Organic Electronics 37 (2016) 213–221

Contents lists available at ScienceDirect

Organic Electronics

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

# A dual electrochromic film based on nanocomposite of aniline and o-toluidine copolymer with tungsten oxide nanoparticles

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ARTICLE INFO

*Article history:*
Received 12 March 2016
Received in revised form
21 May 2016
Accepted 29 June 2016
Available online 7 July 2016

*Keywords:*
Electrochromic
Tungsten oxide
Aniline
O-toluidine
Electrodeposition

ABSTRACT

A dual electrochromic (EC) film was prepared based on composite of tungsten oxide nanoparticles and copolymer of aniline and o-toluidine, by electrochemical polymerization method. In this method, aniline and o-toluidine monomers were dispersed in the solution containing tungsten oxide ($WO_3$) nanoparticles and the final mixture was used for electrodeposition of film on fluorine doped tin oxide (FTO) coated glass. $WO_3$ nanoparticles were incorporated in the copolymer matrix structure, and a dual EC film was constructed. EC properties of $WO_3$, copolymer and $WO_3$-copolymer nanocomposite films were evaluated by cyclic voltammetry (CV) and the UV–Vis spectrophotometry. Also, the optical response and coloration efficiency (CE) of samples were investigated. The composition of organic-inorganic EC materials have improved properties in application of the EC film such as significant optical modulation (37.35% at 633 nm) and high switching speed and high coloration efficiency (116.6 $cm^2\ C^{-1}$ at 633 nm). These achievements were better than $WO_3$ or copolymer films. The improved EC properties were appertained to the mixture of prominences of both materials.



## 1. Introduction

The energy demand in the world is rising as result of population growth. On the other hand, energy demand yield to global warming. Global warming occurs from carbon dioxide emission to the atmosphere as a consequence of energy producing from fossil fuels [1,2]. The fraction of the land energy reserves use in buildings for heating, cooling, ventilation, and appliances amounts to 30–40%. The capacity of energy saving is significant and economic in building domain [3,4]. Because windows are weak links in buildings for energy saving that cannot be eliminated, then the technologies for energy efficiency can lead to large energy saving [5,6]. One of these technologies is electrochromic (EC) window.

Electrochromism is a phenomenon related to color change with a reversible electrochemical process due to the generation of different electronic absorption bands in the visible region. The color change is commonly between a transparent state (bleached state) and a colored state, or between two colored states. EC materials are able to change the optical properties persistently and reversibly by an external voltage [7–10]. Major known EC materials can be classified into three groups: inorganic oxides, single molecular and organic polymeric materials [11–16].

EC materials can be divided into anodic or cathodic materials. The complementary or dual EC devices (ECDs) such as smart windows are devices in which both anodic and cathodic EC materials can simultaneously be bleached or colored [17]. For example when the voltage is applied to the ECD, cathodic EC material is colored by insertion ions (or extraction electrons) and anodic EC material is colored by extraction ions (or insertion electrons), simultaneously.

$WO_3$ as a well known inorganic EC material is the most investigated material, not only it has genuine color switching but also it has good chemical stability and strong adherence to substrate [18–20]. However, apart from these advantages, single color change and slow switching speed are defects that limit its usage. On the other hand, an organic EC material (i.e. conducting polymer), not only can eliminate these defects, but also has advantages such as multicolor, fast switching speed, flexibility and easy to optimize their EC properties through molecular tailoring [21–26]. Regrettably, lack of film uniformity, low material recovery and narrow range of colors are limitations that bound their engineering applications [27,28].

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http://dx.doi.org/10.1016/j.orgel.2016.06.038
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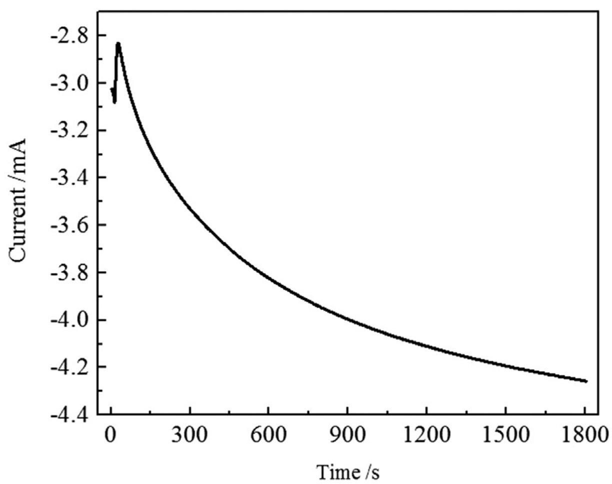


**Fig. 1.** Electrodeposition of $WO_3$ film with chronoamperometry technique.

Copolymerization is an important process for optimizing of the electrochemical or optical properties of the EC materials, which could modify the structures and properties by combining the advantages of both monomers. The EC properties of the copolymers have showed that they exhibit stronger formability and uniformity, better electroactivity and tricolor electrochromism than monomers [29,30].

The purpose of this article is to prepare new nanocomposites based on copolymers and metal oxides exhibit the improved EC properties compared with those of pure conducting polymers and inorganic materials, or even nanocomposites based on polymers and metal oxides. Because of the scarce efforts performed by researchers about composite of EC copolymers and EC metal oxides, the EC properties of the $WO_3$-copolymer nanocomposite thin film investigate in this research. In the present work, inasmuch as the coloration of $WO_3$ film with the bleaching of copolymer are perfectly simultaneous, the $WO_3$-copolymer nanocomposite thin film with dual EC property based on the aniline and o-toluidine is prepared by electropolymerization method.

## 2. Experimental

### 2.1. Materials

Sodium tungstate ($Na_2WO_4.2H_2O$), aniline, o-toluidine, sodium dodecyl sulfonate (SDS), sulfuric acid, hydrochloric acid, hydrogen peroxide (35%), ethanol and acetone were purchased from Merck. The FTO-coated glass was purchased and cut into

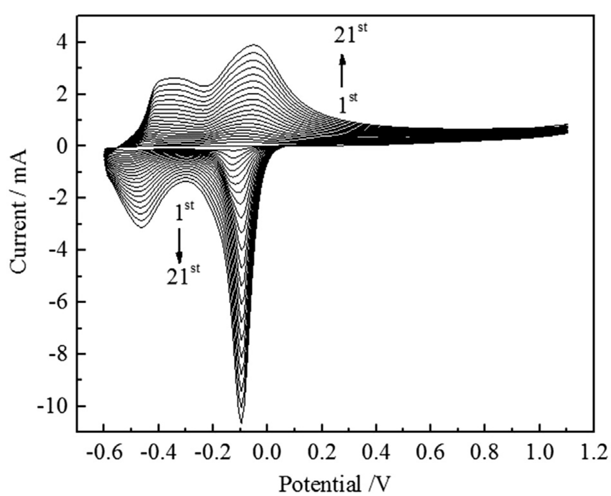


**Fig. 2.** Cyclic voltammugrams of copolymer polymerization at 50 mV/s.

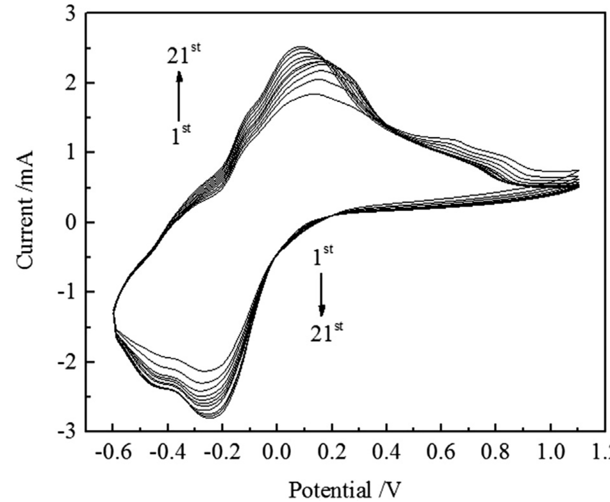


**Fig. 3.** Cyclic voltammugrams of $WO_3$-copolymer polymerization at 50 mV/s.

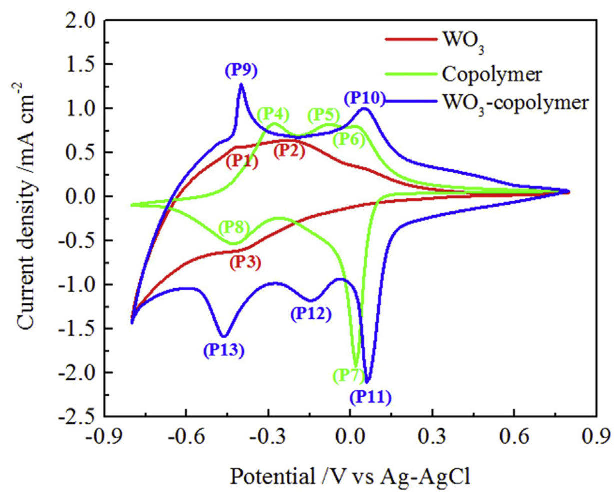


**Fig. 4.** Cyclic voltammograms of $WO_3$ film (dash line), copolymer film (line) and $WO_3$-copolymer nanocomposite film (dote line) in a 0.5 M solution of $H_2SO_4$.

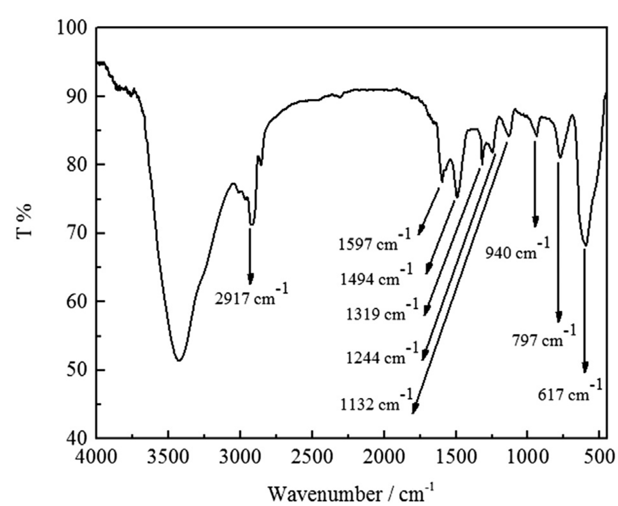


**Fig. 5.** FTIR spectrum of the $WO_3$-copolymer nanocomposite film.