

Visible Light Drived N, S -codoped TiO₂ Photocatalysts Grown by Microplasma Oxidation Method

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N, S-codoped TiO₂ films were grown in situ on titanium sheet by micro-plasma oxidation method in electrolyte with (NH₄)₂SO₄ and H₂NCSNH₂. X-ray diffraction, spectrophotometer and scanning electron microscopy equipped with energy dispersive X-ray microanalysis were applied to characterize the films. A model textile industry pollutant (Rhodamine B) was used to study the photo-catalytic properties of the modified films. The result shows that N,S-codoped TiO₂ films exhibits higher photocatalytic activity, which can be attributed to the increase of surface area and light utilization of N,S-codoped TiO₂ films.

Keywords: Micro-plasma oxidation; doping; Titanium dioxide; Photocatalyst

1. INTRODUCTION

TiO₂ has a lot of merits, such as its photo-stability, strong oxidizing power, non-toxicity, chemical and biological inertness, stability, as well as its low cost. So it is one of the most studied semiconductors for photocatalytic reactions [1-4]. However, the main drawback of TiO₂ is its relatively large band-gap (3.2eV), which make it absorb only near-ultraviolet region of the solar irradiation, limiting its practical applications since UV comprises only a small fraction of solar radiation [5].

In order to improve photo-catalytic efficiency, tremendous efforts have been made in recent years. TiO₂ doped by certain types of transition metals and nonmetals has been extensively studied [[4]]. Asahi et al. [6] prepared N-doped TiO₂ materials with visible light activity. Subsequently, TiO₂ photocatalysts doped with nonmetals (N [7], F [8], S [9], etc.) have been reported; their photo-catalytic

performance in the visible light region was enhanced. Nonmetals doping can enhanced visible light absorption results from: (1) an isolated narrowband forms above the valance band of TiO_2 after nonmetals replacing oxygen [6]; (2) the nonmetals should be sat at a weak interaction site like an oxygen-deficient site. Several reports describe the subband-gap levels in their electron structures, which is responsible for the vis-activity [10].

TiO_2 films have been prepared by a variety of deposition techniques such as sol-gel process, colloid baking, chemical vapor deposition, evaporation and various reactive sputtering depositions, microplasma oxidation(MPO) [4, 5, 11-19]. Among these methods, micro-plasma oxidation method is based on the anodic oxidation, which occurs at potentials above the breakdown voltage of the oxide film growing on the anode surface [20]. The process consists of numerous simultaneous and uniform plasma discharges over the metal surface. And the instantaneous temperature of the films can exceed $2000\text{ }^\circ\text{C}$ in this method, which makes it easy for dopant to be added in TiO_2 films [21].As the process combines electrochemical oxidation with a high-voltage spark treatment in anelectrolyte bath, oxide is synthesized inside high-voltage breakthrough channels across the former oxide layer and have good adherence with substrate metal. In this way, producing TiO_2 thin films only needs very short time.

In this paper, nitrogen and sulfur co-doped TiO_2 photocatalyst was grown on the titanium substrate by use of the MPO method. $(\text{NH}_4)_2\text{SO}_4$ and H_2NCSNH_2 were selected as sulfur and nitrogen source to modify the TiO_2 during the MPO. The objective of the research was to investigate the effects of H_2NCSNH_2 in the $(\text{NH}_4)_2\text{SO}_4$ electrolyte solution in the MPO process, on the structural property, the surface morphology and the photo-catalytic activity of the modified films under the visible light.

2. EXPERIMENTAL

2.1. Catalyst preparation

A titanium sheet (99.9% in purity) was selected as an anode, with a reaction area of $25\text{mm}\times 10\text{mm}\times 0.5\text{mm}$ and a copper sheet was introduced as a cathode. The set-up scheme of the oxidation equipment is shown in reference [22]. 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 of $10\text{ A}/\text{dm}^2$ was first performed until a anode-to-cathode voltage of 200 V was reached, and then the voltage was maintained. The oxidation time was 10 min. The temperature was controlled in the range $(20\pm 0.2\text{ }^\circ\text{C})$ by a cold water jacket. The electrolyte solution consisted of 0.5M analyticalgrade $(\text{NH}_4)_2\text{SO}_4$ (supplied by Beijing Chemical Reagent Plant) and analytical-grade H_2NCSNH_2 (0 g/L, 15 g/L) solutions(supplied by Tianjin 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_2 and N,S- TiO_2 , respectively.

2.2. Characterizations of TiO_2 films

The surface morphology of the films was observed on an S-570 scanning electron microscope (SEM) from Hitachi. The X-ray diffraction (XRD) with a Cu K source (D/max-r B from Ricoh) was

applied to study the crystalline structure of the films with an accelerating voltage and an applied current of 40 kV and 30mA, respectively. The elemental distribution was analyzed by energy dispersion spectroscopy (EDS).

2.3. Evaluation of photocatalytic property of the films

The bench-scale photoreactor system consisted of a cylindrical quartz cell with the size of 25 mm in diameter and 50 mm in height and a 500 W xenon lamp. The photo-catalytic activity of each films produced by MPO was examined by measuring the degradation of the Rhodamine B dye solution. Films of 2.5 cm² were immersed into the 10 mL aqueous Rhodamine B solution (10 mg/L). The solution was stirred continuously and supplied with air in the reaction process. The Xenon light was irradiated for 180 min perpendicularly to the surface of the samples through the sidewall of the cylindrical quartz cell. Rhodamine B had the maximum absorbance at the wavelength of 552 nm in the UV spectrometry. The change of Rhodamine B concentration with the irradiation time was measured by UV spectrophotometry at the wavelength of 552 nm.

3. RESULTS AND DISCUSSION

3.1. Morphology of the Films

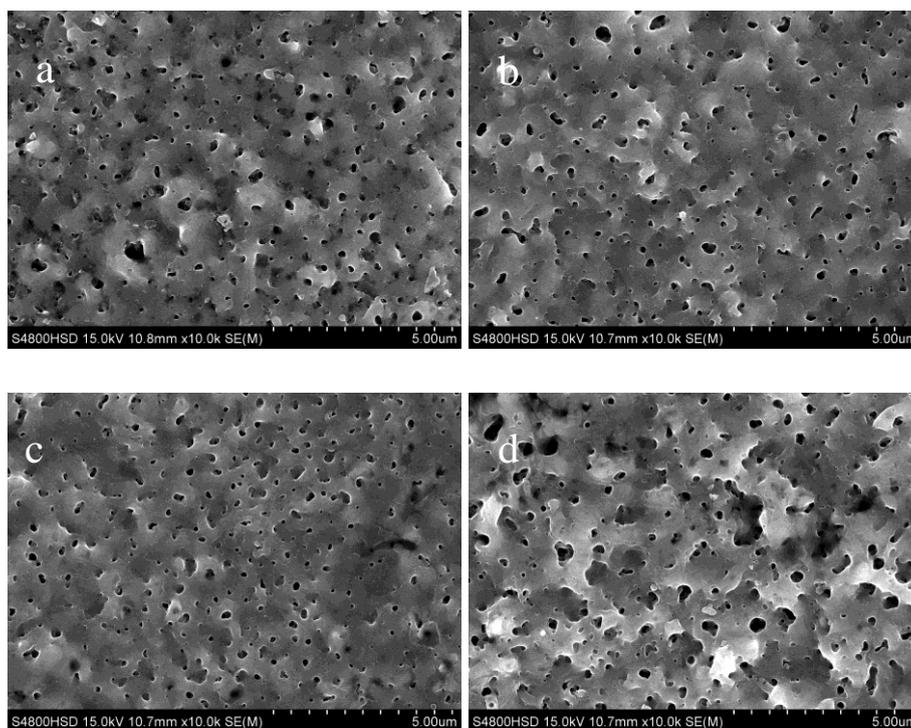


Figure 1. SEM images of TiO₂ films grown with MPO at the different concentration of H₂NCSNH₂; a) bare b) 10g/L c) 15g/L d) 20g/L

Characteristic SEM photographs of the films magnified by 1000 times are presented in Fig.1. It

can be seen that the surface of micro-plasma oxidation films are mesoporous. Compared with pure TiO_2 , the surface density of the pores on N,S-TiO₂ films increase, which can produce more reactive sites to absorb and oxide pollutants.

3.2. Structural Analysis of the Films.

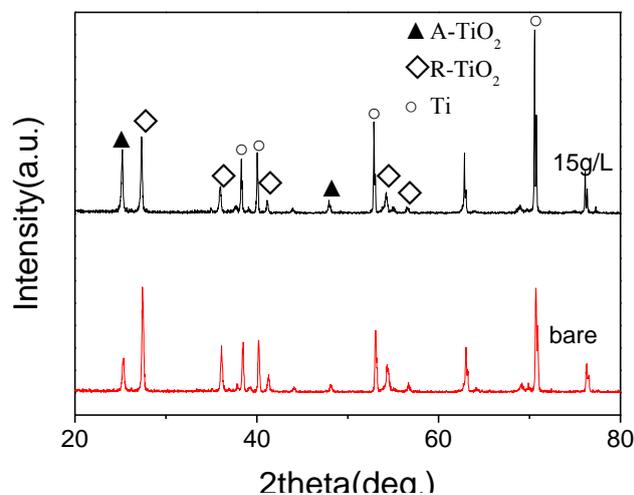


Figure 2. XRD spectra of films grown before and after H_2NCSNH_2 addition

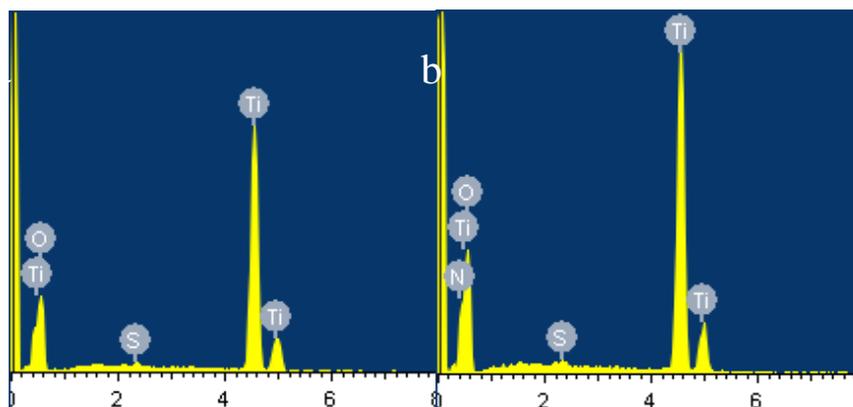


Figure 3. EDS analysis of TiO_2 grown with MPO methods in different electrolytes; a) $(\text{NH}_4)_2\text{SO}_4$ b) $(\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{NCSNH}_2$

The XRD patterns of the films prepared are shown in Fig. 2. It can be seen that there are many sharp peaks in the XRD patterns, which indicate that the prepared films have been well crystallized. And the films mainly consist of anatase and rutile TiO_2 . It can be noticed that content of anatase TiO_2 increases when the H_2NCSNH_2 is added into the electrolyte. Fig. 3 shows the EDS analysis of TiO_2 films. From Fig. 3, it is clear that the film composes of titanium, oxygen, nitrogen and sulfur when the H_2NCSNH_2 is added into the electrolyte. From the EDS spectra, it can be deduced that nitrogen and sulfur in the electrolyte can introduce into TiO_2 films during higher momentarily temperature process of MPO.

3.3. UV-vis DRS

The UV-vis absorption spectra of pure TiO_2 and N,S-codoped TiO_2 samples prepared by the MPO are shown in Fig. 4. The band-gap of TiO_2 can be estimated from the intercept of UV-vis DRS of using the following equation: $E_g = 1240/\lambda$. The absorption threshold of pure TiO_2 is 419.0 nm, which is corresponding to a band-gap of 2.96 eV. For N,S-codoped TiO_2 , the band gap energies were respectively 2.885 eV, narrower than those of pure TiO_2 , which demonstrated that doped TiO_2 can improve the absorption of visible light.

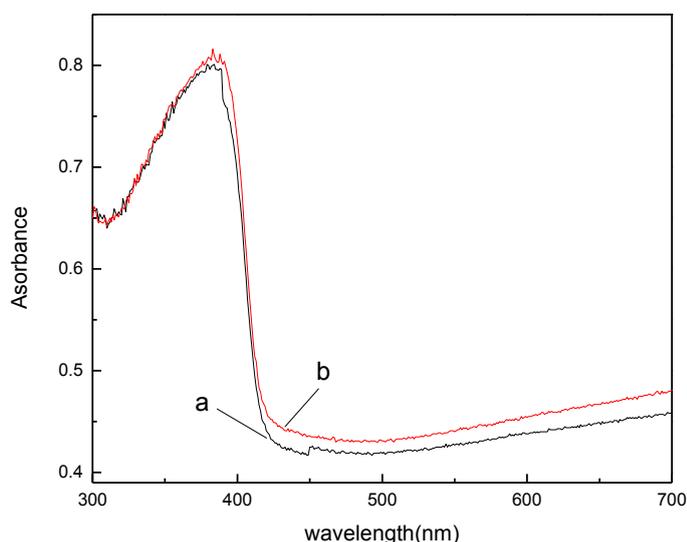


Figure 4. Figure UV-vis diffuse reflection spectroscopy of TiO_2 films in different electrolytes; a) $(\text{NH}_4)_2\text{SO}_4$ b) $(\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{NCSNH}_2$

3.4 Photocatalytic properties of the films

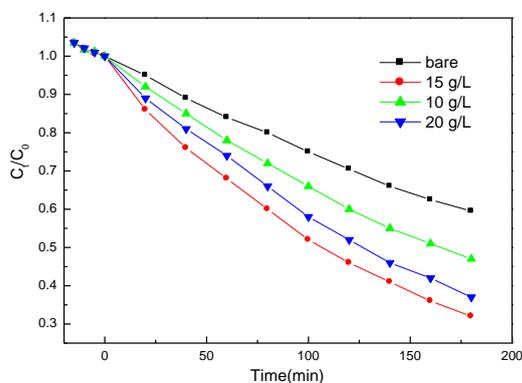


Figure 5. Photo-catalytic degradation of Rh. B by TiO_2 films produced before and after adding H_2NCSNH_2

The degradation efficiency of Rhodamine B using the produced films with the different doped

concentration of H_2NCSNH_2 are shown in Fig. 5. It can be seen that the doped films enhance the efficiency of degradation. The removal of Rhodamine B using the produced film with Xenon-irradiation of 180 min reaches about 70% when the doped concentration of H_2NCSNH_2 is 15 g/L, which is 30% higher than that using the films produced in the pure $(\text{NH}_4)_2\text{SO}_4$ electrolyte solution. The N,S-TiO₂ films are used repeatedly as many as 20 times. The degradation of Rhodamine B for 180 min is shown in Fig. 6. It can be seen that the removal efficiencies of Rhodamine B all exceed 65%. Though the efficiencies is a little lower than the latest papers, our preparation method is with only one step and it can be easily controlled, it shows a promising method in the preparation of TiO₂ Photocatalysts[23-26].

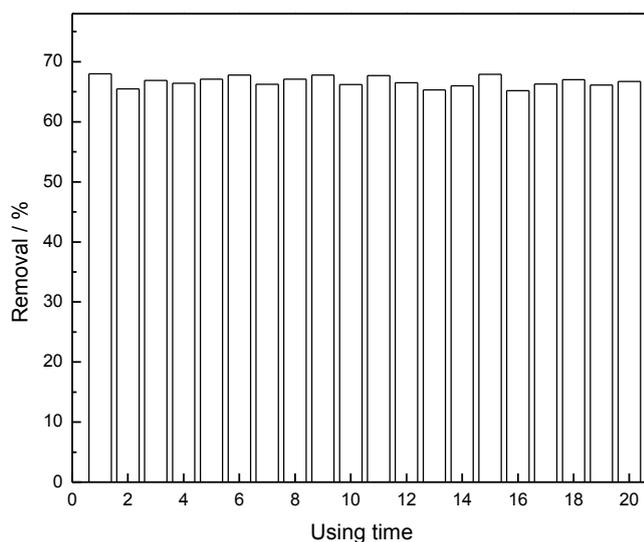


Figure 6. Reuse of N,S-codoped TiO₂ films grown with MPO method.

4. CONCLUSION

TiO₂ films have been prepared with the $(\text{NH}_4)_2\text{SO}_4$ electrolyte using MPO oxidation method in 10 min. H_2NCSNH_2 is added into the above solution in order to obtain N,S-codoped TiO₂ films. The films produced by MPO method have good adherence to substrate, better reuse properties. The produced TiO₂ films exhibit higher photo-catalytic activities than that prepared in the pure electrolyte. The increase activity is related to red shift absorption and the increase of anatase phase and surface pores density caused by nitrogen and sulfur doping.

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