Factors affecting the electro-catalytic characteristics of Eu doped SnO$_2$/Sb electrode

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ABSTRACT

Different compositions of Eu doped electrodes were prepared by a pyrolysis method in order to investigate the effect of Eu on the electro-catalytic behavior of Ti-based SnO$_2$/Sb electrodes. The electrodes were characterized by SEM, EDS, XRD and their degradation abilities were evaluated using phenol. The electro-catalytic performance of prepared electrodes was strongly influenced by the heat-treatment temperature and Eu doping content. A temperature of 750 °C and a Eu content of 2% provided optimal catalytic activity for the SnO$_2$/Sb electrode. Phenol removal percentage was lowered by 13.2% compared to the control when higher Eu doping (5%) was applied due to the potential concentration of oxygen vacancies and the enrichment of Eu atoms on electrode surface. The unit cell of SnO$_2$ expanded by about 2% after Eu doping due to the replacement of the smaller Sn^{4+} by larger Eu^{3+}. The average size of the SnO$_2$ grains on the electrode surface for the Eu doped samples ranged from 8 to 9 nm, which was smaller than that of the control, suggesting catalysis improvement since smaller grain sizes produced more active sites on the electrode surface.

1. Introduction

Electrochemical (EC) processes are attractive for their low-volume requirements and environmental compatibility for treatment of industrial wastewaters containing toxic or non-biodegradable compounds [1–5]. In previous research [6–10], EC oxidation of a model organic pollutant (phenol) was examined with several different electrode materials, it was observed that different electrode produced a wide range of electrochemical reactions. For example, traditional anode materials such as Pt or Ti-based IrO$_2$ electrodes, and Ti-based RuO$_2$ electrodes, favored electrochemical transformation of non-biocompatible organics into forms compatible with subsequent biological treatment. In contrast, Ti/SnO$_2$ and Ti/PbO$_2$ anodes tend to result in electrochemical incineration, where organics are completely oxidized to CO$_2$. Research on the relationship between the anode materials and their structures on EC catalyst characteristics is helpful in selecting anode materials for high-efficiency EC processes.

Anodes with high stability, high activity, and low cost are important for a successful organic oxidation processes. The composition and structure of coatings on the electrode surface are the main factors that influence the electro-catalytic characteristics and stability of electrodes. Some researchers have found that Sb doped Ti-based SnO$_2$ anodes (SnO$_2$/Sb) are useful due to high oxygen evolution over-potentials and favorable electro-catalytic characteristics toward electrochemical incineration of certain recalcitrant and toxic organic compounds [7,8,11–14].

Previous research in our lab has found that introducing Gd or Co atoms onto the anode surface can change the conductivity and stability of a SnO$_2$/Sb electrode [15,16], as well as its electro-catalytic properties primarily by changing the concentration of oxygen vacancies in the SnO$_2$ crystal lattice [17]. Doping RuO$_2$ anodes with 3% gadolinium (Gd) increased electrochemical oxidation of phenol by 38.4% after a total of 1000 C of charge was applied [9]. Additionally, with proper doping of Gd (2%) in a SnO$_2$ anode, the phenol removal rate was 41% higher than the control electrode (0% Gd) [16]. Doping SnO$_2$/Sb electrodes with several kinds of RE elements can improve their electro-catalytic performance [18], but the reasons for this improved performance need additional investigation since the preparation procedure may significantly influence the composition and structure of the electrode.

Some researchers found that doping of europium (Eu) is benefit to get fine grains for a RuO$_2$ coating electrode and then its electro-catalytic ability was improved [19]. Here we examined europium

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(Eu) and the effect of different preparation parameters including the heat-treatment temperature and the Eu content. The Eu doped Ti-based SnO_2/Sb electrodes were prepared under different conditions, and their electrochemical performance was evaluated based on the degradation of phenol. The performance of the electrodes was then related to changes in the morphology and physical structures of the electrode surface.

2. Experiments and methods

2.1. Electrode preparation

Ti plates (99.5% pure), used as the base metal, were 2 cm × 3 cm and had a thickness of 1.5 mm. They were thoroughly polished with sandpaper (320-grit), degreased in 40% NaOH at 80 °C for 2 h, etched in 15% oxalic acid at 98 °C for 2 h, and then thoroughly washed with de-ionized (DI) water. Treated Ti plates became grey, losing their metallic sheen.

Eu doped Ti-based SnO_2/Sb electrodes were prepared by electro-deposition, followed by thermal oxidation of the inner coating layer and pyrolysis of the dipped outer layer using previously described procedures [17]. For inter layer preparation, the Ti plate was used as the cathode in 100 mL of an ethanol solution containing 17.5 g $SnCl_4 \cdot 5H_2O$, 0.73 g Sb_2O_3, and 2 mL of concentrated HCl (37%), with Ti/RuO_2 as the counter electrode. A constant DC current of 0.12 A was charged for 25 min for cathode electroplating. The layer on Ti plate was then annealed at 400 °C for 2 h. For the outer layer, the Ti plate was dipped into a coating solution consisting of 30 g $SnCl_4 \cdot 5H_2O$, 0.8 g Sb_2O_3, 2.5 mL concentrated HCl (37%) and a variable amount of $Eu(NO_3)_3$ concentration (Eu/Sn mole ratios of 0.5, 1.0, 2.0, 3.3, and 5.0%) in 50 mL n-butanol. The electrode was then dried in an infrared oven. After five cycles of both dipping and drying, the Ti plates were heated in a muffle oven (450 °C for 20 min) for pyrolysis of the coating. The above process (dipping, drying and pyrolysis) was repeated three times and finally, the electrodes were individually heated at different temperatures of 450, 550, 650, 750 and 850 °C for 2 h.

2.2. Phenol electrolysis

EC phenol degradation was conducted in 100 mL glass beakers. For each cell, a 6 cm^2 (2 cm × 3 cm) anode, prepared as described above, and a stainless steel cathode having the same area was placed in the beaker with a 15-mm spacing between the electrodes. A DC potentiostat with a voltage range of 0–30 V was used as the power supply for organic degradation studies. Electrolysis was performed under galvanostatic control at 0.12 A. The phenol solution (80 mL, 100 mg L^{-1}) was placed in each cell with a 0.25 M Na_2SO_4 electrolyte. The solution in the cell was analyzed every 30 min for the concentration of phenol and total organic carbon (TOC). Concentration of phenol was measured using a standard spectrophotometric method [20]. TOC was analyzed using a TOC Analyzer (Shimadu 5000A). Experiments of phenol electrolysis were conducted in triplicate. The data were given as the means of the triplicate, and the corresponding standard deviations were found to be less than 5%.

2.3. Structural characterization of the electrodes

The morphology and element analysis of the electrodes were obtained using a scanning electron microscope (KYKY-AMRAY MODEL-1000B) equipped with an energy dispersive spectrometer (EDS). X-ray dot-mapping was used to analyze the distribution of coating elements. X-ray diffraction (XRD) patterns of the coating films on these electrodes were recorded on a D/max-rB XRD
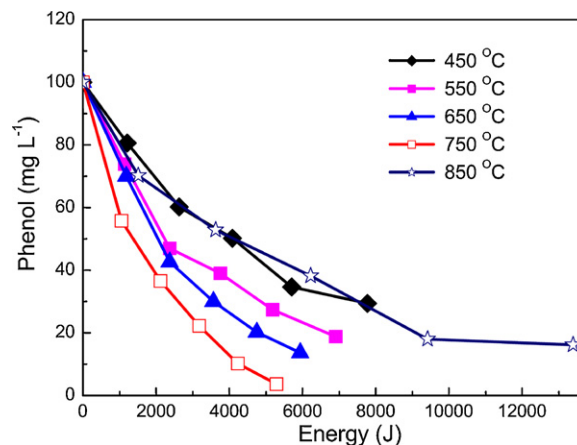

Fig. 1. Effect of pyrolysis temperature for 3.3% Eu/Sn doped SnO_2/Sb electrodes on phenol removal.

instrument (Rigaku, Japan) equipped with graphite monochromator using Cu Kα radiation, with an operating voltage of 45 kV and a current of 50 mA.

3. Results

3.1. Effect of pyrolysis temperature on the electro-catalytic performance of Eu doped Ti-base SnO_2/Sb electrodes

The effect of final pyrolysis temperature on the anode performance was investigated at a fixed Eu content of 3.3% (Eu/Sn). Considering that a same current may cause different voltages on the electrolytic cells due to different anodes, phenol removal efficiency is presented as a function of energy consumption (Fig. 1). It is obvious that phenol removal is dependent on the pyrolysis temperature used in the anode preparation process and different power consumption was found for different anodes. Using an electrode heat-treated at 750 °C, 96.4% of phenol was removed after 5290 J of power consumed (corresponds to 2.5 h electrolysis). Lower phenol removal efficiencies were found at temperatures of 450 °C (61.4%), 550 °C (73.8%), 650 °C (83.0%) and 850 °C (56.7%) with same power consumption. At the end of electrolysis (2.5 h), phenol removal of 70.6% (450 °C), 81.2% (550 °C), 86.4% (650 °C) and 83.8% (850 °C) can be obtained with different power consumptions. It was thought that these different pyrolysis temperatures affected the structure of the electrode coating, as discussed further below.

3.2. Effects of Eu content on the electro-catalytic performance of Eu doped Ti-base SnO_2/Sb electrodes

Different Eu contents were examined for their effect on phenol removal using a fixed pyrolysis temperature of 750 °C (Fig. 2). A 2.0% doping of Eu into the SnO_2/Sb electrode provided the maximum phenol degradation rate, with 72% phenol removal after 1770 J power consumed (corresponds to 1 h electrolysis). This was 15.8% higher than the control (no Eu) with same power consumption. After 2 h of electrolysis, 95% of the phenol was removed using the 2% Eu electrode with a power consumption of 3540 J, compared to 2.5 h needed for 97% phenol removal by the control with 4700 J power consumption. There were small differences in phenol removal using electrodes with Eu/Sn contents of 0%, 0.5%, 1.0% and 3.3%. However, phenol removal efficiencies were substantially decreased using a higher Eu/Sn ratio of 5.0%, with a phenol removal percentage lowered by 13.2% compared to the control, and by 17.8% compared to the 2.0% electrode after 2 h of electrolysis and with more power consumption.
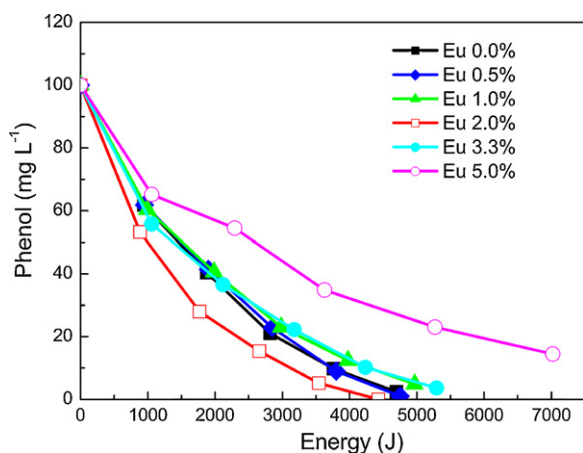
Fig. 2. Effect of Eu content for doped SnO$_2$/Sb electrodes calcined at 750 °C on phenol degradation.

3.3. Removal efficiency of TOC with Eu doped SnO$_2$/Sb electrode in phenol degradation process

To investigate the mineralization of organic compounds in the EC treatment process, the experiments were performed to detect the removal efficiency of TOC with selected Eu doped SnO$_2$/Sb electrode. The results are represented in Fig. 3. About 70% of TOC was removed in 1.5 h with the 2% electrode, which is higher than the control and the power consumption is lower for 2% electrode than the control. After 2.5 h of electrolysis, 90% of TOC was removed with the 2% electrode, showing a good capacity on intermediate organics degradation.

3.4. Crystal structure analysis of the coating layer

The XRD patterns of Eu doped SnO$_2$/Sb electrodes are shown in Figs. 4 and 5, with the main diffraction peaks labeled for composition. Aside from a series of diffraction peaks corresponding to rutile type SnO$_2$ in both of the samples, there were also peaks for TiO$_2$ in the XRD spectra. The results shown in Fig. 4 demonstrate that the intensities of the peaks corresponding to rutile type SnO$_2$ increased with pyrolysis temperatures in the range of 550–750 °C. This suggests that a well-developed SnO$_2$ crystal was obtained when with increased pyrolysis temperature.

Compared to the control samples lacking any Eu, it was found that the intensities of SnO$_2$ diffraction peaks were weakened
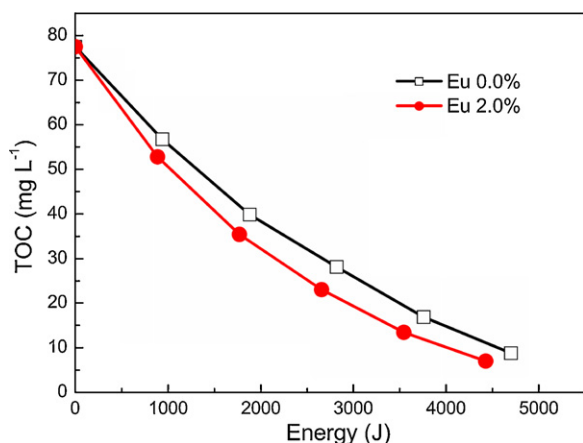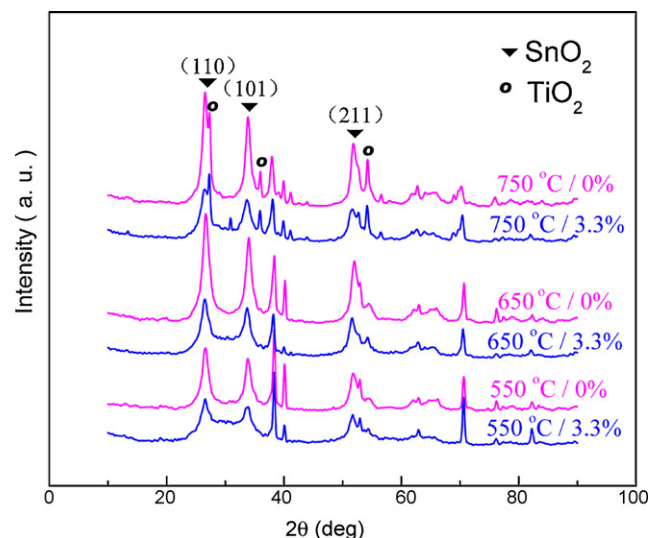

Fig. 4. XRD patterns of Eu doped SnO$_2$/Sb electrodes calcined at different temperature for Eu/Sn ratios of 0% and 3.3%.

after Eu doping (Figs. 4 and 5). Another interesting phenomenon observed in Fig. 5 is that the intensities of the SnO$_2$ diffraction peaks of Eu doped SnO$_2$/Sb electrodes (heat-treated at 750 °C) increased as the Eu content was increased from 2% to 5%. However, this increase was associated with a decreased performance with Eu contents of 2–5% (Fig. 2). Thus, it appears that a Eu addition of 2% is optimal for enhancing the electro-catalytic ability of the electrode without well SnO$_2$ crystal formation.

3.5. Morphology and elemental composition

The morphology of freshly prepared metal oxide coatings of Eu doped SnO$_2$/Sb electrodes were examined by SEM. The surface coating of 2% Eu/Sn electrode appeared to be more uniform and composed of smaller cracks than the other two electrodes (control and 5% Eu/Sn) (Fig. 6). X-ray dot-mapping, which was used for analyzing the distribution of coating elements, indicated a uniform distribution of Sn, Sb, and Eu on the electrode surface (Fig. 7). Enrichment of doping elements, including Sb and Eu, was observed using energy dispersive spectrometry (Table 1), where *theoretical value* stands for the additive ratio in the coating solution and the *actual value* is the EDS test result.
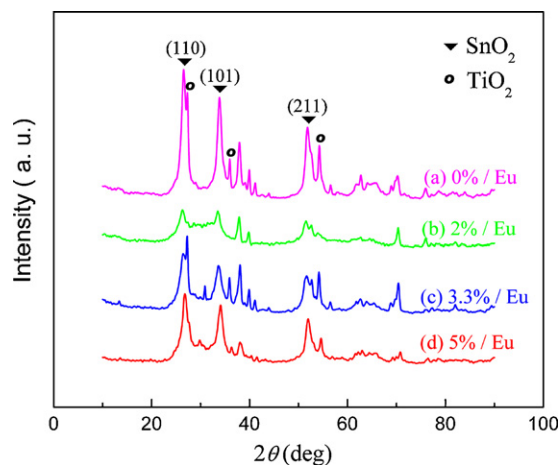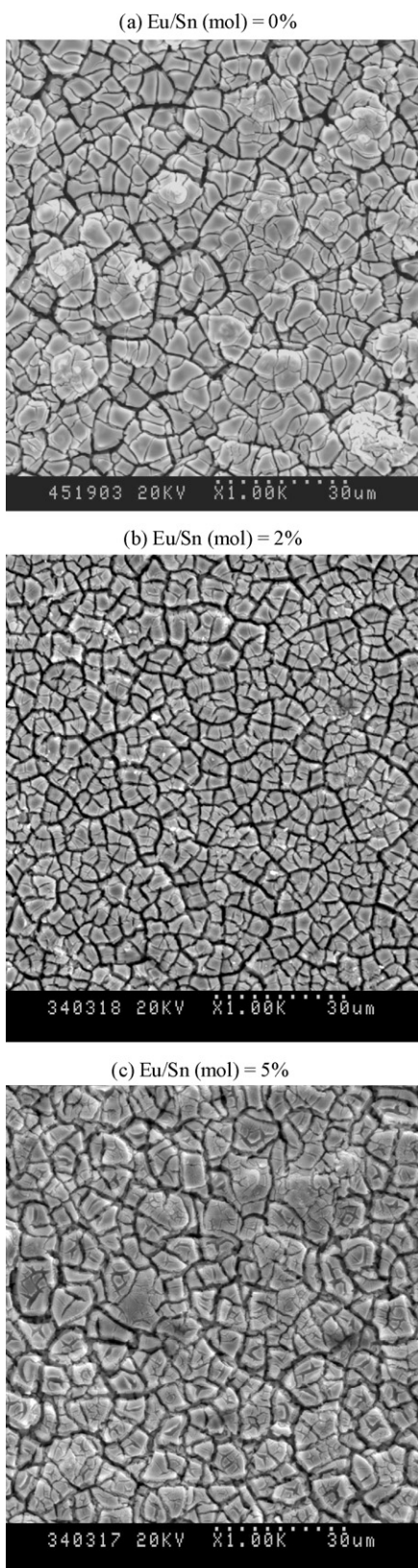

Fig. 3. Removal efficiency of TOC with Eu doped SnO$_2$/Sb electrode on phenol degradation.

Fig. 5. XRD patterns of Eu doped SnO$_2$/Sb electrodes calcined at 750 °C for Eu mole percentages of: (a) 0%, (b) 2%, (c) 3.3% and (d) 5%.

(a) Eu/Sn (mol) = 0%

(b) Eu/Sn (mol) = 2%

(c) Eu/Sn (mol) = 5%

Fig. 6. SEM micrographs of Eu doped SnO_2/Sb electrodes calcined at 750 °C for Eu/Sn molar ratios of: (a) 0%, (b) 2% and (c) 5%.

Table 1
Composition of metal elements on electrodes surface.

Electrode	Element				
	Sn	Sb (at.%)		Eu (at.%)	
		Theoretical	Observed	Theoretical	Observed
Eu/Sn 0%	100		14.2	0	0
Eu/Sn 2%	100	6.4	13.7	2.0	10.6
Eu/Sn 5%	100		14.0	5.0	26.2

4. Discussion

In an EC process using a metal oxide anode, it is thought that the hydroxyl radicals generated from water electrolysis play a critical role in the degradation of the organic substance [21,22]. A possible oxygen transition may occur from the adsorbed hydroxyl radicals ($MO_x[•OH]$) to the lattice of the metal oxide anode, forming the higher oxide MO_{x+1}, and the oxygen forms oxidizing organic substance to different products [21,23]. Since $MO_x[•OH]$ favors electrochemical combustion while MO_{x+1} favors electrochemical conversion [23], the ratio of $MO_x[•OH]$ vs. MO_{x+1} on the anode surface is an essential factor affecting catalytic performance of an oxide anode. SnO_2 is known as an n-type semiconducting metal oxide and its properties depend strongly on its non-stoichiometric composition (i.e. O:Sn ratio <2). Oxygen vacancy is the predominant atomic defect in SnO_2 crystal [24] which provide more opportunities for oxygen atom transfer from adsorbed •OH to the crystal lattice [16]. Thus, the performance of Eu doped SnO_2/Sb electrodes should depends strongly on the number of active sites that can adsorb hydroxyl radicals, and the concentration of oxygen vacancies needed for the formation of MO_{x+1}. More active sites and less oxygen vacancies on anode surface are expected for improved performance.

When lower Eu contents were used, the lattice parameter of the Eu modified samples were larger than that of reference samples without Eu doping (Tables 2 and 3), consistent with our previous studies [16]. A reasonable explanation for the lattice expansion is that Eu^{3+} ion entered the unit cell of SnO_2 and the larger ionic radii of Eu^{3+} (95 pm) replaced the Sn^{4+} with smaller ionic radii (71 pm).

Nanometer sized SnO_2 crystallites were observed in our samples, with grain sizes ranged from 8 to 10 nm. The SnO_2 grain size of Eu modified samples was smaller than that of control samples

Table 2
Refinements to the XRD patterns of SnO_2 grains on Eu doped SnO_2/Sb electrodes calcined at different temperature.

Eu doped SnO_2/Sb electrode samples		Average grain size, D (nm)	Lattice parameters (Å)	
			a	c
550 °C	0%	8.8	4.7177	3.1992
	3.3%	–	–	–
650 °C	0%	9.7	4.7281	3.172
	3.3%	9	4.7597	3.2023
750 °C	0%	10	4.7455	3.1888
	3.3%	8	4.777	3.2108

Table 3
Refinements to the XRD patterns of SnO_2 grains on SnO_2/Sb electrodes calcined at 750 °C with different Eu content.

Eu doped SnO_2/Sb electrode samples	Average grain size, D (nm)	Lattice parameters (Å)	
		a	c
0%	10	4.7455	3.1888
2%	–	–	–
3.3%	8	4.777	3.2108
5%	8.5	4.6935	3.170

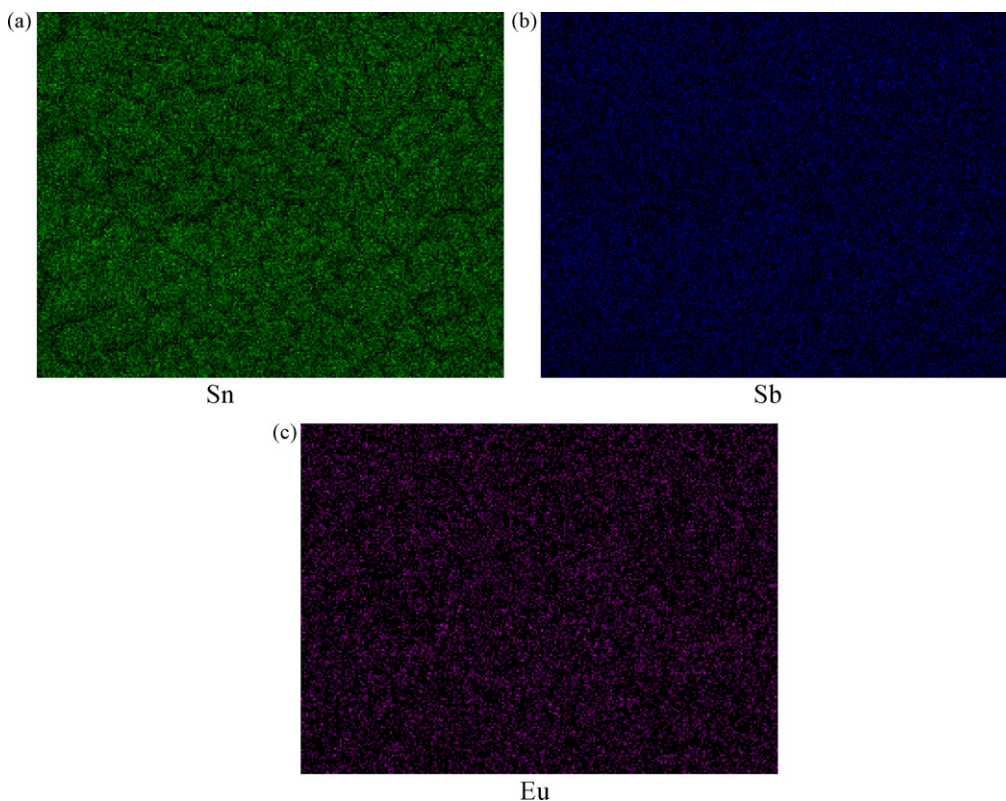**Fig. 7.** X-ray dot-mapping of Eu (2 mol%) doped SnO$_2$/Sb electrodes calcined at 750 °C for (a) Sn, (b) Sb, and (c) Eu elements.

without Eu doping (Tables 2 and 3). The reduction of SnO$_2$ grain size with Eu addition suggests that improvement in catalytic ability was associated with a smaller grain size and thus more active sites and surface area. As reported before, the Sb^{5+} in SnO$_2$ lattices is thought to be helpful for adsorption of polar species and may act as active site [25]. Smaller grain size of Eu doped samples implies more surface atoms including Sb^{5+} and therefore can enhance the electro-catalytic capacity of the electrode.

However, Fig. 2 shows that not all Eu doped SnO$_2$/Sb electrodes produced better performance in terms of phenol reduction compared to controls SnO$_2$/Sb (no Eu). This shows that a high Eu content alone does not favor improved catalysis with SnO$_2$/Sb electrodes. From the perspective of an electron balance, there should be more oxygen vacancies accompanying the substitution of Eu^{3+} (three electrons) for Sn^{4+} (four electrons) [16]. Additionally, EDS analysis indicated enrichment of Eu atoms on the electrode surface (26.2% Eu in the surface compared to 5% in the preparation solution). The deviation of the element contents in the oxide coating layer from the original dipping solutions was thought to be caused by thermal decomposition, which resulted in different volatility of the components and elements diffusion in the coating layers. The concentrated Eu^{3+} on electrode surface implies a potential of higher concentration of oxygen vacancies on the actual electrode surface than that expected from theory. Thus, high doping content of Eu (more than 3.3%) resulted in deceased performance for the SnO$_2$/Sb electrode.

The electrochemical degradation of phenol on different Eu doped SnO$_2$/Sb electrodes also indicates that the heat-treatment temperature has a remarkable influence on the electrode's catalytic performance and stability. Raising temperature moderately favors enhancement of the catalytic activity with Eu doped SnO$_2$/Sb electrodes. Fig. 4 showed that the intensities of the SnO$_2$ diffraction peaks were enhanced with increased temperature, indicating a better crystallinity which would favor improved catalytic activity. On the other hand, there were TiO$_2$ peaks in the XRD patterns

and their intensity increased with pyrolysis temperature (Fig. 4). The generation of TiO$_2$ at the interface between Ti substrate and SnO$_2$ coating could decrease conductivity and thus cause a loss in electrode performance (Fig. 1).

5. Conclusions

Heat-treatment temperature and Eu content were studied to reveal their effects on catalytic performance of the electrodes. The electrochemical degradation of phenol was strongly influenced by the preparation parameters. A moderately high pyrolysis temperature of 750 °C and Eu content of 2% produced the best performance with SnO$_2$/Sb electrodes. The introduction of the Eu produced smaller grain sizes of SnO$_2$, resulting in larger surface areas and active sites on the electrode surface that improved electro-catalytic oxidation. Higher Eu contents were not expected to improve performance due to the expected increase of oxygen vacancies. It is suggested that Eu doping has two opposite effects on structure of SnO$_2$/Sb electrodes, which are reduction of grain sizes and increase of oxygen vacancies of SnO$_2$; the former effect is welcome but the latter is undesirable for better performance of SnO$_2$/Sb electrodes.

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