Electrochemistry Communications 57 (2015) 65–69

Contents lists available at ScienceDirect

Electrochemistry Communications

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

Short communication

# Enhanced electrochromic properties of hybrid P3HT/$WO_3$ composites with multiple colorations

Tae-Ho Kim, Hyeong Jin Jeon, Jae-Wook Lee, Yoon-Chae Nah *

*School of Energy, Materials, and Chemical Engineering, Korea University of Technology and Education, Cheonan 330-708, Republic of Korea*

ARTICLE INFO

*Article history:*
Received 2 May 2015
Received in revised form 19 May 2015
Accepted 19 May 2015
Available online 27 May 2015

*Keywords:*
P3HT/$WO_3$ composites
Nanoporous $WO_3$ layers
Electrochromism
Multi-color
Response time

ABSTRACT

We investigated the enhanced electrochemical and electrochromic properties of P3HT (poly 3-hexylthiophene)/$WO_3$ composites. Nanoporous $WO_3$ layers were prepared using electrochemical anodization. P3HT was spin coated on these layers to obtain hybrid P3HT/$WO_3$ composites. After annealing at 300 °C for 1 h, the monoclinic phase of the $WO_3$ layer and self-organized lamella structure of P3HT were examined. The P3HT/$WO_3$ composites exhibited enhanced current densities and three different reflective colors with a combination of pristine P3HT and $WO_3$ during the redox reaction. Furthermore, the composites exhibited faster switching speeds compared with $WO_3$ layers, which might be attributed to the easy $Li^+$ insertion/extraction resulting from the incorporation of P3HT.

## 1. Introduction

The electrochromic (EC) phenomenon can be observed when voltage is applied to materials including transition metal oxides and conducting polymers, in which the electrochemical reaction occurs via the double insertion/extraction of electrons and ions [1]. Because of their attractive characteristics, such as lower power consumption and no limitations on viewing angle and memory effects under open-circuit conditions, EC devices can be used for applications in smart windows, switchable mirrors, and information displays [2–4].

Of EC transition metal oxides, tungsten oxide ($WO_3$) exhibits the most efficient electrochromic properties both in the visible and near infrared regimes [5]. These properties are highly dependent on the crystal structure, which affects the electronic properties of the layer or ion insertion/extraction during electrochemical reactions [6]. The crystal structure of $WO_3$ can be controlled by synthetic methods or deposition processes. Several methods can be used to fabricate $WO_3$ electrodes for EC applications, including chemical vapor deposition [7,8], sputtering [9], thermal evaporation [10], sol–gel coating [11,12], and electrochemical methods [13]. In addition to bulk-type electrodes, nano-structured $WO_3$ has been increasingly investigated because its morphology provides a high surface area for electron and ion transport [14].

Recently, $WO_3$ nanoporous layers were prepared by the electrochemical anodization of W in a fluoride-containing electrolyte [15]. Controlled growth of $WO_3$ layers resulted in a randomly oriented nanoporous structure rather than a highly ordered pore distribution. Compared with the compact layers fabricated without the addition of fluoride ions in the electrolyte, the porous $WO_3$ layers exhibited enhanced electrochemical properties and thus superior electrochromic coloration and kinetics [16].

However, as observed for most inorganic electrochromic materials, $WO_3$ undergoes a single color modulation from transparent to deep blue with a higher absorption in the wavelength range of 600–700 nm. In contrast, polymeric materials exhibit multicolor electrochromism, which is mainly observed in polyaniline [17], polypyrrole [18], and polythiophene [19], and their derivatives can exhibit various colorations by tailoring the electronic structures of the materials [20]. Among polymeric electrochromic materials, P3HT (poly (3-hexylthiophene)) has recently been studied as a red-colored candidate [21].

The development of organic and inorganic hybrid materials has been extensively studied because the combination of two components can yield enhanced properties [22]. Intensive studies on electrochromic systems composed of a metal oxide and conducting polymers have recently been performed, including that on a $WO_3$/PANI composite, which exhibited blue to green coloration [23]. To achieve diverse colorations, the

---

* Corresponding author. Tel.: +82 41 560 1322; fax: +82 41 560 1370.
*E-mail address:* ycnah@koreatech.ac.kr (Y.-C. Nah).

http://dx.doi.org/10.1016/j.elecom.2015.05.008
1388-2481/

hybridization of blue $WO_3$ and red P3HT could yield a promising electrochromic material.

In this paper, we report on the formation of organic–inorganic hybrid materials composed of nanoporous $WO_3$ and P3HT that exhibit enhanced electrochemical and electrochromic properties with multiple colorations.

## 2. Experimental

W (tungsten) sheets (0.1-mm thick, 99.95%, Nilaco) were sonicated in acetone, isopropanol, and methanol solutions, followed by rinsing with deionized water. To obtain nanoporous $WO_3$ layers, the W sheet was anodized at 40 V for 1 h in 1 M $H_2SO_4$ solution with the addition of NaF, as reported elsewhere [16]. The samples were then heat-treated at 300 °C for 1 h in air ambient.

After preparation of a nanoporous $WO_3$ layer, a 0.5 wt% solution of P3HT (Aldrich Co.) in dichlorobenzene (Aldrich Co.) was spin coated on top of the $WO_3$ layers at 1000 rpm for 30 s and dried on a hot plate at 60 °C for 30 min. The morphology and crystal structure of the samples were investigated using field-emission scanning electron microscopy (FESEM, FEI) and X-ray diffractometry (XRD, Bruker).

For the electrochemical and electrochromic measurements, a three-electrode system was used in propylene carbonate solution containing 0.4 M $LiClO_4$. The samples were contacted with a Cu back-plate and then pressed against an O-ring in the wall of the electrochemical cell. A platinum ring and silver wire were used as the counter and reference electrodes, respectively. Cyclic voltammetry (CV) and chronoamperometry measurements were performed using an Autolab PGSTAT 302N potentiostat/galvanostat. In situ reflectance measurements were performed using a fiber optic illuminator (tungsten halogen lamp, Ocean Optics).

## 3. Results and discussion

Fig. 1(a) presents an FESEM surface image of the anodized $WO_3$ layers. A highly nanoporous oxide structure is observed, with a typical pore size of approximately 80 nm. The annealing process at 300 °C does not affect the morphology of the $WO_3$ layers (not shown). The porous $WO_3$ layers coated with P3HT are shown in Fig. 1(b). Even though the P3HT solution was spin coated on the $WO_3$ layers, the porous structure of $WO_3$ still exists, which implies that the solution is successfully infiltrated into the porous layers. However, the pore size appears to be reduced by ~50 nm, which also indicates that P3HT is mainly coated inside the pore walls. To investigate the crystalline structure of the samples, XRD patterns of the pure $WO_3$ and P3HT/$WO_3$ layers were obtained. For the as-anodized $WO_3$ layers in Fig. 1(c), the oxide layer consists of an amorphous structure with no distinctive peaks and only two (110) and (200) peaks from the tungsten metal substrate. The porous $WO_3$ layer annealed at 300 °C exhibits peaks at $2\theta = 23.05°$, 23.50°, 24.25°, and 34.06°, which represent the (002), (020), (200), and (202) planes of the monoclinic phase, respectively. These findings indicate that the amorphous $WO_3$ layer transformed into the crystalline structure of the monoclinic phase after annealing [24,25]. The XRD pattern of the P3HT/$WO_3$ layer is shown in Fig. 1(d). The sample exhibits a single peak at $2\theta = 5.24°$, which is associated with the self-organized lamella structure of thiophene rings in P3HT. In particular, this peak corresponds to the a-axis orientation, with the polymer main chain parallel to and the side chains perpendicular to the substrate [26,27].

CV measurements for $WO_3$, P3HT, and the P3HT/$WO_3$ composites were performed at −0.7 V and 1.0 V at a scan rate of 50 mV/s in a propylene carbonate solution containing 0.4 M $LiClO_4$. Fig. 2(a) presents a CV graph of the nanoporous $WO_3$ layers annealed at 300 °C, in which the charge densities exchanged during cathodic ($Q_c$) and anodic ($Q_a$) reactions are −1.84 and 1.80 mC/cm$^2$, respectively. The reversibility

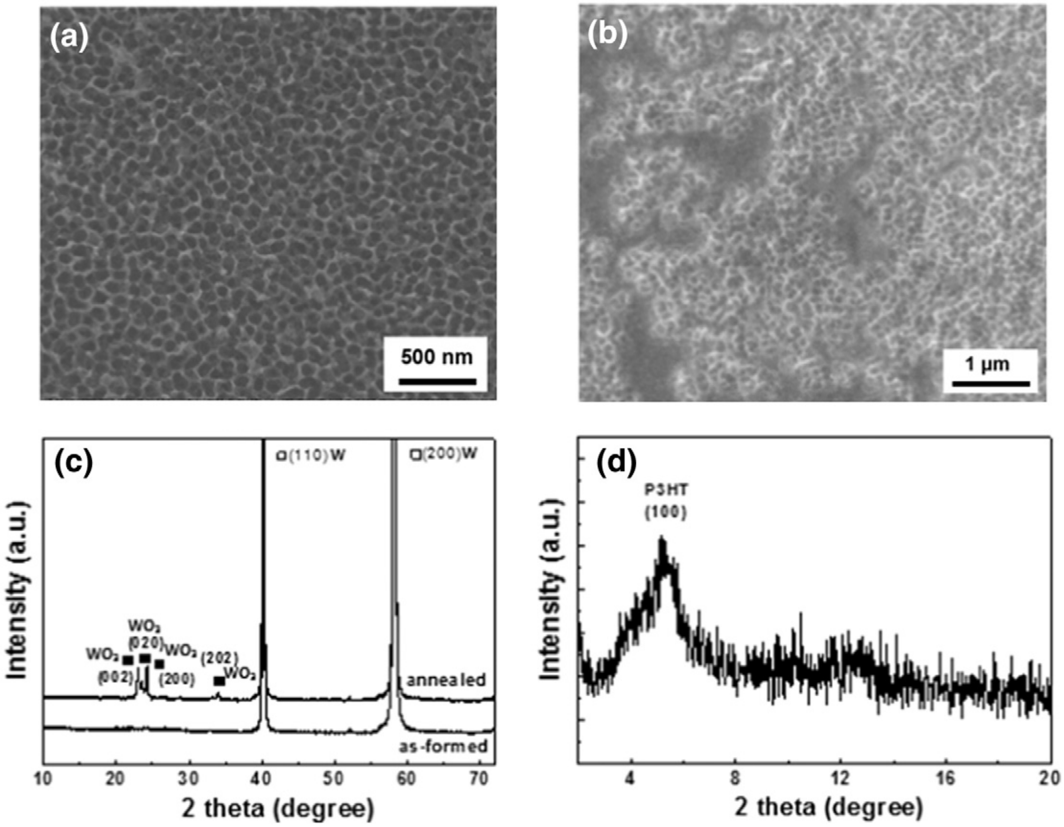

**Fig. 1.** SEM surface views of (a) anodized $WO_3$ nanoporous layer and (b) P3HT-coated porous $WO_3$ layers. XRD patterns of (c) $WO_3$ and (d) P3HT/$WO_3$.