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Preparation and Characterization of TiO_2 Photocatalytic Thin Film and Its Compounds by Micro-Arc Oxidation Technique

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ABSTRACT

Mesoporous TiO_2 ceramic films have been prepared upon the Ti alloy substrate by the micro-arc oxidation (MAO) technology. To enhance the photo-catalytic property of the films, Eu_2O_3 particles were added into the electrolyte solution of Na_2CO_3/Na_2SiO_3. Scanning electron microscope (SEM), energy dispersive (EDS), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) are employed to characterize the modified films. Diffuse reflectance spectra (DRS) test, photo-generated current test and photo decomposition test are applied to evaluate the photo-catalytic property of the modified films. The results show that Eu_2O_3 transformed into one-dimensional (1-D) nano-wires embedded within the composite film, and the film has high photo-catalytic property.

Keywords: TiO_2; Eu_2O_3; Compound; Photo-Catalytic Property

1. Introduction

Rice Titanium dioxide (TiO_2) is one of the most important semi-conductor materials, which is widely used as an efficient photo-catalyst. In terms of environmental protection and new energy, TiO_2 has obtained widespread concern and research because of its chemical stability, biological compatibility and photo-catalytic ability since the report of photolysis of water on titanium dioxide (TiO_2) by Fujishima in 1972 [1]. However, the application of TiO_2 is limited. For the photo-catalytic applications, the band gap energy (Eg) of the semiconductor is critical. Because of the wideness (3.2 eV) of the Eg of TiO_2, and the ultra-violet (UV) light absorption and weak absorption of visible light [2], considerable efforts have been directed to extend the absorption edge of TiO_2 toward the visible part of the spectrum in the last three decades. So many researchers have been concentrating on finding an apt process and a modification technology to improve the photo-catalytic property of the TiO_2.

TiO_2 powder and TiO_2 film are the most common existence forms of TiO_2. However, due to the hard recycle in polluted water and limited depth of photo-radiation, TiO_2 powder is not widely used, and thus many researches have been focusing on the preparation of TiO_2 film recent years [3-5]. It is well-known that there are many different methods for preparing TiO_2 film, such as sol-gel [6-9], liquid phase deposition (LPD) [10], hydrolysis precipitation [11] and chemical vapor deposition [12,13], etc. TiO_2 film can also be produced via micro-arc oxidation (MAO) technology [14,15]. Generally speaking, MAO is a useful approach for forming a ceramic coating on the surface of valuable metals, such as Al, Mg and Ti, and their alloys [16]. MAO is a process based on the anodic oxidation and occurs at potentials above the breakdown voltage of the oxide layer formed on the anode surface [17]. Now, micro-arc oxidation (MAO) is most frequently used to prepare TiO_2 film. The TiO_2 film that is prepared through MAO has much high quality, such as high wear resistance and corrosion resistance [18], favorable biological activity [19] and

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photo-catalytic activity. To enhance the efficiency of photo-catalytic property of TiO_2 film prepared by MAO, rare earth metals with incompletely occupied 4f and empty 5d orbit also often serve as catalysts or promote catalysis. Besides, it has been proved that metal Eu, as one of the rare earth metals, has the ability to improve the photo-catalytic activity of the TiO_2 films, because of the electrons trap effect supplied by the alterable chemical valence (Eu^{2+} and Eu^{3+}) sites [20].

In the present work, we have prepared TiO_2 film upon Ti alloy substrate via MAO technology. Meanwhile, in order to get high efficient photo-catalytic property, rare earth metal oxide Eu_2O_3 was compounded into the TiO_2 film, and methyl blue dye was used to test the photo-catalytic efficiency under UV-Vis irradiation. The grain could be combined on the surface of the TiO_2 layer directly by the MAO process of high temperature and fast solidification, which could improve its photo-catalytic property.

2. Experimental

All chemicals were of analytical grade and used without further purification. In our work, Eu_2O_3 particles were added into the electrolyte directly after ultrasonic dispersion in distilled water. We prepared uniform TiO_2/Eu_2O_3 film upon Ti alloy substrate by using the high temperature and fast solidification of MAO process. Meanwhile, we also prepared pour TiO_2 film, so as to make a contrast with films were produced without adding semiconductor compound into the electrolyte. Follow these steps：

At first, we made up 5 L electrolyte. The electrolyte was a mixed solution of sodium carbonate (20 g/L) and sodium silicate (8 g/L). The anode was TC4 substrate with reaction area of 20 × 20 × 5 mm. After polishing, the substrates were cleaned by ethanol, acetone and distilled water. A stainless steel container was used as electrolyte cell and cathode. MAO of titanium alloy substrate was carried out at a constant current using a 60 KW AC power supply. Different current densities were reached by adjusting the voltage between two working electrodes. The temperature was controlled below 40˚C within a small circulating water channel. Oxidation time was ten minutes. And then, the pure TiO_2 film was prepared upon TC4 substrate when the voltage was 400 V and stable. Last, 10 g Eu_2O_3 particles were added into the same electrolyte (the concentration of Eu_2O_3 was 2 g/L). The TiO_2/Eu_2O_3 composite films were prepared at different voltage, 300 V, 350 V and 400 V. The detail experimental conditions were listed in **Table 1**.

The morphologies of the films and their chemical compositions were characterized by using scanning electron microscope (SEM), energy dispersive spectrometer (EDS) and X-ray photoelectron spectroscopy (XPS). The crystal structure was measured by using X-ray diffract meter (XRD) (D8 Advanced, Bruker AXS, Germany) with Cu Ka radiation (the scanning speed is 6˚ per minute). Photo-catalytic property was tested by diffuse reflectance spectra (DRS) test, photo-generated current test, and photo decomposition test.

Diffuse reflectance spectra (DRS) test UV-Vis diffuse reflectance spectra (DRS) of the TiO_2 layers were measured on the diffuse reflectance accessory of UV-Vis recording spectro-photometer (UV-2550, Shimadzu, Japan).

Photo-generated current test The TiO_2 layer, saturation calomel electrode and the platinum electrode, which were immersed in 1 mol/L NaOH aqueous solution, were chosen to the working electrode, reference electrode and counter electrode respectively. The working electrode was irradiated by using a high pressure mercury lamp (160 W) in 10 cm horizon distance away. The photocurrent was detected using an electrochemical workstation (CHI 660C, Chenhua, Shanghai).

Photo decomposition test The methyl blue solution of 12 mg/L was pour into two beakers. The TiO_2 layer without complex and the compounded layers were immersed in them, and the left was used as reference. All of them were illuminated by a high pressure mercury lamp (160 W) under 15cm vertical distance. The absorbance of methyl blue solution was measured by a UV-Vis spectrophotometer (UV-2550, Shimadzu, Japan).

Table 1. Experimental conditions of the TiO_2/Eu_2O_3 compounded film.

Samples	Electrical					Electrolyte		
	Voltage		Frequency	Duty cycle	Time	Na_2CO_3	$Na_2SiO_3 \cdot 9H_2O$	Eu_2O_3
	Forward	Negative						
TiO_2	400 V	10 V	1 KHz	20%	10 min	20 g/L	8 g/L	No
TiO_2/Eu_2O_3	300 V	10 V	1 KHz	20%	10 min	20 g/L	8 g/L	2 g/L
TiO_2/Eu_2O_3	350 V	10 V	1 KHz	20%	10 min	20 g/L	8 g/L	2 g/L
TiO_2/Eu_2O_3	400 V	10 V	1 KHz	20%	10 min	20 g/L	8 g/L	2 g/L

3. Results and Discussions

The SEM morphologies of the pure TiO_2 film at 400V are shown in **Figure 1**. From **Figure 1**, we can see clearly that the pure TiO_2 film is porous with diameter of pores (the diameter of pores is about 1 - 5 μm). **Figure 2** shows the SEM morphologies of the TiO_2/Eu_2O_3 composite films at 300 V, 350 V and 400 V. Meanwhile, **Figure 2** gives its two different magnifications photos at 400 V. It can be seen that the MAO TiO_2 surface exhibits a typical crater and porous microstructure with a diameter around 1 - 2 μm. At 300 V and 350 V, the surface of the TiO_2/Eu_2O_3 composite film present micro pore structure, as shown in (a) and (b), which is just ordinary film prepared by MAO technology. However, at the high voltage 400 V, there are many one-dimensional (1-D) structures homogeneously embedded within the film, as shown in (c-1) and (c-2). Due to the small size effect, these 1-D structures can enhance the photo-catalytic property of TiO_2 film. So, our researches were concentrated on the TiO_2/Eu_2O_3 composite film prepared at 400V. In order to get more detail information about the 1-D nano-wires materials on the surface of TiO_2/Eu_2O_3 film, we made size statistics about it. It can be noticed that these 1-D nano-wires have the average length of 1.26 μm and the average width of 87.5 nm from **Figure 3**.

In order to prove that the 1-D nano-wires were Eu_2O_3,

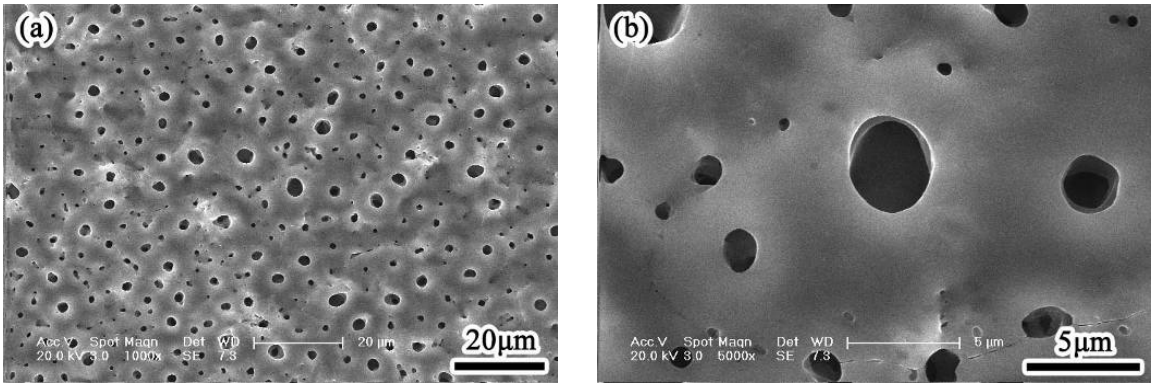


Figure 1. SEM morphologies of TiO_2 film without composites. (a) Low magnification; (b) High magnification.

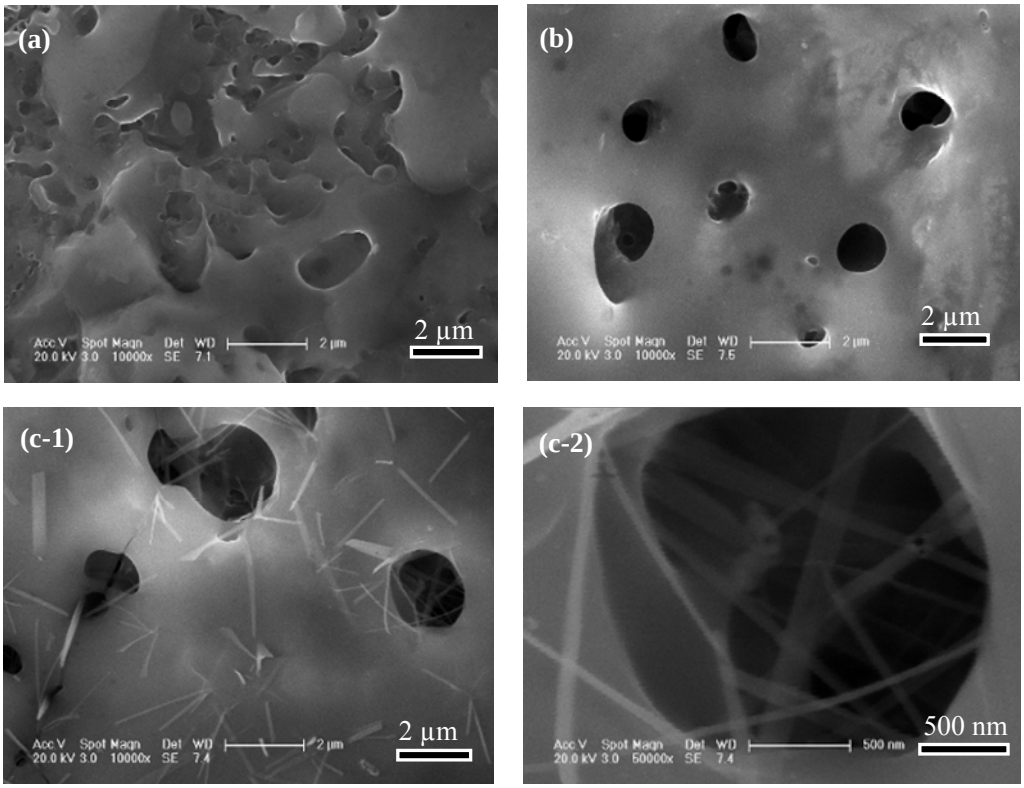


Figure 2. SEM morphologies of the TiO_2/Eu_2O_3 film by different voltage. (a) 300 V, (b) 350 V, (c-1) 400 V, (c-2) 400 V.

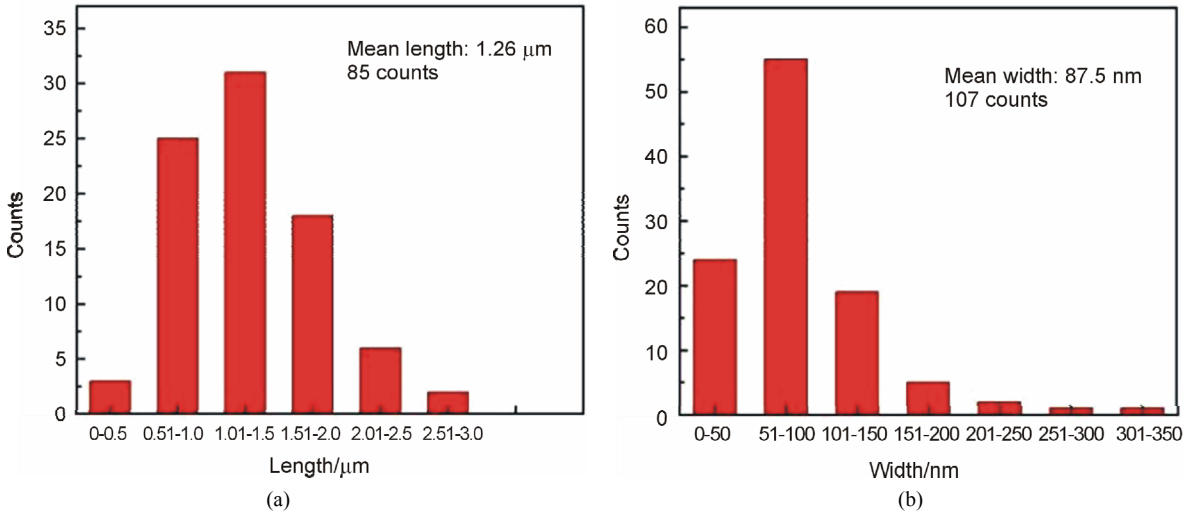


Figure 3. Statistical size distribution of the nano-wires on TiO_2/Eu_2O_3 composite film: (a) Length; (b) Width.

which were added into the electrolyte and entered into the micro-porous of the TiO_2 films, we made EDS test. EDS measurement revealed that these 1-D nano-wires were composed of Eu and O elements, as shown in **Figure 4**, which implies that original Eu_2O_3 particles have transformed into 1-D nano-wires during MAO process. At the same time, we know that Ti and some O elements come from the TiO_2 film, and Au elements come from SEM observation of injection of the sample, and Na elements come from the electrolyte.

XPS technique was applied to confirm Eu_2O_3 existence in the TiO_2/Eu_2O_3 composite film and investigate the chemical states of the elements, whose result is presented in **Figure 5**. It can be seen that the peaks mainly contain the Ti 2p, O 1s, C 1s and Eu $3d^5$, which also demonstrates the existence of Eu_2O_3 inside the film.

Figure 6(a) illustrates XRD patterns of the pure TiO_2 and the TiO_2/Eu_2O_3 composite film (400V). It can be noticed clearly that both of them mainly contain anatase phase with few rutile phase. At the same time, we know that 1-D nano-wires have little affection to the crystal structure of the films. **Figure 6(b)** displays the enlarged XRD peaks of anatase TiO_2 plans A (101) in the 2θ region of 24.0˚ - 27.0˚. We measured the full width half maximum (FWHM) of the main peak of anatase TiO_2 plans (101) in the 25.3˚. The result is that the FWHM of the pure TiO_2 film is 0.24 and the TiO_2/Eu_2O_3 composite film is 0.28. Using the Scherrer Formula, we calculated that in pure TiO_2 film, the grain size of anatase TiO_2 is about 33 - 34 nm but in the TiO_2/Eu_2O_3 composite film, the size is around 28 - 29 nm. From calculation results, we found that the grain size of anatase in the TiO_2/Eu_2O_3 composite film decreased obviously, compared with pure TiO_2 film. The reason is that rare earth metals has incompletely occupied 4f and empty 5d orbit and the growth of TiO_2 grains was inhibited after Eu_2O_3 was compounded in TiO_2 films.

For the sake of studying the photo-catalytic properties of the TiO_2/Eu_2O_3 composite film (400 V), diffuse reflectance spectra (DRS) test was employed and its result is presented in **Figure 7**. Obviously, the composite film exhibits a higher absorption of UV and visible light with an Einstein shift about 10 nm. Before Eu_2O_3 was compounded, the pure TiO_2 film only has little absorption of visible light. The results reveal that improved absorption in UV and visible light ranges is contributed from the addictive phase Eu_2O_3. Eu^{3+} possesses abundant energy levels, so Eu_2O_3 can increase the absorption of UV and visible light and improve the photo-catalytic properties of the composite film.

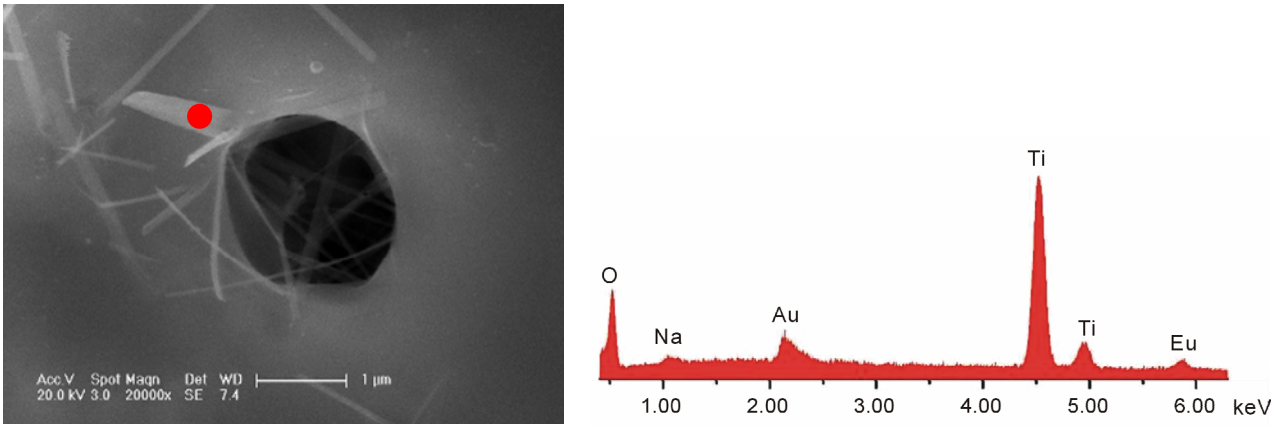
To study the photo-catalytic efficiency of the TiO_2/Eu_2O_3 composite film (400 V), we also measured the intensity of photo-generated current of it, as shown in **Figure 8**. The reason why the TiO_2/Eu_2O_3 composite film has a higher intensity of photon generated current is that in Eu_2O_3, iron Eu^{3+} has an incomplete 4f orbital track and an empty 5d orbital track, which tends to produce multi-electron configuration and therefore can effectively inhibit the recombination of photo-electrons and holes.

Figure 9 shows the result of the degradation experiments of methyl blue. It revealed that the photo-catalytic performance of the TiO_2/Eu_2O_3 composite film (400 V) exhibited two times higher than that of the pure TiO_2 film. We can see that after four hours, the degradation of methyl blue reaches to 90% when using the TiO_2/Eu_2O_3 composite film (400 V), while only 45% when using the film without Eu_2O_3.

4. Conclusion

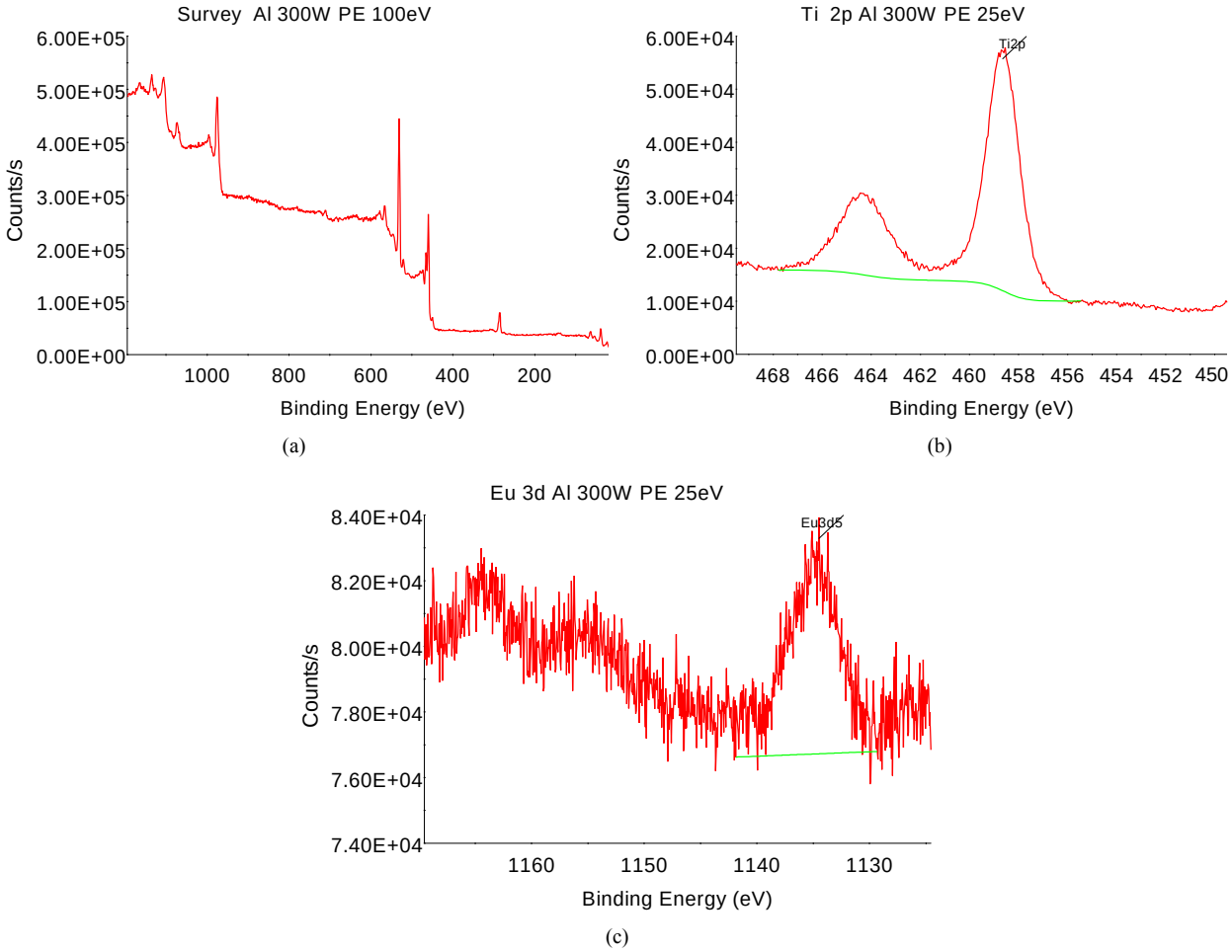
In conclusion, the TiO_2 films were prepared upon Ti alloy substrate by micro-arc oxidation (MAO) process. The

films had a porous structure with a rough surface which is suitable for modification. When rare earth metal oxide Eu_2O_3 was added into the electrolyte, a composite film was produced during MAO and Eu_2O_3 transformed into one-dimensional (1-D) nano-wires embedded within the composite film. Comparing with the pure films, the composite films exhibited high efficient photo-catalytic properties, such as high absorption in UV and visible light ranges, high photo-generated current intensity and high photo degradation rate.



(a) (b)

Figure 4. EDS analysis of the TiO_2/Eu_2O_3 composite film.



(a) (b) (c)

Figure 5. XPS spectra of the TiO_2/Eu_2O_3 composite film.

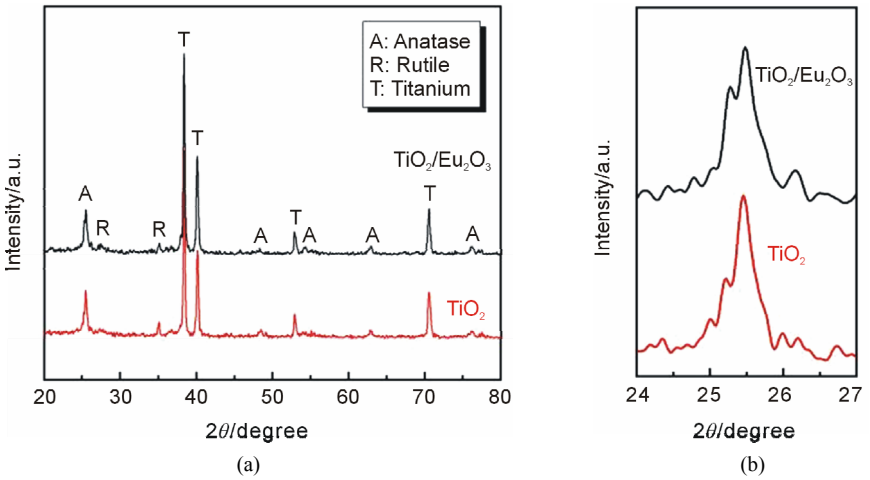


Figure 6. XRD patterns of the TiO_2 and the TiO_2/Eu_2O_3 composite films prepared by MAO (a)survey, (b) anatase (101) peak.

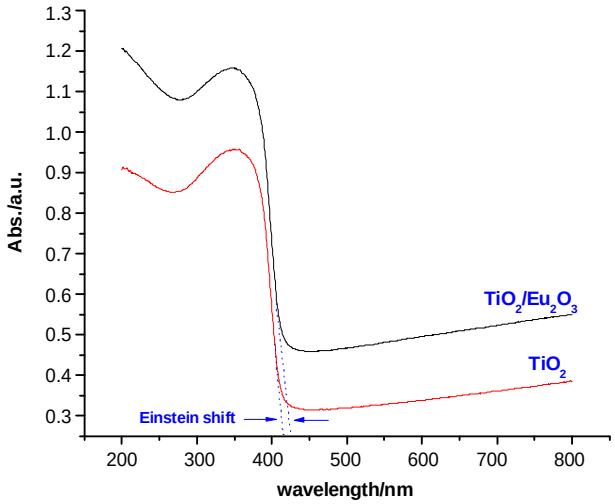


Figure 7. UV-Vis spectra of the TiO_2 film and the TiO_2/Eu_2O_3 composite film.

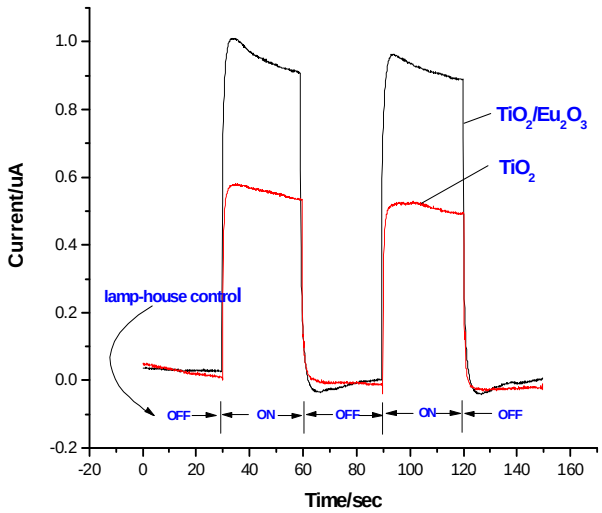


Figure 8. Photo-generated current of pure TiO_2 and TiO_2/Eu_2O_3 composite film.

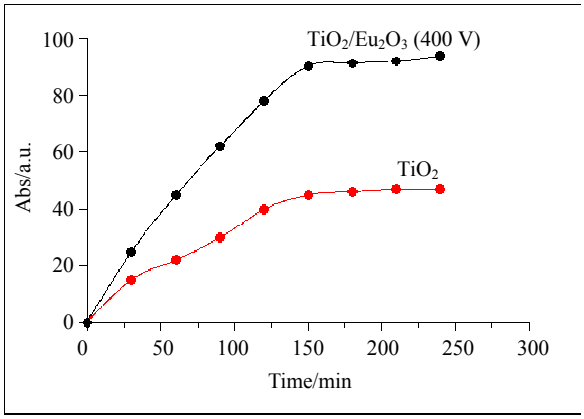


Figure 9. The concentration of methylene blue photo-degraded by pure TiO_2 and TiO_2/Eu_2O_3 film.

5. Acknowledgement

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