Journal of Colloid and Interface Science xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Regular Article

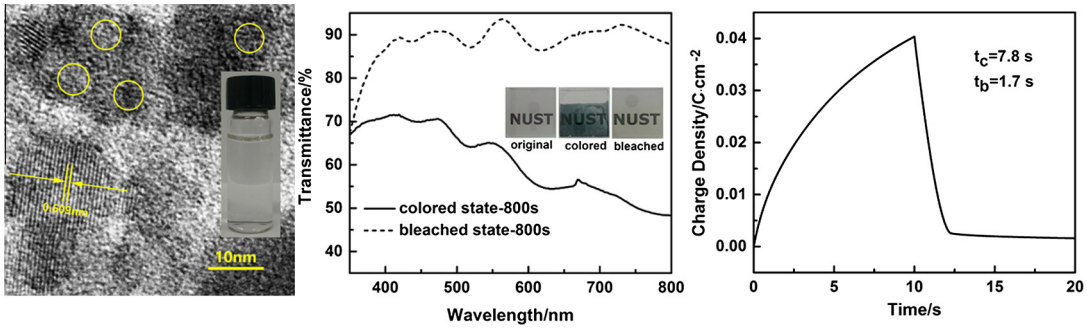
Assembling tungsten oxide hydrate nanocrystal colloids formed by laser ablation in liquid into fast-response electrochromic films

Shalong Wang [1], Kang Dou [1], Yousheng Zou *, Yuhang Dong, Jubin Li, Dan Ju, Haibo Zeng *

Institute of Optoelectronics & Nanomaterials, School of Material Science and Engineering, Nanjing University of Science and Technology, Nanjing 210094, China

GRAPHICAL ABSTRACT

The mesh-like porous tungsten oxide hydrate film exhibited a wide optical modulation of 32% at 632 nm, fast coloring and bleaching response speed of 7.8 s and 1.7 s, respectively.



ARTICLE INFO

Article history:
Received 30 June 2016
Revised 26 August 2016
Accepted 27 August 2016
Available online xxxx

Keywords:
Tungsten oxide hydrate
Electrochromic properties
Laser ablation in liquid
Electrophoresis
Colloidal nanocrystals

ABSTRACT

High-performance electrochromic films based on tungsten oxide hydrate ($[WO_2(O_2)H_2O]\cdot 1.66H_2O$) colloidal nanocrystals with fast switching speed were fabricated by laser ablation in a mixture of water and hydrogen peroxide followed by electrophoretic methods. Through electrophoretic deposition, the nanoparticles in the colloids synthesized by laser ablation aggregated onto the FTO coated glass substrate forming a lager cell with a uniform size of around 200 nm, which subsequently self-assembled into a porous tungsten oxide hydrate film. By optimizing the electrophoretic time (800 s) and voltage (−0.5 V), the mesh-like porous tungsten oxide hydrate film achieved a wide optical modulation of 32% at 632 nm, fast coloration and bleaching response speed of 7.8 s and 1.7 s respectively due to the synergetic effect of the unique atomic structure of $[WO_2(O_2)H_2O]\cdot 1.66H_2O$ and porous structure with large surface area that facilitates the ion insertion/extraction. Thus the tungsten oxide hydrate can be a promising electrochromic material for practical applications.

1. Introduction

Information transformation plays a vital role in the rapid development of modern society. Besides electronic communication, display performance is also an important component for conveying information. As a potential screening functional material, elec-

* Corresponding authors.
E-mail addresses: yshzou75@njust.edu.cn (Y. Zou), zeng.haibo@njust.edu.cn (H. Zeng).
[1] These authors contribute this work equally.

http://dx.doi.org/10.1016/j.jcis.2016.08.072
0021-9797/

trochromic materials are widely used in internet technology, electronics, energy, architecture and national security field. Moreover, electrochromic materials are also applied in smart windows, reflect mirror, information displays, sunroofs, etc. [1–8], owing to their controllable transmittance, memory effect and fast response.

Electrochromic materials can undergo reversible change of transmittance by the application of an electrical voltage which induces insertion/extraction of charges (ions or electrons), and exhibit a dynamic changing between two different colors. Typically, electrochromic materials are divided into three categories: inorganic materials, organic small molecules (OSM), and conjugated polymers. Inorganic materials are mainly transitional metal oxides (TMO), including cathode colored materials (e.g. V/Mo/W/Nb/Ti oxides) and anode colored materials (e.g. Prussian blue or Ni/Co/Ir oxides). Among these TMOs, WO_3 earns a lot of attentions owing to its outstanding color efficiency and electrochromic stability. Moreover, WO_3 is a potential display material as the colored state of WO_3 (blue) can compensate the weak sensitivity to blue light of human eyes. The electrochromic mechanism of WO_3 can be simply described as the insertion and extraction of ions and electrons, the corresponding reaction formula is described as:

$$xM^+ + xe^- + WO_3 \leftrightarrow M_xWO_3 \quad (1)$$

Normally, $M^+ = H^+$, Li^+, Na^+ [9], can be inserted/extracted into/from WO_3 quite fast due to their light weight. The colored and bleached states are bright blue and transparent, respectively.

Although the electrochromic properties of WO_3 have been extensively studied, its practical application is still limited by its long response time. Since WO_3 is a semiconductor, the poor conductivity slows down the transfer of charge carriers. On the other hand, WO_3 films prepared by traditional methods [10,11] usually have compact structure, which also hampers the transport of ions in the electrolyte. Therefore, the chemical reaction between WO_3 and ions is quite slow limiting the speed of electrochromic process.

Recently, some efforts have been made to improve the response time of WO_3. Nanostructured WO_3 with large specific surface area and high chemical activity is expected to reduce the transfer distance for the charge carriers and improve the switching characteristic of electrochromic process. Using ultrathin $W_{18}O_{49}$ nanowire assemblies, Yu et al. [12] fabricated the electrochromic nanodevices based on the well-organized $W_{18}O_{49}$ nanowire monolayer film with stable and fast response of less than 2 s. Cai et al. [13] prepared a Ti-doped WO_3 film with high conductivity to improve the transfer speed of carriers and the presence of amorphous structure in the film is also in favor of the insertion and extraction of charges. Meanwhile, Cai et al. [14] realized an electrochromic application with fast speed based on a two-dimensional WO_3 ordered nanoporous film via a step-by-step template-assisted strategy, indicating that the porous structure can also improve the coloring/bleaching speed of WO_3 films by offering more available paths for the ions and electrons transport. Another approach to speed up the electrochromic response is by changing the microstructure of tungsten oxide with water molecules. There have been some literatures demonstrating that tungsten oxide hydrates such as $WO_3{\cdot}2H_2O$ (dihydrate), $WO_3{\cdot}H_2O$ (monohydrate), $WO_3{\cdot}0.5H_2O$ (hemihydrate), and $WO_3{\cdot}0.33H_2O$ [15–19] also exhibit good electrochromic performances. Judeinstein and Livage [20] once reported that the lithium diffusion coefficient in WO_3 monohydrate is 10–100 times greater than that in anhydrous WO_3, and they suspected that H_2O molecules are strongly involved in the ionic conduction mechanism. Xie et al. [21] clarified that, since $WO_3{\cdot}2H_2O$ possesses a layered structure, the existence of interlaminar water can increase the distance between adjacent layers to supply a larger spacing [22], facilitating ionic intercalation/extraction during electrochromic process for the electrochromic device based on the assembled $WO_3{\cdot}2H_2O$ ultrathin nanosheets film.

Herein, we propose a novel strategy to fabricate high-performance electrochromic films based on tungsten oxide hydrate colloidal nanocrystals. The tungsten oxide hydrate nanoparticles were synthesized using laser ablation in liquid (LAL), which is a facile and green method for synthesizing nanoparticles (NPs) with high chemical reactivity and complex nanostructure. Subsequently, these nanoparticles assembled into a porous tungsten oxide hydrate film using electrophoresis technique. The structure, morphology and electrochromic performances of the porous tungsten oxide hydrate film were investigated, which shows extremely fast response speed under both coloration and bleaching voltages.

2. Experimental

2.1. Fabrication of tungsten oxide hydrate colloid

First, a tungsten target (>99.9%) was polished with sandpaper and rinsed by ethanol and deionized water respectively. Then the cleaned tungsten target was immersed in a quartz chamber containing 60 mL deionized water and 0.2 mL H_2O_2 (30 wt.%). A focused Nd: YAG laser (1064 nm, pulse duration 10 ns, 10 Hz) with a power of 250 mJ/pulse and a facula of 2 mm irradiated on the tungsten target for 2 h to obtain a colloid containing tungsten oxide hydrate NPs.

2.2. Fabrication of tungsten oxide hydrate films

The as-prepared colloid was subsequently transferred to an electrolytic cell and the electrophoretic deposition progress was carried out in a three-electrode system (shown in Fig. 1). Transparent FTO substrate was used as working electrode while a Pt sheet acting as the counter electrode and the distance of these two electrodes were fixed as 1 cm. The reference electrode was a calomel electrode. Electrophoretic deposition was done at a constant voltage of −0.5 V, eventually, an optically transparent tungsten oxide hydrate film with porous structure was fabricated.

2.3. Characterization of tungsten oxide hydrate colloid and film

The microstructure and size of the as-synthesized tungsten oxide hydrate nanoparticles after LAL were measured by high resolution transmission electron microscope (HRTEM, FEI Tecnai20). The crystal structures of the NPs were also investigated by X-ray diffraction (Bruker-AXS D8 Advance) and Raman spectroscopy (Aramis). The morphologies of the as-deposited EC films were obtained on field emitting scanning electron microscope (FESEM, FEI Quanta 250F).

2.4. Electrochromic measurements

The electrochromic performances of the films were measured through the electrochemical workstation (CHI660E, Chenhua, Shanghai) with a three-electrode system. The as-deposited films were immersed in 1 M $LiClO_4$ in propylene carbonate solution so that its electrochromic performance can be studied. The coloration and bleaching voltage were set to −1.5 V and 1.5 V respectively and the switching response was recorded in the sweep mode. The transmittance spectra of the films at colored/bleached state were measured by UV–Visible spectrum (UV-3600).

Please cite this article in press as: S. Wang et al., J. Colloid Interface Sci. (2016), http://dx.doi.org/10.1016/j.jcis.2016.08.072