



Full Length Article

Switching electrochromic performance improvement enabled by highly developed mesopores and oxygen vacancy defects of Fe-doped WO₃ filmsBon-Ryul Koo^a, Kue-Ho Kim^b, Hyo-Jin Ahn^{a,b,*}^a Program of Materials Science & Engineering, Convergence Institute of Biomedical Engineering and Biomaterials, Seoul National University of Science and Technology, Seoul 01811, Republic of Korea^b Department of Materials Science and Engineering, Seoul National University of Science and Technology, Seoul 01811, Republic of Korea

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ABSTRACT

In recent years, owing to the capability to reversibly adjust transparency, reflection, and color by the low electric field, electrochromic devices (ECDs) have received an extensive attention for their potential use in optoelectronic applications. However, considering that the performances of the ECDs, including coloration efficiency (CE, < 30.0 cm²/C) and switching speed (> 10.0 s), are still low for an effective applied use, critical efforts are needed to push the development of a unique nanostructure film to improve electrochromic (EC) performances. Specifically, as the large-scale applications (e.g. refrigerators, vehicles, and airplanes) of the ECDs have been recently developed, the study for improving switching speed is urgently needed for commercialization of the devices. In this context, the present study reports a novel nanostructure film of Fe-doped WO₃ films with highly developed mesopores and oxygen vacancy defects, fabricated using the Fe agent and the camphene-assisted sol-gel method. Fe-doped WO₃ films with highly developed mesopores and oxygen vacancy defects show remarkable EC performances with both fast switching speed (2.8 s for the coloration speed and 0.3 s for the bleaching speed) and high CE (71.1 cm²/C). These two aspects contribute to the synergistic effects of optimized Fe doping and camphene on the films and have outstanding values as compared to previously reported results of WO₃-based materials. Specifically, the fast switching speed is attributed to the shortened Li⁺ diffusion pathway of the highly developed mesopores; and the other is the improved electrical conductivity of the highly increased oxygen vacancy defects. In addition, the high CE value is due to an efficient charge transport as the result of a more effective electroactive contact of the morphology with highly developed mesopores, resulting in a large transmittance modulation with a small intercalated charge density.

1. Introduction

Today, with an increase of the need for energy-efficient and convenient environments in daily life, electrochromic devices (ECDs) have attracted extensive attention in terms of their promising applications, such as energy-save “smart window”, electronic displays, and adjustable mirrors [1–3]. These devices have many advantages, such as visibility in the sunlight, color variations, low operating voltage, and low memory effect; they can also reversibly and persistently vary transparency, color, or other optical properties (such as absorption and reflection) by the application of a small electric field, which is based on a change in the electronic structure of electrochromic (EC) materials as a result of electron-ion behavior [3,4]. The typical ECD structure consists of five superimposed layers: the two different EC layers, the ion conductor layer, and the two transparent conducting layers [5]. The EC layers are the most fundamental components in ECDs that strongly

dominate the EC performances of optical modulation, coloration efficiency (CE), and switching speed and can be classified into two types: cathodic materials (WO₃, MoO₃, and polythiophene derivative) coloring under ion intercalation and anodic materials (NiO, IrO₂, and polyaniline) coloring under ion deintercalation [6]. Specifically, an important parameter for the ECDs is the switching speed defined as the time required for electronic switching of light transmittance, absorption, and coloration [7]. However, as the ECDs exhibit a slow switching speed, more than 10.0 s for the full color transition, this can hinder commercialization of the devices. In addition, the switching speed is extremely slowed with the increase of the operating area in the devices (3.0–5.0 min for 1524 × 3048 mm² of SageGlass®) [8]. Therefore, further research seeking to improve the switching speed remains a critical issue for the development of the ECDs [9,10].

Due to the outstanding characterizations of harmlessness, low cost, good stability, and wide optical modulation among various EC

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materials, tungsten oxide (WO₃) corresponding to an indirect semiconductor with the band gap of 2.50–3.65 eV, has been conventionally used as one of the most representative cathodic EC materials in ECDs [11–13]. The WO₃ shows a reversible color change between the deep blue and the colorless by a response of the cathodic and anodic reaction. This phenomenon is attributed to intercalation/deintercalation of small protons (M = H⁺, Na⁺, and Li⁺) into WO₃ lattices (see Eq. (1)): [14]



Unfortunately, since CE (< 30.0 cm²/C) and switching speed (> 10.0 s) of the formed WO₃ film are relatively small, WO₃ is a critical limitation for the effective use in the applications. In particular, with recent advances in the development of large-scale applications (e.g. refrigerators, vehicles, and airplanes) using WO₃-based ECDs, improving the switching speed of the devices has been highlighted as an important venue of future research and development. It is known that an increase of switching speed can be mainly achieved by strategies of 1-dimensional (D) and porous nanostructures and doping of metal ions [15–21]. First of all, the development of 1-D and porous nanostructures is useful in terms of enhancing switching speed due to providing a more effective contact area with electrolyte and reducing the diffusion length of ions during the EC reaction [22,23]. For example, using the hydrothermal method, Ma et al. synthesized vertically aligned 1-D WO₃ films that showed a faster switching speed (6.7 s for the coloration speed and 3.4 s for the bleaching speed) as compared to those of the bare nanorod WO₃ films [22]. Furthermore, Cronin et al. demonstrated that the porous WO₃ films prepared by the dip coating method at the optimum viscosity of dipping solutions showed an improved switching speed (37.0 s for the coloration speed and 5.0 s for the bleaching speed) as compared to that of the dense WO₃ films [23]. In addition, the doping of metal ions such as Ni into WO₃ lattices were reported to be able to enhance the switching speed by the reduced charge transfer resistance [24,25]. Using the hydrothermal method, Zhou et al. prepared Ni-doped WO₃ films and their results indicated that the 0.5% Ni doping could have an enhanced switching speed (7.8 s for the coloration speed and 6.0 s for the bleaching speed) as compared to those of bare WO₃ films [24]. Yet, despite these efforts, the implementation of fast switching speed below 1.0 s has yet been limited for WO₃-based ECDs. Hence, in the present study, we applied a novel way to obtain the fast switching speed of WO₃-based films by both Fe doping and highly developed mesopores.

In the present study, we report a novel nanostructure film of Fe-doped WO₃ films with highly developed mesopores and oxygen vacancy defects using the Fe agent and the camphene-assisted sol-gel method. The Fe agent and camphene play a particularly attractive role causing the nanostructure film with highly developed mesopores and oxygen vacancy defect on the WO₃, resulting in an impressive improvement of their EC performances, including both fast switching speed below 1.0 s and high CE.

2. Experiments

Fe-doped WO₃ films with highly developed mesopores and oxygen vacancy defects were prepared by the spin-coating sol solution with both Fe agent and camphene on a commercial FTO glass (Pilkington, 8.0 Ω/□). For the preparation of the sol solution, tungsten (VI) chloride (WCl₆, Aldrich) and iron (III) nitrate nonhydrate (Fe(NO₃)₃·9H₂O, Aldrich) as the agent for Fe doping were dissolved in 2-propanol ((CH₃)₂CHOH, Aldrich), in which amount of Fe/W varied to be 3, 5, and 7 at% to optimize the EC performances of the Fe-doped WO₃ films. Thereafter, in order to obtain the Fe-doped WO₃ films with highly developed mesopores and oxygen vacancy defects, 10 wt% camphene (Hill Notation)C₁₀H₁₆, Aldrich) as the organic additive to the solvent were added into the sol solutions with 5 at% Fe as an optimized condition. After stirring for 3 h at room temperature, the resultant solutions

were deposited on the commercial FTO glass using the spin coating method, which was performed at 2000 rpm for 30 s and then repeated 2 times. In the next step, the samples were annealed at 300 °C in air to form the Fe-doped WO₃ films with highly developed mesopores and oxygen vacancy defects. For comparison, bare WO₃ films and Fe-doped WO₃ films were fabricated by spin-coating the WCl₆ sol solution without additive and with the amount of 3, 5, and 7 at% Fe. Therefore, we obtained five types of bare WO₃ films, Fe-doped WO₃ films with 3, 5, and 7 at% Fe, and Fe-doped WO₃ films using camphene with 5 at% Fe. The obtained films were marked as bare WO₃, 3Fe-WO₃, 5Fe-WO₃, 7Fe-WO₃, and CFe-WO₃, respectively.

The thermal behaviour of the samples was identified by differential scanning calorimetry (DSC, DSC-60, Shimadzu). The surface morphology was investigated using a field-emission scanning electron microscopy (FESEM, Hitachi S-4800) and an atomic force microscopy (AFM, diDimensionTM 3100). The crystal structure and chemical state were investigated by X-ray diffraction (XRD, Rigaku D/Max-2500 diffractometer using Cu K_α radiation) and X-ray photoelectron spectroscopy (XPS, AXIS ultra-delay line detector equipped with an Al K_α X-ray source, KBSI Daedeok Headquarters), respectively. The electrical and optical properties were analyzed by a Hall-effect measurement system (Ecopia, HMS-3000) and ultraviolet-visible (UV-vis) spectroscopy (Perkim-Elmer, Lambda-35), respectively. The electrochemical and EC performances were characterized using a potentiostat/galvanostat (PGSTAT302N, FRA32M, Metrohm Autolab B.V., the Netherlands) in a three-electrode electrochemical cell with 1 M LiClO₄ as the electrolyte, Pt wire as the counter electrode, and Ag wire as the reference electrode. *In situ* optical properties related to switching speed were measured using ultraviolet-visible (UV-vis) spectroscopy (Perkim-Elmer, Lambda-35) in the wavelength at 633 nm.

3. Results and discussion

We constructed the Fe-doped WO₃ films with highly developed mesopores and oxygen vacancy defects through the sol-gel method using Fe dopant and camphene. To trace the formation behavior of the highly developed mesopore on the films, the thermal analysis on the sol solutions for forming bare WO₃, 5Fe-WO₃, and CFe-WO₃ using DSC was performed under air in the range of 25–300 °C (see Fig. 1a). All samples mainly included two major stages at 25–75 °C and 115–135 °C. The rapid endothermic peak observed at 25–75 °C was due to the elimination of the solvent in the samples. The major endothermic peak from 115 to 135 °C could be attributed to the hydrolysis of WCl₆ related to formation of the WO₃ [26]. For 5Fe-WO₃, there was an extra endothermic peak at 95–115 °C induced by thermal decomposition of the Fe(NO₃)₃·9H₂O for Fe doping into WO₃ lattices [27]. Furthermore, CF-WO₃ showed a broad endothermic peak at 84–115 °C. This included two major peaks of the thermal decompositions related to camphene at 84–102 °C and Fe(NO₃)₃·9H₂O at 95–105 °C [28]. These DSC results demonstrate the formation behavior of the nanostructure film with highly developed mesopores (CF-WO₃) (see Fig. 1b). During the annealing process, the critical two steps were generated by the thermal decomposition of the camphene and the Fe agent. In the first step (centered at 95 °C), the thermal decomposition of the camphene could cause the partial Kirkendall effect of W⁶⁺ electrostatic-interacted with isobornyl alkyl ether converted by camphene and 2-propanol, which was due to a higher diffusion coefficient of the camphene ($D = 12 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$) than that of pure W⁶⁺ ($D = 70 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$) [28,29], resulting in the formation of the mesopores with the average diameter of 23.2 nm on the WO₃ films. In the second step (centered at 105 °C), Fe doping into WO₃ could result in the distortion of the WO₃ structure due to a mismatch (0.02 Å) of the ionic radius between Fe³⁺ (0.64 Å) and W⁶⁺ (0.62 Å) [29,30], which could form the mesopores with the average diameter of 35.9 nm [31]. The resultant nanostructure film consisted of the highly developed mesopores with the two different average diameters of 23.2 nm and 35.9 nm by the synergistic effect of

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