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Electrochromic behavior of WO_3 nanoplate thin films in acid aqueous solution and a protic ionic liquid

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ABSTRACT

WO_3 nanoplates were synthesized in non-aqueous solvent using a one-step process ultrasonic irradiation. The nanostructured morphology was maintained in the films prepared by electrophoretic deposition (EPD) process onto ITO substrates. Spectroelectrochemical experiments were carried out by using both, H_2SO_4 and a protic ionic liquid (PIL) *N*-methyl-pyrrolidinium tetrafluoroborate, electrolytes. Cyclic voltammograms (CVs) were combined with transmittance measurements for all films that undergo typical reversible color change from colorless to blue. The integrated cathodic current of intercalation/deintercalation was used to calculate the coloration efficiency (CE) of films; the value obtained being in good agreement with nanostructured WO_3 films. The coloration/bleaching processes showed good color efficiency, fast coloration time and optical contrast in acid electrolytes. The results using PIL as electrolyte, instead of H_2SO_4, show that all electrochromic parameters were improved, including the cyclic durability that was higher in this medium. Therefore, the use of a PIL enables proton intercalation but no dissolution suggesting its use as a suitable electrolyte for electrochromic devices.

1. Introduction

Electrochromic materials are capable of changing their optical properties, reversibly or persistently when an electrical voltage is applied [1–3]. Electrochromism of tungsten oxide (WO_3) nanostructures has been widely studied in the last years. From all these studies a large majority of authors agree in assuming that the electrochromic effect in WO_3 can be summarized by the overall reaction:

$$\underset{(Colorless)}{WO_3} + {}_xM^+ + xe^- \leftrightarrow \underset{(Blue)}{M_xWO_3} \quad (1)$$

where M^+ is generally H^+, Li^+ or Na^+. Several physical studies of the reaction product, i.e. the "bronze" M_xWO_3, have been performed [4]. It is widely accepted that the mechanism for coloration is related to the intervalence charge transfer (IVCT) model for WO_3, first proposed by Faughnan et al. [5]; it was based on the assumption that the injected electrons are localized on W^{6+} ions to form W^{5+}, the coloration being due to transferring electrons from W^{5+} to the adjacent W^{6+} sites. However, unless these two W sites are non-equivalent, the two configurations are energetically equivalent.

An alternative model is based on the concept of polaron formation, that displacing atoms or ions in a material from their carrier free equilibrium position produces a potential that will bind a charge carrier by self-trapping [6]. It has been suggested that the coloration in amorphous WO_3 is due to small polaron formation [7].

Electrochromic tungsten oxide is potentially applied in energy-efficient smart windows, display devices, switchable mirrors and photoelectrochromic devices. The performance of electrochromic devices in visible wavelength range for civil applications has been extensively studied [8,9]. However, diffusion of positive ions into the tungsten oxide layer is often slow, sometimes taking minutes to complete. Many efforts have been made in this area to understand the intercalation phenomena in WO_3 thin films using electrogravimetric studies [10–12]. Since the chemical diffusion coefficient of protons (D_{H+}) is one order of magnitude larger than that of lithium ions (D_{Li+}), electrochromic systems based on proton electrolytes (e.g., aqueous H_2SO_4) are mandatory for display applications and preferred for other applications. Unfortunately, proton insertion from aqueous H_2SO_4 solution currently results in rapid degradation of the electrochromic films [13].

There are two important criteria for selecting an electrochromic material. The first one is the time constant of the intercalation reaction, which is limited both by the diffusion coefficient and by the length of the diffusion path. While the former depends on the chemical and crystal structure of the metal oxide, the latter one is determined by the material's microstructure [14]. In the case of nanoparticles, the smallest dimension is related to the diminution of the diffusion path length phenomena. Thus, designing a nanostructure with a small size, while maintaining the proper crystal structure, is a key to obtaining a material with fast insertion kinetics, enhanced durability, and superior performance.

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The second important criterion is coloration efficiency (CE), the change in absorbance (A) per inserted charge unit (Q), that is, CE $= \Delta A/Q$ [4]. A high CE provides large optical modulation with a small charge insertion or extraction. This is a crucial parameter for electrochromic devices, since a lower charge-insertion or extraction rate enhances the long-term cycling stability.

Different methods to obtain tungsten oxide nanoparticles has been reported, including sol–gel process [15], chemical vapor deposition [16], solvothermal [17] and electrochemical [18]. Sonochemical synthesis was used to prepare tungsten oxide nanomaterials using different precursors such as tungsten hexacarbonyl and tungsten chloride [19, 20] and different solvents such as ethanol [21] and benzyl alcohol [22]. Electrophoretic deposition is an important method of film formation, where charged nanostructures dispersed in an appropriate solvent can be deposited onto transparent substrates under influence of an electric field. There are some articles reporting electrochromic tungsten oxide films obtained by immobilization of nanoparticles using EPD technique [23,24].

As stated, tungsten oxides have been most extensively studied but because of their high dissolution rate in acidic electrolyte solutions, these films can only be used in lithium-based organic electrolytes, resulting in slower response times. Furthermore, extended durability, even in Li^+ systems, has not yet been demonstrated.

Ionic liquids (ILs) are a class of solvents which are increasingly being used in a variety of applications due to a number of desirable properties [15,16]. ILs are defined as those fused salts which have a melting point below 100 °C, while those with higher melting points are frequently referred to as molten salts. ILs can be divided into two broad categories: aprotic ionic liquids and protic ionic liquids (PILs). PILs are produced through proton transfer from a Brønsted acid to a Brønsted base. They are an interesting subset of ILs, with some distinguishing features when compared to aprotic ionic liquids. The majority presents no negligible vapor pressures, but their beneficial properties for certain applications outweigh this potentially negative property.

The protic nature of PILs is a crucial feature in a number of applications, including biological applications [25–27], organic synthesis [28], proton conducting electrolytes for polymer membrane fuel cells and catalysts [29]. PILs have attracted attention as electrolytes for their suitable electrochemical properties, including high electrochemical and dimensional stability, good ionic conductivity, and long-term durability. Some systems have been investigated and applied in batteries, double-layer supercapacitors, fuel cells and chemical sensors [30].

For the electrolyte application in electrochromic devices (ECDs), the properties mentioned above have to include also the excellent optical transparency and high photostability of the electrolyte. PILs systems based on pyrrolidinium meet these requirements. Moreover, they are environmentally friendly and exhibit only a low toxicity when comparable to other electrolytes like propylene carbonate (PC).

In this article we report our strategy for building up electrochromic nanostructured films with tungsten oxide nanoplates synthesized by sonochemical method and deposited using electrophoretic deposition (EPD) technique onto a transparent conductor substrate (ITO) and proton intercalation/deintercalation of the as-prepared films in both aqueous and PIL electrolytes.

1.1. Experimental methods

Materials: Tungsten (VI) chloride (99.99%) was purchased from Aldrich. Benzyl alcohol (anhydrous, 99.8%), ethanol, Tetra hydrofurane (THF) and acetonitrile were purchased from Synth. All chemicals were used without further purification.

1.2. Synthesis of tungsten oxide nanoplates

WO_3 nanoparticles were prepared by modification of previous method described in literature [20]. First, 100 mg of WCl_6 (0.25 mmol), was slowly added to 10 mL of benzyl alcohol (86.50 mmol) under vigorous stirring at room temperature. The solution was introduced into the sonication cell with a probe from Sonics-Vibracell. The reaction mixture was sonicated during 9 min at 60% amplitude to fully react. The sonication was carried out without cooling, so that, a temperature of 92 °C was reached at the end of the reaction. The resulting suspension was centrifuged and the precipitate was thoroughly washed several times with ethanol and THF. The collected material was left to dry in air and finally ground into a powder. The as-prepared powder was green-yellow due to the sub-stoichiometric state of the as-synthesized WO_3 nanoplates, but became slightly yellow after annealing in air at 300 °C for 2 h.

For Raman and XRD characterization, powder of nanoplates were obtained by centrifugation (Eppendorf centrifuge, 13,400 rpm) during 1 h followed by vigorous washing with deionized water in order to remove superficially adsorbed ions, and further centrifugation for one additional hour. The residual solution was removed and the solid obtained was dried at low pressure and room temperature in a desiccator. The phases of the synthesis products were identified by powder X-ray diffraction (XRD, Rigaku Miniflex 30 kV/15 mA, $\lambda = 1.54056\ \AA$). Average crystallite/grain size was calculated using the Debye–Scherrer equation after carrying out background subtraction. Crystallite size values calculated using the XRD results obtained are only approximate since the effect of instrumental line broadening on these was not taken into account. Raman spectra were obtained in a Renishaw Raman Imaging Microscope (System 3000), connected to a CCD detector (Wright, 600 × 400 pixels), using the 514 nm excitation radiation (He-Ne laser -Spectra Physics, model 127).

The transmission electron microscopy images were collected using Jeol 1200 EXII electron microscope. The samples were dispersed in acetonitrile and a drop of the suspension was air dried onto carbon-coated copper grids.

1.3. Film formation

The substrates, indium-doped tin oxide substrates (ITO, Delta Technologies, sheet resistance 15–25 $\Omega\ cm^{-1}$, surface area 0.5 cm^2) (0.7 cm × 3 cm in size), were cleaned by ultrasonication in acetone, ethanol and water for 15 min, respectively. Then the substrates were further washed thoroughly with water.

The nanoplate suspension was prepared by dispersing the WO_3 nanoplates in acetonitrile with 2 mg cm^{-3} concentration using an ultrasound probe from Sonics-Vibracell. Films were made by using the EPD technique with nanoparticles immobilized onto indium-doped tin oxide substrates used as the anode and a platinum foil as the cathode by applying potentials at different range from 100 to 300 V, during 60 s between the two parallel electrodes placed 1.0 cm apart in an electrochemical cell containing the nanoparticle suspension. The coated substrates were overnight air-dried before morphological and electrochromic studies.

The morphologies of the as-prepared thin films were observed by scanning electron microscopy (SEM) with a Jeol microscope, model JSM-7401F. Thin film growth was monitored by UV–vis spectroscopy with an HP 8452A spectrophotometer.

1.3.1. PIL electrolyte preparation

Equimolar amounts of the tetrafluoroboric acid solution were slowly added while stirring to the *N*-methylpyrrolidine contained in a round-bottom flask over ice. The reaction with strong inorganic acids is extremely aggressive and care should be taken. The temperature during reaction was maintained below 15 °C. Excess water was removed by drying under vacuum at 60 °C. The final product was *N*-methylpyrrolide tetrafluoborate ($[C_3mpyr][BF_4]$) which is typically hygroscopic and required vacuum freeze-drying prior to use [31].

The amount of water contained in the PILs was determined using a coulometric Karl-Fisher titrator from Metrohm (model 831). Samples