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Facile preparation of WO_3/PEDOT:PSS composite for inkjet printed electrochromic window and its performance for heat shielding

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ABSTRACT

In this study, we have prepared an electrochromic (EC) ink composed of WO_3 nanoparticles and poly (3,4-ethylenedioxythiophene):poly (styrene sulfonate) (PEDOT:PSS). The ink formulation can be processed through inkjet-printing or spray coating to deposit high-quality EC layers. The PEDOT:PSS acts as an conductive binder to connect the WO_3 nanoparticles leading to reduced impedance and better electrochemical properties. The WO_3/PEDOT:PSS (PH1000) exhibits an optical modulation of 54.1%, a response time of 1.1 s, and a coloration efficiency of 83.87 cm^2/C. A hybrid type electrochromic device (ECD) incorporated with WO_3/PEDOT:PSS with excellent durability has been fabricated. The performance of WO_3/PEDOT:PSS based ECD for sun shielding property is also evaluated. The ECD can efficiently block the sunlight and reduce solar heat gain. As a result, the indoor temperature can be modulated from 32.7 °C (bleached state) to 29.4 °C (darken state) under illumination.

1. Introduction

Electrochromism is the phenomenon displayed by electroactive materials that show a reversible color change when a small DC voltage is applied. EC materials have been shown much promising properties such as low power consumption, no limitation of view angle and excellent memory characteristic under open circuit condition. As the color change is persistent and energy need only be applied to affect a change, electrochromic materials are applied for smart window and used to control the amount of light and heat allowed to pass through windows [1,2]. Another popular application is in the automobile industry where it is used to switchable rear-view mirrors in various lighting conditions.

Various types of materials can be used to construct electrochromic devices (ECDs) such as inorganic materials [3–6], conjugated polymers [7–13] and small molecules [14–18]. Among the inorganic materials, transition metal oxides are a large family of materials possessing various interesting properties in the field of electrochromism. Tungsten oxide (WO_3), has been the most extensively studied material, used in the production of electrochromic windows or smart glass due to its high coloration efficiency and good cyclic stability [19–23]. In recent years main attention has been focused on nanostructured WO_3 prepared by using a variety of techniques including plasma sputtering [24], electrophoretic deposition [25], hydrothermal [26], chemical vapor deposition [27], electrospinning [28], Langmuir–Blodgett [29] and lay-by-layer deposition [30]. Although the WO_3 films prepared from these approaches can deliver attractive EC performance, the fabrication process is difficult to be scaled up. Additionally, the low-temperature and solution process is the basic requirement for the next generation of flexible ECDs. Inkjet printing [31] is a low-cost and low-temperature method which can process WO_3 on various substrates. Moreover, the inkjet printing can pattern the EC materials on a desirable location without additional lithography process or complicated masking steps. The thickness of the EC layer also can be precisely controlled by changing the number of printed layers.

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However, the problems of the spray coating or inkjet printing commonly encountered are the blockage of nozzle due to the too large particle or aggregation and the crack of the resultant films. Moreover, the resistance of the resultant films should be very large due to the much grain boundary formed by the WO_3 nanoparticles. Therefore, the key to achieve uniform and electrochemically active WO_3 film by using inkjet printing method rely on the following characteristics: (1) preparation of uniform WO_3 nanoparticle; (2) efficient dispersion and (3) introduction of conductive binder and dispersant. In the recent years, the conducting polymer, PEDOT:PSS, has been demonstrated as an efficient surfactant and binder for WO_3 based EC application [32]. Both PEDOT:PSS and WO_3 are cathodically coloring materials, and can be simultaneously changed colors between colored and bleached state. In addition, the commercial PEDOT:PSS has been demonstrated as an efficient surfactant to disperse much nanomaterials such as carbon nanotube [33], TiO_2 [34], Fe_3O_4 [35]. Therefore, the PEDOT:PSS is an excellent candidate used as a conductive binder to prepared WO_3 suspension for inkjet printing.

In this study, we tend to develop an EC ink which can satisfy the three requirements described above. This is an easy-to-process and economical method to prepare stable and well-dispersed EC formulation which can be readily deposited on various substrates by inkjet printing. We applied a wet-grinding method to miniaturizate and disperse pure WO_3 powder with PEDOT:PSS as a polymeric and conductive surfactant. The WO_3/PEDOT:PSS solution after grinding can form a stable colloidal without precipitation. With the polymeric nature of PEDOT:PSS, the resultant composite films prepared by inkjet printing are crack-free with uniform surface. The PEDOT:PSS can also act as a conductive binder to facilitate the electron transport between the WO_3 nanoparticles. Most importantly, the proposed strategy is not only useful for WO_3 but also other inorganic materials. We also performed a systematic investigation for the effect of conductivity of PEDOT:PSS on the EC performance of hybrid films. Moreover, A hybrid type electrochromic device was also fabricated and the sun shielding property is also evaluated for the first time. The resulting EC films reveal a large optical modulation (54.1%), fast response time (1.1 s) and a coloration efficiency of 83.87 cm^2/C. The hybrid ECD also shows outstanding sun shielding property which can decrease the indoor temperature from 32.7 °C (bleached state) to 29.4 °C (darken state) under illumination.

2. Experimental section

2.1. Preparation of WO_3/PEDOT solution

At first, the commercial WO_3 powder (Aldrich, > 99.0%) was sonicated in ethanol with a concentration of 1.0 wt%. After sonication for 1 h, the WO_3 suspension was mixed with 10 vol% of the PEDOT:PSS with stirring. Then, the high-energy ball milling was performed at a speed of 2000 rpm at room temperature using a circulation-type grinder (JBM-C020). After grinding for 12 h, the WO_3 can be dispersed well without precipitation. The WO_3 suspension can maintain its highly disperse without aggregation for at last three month.

2.2. Fabrication of ECDs

The ECDs were fabricated by assembling two ITO substrates (3.0×4.0 cm^2) with a cell gap of 60 μm (DuPont Surlyn®). Before assembling of the ECD, the ITO substrates cleaned by isopropyl alcohol and treated with O_2 plasma. At first, the WO_3/PEDOT:PSS composite was deposited on the ITO substrate through spray coating. Then, the electrolyte solution was dropped onto the WO_3/PEDOT:PSS modified ITO substrate. Subsequently, the working electrode was covered with a blank ITO substrate. The electrolyte used to fill the ECDs was composed of 0.01 M 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and 0.1 M $LiClO_4$ in acetonitrile (ACN).

2.3. Charaterization

A JEOL 2010 transmission electron microscope (TEM) was used to examine the morphology and particle size of the WO_3 nanoparticles. The crystalline structures of WO_3 were characterized using grazing-incidence X-ray diffraction (XRD) (GIXRD; Philips PANalytical X'Pert PRO MRD apparatus; Cu Kα radiation); the incident X-ray beam angle was fixed above the critical angle at 5°. The zeta potential of the WO_3 was measured by the Zetasizer (Nano-ZS) from Malvern Instruments and its software, Dispersion Technology Software (DTS). The zeta potential of WO_3 was recorded under a PH value of 7.0 with a concentration of 0.1 wt%. The surface morphologies of the WO_3/PEDOT:PSS films were investigated using scanning electron microscopy (SEM, Hitachi S-4700) and atomic force microscope (AFM, Digital Instrument NS 3a controller equipped with a D3100 stage). The absorbance and transmittance spectra of the EC films were obtained using a UV–Vis spectrophotometer (GBC Cintra 2020). All the electrochemical experiments were performed using Autolab potentiostat/galvanostat (Eco Chemie, model PGSTAT30) at room temperature. Cyclic voltammetry (CV) was performed using a three-electrode cell with 0.1 M $LiClO_4$/ACN as electrolyte, ITO-glass modified with WO_3/PEDOT:PSS as the working electrode, a platinum sheet as the counter electrode, and nonaqueous Ag/Ag^+ as the reference electrode. The impedance test was carried out at 10 mV amplitude in frequency range from 10^{-1}~10^4 Hz in 0.1 M $LiClO_4$/ACN solution. The thermal image of the EC window was recorded by an infra-red thermograph (TiX 1000). Raman spectrum and mapping were recorded using a WITEC confocal spectrometer with 600 lines/mm grating, and 514.5 nm excitation. The temperature of the ECD window was recorded by an infra-red thermograph (TiX 1000).

3. Results and discussion

The TEM images and their corresponding selected area electron diffraction (SAED) of WO_3 powder before and after grinding are shown in Fig. 1a and b. The starting material reveals a clear crystal structure with a particle size ranged between 50 and 500 nm. After grinding, the structure of WO_3 is destroyed and broken into much thin and small sheet-like particle. The particle size also decreases dramatically to less than 20 nm. The SAED as shown in the inset also suggests the crystallinity of WO_3 is considerably weaker after grinding process. Fig. 1c presents the XRD of raw and ground WO_3 powder. The XRD pattern can be indexed to a pure phase of monoclinic for the raw WO_3 with strong diffraction peaks. In comparison, the XRD pattern of ground WO_3 shows a significant broadening and simultaneous decrease in intensity, indicating the decrease in grain size during the grinding process. The zeta potential of raw WO_3 and ground WO_3 is also shown in Fig. 1d. The negative value of both raw and ground WO_3 is due to the hydroxyl group on the surface of WO_3. The zeta potential of raw and ground WO_3 is −14.4 and −38.5 mV, respectively. A more negative zeta potential corresponds to a larger repulsive electrostatic forces between particle surfaces, and consequently a more stable colloid suspension. Generally, the absolute values of zeta potentials on the particle surfaces should be greater than 40 mV to maintain a relatively stable suspension.

The surface morphology of the PEDOT:PSS, WO_3 and hybrid film are also investigated by SEM and AFM analysis. The PEDOT:PSS film reveals a smooth and featureless morphology as shown in Fig. 2a.