



Photocatalytic Degradation of Dye Pollutant Acid Yellow-17 by La Doped TiO₂/Indium-Tin Oxide Thin Layer Photocatalytic Electrode

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(Received: 10 June 2013;

Accepted: 30 October 2013)

AJC-14322

La-doped TiO₂ photocatalytic electrode has been successfully synthesized using tetraisopropyl orthotitanate, isopropyl alcohol, acetic acid and La₂O₃ as precursors by sol-gel method. Different molar ratios of La/Ti were supported on indium-tin oxide glass to produce photocatalytic electrodes. All catalysts have been further characterized by using XRD, XPS and contact angle analysis. The La/Ti molar ratio 0.05 photocatalytic electrode shows the best decolorization and mineralization rate after 4 h reaction. Applied potential would effectively increase the decolorization rate under visible light irradiation.

Key Words: Lanthanum, Indium-tin oxide, Photoelectrocatalytic, Photoelectrocatalytic reaction.

INTRODUCTION

In advanced oxidation processes (AOPs), application of UV light combining with semiconductors is a new technology which develops fast in recent years. Titanium dioxide is the most popular semiconductor in degrading organic pollutants¹⁻³. It has the advantage of being non-toxic, photo-stable and water insoluble⁴. Titanium dioxide widely used in advanced oxidation processes for liquid phase or gas phase.

UV light takes possession of only 5 % sunlight and the remaining 95 % being visible light that TiO₂ photocatalyst can not absorb. Let TiO₂ to absorb visible light and to make oxidation process will be a more economical and effective method. Many former studies point out modification technologies advantage TiO₂ to absorb visible light and make photodegradation effective. Modificatory materials often been sorted out metal modify and non-metal modify^{5,6}.

La₂O₃ be used to modify TiO₂ and coated La₂O₃-TiO₂ on stainless steel plate. It was observed that La₂O₃ can effectively adsorb contaminants onto the La₂O₃-TiO₂ photocatalyst and increases the total photocatalytic ability. Another hand applied voltage can enhance the reactive dynamics⁷.

In this work, uses sol-gel method to synthesize TiO₂ photocatalyst and adds lanthanum metal during the preparation to make it able to utilize visible light and reduce electron-hole recombining. In order to increase the process efficiency of photocatalyst voltage is applied; such photocatalyst is further coated on glass of indium-tin oxide (ITO), to prepare catalyst electrode. How well the catalyst electrode treats the azo dye,

acid yellow-17 (AY-17), before and after modification is investigated; voltage is also applied to it in hope of elevating its catalytic efficiency in the visible light system.

EXPERIMENTAL

Synthesis of catalyst: The impregnation of TiO₂ photocatalyst for coating in this experiment includes the following steps:

First, continuously mix, agitating of isopropyl alcohol (IPA), tetraisopropyl orthotitanate (TTIP) and acetic acid mole ratio 1:2:8 and stirred for 10-15 h. And then immerse indium-tin oxide glass in the sol and left it at a constant speed after impregnation for 1 min. Dry the impregnated indium-tin oxide glass for 15 min in an oven preheated at 105 °C. Put indium-tin oxide glass in a high-temperature oven at 500 °C for 1.5 h. Finally, repeat above step for many times, followed by heating at 500 °C for 24 h.

Modify photocatalyst electrode: The La-TiO₂/ITO preparation process, based on the process of TiO₂/ITO photocatalyst electrode, uses lanthanum oxide as the precursor and adds it directly in the mixed solution of tetra isopropyl orthotitanate isopropoxide (TTIP), acetic acid and isopropyl alcohol for preparing TiO₂ photocatalyst sol, by different molar ratios of lanthanum to titanium; the subsequent steps are the same as the preparation of TiO₂/ITO photocatalyst. In this experiment, the La-Ti molar ratios are 0.025, 0.05, 0.075 and 0.1, respectively, denoted hereinafter by 0.025 LTI, 0.05 LTI, 0.075 LTI and 0.1 LTI, while unmodified TiO₂/ITO photocatalyst is denoted by TI.

Catalyst and photodegrade characterization: All commercial TiO_2/ITO (TI) and $\text{La-TiO}_2/\text{ITO}$ (LTI) were characterized by field emission scanning electron microscope (SEM), high-resolution X-ray diffract meter (HR-XRD), X-ray photoelectron spectroscopy (XPS), surface area and porosity analyser (BET) and Contact angle analysis meter to analyse the surface of the catalysts and uses UV/visible spectrophotometer (JASCO Model V-5000) and total organic carbon (TOC, Shimadzu TOC-VCSN) to measure the photo degradation rate by AY-17.

RESULTS AND DISCUSSION

SEM and BET characterization: Figs. 1-5 is 100000 times SEM images of TI catalyst and different La/Ti molar ratio photoelectrocatalysts. TiO_2 particle is almost round sphere and about 20 nm in diameter. It can be clearly seen that all the La-modified photocatalyst electrode has smaller particle sizes and diameters, which all are less than 20 nm. The 0.025 LTI catalyst is linear structure, which piles by 10 nm particles. Another hand, adding La/Ti 0.05, 0.075 and 0.1 the particle would uniform and less than 10 nm. All results observe that using La modify TiO_2 could make particle size smaller and more uniform.

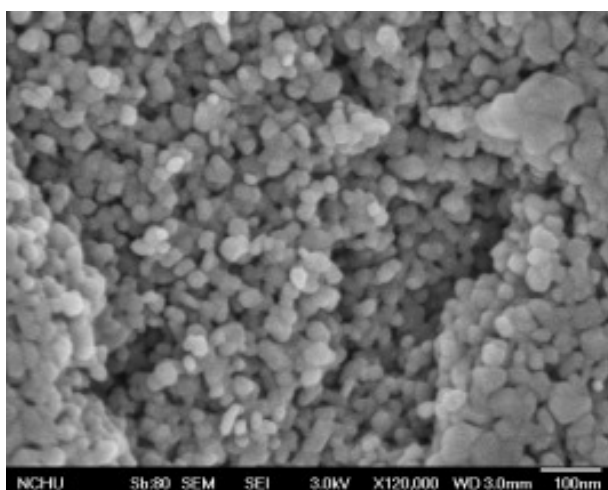


Fig. 1. 100000 times SEM images of TI photocatalytic electrode

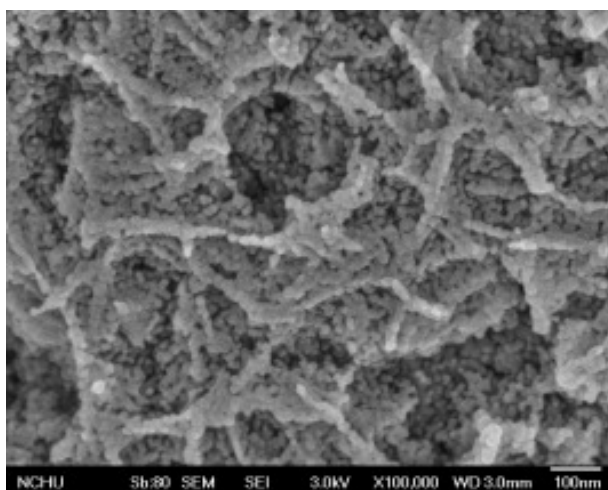


Fig. 2. 100000 times SEM images of 0.025 LTI photocatalytic electrode

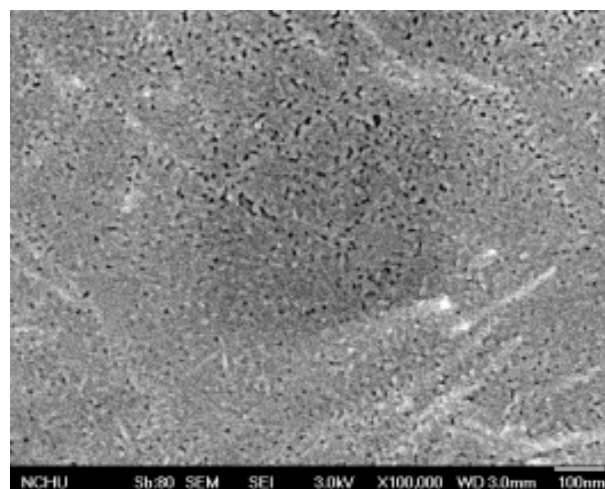


Fig. 3. 100000 times SEM images of 0.05 LTI photocatalytic electrode

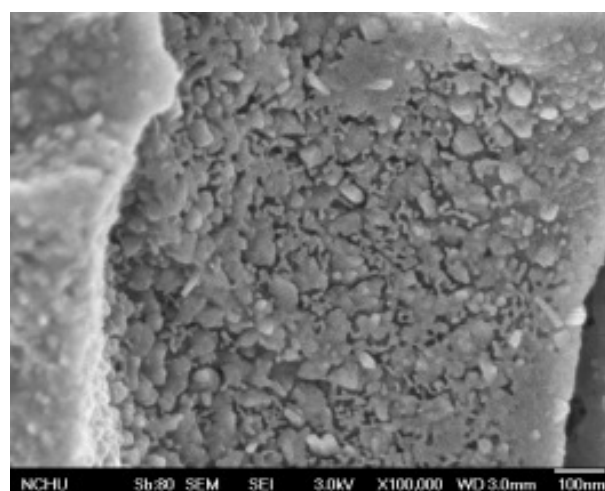


Fig. 4. 100000 times SEM images of 0.075 LTI photocatalytic electrodes

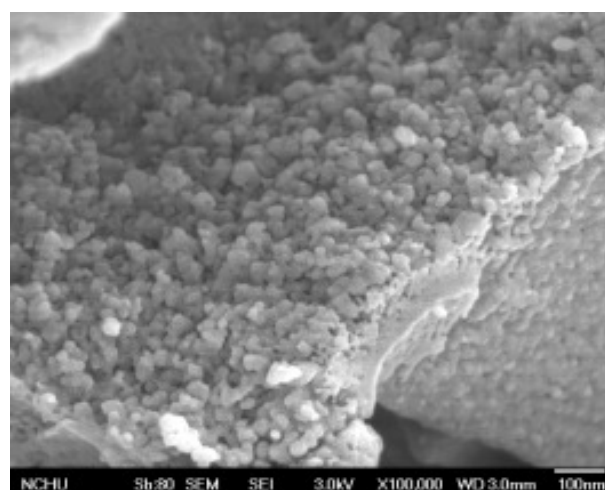


Fig. 5. 100000 times SEM images of 0.1 LTI photocatalytic electrode

Table-1 lists the particle size and specific surface of all photocatalysts. The result indicates that 0.05 LTI has the largest specific surface area. Due to the effect of aggregation catalysts with higher content (0.075 LTI and 0.1 LTI) and lower content (0.025 LTI) of additive La have specific surface smaller than 0.05 LTI catalyst.

TABLE-1
SPECIFIC SURFACE OF THE PHOTOCATALYSTS

Photocatalyst	Particle size (nm)	BET (m ² /g)
Ti	20	51
0.025 LTI	10	42
0.050 LTI	< 10	60
0.075 LTI	< 10	45
0.100 LTI	< 10	46

XRD analysis: Fig. 6 shows the XRD patterns both the La doped catalysts and pure TiO₂ catalyst. The TiO₂ catalyst all peaks are indexed to pure anatase phase of TiO₂ (JCPDS-No. 21-1272). Another hand the XRD analysis of La-TiO₂ photocatalytic shows in Table-2. It can be clearly observed that the crystal type of rutile (JCPDS-No. 21-1276) and anatase appears in LTI photocatalyst electrodes.

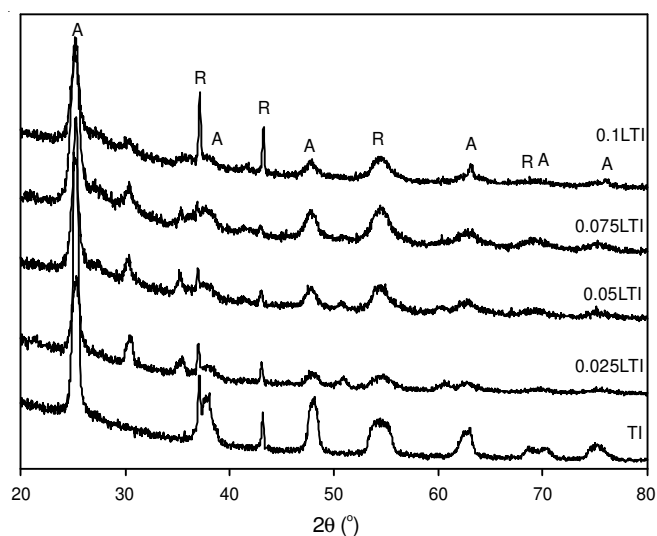


Fig. 6. XRD patterns of La doped and TiO₂ catalysts

TABLE-2
ANATASE AND RUTILE RATIO IN CATALYSTS
OF DIFFERENT La-Ti MOLAR RATIOS

Sample	Anatase (%)	Rutile (%)
0.025 LTI	89	11
0.050 LTI	83	17
0.075 LTI	82	18
0.100 LTI	76	24

The per cent of the rutile phase crystal increased with the increase of the La/Ti molar ratio⁸. No peak of lanthanum oxide is found in the XRD patterns, implying that La ion may be combined with the lattice of TiO₂ as particles of small size below the detectability limit of XRD⁹.

XPS studies: The XPS spectra of different molar ratios La doped TiO₂ photoelectrocatalytic are shown in Fig. 7. Ti 2p binding energy for different La modified TiO₂ is equal to 458 eV and 464 eV indicating that Ti⁴⁺ exist at the catalytic structure¹⁰. The peak of O 1s at 529 eV is the characteristic chemical band of Ti-O band. From the La 3d pattern, it clearly observed that the lanthanum exists at photocatalytic LTI in La³⁺ state. Based on the above XPS pattern, La-O-Ti compounds is the primary construction in the photoelectrocatalytic.

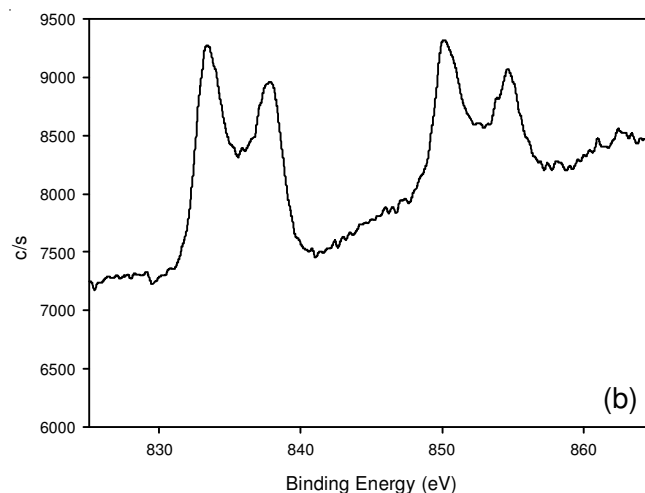
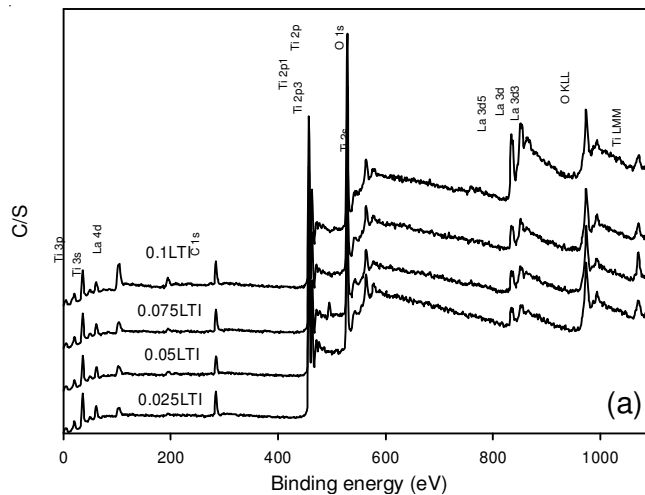


Fig. 7. (a) XPS spectra of all photocatalytics (b) La 3d XPS spectra

Contact angle analysis: The attention has been paid to the influence of modify TiO₂ by contact angle analysis. Fig. 8 shows the images of pure TiO₂ and La doped photoelectrocatalytic contact angle. It can be observed that the angle of TiO₂ photocatalytic is about 8.3°. When using La doped TiO₂ the contact angle decreased to 2.9°. The results show that the all catalytic are super-hydrophilicity (less than 10°), the modify catalytic is better hydrophilicity¹¹. It could be changed by adding the transition metal to high hydrophilicity and prevented water drops. So that light can penetrate to the electrode surface and have high wettability for water, which does not cause light scattering.

Although UV light can make TiO₂ surface hydrophilic¹², but Fig. 8(b) show small contact angle in the dark. The result is that the gel on the carriers be calcined at 500 °C and become micro-pore structure on surface. When water contacts with the thin catalytic film, capillarity make surface strong absorb and take drops develop. It would make contact angle to become small.

UV light test at varied pH: The efficiencies of photo-catalytic process strongly depend upon the pH of the reaction solution. It was due to the surface adsorption with the change of solution pH. The results shown in Fig. 9. It clearly seen that the increase of AY-17 degradation rate was irradiation to strong AY-17 absorption in acidic condition. At pH 4, after the 0.05 LTI

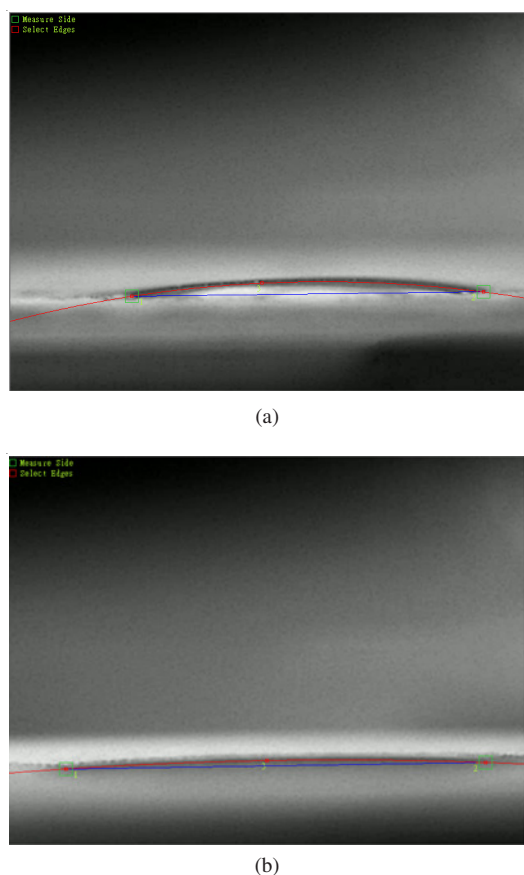


Fig. 8. Contact angle image of (a) TI and (b) 0.05 LTI photoelectrocatalytic

photocatalytic electrode undergoing photo-reaction for 4 h. Total organic carbon remaining rate is less than 27 % and unmodified photocatalytic have about 70 %. In all modified photocatalytics, only 0.05 LTI has better effect, other different molar ratios are similar to the unmodified catalytic, even are poor. It is thus inferred that the La-Ti molar ratio for best light utilization efficiency is about 0.05. With the lower molar ratio (0.025 LTI), photocatalyst has little La on the surface and exhibits no effect. While with over-addition of La (0.075 LTI and 0.1 LTI), the photocatalytic activity is similar to unmodified one. It dues to that the La on the catalyst surface becomes a center for electron-hole pair recombination. The center decreases the quantity of holes creating and further lowering the photocatalytic efficiency¹³⁻¹⁷.

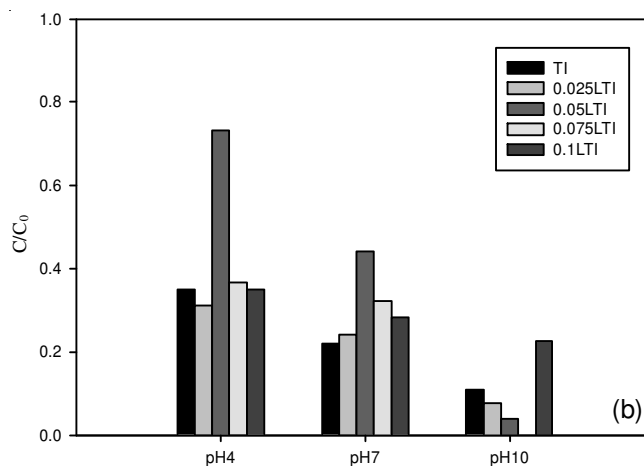
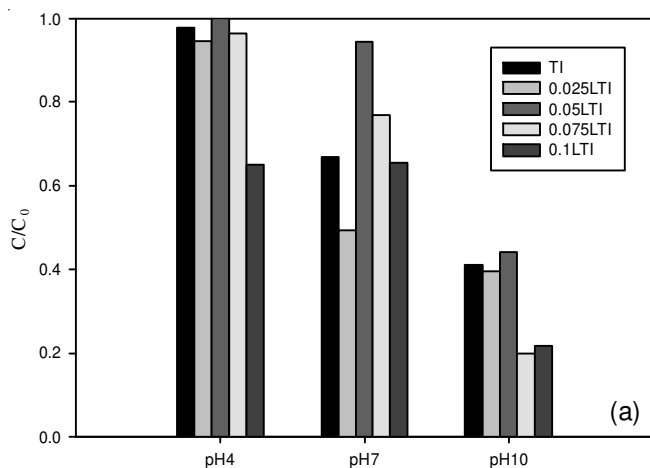


Fig. 9. (a) AY-17 degradation rate and (b) mineralization rate of all photocatalytic electrodes at different pH value under UV light

Different initial concentration: Dye of different initial concentration at 5, 10, 20 and 40 mg/L in solution whose condition was controlled at pH 4; 0.05 LTI photocatalyst electrode was exposed to UV light to investigate its AY-17 degradation rate and mineralization rate.

The results (Fig. 10), where the efficiency in elimination is apparently poor with higher initial concentration (20 and 40 mg/L), which cause is speculated to be shielding effect of the dye that affects the exposure of the electrode surface to the light, further with affecting the overall elimination efficiency. On the other hand, with a lower initial concentration (5 mg/L), the elimination efficiency of total organic carbon after 4 h is less than the pattern of initial concentration at 10 mg/L, which is speculated to the chances of contact between dye particles and electrode surface are small at lower concentration, so that the mineralization rate is low.

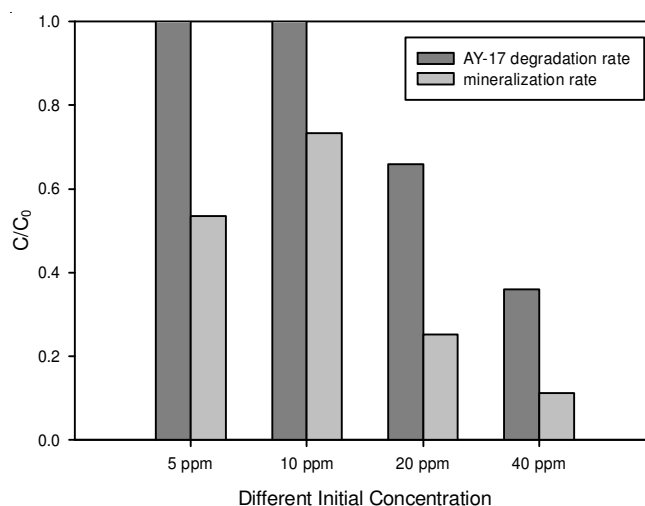


Fig. 10. Photocatalytic activity of different AY-17 initial concentration

Light intensity: The experiment was controlled in acidic condition (pH 4), with initial dye concentration at 10 ppm, the 0.05 LTI photocatalyst electrode was exposed to ultraviolet lamp in varied light intensity (4.7, 6.45 and 8.2 mW/cm²).

Fig. 11 shows that in higher light intensity (8.2 mW/cm²), it was observed that there is hardly difference between the eliminating effect at this time and that in previous test (6.45

mW/cm²). It is thus speculated that in various light intensity, the modified photocatalyst electrode has a critical value, beyond it the eliminating effect would not increase.

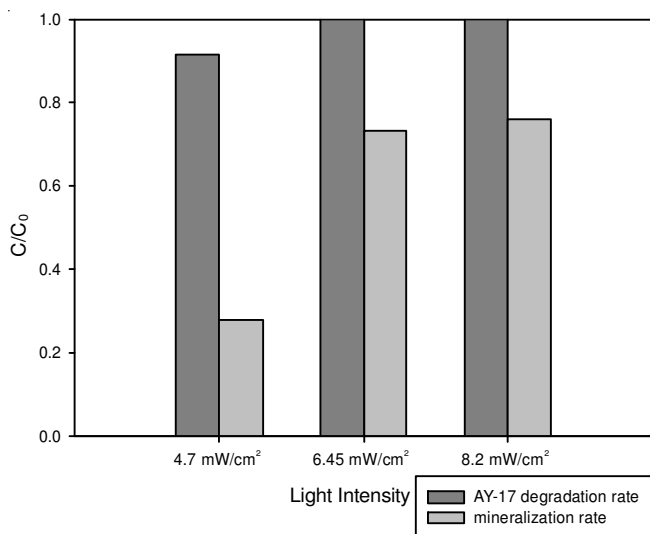


Fig. 11. Pphotocatalytic activity of different light intensity

Applied potential: In order to investigate what applied potential affect the elimination of acid yellow 17. To enhance the economic benefit, this study will first conduct test in respect of source of visible light, hoping to identify the optimal operational condition and upgrade the whole process technology toward application.

The experimental conditions are that initial acid yellow 17 concentration at 10 ppm into the reaction; 0.05 LTI photocatalyst electrode was used to visible light lamp of 419 nm wavelength. With different voltages of 0.2, 0.4, 0.8, 1.0, 2.0 and 4.0 V applied and solution controlled at pH 4.0 ± 0.1 without addition of electrolyte in the reaction tank.

The experimental results (Fig. 12) revealed that when over-voltage (4 V) or insufficient voltage (0.2 V, 0.4 V, 0.8 V) were applied, the total photocatalytic efficiency was close to exposed in visible light, where the increase in eliminating effect was limited. However, to add appropriate voltages (1.0 V, 2.0 V) applied, the eliminating effect increased by about 15 %, compared with exposure to direct visible light. When the applied voltage is too low, it might be that driving force of the electric field is too low to effectively provide enough energy to keep electron-hole pairs separation, which results in the effect similar to that under direct visible light. Conversely, when the applied voltage is too high, the photocatalytic efficiency decreases probably because the electrons from the applied voltage combine with the holes separated from the catalyst, while over-voltage might cause photocatalyst to come off, which destroy the stability of the photocatalyst electrode.

Conclusion

Different La/Ti molar ratios photocatalysts were successfully synthesized on the indium-tin oxide glass by sol-gel method and dip-coating method. Particle size of La doped TiO₂ (<10 nm) are smaller than pure TiO₂ catalyst evident from SEM patterns. From XRD results, TiO₂ catalyst are pure anatase

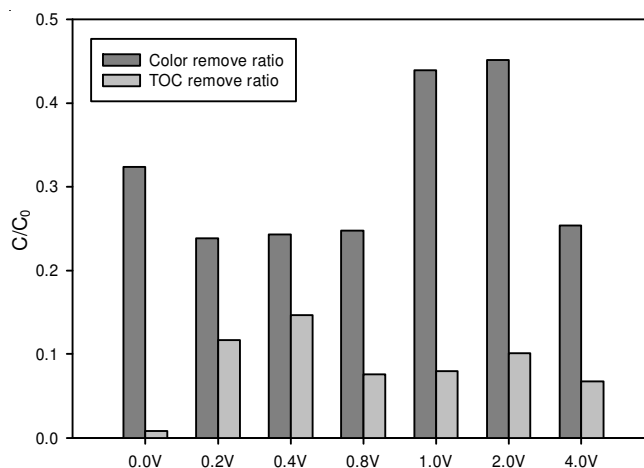


Fig.12. Photocatalytic activity of applied potential

phase and the per cent of the rutile phase crystal increased with the increase of La/Ti molar ratio. The XPS patterns shows that the La ion on the crystallization is La³⁺ state and combines with La-O-Ti band. Another La modify TiO₂ semiconductors can decrease the contact angle from 8.3° to 2.9°.

In photoreaction experiment, 0.05 LTI photocatalyst in acid condition has best light utilization efficiency under UV light irradiation. On this condition, AY-17 concentration about 10 ppm and light intensity above 6.45 mw/cm² is best photolysis parameters. In order to increase photolysis effect under visible light irradiation, adding applied potential 2.0 V would increase 15 % AY-17 degradation rate.

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