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Research paper

Synthesis of ordered bowl-like polyaniline film with enhanced electrochromic performances

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A R T I C L E I N F O

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A B S T R A C T

A bowl-like polyaniline (PANI) film is synthesized by the combination of electrodeposition and monolayer colloidal crystal template (MCCT). The resulting film exhibits an ordered hexagonal close-packed bowl-like arrangement that is made up of macrobowls with a diameter of 450 nm. The unique bowl-like structure endows PANI film with enhanced electrochromic performances due to its increased accessible intercalation sites originating from larger surface areas and shortened diffusion distances of ions resulting from macroporous structure. It is found that the bowl-like PANI film possesses faster switching responses (1.45 s for coloration and 0.62 s for bleaching), larger optical transmittance modulation (52.1% at 740 nm) and higher coloration efficiency (118.2 cm^2C^{-1}) than the dense PANI film prepared without the MCCT. Moreover, the bowl-like film also exhibits IR electrochromic performances in the wavelength range from 2.5–25 µm, which depicts a reflectance modulation ~ 36.5% at 10 µm. This work provides a promising strategy for constructing other bowl-like polymer electrochromic films.

1. Introduction

Electrochromic materials possess a capability of reversible color switch under applied voltages. The theory of electrochromism was proposed by Platt in 1961, and subsequently was first demonstrated by Deb in 1969 [5]. Electrochromism have been extensively studied for applying in optical display, smart windows, rear-view mirrors for automobiles due to low power consumption, high coloration efficiency, and stable memory effect under open circuit condition [1–4]. Among the wide variety of electrochromic materials, polyaniline (PANI) is particularly attractive because of its low cost, good environmental stability, ease of synthesis, as well as excellent controllability through an acid/base doping/dedoping chemistry [6–10]. It is well known that electrochromic process is essentially an electrochemical reaction associated with intercalation (de-intercalation) of ions to (from) the film [11–15]. For PANI film, its color change is due to the transition between different oxidation states accompanying intercalation (de-intercalation) of ions. The optical contrast is closely related with the amount of accessible intercalation sites. Usually, larger surface areas can provide more accessible intercalation sites, thus representing a higher optical contrast. Switching time is restricted by the rate of ion transport into the EC film, which strongly depends on microstructures and morphology of films. In view of nanosized and porous processing of electrochromic film can obtain larger surface-to-volume ratio, the development of nano-porous structure is an ideal strategy for improving electrochromic performances of PANI.

Template assisted synthesis is one of the mostly used methods to fabricate nano-porous structure of PANI films owing to its controllability and versatility [16–18]. For example, vertically oriented nanorod arrays were prepared using supramolecular assemblies of block copolymer as scaffold material [16], and ordered nanotubes were synthesized via the introduction of anodic aluminum oxide as template [17]. Recently, three-dimensional ordered macroporous (3DOM) structure of PANI film obtained by the replication of colloidal crystal template was also demonstrated to possess enhanced electrochromic performance compared with dense film owing to the interconnected pores [19]. These interconnected pores provide inter-continuous pore spaces for good electrolyte penetration, while the continuous walls give effective transport pathways for ions. Generally, a smaller porous size implies better electrochromic performances in 3DOM structure because

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it possesses larger surface areas [13]. The colloidal crystal template is an ordered and multilayer colloidal microsphere (typically polystyrene (PS) or silica spheres) array with a hexagonal close-packed alignment [20,21]. Actually, the synthesis of the colloidal crystal template is quite tedious, which usually requires three days or more. However, the monolayer colloidal crystal template (MCCT) can be easily self-assembled in a short time, and the resulting two-dimensional ordered macroporous (2DOM) structure exhibits similar properties with 3DOM structure [22–24].

Motivated by above efforts, we herein fabricated a bowl-like PANI film with 2DOM structure by the MCCT assisted electrodeposition for the first time. Compared with dense PANI film prepared without MCCT, such bowl-like structure possesses larger surface-to-volume ratio, and thus improves electrochromic performances in the spectral range of 400–1100 nm. Moreover, IR electrochromic performance of the bowl-like PANI film in the spectral range of 2.5–25 μm was also investigated.

2. Experimental section

2.1. Assembly of the MCCT

The fabrication process of the bowl-like PANI film involves three steps, which is depicted in Fig. 1. The first step was to prepare MCCT by self-assembly. Monodispersed PS latex spheres with a diameter of 510 nm were obtained by an emulsifier-free emulsion polymerization method [25,26]. The resulting PS spheres were washed several times with deionized water and ethanol, collected by centrifugation, and dried at 50 °C for 6 h in a vacuum oven. Then the precipitate was redispersed at 1 wt% in a 1:1 by volume mixture of deionized water:-ethanol to obtain PS spheres suspension. ITO glass was ultrasonically cleaned in NaOH solution (0.5 M), ethanol, and distilled water for 15 min, respectively. The hydrophilic ITO glass was placed at the middle of a Petri dish to which deionized water was added slowly to a level of slightly higher than the upper glass surface without submersion. Subsequently, the PS spheres suspension was dropped carefully onto the upper surface of ITO glass to form a floating monolayer of PS spheres. With a few drops of sodium dodecylsulfate solution (2 wt%) added into the deionized water, the floating PS spheres were pushed aside and became tight because of the change of surface tension. The monolayer of close-packed PS spheres was easily picked up by the hydrophilic ITO glass. After naturally dried in air, the MCCT was obtained finally and stored in a desiccator for further use.

2.2. Synthesis of the bowl-like PANI film

The bowl-like PANI film was prepared in an aqueous solution of 0.1 M H_2SO_4 and 0.1 M aniline monomer by potentiostatic method at 0.8 V for 300 s. The above MCCT, Ag/AgCl and Pt foil were used as the working electrode, reference electrode and counter electrode, respectively. After electro-polymerization, the resulting PANI/PS composite film was washed carefully using deionized water, and then naturally dried in air. Subsequently, the composite film was immersed in toluene for 24 h to remove the MCCT. Finally, the bowl-like PANI film was obtained after dried at 50 °C. The dense PANI film was synthesized under the same conditions in the absence of MCCT.

2.3. Characterizations

Scanning electron microscope (SEM) images were obtained using a FEI Helios Nanolab600i. Fourier transform infrared (FT-IR) spectra were performed on a Bruker VERTEX-70 spectrophotometer using the standard KBr disk method. Cyclic voltammetry (CV) and chronoamperometry (CA) tests were carried out using a CHI760D electrochemical workstation in a three-compartment system with an aqueous solution of 0.5 M H_2SO_4 as the electrolyte, Ag/AgCl as the reference electrode and a Pt wire as the counter electrode. The optical transmission spectra (400–1000 nm) and IR reflectance spectra (2.5–25 μm) of electrochromic films in the fully colored and fully bleached states were recorded respectively using a MAYA 2000-Pro (Ocean Optics) and a VERTEX 70 (Bruker) FT-IR spectrometer with an A562 integrating sphere after the films were subjected to CA tests with a potential step 0.55 V (10 s) and −0.25 V (10 s).

3. Results and discuss

3.1. Morphology and structure

The surface profiles of films were investigated by electron microscopic studies. Fig. 2a–c presents SEM images of the MCCT, the bowl-like PANI film and the dense PANI film. The MCCT shows a typically close-packed array with long-range order perpendicular to the ITO glass (Fig. 2a). After removing the MCCT by toluene etching, the obtained

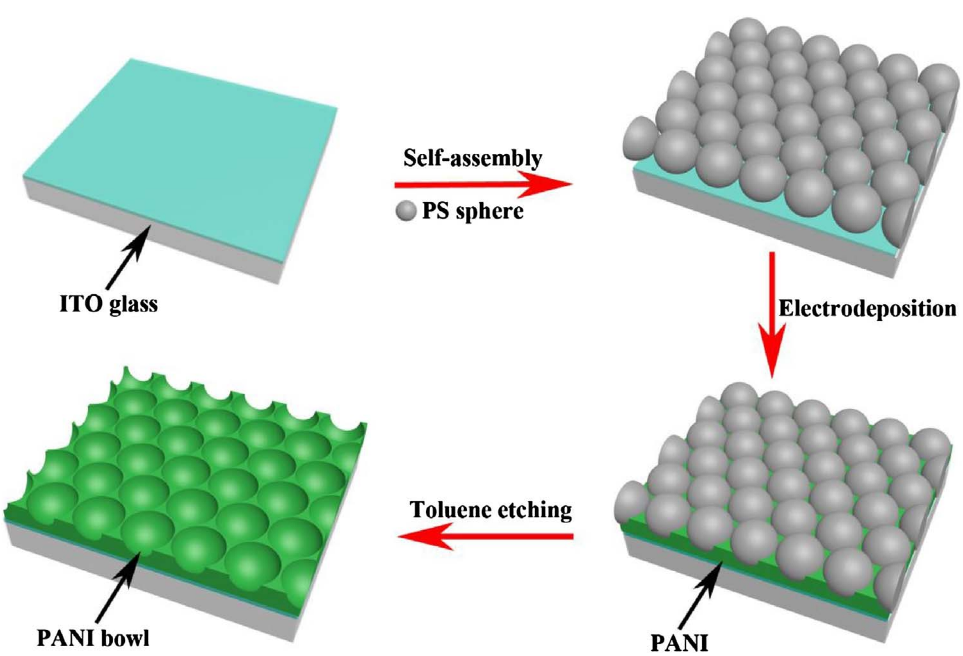

Fig. 1. Schematic illustration for the formation of the bowl-like PANI film.