

# Enhanced Coloration Efficiency of Electrochromic Thin Film Based on $\text{TiO}_2$ and Chitosan

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**Abstract**—Self-assembled multilayer films containing  $\text{TiO}_2$  and chitosan (CS) were prepared using layer-by-layer method (LbL). The composite film fabricated on quartz and fluorine-doped tin oxide substrates was investigated using UV-vis spectroscopy, scanning electron microscopy (SEM), cyclic voltammetry (CV) and in situ chronoamperometric (CA) electrochemical measurements. The results of the UV-vis spectra confirm the uniformity of each deposition cycles. The electrochemical behavior of  $\text{TiO}_2$  has the typical property of a surface-confined electrochemical process. The composite film displays high electrochromic performance, with the coloration efficiency  $33.3 \text{ cm}^2/\text{C}$  of and optical contrast of 17.1% at 800 nm. Furthermore, the film achieved a fast switching speed of 6.0 s and 0.5 s for coloration and bleaching, respectively. The composite material undergoes transitions from colorless to dark blue when the potential is switched from +2 V to -2 V. The electrochromic performance of the LbL film containing  $\text{TiO}_2$  and CS indicates that this material is highly beneficial in view of an application in electrochromic devices.

**Keywords**- *Electrochromic;  $\text{TiO}_2$ ; Chitosan; Layer-by-layer; coloration efficiency*

## I. INTRODUCTION

Electrochromic materials (EC) which are able to change their optical properties by the application of an electrical voltage have been proved especially useful for smart windows, large-area displays and antiglare mirrors [1,2]. Recently, extensive efforts have been dedicated to the improvement of electrochromic properties such as optical contrast and coloration efficiency in terms of the practical application for electrochromic devices. Among these EC materials,  $\text{TiO}_2$  was widely studied and can switch between colorless and a blue color due to the injection/extraction of electrons and cations [3]. Recently, several techniques have been used to prepare  $\text{TiO}_2$  film including sol-gel method [4], hydrothermal method [5], electrodeposition [6] and self-organizing anodization [7].

However, the above-mentioned methods have one or more characteristic drawbacks such as high temperature and dangerous reagents, expensive equipment, rigorous preparation procedure.

An attractive, effective and convenient approach for the preparation of  $\text{TiO}_2$ -based film is the layer-by-layer (LbL) assembly technique, which offers several advantages over other thin film deposition methods, e.g. high control of the thickness, uniformity and orientation of each layer. Recently, several groups have reported the successful fabrication of  $\text{TiO}_2$  film using the LbL assembly method. Huguenin et al. prepared an LbL film from  $\text{TiO}_2$  nanoparticles and tungsten-based oxides, and then investigated chromogenic properties [8,9]. Peng and co-workers incorporated tungsten bronze nanorods and  $\text{TiO}_2$  nanoparticles into a thin film by LbL technique [10]. We fabricated electrochromic film consisting of polyoxometalate ( $\text{P}_2\text{W}_{18}$ ) and  $\text{TiO}_2$  using LbL method [11,12]. Obviously,  $\text{TiO}_2$  was chosen as a candidate for improving the electrochromic properties of tungsten-based material. To the best of our knowledge, the electrochromic performances such as coloration efficiency of  $\text{TiO}_2$ -based film by LbL have been virtually unexplored so far. Furthermore, it will be of practical importance to investigate the film structure and assembling procedure of  $\text{TiO}_2$  film.

In this paper, we successfully fabricate a nanocomposite film containing  $\text{TiO}_2$  and chitosan (CS) by LbL assembly method. Chitosan was chosen as cationic polyelectrolyte for assembled with anionic  $\text{TiO}_2$ . The composite film exhibits a classical linear increase in film absorption with the number of layers and excellent smoothness. Furthermore, the composite film exhibits enhanced electrochromic properties in terms of high optical contrast, coloration efficiency and switching times. Obviously, it can be helpful for exploring applications in electrochromic devices.

## II. EXPERIMENTAL

### A. Materials

All solvent and chemical used were of analytical grade and used without further purification. Chitosan was purchased from Amresco. The colloidal dispersion of  $\text{TiO}_2$  was synthesized by the hydrolysis of tetra-n-butyl titanate. Briefly, 10 mL of the organic titanate was dissolved into 10 mL of 2-propanol. The solution was added slowly to 100 mL of deionized water with continuous stirring and then 0.7 mL of nitric acid (70%) was added into the solution. The mixture was stirred at room temperature for 2 h, and then was heated at 80 °C while stirring for 4 h, giving rise to a stable and transparent (slightly cloudy)  $\text{TiO}_2$  sol.

### B. Preparation of the composite film

Layer-by-layer films were assembled onto FTO-coated glass and quartz substrates. First, the substrates were immersed into CS solution (1 g/L) for 2 h. Then the CS-supported substrates were alternately dipped into the  $\text{TiO}_2$  sol for 2 min, CS solution (0.8 g/L) for 10 min. After deposition of each layer, the substrates were rinsed with deionized water after each dipping. Repeat the above process until the desired number of  $[\text{TiO}_2/\text{CS}]_n$  was obtained. All adsorption process was performed at room temperature.

### C. Characterization

A conventional three electrodes system was used, with the FTO electrode coated by the self-assembled film as the working electrode, Ag/AgCl (3 M KCl) as the reference electrode and platinum coil as the counter electrode. The electrolyte was 1 mol/L  $\text{LiClO}_4$  in propylene carbonate (PC). All the electrochemical experiments were performed on the CHI 605C electrochemical workstation (Shanghai Chenhua Instrument Factory, China). UV-vis absorption spectra of quartz-supported and FTO-supported films were recorded on Varian Cary 50 Conc UV-vis spectrophotometer. Scanning electron micrographs (SEM) were obtained with a Hitachi S-4800 instrument. Spectroelectrochemical measurements of the composite films were performed by combining the in situ UV-vis spectrophotometer with the electrochemical workstation.

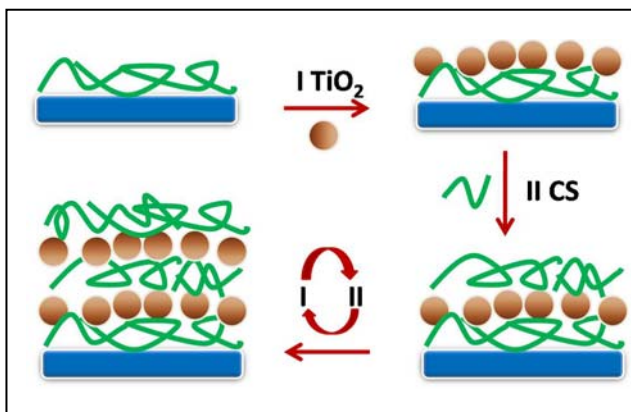


Figure 1: The schematics of the self-assembly of the  $[\text{TiO}_2/\text{CS}]$  film.

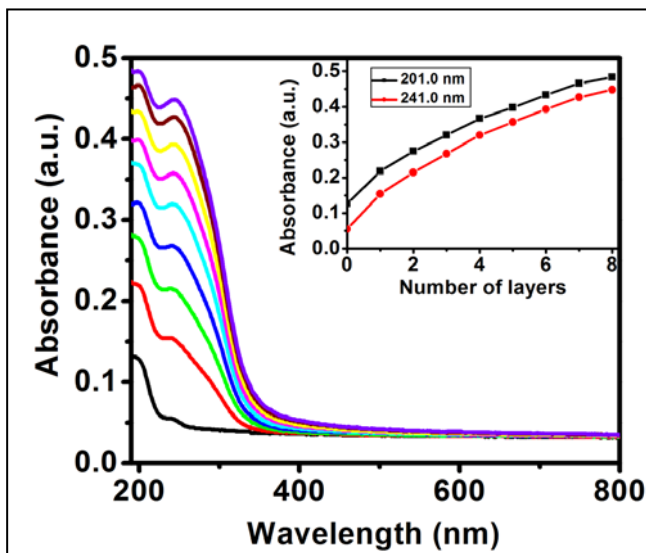


Figure 2: UV-vis absorption spectra of  $[\text{TiO}_2/\text{CS}]_n$  film (with  $n = 1-8$ ) film. Inset: plots of the absorbance values for quartz supported  $[\text{TiO}_2/\text{CS}]_n$  composite films at 201 and 241 nm.

## III. RESULTS AND DISCUSSION

### A. Fabrication and morphology of the composite film

The  $[\text{TiO}_2/\text{CS}]_n$  composite film was assembled onto ITO-coated glass via ionic attraction of oppositely charged  $\text{TiO}_2$  and CS. The schematics of the self-assembly of the  $[\text{TiO}_2/\text{CS}]_n$  film are illustrated in Fig. 1.

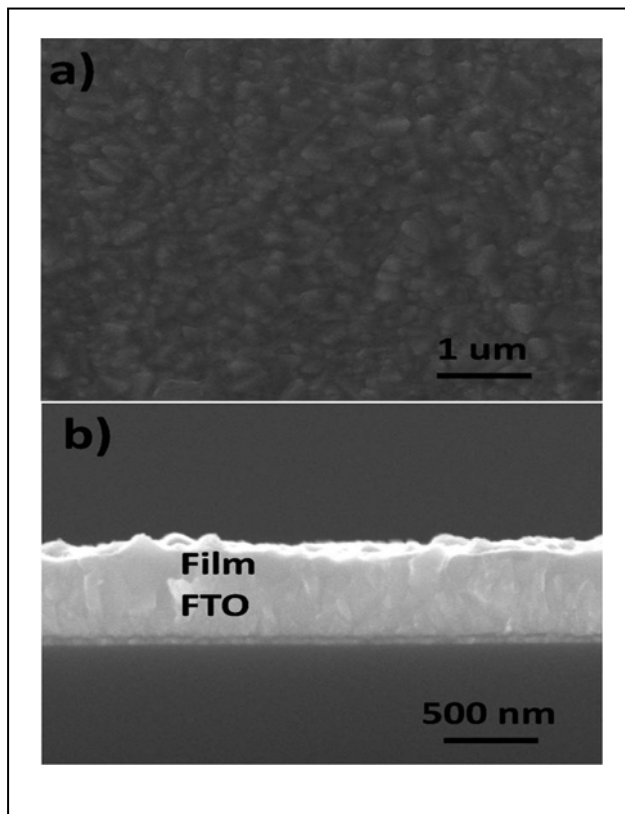


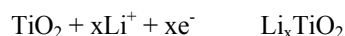
Figure 3: The schematics of the self-assembly of the  $[\text{TiO}_2/\text{CS}]$  film.

UV-vis spectra was used in present work to monitor the layer-by-layer assembling process of  $[\text{TiO}_2/\text{CS}]_n$  films due to its facility in evaluating the growth process of the multilayers. Fig. 2 displays the UV-vis absorption spectra of  $[\text{TiO}_2/\text{CS}]_n$  (with  $n = 0-8$ ) assembled on a quartz substrate. The inset in Fig. 2 shows the plots of the absorbance values for quartz-supported  $[\text{TiO}_2/\text{CS}]_n$  (with  $n = 0-8$ ) multilayer films at 201 and 241 nm as a function of the number of  $[\text{TiO}_2/\text{CS}]$  bilayers. The former is owing to an overlap of  $\text{TiO}_2$  (203 nm) and CS (201 nm) bands, and the latter is due to the characteristic absorption of  $\text{TiO}_2$  (241 nm), as compared to that of  $\text{TiO}_2$  and CS solution.

The morphology and thickness can be examined by scanning electron microscopy (SEM). Fig. 3 displays the SEM of the  $[\text{TiO}_2/\text{CS}]_{20}$  film assembled on FTO glass. The film surface is relatively smooth over a large area and consists of a multitude of small domains, which perhaps arises from the absorption of bi- and multilayer aggregates of the  $\text{TiO}_2$  nanoparticles and/or the CS chains. From the cross-section observations, the thickness of the composite film was approximately 210 nm.

### B. Electrochemical behavior of the composite film

Cycle voltammetry (CV) was used to investigate the electrochemical behavior of the composite films. Fig. 4 shows the CV of the as-prepared  $[\text{TiO}_2/\text{CS}]_{20}$  film in 1 mol/L  $\text{LiClO}_4$  in PC, and one redox peaks is noted in the potential range 0 to -1.0 V. The evidence cathodic and anodic peaks appeared at approximately -0.128 and -0.038V, respectively, for the  $\text{Li}^+$  intercalation into and extraction from the  $\text{TiO}_2$  framework following the reactions:



### C. Electrochromic performance of the composite film

Fig. 5 displays the UV-vis transmittance spectra of the  $[\text{TiO}_2/\text{CS}]_{20}$  composite film under an applied potential of 0 V, -1.2 V, -1.4 V, -1.6 V, -1.8 V and -2.0 V in 1 mol/L  $\text{LiClO}_4/\text{PC}$  solution. The spectroelectrochemistry presents complete color conversion from colorless to blue under different potentials. At first, the composite film is colorless

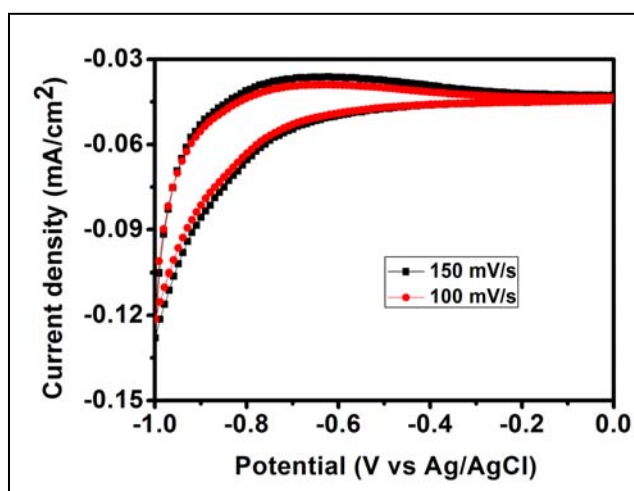


Figure 4: Cycle voltammograms of  $[\text{TiO}_2/\text{CS}]_{20}$  film in 1 mol/L  $\text{LiClO}_4$  PC solution at different scan rates.

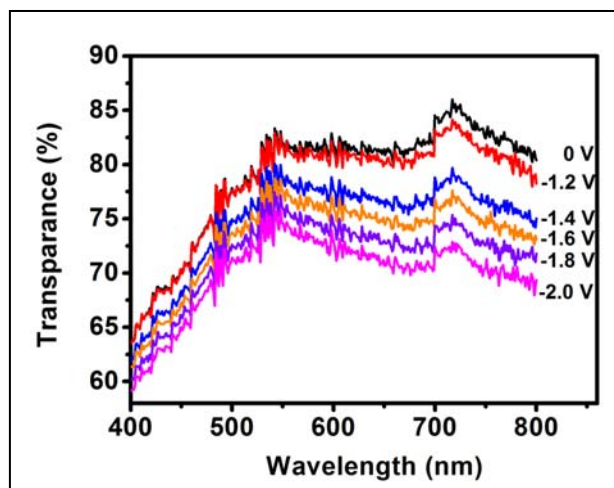


Figure 5: Visible spectra of  $[\text{TiO}_2/\text{CS}]_{20}$  film under different potentials.

at an applied potential of 0 V. As the potential increases from -1.2 to -2.0 V, the reduction of  $\text{TiO}_2$  begins and the film immediately turns to dark blue. The composite film shows a broad absorption band in the visible region at  $\lambda > 550$  nm, indicating that the color change results from the electrochemical reduction of  $\text{TiO}_2$ . When positive potential (+2.0 V) is applied, the composite film is bleached.

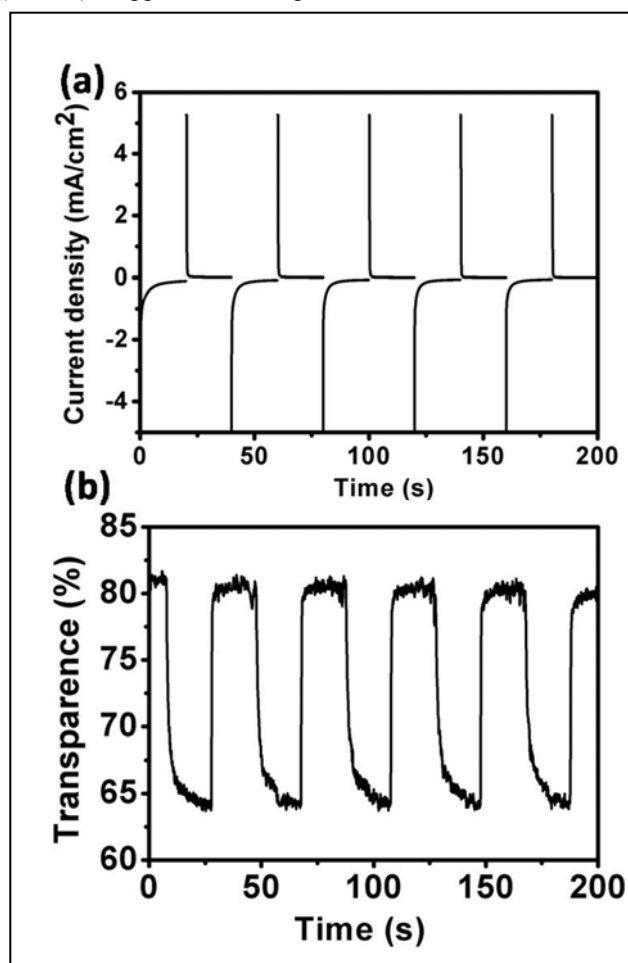


Figure 6: (a) Chronoamperometry curves and (b) optical transmittance change at 800 nm of  $[\text{TiO}_2/\text{CS}]_{20}$  film during subsequent double-potential steps (-2.0 V and +2.0 V).

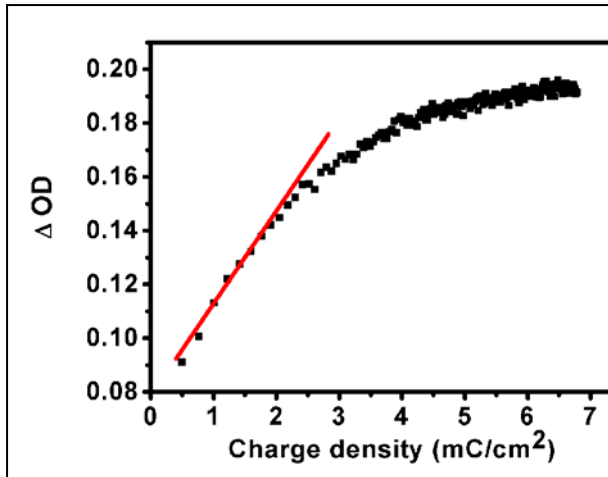


Figure 7: Coloration efficiency at 800 nm of  $[\text{TiO}_2/\text{CS}]_{20}$  film during subsequent double-potential steps ( $-2.0$  V and  $+2.0$  V).

Fig. 6 shows the current and transmittance at 800 nm of the  $[\text{TiO}_2/\text{CS}]_{20}$  composite film during subsequent double-potential steps ( $-2.0$  V and  $+2.0$  V). The response time is defined as the requirement for 90% of the total transmittance change to be reached. In this experiment, the coloration and bleaching time is 6.0 s and 0.5 s, respectively. The bleaching is observed to be faster than the coloration, which is in accordance with the time needed for the oxidation and reduction of the  $\text{TiO}_2$ . As shown in Fig. 6b, the optical contrast of  $[\text{TiO}_2/\text{CS}]_{20}$  film is 17.1%.

Aside from optical contrast and response time, coloration efficiency (CE) is an important factor for the utility of electrochromic materials in ECDs applications. The CE represents the change in the optical contrast ( $\Delta\text{OD}$ ) for the charge consumed per unit of electrode area.

$$\text{CE} (\eta) = \Delta\text{OD} (\lambda) / (q/S) = \log(T_b/T_c) / (q/S)$$

Where  $\Delta\text{OD}$  is the optical contrast at a given wavelength  $\lambda$ ,  $q$  is injected/ejected electronic charge,  $S$  is the electrode area,  $\Delta A$  is the absorbance change,  $T_b$  and  $T_c$  is the transmittances in the bleached and colored states respectively. The CE was extracted as the slope of the line fitted to the linear region of the curve. Fig. 7 displays the plots of  $\Delta\text{OD}$  versus the extracted charge density. The CE value of the  $[\text{TiO}_2/\text{CS}]_{20}$  composite film is  $33.3 \text{ cm}^2/\text{C}$  at 800 nm, which lies in a typical range of  $20\text{--}50 \text{ cm}^2/\text{C}$ . The calculated CE is larger than that mesoporous  $\text{TiO}_2$  film prepared by Schmuki et al. ( $15.58 \text{ cm}^2/\text{C}$ ) [4] and  $\text{TiO}_2$  nanowires fabricated by Lin et al. ( $13.87 \text{ cm}^2/\text{C}$ ) [13]. In addition, the estimated charge and discharge densities ( $Q_c$  and  $Q_d$ ) are  $6.93 \text{ mC}/\text{cm}^2$  and  $3.39 \text{ mC}/\text{cm}^2$ , respectively. The reversibility ratio which can be calculated from values of  $Q_c$  and  $Q_d$  is 48.9%.

The stability was further evaluated by the transmittance change of the composite film. Fig. 8 shows the transmittance results for the double potential experiment performed on the  $[\text{TiO}_2/\text{CS}]_{20}$  at 800 nm. After 100 cycles the transmittance retained 51.1% of its original value and it was reduced to 33.1% of its original value after 200 cycles. The coloration and bleaching time is 5.8 s and 0.6 s, respectively. The slight decrease of optical contrast after 200 cycles still indicates good cycle stability of the composite film.

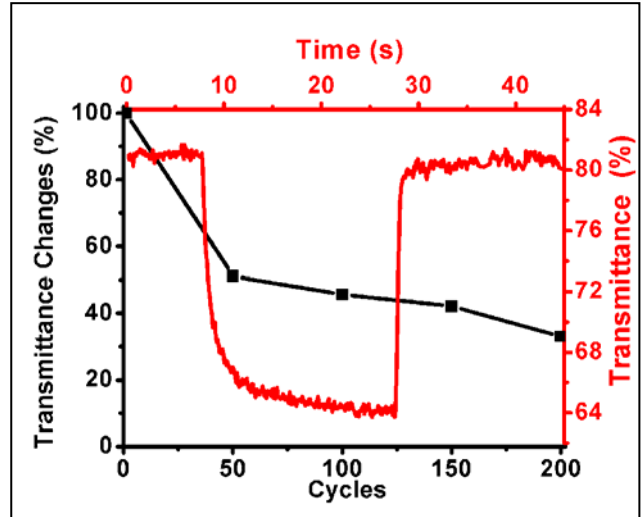


Figure 8: Cycle stability of  $[\text{TiO}_2/\text{CS}]_{20}$  film at 800 nm under a square wave potential of  $-2.0$  and  $+2.0$  V.

#### IV. CONCLUSIONS

In conclusion, we demonstrate an effective approach to prepare the  $\text{TiO}_2$ -based film. A composite film composed of inorganic nanoparticles ( $\text{TiO}_2$ ) and polyelectrolyte (CS) was fabricated by the layer-by-layer assembly method. The  $\text{TiO}_2$ -CS film showed a transmittance modulation of up to 17.1% and coloration efficiency was calculated to be  $33.3 \text{ cm}^2/\text{C}$ . In addition, the multilayer film also showed fast coloration and bleaching speed during voltage switching. Therefore, the composite film based on  $\text{TiO}_2$  with high electrochromic properties could become a promising candidate for possible applications in electrochromic devices.

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