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Research Article

Novel Synthesis of Good Electrochromic Performance WO_3 Nanoplates Grown on Seeded FTO

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Abstract

Tungsten trioxide (WO_3) has applications in various electrochromic devices and is fabricated using various techniques, which affect its electrochromic properties. In this study, tungsten trioxide (WO_3) nanoplates were synthesised via a two-step facile synthesis process using a hydrothermal technique on seeded fluorine-doped tin oxide (FTO) glass substrates. WO_3 nanoplates with high porosity were obtained using a fast and simple hydrothermal method. First, a seed layer was grown on FTO using a spin coating process. WO_3 nanoplates were then quickly synthesised on the seeded FTO glass using a hydrothermal technique at 200 ˚C for 1h. The nanoplates were characterizated by using XRD, SEM, Chronoamperometry and Cyclic Voltammetry techniques. The WO_3 nanoplates have got a crystal structure mixed monoclinic and hexagonal phases. The crystal grain sizes of the film was found to be 36 and 53 nm for the (011) and (200) sharpest crystal planes of monoclinic and hexagonal crystal phases respectively. The switching times of WO_3 nanoplates were determined as 1.28 s for colouration and 5.50 s of bleaching, and the diffusion coefficient was calculated as 4.2×10^{-10} cm^2/s. As a result, the nanoplate structures with high porosity were successfully obtained and the WO_3 nanoplates showed good electrochromic performance with a good crystal structure, high diffusion coefficient, and short ion insertion time.

Keywords: Nanoplates, WO_3, Hydrothermal Method.

İyi Elektrokromik Performans Gösteren WO_3 Nanoplakaların Çekirdeklenmiş FTO Üzerine Yeni Sentezi

Öz

Tungsten trioksit (WO_3), çeşitli elektrokromik cihazlarda uygulamalara sahiptir ve elektrokromik özelliklerini etkileyen çeşitli teknikler kullanılarak üretilir. Bu çalışmada, tungsten trioksit (WO_3) nanoplakalar, tohumlanmış flor katkılı kalay oksit (FTO) cam altlıklar üzerinde hidrotermal teknik kullanılarak iki aşamalı bir kolay bir sentezleme süreci ile sentezlenmiştir. Yüksek gözenekli WO_3 nanoplakalar hızlı ve kolay hidrotermal metot kullanılarak sentezlenmiştir. Öncesinde Döndürmeli Kaplama işlemi kullanılarak FTO üzerine bir çekirdek tabaka büyütülmüştür. WO_3 nanoplakalar ise, 200 ˚C de 1 saat süreyle hidrotermal teknik kullanılarak çekirdek tabaka oluşturulmuş FTO camların üzerine hızlı bir şekilde sentezlenmiştir. Bu yapılar XRD, SEM, Kronoamperometri ve Döngüsel Voltametri teknikleri ile karakterize edilmiştir. WO_3 nanoplakalar, monoklinik ve hegzagonal kristal fazın karışımı olan bir kristal yapısına sahiptirler. Filmin kristal parçacık boyutu sırasıyla (011) ve (200) en şiddetli monoklinik ve hegzagonal kristal fazları için 36 ve 53 nm olarak hesaplandı. WO_3 nanoplakaların anahtarlanma süreleri renklenme için 1.28 s ve şeffaflaşma için 5.50 saniye olarak bulundu aynı zamanda difüzyon katsayısı da 4.2×10^{-10} cm^2/s olarak belirlendi. Sonuç olarak yüksek gözenekliliğe sahip nanoplaka yapılar başarıyla elde edilmiş ve WO_3 nanoplakalar, iyi bir kristal yapısı, yüksek difüzyon katsayısı ve kısa iyon ekleme süresi ile iyi elektrokromik performans göstermiştir.

Anahtar Kelimeler: Nanoplakalar, WO_3, Hidrotermal Metot.

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1. Introduction

As a wide-band-gap n-type semiconductor and due to multiple oxidation states, WO_3 has been used in various devices such as electrochromic devices, gas sensors, and photocatalytic cells [1]. WO_3, which has been widely studied because of its high colouration efficiency and high cyclic stability compared with other transition metal oxides, can switch between colourless and a blue colour reversibly with oxidation/reduction reactions (injection/extraction of the ions such as H^+, Li^+, Na^+ by alternately applying a small positive or negative voltage [2,3].In particular, h-WO_3 thin films show good electrochromic colouration efficiency [4].

Electrochromic WO_3 thin films have been synthesised by several techniques such as sol-gel [5],pulsed spray pyrolysis [6], thermal evaporation [7], sputtering [8], and hydrothermal synthesis [9, 10]. In this paper, we report the synthesis of WO_3 nanoplates prepared by a simple hydrothermal synthesis method..

Several studies have reported the production of tungsten oxide using hydrothermal techniques but tungsten oxide structures have been obtained as a powder by long-term synthesis at high temperatures by a salt-acid assisted process [1, 9, 11–14]. It has also been formed without the use of any seed layers on the substrate [15–20].

In this study, WO_3 nanoplates with high porosity were obtained using a fast and simple method in two steps. First, a seed layer was grown on FTO using a spin coating process. WO_3 nanoplates were then synthesised on the seeded glass using a hydrothermal technique. Spin Coating and Hydrothermal synthesis techniques have several advantages such as a broad deposition area, low cost and easy of use for the technological applications, and especially hydrothermal method is used for obtaining nanostructures in specific shape and size [21].

In this study, a rapid and simple methodology was developed to synthesize WO_3 nanoplates with highly crystalline and high-electrochromic performance. The nanoplates which were easily obtained firstly in a short time and high temperature with using Hydrothermal Method can be exhibited high performance in the Electrochromic applications.

2. Material and Method

A WO_3 seed layer was grown on FTO substrates using the spin coating method. Tungsten powder was dissolved in 30 % hydrogen peroxide within a temperature range of 0–10 °C. Ethanol was added to the solution at a volume ratio of 1:3. The solution was aged for two months to obtain stability. The spin coating process was performed on FTO at 3000 rpm for 25 s. The WO_3 seed layer was achieved by repeating the spin process 10 times. After each spin process, the samples were dried at 200 °C for 5–10 min. The seed layers were then annealed at 400 °C for 2h.

Atypical hydrothermal synthesis was used; 3.29 g sodium tungstate dihydrate powder (Na2WO42H2O) was dissolved in 40 mL deionised water. Solution pH was adjusted to 2 pH by adding HCl (3 M). The solution was stirred for 60 min. The resulting solution was transferred to a 50 mL Teflon stainless steel autoclave. The hydrothermal synthesis was carried out at 200 °C for 1h and the nanoplates were obtained during the hydrothermal reaction. After hydrothermal process, the films were washed with deionized water a few times to clean up residues. Finally, The films were dried in the air oven 80-100 ˚C for 10 minutes.

3. Results and Discussion

X-ray diffraction (XRD) datas were recorded using Panalytical Empyrean X-ray diffractometer (operated at 45 kV and 40 mA with CuKα radiation (λ = 1.5406 Å), Scanning type: continuous, incidence angle: ~ 50˚ (2Th)) for structural properties of the films. The XRD patterns of the films are shown in Figure 1. The XRD pattern of WO_3 showed highly intense and sharp diffraction peaks positioned at 2θ between 24° and 30°. The sharp peak can be indexed to the (200) plane, which belongs to the hexagonal phase of WO_3,in accordance with the powder diffraction film number 33-1380 of the International Centre for Diffraction Data (ICDD). The other sharp peak can be indexed to the (011) plane, which belongs to a single phase of WO_3 with a monoclinic crystal structure, in accordance with the powder diffraction film number 43-1035 of the ICDD. Mixed crystal structure was obtained. However, the hexagonal crystal phase is more dominant than the monoclinic crystal phase in the structure. Therefore a and c lattice parameters for the (200) and (002) reflection of the hexagonal crystal phase were determined by using Equation 1 :

$$\frac{1}{d^2} = \left[\frac{4}{3} \times \frac{h^2+hk+k^2}{a^2}\right] + \frac{l^2}{c^2} \quad (1)$$

where d was determined which is measured by XRD device as 3.07927 Å for (200) reflection and 1.95436 Å for (002) reflection. The lattice parameters of hexagonal crystal phase were calculated as a= 7.112 Å and c= 3.909 Å which are in good agreement with the literature value (a = 7.298 Å and c= 3.899 Å) [22]. The unit cell volume of the hexagonal crystal was calculated as 171.217 $Å^3$ using hexagonal unit cell volume formula [23].

The grain size (D) using Scherrer's formula, as given in Equation 2 and the dislocation density (δ) was estimated using Equation 3 [24] :

$$D = \frac{0.9\,\lambda}{\beta \cos\theta} \quad (2)$$

$$\delta = \frac{1}{D^2} \quad (3)$$

XRD data of the WO_3 nanoplates were given at Table 1. According to Table 1, it was concluded that the maximum peaks of WO_3 nanoplates with hexagonal and monoclinic crystal systems, which have small δ-values and large D-values, indicate a good crystal structure.

Table 1. XRD data of (011) monoclinic and (200) hexagonal planes of the WO_3 nanoplates

(hkl)	2θ°	d-spacing Å	FWHM [°2Th.] (lines/m²)	D(nm)	δ x10¹⁵
(011) monoclinic	25.1439	3.53891	0.235	36	0.7716
(200) hexagonal	28.3936	3.07927	0.159	53	0.3560

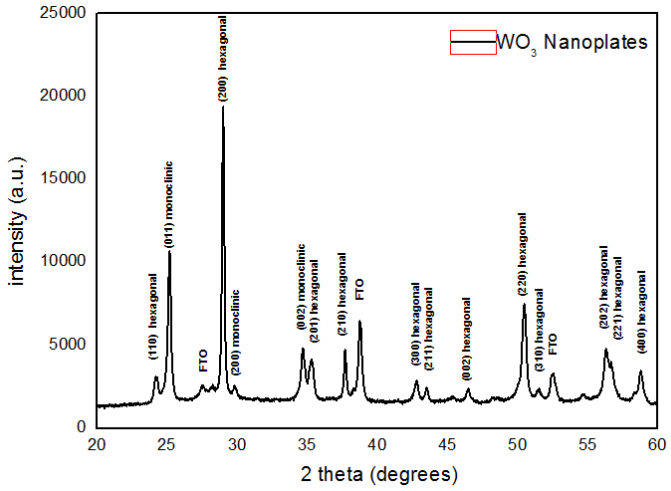


Figure 1.XRD spectra of the WO_3 nanoplates

The electrochromic performance of WO_3 is closely related to its crystalline, and by increasing the porosity and precisely controlling the crystal size, crystalline WO_3 films with both good electrochromic stability and fast response can be achieved [3].

Field emission scanning electron microscopy (FESEM) is FEG Quanta 259 model for using investigation of morphological properties of the films. SEM images of the samples are shown in Figure 2. The growth process on the FTO substrates occurred in two steps: the nucleation form, which involves the decomposition of clusters of molecules by the spin coating method and growth of the nanoplate form that is obtained by reactions with the particles combining to form nuclei on the substrate.

The high-porosity WO_3 nanoplate arrays were grown smooth and directly oriented due to the seeded FTO substrate. After the hydrothermal process, the WO_3 film consisted of regular aggregated nanoplates with sizes ranging from tens to hundreds of nanometres. The average size of the nanoplate arrays was estimated to be 125 nm s 625 nm.

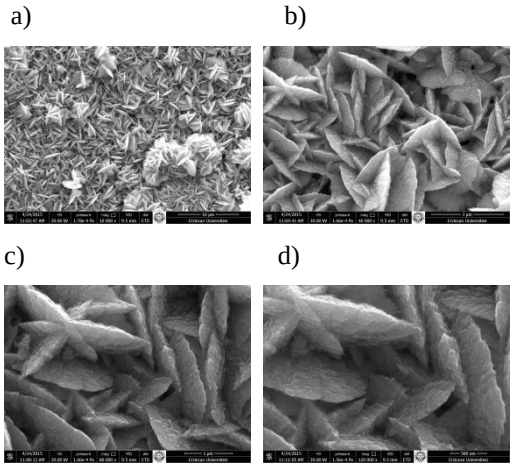


*Figure 2. SEM images of the WO_3 nanoplates at **a)**10000, **b)** 40000, **c)** 80000 and **d)** 120000 magnifications.*

EC (Electrochromic) performance of the WO_3 nanoplates were studied by using cyclic voltammetry (CV) and Chronoamperometry (CA) methods using a Gamry Potentiometer. CV and CA curves recorded for the thin films are shown in the Figure 3 with a linear potential sweep between -2 and 1V. Intercalation and deintercalation process of Li^+ ions were carried out using a 0.5 M $LiClO_4$/propylene carbonate electrolyte solution and the Platine is used as the counter electrode, AgCl is used as the reference electrode, and the thin film is used as the working electrode. The WO_3 nanoplates exhibited good electrochromic performance.

The diffusion constant for the Li^+ ions was calculated as 4.2×10^{-10} cm^2/s using the Randles-Servcik equation, for the intercalation process. The high diffusion coefficient for intercalation of Li^+ ions into WO_3 was in the range of $1.5\times10^{-12} < D\ (Li^+) < 5\times10^{-9}$ cm^2/s; additionally, the diffusion coefficient was found to be in good agreement with the diffusion coefficient calculated by hydrothermal and CBD methods [25–27].The threshold voltage (Et) is indicated in Figure 3, which corresponds to the rapid surge of Li^+ ionic intercalation into the WO_3 structures [26].

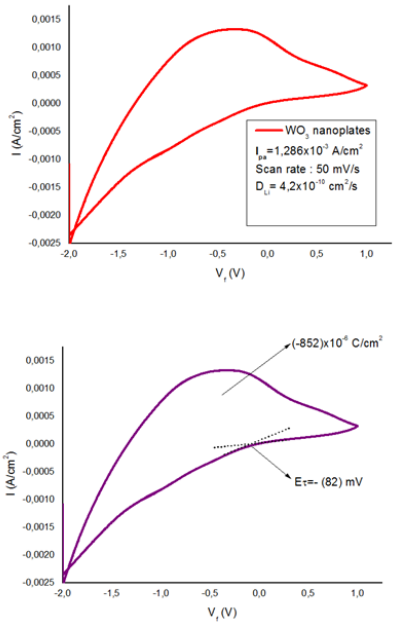
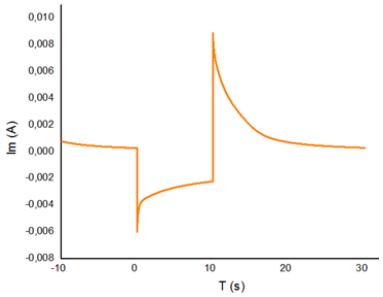


Figure 3. Cyclic voltammetry curves of the WO_3 nanoplates.

Figure 4 shows the CA curves recorded for the WO_3 nanoplates. The switching time for the WO_3 nanoplates between the colouration state (t_c) and the bleaching state (t_b) was recorded. According to the CA curve, the WO_3 nanoplates exhibited colouration times of 1.28 s and bleaching times of 5.50s. A good electrochromic response was observed in the WO_3 nanoplates, and the colouration time was faster than the bleaching time during the transition from the semi-conductor (WO_3) to the conductor (Li_xWO_3).



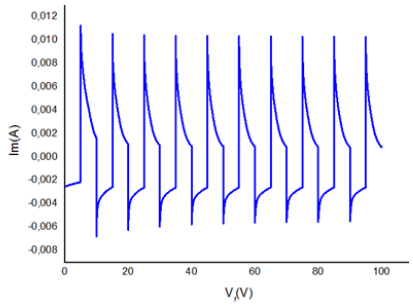


Figure 4. Chronoamperometric measurements of the WO_3 nanoplates.

4. Conclusions and Recommendations

In this study, WO_3 nanoplates were fabricated using a simple hydrothermal method at 200°C for 1 h. Monoclinic and hexagonal mixed phases were obtained for the WO_3 crystal. High-crystalline WO_3 nanoplates were grown by a novel facile hydrothermal technique, and the nanoplates showed good electrochromic performance with a fast switching time (colouration time = 1.28 s, bleaching time = 5.50 s) and a high diffusion coefficient (4.2×10-10 cm2/s).

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