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Layer-by-Layer Assembly of PEDOT:PSS and WO_3 Nanoparticles: Enhanced Electrochromic Coloration Efficiency and Mechanism Studies by Scanning Electrochemical Microscopy

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ABSTRACT

Layer-by-layer assembly method is employed to fabricate multilayer hybrid films based on poly (styrenesulfonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT:PSS) and tungsten oxide nanoparticles (WO_3 NPs). Polyethylenimine (PEI) is deposited in between to introduce electrostatic force between the components. In the hybrid films, randomly oriented disk-like WO_3 NPs are homogeneously distributed in the polymers and form an interdigitated structure. This very rough surface morphology hinders the formation of a continuous PEI layer between the electrochromic layers. Owing to the efficient charge transfer between the two active components and complementary electrical conductivity of the two components in the redox switching process, the coloration efficiency of the hybrid film is significantly improved to 117.7 cm^2/C at wavelength of 633 nm. The underlying mechanism for the enhancement is verified by scanning electrochemical microscopic studies through probing the conductivity changes of PEDOT:PSS, WO_3-NP and hybrid films under various applied potentials.

1. Introduction

Electrochromism is a phenomenon related to the reversible change in optical absorbance/reflectance of a material induced by externally applied potentials [1]. Electrochromic materials have great potentials for flexible displays, smart windows and numerous other applications owing to their abilities to achieve different optical states under fairly low potentials and the low power consumption for maintaining the states [1]. Two major classes of common electrochromic materials are transition metal oxides (TMOs) and conjugated polymers (CPs) [2–4]. As the most widely used electrochromic TMO, tungsten trioxide (WO_3) has been extensively studied since its electrochromic properties were discovered in 1969 [5]. WO_3 can be reversibly switched between transparent and blue states upon electrochemical insertion/extraction of small cations and simultaneous insertion/extraction of charge-balancing electrons through an outer circuit. The relatively high optical contrast and environmental stability of WO_3 make it very attractive for many practical applications. Amorphous WO_3 (a-WO_3) exhibits fast electrochromic switching during the injection/extraction process because its porosity provides large specific surface area [6]. However, a-WO_3 can only be applied in lithium based electrolyte, since it can dissolve in acidic solutions [6,7]. Polycrystalline WO_3 has better chemical and electrochemical stabilities than a-WO_3, whereas the electrochromic switching process for the polycrystalline WO_3 is slower than that for a-WO_3 because the diffusion of ions is hindered by the crystalline regions [7]. Electrochromic CPs usually exhibit relatively fast switching speed and high coloration efficiency, and hence have been combined with WO_3 to improve its electrochromic properties [8,9]. In particular, both poly(styrenesulfonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT:PSS) and WO_3 are cathodically coloring materials, and can be simultaneously switched to colored or bleached state [8]. As reported by Deepa et al., PEDOT:PSS/WO_3 composite films with PEDOT:PSS as the major component can exhibit a high coloration efficiency comparable to that of PEDOT:PSS; while the electrochemical response of WO_3 was preserved in the hybrid [10]. The interactions between the organic and inorganic components also stabilize the defects in WO_3, leading to good electrochemical stability of the hybrids with WO_3 as the major component [8,9,11]. Furthermore, although with cations ($M = H^+$, Na^+ and Li^+) inserted, M_xWO_3 displays metallic conductivity due to its oxygen-vacancy defects [12], the fully oxidized WO_3 is an n-type semiconductor with extremely low electrical conductivity. By contrast, PEDOT exhibits high electronic conductivity at its oxidation state [12]. Thus under

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positive potentials, the high conductivity of PEDOT:PSS may facilitate electron transport in WO_3/PEDOT hybrids. So far, the effects of redox reaction-induced electrical conductivity change on electrochromic properties of TMO/CP hybrid systems are, however, rarely studied [13].

Layer-by-layer (LBL) assembly is a versatile thin-film fabrication method, which allows deposition of oppositely charged species to form multilayer films [14,15]. Various nanostructures, such as nanoparticles, nanotubes and nanosheets, can be used as building blocks of LBL-assembled thin films [14,16]. Compared with other thin-film fabrication methods, such as electrodeposition, the LBL process allows precise control over the deposition of each component from solution [17,18] and hence is very useful for fabrication of hybrid films with tailored morphologies for mechanism studies. A significant advantage of LBL assembly process for the fabrication of electrochromic thin films is the ease in incorporation of EC materials with polyelectrolyte, which can act as ionic conductors to aid insertion/extraction of ions into/from the electrochromic materials [19,20]. However, these polyelectrolytes are mostly electrical insulators, which reduce the electrical conductivity of the films. An alternative is to fabricate electrochromic films by LBL assembly of CPs and conducting electrolytes, where the electron hopping between the layers could facilitate charge transfer [21,22]. As for WO_3-based layered electrochromic structures, Wang and Zeng et al. reported LBL-assembled electrochromic films based on crystalline WO_3 nanosheets, which have good electrochemical stability [23]. However, although in principle the small thickness of the nanosheets could shorten the ion diffusion path, in reality the stacking of the nanosheets leads to a slow coloration process. Several research groups also reported the LBL assembly of electrochromic thin films based on polyoxometalates (POMs) and polyelectrolyte, such as tungstophosphate anion (P_2W_{18}) and poly(allylamine hydrochloride) (PAH) [24]. Gold nanoparticles (AuNPs) have also been incorporated into POMs/polyelectrolyte system to enhance its electrochromic properties [25]. As introduced earlier, WO_3 and PEDOT:PSS have the potential to be simultaneously switched to colored states and their electron transport properties could be complementary, which make WO_3 and PEDOT:PSS multilayer thin films attractive for electrochromic applications. Furthermore, understand charge transfer process in such layered electrochromic structures may provide useful design guideline for other electrochromic TMO/CP hybrid systems.

In this work, we employed LBL assembly method to fabricate electrochromic hybrid films from crystalline WO_3 nanoparticles (WO_3 NPs), PEDOT:PSS and polyethyleneimine (PEI). Herein we demonstrate that the hybrid system with WO_3 as the major component exhibits enhanced electrochromic properties, especially remarkably improved coloration efficiency compared with those of WO_3/PEI and PEDOT:PSS/PEI systems. Scanning electrochemical microscopy (SECM) technique is employed to study the charge transfer process across the hybrid films under various potentials, providing insight into the mechanism underlying the enhanced electrochromic properties.

2. Experimental

2.1. Materials

All chemicals, namely PEI (50 wt.% in H_2O), PEDOT:PSS (1.3 wt.% dispersion in H_2O), W powder, H_2O_2 (30 wt.% in water), H_2SO_4 (98%), NH_4OH (28~30% NH_3 basis in water), $LiClO_4$ and propylene carbonate (PC), were purchased from Sigma-Aldrich and used without further purification. Unless specified, all solutions or suspensions were prepared using deionized water (DIW, 18 $M\Omega/cm^2$), which was purified by Milli-Q integral water purification system. The substrates used were Si wafer (Sigma–Aldrich), quartz glass, and indium tin oxide (ITO)-coated glass with sheet resistance $R_s = 5\text{-}15\ \Omega$ (Delta Technology, USA). The Si wafers were cleaned by sonication in 1:1 (vol. ratio) DIW/acetone mixture for 20 min, followed by immersing in 3:1 (vol. ratio) H_2SO_4 (98%)/H_2O_2 (30%) solution for 30 min. The glass and ITO-coated glass were cleaned by sequential bath sonication in ethanol, 1:1 (vol. ratio) NH_4OH/H_2O_2, and DIW for 10, 30, and 10 min respectively. After cleaning, they were washed by DIW and blow-dried by N_2 gas before use. Standard three-electrode cell was employed in electrochromic studies. Pt and Ag wires were used as counter and reference electrodes, respectively. While, in electrochemical tests, Ag/AgBr wire was used as reference electrode.

2.2. Sample preparation

The WO_3 NPs were prepared via hyrdrothermal process from metallic W powder, which could be dispersed in water without any additives [26,27]. The electrochromic thin films were obtained by LBL self-assembly. Clean substrates were immersed into 1 wt.% PEI and 0.2 wt.% PEDOT:PSS (or 0.4 wt.% WO_3-NPs) solutions for 30 min and 1 hour alternatively to obtain single component films. Multilayer hybrid films were fabricated by immersing the substrates sequentially into PEI, PEDOT:PSS, PEI, and WO_3-NP solutions for 30 min, 1 hour, 30 min, and 1 hour repeatedly. Between any two adsorption steps, the substrates were washed by DIW, and also blow-dried by N_2 gas for building uniform self-assembled layers. The obtained thin films are denoted as Pn, Wn and Hn, where n represents the number of layers; while P, W and H are abbreviation for [PEI/PEDOT:PSS], [PEI/WO_3 NPs] or [PEI/PEDOT:PSS/PEI/WO_3 NPs].

2.3. Characterization

The XRD pattern of WO_3 NPs was measured using a Shimadzu diffractometer with Cu Kα radiation (ESI, Fig. S1). The thickness of the multilayer films was measured using a surface profiler (alpha-step 500 profilometer) on Si substrate. The surface morphology of the films were examined on a scanning electron microscope (SEM, SIRION, FEI Ltd.), which is equipped with energy dispersive X-ray spectrometer (EDX, X-Max 20, Oxford Instruments, UK) system for examining the composition. The topography of the films was also characterized by atomic force microscope (AFM Dimension ICON, Bruker) using tapping mode at a scale of 5 μm. The chemical structure and composition of the films were studied by X-ray photoelectron spectroscopy (XPS, AXIS ULTRA, Kratos Analytical) using Al Kα (1486.7 eV) X-ray source.

The spectra-electrochemical properties were measured by potentiostat (1470E, Solartron) and a UV-Vis-NIR spectrophotometer (UV3600, Shimadzu). The transmittance of each film was recorded at potentials of +0.8, 0, and −1.0 V in a wavelength range of 300 to 800 nm. Moreover, to obtain dynamic transmittance, square-wave potentials oscillating between +0.8 and −1.0 V were applied to sample films at time interval of 40 and 50 s for hybrid and PEDOT:PSS/WO_3-NPs films respectively. A standard three-electrode system was used in all tests, where sample films coated on ITO glass served as working electrode, and platinum (Pt) and silver (Ag) rods were used as counter and reference electrode, respectively, in a solution of 1 M lithium perchlorate ($LiClO_4$) in propylene carbonate (PC).

Scanning electrochemical microscope (SECM, CHI 920C) was employed to conduct cyclic voltammetry (CV) and other electrochemical tests. CV was also carried out with the same apparatus and solution as the electrochromic tests. Approach curves were measured by approaching a Pt microelectrode (25 μm diameter, RG = 10, E = +300 mV *vs.* Ag/AgBr quasi reference electrode (QRE))