

THE EFFECT OF DYSPROSIUM DOPING ON WO₃ ELECTROCHROMIC FILM

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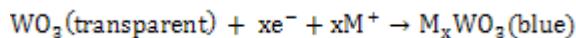
The influence of dysprosium (Dy) doping on the structural properties and electrochromic performance of WO₃ films were investigated. Dy-doped WO₃ films were prepared by sol-gel method with peroxotungstic acid precursor, and deposited on F-doped tin oxide (FTO) substrates by dip-coating. The effect of Dy doping on the structural properties, surface morphology, were examined using X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX), atomic force microscope (AFM). The XRD results suggest that WO₃ exists as nanocrystalline monoclinic phase-dispersed in amorphous phase in both the doped and undoped samples. AFM analyses indicates that Dy doping increases the roughness, and effective surface of the films. Using cyclic voltammetry (CV), the electrochemical properties of the films were studied. Dy-doped films exhibited better ion diffusion than the undoped films, which is a result from the increase in the effective surface area. Furthermore UV-vis spectroscopy analysis shows that the optical modulation of the films could be improved from 43.5% to 56.9% with 0.50 at% Dy doping.

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1. Introduction

An Electrochromic material, which changes their optical properties when an electric field is applied, has attracted considerable attention for their applications in smart windows, self-dimming mirrors and optical displays [1, 2]. Among these materials, tungsten trioxide (WO₃) has been widely studied due to their fast switching kinetics, chemical reversibility, and electrochromic efficiency [3, 4]. The coloration of WO₃ from transparent to blue occurs when an electron and a cation (M⁺), usually H⁺ and Li⁺, is inserted according to the following reaction.



Various techniques such as sol-gel [5], electrodeposition [6], sputtering [7], hydrothermal process [8] and evaporation [9] have been developed to synthesize and deposit WO₃ thin films. Due to its low cost, simplicity, and possibility for large scale production, the sol-gel method is preferable for the preparation of electrochromic WO₃ films [10, 11].

In the recent years, various studies have been conducted to improve the electrochromic performance of WO₃. Doping WO₃ with other metals including lithium (Li) [12], molybdenum (Mo) [13], titanium (Ti) [14] and niobium (Nb) [15] have already been reported to enhance the electrochromic properties of the films. Dysprosium is a promising dopant to improve the electrochromic WO₃ films, since it has been reported to improve photocatalytic properties [16, 17], and the electrochromic properties [18] of transition metal oxides. Thus in this paper, the effect of Dy doping on the structural and electrochromic properties of WO₃ films prepared by sol-gel dip coating was studied.

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2. Experimental

2.1. Synthesis of Dy-doped WO₃ Films

The synthesis of the WO₃ films were done via sol-gel method with peroxotungstic acid (PTA) precursors, similar to works by Wu, Wang [1]. The PTA precursor was prepared by dissolving 6.5 g of tungsten powder (99.9%, Merck) in a hydrogen peroxide solution, containing 35 ml of hydrogen peroxide (35%, Chem-Supply) and 9 ml of distilled water, under stirring for 24 hours. The PTA precursor was mixed with an equal amount of ethanol (reagent grade, J.T. Baker) and Dy(NO₃)₃ (99.9%, Aldrich) and sonicated for 30 min to yield a PTA sol with 0, 0.25, 0.5 and 0.75 at% Dy concentrations. The sol was deposited by dip coating with withdrawal speed of 25 mm/min on FTO glass substrate (7 Ω/sq., Sigma-Aldrich), which was cleaned by sonication in distill water, acetone and ethanol. The films were then dried in ambient temperature, and annealed at 300°C for 2 h with heating rate of 5°C min⁻¹.

2.2. Characterization

X-ray diffraction (XRD, Philips X'Pert MPD system, Netherlands) with Cu Kα radiation was performed on the annealed tungsten oxide powder to examine the crystal structure. The elemental analysis and surface morphology of the films were characterized using energy-dispersive X-ray spectroscopy (EDX) and atomic force microscope (AFM; Nanosurf easyScan2), respectively. The electrochemical properties of the films were studied by cyclic voltammetry (CV; Powerlab 2/20 Potentiostat, ADInstrument) using a potentiostat with 0.5 M H₂SO₄ electrolyte solution. The working electrode, counter electrode, and reference electrode were the FTO/WO₃ film, platinum, and Ag/AgCl, respectively. The CV measurements were performed with scan rate of 100 mV/s. Optical modulations of the films were investigated using a UV-vis spectrophotometer (UV-2401, Shimadzu).

3. Results and discussions

3.1. Morphology and Structural Characterization

XRD patterns of the undoped and Dy-doped WO₃ powder are illustrated in

Fig. 1. In all samples, a single sharp peak around 23.17° is observed, similar to that reported by Kim, Lee [19] and Vemuri, Bharathi [20]. The single peak at 23.17° corresponds to the (002) plane of the WO₃ monoclinic phase (JCPDS Card No.43-1035), and it indicates the presence of nanocrystalline phase-dispersed amorphous WO₃ [19]. However, no significant change in the XRD pattern is observed between the doped and undoped samples, suggesting that Dy-doping has no effect on the crystal structure.

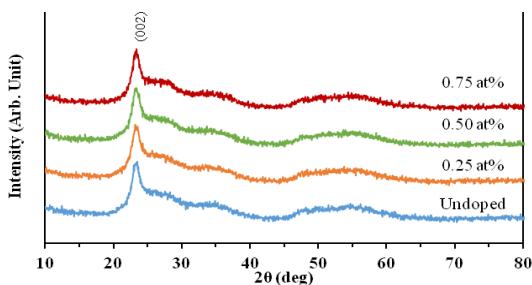


Fig. 1. XRD patterns for WO₃ powder with different Dy-doping concentrations

The elemental analysis of the films was studied by energy-dispersive X-ray spectroscopy (EDX). The EDX spectrum and mapping of the 0.5 at% Dy-doped film is shown in Fig. 2. The spectrum confirms the presence of Dy, and the mapping indicates that all the elements are

distributed throughout the film. The EDX results for other Dy concentrations yielded similar results to that of the 0.5 at% Dy-doped samples, thus they are not shown. However the amount of Dy in the EDX results varied according to the doping concentration.

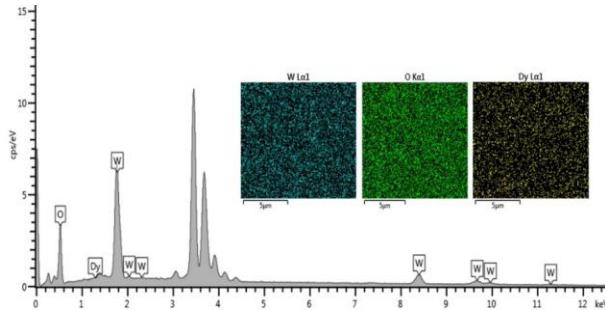


Fig. 2. EDX spectrum and element mapping of 0.5 at% Dy-doped WO_3 films

The surface morphology of the films studied by AFM is shown in

Fig. 3. A significant increase in the films roughness is observed with Dy doping. The roughness (R_{ms}) increased from 13.24 nm of the undoped film to 28.35, 20.58 and 23.57 nm of the 0.25, 0.5, and 0.75 at% films, respectively. Increasing the roughness of the films results to more effective surface area [21].

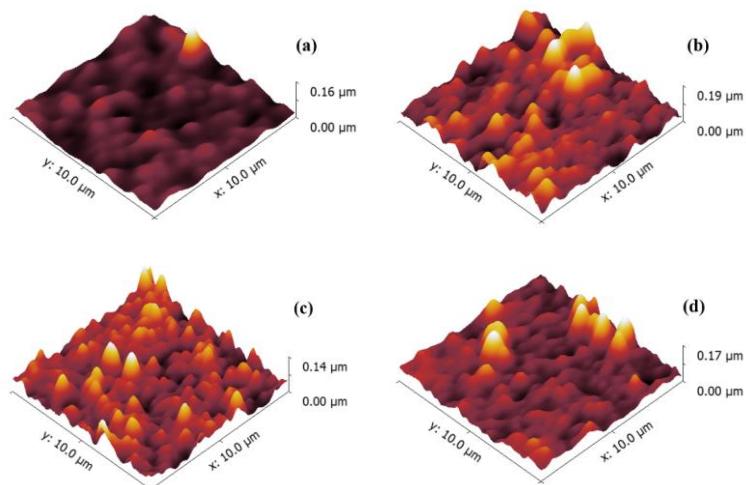


Fig. 3: AFM images of undoped (a), 0.25 at% (b), 0.5 at% (c) and 0.75 at% (d) Dy-doped WO_3 films

3.2. Electrochromic Performance

Cyclic voltammograms of the electrochromic films are displayed in

Fig. 4. Films with Dy-doping exhibits higher current density peak and larger CV loops, indicating more electron and ion transfer at the interface between the film and electrolyte. This is in good correspondence with the surface morphology results. Since Dy-doping increases the effective surface area of the film, more ions can be intercalated into the film [21-24]. The diffusion coefficient (D) was calculated using Randles-Sevcik equation [5]. The films with 0.5 at% Dy-doping had highest diffusion coefficient ($7.33 \times 10^{-10} \text{ cm}^2/\text{s}$), significantly higher than the undoped films ($3.55 \times 10^{-10} \text{ cm}^2/\text{s}$).

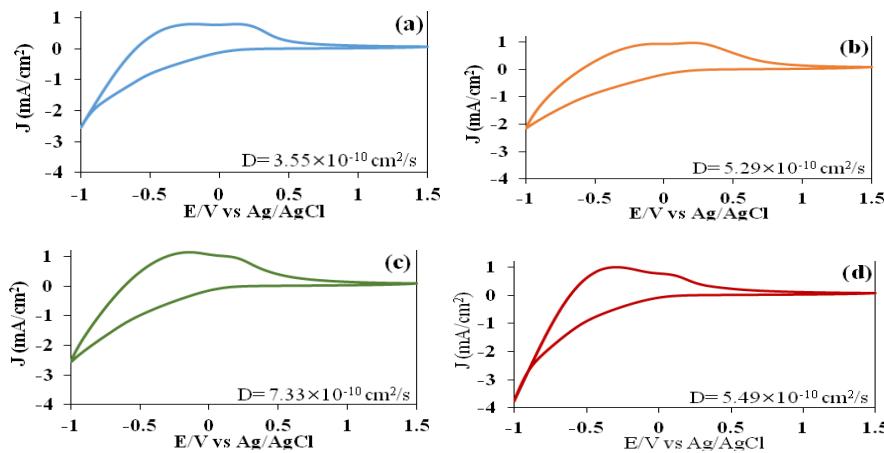


Fig. 4. Cyclic voltammogram for undoped (a), 0.25 at% (b), 0.5 at% (c) and 0.75 at% (d) Dy-doped WO_3 films

UV-vis transmittance spectra of the as deposited, colored and bleached films were measured between 300-1100 nm, shown in

Fig. 5. Optical modulations (ΔT) of the films were compared at 635 nm. The undoped films had an optical modulation of 43.5%. By doping 0.5 at% Dy, the optimal optical modulation of 56.9% is achieved; this is 13.4% higher than the undoped films. This result is in agreement with the CV results, in which 0.5 at% Dy doped films had highest diffusion coefficient.

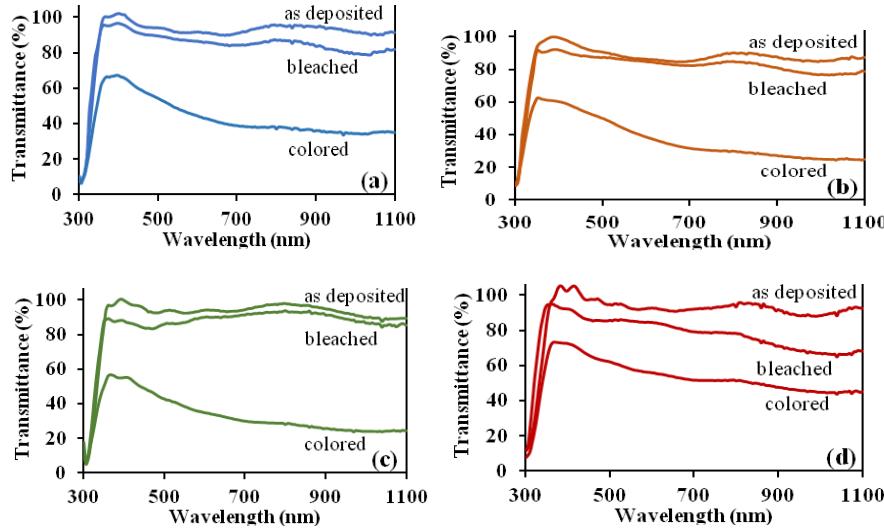


Fig. 5. Transmittance of the undoped (a), 0.25 at% (b), 0.5 at% (c), 0.75 at% (d) Dy-doped WO_3 films

4. Conclusions

Dy-doped WO_3 films were successfully prepared by sol-gel method with peroxotungstic acid (PTA) precursor, and deposited on FTO glass substrate by dip-coating. Dy doping was found to increase the roughness of the WO_3 electrochromic films, improving the ion diffusion and electrochromic properties of the film. It was found that the electrochromic film with 0.5 at% Dy doping exhibited highest optical modulation, and had good reversibility.

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