Available online at www.sciencedirect.com

Chinese Chemical Letters 18 (2007) 883–886

CHINESE CHEMICAL LETTERS

www.elsevier.com/locate/cclet

The research on the high quality TiO_2, MoO_3-doped WO_3 electrochromic film

Wei Luo, Xiang Kai Fu *, Li Hua Ma

College of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China

Abstract

The high quality TiO_2, MoO_3-doped WO_3 electrochromic film was prepared by the sol–gel method for the first time. The sol, which has hydrogen peroxide (H_2O_2) and oxalic acid ($H_2C_2O_4$), was very stable at room temperature and quite suitable for the deposition of films. The WO_3 electrochromic film prepared from this doped sol had excellent performance, such as short response time, no cracks, good adhesion to the substrate, high coloring efficiency and longevity of service.

Keywords: TiO_2; MoO_3; WO_3; Oxalic acid; Sol–gel; Electrochromic

The electrochromic materials have an excellent application prospect. They are widely used on smart windows with controllable throughput of radiant energy and electronic information displays. In recent years, research on the smart window has been receiving more and more attention. By controlling the solar radiation to buildings or automobile interiors, the uptake of illumination and heat can be modified to improve the energy conversion, which will meet the low power requirement. Among the electrochromic materials used in smart windows, WO_3 has attracted much attention recently due to its high coloring efficiency, high stability and low material cost. Working as a promising electrochromic material, WO_3 is usually doped with one or two efficient additives to improve its properties [1]. For example, H_2O_2 and $H_2C_2O_4$ can stabilize the tungstic acid sols, decrease the electrochromic potential of the prepared electrochromic film and shorten the response time; while TiO_2 and MoO_3 can improve the adhesive ability, coloring efficiency, and prolong the cycle life of the WO_3 electrochromic film. Many researches have been done on doped WO_3 electrochromic films, but there are no reports concerning doping the WO_3 electrochromic film in this way presented in this work [2–5].

There are several methods to prepare WO_3 film material, such as electrode position, chemical vapour deposition, electron beam deposition, and sol–gel process. Among these methods, the sol–gel process has been proposed as a simple and innovative technique because of its low processing temperature, simple equipment and ready control of the film morphology, which is the key for preparing an excellent WO_3 electrochromic film. In this paper, a high quality TiO_2, MoO_3-doped WO_3 electrochromic film was prepared by the sol–gel method for the first time, and an explanation for its excellent performance had also been proposed.

---

* Corresponding author.
E-mail address: fxk@swu.edu.cn (X.K. Fu).

1001-8417/$ – see front matter © 2007 Xiang Kai Fu. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.
doi:10.1016/j.cclet.2007.05.003

1. Experimental

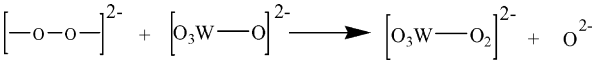
MoO_3-doped WO_3 sols were formed upon acidification of sodium tungstate aqueous solution with sodium molybdate passed through a proton exchange resin, H_2O_2 and $H_2C_2O_4$ were added afterwards. TiO_2 sols were formed upon the hydrolysis of $Ti(OBu)_4$ in the mixture of water and ethanol (20:80, w/w), H_2O_2 and $H_2C_2O_4$ were also added. For the preparation of TiO_2, MoO_3-doped WO_3 sols, TiO_2 sols, were dissolved in the foregoing MoO_3 doped WO_3 sols directly. With this procedure, clear, homogeneous and stable sols were obtained for deposition.

Films were deposited by dip-coating on indium tin oxide (ITO) coated glass with a pull rate of 2 mm/s under the controlled relative humidity of 55%. The ITO film has a sheet resistivity of 50 Ω. After the substrates were cleaned with detergent, they were firstly flushed with de-ionized water and then rinsed with acetone and ethanol. Multiple coatings with intermittent drying at room temperature were used to generate thicker films. In this work, each sample was dipped for twice. The as-deposited films were dried in air for 30 min at 80 °C to evaporate the solvent and then heated to 150 °C at a rate of 5 °C/min; after 150 °C was reached, the films were kept at this temperature for other 2 h. Final thicknesses of the mixed oxides films were in the range of 300–400 nm for all the samples characterized in this work.

2. Results and discussion

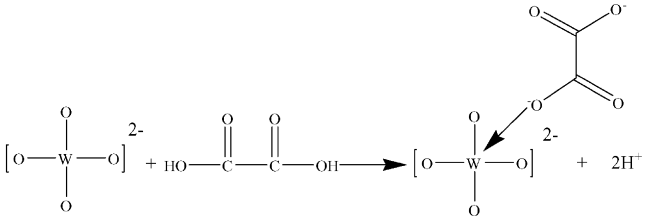
The pure WO_3, MoO_3 or TiO_2 sols could change into gels within 20 min; therefore, they were not stable enough for the preparation of WO_3 electrochromic film. However, the addition of stabilizers, such as H_2O_2 and $H_2C_2O_4$, could increase the stability as well as the electrochromic performance of theWO$_3$ film, without affecting the viscosity of the sols within 6 months.

The reason why adding H_2O_2 and $H_2C_2O_4$ help stabilize the sols is that the addition of H_2O_2 into doped tungstic caused the formation of peroxo tungstic acid by partly replacing the O^{2-} in $[WO_4]^{2-}$ with $O_2{}^{2-}$:



$$[-O-O-]^{2-} + [O_3W-O]^{2-} \longrightarrow [O_3W-O_2]^{2-} + O^{2-}$$

This reaction decreased the number of O^{2-} ligands in $[WO_4]^{2-}$, decelerated the condensation among tungstic acid and stabilized the tungstic acid sols. The small ligand molecules $H_2C_2O_4$ could also coordinate with W^{6+} to stabilize the tungstic acid sols [6]. The possible mechanism is described as follows:



The increased ligands around W^{6+} could result in steric effect and decrease the condensation among tungstic acids. The H_2O_2 and $H_2C_2O_4$ have the same reactions with the Mo^{6+} and Ti^{4+} to make the doped sols more stable.

In order to estimate the color change, the electrochemical workstation was upgraded with an optical system, UNIC®4802. A quartz cell was used as the electrochemical cell, in which the three electrodes were immersed. Thus, the current, the passed charge and the light transmittance can be measured "*in situ*" as a function of applied voltage at different wavelengths. Cyclic voltammetry curves had been recorded within −1.5 to 1 V range (*vs*. SCE) at a scanning rate of 50 mV/s. The number of charges Q exchanged during these experiments can be read from the records and the reversibility of one cycle can be expressed by the coulombic ratio $\tau = Q_{ox}/Q_{red}$. The optical density of the films can be measured simultaneously during cyclic voltammetry runs.

The cyclovoltametric curves for the film (Fig. 1) do not show any distinct cathodic peaks, which indicate the amorphous structure of the film since the classical amorphous tungsten oxide films have a broad distribution of energetically different intercalation sites [5,7]. In contrast, there is a very well-defined anodic peak at −0.2 V, which is the evidence of improved kinetic performance. This improved performance is caused by the highly porous structure that greatly reduces the diffusion length of lithium ions [8].