A visible-to-infrared broadband flexible electrochromic device based polyaniline for simultaneously variable optical and thermal management

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A B S T R A C T

A visible-to-infrared broadband flexible electrochromic device based on H₂SO₄-doped polyaniline films has been constructed for simultaneously variable optical and thermal management. Upon electrochemically manipulating, the demonstrated electrochromic device could change from a wide bandgap semiconductor to an insulator, causing the device to transform from a high thermal emitter with dark green to an optical reflector with bright yellow. High infrared emission changes of 0.4 and 0.3 for the device are observed at the wavelength ranges of 8–14 μm and 2.5–25 μm, respectively, which are higher than most reported electrochromic devices. A promising cycling stability and flexibility of the device are also observed. The thermal imaging results reveal that the device can be electrochemically and reversibly tuned to blend them with their environment. Furthermore, both the theoretical calculation and experimental results demonstrate that the device exhibits different heat transfer rates, facilitating the thermal management of the indoor object. The illustrated capabilities of the device make the electrochromic device highly promising for the optical management in visible-infrared regions and thermoregulation in indoor environment.

1. Introduction

Broadband smart materials from visible to infrared wavelengths is attractive for applications like smart windows, thermal camouflage, and thermal management to reduce energy consumption and carbon footprint in residential environment [1]. To date, there were many intensive efforts for the engineering of various artificial optical and thermal management platforms with smart tunable properties from visible to infrared wavelengths, including thermochromic materials [2,3], soft machines [4], liquid crystal (LC) materials [5] and electrochromic (EC) materials [1,6,7]. However, most of these efforts still suffer from issues, such as complex manufacturing processes, high operating voltages for the devices, and most importantly, only a single function could be achieved, making the development of these technologies extremely challenging. In contrast, conducting polymer (CP)-based EC materials have a great potential due to the ability of tunable absorptivity at visible to infrared (IR) wavelength and the low operating voltages.

Among them, polyaniline (PANI) has been studied extensively due to its excellent EC behaviors. For example, P. Topart et al. firstly reported an IR switching electro-emissive device with the PANI film as an active layer and the WO₃ film as a counter electrode. The specular reflectance of the device could be continually adjusted between 0.2 and 0.65 at 12 μm by applying potentials [8]. P. Chandrasekhar et al. assembled the PANI films on the gold substrates into a reflective EC device, the IR emittance of which can vary from 0.32 to 0.79 in the range of 0–40 μm [9]. Li et al. used H₂SO₄-doped PANI films as the electrodes to prepare the EC devices and studied the performances of variable IR emissivity. The devices could yield an emissivity change (Δε) of ca. 0.24 in the range of 8–12 μm [10]. In addition, our group has also carried out the research of PANI EC films and devices [11–14]. For example, we have used camphorsulfonic acid as the dopant to prepare the PANI films and assembled them into the device with an Δε of 0.4 at 2.5–25 μm [13]. However, despite these achievements, there have been no studies about achieving a dual-function of visible-infrared concealing and thermal regulations with radiative heating or cooling in one device to the best of our knowledge. In addition, most previously reported devices are rigid, significantly hindering their use in practical applications.

To overcome this limitation, here we prepared H₂SO₄-doped PANI...
films and assembled them into a flexible broadband EC device with dual-function of optical and thermal regulation. The optical and thermal emission properties of the device were characterized in the visible-infrared wavelengths which exhibit the suitability of broadband concealing. In addition, the device successfully achieved the thermal management of indoor objects in theoretical calculation and practical application. We believe that this study will provide an exciting perspective and avenue for developing dual-functional devices for simultaneously variable optical and thermal management.

2. Experimental section

2.1. Materials and instruments

Aniline (99.5%) was supplied from energy chemical and was reduced pressure distilled before use. Propylene carbonate (PC), lithium perchlorate and the microporous nylon 66 was obtained from commercial suppliers. Thermal evaporation was used to deposit gold on the nylon 66 porous substrate. Electrochemical workstation (CHI760D, Shanghai Chenhua Instruments, China) were used to deposit the PANI films and test cyclic voltammetry (CV). Spectral emittance (2.5–25 μm) of the PANI films and the devices were measured by a VERTEX 70 (Bruker) FT-IR spectrometer with an A562 integrating sphere. IR thermal imager (TI450, Fluke) with a spectral range of 7.5–150 μm was used to record the thermal images of films and the device. Flexibility testing of the device was operated on a flexible bending instrument (Dongguan Xinken Instruments, China).

2.2. Preparation and assembly of the H2SO4-doped PANI devices

H2SO4-doped PANI films were prepared using the synthetic procedure shown in Scheme 1. Firstly, 10.86 mL H2SO4 and 9.33 g aniline monomer were added to 200 mL water and stirred for 30 min at room temperature. Then, Au/nylon 66 porous substrates (the working electrode), Pt foil (the counter electrode), Ag/AgCl (the reference electrode) and 30 mL mixed solution were used for the polymerization of PANI by a galvanostatic method with different polymerization current densities (0.1 mA/cm² and 0.2 mA/cm²) and polymerization charges (0.5 C, 0.6 C, 0.7 C, 0.8 C, 0.9 C and 1.0 C), respectively. The route for the assembly of the device has been previously described in our previous literature [13]. Briefly, as shown in Scheme 1, a device with a sandwich structure was assembled using the H2SO4-doped PANI porous films on the Au substrate as both the front and back electrodes, with polyethylene (PE) as a protective layer. The P(VDF-HFP) porous film containing electrolyte was used as the electrolyte film. After each layer was assembled together, the device was firmly compressed using a roll-to-roll mode at 150 °C.

3. Results and discussions

SEM images of the PANI films deposited at different current densities with polymerization charges from 0.5 C to 1.0 C were shown in Fig. 1 and Fig. S1. Fig. S1a shows the morphology of the Au film on the nylon film, which is a porous structure constructed by the network of intersecting fibers with the diameter of about 0.25 μm. With the increasing of the polymerization charges, the diameter of the fibers gradually increases and the porosity of the film is continuously decreased due to the deposition of PANI during the polymerization process (Fig. 1 and Fig. S1). Moreover, the growth speed of the films at 0.2 mA/cm² is faster than that of at 0.1 mA/cm², which mainly ascribes to the faster polymerization speed at larger polymerization current.

CV curves at a scan rate of 30 mV/s between -0.3 V and 0.8 V were measured to determine the electrochemical performance of the PANI films at different polymerization current densities. As shown in Fig. 2, with the increasing of the polymerization charges, the areas of the CV curves enlarge, indicating an increasing in the mass of PANI films. It can also be confirmed to use the cross section SEM images to determine the thickness of the film, where the thickness of the films increases with the increase of polymerization charges (Fig. S2, Fig. S3 and Fig. S4). Generally, under the external voltage, the PANI film can be reversibly transformed from leucoemeraldine base (LB) with low emittance [9]. All the CV curves of the PANI films exhibit one oxidation peak at 0.3 V corresponding to the transformation from LB to ES and one reduction peak at 0.05 V, which are chosen as the actuating potentials to study the EC performance of the PANI films, which are lower than the previously reported devices [13–20], suggesting that more energy could be saved at low voltages. In addition, the oxidation peaks shift positively and the corresponding reduction peaks shift negatively with increase in the polymerization charges due to the increasing in the resistance of the PANI films (Fig. S5) [14,21–23]. In addition, the EIS measurements were carried out in a frequency range of 0.01 Hz to 100 kHz to understand the electrochemical behaviors of the PANI films at 0.3 V and −0.05 V, respectively. As shown in Fig. S6 and Fig. S7, the charge-transfer resistance (Rct) of the PANI films increase with the increase of the
polymerization charges whether the PANI films is in an oxidation state or a reduced state. And, the radius of semicircle for PANI film at the oxidation state is lower the reduced film, which means that the PANI film at reduced state has a higher the charge-transfer resistance ($R_{ct}$).

Moreover, the low frequency straight line for the PANI films deposited at different conditions is much steeper and closer to 90° which denotes the shorter ion-diffusion path, lower resistance to diffusion in the electrode [24, 25].

The emittance curves of PANI films at polymerization current densities of 0.1 mA/cm$^2$ and 0.2 mA/cm$^2$ with different polymerization charges at potentials of $-0.05$ V and 0.3 V were measured and the results were shown in Fig. S8 and Fig. S9. With the increasing of polymerization charges, the $\varepsilon$ of the film at 0.1 mA/cm$^2$ at 2.5–25 $\mu$m at 0.3 V displays an increasing trend due to the increasing of the films' thickness, but the $\varepsilon$ of the film at 0.9 C is lower that of at 0.8 C owing to the lower carrier concentration [9]. The $\varepsilon$ values of the films from 0.5 C to 0.9 C at $-0.05$ V remain around 0.2 due to the high IR permeability state at the reduced state, while the $\varepsilon$ values of the film at 1.0C are the highest, attributing to the low IR transmittance. At the polymerization current density of 0.2 mA/cm$^2$, the $\varepsilon$ values at both 0.3 V and $-0.05$ V gradually increase. However, the increasing rate at 0.3 V is higher than that of at $-0.05$ V, thus leading to the increasing of the $\Delta\varepsilon$ values. The $\Delta\varepsilon$ values of the films were also calculated according to Equation (3) (Supporting information), which were shown in Fig. 3a. According to previous studies by our

Fig. 1. SEM images of PANI films at 0.1 mA/cm$^2$ with polymerization charges from 0.5 C to 1.0 C. (a) 0.5 C (b) 0.6 C (c) 0.7 C (d) 0.8 C (e) 0.9 C (f) 1.0 C.

Fig. 2. CV curves of the PANI films at different polymerization current densities with polymerization charges from 0.5 C to 1.0 C measured in an aqueous solution of 0.2 M H$_2$SO$_4$ with a scan rate of 30 mV/s between $-0.3$ V and 0.8 V. (a) CV curves of PANI films at the polymerization current density of 0.1 mA/cm$^2$ (b) CV curves of PANI films at the polymerization current density of 0.2 mA/cm$^2$.

Fig. 3. Spectral test results of the PANI films in visible-infrared regions. (a) The $\Delta\varepsilon$ of the PANI films prepared at the polymerization current density of 0.1 mA/cm$^2$ with polymerization charges from 0.5 C to 1.0 C. (b) Reflectance curves of the PANI films prepared at the polymerization current density of 0.1 mA/cm$^2$ with the polymerization charge of 0.8 C. Inset: The visual color change of the PANI films at 0.3 V (right) and $-0.05$ V (left). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)
group [13], the PANI film has the high IR absorption at the ES state originating from bipolarons, thus leading to a high ε value. Conversely, the PANI film appears to be substantially IR-transparent at the LB state and has a low ε value owing to the strong reflecting effect of the Au layer. Obviously, the ε values of the films at 0.1 mA/cm² from 0.5 C to 1.0 C are consistent with the previous results, that is, the lowest ε is at LB state, and the highest ε is at the ES state. At 0.2 mA/cm², the ε values from 0.5 C to 0.6 C are also consistent with the previous results, while the ε of the PANI films at LB state are higher than that of at ES state at the range of 2.5–7 μm when the polymerization charge is above 0.6 C, which is caused by the pseudo-metallic behavior of PANI [26,27]. Therefore, the ε value of the film prepared at the polymerization current density of 0.1 mA/cm² with polymerization charge of 0.8 C is the highest, and thus which is selected for the further study of the optical and thermal management ability in the experiment.

The reflectance curves of the PANI film prepared at a current density of 0.1 mA/cm² with a polymerization charge of 0.8 C at 260–2000 nm was measured. As shown in Fig. 3b, the PANI film shows a reflection peak at 660 nm under −0.05V, which is corresponding to the yellow film in Fig. 3a, and the intensity of the peak increases accompanied by the appearance of a new peak at 1250 nm under 0.3 V corresponding to the green film. The results demonstrate that the PANI films can tuneably blend with green or yellow background under different voltages due to their reversible color change.

To further evaluate the IR regulation performance, IR spectra of the emitted radiation for the PANI films were measured at −0.05 V, 0.1 V and 0.3 V (Fig. 4a). Notably, the intensities of the spectra at the wavelength range of 8–14 μm and 2.5–25 μm increase from −0.05 V to 0.3 V (Fig. 4a1) because of the enhancement carrier concentration through electrochemical oxidation [9]. Furthermore, Δε values of the film were calculated to be 0.4 and 0.3 at wavelength ranges of 8–14 μm and 2.5–25 μm, respectively. Based on Stefan-Boltzmann law, the emissive power of the PANI film at different voltages (−0.05 to 0.3 V) were also calculated, as shown in Fig. 4a2. The distinctly different integral areas indicate that the film has excellent capability of switchable IR modulation. To realize the practical applications, a dual-functional EC device was assembled with the H₂SO₄-doped PANI films and the emissance curves of the device at different voltages were also measured, as shown in Fig. 4b1. The evolution of ε at the wavelength ranges of 8–14 μm and 2.5–25 μm shows a similar tendency to the PANI films, that is, ε gradually increases with the increase of the applied voltage. The absorbance peaks at 3.5 μm, 6.8 μm and 14 μm are ascribed to the absorbance of the PE layer, which are reported to have little impact on the applications [28]. Δε values of the device are calculated to be 0.4 and 0.3 at the wavelength ranges of 8–14 μm and 2.5–25 μm, respectively, exhibiting excellent modulation capacity in the IR region. Notably, the Δε of 0.4 at 8–14 μm is larger than that of most H₂SO₄-doped PANI device [10]. In addition, the emissive power of the device also exhibits excellent capability of switchable IR modulation (Fig. 4b2).

Fast response time is a key factor of the dual-functional EC device for the practical applications. The response time of the device was studied through the I-t curve under applied voltage and the results were shown in Fig. S10a. The coloring time of the device is about 9.8 s and the fading time is about 9.6 s. In order to confirm the structural stability of the EC device, the IR emissivity of the device was measured after multiple cycling. As shown in Fig. S10b, the emissivity of the device remains stable within 500 cycles, hinting the device has excellent structure stability.

To verify the flexibility of our device, the colors and emissivity of the devices were measured at potentials of −0.05 V and 0.3 V during and after the bending test by repeated bending/unbending motions, as shown in Fig. 5a–c and Video S1 (Supporting Information). The device could be bent more than 90° without breaking, and still retains the EC ability under external voltage at the bended state (Fig. 5a). Meanwhile, IR spectra of the device after multiple bending shows that Δε of the device gradually decreases with the bending process. The Δε almost remains constant after bending for 40 cycles indicating that our device has good stability (Fig. 5b). Fig. 5c shows the digital photos of the device at colored states before and after 100 bending cycles. The color of the device has a large deviation from the initial state, which is mainly due to the breaking of circuit inside the device caused by bending.

Supplementary video related to this article can be found at https://doi.org/10.1016/j.solmat.2019.110356.

The high Δε of the PANI films and devices make them appealing for
thermal imaging applications. To verify the suitability for thermal imaging, we firstly tested the ε of PANI films under different temperatures. As shown in Fig. S11, there are no evident changes for the emissivity of both oxidized and reduced PANI films under different temperatures. Then the PANI films and devices were placed on the Al plate to capture IR thermal imaging. As shown in Fig. 6a and Fig. 6b, the non-emissive reduced state of the samples appears colder and the emissive oxidation state appears hotter, similar with those of glass and paper, respectively. Meanwhile, a dynamic video of the device in the voltage range between -0.05 V and 0.3 V exhibits that the device could change reversibly from green to yellow and hotter to colder (Video S2). It is also observed that the apparent temperature \( T_r \) has the consistent results under different temperatures. These observations can be explained using the following relation from the principle of thermal imager [1].

\[
T_r = εT_b^4 + RT_a^4
\]

where \( T_b \) is the real temperature of the PANI films or devices, \( T_a \) is the effective temperature of the environment, \( ε \) is the emittance of the PANI films or devices, and \( R = (1 - ε) \) is its reflectance. As evident from the above formula, the PANI films or the devices show a strong emissivity at the oxidation state, so \( T_r \) displayed by the thermal imager is high, while \( T_r \) at the reduced state is the temperature of cold environment reflected due to the high reflectivity of the PANI films. These variable IR behaviors imply that the films or devices can blend with the surroundings changes. As exhibited in Fig. 6c, the oxidized and reduced devices placed on a hand show the temperatures (31.3 °C and 22.1 °C) are close to those of human skin (\( \sim \)32 °C) and the ambient (20 °C), respectively. Therefore, the dual-functional EC device based on the PANI film is capable of applications for thermal imaging, whose performances are superior to those reported EC devices (Table S1).

The excellent IR optical properties of the dual-functional EC device encourage us to continue to study its applications in regulating thermal radiation of indoor objects. Firstly, we performed theoretical calculations of cooling power at different surface temperatures according to Equations (4)–(7) (Supporting Information). The calculated relationship between the cooling power and temperature is presented in Fig. 7a. It can be seen that if the non-radiative heat transfer can be avoided (\( h = 0 \)), the device can continuously achieve cooling ability with more than 20 °C below the ambient temperature both at the oxidation and the reduction states. In addition, the device shows larger cooling power (about 65 W/m²) at the oxidation state and a lower cooling power at the reduction state, when the surface temperature is the same with the ambient temperature (\( h = 5 \)), which could make the indoor object of rapid cooling and insulating. At the oxidation state, the device can reach the stagnation temperature, which is about 8 °C below ambient, while there is almost no change at the reduced state. The results theoretically indicate that the dual-functional EC device has excellent ability of thermoregulation for indoor objects. Followingly, an experimental platform was established to verify the thermoregulation capability of the device for the indoor object using a thermal imager (Fig. 7b). The details of the measurement setup were shown in the Supporting Information. As shown in Fig. 7c and Fig. 7d, the apparatus without the EC device could lower its temperature through non-radiative heat transfer, and the device at the oxidation state or reduced state could achieve different cooling effects based on mixed heat transfer. Undoubtedly, the results

Fig. 5. Characteristics of the dual-functional EC device during dynamic bending tests at the bending radius of 8 mm. (a) Digital photos of the device under different voltages after and during bending. (b) The Δε values of the device after different numbers of bending cycles. (c) Digital photos of the device at 0.3 V before and after 100 cycles.

Fig. 6. (a) Digital photos of PANI films and devices. (b) IR images of PANI films and devices on Al plate, showing their behaviors at different temperatures. (c) IR images of PANI EC devices at oxidation and reduction states on human skin.
have clearly implied the practical applications of the device for variable thermoregulation.

4. Conclusions

In conclusion, we demonstrate a dual-functional flexible device for simultaneously optical and thermal management based on H2SO4-doped PANI EC films. The color and emissivity of the device can be controlled reversibly between −0.05 to 0.3 V, which could change from green to yellow color and from high to low IR emission states simultaneously, making it appealing for both camouflage and thermal regulation applications. The IR emissivity change (Δε) of the device is 0.4 and 0.3 at the wavelength ranges of 8–14 μm and 2.5–25 μm, respectively. Moreover, the device exhibits high durability and structure stability after 500 cycles and applications of mechanical bending. The dual-functional EC device is capable of realizing the different radiative cooling rate for the object at oxidation and reduction states, showing excellent ability of thermoregulation for indoor objects. Therefore, the dual-functional device will facilitate their applications in the field of thermal control, radiative cooling and other color-related areas.

Author contributions

Gaoping Xu directed the research and conceived the project with Leipeng Zhang, Bo Wang and Xi Chen. The experiments were performed by Shuliang Dou, Mengyao Pan and Feifei Ren. All the authors analyzed the data. Xiaobai Li and Yao Li contributed to the manuscript writing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.solmat.2019.110356.

References


