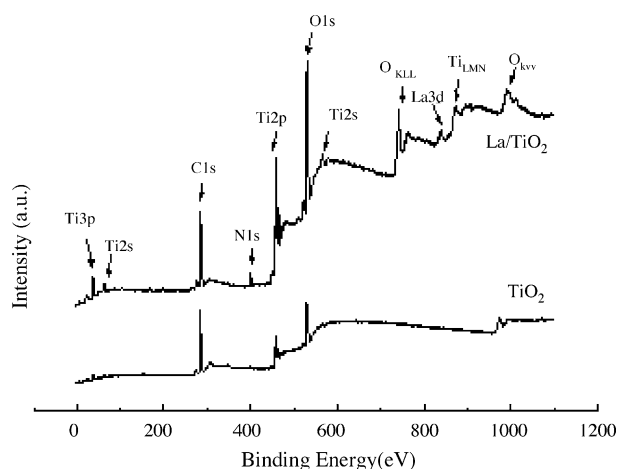


Fig. 5. XPS spectroscopy of  $\text{TiO}_2$  and  $\text{La/TiO}_2$  by MPO.



mainly contain the Ti 2p, O 1s and C 1s. The peaks of the N 1s (400.19 eV) and La 3d (839.61 eV) appear in the survey spectra of the TiO<sub>2</sub>/La films, which implies that La ions entered into the TiO<sub>2</sub> films in the experiments. However, the intensity of the La ion's peak is weak, which indicates that the amount of the La ions in the films is small.

From the XPS and XRD spectra, it can be deduced that La<sup>3+</sup> ion in the electrolyte can introduce into TiO<sub>2</sub> films during its formation and bring about the increase of TiO<sub>2</sub> lattice parameters and cell volume, which results in the formation of structural defects.

A general mechanism for heterogeneous photo-catalysis on TiO<sub>2</sub> under UV irradiation is shown as [1–5,20]:



Upon excitation, a conduction-band electron and a valence-band hole separate. Then the hole initiates an oxidative reaction while the electron initiates a reductive reaction if recombination does not occur. Organic compounds are believed to be destroyed through direct oxidation by the trapped holes or to be attacked by hydroxyl groups [21,22].

Sclafani and Herrmann have found that metal oxides with more structure defects on surface could ionosorb oxygen as O<sup>-</sup> species, which can cause hole trap reaction and produces more OH<sup>•</sup> radical [23]. So, the above lattice distortion can reduce the recombination rate of e<sup>-</sup>/h<sup>+</sup> pairs and produce more OH<sup>•</sup> radical, which will have a positive influence on the photo-catalytic activity of the films. When the dopant concentration is 0.075 g/L, the lattice distortion of TiO<sub>2</sub> is maximal. Therefore, the film has higher photo-catalytic activity, which is consistent with the results of the photo-catalytic degradation experiments.

However, when the concentration of La(NO<sub>3</sub>)<sub>3</sub> increase above 0.075 g/L, degradation efficiency of the produced films decrease instead. It is likely to form the La<sub>2</sub>O<sub>3</sub> on the surface of TiO<sub>2</sub> particles when doping La<sup>3+</sup> is more, which could decrease the quantity of La ions entering into the TiO<sub>2</sub> lattice, reduce the distortion, and counteract the photoreaction. Because the amount of La<sub>2</sub>O<sub>3</sub> in the films is very small, so the La<sub>2</sub>O<sub>3</sub> phase cannot be detected by XRD. Another reasonable explanation ascribes to the more doping La<sup>3+</sup>, which is deleterious to the separation of electron–hole pairs. It acts as a recombination centre leading to a shorter lifetime of the electron–hole pairs. In order to improve the photo-catalytic activity of the TiO<sub>2</sub> film, further tests and explanation are actually underway.

#### 4. Conclusion

In conclusion, TiO<sub>2</sub> films were gained by the micro-plasma oxidation method in the H<sub>2</sub>SO<sub>4</sub> electrolyte solution. When La ions were doped, the films exhibit higher photo-catalytic activity.

The removal rate of Rhodamine B reached to 76% in the initial 15 min, which was 38% higher than that of films produced in pure electrolyte solution, when the La(NO<sub>3</sub>)<sub>3</sub> concentration was 0.075 g/L. The enhanced activity was related to the changes of the lattice parameters and surface structure induced by La doping.

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