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Short Communication

Preparation and Electrochromic Performance of TiO_2 Thin Film

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TiO_2 films were prepared by sol–gel methods with butyltitanate as main raw materials. Structural and electrochromic properties were investigated by XRD, SEM, electrochemical workstation and Ultraviolet visible spectroscopy. The results indicate that the TiO_2 films have better electrochromic properties when the films are amorphous with heat treatment temperature at 250℃ and applied voltage of ± 2V with respect to the reference electrode. And injected charge density is at 5.13 $mC\cdot cm^{-2}$， cyclic reversibility K value is at 0.48, transmittance is below 60% and the difference of transmittance between colored state and bleached state is 20%.

Keywords: TiO_2 Thin Film; Electrochromism; Sol-Gel; Heat Treatment

1. INTRODUCTION

As a very important functional material, the preparation, structure, performance and application of TiO_2 thin film have become the hot topic in these years[1-4]. Many researchers have prepared TiO_2 films by using different raw materials in different ways such as DC magnetron sputtering [5], sol-gel[6]and ion beam assisted depositing[7]. They also have studied its electrochromic performance as an electrochromic material.

TiO_2 thin film prepared in sol-gel method has several remarkable characteristics such as easy for control, convenient for massive preparation and low in cost, etc. In order to obtain the homogeneous and compact TiO_2 film firmly attached to the base, it is necessary to adopt the heat treatment with the gel thin film. Nevertheless in the heat treatment process, components, structures and performances of the film will be changed. In previous document[8], people have studied influence of heat treatment on the crystal transformation of TiO_2 film, and the result indicates that with the rise of heat treatment temperature, TiO_2 film is converted from amorphous state to anatase structure before it is converted to rutile structure. In document[9], people have studied sputtering TiO_2 film structure and performance, which indicates that amorphous TiO_2 film is more conducive to the ion injection and extraction. In document[10], people have studied spin-coating TiO_2 film, the result indicates that with the rise of heat treatment temperature, the grain size is larger, thin film's thickness is lessened and refractive index becomes larger.

In this paper, we use butyltitanate as the main component to prepare TiO_2 film on the surface of conducting glass in sol-gel method and systematically study the structure and electrochemical properties of TiO_2 film.

2. EXPERIMENTAL

2.1 Sol Preparation

Taking butyltitanate（$Ti(OC_4H_9)_4$））as the main component, absolute ethyl alcohol as solvent, glacial acetic acid as chelating agent and using hydrogen nitrate to adjust pH Value, precursory sol of TiO_2 is prepared. The details are as follows: a certain amount of $Ti(OC_4H_9)_4$）with vigorously stir slowly drops into absolute ethyl alcohol and stir it for two hours to obtain the homogeneous and transparent jasmine precursor A. The solution mixed by H_2O, glacial acetic acid and absolute ethyl alcohol drop into the precursory A at the speed of 3 drops/s in vigorously stir. And keep stirring it for 1 hour, placing and aging for 3 hours to obtain jasmine TiO_2 precursory sol.

2.2 Thin Film Preparation.

Prepare TiO_2 Film on ITO conducting glass substrate surface with sheet resistance at 40Ω in dipping-coating method. At first, place the conducting glass substrate in the glass container in vertical position. Slowly inject the aged TiO_2 precursory sol. After the conducting glass is completely dipped in the sol, let stand for 15 minutes before make the sol in the glass container flow out at the speed of 3 drops/s. Then keep drying the coated conducting glass in the drying cabinet for 15 minutes, by which the 1-layered film coating work is done. Repeat the above-mentioned steps to prepare the 3-layered film samples. Finally, deal with heat treatment with the coated glass substrate at 150℃, 200℃, 250℃, 300℃ and 400℃ for 2 hours. With the furnace cooling to room temperature, obtain the homogeneous and transparent TiO_2 thin film and make it into 5mm*5mm working electrode for later use.

2.3 Instrumental

Use X'Pert PRO X-ray diffractometer (Cu Kα radiographic source, voltage at 40KV, current at 40mA and wave length at 0.15405nm) manufactured by PANALYTICAL B.V. from Netherland to test the phase structure of sol powder; use SSX-550 scanning electron microscope by Shimadzu to test the microstructure of film; use LAMBDA950 UV visible spectrophotometer to test the transmitted spectrum of the thin film in the colored state and bleached state; use CS300UA electrochemical workstation manufactured by Huazhong University of Science and Technology to test the thin film's cyclic voltammetry curve; the test adopts the standard 3-electrode method: platinum black electrode is counter electrode, saturated calomel electrode is reference electrode and thin film sample is work electrode and the electrolyte is 1mol/L $LiClO_4$ + propylene carbonate (PC)solution. In the test, the scan speed is at 50mv/s.

3. RESULT AND DISCUSSION

3.1 XRD Analysis

Fig 1 is the XRD pattern of TiO_2 sol powder under different heat treatment temperatures. We can see from Fig 1 that when the heat treatment temperatures are at 150℃, 200°Cand 250°C, there is only one peak package in the diffraction pattern without the appearance of obvious crystallization peak, which indicates that TiO_2 thin film under these temperatures has amorphous structure. When the heat treatment temperature is at 300°C, with 2θ＝25.4°, 37.9°, 48.0°, 54.0°, 55.0°, 62.8°, the widened dispersion peaks appear in correspondence with crystal plane (101), (004), (200), (105), (211) and (204) of anatase phase. In this occasion, the diffraction peak is weak with incomplete crystal growth. When the heat-treatment temperature is at 400°C, TiO_2 diffraction peak is gradually sharpened, which indicates the TiO_2 grains gradual grow up and crystallization degree strengthen，the film has complete anatase structure. However, sputtering TiO_2 film is amorphous when the heat treatment temperature is less than 350℃, the anatase crystal is formed at 450℃[11]. The anatase crystal is formed at 350℃ when TiO_2 film is prepared by sol–gel methods with titanic chloride as main raw materials[12]. Therefore, the anatase crystal is formed at about 400℃ in the process of TiO_2 film preparation. The crystallization temperature of TiO_2 film varies slightly when preparation process and raw materials are different.

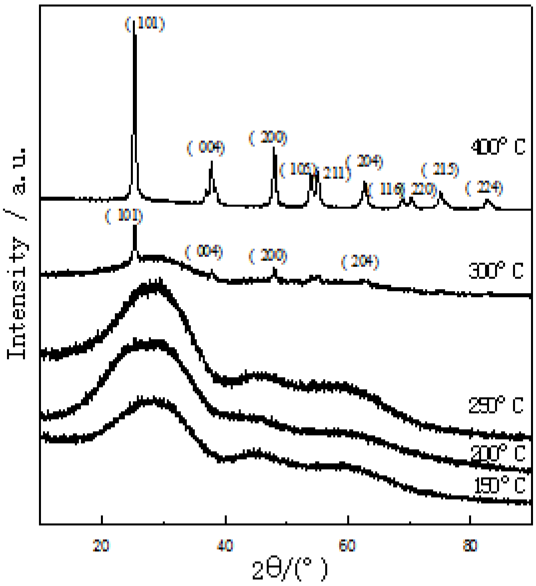

Figure 1. XRD spectra of TiO_2 powder under different heat treatment temperature

3.2 SEM Analysis

Figure 2 is SEM morphology of TiO_2film under different heat treatment temperatures. We can see from Fig 2 that when the heat treatment temperature is at 150°C and 250°C, the film is more flat, smooth and no obvious particles. When the heat treatment temperature is at 300°C, the film starts crystallizing. The TiO_2 film is rough and uneven, which is composed of particles and particle aggregates. When the heat treatment temperature is at 400°C, TiO_2 particles grow up. In document[10], TiO_2 particle is smaller with average grain size of about 7nm when heat treatment temperature is at 120℃. When heat treatment temperature is at 350℃, TiO_2 particles grow up and the distribution is more uniform and compact. Some interlinked cracks are observed in the films surface. Therefore with the rise of heat treatment temperature, the grain size is larger and roughness increases.

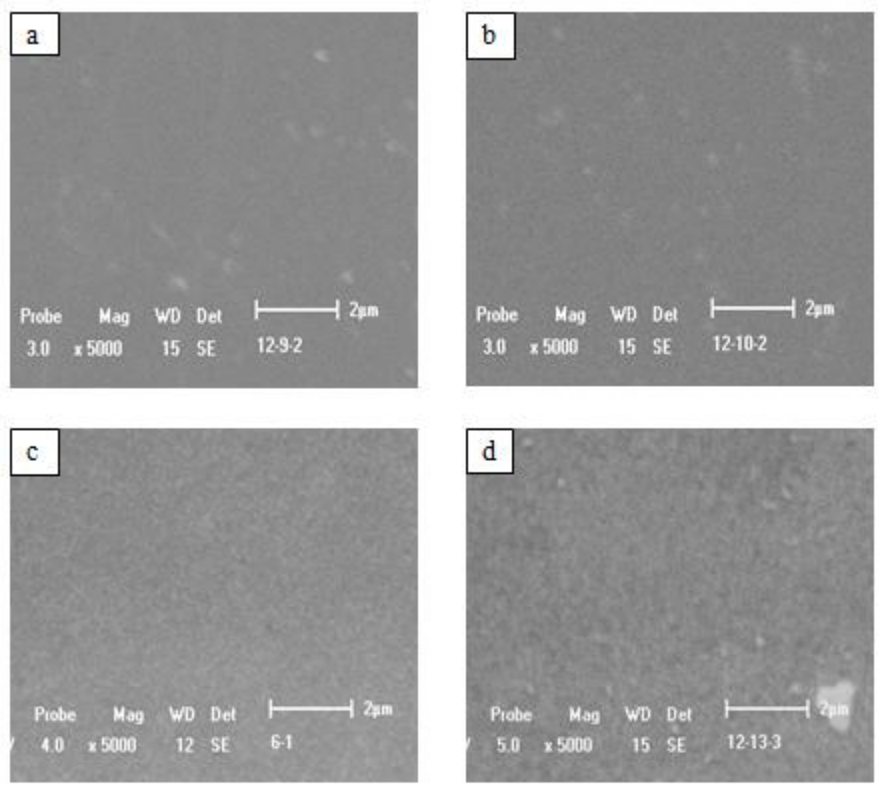

Figure 2. The SEM photographs of TiO_2 thin films under different heat treatment temperatures (a)150℃；(b) 250℃；(c)300℃；(d)400℃

3.3 Electrochemical Performance Analysis

3.3.1 Influence of heat treatment temperature

Fig 3 is the Cyclic Voltammetry（CV）curves of TiO_2 films in different heat treatment temperatures. We can see from Fig 3 that the TiO_2 thin film’s peak current gradually descends with the heat treatment temperature rises. When the heat treatment temperatures is at 150°Cand 200°C, the film has larger response current. But current fluctuation is larger, which indicates the instability of TiO_2 film in this temperature. When the heat treatment temperature is at 250°C, the organic components in the thin film are gradually decomposed, peak value current dramatic decline and its color becomes the vivid blue. When the heat treatment temperatures is at 300°C, the film starts crystallizing. The response current continues to decline. When the heat treatment temperatures is at 400°C, with the enhancement of crystallization degree, the response current is very low and the color of the film fades in the colored state.

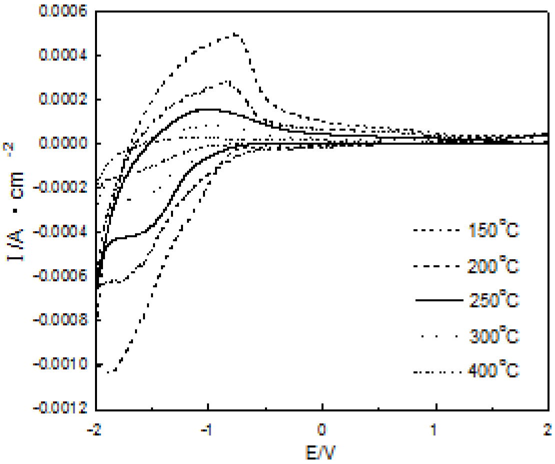

Figure 3. The CV curves of TiO_2 film under different heat treatment temperature

Table 1 is the TiO_2 film injected and extracted charge amount and reversibility in the test as illustrated in Fig 3. We can see from Table 1 that with the rise of heat treatment temperature, the charges density of injected and extracted from TiO_2 film gradually drops with the descending of charge storage capability and obvious promotion of the cyclic reversibility.

The analysis indicates that when the heat treatment temperature is low, TiO_2 film contains a large amount of non-decomposed organic framework and TiO_2 particles are distributed in organic framework with tiny dispersed state, which have larger superficial area and provide more active points for the injection of Li^+ and electrons. But the unstable organic framework makes the above-mentioned Li^+ and electrons have bad injection and extraction cyclic reversibility. Therefore, the film has larger charge storage capability when the heat treatment is at 150°C and 200°C, but K Value is only at 0.31 and 0.37. When the heat treatment temperature is at 250°C, the organic components in the film are gradually decomposed and the distributed TiO_2 particles in dispersed state gradually become larger with the reduction of superficial area, diminishing of Li^+ and electrons injection active points, which lead to decline of film's charge storage capability, but the stability is improved with K Value increased to 0.49. When the heat treatment is at 300°C and 400°C, film starts crystallizing with the grain growth and the film's stability is also increased, K Value is at around 0.6. But the diminishing of superficial area also reduce the Li^+ and electrons injection active points and the descending of charge storage capability.

In document[13], when the heat treatment temperature changes from 120℃ to 450℃, the K value of the films increases from 0.56 to 0.73, while injected charge density decreases from

14.12mC/cm^2 to 6.79mC/cm^2. The non constancy of thin film is good for improving the ion storage capability[14].

Therefore, when the heat treatment temperature is at 250°C and TiO_2 film is amorphous structure, which is more favorable for ion injection and extraction with most obvious color change and better charge storage capacity and cyclic reversibility.

Table 1. Charge density inserted into or extracted from TiO_2 film under different temperature

Heat treatment temperature /(℃)	150	200	250	300	400
Q_{in} /(mC/cm^2)	29.77	13.55	5.13	4.17	2.95
Q_{ex} /(mC/cm^2)	9.23	5.12	2.51	2.50	1.79
K values	0.31	0.37	0.49	0.60	0.61

3.3.2 Influence of external voltage

Figure 4 is cyclic voltammetry curves of TiO_2 films under different external voltage. The external voltage respectively is ±0.5V, ±1V and ±2V, scan rate is 50mV/s. We can see from Figure 4, with the increase of external voltage, the response current of TiO_2 film also increases gradually, and the color effect is becoming more and more obvious. This is because Li^+ can not be fully into the TiO_2 film when external voltage is low. But when the external voltage is larger than 2.50V, TiO_2 film will be the broken. Therefore applying external voltage of ±2V on TiO_2 film is most suitable.

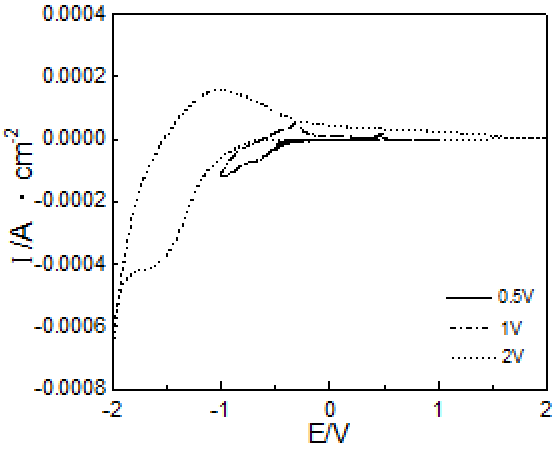

Figure 4. The CV curves of TiO_2 film under different voltage

3.4 Optical Performance Analysis

Fig 5 is the UV Visible Transmission Spectrum in colored and bleached state of TiO_2 film under 250℃ and 400℃ heat treatment with external voltage at ±2.0V.

We can see from Fig 5 that when the heat treatment temperature is at 250℃, spectral transmittance of colored state is below 60%, the difference in transmittance between colored state and bleached state, that is, △T is at around 20%.When the heat treatment temperature is at 400℃, transmittance of TiO$_2$ film in colored state at around 70% to 75% and the △T is less than 10%. With the rise of the heat treatment temperature, the color of film shallows and transmittance is obviously improved[15].As far as electrochemical deposition TiO$_2$ film is concerned[16], △T is only 5% with the heat treatment temperature at 250℃. The color of film shallows and electrochromic effect is weak.

Therefore, TiO$_2$ film used by sol-gel method has the most obvious color change and better electrochromic performance with the heat treatment at 250℃.

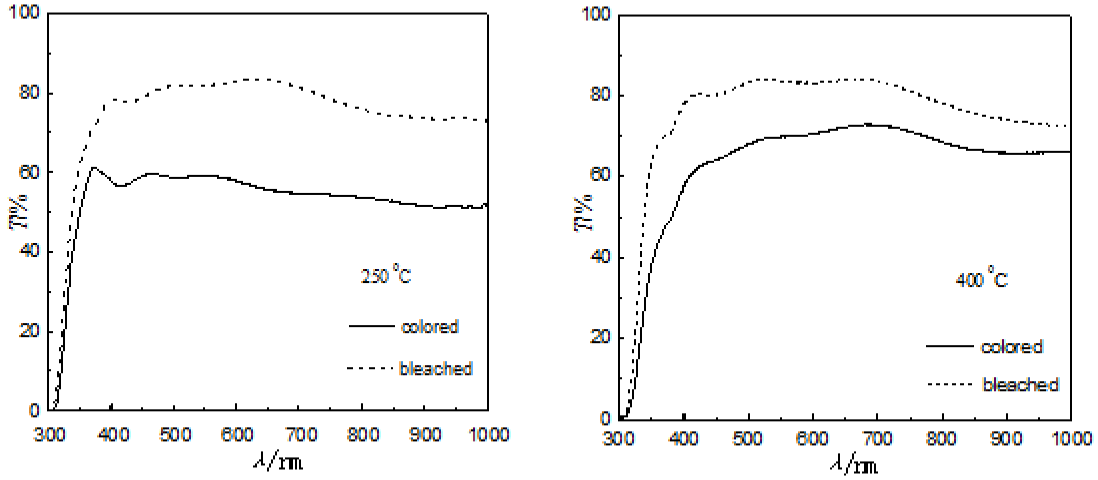

Figure 5. The UV-vis transmission spectrum of TiO$_2$ film under different heat treatment temperature

4. CONCLUSIONS

Using sol-gel method to prepare TiO$_2$ electrochromic film, which goes through heat treatment at 150℃, 200℃, 250℃, 300℃ and 400℃ respectively and the effects of heat-treatment temperature on structure and electrochromic performance are studied. The result indicates that the TiO$_2$ film has amorphous structure under 250°C; TiO$_2$ film starts crystallizing at 300°C; TiO$_2$ film forms complete anatase structure at 400°C. With the rise of heat-treatment temperature, the charge storage capacity of film drops, cyclic reversibility is promoted and optical modulation amplitude descends. When the heat-treatment temperature is at 250℃ and the TiO$_2$ film is amorphous, it has the most obvious color change and better electrochromic characteristics. The density of injected charge is at 5.13 mC·cm^{-2} with cyclic reversibility K Value at 0.48, transmittance is below 60% and the difference of spectral transmittance between colored state and bleached state is at 20%.

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