Enhancement of Electrochromic Properties of Polyaniline Induced By Copper Ions

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Abstract

Driven by the urgent need for adaptive infrared (IR) electrochromic devices, the improvement of electrochromic properties based on polyaniline (PANI) conducting polymers has become one of the research focuses. In recent years, the doping strategy has been proven to efficiently increase the IR modulation ability of PANI, but only limited to the acid species. Herein, the effects of copper ions on the structure and electrochromic properties of polyaniline were investigated. Compared to the pure polyaniline, the Cu-doped PANI porous films show better IR modulation ability. With the increasing concentration of copper ions, the emittance variation ($\Delta\epsilon$) of Cu-doped PANI films exhibits a trend in volcanic pattern due to the critical role of the polarons and bipolarons. The optimal IR emissivity (ϵ) modulation obtained on Cu-doped PANI films shows the $\Delta\epsilon$ modulation of 0.35 and 0.3 in the wavelength range of 8–14 μm and 2.5–25 μm , superior to previous reported pure sulfuric acid-doped PANI. Furthermore, a flexible IR electrochromic device was fabricated with the present Cu-doped PANI porous films. The modulation of the emittance variation varied between 0.513 and 0.834 ($\Delta\epsilon = 0.32$ in ranges of wavelength 8–12 μm), suggesting the great potential for applications in military camouflage and intelligent IR thermal management.

1. Introduction

Electrochromic materials and devices that respond in the mid-to-far IR region are very important, because of their wide applications in smart windows, infrared camouflage and thermal IR optical switches.^[1–6] The commonly reported materials mainly include transition metal oxides (WO_3 ^[7–9]) and conducting polymers (CPs) (polythiophene^[10], polypyrrole^[11], and polyaniline^[12, 13]). Among these, polyaniline (PANI) shows rich color change characteristics and large infrared control due to the tunable structure and reversible redox properties. Meanwhile, the doping strategy has been proved to effectively improve the IR electrochromism of PANI systems. For example, P. Chandrasekhar et al.^[14] first put forward the poly (anethosulfonate)-doped PANI films on the gold substrates as functional layer of electrochromic device. The excellent IR emissivity (ϵ) of the polymeric matrix doped PANI varied from 0.32 to 0.79 in ranges of wavelength 0–40 μm . However, the used macromolecular polymer dopant is very expensive. Following this work, Li et al.^[15] investigated the performances of the EC devices that was prepared by using H_2SO_4 -doped PANI films as the electrodes. The devices showed modulation of the emittance variation ($\Delta\epsilon$) of 0.24 in ranges of wavelength 8–12 μm . Topart et al. prepared a non-flexible IR electrochromic device based on the camphor sulfonic acid (CSA)-doped PANI film deposited by spin coating, which showed the dynamic ϵ variation from 0.35 to 0.8 at 12 μm ^[16]. In addition, Y. Li's^[12, 17–19] team had used different acid as the dopants to prepare the PANI films and assembled them into the device, achieving an $\Delta\epsilon$ of 0.4 in ranges of wavelength 2.5–25 μm . However, despite these achievements, the dynamic IR modulate ability of PANI film is restrictive, suggesting the importance of new strategies and electrochromic mechanism analysis.

As reported, the state of polarons and bipolarons was the key factor to affect the variable IR emissivity of PANI films. Changing the content and state of polarons and bipolarons can effectively control the infrared electrochromic performance of PANI films. In Chandrasekhar's work,^[14] the different IR transmittances of the overlying PANI layer under different oxidation states affected the reflection from the underlying Au layer. By analyzing different reflection and ϵ values of the PANI Au/porous substrate films, it demonstrated that the IR spectral regions of PANI mainly contributed by bipolaron states of PANI.^[20] Zhang et al.^[6] also reported that the occurrence and disappearance of polarons and bipolarons delocalizing on the PANI chains were the key parameters affecting the variable IR emissivity of PANI films, which was illustrated by analyzing the electrochemical oxidation/reduction process and structural evolution of PANI. Meanwhile, the part of the PANI film without participating in the redox reaction (called inactive PANI) was revealed to result in the higher actual emissivities. As is well-known, metal ions, as a Lewis acid, can coordinate with nitrogen atoms to modulate carriers transfer, and contribute to catalyze the reaction for inactive PANI. Therefore, it is believed that numerous polarons and bipolarons delocalized on the PANI chains will presented by doping of copper ions.

In this paper, the Cu-doped PANI porous films were prepared by electropolymerized on an Au/PES porous substrate. The optimal emissivity variation ($\Delta\epsilon$) of Cu-doped PANI film achieves 0.35 and 0.3 in ranges of wavelength 8–14 μm and 2.5–25 μm , respectively. Compared to the traditional acid-doped PANI films, the stronger IR regulation ability from present Cu-doped PANI porous film is attributed to the more polarons and bipolarons delocalized on the PANI chains, as revealed by X-ray diffraction (XRD), Raman spectra, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) techniques. The switching times of the Cu-doped PANI porous film for the coloration and bleaching are 1.5 s and 0.7 s, respectively. Moreover, an IR electrochromic device constructed with Cu-doped PANI Au/porous substrate films exhibit a higher IR modulation ability ($\Delta\epsilon = 0.32$ in the wavelength range of 8 to 12 μm). We believe that the results in this work will provide a novel perspective and avenue for improving IR modulation ability of electrochromic devices based on polyaniline conducting polymers.

2. Experimental Section

2.1. Materials

Aniline (99.5%, AR) was purchased from Aladdin and distilled under reduced pressure before using it. Microporous substrates of Polyethersulfone (PES) with a pore size of 1 μm and polyethylene (PE) with 5-mm-thick films were obtained from commercial suppliers. A 200-nm-thick Au layer was deposited on the PES porous substrate by thermal evaporation. Copper Sulfate (CuSO_4 , 99%, AR) and polyvinyl alcohol (PVA, average MW 105,000) were received from Alfa-Aesar Company. Ultrapure water was prepared with an Aquapro system (18.2 $\text{M}\Omega\cdot\text{cm}$).

2.2. Preparations of Cu-doped PANI porous films

The synthesis of Cu-doped PANI films were completed through the electropolymerization on the Au/PES microporous membrane ($1 \times 1 \text{ cm}^2$) in an aqueous solutions of 1 M H_2SO_4 , 0.5 M aniline monomer, and different content doping of CuSO_4 (0 M, 0.005 M, 0.01 M, 0.02 M, 0.03 M, respectively) by a chronoamperometry method at the potential of 0.65 V and a polymerization charge of 0.37 C/cm^2 . An Ag/AgCl and Au/PES microporous membrane ($2 \times 2 \text{ cm}^2$) were used as the reference electrode and counter electrode, respectively. After the electropolymerization, the prepared films were washed with ultra-pure water and then air-dried at the temperature of 40°C . The final product was marked PANI-0, PANI-0.5, PANI-1, PANI-2, and PANI-3 depending on the copper ion concentration, respectively.

2.3. Device assembly

Scheme 1 shows the route followed for the assembly of the device. A device with a “sandwich” structure was assembled using the Cu-doped PANI porous films on the Au/PES substrate as both the front and back electrodes. Then, a 5 mm-thick IR-transparent encapsulant layer of PE was heat-bonded directly to the surface of the front electrode, protecting the PANI functional layer from the external environment. Subsequently, the back of the front electrode and the surface of the counter electrode were coated with a gel electrolyte and allowed to dry over 72 h (The electrolyte comprised PVA, sulfuric acid and ultrapure water in 12% / 6% / 82% weigh ratio. The electrolyte mixture was heated to 80°C until the PVA was dissolved. The electrolyte was reheated before using). Finally, the working electrode and the counter electrode with the gel electrolyte were assembled in a two-electrode configuration by hot-pressing at 150°C .

2.4. Measurements

Cyclic voltammetric (CV) and chronoamperometric (CA) experiments were carried out on electrochemical workstations (CHI760E, Shanghai Chenhua Instruments, China). The electrochemical measurements of Cu-doped PANI porous film were performed in a three-compartment system with 0.5 M H_2SO_4 aqueous solutions as the electrolyte. An Ag/ AgCl electrode and a graphite rod were utilized as the reference electrode and counter electrode, respectively. X-ray diffractions (XRD) measurements were conducted on a Rigaku Dmax 2500 Powder Diffractometer with Cu-K α radiations ($\lambda = 0.15406 \text{ nm}$). Raman spectra were recorded using an inVia Qontor (Renishaw, UK) system at the wavelength of 532 nm. The scanning electron microscopy (SEM) measurements were operated on a Hitachi S4800 with a working accelerating voltage of 10 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on an AVG Thermo ESCALAB 250 spectrometer (VG scientific) operated at 120 W. IR reflectance and transmittance spectra of the Cu-doped PANI films at different voltages were carried out by Nicolet IS50 Fourier IR spectroscopy (America), Owing to the opaque nature of the PANI porous film, the value of IR emissivity of the Cu-doped PANI films and devices can be calculated by weighting $[1 - R(\lambda)]$ (namely spectral emittance) with the black body spectrum for a particular wavelength and integrating this in a spectral range of 2.5 to $25 \mu\text{m}$ according to the following two equations ^[21, 22]:

$$B(\lambda) = \frac{2\pi hc^2}{\lambda^5} \frac{1}{e^{\left(\frac{hc}{\lambda kT}\right)-1}} \quad (1)$$

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

where h is the Plank constant ($6.6261 \times 10^{-34} \text{ J s}^{-1}$), c is the speed of light ($2.998 \times 10^8 \text{ m s}^{-1}$), λ is the wavelength, T is the temperature (K), $B(\lambda)$ is spectral radiance of the black body at λ and $R(\lambda)$ is the reflectivity at λ .

3. Results And Discussion

Scheme 1 displayed the synthetic procedures of Cu-doped PANI porous films and corresponding devices. The Cu-doped PANI porous films were obtained by in situ electrochemical deposition of aniline molecules in H_2SO_4 aqueous solution. The Au porous substrate layer has two functions: one is to provide conductive framework and external electrode for the electrode of IR electrochromic device; Second, the gold metal has a high reflectivity in the IR range, which can effectively reflect the IR energy through the working electrode of PANI films. When polymerized in acid dopant, the PANI begin to aggregate on the surface of Au/ PES porous membrane. Meanwhile, the color of the membrane surface changes from golden to yellowish green and to dark green as the polymerization charge increased. To reveal the composition information, the XRD patterns are collected. As shown in Fig. 1(a) and Fig. S1, all the samples present a wide peak centered at 18.5° , which could be from the amorphous structure of the PES substrate^[23]. As a comparison, the pure PANI film shows a diffraction peak at $2\theta = 25.4^\circ$, indicating the semicrystalline nature of polyaniline and in consistent with the previous results^[24]. With the introduction of copper ions, the PANI signal peaks from Cu-doped PANI porous films become stronger and sharper. According to the previous reports^[25], the sharpness of the diffraction peak usually relates to the mono-distributions of the periodicity between the polymer backbone chains. This suggests the enhancement of the molecular arrangement order in Cu-doped PANI porous films. Furthermore, it is found that two signal peaks from $\text{Cu}_3(\text{SO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ and $(\text{NH}_3)_2\text{Cu}(\text{NO}_3)_2$ exist in the prepared Cu-doped PANI porous films, as marked by the diamonds and clubs (PDF# $\text{Cu}_3(\text{SO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ and PDF# $(\text{NH}_3)_2\text{Cu}(\text{NO}_3)_2$). It is indicated the possible existence of Cu-N coordination bonds in Cu-doped PANI porous films, and the simultaneous doping of sulfuric and nitric acid. The signal peaks of $(\text{NH}_3)_2\text{Cu}(\text{NO}_3)_2$ from PANI-2 porous film is sharpest among the prepared PANI porous films (Fig. S1). This suggests the existing $\text{Cu}_3(\text{SO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ and $(\text{NH}_3)_2\text{Cu}(\text{NO}_3)_2$ may has a great impact on the subsequent electrochromic properties.

To analyze the chemical bonds in the PANI films, the Raman spectra were measured in the range of 100–2000 cm^{-1} . In Fig. 1b, all the copper-doped PANI porous films present the signals at the same positions. Specifically, the characteristic peaks observed at 1622 and 1572 cm^{-1} are assigned to the C-C stretching vibration of the benzenoid ring and C = C stretching vibration of the quinoid ring, respectively. The peak at 1480, 1313 and 1252 cm^{-1} in the spectra are attributed to the C = N stretching vibration of the quinoid ring and the C-N stretching vibrations of the benzenoid ring and quinoid ring, respectively. The C-N⁺ stretching vibration of more delocalized polaronic structures is represented by the peak at 1343 cm^{-1} , and the benzenoid ring deformation in polarons is suggested by the signal at 868 cm^{-1} [26]. Compared with the Raman spectrum of the PANI-0 porous film, the Cu-doped PANI porous films show a stronger and sharper absorption peak at 1343 cm^{-1} . As expected, this reveals that a large number of polarons and bipolarons delocalized on the PANI chains with the introduction of copper ions. The peaks at 1198 cm^{-1} and 812 cm^{-1} represent the C-H in-plane bending vibration and out-plane bending vibration in the quinoid ring [27]. Note that the intensity of the peak at 1198 cm^{-1} increases with the introduction of copper ion, suggesting the increased oxidation degree of Cu-doped PANI porous films. The similar intensity of the PANI-1, PANI-2 and PANI-3 indicate the comparable REDOX components.

The geometric structure of the material is critical to optical response performance, since the ion transfer between electrode material and electrolyte plays a decisive role during the electrochemical redox process. Herein, the morphologies of PANI porous films were investigated by SEM images. As shown in Fig. S2, similar to that of the PES and Au/PES membranes with a linear porous network structure, pure PANI film presents a fibrous structure, which constructs a reticular membrane. The porous structure benefits to electrolyte infiltration and ion transmission. The surface morphology of the Cu-doped PANI porous films are exhibited in Fig. 2(a)-(d). With the addition of copper concentration, the diameter of the porous structure from Cu-doped PANI films becomes smaller resulting from the filling of smaller PANI nanoparticles, even though the general frameworks remain consistent. Correspondingly, the surface morphologies of Cu-doped PANI porous films become more compact and rougher. Figure 2(e)-(h) show the cross sections of the prepared Cu-doped PANI films. Obviously, all the PANI layer with the thickness of 40 μm are tightly attached to the Au/PES porous membrane, and uniform voids can be found in the porous structures. The EDS mapping images of Cu-doped PANI film surface are shown in Fig. 3(a), (c)-(f)). The results show that the elements of carbon, oxygen, copper, and nitrogen are uniform distribution on surface of PANI-2 porous films. Compared to that in spectrum 4/6, the higher copper content in spectrum 5 indicates that the copper element uniformly distributed in the prepared films, rather than the local larger nanoparticles, as shown in Fig. 3(b).

To reveal the elements' electronic state, XPS analysis were conducted. As shown in Fig. S3, all the Cu-doped PANI films show the presence of carbon, nitrogen, oxygen, sulfur and copper element (Fig S3). As a comparison, the copper signals are missing in PANI-0 films. As reported, the electron polarization in the PANI films occurs mainly on nitrogen atoms. Therefore, a fine analysis of the N 1s core level spectra was performed. As shown in Fig. 4(a)-(e), all the spectra from PANI films can be fitted into three major components located at 398.5, 399.5, 401.1 and 402.2 eV, which are attributed to the quinonoid imine (=

N-), benzenoid amine (-NH-), protonated amine ($-\text{NH}_2^+$) and protonated imine ($=\text{NH}^+$), respectively.^[28] Compared to PANI-0 porous film, the quinonoid imine ($=\text{N}-$) peak disappears in the XPS N 1s spectra from Cu-doped PANI films. This indicates that the copper ions doping induced the transformation of quinonoid imines in PANI films. The $=\text{N}-$ structure in the Cu-doped PANI films is converted to a positively charged $-\text{N}^{+\bullet}$ - structure, corresponding to the two peaks in the XPS spectra with binding energy greater than 400 eV (i.e. protonated amine and protonated imine). Specifically, with the increase of copper concentration from 0.005 M to 0.02 M, the percentage of the protonated amine and protonated imine increases from 50–66%, while the content of benzenoid amine decreases. It hints that the initial introduction of copper ions promotes the protonation, leading to the formation of protonated amine. When the concentration is further increased to 0.03 M, PANI-3 porous film occur a reverse trend, which the content of protonated amine and protonated imine decrease to 52%. Because the $-\text{N}^{+\bullet}$ - structure is polaron structure in the PANI chain^[29], the percentage of protonated amine ($-\text{NH}_2^+$) and protonated imine ($=\text{NH}^+$) represent the number of polarons and bipolarons. As mentioned above, the formation and the elimination of polarons and bipolarons delocalized on the PANI chains are the direct and most critical factors in realizing excellent emissivity modulation performance. Thus, based on the maximum number of polarons and bipolarons, the PANI-2 porous film is expected to exhibit the best infrared electrochromic performance.

To analyze the chemical valence state of copper element and disclose its role on polarons, the high resolution Cu 2p spectra are exhibited in Fig. 5. Benefitting from the sensitivity of X-ray photoelectron energy spectra toward the element coordination environment, the copper signals from all the Cu-doped PANI films can be fitted into two components with the presence of two satellite peaks. The binding energies at 934.98 and 955.7 eV are originated from the characteristic peak of Cu 2p_{3/2} and Cu 2p_{1/2} from Cu(II) species, while the two peaks located at 933.3 and 952.5 eV correspond to the Cu 2p_{3/2} and Cu 2p_{1/2} from Cu(δ) species, respectively^[30–32]. The Cu $^{\delta+}$ ($+1 < \delta < +2$) with lower oxidation state could be from Cu-N coordination bonds, and the Cu(II) species come from the metal salt. These are in consistent with those from the above XRD. Such results indicate that the introduction of copper ions not only facilitate protonation of quinonoid imine, but also form metal-nitrogen coordination compounds in polymer films.

According to the above structural analysis, it is anticipated the obvious differences in infrared emission modulation on the Cu-doped PANI films prepared with different copper ions concentration. Cyclic voltammetric measurements were performed to preliminarily determine the electrochemical performance of the Cu-doped PANI porous films. As displayed in Fig. 6, the CV curves of Cu-doped PANI porous film present a pair of redox peaks corresponding to the state of emeraldine salt (ES) and leucoemeraldine (LE). The electrochemical active area under the CV curves is increasing with the increase of copper ions concentration. The PANI-2 porous film shows the largest electrochemical active area, suggesting the maximum amount of charge transfer and the potential optimal infrared electrochromic regulation performance. As reported, the IR electrochromic properties of PANI-based films are directly related to their existential states^[33, 34]. Hence, the potentials of -0.25 V and 0.5 V were chosen on account of the films' states completely transforming between LE and ES. Chronoamperometric (CA) experiment was

conducted to investigate of the IR electrochromic performance of PANI-2 and PANI-0 porous films. As shown in Fig. 6(b), the color of the film materials obviously changed from yellow to atrovirens in the voltage positive conversion process. For the PANI-2 porous film, the response time, defined as the times required for achieving 95% change of the full current density, from coloring state to bleaching state (the bias voltage: -0.25 V) can be calculated to be 0.7 s. When the bias voltage of 0.5 V is applied, the response time is determined to be 1.5 s (Fig. S4(a)), much superior to that of pure PANI and previous reports [13, 14, 19, 35]. This can be reasonable by the reticular structure that provides more ion channels and larger reactive area, improving the electrochemical reaction rate. The faster response time of the PANI-2 porous film suggest a more sensitive device. Furthermore, the response time of the present PANI-2 porous film is respectively about 1.3 s and 2.7 s for bleaching state and the coloring state after 50 cycles durability test, as shown in Fig. 6b and Fig. S4(b). Therefore, the prepared PANI-2 films not only show the excellent response ability, but also the good stability.

To quantitatively analyze and compare the IR emissivity change of PANI-based films, the Fourier transform infrared spectra were studied in the whole wavelength range from 2.5 to 25 μm and the values of ε are calculated according to Eqs. (1) and (2). Figure 7 presents the emittance curves of Cu-doped PANI porous films at potentials of -0.25 V and 0.5 V. The emittance curves at 0.5 V gradually rise with the copper ions concentration changing from 0.005 M to 0.02 M, while a decrease is observed for the further increasing to 0.03 M. This trend is in consistent with the number of polarons and bipolarons obtained in XPS results. As discussed above, the copper ions can activate the part of the inactive PANI film. Therefore, the Cu-doped PANI films, especially for PANI-1 and PANI-2 films, have low IR emissivity at -0.25 V. Similar to the emittance curves, the $\Delta\varepsilon$ between the curves at -0.25 V to 0.5 V presents a change in volcanic patterns. The maximum $\Delta\varepsilon$ from the PANI-2 porous film is 0.35 in ranges of wavelength 8–12 μm . By contrast, the PANI-0, PANI-0.5, PANI-1 and PANI-3 only provides the $\Delta\varepsilon$ of 0.1, 0.12, 0.21 and 0.06, respectively, as shown in Fig. 7(e). The decreased $\Delta\varepsilon$ of PANI-3 may be caused by the dense microstructure of PANI-3 porous film, hindering the transmission of carriers [33, 36]. Therefore, the PANI-2 porous film exhibits the best infrared modulation performance in this work ($\Delta\varepsilon$ in the wavelength ranges of 2.5 to 25 μm). It indicates that the evolution of the emittance curves largely depend on the copper ions concentration and microstructures of PANI on the porous films.

Based on the best $\Delta\varepsilon$ value, the PANI-2 porous film is selected as the functional layer to assemble IR electrochromic (EC) device. Figure 8(a)-(d) exhibits the digital photographs of the Cu-doped PANI IR EC device at different voltages. When the applied voltage is fixed at 0.3V, the device presents the color change from yellow to green. As the applied voltage increases to 0.5 V, the color of the device changes to dark green. When the applied voltage reaches 0.8 V, the device presents atrovirens. The results demonstrate that the Cu-doped PANI IR devices can tunably blend with green or yellow background under different voltages.

In order to explore the application potential of the Cu-doped PANI IR EC device in optical and thermal management, the IR emissivity of EC device was also investigated in the wavelength ranges of 3–5 μm and 8–12 μm at the different voltages. As shown in Fig. 8(e), the evolution of ε in two wavelength ranges

shows a similar tendency. That is, the emissivity gradually increases along with the applied voltage. When the applied voltage reaches 0.5 V, the emissivity of device increases a little and tends to be stable as a result of the PANI layer in the ES state. Note that the present $\Delta\epsilon$ of 0.32 in 8–12 μm is much larger than that (0.24) from the previous pure sulfuric acid-doped PANI device ^[15]. In addition, the response time and stability of the device were also studied in Fig. 9(f). The coloring time of the device is about 5.74 s (1st cycle) and 6 s (50th cycle), while the fading time is about 3.77 s (1st cycle) and 5 s (50th cycle). Meanwhile, the current density of device still retains less than 0.3 mA cm⁻² loss after the 50 cycles. Therefore, the present IR electrochromic device exhibits the superior tenability and the good electrochromic stability.

4. Conclusions

In summary, various Cu-doped PANI porous films have been prepared via the electropolymerization procession the surfaces of Au/porous substrates. The influence of copper ions on the polarons and bipolarons were revealed by the XRD spectra and XPS analyses. The geometric structures of the prepared Cu-doped PANI porous films were investigated by SEM spectra. Based on the electronic structure and appropriate porous structure, the Cu-doped PANI porous film prepared at the concentration of 0.02 M showed the optimal IR electrochromic properties and the best emissivity modulation. Furthermore, a flexible IR electrochromic device has been fabricated and shows good modulation of the emittance variation in the wavelength ranges of 8–12 μm . The results in this work will not only provide new insights into the redox states and protonation levels of the PANI, but also a new thought for enhancing the IR emissivity modulation ability of electrochromic films. This will promote the applications of IR electrochromic devices in military camouflage and thermal control of satellites.

Declarations

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Conflict of Interests

The authors declare no competing financial interests.

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Figures

Figure 1

(a) The XRD image of Au/PES substrate, PANI-0 and PANI-2 porous films. (b) Raman spectra of the PANI porous films at different copper concentration.

Figure 2

SEM images of (a) PANI-0.5, (b) PANI-1, (c) PANI-2, (d) PANI-3 porous films, and cross sections of (e) PANI-0.5, (f) PANI-1, (g) PANI-2, (h) PANI-3 porous films.

Figure 3

(a) SEM images of PANI-2 porous film, (b) Copper ions content of above area, EDS elemental mapping images of the: (c) C element, (d) O element, (e) Cu element, (f) N element.

Figure 4

XPS spectra of N 1s spectrum for (a) PANI-0, (b) PANI-0.5, (c) PANI-1, (d) PANI-2, (e) PANI-3 porous films, and (f) the ratio of nitrogen species to total nitrogen content for N 1s spectrum.

Figure 5

XPS spectra of Cu 2p spectrum for (a) PANI-0.5, (b) PANI-1, (c) PANI-2, and (d) PANI-3 porous films.

Figure 6

(a) The CV curves of Cu-doped PANI porous films measured in 0.5 M H₂SO₄ aqueous solutions with a scan rate of 50 mV/s sweeping between -0.3 and 1.2 V. (b) The CA curves of 1st and 50th cycles and digital camera images of the PANI-0 and PANI-2 porous films at 0.5V and -0.25V.

Figure 7

Emittance curves for (a) PANI-0, (b) PANI-0.5 (c) PANI-1, (d) PANI-2, and (e) PANI-3 porous films. (f) The $\Delta \epsilon$ regions of the spectrum (2.5-25 μm and 8-12 μm) for Cu-doped PANI porous films at different Cu ions concentrations.

Figure 8

(a)-(d) Digital camera images of Cu-doped PANI IR electrochromic device at different voltages. (e) The emissivity value (ϵ) of Cu-doped PANI IR electrochromic device at regions of the spectrum (3-5 μm and 8-12 μm). (f) The CA curves of 1st and 50th cycles of the Cu-doped PANI IR electrochromic device at 0.8V and -0.8V.

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