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Effect of etching on current and optical density for WO_3 thin film

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Abstract
We present, an electrochromic film of WO_3 fabricated on an ITO by etching process, adopting a low-cost, facile and template-free fabrication process, for a first time, by using hydrothermal method, we obtained WO_3 films with a simplified architecture (ITO/HCl/WO_3). Compared to ITO/WO_3 configuration, the ITO/HCl/WO_3 configuration exhibited a strong enhancement in terms of roughness, porosity, open-tunnel structure, current density and optical density. Moreover, electro-optical characterization illustrates high transmittance modulation (about 49% at 630 nm) with excellent stability, making it attractive for a practical application.

Keywords:current density, optical density, electrochromic property, etching, enhancement in porosity.

Introduction

The interest in electrochromic (EC) devices has increased over the last decade due to their application in solar light control and energy saving in smart windows fabricated using EC materials [1].These materials can change their optical properties under the applied voltage. Among various EC materials, tungsten oxide (WO_3) has been widely studied because of its high coloration efficiency in the visible region of the electromagnetic spectrum, high cyclic stability compared with other transition metals, suitable energy band gap (2.5-2.8eV), electron mobility (~12$cm^2V^{-1}s^{-1}$), long holes diffusion length (~150nm), and stability against photocorrosion in acidic solution [2-3].Three-dimensional assembled structures of WO_3 in nanometer or micrometre-scale have a large surface-to-volume ratio because of the porous structure, thereby yielding superior optical modulation with an enhanced chromic response time [4-5]. Among the several WO_3 polymorphs, the hexagonal form is of great interest due to its open-tunnel structure [6].

Various methods such as electrodeposition [7], sol-gel method [8], atmospheric pressure chemical vapour deposition [9],pulsed laser deposition [10], spin coating [11]havebeen used to synthesize WO_3 thin films. However these methods require strict reaction conditions such as high-low temperatures, accurate gas concentrations, toxic chemical reagents, and expensive complex equipment. Among the various methods, hydrothermal synthesis is a favourablealternative, because of low growth temperature, wherein microstructures of WO_3 films can be precisely tailored by varying the precursor concentration, temperature, and duration and by adopting various surfactants and capping agents. Moreover, directly growing WO_3 thin films with strong adhesion on substrates by using the hydrothermal method is difficult. Additional studies must be conducted on the synthesis of WO_3 crystals or thin films [3, 12-14].

The surface roughness, sheet resistance and transmittance of indium tin oxide (ITO) films affects the performance of EC devices [15]. Etching plays an inherent role in enhancing these parameters [16-18]. However, very few studies have performed etching in the hydrothermal method. For instance, a study analysed the photoelectrochemical properties [19], wherein citric acid was used to perform etching on the synthesized WO_3 thin films. The study reported that the etching process modifies the nanoplates surface with increasing voids. In addition, it enhances the intensity of photocatalytic active crystal planes. Therefore, in this study we performed etching by using hydrochloric acid (HCl) in the hydrothermal method to synthesize stable WO_3 thin films for EC applications.

In this study, we present a novel and convenient strategy to synthesize WO_3 film through wet etching of ITO glass substrates by using HCl followed by the one-step hydrothermal method without a seed layer. Untill now, the process of etching by using HCl has not been introduced in the hydrothermal synthesis of WO_3 thin films. HCl etching on ITO produces free radicals, consequently increasing the chemical reaction rate. In addition, etching changes the phase from crystallised to amorphous, thus enhancing the adhesivity of WO_3 films on ITO substrates and markedly improves its EC performance.

Experimental

Materials:

Sodium tungstate ($Na_2WO_4{\cdot}2H_2O$), oxalic acid ($C_2H_2O_4{\cdot}2H_2O$), and HClwere purchased from LobaChemie and all these analytical reagent-grade chemicals were used without further purification. ITO glass plates (25ohm cm^{-2}, 3×1 cm^2) were used as substrates. All aqueous solutions were prepared using double distilled water (DDW).

Method:

The glass substrates were cleaned with an aqueous detergent, ultrasonicated in DDW, and acetone and rinsed with DDW. For etching the ITO glass substrates, 4M HCl solution was prepared because ITO was reported to be dissolved in etchants of halogen acids with a concentration exceeding 4M [20-22]. Furthermore, ITO glass plates were kept in HCl (4M) for 1min. Here, H^+ and Cl^- ions collides with ITO, and generates indium chloride [InCl; eqn (1)], which is highly reactive chemically [23]. Moreover, it increases the reaction rate by breaking the chemical bonding of ITO [eqn (1)]. The ITO plates were dried naturally at room temperature. The bright spots observed on the ITO glass substrates entailed the etching process, represented as ITO/HCl.

$$In_2O_3 + 2HCl \rightarrow 2InCl + H_2O + O_2 \quad (1)$$

Following this reaction, the ITO glass substrates were impregnated with water, facilitating not only the strengthening of the adhesive nature of the ITO glass substrates [24], but also the nucleation of WO_3.

A precursor solution of 0.2M $Na_2WO_4{\cdot}2H_2O$ was prepared in DDW; the pH of this solution was 8.5. Acidification was performed by the dropwise addition of HCl to obtain a pH of 1. A white precipitate was formed, which was dissolved by vigorously adding 30mL of oxalic acid (0.1M). After stirring for 15 min, a transparent yellow solution was obtained [25]. These solutions were transferred into a 25 mL teflon-lined stainless steel autoclave. In the first instance, a bare ITO substrate was dipped vertically in the autoclave, maintained at 100°C and 4 psi (0.2 kg cm^{-2}) for 1h to obtain deposition on the bare ITO glass substrate by using the hydrothermal method. These films are represented as ITO/WO_3. Later, the etched ITO substrates were dipped in an autoclave with previously prepared yellow solution at the aforementioned conditions. Thereafter, WO_3 films get deposited on the etched ITO represented as ITO/HCl/WO_3.

A scanning electron microscope (SEM) was used to characterise morphologies of an as-prepared film (Hitachi S-4700 II, 25 kV). X-ray diffraction (XRD) pattern (Thermo ARLSCINTAG X'TRA with CuKa irradiation, L ¼ 0.154056 nm) was used to analyse the crystallinity. An electrochemical study was performed using a three-electrode system (Electrochemical Analyzer 608, CH Instruments), a graphite rod as the counter electrode, a standard calomel electrode (SCE) as the reference electrode and the ITO/WO_3, ITO/HCl/WO_3 as a working electrode with an electrolyte solution containing 0.5M lithium perchlorate ($LiClO_4$) in propylene carbonate (PC).

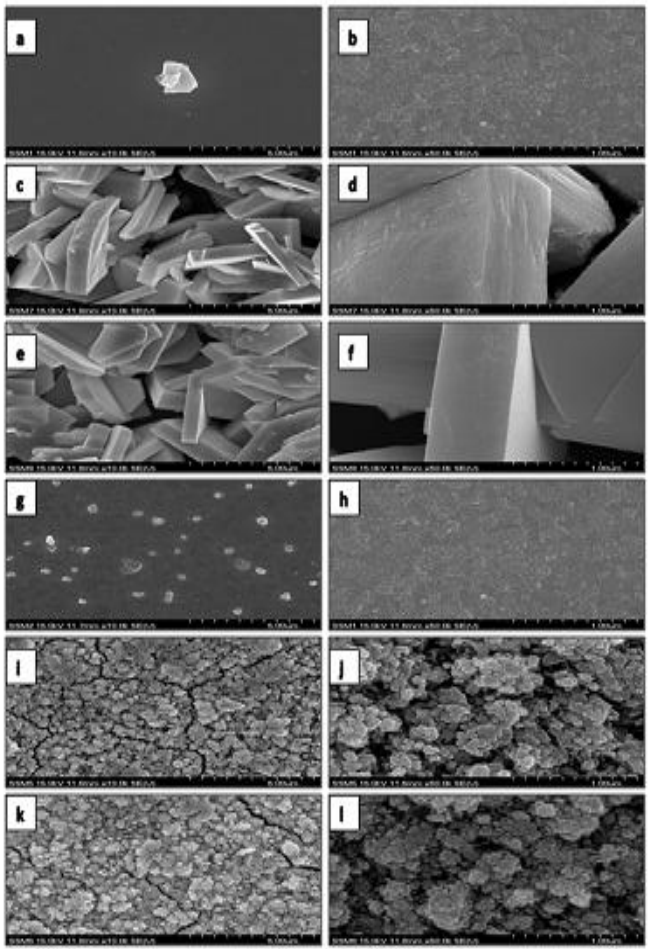

Figure 1: Scanning electron microscopy for (a,b) ITO, (c,d) ITO/WO_3 before annealing, (e,f) ITO/WO_3 after annealing, (g,h) ITO/HCl, (i,j) ITO/HCl/WO_3 before annealing and (k,l) ITO/HCl/WO_3 after annealing samples on conducting glass substrates. All the films are recorded at low and high magnifications.

Table 1: Pore size and grain size for ITO/WO_3 and ITO/HCl/WO_3

Particulars	ITO/WO_3		ITO/HCl/WO_3	
	Before Annealing	After Annealing	Before Annealing	After Annealing
Grain Size	500-700nm	400-700nm	80-100nm	50-70nm
Pore Size	100nm	100nm	200nm	400nm

Results

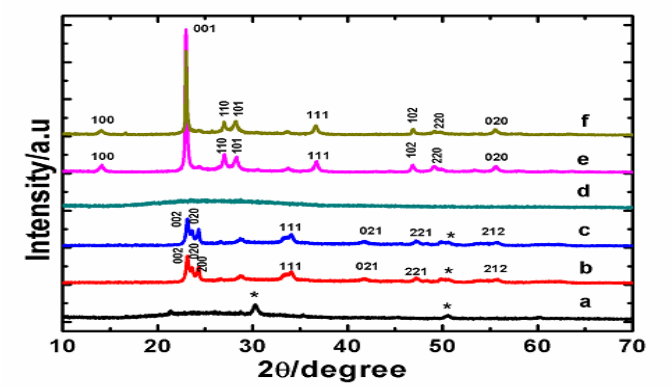

Figure 2:X-ray diffraction patterns for (a) ITO, (b,c) ITO/WO_3 before and after annealing the samples, (d) ITO/HCl and (e,f) ITO/HCl/WO_3 before and after annealing the samples, where asterisk specifies the peaks of ITO. The standard JCPDS no. 00-005-0364 for ITO/WO_3 and JCPDS No. 00-033-1387 for ITO/HCl/WO_3 is indicated as sample peaks.

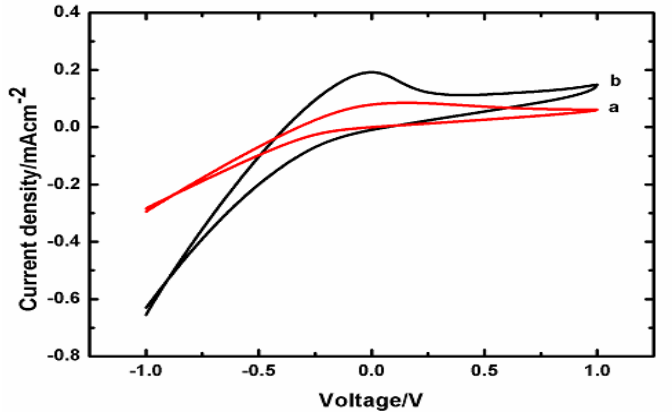

Figure 3: CV recorded in 0.5 M $LiClO_4$-PC electrolyte for (a) ITO/WO_3 and (b) ITO/HCl/WO_3 configuration after annealing the sample at the scan rate of 20 mV s^{-1}

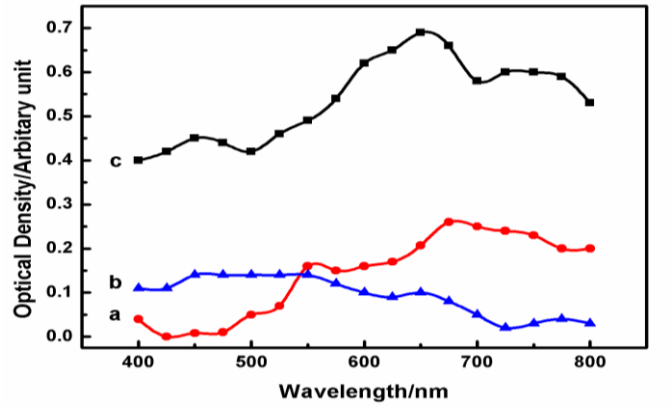

Figure 4: Variation of optical density vs wavelength for a) ITO/WO_3 after annealine b) for ITO/HCl/WO_3 before annealine and c) for ITO/HCl/WO_3 after annealine.

Discussion

SEM

Figure 1 (a-l) present the SEM images for all the samples; the grain and pore sizes are elaborated in Table 1. The bare ITO glass substrates showed agglomerated particle size of 1500nm [Figures 4 (a and b)]. Moreover, the ITO/WO_3 film showed a clear, fine nanobrick thickness of 500-700 nm, with fewer changes before and after annealing [Figures 4 (c-f)] and a porous structure. However, the ITO/HCl film isolated the agglomerated ITO particles [Figures 4 (g and h)], increasing the film roughness [26].The ITO/HCl/WO_3 films before annealing [figures4 (i and j)] exhibited tiny nanoflowers having a grain size of 80-100 nm with an incorporated cracky nature and a pore size of 200nm. However, after annealing [figures4 (k and l)], the films revealed tiny nanoflowers having grain size of 50-70 nm, with an integrated cracky nature, and a pore size of 400nm. Indeed, the ITO/HCl/WO_3 film showed a decreased grain size and increased pore size with an open surface, wherein etching plays a key role in the architecture of WO_3 thin films.

XRD

The XRD patterns of the ITO, ITO/WO_3, ITO/HCl and ITO/HCl/WO_3 films are shown in Figures 2(a-f). Figure 2a exemplifies the crystalline peaks of the bare ITO substrate (indicated by an asterisk) and the XRD patterns of the films before (Figure 2b) and after (Figure 2c) annealing. It possesses a monoclinic phase (JCPDS no. 00-005-0364) of WO_3 with well indexed peaks at 23.14° (002), 23.65°(020), 24.39°(200), 26.11°(011), 8.96°(111), 33.38°(021), 42°(221), 50°(140), 55.54°(212), with less variation in the intensity. The asterisk (*) indicates the ITO peaks (JCPDS no. 00-06-0416) [27]. Figure 2d represents the amorphous nature of the ITO/HCl film. The occurrence of amorphous phases is a particularly interesting phenomenon for studying thin film growth [24]. TheXRD patterns of the ITO/HCl/WO_3 film [Figures 2 (e and f)] represents the hexagonal phase of WO_3 (JCPDS card no. 00-033-1387). with well-indexed peaks at 13.85° (100), 24.37° (110), 26.84°(101), 28.20°(200), 33.57°(111), 36.6°(201), 42.81°(300), 48.69°(102), 49.87°(220), 55.25°(202), 49.87°(220), with an additional peak at 22.69° (001), indicating that most (001) planes are parallel to the substrate [2]. Herein, the ITO peaks were absent due to the amorphous nature, thus increasing the adhesivity of WO_3 films. The XRD results are analogous with SEM. Intense and sharp XRD peaks of the ITO/WO_3 and ITO/HCl/WO_3 films ensure a high degree of crystallinity, improving performance of EC devices.

Electrochemical study

The electrochemical study of the ITO/WO_3 and ITO/HCl/WO_3 films for the annealed film in 0.5 M $LiClO_4$ + 1mM PC was typically characterised through cyclic voltammetry (CV) in the potential range of -0.9 to +1.0 V vs the SCE at a scan rate of 50mVs^{-1} [Figures 5 (a and b)]. A significant shift was observed in the shape of the CV curves. Upon cycling, the ITO/WO_3 film, yellow when deposited, switch from blue to slight transparent in a reversible manner. Contrastingly, the ITO/HCl/WO_3 film slightly yellow when deposited, switch from being deep blue to considerably transparent in a reversible manner. The blue colouration of the film is associated with the cathodic peak before current reduction due to oxygen evolution, whereas the bleaching process is associated with the oxidation peak, in agreement

with the cathodic electrochromism nature of tungsten trioxide [5].

Optical Density Spectra

Figure 4 shows the optical density spectra for a) the WO_3 film deposited on etched ITO as compared to the WO_3 thin film deposited on bare ITO. It can be seen from the absorption curves that a weak broad peak was formed for the annealed ITO/WO_3 film. This peak becomes more intense for the annealed ITO/HCl/WO_3 film, peaks were not observed for ITO/HCl/WO_3 before anneiline. It is known that for a metal nanoparticle with dimension much smaller than the wavelength of light, an electromagnetic wave with certain wavelength induces a resonant coherent oscillation of the free electrons across the nanoparticle. This wavelength depends on the metal composition, nanoparticle size and shape and the dielectric properties of the surrounding media [29].

Conclusion

In summary, we demonstrated the EC configuration of ITO/WO_3 and ITO/HCl/WO_3 fabricated via a cheap, facile and seed layer free green technique of hydrothermal method by adding $C_2H_2O_4.2H_2O$ as the capping agent. ITO/WO_3 configuration composed of aggregated microbricks. HCl provides a simplified architechture to WO_3 films forming uniform and well-adhesive layer with amendment of monoclinic to hexagonal phase with nanoflowers of grain size 50-70 nm. It also lowers the thickness of the ITO/HCl/WO_3 film with enhanced pore size providing open tunnel structure for charges. In particular, etching provides superior optical modulation (49.3% at 630 nm) with better change in current density. Noticeably, the ITO/HCl/WO_3 configuration holds great promise for potential applications in energy-saving smart windows.[28]

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