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A dual electrochromic film based on nanocomposite of copolymer and WO_3 nanoparticles: Enhanced electrochromic coloration efficiency and switching response

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ABSTRACT

A dual electrochromic (EC) film based on composite of tungsten oxide nanoparticles and copolymer of aniline and *o*-anisidine was prepared by electrochemical polymerization method. In this method, aniline and o-anisidine monomers were dispersed in the solution containing WO_3 nanoparticles and the final solution was used for electrodeposition of film on fluorine doped tin oxide (FTO) coated glass substrate. The WO_3 nanoparticles were embedded in the copolymer matrix, thus a dual EC film was formed. The EC film with the approximate thickness of 374 nm and the grain size of nanocomposite under 100 nm was obtained. EC properties of WO_3, copolymer and WO_3-copolymer nanocomposite films were investigated by cyclic voltammetry (CV) and the visible transmittance. Also, the optical response and coloration efficiency (CE) of samples were investigated. In particular, a significant optical modulation (42.86% at 633 nm), fast switching speed and high CE (99.4 $cm^2 C^{-1}$ at 633 nm) are achieved that are much better than films only composed of WO_3 and copolymer. The improved EC properties are ascribed to the mixture of prominences of both materials and the formation of the donor-acceptor mechanism.

1. Introduction

Increasing of the world population and subsequently growth of the energy demand cause the awareness toward renewable energy sources. However, uncontrollable and periodic natures of these energy sources intensifies the need for an efficient energy storage system. Electrochemical devices (ECDs) which are formed of EC materials, electrolytes and electrodes can store energy and/or convert energy [1,2]. Since Balzers in 1953 presented a very clear description of electrochromism in tungsten oxide films or when Deb in 1969 changed the situation of EC knowledge by his publications, more and more scientists engage in the research field of EC materials, and subsequently more EC materials were discovered and reported [3,4]. A material with EC property exhibits a reversible and optical change due to oxidation/reduction mechanism after applying different electric potentials (≤3 V) [5–7]. In this process, injection and extraction of electrons and ions lead to optical changes that usually is companied with color change. Based on electrochromism definition, various applications such as intelligent optical displays, smart windows, rear-view mirrors and military camouflages can be planed [3].

Of all electrochemical reactions that can lead to visible changes at the electrode, only a little number of them are with adaptable intensity to be useful in devices. Moreover, a lower number of them can exhibit the specified color change to guarantee usefulness; and so the rest reactions can be used as practical EC reactions. Inorganic materials (such as transition metal oxides), single molecular materials and organic polymeric materials (π-conjugated conducting polymers) can play EC role [8–15]. The main change in the optical transmittance spectrum of conducting polymers occurs upon doping, while the change in the optical transmittance spectrum of inorganic materials become stable on the insertion/extraction of ions. These changes make these EC materials first applicants for research in the field of ECDs.

Yet, researchers in EC field have been put forth more effort on ECDs based on inorganic EC materials and organic conducting polymers. Organic/inorganic composite materials in general introduce the natural interface between two worlds of material science. In this scientific scope, the major problem is overcoming to synthesize inorganic–organic hybrid combinations that keep or enhance the best properties of each of the components while eliminate or reduce their particular deficiencies.

WO_3 as a famous 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 [16–19]. However, apart from these advantages, single color change and slow switching

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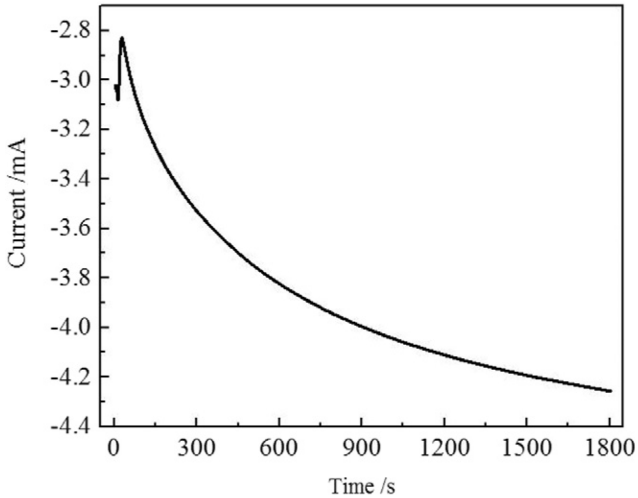

Fig. 1. Electrodeposition of WO_3 film with chronoamperometry technique.

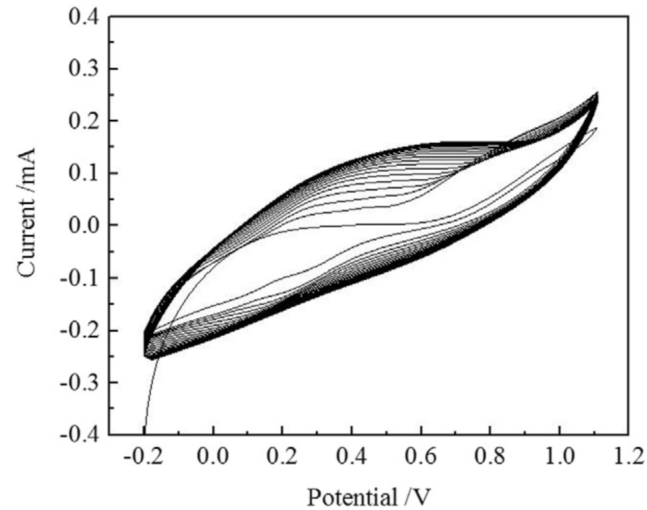

Fig. 3. Cyclic voltammogram of WO_3-copolymer polymerization at 50 mV/s.

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 [20–24].

Polyaniline (PANI) and its derivatives such as *o*-anisidine have attracted considerable attention due to their use in ECDs [25–28]. Moreover, 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 [29,30]. The EC properties of the copolymers showed that the copolymers exhibit stronger formability and uniformity, better electroactivity and tricolor electrochromism than monomers [30]. Li et al. [29] reported the EC properties of the copolymers of *o*-phenylenediamine and aniline. The results showed that the copolymers exhibit stronger formability and uniformity, better electroactivity and tricolor electrochromism than *o*-phenylenediamine and aniline homopolymers. Camurlu et al. [31] reported a dual conducting copolymers based on 1-(2-ethyl-hexyl)-2,5-di-thiophen-2-yl-2,3-dihydro-1H-pyrrole and 3,4-ethylenedioxythiophene. The results showed that the copolymers revealed shorter switching times and higher optical contrast.

In the last years, many researchers were dedicated to incorporate EC metal oxides into conjugated polymers to form organic/inorganic composite films [21,32–36]. Nwanya et al. [37] reported the EC properties of the WO_3 and PANI nanocomposite. The result showed that the composite film has EC behavior during the CV and led to the formation of a true EC capacitor. Zhang et al. [21] reported the EC properties of the WO_3 nanorod and PANI. The result showed that the composite exhibits faster switching response and higher durability than WO_3 nanorod film. Cai et al. [20] reported the dual EC properties of the WO_3 and PANI nanocomposite. The result showed that WO_3/PANI nanowire exhibits high coloration efficiency, fast switching speed and good cycling stability. However, the scarce efforts were performed by researchers to test and examine the composite of the EC copolymers with EC metal oxides.

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*-anisidine was prepared by electropolymerization method. 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. In this process, if cathodic EC material accepts the same charge carrier that anodic EC material extrudes it, then the donor-acceptor mechanism will be formed. This mechanism can be enhanced the EC properties in ECDs. With regard to donor-acceptor mechanism, we chose the WO_3 as a famous EC metal oxide and the monomers of aniline and o-anisidine as EC conducting polymers. The EC properties of the WO_3-copolymer nanocomposite thin

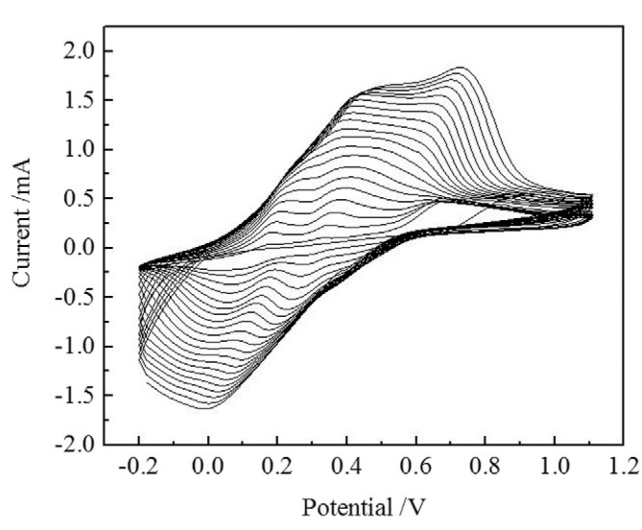

Fig. 2. Cyclic voltammogram of copolymer polymerization at 50 mV/s.

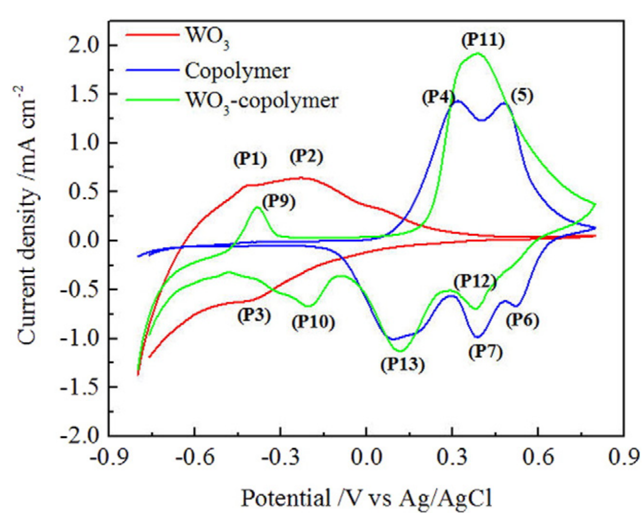

Fig. 4. Cyclic voltammogram of WO_3 film (dash line), copolymer film (line) and WO_3-copolymer nanocomposite film (dote line) in a 0.5 M solution of H_2SO_4.