

Low-Spin Fe Redox-Based Prussian Blue with Excellent Selective Dual-Band Electrochromic Modulation and Energy-Saving Applications

Dajiang Tang¹, Junxin Wang², Xue-An Liu¹, Zhangfa Tong¹, Hongbing Ji¹, Hui-Ying Qu^{1,*}

¹ Guangxi Key Laboratory of Petrochemical Resource Processing and Process Intensification Technology, School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China

² Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge CB3 0FS, United Kingdom

*Corresponding author: Hui-Ying Qu, E-mail: huiying.qu@gxu.edu.cn

Abstract

Dual-band electrochromic materials (DBEMs) are of utmost importance for smart windows to realize independent control of the visible (VIS) and near-infrared (NIR) light. However, very few single-component DBEMs are capable of independently and effectively controlling both VIS and NIR light. Here, we present Prussian blue (PB) with remarkable performance to replace the composite DBEMs that require deliberate design and complicated preparation. Excellent durability and capacity were achieved simultaneously due to the activated low-spin Fe in PB. A dual-band electrochromic device (DBED) by using PB thin films as electrochromic layers was constructed, exhibiting superior dual-band electrochromic performance, energy storage performance and memory effect. We show that the energy-saving DBED can be bleached without applying any external bias potential, and can be colored by using a commercial photovoltaic solar panel under ambient solar irradiation. The stored energy during coloration can be further used to light up the lights. Finally, the coloration mechanism of the DBED was studied by the density functional theory calculations, to shed light on the large optical transmittance modulation in both VIS and NIR regions. The new insights will advance the design of efficient and durable DBEMs and the development of bi-functional smart windows.

Keywords Dual-band electrochromism; smart window; Prussian blue; energy storage; bi-functional device

1. Introduction

Independent modulation of the visible (VIS) and near-infrared (NIR) light as desired is an important prerequisite for the energy-saving glazing to regulate indoor lighting and temperature. Electrochromic smart windows can dynamically modulate solar radiation into the interior. Their optical properties can be switched reversibly and persistently between bleached and colored states by applying a small electrical signal (~ 1 V) [1, 2], thus lessening the strain on lights, heating and air-conditioning equipment, and decreasing up to 40% energy consumption of buildings, exhibiting promising prospect for next-generation intelligent systems[3, 4]. However, traditional electrochromic smart windows only involve VIS light modulation while cannot selectively regulate the VIS and NIR light, resulting in ineffectively block of the solar radiant heat[5-10]. The NIR light, accounting for $\sim 50\%$ of the total solar radiation, passes through the windows and significantly raises the temperature of the room[11]. In this regard, the exploration of dual-band electrochromic smart windows has gained an increasing number of interests to realize selective and independent modulation of the VIS and NIR light.

The most widely studied and implemented electrochromic smart windows consist of the central electrolyte layer joining the electrochromic electrode and the counter electrode on both sides[1, 12-14]. It is clear that the dual-band electrochromic materials (DBEMs) are the key components in the dual-band electrochromic smart windows, and great efforts have been devoted to synthesizing various materials with dual-band electrochromic performance. Milliron's group has pointed out that dynamic and

independent dual-band control can be realized by the nanocomposite of tin-doped indium oxide (ITO)-NbO_x[15]. Inspired by this work, other composite DBEMs such as WO_{3-x}-NbO_x[16], polythiophenes-ITO[17], polyaniline-ITO[18], PANI/WO₃-ITO[19] Ta-doped TiO₂[20], W₁₈O₄₉-K₂₈Li₅H₇P₈W₄₈O₁₈₄·92H₂O[21] and WO₃-VTiO₂[22] films are continually developed. However, they usually need to be deliberately designed, and the preparation methods are always complicated. Compared with the composite DBEMs, single-component DBEMs are more attractive due to their easily controlled structures at the molecular level. Unfortunately, only tungsten oxide- and TiO₂-based DBEMs are reported to be able to control both VIS and NIR light[20, 23], but the response speed and memory effect are unsatisfactory yet. Therefore, it is of great importance to develop efficient, green and energy-saving glazing consisting of single-component DBEMs with excellent dual-band electrochromic performance, to reduce the energy demand of the buildings.

Prussian blue (PB, KFe^{III}[Fe^{II}(CN)₆] or KFeHCF) is known for its superior VIS light modulation during the electrochromic process[24]. However, previous studies did not show the ability of PB to regulate the NIR region selectively. For example, the W₁₈O₄₉/PB composite film designed by Zhao et al. realized VIS modulation by PB and NIR-modulation by W₁₈O₄₉[25]. Wang et al. reported a self-powered electrochromic device by using PB as the cathode and Al as the anode, a large transmittance modulation of 52.2% at 670 nm was achieved[26]. However, a short lifespan (≤1000 cycles) was observed in PB and other PB analogues film[27, 28]. Their unsatisfactory durability is due to the limited utilization of the low-spin Fe in them, resulting in the inferior

conductivity and spatial resistance caused by the tight cooperative interaction between Fe and the surrounded cyano group[29]. To our knowledge, the literature is currently lacking in studies using single-component PB as the DBEMs to fabricate dual-band electrochromic smart windows with long-term durability.

Herein, we explored a facile method to prepare the durable single-component PB thin film that can selectively and independently modulate the VIS and NIR light for the first time. It presents a wide range of switchable colors including blue, green, yellow, and transparent, allowing for three distinct operating modes (bright and warm, colored, dark and cool) during the electrochromic process. Large transmittance modulation of both VIS and NIR light, high coloration efficiency (*CE*) and fast switching speed were also achieved. Experimental and theoretical analysis demonstrates that the low-spin Fe in PB can be activated, leading to long-term durability and high energy storage capacity of the thin film. Moreover, an energy-saving dual-band electrochromic device (DBED) applying PB as the cathode and Zn foil as the anode was fabricated. It exhibits remarkable dual-band electrochromic performance, energy storage performance and the optical memory effect. The coloration mechanism of the DBED was further illustrated by the DFT calculations.

2. Experimental Section

2.1. Materials

All the solvents and chemicals were of analytical grade and were used without further purification. Ferric chloride (FeCl_3 , 98%) was purchased from Energy Chemical. Potassium chloride (KCl , 99.5%), potassium hexacyanoferrate (III) ($\text{K}_3[\text{Fe}(\text{CN})_6]$),

99.5%), hydrochloric acid (HCl, 36 wt.%), acetone ($\text{CH}_3\text{COCH}_3 \geq 99.5\%$) and ethyl alcohol ($\text{C}_2\text{H}_5\text{OH} \geq 99.7\%$) were purchased from Guangdong Guanghua Sci-Tech., Ltd. Zinc foils (Zn, 99.9%) were purchased from Qinghe Jinxuan Metal Trading Co., Ltd. Epoxide resin (E-51) and poly (vinyl alcohol) (PVA, 87.0-89.0 mol%) were purchased from Shanghai Macklin Biochemical Co., Ltd. ITO-coated glass substrates with a resistance of $6 \Omega \cdot \text{sq}^{-1}$ were purchased from Advent South China Xiang Science and Technology.

2.2. Synthetic Procedure

2.2.1. Synthesis of the Precursor Solution

The precursor solution used for electrodepositing PB thin films was prepared as follows. Firstly, FeCl_3 (10 mmol), $\text{K}_3[\text{Fe}(\text{CN})_6]$ (10 mmol) and KCl (500 mmol) were ultrasonically dissolved in 25 mL deionized water (DI water) to form a uniform greenish-yellow solution[30]. Subsequently, the solution was stirred at 850 rpm at room temperature for 24 h to obtain the precursor solution. For comparison, precursor solutions containing the same components but stirring at 0, 550 and 1150 rpm were also prepared.

2.2.2. Electrodeposition of the Prussian blue Thin Films

$1 \times 2 \text{ cm}^2$ ITO-coated glass substrates were sequentially washed by acetone, ethyl alcohol and DI water, and dried at 70°C in air. The PB thin films were electrodeposited according to the Neff method[31] using a three-electrode system with an ITO-coated glass substrate, a Pt sheet and Ag/AgCl as working electrode, counter electrode and

reference electrode, respectively, at a constant current density of $25 \mu\text{A}\cdot\text{cm}^{-2}$ for 600 s.

After electrodeposition, the PB thin films were rinsed by DI water and then dried at $80\text{ }^{\circ}\text{C}$ for 12 h in vacuum.

2.3. Dual-Band Electrochromic Device Assembly

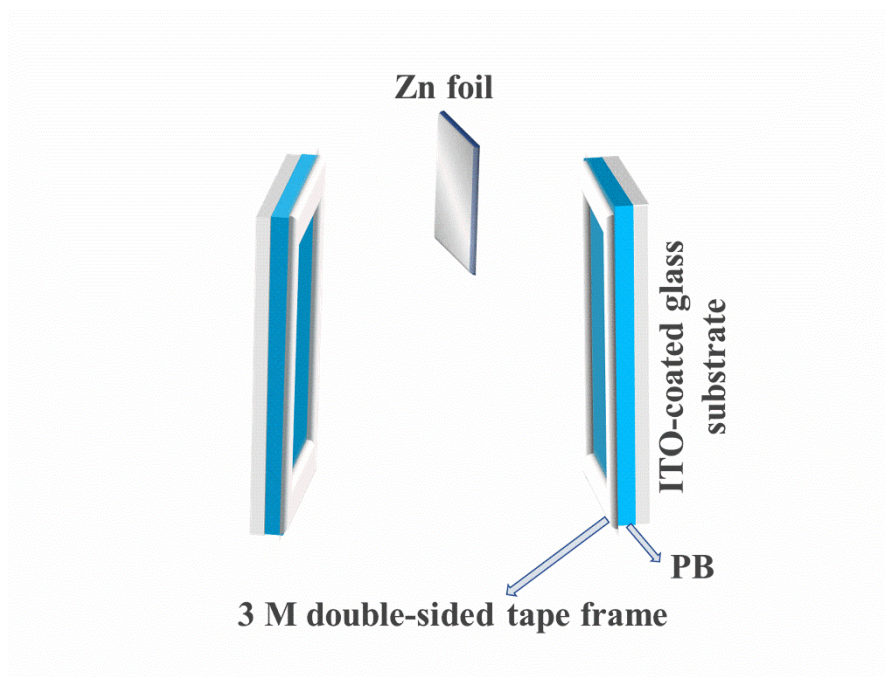
2.3.1. Preparation of the Gel Electrolyte

The gel electrolyte containing PVA, KCl, and hydrochloric acid was selected due to its superior ionic conductivity at room temperature, high optical transparency and electrochemical stability in both VIS and NIR spectral ranges. This polymer gel electrolyte was synthesized by a sol-gel method. Firstly, 0.7 g KCl was added to 100 g DI water, the pH of the solution was adjusted to 4 by adding hydrochloric acid. Then, 8.0 g PVA was dissolved in the solution by continuous stirring at $90\text{ }^{\circ}\text{C}$ for 4 h using oil bath heating.

2.3.2. Assembly of the Dual-Band Electrochromic Device

The DBED with dimensions of $3\times 4\text{ cm}^2$ was assembled by using two PB thin films as the cathodic electrochromic (EC) layers on both sides of the device, a commercial Zn foil ($2\times 2.5\text{ cm}^2$) as the anode, and the above-mentioned gel electrolyte as the electrolyte. Specifically, a 1.0 mm-thick 3 M double-sided tape was laid on the edge of the two PB thin films as a spacer to avoid the short-circuit. The Zn foil was sandwiched between the two facing PB thin films, and the gel electrolyte was injected into the device through the tape with a syringe. The opaque Zn foil can block the incident light, therefore Zn anode was positioned on the upper part of the device to allow the VIS and

NIR light to pass through, as displayed in Schematic 1. Such a three-electrode configuration is more complicated than the traditional 2-electrode electrochromic devices, thus, the device was sealed with epoxide resin finally to improve the sealing performance.



Schematic 1. Schematic illustration of the dual-band electrochromic device assembly.

2.4. Electrochemical and Electrochromic Measurements

Cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS) were performed in a three-electrode electrochemical workstation (CHI760E, Shanghai Chenhua Instruments, Inc.), galvanostatic charge/discharge (GCD) curves were recorded by the three-electrode LAND test system. For the three-electrode system, the PB thin film served as the working electrode, Pt sheet as the counter electrode, and Ag/AgCl as the reference electrode. The electrolyte

used was 0.5 M KCl aqueous solution with a pH of 4 adjusted by adding hydrochloric acid. In-situ transmittance of the PB thin films in the wavelength range of 350–2500 nm was studied together with the electrochemical measurements using an Ocean Optics fiber-optic setup. A vessel containing only the electrolyte was employed to obtain the 100% level for the transmittance of the films. For the DBED, In-situ optical transmittance in the wavelength range of 350–1100 nm was studied in air, air was used as the 100% level for the transmittance of the device without subtracting the transmittance loss due to the ITO layer. The experiments were repeated on hundreds of samples and showed the same results.

2.5. Computational Details

Density Functional Theory calculations were carried out using the Vienna Ab Initio Simulation Package (VASP.6.1.0). We built a model with a face-centered $F\bar{4}3m$ unit cell. Four and eight K^+ cations were placed in the tetrahedral positions of the PB and PW lattices, respectively. The Projector Augmented Wave (PAW) was used to replace the inner electrons. For structure optimization, we apply the small PAW pseudopotentials to all metals in the lattice, extending valence and valence-subshell s- and p-electrons. The electronic structures of PB and PW were calculated by the generalized gradient approximation (GGA) parametrized by Perdew-Burke-Ernzerhof (PBE) with Hubbard parameter U (denoted as GGA+ U), in which the U value was set to 6.0 eV[32]. The energy cutoff of 600 eV and Monkhorst-Pack k-point mesh with $5 \times 5 \times 5$ k-points were used for lattice optimization calculations. For density of state (DOS) calculations, Monkhorst-Pack k-point mesh with $9 \times 9 \times 9$ k-points was used.

2.6. Characterization

A field emission scanning electron microscope (FESEM, Hitachi SU8220) was used to examine the surface structures of the PB thin films with an acceleration voltage of 10 kV. The cross-section was determined by the scanning electron microscope (SEM, ZEISS Gemini 300) with an acceleration voltage of 2 kV. Morphology and structure were examined by transmission electron microscope (TEM, JEM-F200 URP) equipped with an energy dispersive spectrometer (EDS) operating at 200 kV. Raman (LabRAM HR Evolution) was performed using a 50× objective lens and a 532 nm wavelength laser in the wavenumber range of 300–3200 cm^{-1} . ATR-FTIR spectra were recorded by SHIMADZU UV-3600 Plus in the air with a resolution of 0.1 nm. X-ray photoemission spectroscopy (XPS, Thermo Fischer, ESCALAB 250Xi) was carried out using a monochromatic Al K α irradiation source at 14.6 kV (1486.6 eV). The crystalline structure was measured by an X-ray diffractometer (XRD, RIGAKU Ultima IV, 3 KW) using the Cu K α radiation.

3. Results and Discussion

3.1. Characterization of the Prussian blue Thin Films

The preparation procedure of the PB thin films is illustrated in the Experimental Section and Supporting Information (Fig. S1). It is reported that the adjustment of the stirring rates controls the nucleation rates of PB solution[33]. SEM images of the powder obtained by drying the precursor solution stirred at 0, 550, 850 and 1150 rpm are shown in Fig. S2. The as-prepared PB exhibited a more homogeneous nanocube

structure with the increased stirring speed. Consequently, the morphologies and sizes of PB particles are tailorable by controlling the stirring rates during the preparation process of the precursor solution. The corresponding growth mechanism can be explained by the Kossel's model: growth units including atoms, molecules, and ions are adsorbed on the crystal surface, migrating and nucleating on the face to form an ordered and active monolayer, eventually growing layer-by-layer into a cube under ideal conditions[34]. In addition, it was found that the magnetic reactants of FeCl_3 and $\text{K}_3[\text{Fe}(\text{CN})_6]$ would be absorbed onto the magnetic stirrer without ultrasonic treatment. Therefore, the precursor solution was ultrasonicated before stirring, to ensure a good homogeneity of the solution. The PB thin film deposited from the precursor solution stirring at 850 rpm was denoted as 850-KFeHCF. For comparison, PB thin films deposited by the same procedure but using different stirring rates of 0, 550, and 1150 rpm were also prepared, and were denoted as 0-KFeHCF, 550-KFeHCF, and 1150-KFeHCF, respectively.

Crystalline structure and composition of the PB thin films were ascertained firstly. The X-ray diffraction (XRD) pattern of 850-KFeHCF was well matched with the crystal planes of the face-centered cubic (FCC) PB (JCPDS No.73-0687) [29, 35] (Fig. 1a, S3a and S3b). Feature peaks at 2096 and 2144 cm^{-1} in the Raman spectrum of 850-KFeHCF are the fingerprints of the low-spin Fe (LS-Fe) and high-spin Fe (HS-Fe) coordinated with C and N in the cyano group, and their valences are +2 and +3 [29, 36], respectively (Fig. 1b). Peaks at 488 and 596 cm^{-1} correspond to the vibration of Fe–C and Fe–O, respectively [35]. The attenuated total reflectance Fourier transform infrared (ATR-

FTIR) absorption peaks at 3624 and 1618 cm^{-1} (Fig. 1c) can be assigned to the stretching and bending vibrations of water and hydroxyl ($-\text{OH}$) [36, 37], respectively, implying the presence of water in the framework of PB [35, 38]. The peak at 2046 cm^{-1} can be attributed to the characteristic stretching mode of $\text{C}\equiv\text{N}$ [35, 36], and the one at 1417 cm^{-1} is due to the stretching vibration of $\text{N}-\text{H}$ [38]. Notably, the XRD patterns, Raman and ATR-FTIR spectra of 0-KFeHCF, 550-KFeHCF and 1150-KFeHCF (Fig. S3c-3e, S4) are the same as those of 850-KFeHCF. Morphology and nanostructure features of the PB thin films were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The thin films are dense and uniform, with noticeable cracks on the surface (Fig. 1d, Fig. S4a-c). It is noticed that the cracks of 850-KFeHCF are smaller than the other three. Thickness of the PB layer in 550-KFeHCF, 850-KFeHCF and 1150-KFeHCF is ~ 265 nm, while 0-KFeHCF is a little thicker (308 nm) due to the relatively loose structure of the PB particles (Fig. 1e, Fig. S5a'-c'). The TEM image in Fig. 1(f) shows that the PB nanocubes in 850-KFeHCF are of an average size of 150 nm. The lattice fringe with the d-spacing of 0.359 nm in the high-resolution TEM image corresponds to the (220) lattice plane of PB (Fig. 1g), which is in agreement with the XRD result. Meanwhile, the selected-area electron diffraction (SAED) pattern (Fig. 1h) exhibits both electron diffraction halos and spots, indicating that the PB particles are polycrystalline with high crystallinity, the well-defined diffraction halos correspond to the (200) and (220) planes of PB. The homogeneous distribution of C, N, K, and Fe elements is also demonstrated by the elemental mapping in Fig. 1(i), suggesting the high crystal integrity of 850-KFeHCF.

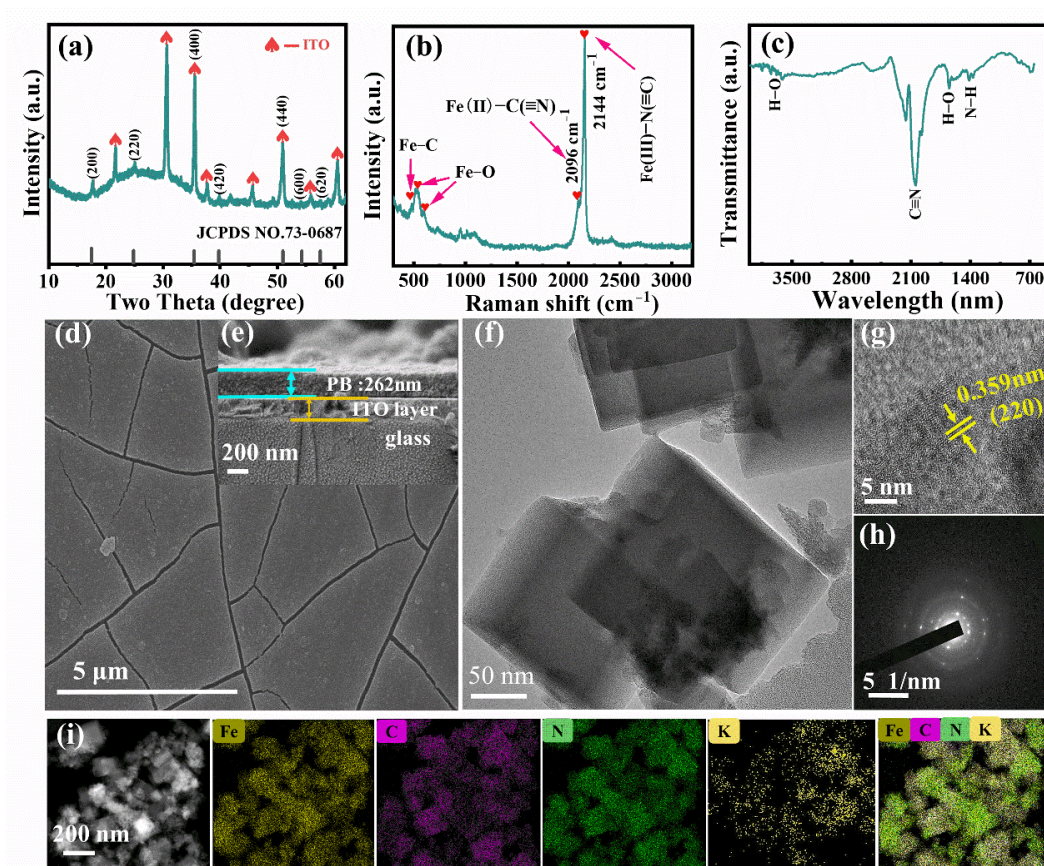


Figure 1. Characterization of 850-KFeHCF. (a) XRD pattern. (b) Raman spectrum. (c) ATR-FTIR spectrum. (d) Surface SEM image. (e) Cross-sectional SEM image. (f) TEM image. (g) High-resolution TEM image. (h) SAED pattern. (i) Elemental distribution of Fe, C, N, and K in the TEM image.

3.2. Effect of Activation of Low-Spin Fe on Durability

Electrochromic smart windows must be durable for decades without essential performance loss. It is therefore important to focus on the durability of the electrochromic films. The cycling stability of the PB thin films was investigated by cyclic voltammetry (CV) and in-situ transmittance spectra in the electrolyte of 0.5 M KCl aqueous solution with a pH of 4. CV measurements were carried out in the potential range of -0.4 to 1.4 V (vs. Ag/AgCl) at a scan rate of $100 \text{ mV} \cdot \text{s}^{-1}$. They started from

the open-circuit potential (OCP) of ~ 0.4 V (vs. Ag/AgCl), scanning to the negative potential direction firstly and then to the positive potential direction. The electrochromic durability of 0-KFeHCF is the worst among the four PB thin films. It started to fall off from the substrate after 80 CV cycles, with a rapid optical modulation decrease in both VIS and NIR spectral ranges (Fig. S6). Improved durability of the PB thin films was achieved by increasing the stirring rate of the precursor solution. 550-KFeHCF degraded substantially after 1100 CV cycles (Fig. S7), in contrast, 850-KFeHCF was still usable after 4000 CV cycles (Fig. 2a-c), exhibiting excellent cycling stability. However, when the stirring rate continued to increase to 1150 rpm, 1150-KFeHCF can only sustain 1200 CV cycles (Fig. S8). The inferior durability could be attributed to the larger cracks and loose structure of the film (Fig. S5c, c'), resulting in easier dissolution into the electrolyte during electrochemical cycling.

CV curves were also used to investigate the effect of the stirring rate on the durability of the PB thin films. Here, we take the most and least durable PB thin films for comparison. In the CV curves of 850-KFeHCF and 0-KFeHCF, two reduction peaks marked peak1 and peak2 can be assigned to the intercalation of K^+ and the concurrent electron to reduce LS-Fe and HS-Fe [39, 40] (Fig. 2d, e). It is specially noted that the peak2 of 850-KFeHCF decreased rapidly within the initial seven cycles, whereas the current density of its peak1 increased continuously during the 100 CV cycles, indicating the activation of LS-Fe. For comparison, the current densities of both peak1 and peak2 of 0-KFeHCF were weakened constantly during CV cycling, and activation of LS-Fe was not observed. It is reported that the origin of the interconversion of Fe(III) and

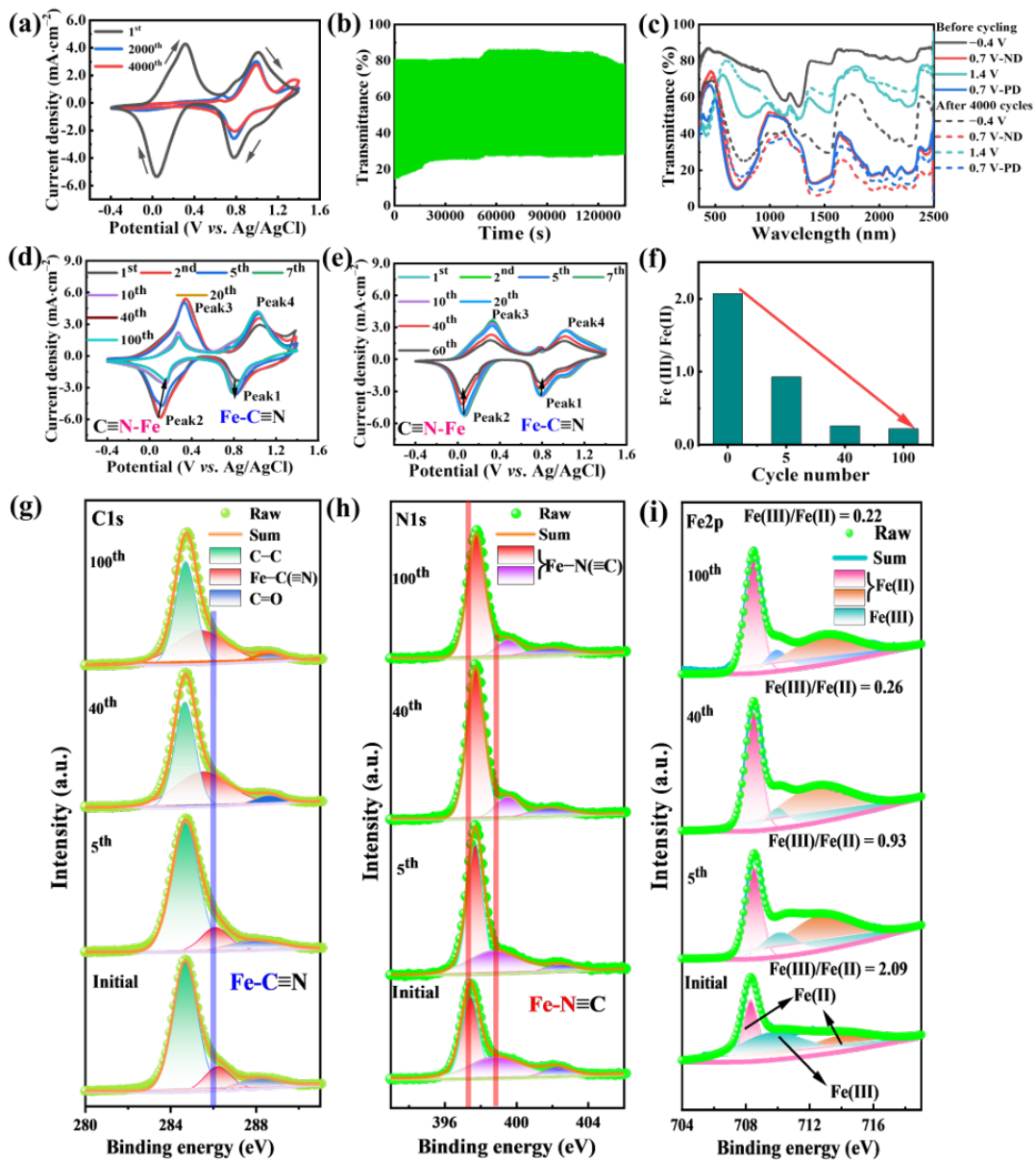


Figure 2. Durability investigation of 850-KFeHCF. (a) CV curves of 850-KFeHCF during 4000 CV cycles. (b) Transmittance modulation at a wavelength of 650 nm. (c) Transmittance spectra before and after 4000 CV cycles. (d, e) CV curve evolution of 850-KFeHCF and 0-KFeHCF, respectively. (f) Fe(III)/Fe(II) ratio at different CV cycles. (g-i) High resolution XPS spectra of C 1s, N 1s and Fe 2p, respectively.

Fe(II) sites lies in the coexistence of two different electronic states that are close in

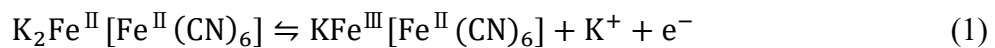
energy, they can be reversibly interconverted into each other by applying an external stimulus such as pressure[41, 42]. Fe in the as-prepared PB was in the high-spin state[29, 43], the high stirring rate with certain pressure will facilitate the HS-Fe to convert to LS-Fe, as illustrated by comparison of the CV curve evolution of 850-KFeHCF and 0-KFeHCF in Fig. 2(d, e).

The redox interaction of intercalation ions (referring to K^+ here) and HS-Fe will result in certain changes in the lattice parameters, whereas that of intercalation ions and LS-Fe does not affect much [35, 44]. Therefore, the X-ray photoemission spectroscopy (XPS) was used to determine the evolution of HS-Fe and LS-Fe in 850-KFeHCF while keeping the film at the OCP. The characteristic binding energy of C at 284.8 eV was used for internal energy calibration. The C 1s spectra of the initial 850-KFeHCF can be deconvoluted into contributions from C–C at 284.8 eV, Fe–C($\equiv$ N) at 285.8 eV and C=O 288.5 eV, as shown in Fig. 2(g) [29, 45]. During CV cycling, the Fe–C($\equiv$ N) peak shifted towards lower binding energy direction, indicating the weakened coordinate bond of Fe–C. Meanwhile, the N 1s spectra in Fig. 2(h) exhibited two main peaks at 397.7 and 399.2 eV attributed to the Fe–N($\equiv$ C) bond [46, 47], and one weak peak at 402.3 eV originated from surface contaminations [47]. The binding energies of the peaks apparently shifted towards higher binding energy direction, demonstrating the enhanced coordinate bond of Fe–N. Such evolution allowed more LS-Fe and less HS-Fe in PB to participate in its electrochromic redox process, which is in agreement with the changes of the redox peaks in Fig. 2(d), and can be further verified by the Fe 2p_{3/2} spectra in Fig. 2(i). The feature peaks at 708.4 and 712.9 eV belong to Fe (II), while the

peak located at 709.8 eV was attributed to Fe (III) [47, 48]. The ratios of Fe (III) and Fe (II) shown in Fig. 2(f) was quantified by integrating the peaks in Fig. 2(i), it was 2.09 and 0.22 before and after 100 CV cycles, respectively. These results show that the improved utilization of LS-Fe can effectively lead to remarkable electrochemical and optical durability of the PB thin films by decreasing the changes of lattice parameters induced by the redox interaction of K^+ and Fe.

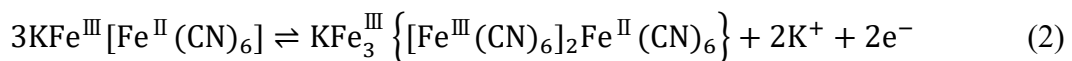
3.3. Electrochromic Performance of the Prussian Blue Thin Films

As shown above, the CV curves of the PB thin films displayed two pairs of redox peaks, corresponding to the reversible intercalation/deintercalation of K^+ . Color changes from Prussian white (PW) to PB, PB to Berlin green (BG), BG to Prussian yellow (PY) happen when scanning from -0.4 to 0.7 V (*vs.* Ag/AgCl), 0.7 to 1.1 V (*vs.* Ag/AgCl), and 1.1 to 1.4 V (*vs.* Ag/AgCl) with K^+ deintercalation. Inverse color changes can be achieved during the opposite scanning from 1.4 to -0.4 V (*vs.* Ag/AgCl) with K^+ intercalation. The photographs at different potentials are displayed in Fig. 3(a). The coloration mechanism can be expressed as [26, 49, 50]



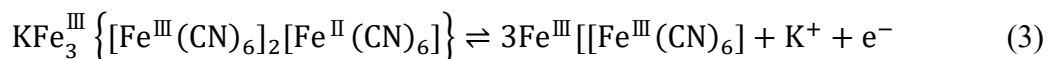
PW

PB



PB

BG



BG

PY

Fig. 3(b) presents the chromaticity diagrams of the PB thin films according to Fig. 3(a) to quantitative their color specifications. The corresponding chromaticity coordinates (x, y) values are shown in Table S1. It clearly shows that the PB thin films present a wide spectral range caused by the reversible color change among transparent, blue, green and yellow. The switching time and coloration efficiency (CE) of the PB thin films were measured in different potential ranges by chronoamperometry (CA). The switching time is defined as the time for bleaching (t_b) and coloration (t_c) to reach 90% of the optical modulation between the fully bleached and colored states. t_b and t_c of 850-KFeHCF from PW to PB are 0.4 and 0.3 s at 650 nm, 1.4 and 1.2 s at 1400 nm, respectively (Fig. 3c), which are much shorter than those of the previous reports (Table S2) and the other three PB thin films (Fig. S9a-c). In addition, t_b and t_c from PB to BG are 2.0 and 1.1 s at 650 nm, 2.1 and 1.7 s at 1400 nm, respectively (Fig. S10a, b), and are 1.1 and 1.2 s at 650 nm, 2.1 and 1.6 s at 1400 nm when switching from BG to PY (Fig. S10c, d), which are also faster than the other three PB thin films (Fig. S11).

The CE is defined as[45]

$$CE = \Delta OD / \Delta Q = \log(T_b / T_c) / \Delta Q \quad (4)$$

where ΔOD is the optical density, ΔQ is the injected charge, T_b and T_c represents the transmittance in the bleached and colored states, respectively. The CE s of 850-KFeHCF thin film in the potential range of -0.4 to 0.7 V (vs. Ag/AgCl), 0.7 to 1.1 V (vs.

Ag/AgCl), and 1.1 to 1.4 V (vs. Ag/AgCl) are $105.6 \text{ cm}^2 \cdot \text{C}^{-1}$, $90.3 \text{ cm}^2 \cdot \text{C}^{-1}$ and $49.2 \text{ cm}^2 \cdot \text{C}^{-1}$, respectively, which are higher than the other three PB thin films (Fig. 3d, Fig. S9a'-c', Fig. S12).

Electrochemical impedance spectroscopy (EIS) was used to analyze the interfacial properties and electrochemical behavior of PB thin films, to illustrate the fast response and high *CE* of 850-KFeHCF. EIS was conducted in a frequency range from 0.01 to 100 kHz at the OCP. Fig. 3(e) displays the experimental and fitting EIS curves of 850-KFeHCF, inset is the magnified diagram in the high frequency range. The charge transfer resistance (R_{ct}) at the interface of the electrolyte and the PB thin film is 5.5Ω , much smaller than those of the other three thin films (7.2Ω , 6.6Ω and 26.4Ω for 0-KFeHCF, 550-KFeHCF, 1150-KFeHCF, respectively) (Fig. S13a-c). In addition, the diffusion (Warburg) element Z_W inside the PB layer is 34.8Ω , which is much smaller than those of the other three thin films (88.7Ω , 132.5Ω and 66.7Ω for 0-KFeHCF, 550-KFeHCF, 1150-KFeHCF, respectively). The excellent charge transfer and ion diffusion ability allows fast response and high *CE* of 850-KFeHCF. The above results show that 850-KFeHCF presents superior optical modulation, cycling stability, switching speed and *CE*. Therefore, it was selected for the following study.

As shown in Fig. 3(f), 850-KFeHCF exhibited a large dual-band optical modulation of 76.6% at 650 nm, 79.8% at 1400 nm and 79.6% at 2000 nm, which is superior than most of the dual-band electrochromic materials that previously reported (Table S2). It should be mentioned that the spectra are not flat, especially at 0.7 V (vs. Ag/AgCl). Part of VIS and NIR light still passed through or was blocked by PB the thin

film. Therefore, the transmittance of 850-KFeHCF in the VIS (380–780 nm) and NIR (780–2500 nm) regions are employed to evaluate its solar irradiation modulation by using Equation (5, 6) [11, 20]

$$T_{sol} = \frac{\int T(\lambda)\psi(\lambda)d\lambda}{\int \psi(\lambda)d\lambda} \quad (5)$$

$$\Delta T_{sol} = T_{sol,high T} - T_{sol,low T} \quad (6)$$

where T_{sol} represents the integrated solar irradiance transmittance, $T(\lambda)$ represents the transmittance at a wavelength of λ , and $\psi(\lambda)$ is the solar irradiance at 1.5 air mass. ΔT_{sol} , $T_{sol,high T}$ and $T_{sol,low T}$ are the solar irradiance transmittance modulation, the highest integrated solar irradiance transmittance and the lowest integrated solar irradiance transmittance, respectively. The results are shown in Fig. 3(g). At -0.4 V (vs. Ag/AgCl), 850-KFeHCF is transparent in the both VIS and NIR spectral ranges while maintaining an excellent VIS (77.0%) and NIR (75.8%) transmittance, corresponding to the bright and warm mode as shown in Fig. 3(h). At 0.7 V (vs. Ag/AgCl), 850-KFeHCF blocks 77.9% of the total solar energy, 75.6% of the visible light, corresponding to the dark and cool mode. The colored mode operating at 1.1 and 1.4 V (vs. Ag/AgCl) allow most of the VIS light (54.5% at 1.1 V vs. Ag/AgCl, 63.2% at 1.4 V vs. Ag/AgCl) to pass through while blocking the NIR light (50.1% at 1.1 V vs. Ag/AgCl, 31.8% at 1.4 V vs. Ag/AgCl), as illustrated in Fig. 3(h). The film can switch among these modes according to personal preference, to decrease the energy consumption of the buildings for lighting and air conditioning.

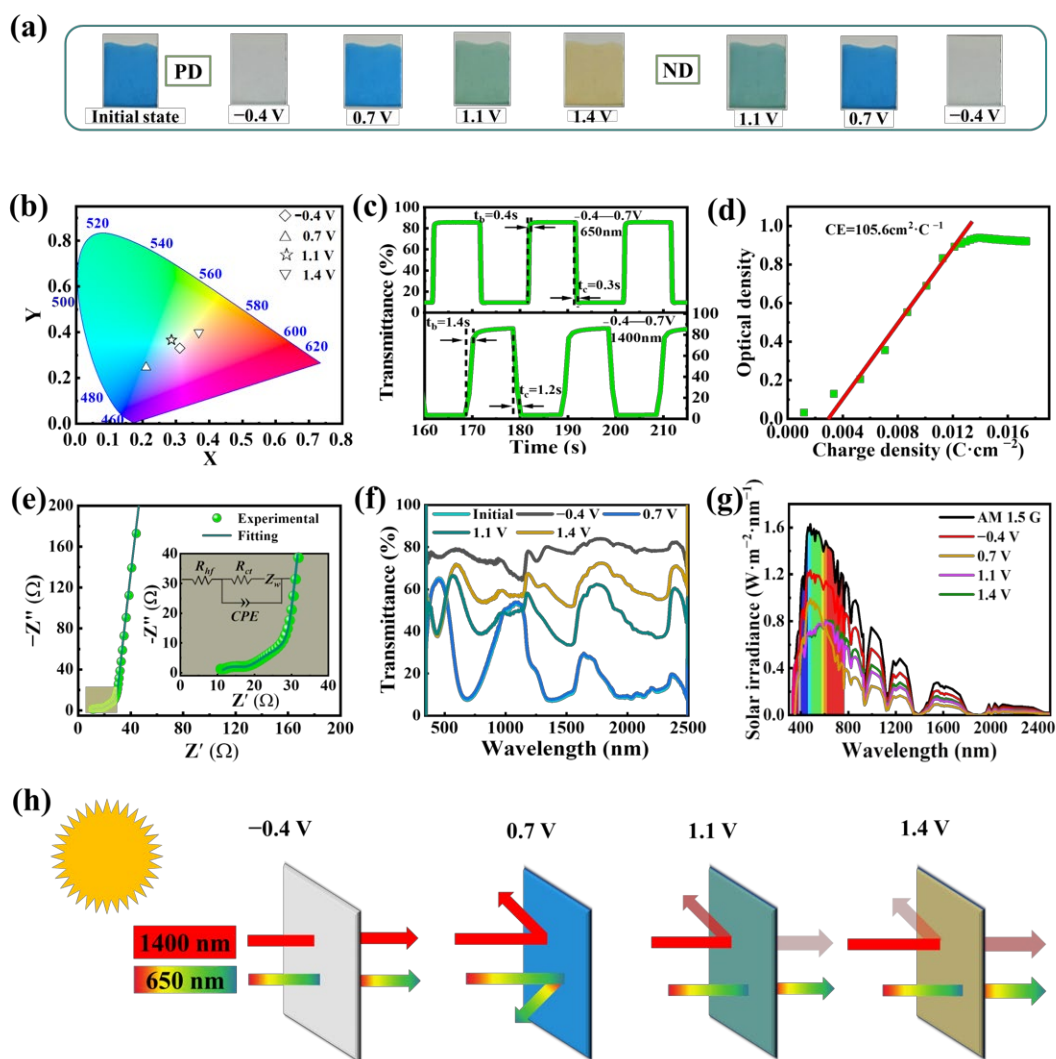


Figure 3. Electrochromic performance of 850-KFeHCF. (a) The digital photos. (b) CIE 1931 chromaticity diagram with (x, y) . (x, y) data were calculated from the RGB values extracted from the photos in (a) by Photoshop. (c) Switching time at 650 and 1400 nm within at $(-0.4 \text{ V vs. Ag/AgCl})$ for 10 s followed by $(0.7 \text{ V vs. Ag/AgCl})$ for 10 s. (d) Coloration efficiency. (e) Nyquist plots and the circuit model used to fit them. (f) Transmittance spectra recorded at different potentials during CV cycling. (g) Solar irradiance spectra at the bright and warm $(-0.4 \text{ V vs. Ag/AgCl})$, dark and cool $(0.7 \text{ V vs. Ag/AgCl})$, and colored $(1.1 \text{ and } 1.4 \text{ V vs. Ag/AgCl})$ modes, respectively. (h) Illustration of three distinct modes of operation.

3.4. Energy Storage of the 850-KFeHCF Thin Film

The energy storage performance was measured by galvanostatic charge-discharge (GCD) and CV within the potential range of -0.4 to 1.4 V (vs. Ag/AgCl) in a three-electrode system. As shown in Fig. 4(a), 850-KFeHCF showed a higher capacity of $51 \text{ mAh}\cdot\text{g}^{-1}$ than $40 \text{ mAh}\cdot\text{g}^{-1}$ for 0-KFeHCF. It is reported that utilization of low-spin Fe benefits superior energy storage performance[29]. Fig. 2(g) provided an unambiguous evidence that the electrochemical reaction relaxed the electrostatic restriction on low-spin Fe imposed by C and enabled more Fe active sites to participate in the redox reaction. Therefore, the improved energy storage performance of 850-KFeHCF is because more LS-Fe ions were involved in the redox process due to the decreased binding energy of C-Fe (low-spin).

As revealed by the EIS data, the reaction rate of PB is controlled by K^+ diffusion, which requires sufficient time. Therefore, the relatively slow scan rates (20 to $50 \text{ mV}\cdot\text{s}^{-1}$) were chosen to analyze the charge storage mechanism and diffusion kinetics of 850-KFeHCF (Fig. 4b). Notably, the profiles at all scan rates manifested two pairs of reversible redox peaks as above, indicating excellent kinetic. According to Equation (7) and (8) [44]

$$i = av^b \quad (7)$$

$$\log i = \log a + b \log v \quad (8)$$

where a and b are both adjustable parameters, i is the current, v is the scan rate. When the value of b approaches 1, the redox process is surface-controlled (capacitive-type behavior); while it is equal to 0.5, the process is ion-diffusion dominated (battery-type

behavior) [12]. As shown in Fig. 4(c), the values of b corresponding to the four redox peaks were 0.80, 0.81, 0.71, and 0.51, suggesting the mixed charge storage mechanism or might be a fractal structure of the film surface or pore surfaces.

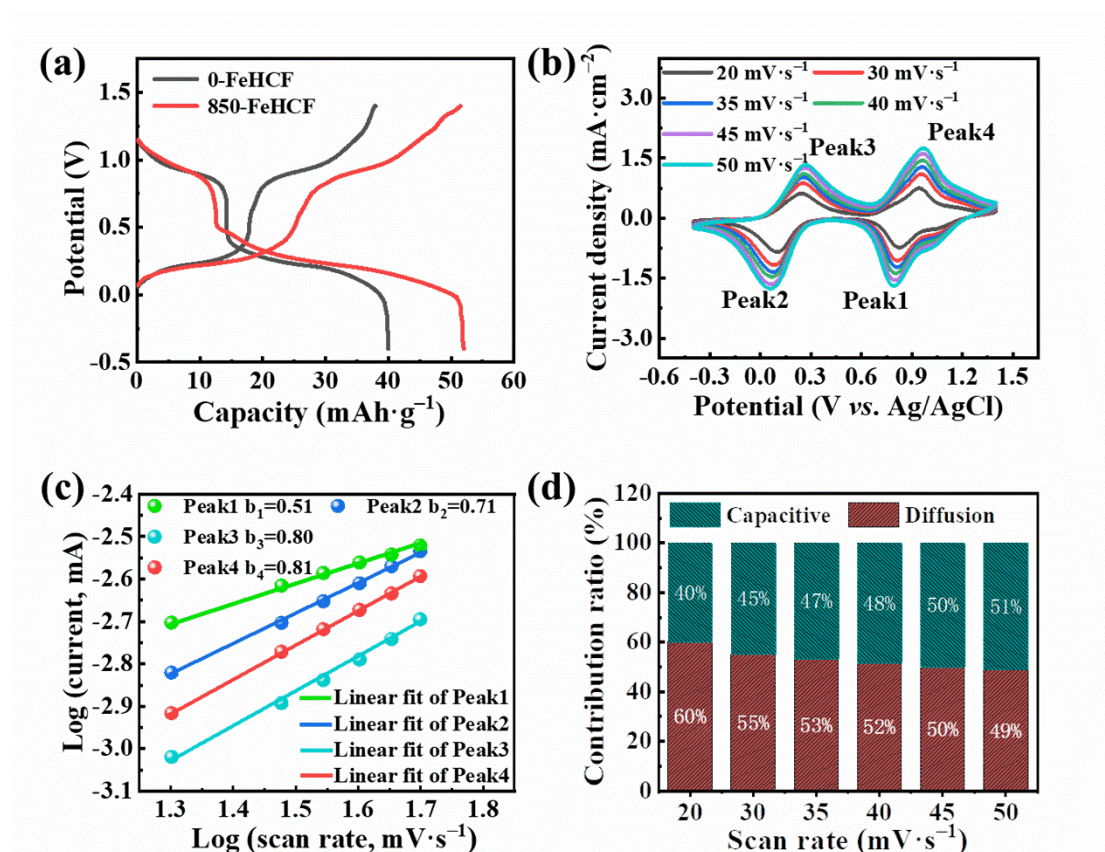


Figure 4. The energy storage performance of 850-KFeHCF. (a) GCD curves of 0-KFeHCF and 850-KFeHCF at a current density of 0.25 A·g⁻¹. (b) CV curves measured at various scan rates. (c) Logarithm relationship between oxidation/reduction peak current density and scan rates. (d) Capacitive and diffusion contributions at various scan rates.

Contributions of the capacitive-type and battery-type charge storage in 850-KFeHCF can be quantified according to Equation (9, 10) [51]

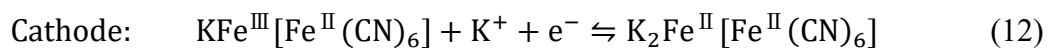
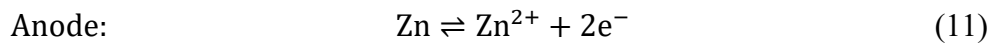
$$i = k_1 v + k_2 v^{1/2} \quad (9)$$

$$i/v^{1/2} = k_1 v^{1/2} + k_2 \quad (10)$$

where $k_1 v$ and $k_2 v^{1/2}$ represent ratios of the capacitive-type and battery-type capacitance, respectively. The results show that the ratio of the battery-type capacitance decreased from 60% to 49% with the scan rate increasing from 0.02 to 0.05 V·s⁻¹, indicating diffusion-controlled charge storage dominated (Fig. 4d). Moreover, the plots of redox peaks at various scan rates show excellent linearity ($R^2 \geq 0.99$) (Fig. S14), implying the redox process is related to the deep penetration of K⁺ ions.

3.5. Electrochromic Performance and Energy Storage of the Dual-Band Electrochromic Device

The DBED using 850-KFeHCF thin films as electrochromic layers was further constructed. It can be switched among the above-mentioned colors (Fig. 5b). As limited by the durable potential range of the ITO conductive layer and the potential window of the electrolyte, measurement of the electrochromic performance of the DBED was carried out in the potential range of 0.3 to 2.4 V in air. CV curves of the DBED is shown in Fig. S15. A pair of redox peaks located at 0.92 and 1.45 V, corresponding to the reduction of PB to PW and oxidation of PW to PB as the following equation



The electrochromic and energy storage processes of the DBED are schematically demonstrated in Fig. 5(a). The DBED presents excellent dual-band electrochromic performance, which can modulate the VIS and NIR light selectively in bright and warm, dark and cool modes with large ΔT of 76.7%, 56.1% at 650 and 900 nm, respectively. This is quite high considering that light must go through two sheets of ITO-coated glass substrates and the gel electrolyte which absorb the NIR light a lot. Transmittance at 650 and 900 nm during CA cycling by switching the potential between 0.3 and 2.4 V with an interval of 10 s were monitored to evaluate the switching time of the DBED in the VIS and NIR regions. t_b and t_c of the DBED are 1.3 and 1.6 s at 650 nm, 1.6 and 1.6 s at 900 nm, corresponding to the discharging and charging processes, respectively (Fig. 5c, d). The DBED exhibits the more excellent performance of electrochromic optical modulation and switching time between the VIS and NIR regions, compared to previously reported electrochromic materials (Table S2).

Interestingly, we found that the as-prepared DBED can be used as an energy-saving electrochromic smart window without applying any external bias potential. As shown in Fig. 5(a) and Supplementary Video 1, the DBED can be quickly bleached to a colorless state (Fig. 5e) by connecting the two PB cathodes and the Zn anode (i.e. connecting S1 and S2) without applying any external bias. In addition, the DBED can be charged to the colored state (Fig. 5f) using a commercial PV solar panel (1.8 V) under ambient solar irradiation by simply connecting S3, S4, and S5, as shown in Fig. 5(a) and Supplementary Video 2. The transmittance of the bleached and colored DBEM

was the same as those obtained when applying an external voltage (Fig. 5b). That is to say, the solar irradiation can be reversibly modulated into the interior based on personal preference and weather conditions. Scenery view and natural daylighting/heating can be realized by simply connect/disconnect the cathodes and the anode, thus reducing the lighting, heating and cooling energy consumption of buildings. Moreover, due to the energy storage ability of the DBED, it supplied a voltage of 2.02 V after the charging/coloration process by solar irradiation (Fig. 5g), which can light up a red LED (Fig. 5h). Therefore, the solar energy stored in the DBED can subsequently be used to light up the lights for further energy saving.

Another key function of the electrochromic device is the optical memory (bistability). It features zero-energy consumption while having the ability to maintain the colored and bleached states without applying any external energy input. It is evaluated at the OCP. Fig. 5(i) shows the transmittance variation of the DBED by applying an external potential (0.3 V for bleaching and 2.4 V for coloring) for 100 s and then powered it off. During the recorded 96 h, the transmittance of the bleached DBED only decreased 3.0% (from 78.1% to 75.1%), while it increased 5.0% for the colored state (from 3.3% increase to 8.3%). This excellent bistability performance is much better than the previous reports (Table S2). The corresponding transmittance spectra of the DBED before and after 96 h were shown in Fig. S16. It decays very slowly. Moreover, the DBED also exhibits an excellent cycling stability, retaining 93.0% of its initial transmittance modulation after 500 CA cycles (Fig. 5j, k). Such an excellent cycling stability is better than the previous reports (Table S2).

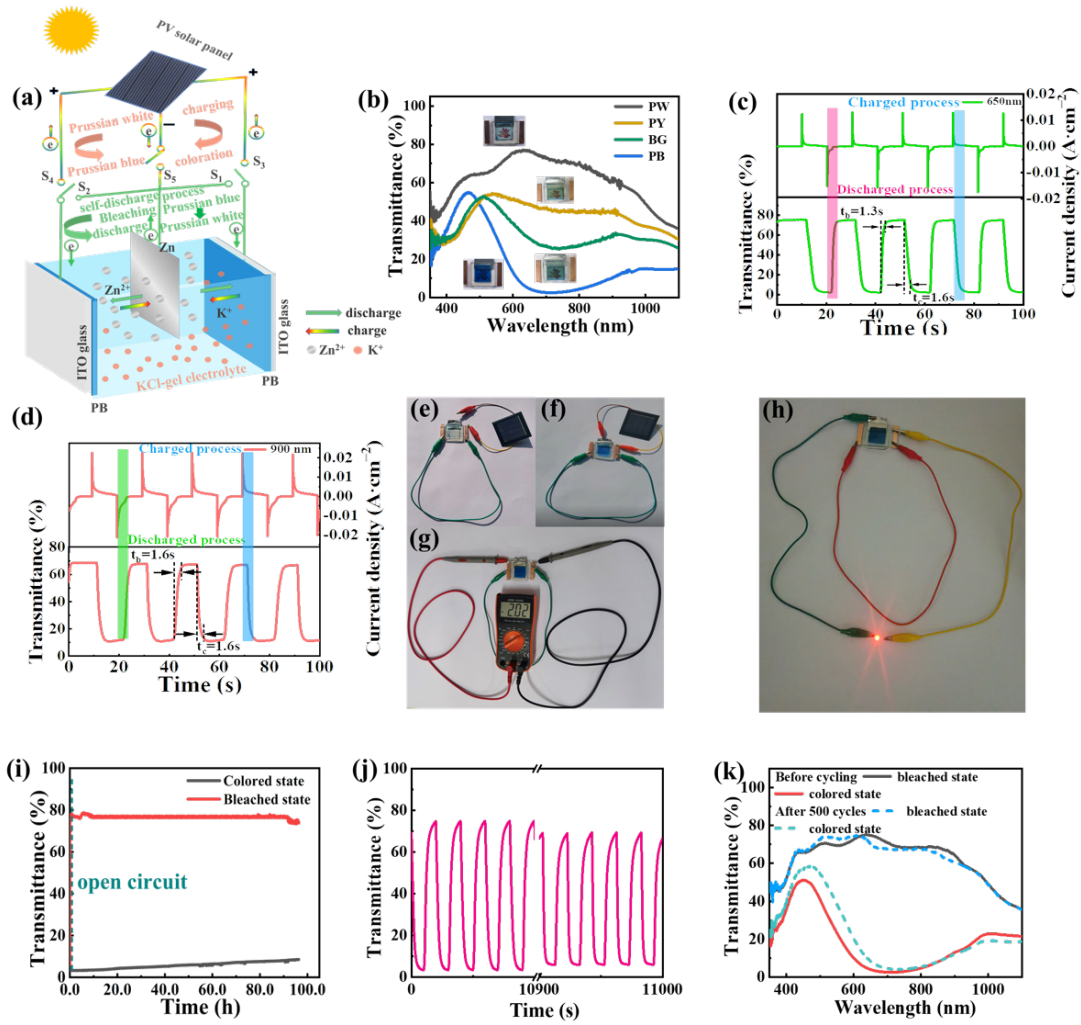


Figure 5. Energy storage and electrochromic performance of the DBED. (a) Schematic illustration of the electrochromic and energy storage processes. (b) Transmittance spectra. Inset shows the digital photos of the DBED. (c, d) CA curves and corresponding in-situ transmittance modulation at 650 and 900 nm, respectively. (e, f) The coloration process of the DBED by connecting the PV solar panel. (g) Voltage supplied by the colored DBED. (h) A red LED powered by the DBED. (i) Memory effect at OCP after a coloring or bleaching stage. (j) Durability. (k) Transmittance spectra before and after 500 CA cycles.

3.6. Density Functional Theory (DFT) Calculations

The coloration mechanism of the DBED was illustrated by calculating the

electronic structure of PB subjected to K^+ intercalation/deintercalation. Fig. 6(a, b) show the total density of electron states (TDOS) of PB and PW. Their partial DOS (PDOS) are also calculated and presented in Fig. S(17a, b). TDOS and PDOS contributions plotted in the positive and negative directions from the zero line on the y axis denote spin-up states and spin-down states, respectively.

The Fermi level of PB is clearly situated in the bandgap close to the valence band (Fig. 6a). During the bleaching process, K^+ intercalated to the tetrahedral holes of PB (Fig. 6a'), accompanied by the electron intercalation through an external circuit to compensate for the charge imbalance. The inserted electrons filled the high-energy states of the valence band and the low-energy states of the conduction band, thus the Fermi level moves up to the conduction band (Fig. 6b) and yields high optical transmittance in both VIS and NIR regions. In contrast, during the coloration process from PW to PB, K^+ deintercalation from the tetrahedral holes of PW (Fig. 6b') and the electrons are extracted from the valence band, leading to the Fermi level shift to the valence band (Fig. 6a) and the increased optical absorption (or decreased optical transmittance) in both VIS and NIR regions.

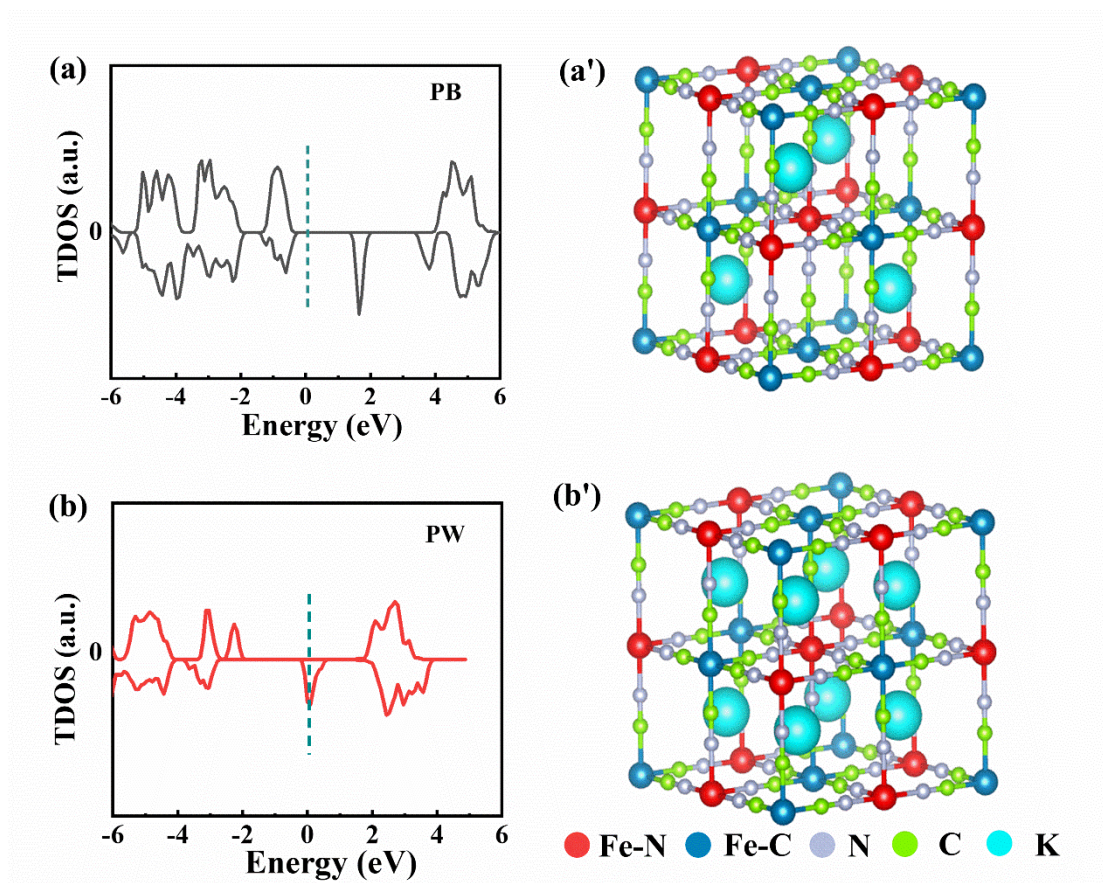


Figure 6. Total densities of electron states and the atomic structures. (a, a') PB, (b, b') PW.

4. Conclusions

In summary, we explored a facile method to prepare the durable single-component PB thin film that can selectively and independently modulate the VIS and NIR light for the first time. The low-spin Fe redox-based PB thin film can serve as the dual-band platform with excellent electrochromic and energy storage performance. The optimized PB thin film can modulate the VIS and NIR light dynamically and independently, providing an excellent optical modulation in the solar spectrum. In particular, the 850-KFeHCF thin film presented large optical modulation (76.6% at 650 nm, 79.8% at 1400 nm and 79.6% at 2000 nm), high CE ($105.6 \text{ cm}^2 \cdot \text{C}^{-1}$), high charge capacity (51

mAh·g⁻¹ at 0.25 A·g⁻¹), fast switching speed (0.4 and 0.3 s for bleaching and coloration at 650 nm, 1.4 and 1.2 s for bleaching and coloration at 1400 nm), and long-term durability (> 4000 cycles). The DBDE using 850-KFeHCF is also fabricated and investigated. Large optical modulation (76.7% at 650 nm, 56.1% at 900 nm), outstanding optical memory effect (>96 h), fast switching speed (1.3 and 1.6 s for bleaching and coloration at 650 nm, 1.6 and 1.6 s for bleaching and coloration at 900 nm), and excellent durability (93.0% transmittance modulation retention after 500 cycles) are achieved. The DBED can be quickly bleached to colorless by connecting the two PB cathodes and the Zn anode, and be colored utilizing the PV solar panel under solar irradiation. Moreover, the energy stored at the colored state of the DBED can be further used for other electric equipment like LEDs. Finally, the coloration mechanism of the DBED was illustrated by the DFT calculations. The PB thin film and its DBED with remarkable electrochromic and energy storage performance exhibit promising practical applications for next-generation intelligent systems and the fields of displays and camouflage.

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