



# The electrochromic performances of single phase VO<sub>2</sub> nanoparticled films



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## ABSTRACT

In the present work, pure phase vanadium oxide VO<sub>2</sub> nanoparticled films were synthesized using acetate based sol–gel precursors. The effect of the water: Vanadyl acetylacetonate ratio on electrochemical and structural properties of nanostructured vanadium oxide films was examined. The X-ray diffraction studies indicated that very strong crystallization of the VO<sub>2</sub> monoclinic phase occurred for the as-deposited films at the annealing temperature of 500 °C. According to the atomic force microscopy and scanning electron microscopy measurements, the size and morphology of the granular structured film depend on the water: Vanadyl acetylacetonate ratio. I-V curve spectra were used to compute several characteristics of the films coated on indium tin oxide substrates such as the optical density, color efficiency and diffusion coefficient. Even though water: Vanadyl acetylacetonate ratio of 0.1 is expected to give the highest color efficiency value (33 cm<sup>2</sup>/C), higher diffusion coefficient (3.15 × 10<sup>-12</sup> cm<sup>2</sup>/s) is observed in the ratio of 0.01. As a result, the correlation between the ratios and electrochromic properties of the films was established.

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## 1. Introduction

Electrochromism has been well documented for transition metals with oxides capable of giving cathodic (Ti, Nb, Mo, W, Ta) and anodic (Ni, Cr, Mn, Co, Fe, Rh, Ir) response. Among the transition metal oxides, vanadium oxide is exceptional due to both its anodic and cathodic behaviors. Furthermore, vanadium oxide (VO<sub>x</sub>) coatings can be used as a counter electrode for electrochromic devices, thermochromic displays, lithium ion batteries (cathode materials), thin-film transistors, energy efficient windows, optical and electrical switching devices, gas sensors, and thermal detectors [1–10]. Electrochromic materials should be low-cost, easily applicable and fast responding on large areas for device applications. In recent years, many techniques have been utilized to produce VO<sub>x</sub> films such as physical vapor deposition, spray pyrolysis, sputtering, chemical vapor deposition, electrodeposition, pulse laser deposition, and an acetylacetonate sol–gel method among other wet chemistry methods [1–13]. Nanofibers, nanorods, nanotubes, and vanadium oxide nanobelts have been mentioned in the literature as differently shaped nano-sized vanadium oxides [5,8,11,12,14]. VO<sub>x</sub> nanomaterials have superior lithium-ion intercalation properties as the diffusion distance for both lithium ions and electrons are reduced. High surface energy and the large surface area allow efficient

intercalation–deintercalation reactions [7,11–13]. Oxidation states (tunable) of vanadium are VO<sub>x</sub> forms such as VO, VO<sub>2</sub>, V<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, and V<sub>6</sub>O<sub>13</sub> etc. owing to an unfilled d-shell. Due to their superior properties, V<sub>2</sub>O<sub>5</sub> phase of the vanadium oxide films have been mentioned many times in literature. The usage of vanadium dioxide VO<sub>2</sub> structures is more popular than other VO<sub>x</sub> forms due to their unique thermochromic properties, polymorphic structures and reversible metal-insulator phase transition (MIT) [9,12–19]. VO<sub>2</sub> has different phase structures such as rutile VO<sub>2</sub>(R), monoclinic VO<sub>2</sub>(M), VO<sub>2</sub>(M1), tetragonal VO<sub>2</sub>(A), and metastable VO<sub>2</sub>(B), VO<sub>2</sub>(C) [12–16]. Especially, Nakano et al. [20] reported that the electrochromic effect is observed in the infrared region of VO<sub>2</sub>/electric-double-layer transistor (EDLT). VO<sub>2</sub> films exhibit superior electrical and optical properties, so they are efficiently used in electrochromic devices and gas sensors, selective catalysts for oxidation and reduction reactions. It is hard to determine the effect of crystalline structure and morphologies on the electrochromic performance of the film. An important problem in the synthesis is to control the reaction and prevent precipitation in the chemical solutions. Parameters such as particle size distribution, surface morphology and the defective structures of the vanadium oxide heavily affect the flow of the reaction. Vanadium oxide films show very different structural, optical and electrochromic properties depending on various coating methods and coating parameters. Among all methods, sol–gel has been adopted due to its cheapness, homogeneity, controllability and its ability of preventing cracking. VO<sub>2</sub> thin films can be prepared with the following

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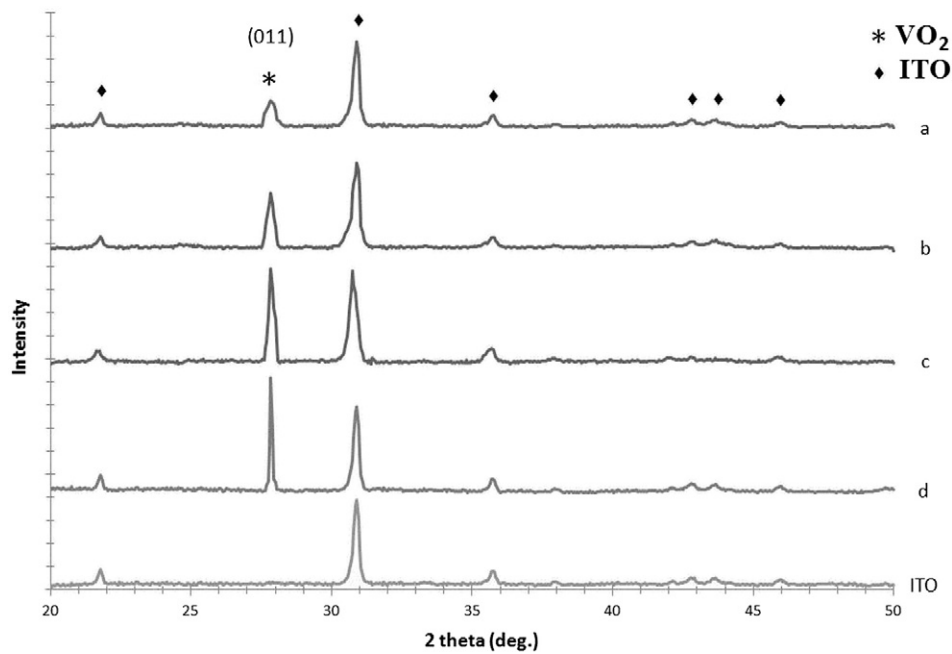


Fig. 1. X-ray diffraction patterns of VO<sub>2</sub> nanoparticled films for different water: vanadyl acetylacetonate volume ratios: (a) 0.01, (b) 0.025, (c) 0.05, (d) 0.1.

sol-gel techniques: hydrolysis of alkoxides, melt quenching, and the chemical method using acetylacetonate [5,6,14–15]. Generally, V<sub>2</sub>O<sub>5</sub> powder and vanadium tri-isopropoxide are used to produce vanadium oxide solution in literature. However, vanadyl acetylacetonate (VO(acac)<sub>2</sub>) is both cheaper and more stable than the other precursors. It is also non-toxic and exhibits stability against precipitation and excessive hydrolysis [6,17]. This work is aiming at uncovering the relationship between the amount of precursor and the optical, structural and electrochromic properties of VO<sub>2</sub> films.

## 2. Experimental

### 2.1. Preparation of VO<sub>2</sub> films

Sol-gel technique was used to produce vanadium oxide from vanadyl acetylacetonate VO(acac)<sub>2</sub> which was dissolved into alcohol. Dissolution of 1 g of VO(acac)<sub>2</sub> powder (Aldrich Chemical, 99.9%) in a mixture of 10 ml of ethanol and 0.1 ml of acetic acid yielded a green color solution. After water was added to the solution, the green solution

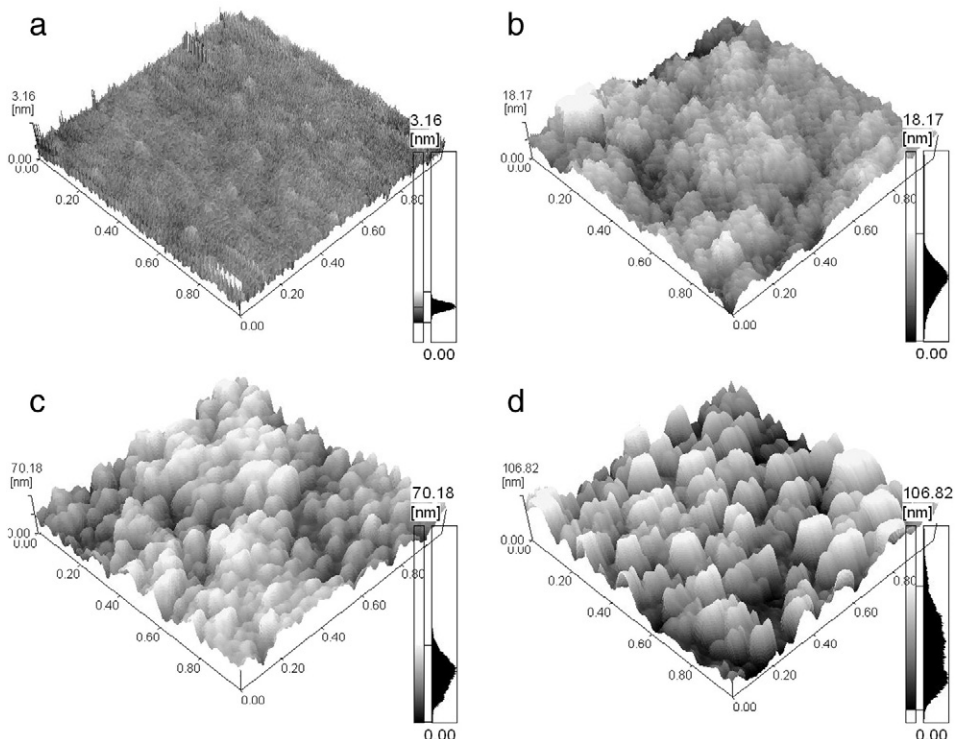


Fig. 2. AFM 3D images of VO<sub>2</sub> nanoparticled films for different water: vanadyl acetylacetonate volume ratios: (a) 0.01, (b) 0.025, (c) 0.05, (d) 0.1.

rapidly turned to red. Four various solutions were prepared for different  $\text{H}_2\text{O}:\text{VO}(\text{acac})_2$  volume ratios: 0.01; 0.025; 0.05; 0.1. The solutions were mixed for 90 min at 55 °C in nitrogen medium. This amount of heating under flowing nitrogen gas is necessary to minimize the sublimation of the aerosol particles encapsulated within the precursor. The obtained solution was deposited on ITO conductive glass substrates by spin coating (2000 rpm/30 s). The films were placed into a tube furnace (Protherm) and nitrogen gas was pumped into the tube for 90 min in order to take the air out. Afterwards, the annealing process started. Films were heated at 500 °C for 1 h, and homogeneous lemon-greenish vanadium oxide films were obtained. They were cooled down to room temperature by pumping nitrogen into the furnace at the same rate as in the pre-heat phase. The coating and annealing procedures were repeated six times in order to gain good electrochemical properties. Each coated layer has an average thickness of 25–30 nm.

## 2.2. Sample characterization

For the identification of the crystal phases of the films, X-ray diffractometer (XRD, Philips PW-1800) with  $\text{Cu-K}\alpha$  radiation ( $\lambda_{\text{Cu-K}\alpha} = 0.15406$  nm) was used. The surface morphology of the deposited thin films was observed using a field emission scanning electron microscope (FESEM, Hitachi S4160) and atomic force microscope (AFM, SPM-9500 Shimadzu). Optical transmittance of films was determined by a spectrophotometer (Perkin–Elmer Lambda 900). The thickness of the films was evaluated using a Stylus Profilometer (Veeco, Dektak 150). Electrochemical properties were determined by a potentiostat (Wenking POS 73, Bank Electronic). Lithium metal was used as both the counter and the reference electrode. The measurements were done in a 1 M solution of lithium perchlorate in propylene carbonate ( $\text{LiClO}_4/\text{PC}$ ) as the electrolyte and cyclic voltammetry (CV) analysis was carried out at a scan rate ranged from 10 mV/s to 100 mV/s.

## 3. Results and discussion

The XRD spectrum of the  $\text{VO}_2$  films annealed at 500 °C is determined for different  $\text{H}_2\text{O}:\text{VO}(\text{acac})_2$  ratios ranging from 0.01 to 0.1 in Fig. 1. For all the ratios, all peaks are well indexed to the monoclinic phase  $\text{VO}_2$  (M). The peak of  $\text{VO}_2$  that appears at  $2\theta = 27.8^\circ$  is sharp and single. The graphs show that the films have  $\text{VO}_2$  (M) structure (JCPDS: 09-0142) with peaks at (0 1 1).

The crystallite sizes calculated by Debye–Scherrer equations are determined to be 6.68, 9.83, 11.88, and 13.10 nm for the nanoparticled  $\text{VO}_2$  films with  $\text{H}_2\text{O}:\text{VO}(\text{acac})_2$  ratios of 0.01; 0.025; 0.05; 0.1, respectively.

$\text{VO}_2$  nanoparticles become smaller as  $\text{H}_2\text{O}:\text{VO}(\text{acac})_2$  volume ratio decreases. This can be explained with slow hydrolysis and condensation reactions. Surface topographical data of the nanocrystalline  $\text{VO}_2$  films for different  $\text{H}_2\text{O}:\text{VO}(\text{acac})_2$  ratios recorded by AFM and SEM are shown in Figs. 2 and 3. Surface roughness of the  $\text{VO}_2$  films was measured Rms: 5.28; 7.36; 8.79; 9.14 nm for 0.01; 0.025; 0.05; 0.1 volume ratios respectively. The results showed that particle sizes of  $\text{VO}_2$  nanoparticled films increased with the increasing  $\text{H}_2\text{O}:\text{VO}(\text{acac})_2$  ratios. The thickness of the films was measured approximately 162 nm by a stylus profilometer.

Fig. 4 shows the cyclic voltammogram of  $\text{VO}_2$  in a lithium electrolyte (lithium intercalation) at scan rate of 50 mV/s. The films are cycled 50 times in the voltage range of  $-1.2$  to 1 V. They exhibit stable characteristics. There are two peaks on the cathodic and anodic scan of  $\text{H}_2\text{O}:\text{VO}(\text{acac})_2$  ratio 0.01 while other volume ratios have a single broad peak. This observation is in agreement with Livage's results [21]. While  $\text{Li}^+$  ions are reversibly intercalated during the cathodic potential sweep and deintercalated during the anodic sweep, the voltammogram recorded with a thin film deposited from vanadic acid exhibits two peaks for both reduction and oxidation as Livage reported. In our case, similar behavior of I–V curve was observed, and there are two peaks for  $\text{H}_2\text{O}:\text{VO}(\text{acac})_2$  ratio of 0.01 due to the amount of vanadyl

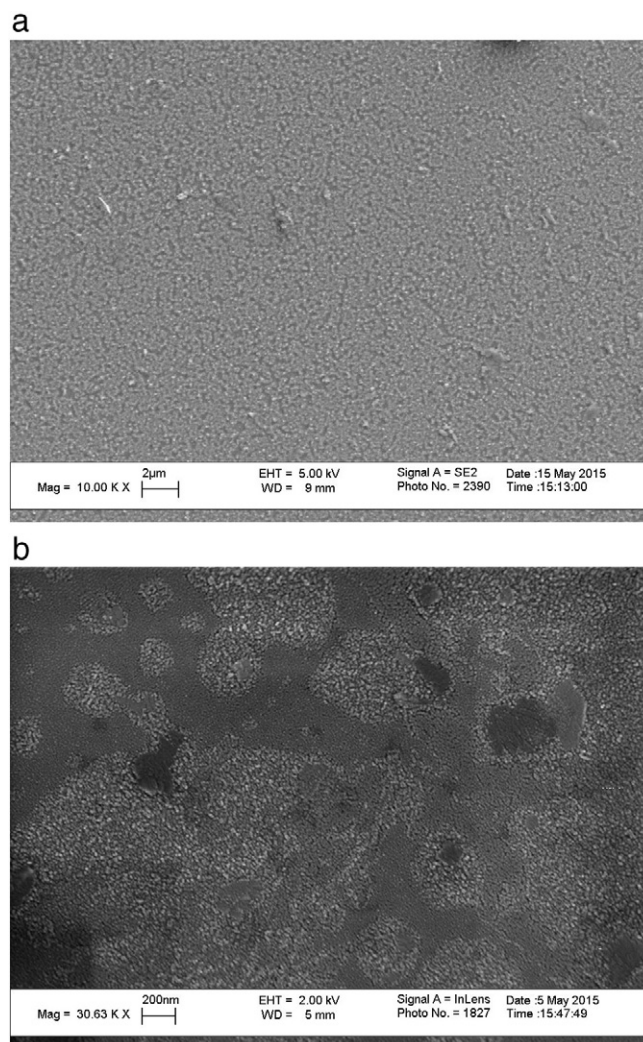


Fig. 3. SEM images of  $\text{VO}_2$  nanoparticled films for different water: vanadyl acetylacetonate volume ratios: (a) 0.01, (b) 0.1.

acetylacetonate. However, for the other ratios, the amount of vanadyl acetylacetonate was decreased in composition, and the effect of this on the I–V curve was observed as convolution of the single broad peak

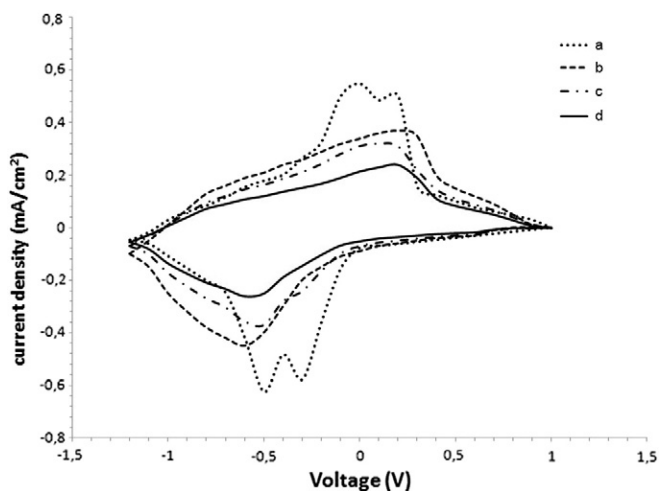


Fig. 4. Cyclic voltammogram of  $\text{VO}_2$  films in a lithium electrolyte at scan rate of 50 mV/s with different water: vanadyl acetylacetonate volume ratios: (a) 0.01, (b) 0.025, (c) 0.05, (d) 0.1. The films are cycled for 50 times in the voltage range of  $-1.2$  to 1 V.



**Table 1**Crystal sizes, diffusion coefficient (D), optical density (OD) and color efficiency values (anodic (CE)<sub>a</sub>, cathodic (CE)<sub>c</sub>) of VO<sub>2</sub> nanoparticles for different H<sub>2</sub>O:VO(acac)<sub>2</sub> ratios.

Data	H <sub>2</sub> O:VO(acac) <sub>2</sub>	Crystal size (nm)	D (cm <sup>2</sup> /s)	OD	(CE) <sub>a</sub> (cm <sup>2</sup> /C)	(CE) <sub>c</sub> (cm <sup>2</sup> /C)
a	0.01	6.68	3.15 · 10 <sup>-12</sup>	0.402	13.26	13.56
b	0.025	9.83	1.17 · 10 <sup>-12</sup>	0.397	14.33	14.61
c	0.05	11.88	1.05 · 10 <sup>-12</sup>	0.491	22.72	23.3
d	0.1	13.1	4.79 · 10 <sup>-13</sup>	0.536	31.6	33

as reported before by Liu et al. [22]. On the other hand, the CV curves indicated the presence of only two peaks: a reduction current peak and an oxidation current peak for ratios: 0.025, 0.05 and 0.1 due to single tunnel in the structure of the VO<sub>2</sub> nanoparticled films.

Diffusion coefficient values were calculated by Randles–Sevcik in Eq. (1):

$$I = (2686 \times 10^5) n^{3/2} A C (D v)^{1/2} \quad (1)$$

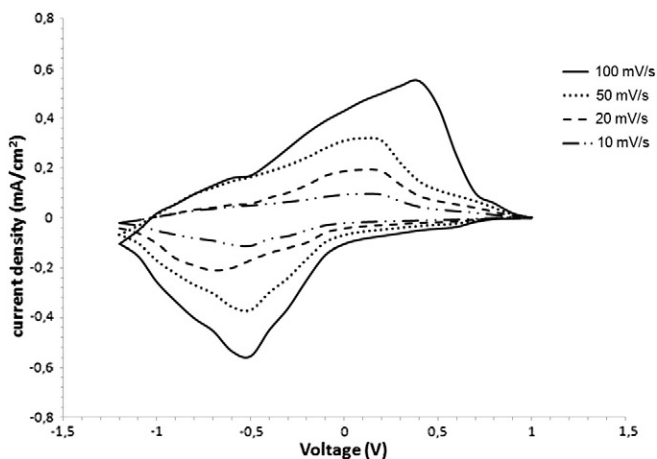
In this equation, D is diffusion coefficient, I is peak current, A is electrode area (cm<sup>2</sup>), n is number of electrons transferred in the redox event, C is concentration of the material (mol/cm<sup>3</sup>) and v is scan rate (V/s) [23]. When H<sub>2</sub>O:VO(acac)<sub>2</sub> ratios were increased, there was a decrease in the current by the slower diffusion of lithium with the increment water ratios due to the water molecules are solvated Li<sup>+</sup> ions. Diffusion coefficient values and peak currents were decreased by increasing the H<sub>2</sub>O:VO(acac)<sub>2</sub> ratio as well as the size of the VO<sub>2</sub> nanoparticles in Table 1.

In order to determine the oxidation–reduction peak potentials of the VO<sub>2</sub> films, the experiments were performed for four scan rates of 10, 20, 50, and 100 mV/s where H<sub>2</sub>O:VO(acac)<sub>2</sub> ratio was 0.025 as presented in Fig. 5.

Scan rate has a direct effect on the diffusion of Li ions into the VO<sub>2</sub> films. The results show that the diffusion is decreased with the decreasing scan rate. The diffusion process causing the coloration of the VO<sub>2</sub> electrochromic film is governed by Eq. (2):



During the measurement, the film exhibits a reversible color change from lemon–green to blue and this observation is in accordance with the insertion of the Li<sup>+</sup> into the VO<sub>2</sub> films. The coloration of the VO<sub>2</sub> films changes progressively during the redox cycle. An important indicator for electrochromism applications is the coloration efficiency (CE) expressed as the ratio of the optical density variation ( $\Delta\text{OD}$ ) to the charge inserted (Q) per area (A). Moreover, the optical density variation can be written in terms of the transmission at visible range of the



**Fig. 5.** Plot of IV curve of VO<sub>2</sub> film (H<sub>2</sub>O:VO(acac)<sub>2</sub> ratio: 0.025) for four scan rates of 10, 20, 50, and 100 mV/s.

bleached (T<sub>b</sub>) and colored (T<sub>c</sub>) states [24].

$$\text{CE} = \Delta\text{OD}/(Q/A) = \log(T_b/T_c)/(Q/A) \quad (3)$$

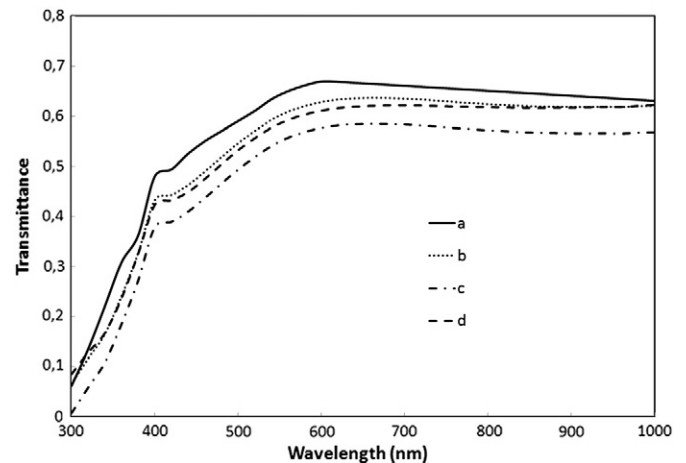
The differences as a function of the H<sub>2</sub>O:VO(acac)<sub>2</sub> content are determined in the transmission modulation in Figs. 6 and 7. These figures illustrate the optical transmittance spectra of the colored/bleached nanoparticled VO<sub>2</sub> films for the ratio after the application of the respective voltage.

The films produced with H<sub>2</sub>O:VO(acac)<sub>2</sub> ratio of 0.1 exhibit the best electrochromic characteristics. As a result of the excellent electrochromic performance, the film is obtained from a sol with this ratio which shows a coloration efficiency of 33 cm<sup>2</sup>/C at a visible range. Diffusion coefficient, optical density and color efficiency values were calculated using Eqs. (1) and (3) and they are given for different ratios in Table 1.

As H<sub>2</sub>O:VO(acac)<sub>2</sub> ratios of the VO<sub>2</sub> nanoparticled films were increased, larger nanoparticles, higher color efficiency values and lower diffusion coefficients were observed.

#### 4. Conclusions

Electrochromic and structural properties of the VO<sub>2</sub> film have been investigated. The VO<sub>2</sub> films have been prepared by the sol-gel method using a VO(acac)<sub>2</sub> powder containing different H<sub>2</sub>O:VO(acac)<sub>2</sub> ratios. Changing the composition of the precursor solution by varying the ratio from 0.01 to 0.1 modified the size of the nanoparticles in films. The results show that there is a single monoclinic phase of vanadium oxide films in the XRD patterns. The observation of the single-phase of a particular oxidation state is a strong indicator that these films exhibit better electrochemical performance. The volume ratio was observed to affect the electrochromic and morphological properties of the vanadium oxide nanoparticled films. It was investigated via both AFM and SEM that an increase in the particle size in surface images of the VO<sub>2</sub> films was observed with an increase of H<sub>2</sub>O:VO(acac)<sub>2</sub> from 0.01 to 0.1, respectively. Cyclic voltammetry measurements revealed that the greater the H<sub>2</sub>O:VO(acac)<sub>2</sub> ratio in compositions of the VO<sub>2</sub> films is, the lower



**Fig. 6.** Transmittance spectra of VO<sub>2</sub> nanoparticled films at bleached state for different water: vanadyl acetylacetonate volume ratios: (a) 0.01, (b) 0.025, (c) 0.05, (d) 0.1.

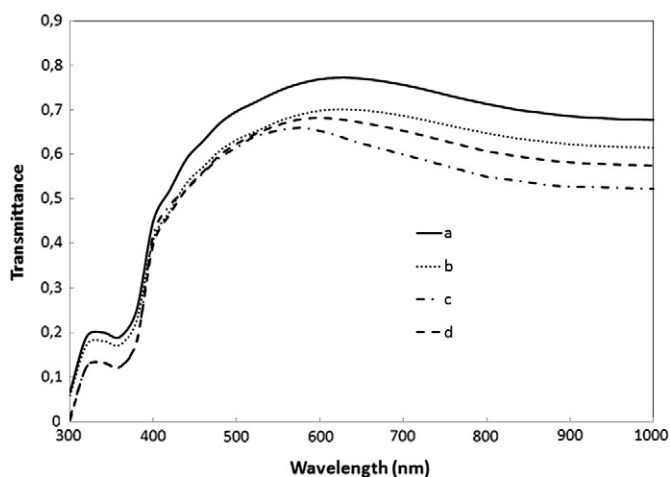


Fig. 7. Transmittance spectra of VO<sub>2</sub> nanoparticled films at colored state for different water: vanadyl acetylacetonate volume ratios: (a) 0.01, (b) 0.025, (c) 0.05, (d) 0.1.

the peak currents are. Additionally, the current versus voltage curves of the different scan rated films were stabilized when cycled 50 times at the sweeping rates varied from  $-1.2$  to  $1.0$  V. Furthermore, the higher transmittance was identified in the ratio of 0.01 for both colored and bleached states. The highest diffusion coefficient value was evaluated for the H<sub>2</sub>O:VO(acac)<sub>2</sub> ratio of 0.01, to be  $3.15 \times 10^{-12}$  cm<sup>2</sup>/s.

This work investigated that decreasing the ratio of H<sub>2</sub>O:VO(acac)<sub>2</sub> in composition increased the diffusion coefficients and also the size of the nanoparticles. The presence of water in the solution has a detrimental effect on all chemical and physical properties of the thin film. The coloration efficiency values increased with the increase in H<sub>2</sub>O:VO(acac)<sub>2</sub> ratios, which is a crucial parameter used to qualify the electrochromic materials and films and should be used frequently. The film produced with H<sub>2</sub>O:VO(acac)<sub>2</sub> ratio of 0.1 displays the highest coloration efficiency of 33 cm<sup>2</sup>/C at a visible range. Owing to these properties, single phase VO<sub>2</sub> nanoparticled films can be preferred to be used in electrochromic devices.

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