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Microstructure and photocatalytic properties of WO_3/TiO_2 composite films by plasma electrolytic oxidation

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ABSTRACT

WO_3/TiO_2 composite films were prepared by plasma electrolytic oxidation in electrolytes containing different tungstate concentration. The morphology, topography, compositions, crystal structure and photophysical properties of films were characterized by SEM, AFM, EDX, XRD, XPS, UV–vis DRS and PL, the surface acidity of films was investigated by ATR-IR. The results showed porous films formed on the titanium substrate, consisted of Ti, O and W, and presented mixed crystal of anatase and rutile. Tungsten species were well-dispersed for WO_3/TiO_2 film formed in lower tungstate concentration, but were in crystalline WO_3 in higher concentration. For WO_3/TiO_2 film prepared in optimal tungstate concentration, the highest content of anatase and the maximum surface acidity were obtained, and the recombination of holes and electrons was effectively inhibited. However, coupled-WO_3 did not shift the optical absorption to the visible region. The improvement of photocatalytic activity was attributed to the increased surface acidity, better separation between photo-induced carriers and higher content of anatase.

1. Introduction

TiO_2 has attracted much attention as a photocatalyst for degradation of organic contaminations, due to its low cost, strong oxidizing power, non-toxicity, photo-stability and chemical inertness [1,2]. A number of researches have been focused on the formation of TiO_2 films because of its reusability. However, practically technological application of pure TiO_2 film is limited by easy recombination of photo-induced hole–electron pairs. Coupling TiO_2 with other semiconductor is considered as a good way because coupling two semiconductors with different redox energy levels can increase the charge separation for their corresponding conduction and valence bands [3,4].

Plasma electrolytic oxidation (PEO) has been widely used to produce oxide films on the valve metals, such as Mg, Al and Ti [5,6]. The distinct properties of oxide films formed via PEO include high porosity and good adhesion to the metal substrates [7,8]. Porous film has larger surface area reacting with fluids contaminated by harmful organic pollutants and good adhesion is beneficial to long term photocatalytic treatment. Furthermore, some elements of the solution could enter the oxide films under electrophoretic effect generated in plasma discharging. So, the composition, structure and physical–chemical properties can be changed by adding different electrolyte ionic composition.

In recent years, several approaches of W doping have been developed to improve photocatalytic activity of TiO_2, it was found that the photocatalytic activity in visible light of TiO_2 nanopowders produced by flame spray synthesis (FSS) was enhanced significantly by the W-doping as well as by additional thermal treatment of those nanopowders [9]. Our previous research [10] reveals that TiO_2 film containing tungsten species can be obtained in tungstate electrolyte.

In this study, we focus on the preparation of WO_3/TiO_2 composite film using PEO technique in an electrolyte containing WO_4^{2-}, because the WO_4^{2-} will be entered the plasma channel and reduced to WO_3 under the external electric field. WO_3 is an appropriate material to couple with TiO_2 because WO_3 has a suitable conduction band potential to allow the transfer of photogenerated electrons from TiO_2 facilitating effective charge separation [11]. The concentration of tungstate on the microstructure, photophysical properties and photocatalytic activity of the oxide films were investigated.

2. Experimental

2.1. Preparation of oxide films

A high purity titanium (99.9%) sheet was selected as anode. Prior to PEO, the rectangular samples with dimensions 0.02 m × 0.02 m × 0.002 m were polished with emery papers (#1200 grit) and degreased using acetone followed by rinsing with distilled water, while a stainless steel plate was used as the counter electrode. A

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home-made 10^4W device using for PEO process consisted of an AC power supply, an electrolyte cell, a stirring and cooling system. The positive voltage, negative voltage, frequency and duty cycle were 400 V, −30 V, 700 Hz and 0.3, respectively. The temperature of the electrolyte was kept under 40 °C. The period of treatment was 300 s. The electrolyte consisted of Na_2WO_4, 50 mol m^{-3} NaOH and 48 mol m^{-3} NaF. The concentration of Na_2WO_4 was 10, 30, 50 and 70 mol m^{-3}, respectively. The as-prepared films were marked as A, B, C and D corresponding to the gradually increased concentration of Na_2WO_4.

2.2. Analyses of oxide films

The morphological features of WO_3/TiO_2 composite films were characterized by Quanta 200 scanning electron microscopy. The topography of films was characterized by SPA 400 atomic force microscopy. The composition of films was analyzed with an energy dispersive X-ray (EDX) detector incorporated into the scanning electron microscopy. The crystalline structure was determined by XRD analysis using a D/Max-IIIB diffractometer (Cu K_α radiation). The chemical states of species were measured by the VG Multilab 2000 X-ray photoelectron spectrogragh (XPS). Diffuse reflectance spectra (DRS) were recorded with a Shimadzu UV-2550 UV–vis spectrophotometer with an integrating sphere attachment. Photoluminescence (PL) spectra were measured using a Shimadzu RF-5301 Fluorescence spectrophotometer with an excitation wavelength of 240 nm at room temperature. The ATR-IR spectroscopy of WO_3/TiO_2 composite films was determined by a Bruker VERTEX 70.

2.3. Evaluation of photocatalytic activity

Photocatalytic activity of WO_3/TiO_2 composite films was measured by monitoring photodecolouration of rhodamine in aqueous solution. Samples of 0.02 m × 0.02 m × 0.002 m were immersed into 10^{-5} m^3 of a 2.1×10^{-2} mol m^{-3} aqueous rhodamine solution for 1800 s prior to UV light irradiation. An ultraviolet germicidal lamp, whose power and wavelength is 40 W and 365 nm, was used as light source. The irradiation time was 3.6×10^4 s. The solution was constantly supplied with air during the reaction. The concentration of rhodamine was calculated from the height of peak at 550 nm in UV–vis spectra (Shimadzu, UV-2550) by using the calibration curve.

3. Results and discussion

3.1. Morphologies, topography and compositions analysis of WO_3/TiO_2 composite films

Fig. 1 shows the morphologies of WO_3/TiO_2 films. The surfaces of WO_3/TiO_2 films were porous, which was beneficial to adsorption of organic compounds and photon absorption. The size of pores on the surface of WO_3/TiO_2 films was 3–10 μm. All the pores were well separated and homogeneously distributed over the films, which were produced by the plasma discharge in the oxidation process. Furthermore, the pore size became bigger slightly and the pore shape became from slender to roundish when the concentration of tungstate increased. The electrical resistance of the electrolyte and, consequently, the total electrical resistance of the electrochemical circuit decreased with the concentration of tungstate increasing, which resulted that the total electrical current of the electrochemical circuit increased. As a result, the plasma discharge became much stronger, which resulted that the pore size increased slightly [12]. Since the electrical current of the electrochemical circuit increased with the concentration of tungstate increasing, stronger electron avalanches take place, which resulted in local melting and solidifying of the growing film in the adjacent electrolyte [13,14], this phenomenon made the pores become roundish easily, because the narrow position of the slender pores melted, solidified and obturated in the PEO process. However, sample D presented a damage surface. As the concentration of tungstate increased, the solution conductivity increased and plasma discharge became stronger. Then, higher temperature caused by plasma discharge made the film surface damaged.

The cross-section view of the sample C was chosen to analyze the structure and bonding conditions of the interface, and shown in Fig. 1e. There was no obvious discontinuity between the deposited films and the underlying substrate. It appeared that the PEO films were well adhered to the Ti substrate, which was beneficial for long-term degradation of organic compounds.

Table 1
Content of surface element of WO_3/TiO_2 composite films.

Element	A		B		C		D	
	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%
Ti	52.81	41.32	51.78	40.61	50.75	39.71	49.81	39.03
O	22.94	53.74	23.05	54.24	23.49	55.04	23.63	55.54
W	24.25	4.94	25.17	5.15	25.76	5.25	26.56	5.43

The AFM surface topography of sample C in a scale 10 μm × 10 μm was showed in Fig. 2., which depicted a rough surface and the surface roughness of sample C was 138 nm. Because the phenomenon of local melting and solidifying of the growing film in PEO process makes the film roughened, a rough surface is usual for PEO-synthesized films, which is beneficial to adsorption of organic compounds and photon absorption.

In order to understand the influence of $WO_4{}^{2-}$ concentration on the compositions of the films, EDX spectra of four films were examined and present in Fig. 3. The content of fluorine was too small to be detected. It was seen that the films mainly consisted of Ti, O and W, the contents of whom were present in Table 1. With the increase of the $WO_4{}^{2-}$ concentration in the electrolyte, it resulted in an increase in the content of O and W, and with an associated decrease in the content of Ti, which meant that the concentration of $WO_4{}^{2-}$ had little effect on the film compositions. The reason of the rather small effect of $WO_4{}^{2-}$ concentration on the incorporation of tungsten could be interpreted as follows. The quantity of $WO_4{}^{2-}$ that can be adsorbed by anode is limited, though the concentration of $WO_4{}^{2-}$ became higher and higher, the quantity of $WO_4{}^{2-}$ adsorbed by anode increased a little, so the content of tungsten in the film increased a little with $WO_4{}^{2-}$ concentration.

3.2. Phase analysis of WO_3/TiO_2 composite films

Crystal structures of WO_3/TiO_2 films were characterized by XRD, seen in Fig. 4. All samples showed the mixed phases of anatase and rutile, but the content between anatase and rutile was different. The relative content of anatase could be determined by the Eq. (1) [15].

$$W_A = \frac{1}{1 + 1.265 I_R/I_A} \tag{1}$$

where I_A and I_R are the diffracted intensities for the major peak of anatase and rutile phase. The results were presented in Table 2. The films of four samples mainly consisted of rutile and the highest content of anatase appeared in sample C, about 18%. It had been reported that higher content of anatase could produce higher photocatalytic activity for mixed-phase TiO_2 [16]. So, sample C would present higher photocatalytic activity.

Because electrical current and voltage applied on the anode surface increased with the concentration of tungstate increasing, the plasma discharge became stronger and stronger, which resulted that the amount of rutile phase and anatase phase both increased

Table 2
Relative content of anatase and rutile in WO_3/TiO_2 composite films.

Sample	Relative content	
	Anatase	Rutile
A	9	91
B	7	93
C	18	82
D	10	90