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### A comprehensive study of electrochromic device with variable infrared emissivity based on polyaniline conducting polymer



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#### ABSTRACT

In this study, dodecylbenzene sulfonate acid (DBSA) doped-polyaniline (PANI) films were synthesized in situ on Au/porous flexible substrate by electrochemical deposition. The emissivity change ( $\Delta \varepsilon$ ) data of PANI films show a reversal from positive to negative as the polymerization charge increases. This trend can be explained by using the Drude free electron theory and the Hagen-Rubens approximation at low frequency due to the pseudo-metallic behavior of conducting polymers. The DBSA doped-PANI film was used as an active layer to fabricate an infrared (IR) electrochromic device. The  $\Delta \varepsilon$  of this IR electrochromic device was measured to be 0.183, 0.388, and 0.315 in the wavelength ranges of 3–5 µm, 8–12 µm, and 2.5–25 µm, respectively. IR thermal images visually obtained from an IR thermal imager suggest that the IR electrochromic device possesses regulating capacity of thermal radiation within the operating waveband of the instrument (7.5–14 µm). The IR electrochromic device developed in this work can be potentially used in IR camouflage for military and thermal control for satellite.

#### 1. Introduction

Electrochromic materials have been widely studied in the past several decades for applications in optical displays, automobile mirrors and optical-modulated windows (smart windows) because of their ability to reversibly switch color under applied alternating voltages [1–5]. Apparently, these applications just involve optical properties of the material in the visible and near infrared (IR) regions. Actually electrochromic materials also possess the ability to modulate light in the mid-IR region, and thus can be used in dynamic thermal IR optical switches [6-8]. For example, the switchable and controllable IR signature variation of electrochromism can act as a military camouflage countermeasure against IR cameras or detectors for all armed forces components (land vehicles and tanks, air-craft, soldiers, etc). Moreover, electrochromism is also a "smart" technique for satellite thermal control to replace bulky and costly mechanical louvers, and traditional fixed emissivity (ɛ) thermal control coatings. The currently reported IR electrochromic materials include tungsten oxide (WO<sub>3</sub>), poly (3,4ethylenedioxythiophene) (PEDOT) and polyaniline (PANI) [9-15]. When compared to transition metal oxides, which have poor processability and low flexibility owing to brittle fracture, conducting polymers exhibit better prospects for practical applications due to their light

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Received 7 March 2017; Received in revised form 22 April 2017; Accepted 21 May 2017 Available online 06 June 2017 0927-0248/ © 2017 Elsevier B.V. All rights reserved. weight, flexibility, ease of deposition, and processability.

As early as 1995, Chandrasekhar et al. reported the first IR electrochromic system based on conducting polymers with a significant and dynamic IR variation [16]. Then through a series of the optimization experiments, they obtained a flexible electrochromic device with reflection mode. This device used poly(anethosulfonate) doped-PANI deposited on a Au/porous substrate as the functional layer, and could adjust effectively  $\varepsilon$  varying from 0.32 to 0.79 [17]. More importantly, the device was tested by mounting it on an actual space craft (NASA's ST5 mission launched in 2003) to evaluate its thermal control efficiency [18]. Recently, they reported a new generation of flexible electrochromic device based on the integrated design of front electrode and back electrode [19]. The device exhibited current state-of-the-art  $\Delta \varepsilon$ (>0.5) due to superduper sustainability of multilayer architectures. Moreover, some special techniques (such as ionic liquid electrolyte and solar absorptance reduction-coating) greatly accelerated the practical progress of the electrochromic devices in thermal control for satellite. However, the macromolecular polymer dopant used is very costly even if the IR electrochromic performance of the polymeric matrix doped-PANI is found to be excellent. Following this original work, Li et al. studied the IR electrochromic property of sulfuric acid doped-PANI using Chandrasekhar's patented device design [20,21]. This inorganic

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acid doped PANI system exhibited a low performance with an average dynamic variation in  $\varepsilon$  values of ca. 0.24 in the 8–12 µm wavelength region, which is much smaller than that observed for poly(anetho-sulfonate) doped-PANI. In addition to the above flexible device design, a non-flexible IR device made from PANI with a camphor sulfonic acid (CSA) dopant has been reported by Topart [22], where the specular reflectance was regulated from 0.2 to 0.65 at 12 µm.

In view of the excellent performances described above, PANI should be an ideal IR electrochromic material. Therefore, it is necessary to carry out an in-depth study on the IR electrochromic mechanism of PANI. Chandrasekhar considered that the different IR transmittances of the overlying PANI layer under different oxidation states affected the reflection from the underlying Au layer, and consequently, the PANI-Au/substrate film showed different reflectance and  $\varepsilon$  values [17]. Li's study also demonstrated that the change in transmittance of the PANI layer under different potentials was the main factor affecting the  $\varepsilon$  value [21]. Although the above two studies illustrated that the change in transmittance resulted in the variation of  $\varepsilon$ , the detailed mechanism of this phenomenon is still not clear.

To address these problems, in this study, we report for the first time, the preparation of PANI films doped with a small molecular organic acid (dodecylbenzene sulfonate acid (DBSA)) by electrochemical deposition on Au/porous substrate, and the assembly of an IR electrochromic device. The device had a sandwich configuration using DBSA doped-PANI-Au/porous substrate films (DBSA doped-PANI porous film) as both working and counter electrodes. The device shows an improved  $\Delta \varepsilon$  of 0.183, 0.388, and 0.315 in the wavelength ranges 3–5  $\mu$ m, 8-12 µm and 2.5-25 µm, respectively. The IR electrochromic mechanism of the DBSA doped-PANI porous film has been discussed in detail. Surprisingly, the obtained  $\triangle \varepsilon$  data reveal a reversal of the change in  $\Delta \varepsilon$  from positive to negative as the polymerization charge increases. This result is not completely consistent with the results reported by Chandrasekhar and Li. The Drude free electron theory and Hagen-Rubens approximation at a low frequency are used to explain our observations.

#### 2. Experimental section

#### 2.1. Materials

Aniline (99.5%) was purchased from Acros and distilled under reduced pressure. A microporous substrate of nylon 66 with a pore size from 0.5 to 2  $\mu$ m was obtained from Haining Zhenghao Filter Equipment Co. China. A 200-nm-thick Au layer was deposited on the nylon 66 porous substrate by thermal evaporation. Propylene carbonate (PC) and lithium perchlorate were received from Alfa. Poly(vinylidene fluoride-*co*-hexafluoropropylene) (P(VDF-HFP)) with an average molecular weight of ca. 400,000, poly(methyl methacrylate) (PMMA) with an average molecular weight of ca. 350,000, N,N-Dimethylformamide (DMF), and DBSA were obtained from Aldrich.

#### 2.2. Preparation of DBSA doped-PANI porous films

DBSA doped-PANI porous films were prepared on the surfaces of Au/nylon 66 porous substrates (2 × 3 cm<sup>2</sup>) in an aqueous solution of 0.1 M DBSA and 0.01 M aniline monomer by a galvanostatic method with a current density of 0.1 mA cm<sup>-2</sup> and a polymerization charge of 3.0C. Ag/AgCl and Pt foil were used as the reference electrode and counter electrode, respectively. For comparison, DBSA doped-PANI porous films with different polymerization charges from 0.5C to 2.5C and 3.5C to 5.0C were also prepared under the same conditions by adjusting the polymerization time.

#### 2.3. Device assembly

As illustrated in Fig. 1, a solid polymer electrolyte film was obtained

by firstly adding P(VDF-HFP) and PMMA into DMF under continuous stirring at 70 °C to form a clear solution. The weight percentages of P (VDF-HFP), PMMA and DMF were 9%, 1% and 91%, respectively. After vigorously stirring for 30 min, the solution was transferred to a watch-glass and maintained at 60 °C to remove DMF. Subsequently, the P (VDF-HFP) porous film was immersed in a PC solution containing 1 M lithium perchlorate for 24 h to ensure the adsorption of PC-lithium perchlorate into the polymer framework. Finally, the solid polymer electrolyte film was dried in air for 6 h and cut into various shapes and sizes for use in further experiments. The PC-lithium perchlorate content in the solid polymer electrolyte film was about 20 wt% obtained by measuring the weight change of the P(VDF-HFP) porous film before and after adsorption. The ionic conductivity of the solid polymer electrolyte film was estimated to be ~  $1.42 \times 10^{-5}$  S cm<sup>-1</sup> using electrochemical impedance spectrum (Fig. S1).

A device with a sandwich configuration was assembled using the DBSA doped-PANI porous film as both front and back electrodes and the solid polymer electrolyte film as the middle layer between the two electrodes. Prior to device assembly, a 30-µm-thick IR-transparent protection layer of polyethylene (PE) was heat-bonded directly to the surface of the front electrode polymer to prevent the permeation of the electrolyte onto the surface of the PANI layer. After each layer was assembled together, the device was suffered transient heating at 100  $^{\circ}$ C by two rollers, providing heat and mechanical pressure simultaneously to make each layers adhere firmly.

#### 2.4. Measurements

Cyclic voltammetry (CV) and chronoamperometry (CA) tests were carried out using an electrochemical workstation (CHI760D, Shanghai Chenhua Instruments, China). Electrochemical impedance spectrum was measured on the electrochemical workstation at open-circuited potential in the frequency range from 0.1 Hz to 1 MHz. Typically, the electrochemical measurements on the DBSA doped-PANI porous films were performed in a three-compartment system with an aqueous solution of 0.1 M DBSA as the electrolyte, Ag/AgCl as the reference electrode and a Pt foil as the counter electrode. For the device, the electrochemical tests were conducted in a system with a two-electrode configuration. Thermal images of the device were obtained using an IR thermal imager (TI450, Fluke) with a spectral range of 7.5-14 µm. Spectral emittance (2.5–25 µm) of the PANI films and the device were measured ex-situ and in-situ via reflection method on a VERTEX 70 (Bruker) FT-IR spectrometer with an A562 integrating sphere owing to the opaque nature of both the PANI film and the device. The value of  $\boldsymbol{\epsilon}$ can be calculated by weighting  $(1 - R_{(\lambda)})$  (namely spectral emittance) with the black body spectrum for a particular wavelength and integrating over the entire measured wavelength range according to the following two equations [23,24]:

$$B_{(\lambda)} = \frac{c_1 \lambda^{-5}}{\exp[c_2/(\lambda T)] - 1}$$
(1)

$$\varepsilon = \frac{\int_{\lambda_{min}}^{\lambda_{max}} (1 - R(\lambda)) B(\lambda) d\lambda}{\int_{\lambda_{min}}^{\lambda_{max}} B(\lambda) d\lambda}$$
(2)

where  $c_1$  is the first radiation constant (3.7418  $\times$   $10^8$  W  $\mu m^4$   $m^{-2}$ ),  $c_2$  is the second radiation constant (1.4388  $\times$   $10^4$   $\mu m$  K),  $\lambda$  is the wavelength, and T is the temperature.

#### 3. Results and discussions

CV measurements were performed (scan rate of 50 mV s<sup>-1</sup> between -0.25 and 0.8 V) to determine the electrochemical performance of the DBSA doped-PANI porous film with varying polymerization charge. As displayed in Fig. 2, all the CV curves exhibit a pair of broad redox peaks corresponding to the transformation between a leucoemeraldine base

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