Electropolymerized polyaniline/manganese iron oxide hybrids with an enhanced color switching response and electrochemical energy storage†

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Polyaniline (PANI) nanocomposites embedded with manganese iron oxide (MnFe2O4) nanoparticles were prepared as thin films by electropolymerizing aniline monomers onto indium tin oxide (ITO) glass slides pre-spin-coated with MnFe2O4 nanoparticles. The shift of the characteristic peaks of PANI/MnFe2O4 in UV-visible absorption spectra and Fourier transform infrared (FT-IR) spectra indicates the formation of composite films and the chemical interaction between the PANI matrix and MnFe2O4 particles. A coloration efficiency of 92.31 cm² C⁻¹ was obtained for the PANI/MnFe2O4 nanocomposite film, higher than that of the pristine PANI film, 80.13 cm² C⁻¹, suggesting a synergistic effect between the MnFe2O4 particles and the PANI matrix. An enhanced areal capacitance of 4.46 mF cm⁻² was also achieved in the PANI/MnFe2O4 nanocomposite film compared with 3.95 mF cm⁻² in the pristine PANI film by CV at a scan rate of 5 mV s⁻¹. The enhanced performances of the composite films were attributed to the pseudocapacitive properties of MnFe2O4 and rougher morphology caused by the embedment of MnFe2O4 particles into the PANI matrix. Finally, the sulfuric acid (H2SO4) concentration and temperature effects on the supercapacitive behavior of the pristine PANI and PANI/MnFe2O4 nanocomposite films were studied, suggesting the positive effects of decreasing H2SO4 concentration and increasing temperature in a low temperature range; higher temperatures can destroy the PANI structure and cause the degradation of PANI.

1. Introduction

As a promising type of sustainable and renewable energy storage device, electrochemical capacitors have merits such as long cycle life, lower maintenance cost and environmental friendliness.1,2 They have been widely applied in portable electronic devices, hybrid electric vehicles, memory backup systems, and large industrial equipment.3–5 The lower power densities of batteries and the lower energy densities of conventional capacitors make electrochemical capacitors a good choice to fill in the gap between the batteries and the conventional electrostatic capacitors.6,7 Electrochemical capacitors are classified into two categories based on different charge storage mechanisms, i.e., (i) electric double layer capacitors (EDLCs), which proceed through a non-faradic process based on ion adsorption between the interfaces of electrodes and electrolytes; and (ii) pseudocapacitors employing a faradic process that store energy through fast surface redox reactions.8 Even though carbon materials are usually employed as EDLC electrodes due to their long cycle life (>10⁵ cycles), their applications are largely restricted by their low energy densities.9 Pseudocapacitors based on the redox reactions of metal oxides and conducting polymer materials are emerging as more competitive candidates due to their higher specific capacitance.10–12 Conducting polymers have received a lot of research interest in pseudocapacitors due to their several beneficial characteristics including tunable electrical properties, flexibility, and high processability from solutions.13,14 Solution-processable conducting polymers have been widely investigated as electrode materials because of the facile inexpensive way to form thin-film electrodes, which offer a tunable thickness, high conductivity, and excellent optical transparency and electrochromism.15,16 In
particular, polyaniline (PANI) has attracted much more attention due to its higher electrochemical and thermal stabilities, low cost, and high conductivity. In particular, highly reversible pseudocapacitance arising from the versatile redox reactions and the corresponding color change make PANI a promising candidate for both electrochemical capacitors and electrochboroic (EC) applications.

Nowadays, different PANI/metal oxide composites have been prepared and employed for various applications. For example, PANI/BaTiO3, PANI/SnO2, PANI/Co3O4, PANI/TiO2, PANI/V2O5 and PANI/WO3 have been investigated demonstrating improved magnetic, dielectric, humidity sensing, catalytic, electrochromic and supercapacitive properties. Furthermore, much work has been focused on spinel transition metal oxides (AB2O4), which contain two metal elements providing the feasibility to tune the energy density and working voltage by varying the metal content. Among the AB2O4, manganese iron oxide (MnFe2O4) as a common ferrite material has been widely utilized in magnetic recording and microwave absorption fields. MnFe2O4 was also reported as an anode material for supercapacitors. Unfortunately, the supercapacitive performance of the MnFe2O4-based electrodes is not satisfactory due to the high charge-transfer resistance originating from the poor electrical conductivity of MnFe2O4. The hybrid of conductive PANI and MnFe2O4 is anticipated to address this challenge and is promising for combined electrochromic and supercapacitive applications.

Different forms of materials have been employed to incorporate metal oxides into polymers to optimize the properties of the synthesized nanocomposites. A film as an efficient one can provide a two-dimensional (2D) nanostructure thus decreasing the diffusion path length of ions and leading to high charge-discharge rates. Nowadays, the structure and composition of the electrode as the main factors affecting the performances of supercapacitors have been widely investigated. However, few studies have been conducted regarding the effects of operating conditions like electrolyte concentration and temperature, which are inevitable factors that need to be considered during practical applications. To the best of our knowledge, a comprehensive study of the electrochemical and electrochromic properties as well as the electrolyte concentration and temperature effects on the supercapacitive behavior of the PANI/MnFe2O4 nanocomposite films has not been carried out yet.

In this work, the PANI/MnFe2O4 nanocomposite thin films were prepared by a facile combined spin coating and electropolymerization method, i.e., the aniline monomers in sulfuric acid solutions were electodeposited onto MnFe2O4 coated indium tin oxide (ITO) glass slides, which were prepared by a spin coating technique. Pristine PANI and pure MnFe2O4 films on the ITO glass were also prepared using the same method as control experiments. The structure and morphology of the composite films were studied using Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). The optical properties and capacitive behaviors of the composite films were investigated using ultraviolet-visible (UV-visible) absorption spectroscopy, spectrophotometry (SEC), cyclic voltammetry (CV) and galvanostatic charge-discharge measurements. The electrolyte concentration and temperature effects on the supercapacitive behavior of the PANI/MnFe2O4 nanocomposite films were investigated by varying the H2SO4 concentration from 0.5 to 2.0 M and applying different temperatures as 2, 22 and 50 °C.

2. Experimental

2.1 Materials

Aniline (C6H5·H·N, ≥99.0%), sulfuric acid (H2SO4, 95.0–98.0%) and hydrogen peroxide solution (PERDROGEN® 30% H2O2 (w/w)), ethanol (HPLC, 99.8%), and ammonium hydroxide (NH4OH, 28.86 wt%) were all purchased from Fisher Scientific. Manganese iron oxide nanopowders (MnFe2O4, 99.99%, 28 nm, stock #: US 3912, CAS # 1344-43-0) were purchased from Nanostructured & Amorphous Materials, Inc., USA. The microscope glass slides and indium tin oxide (ITO) coated glass slides were obtained from Fisher and NanoSci Inc, respectively. Before the usage of the ITO coated glass slides, they were first sonicated in ethanol for 10 min, and then immersed in an aqueous solution containing 4.0 mL NH4OH, 4.0 mL H2O2 and 20.0 mL deionized water for 10 min. Finally, the ITO glasses were sonicated in deionized water for another 10 min and dried naturally. Deionized water was used throughout the experiments.

2.2 Thin film electrode preparation

For the synthesis of a MnFe2O4 film, 1.0 mg MnFe2O4 was dissolved in 10.0 mL ethanol solution under 30 min sonication. The MnFe2O4 film was prepared by drop casting about 1.0 mL MnFe2O4 suspension onto the ITO glass and maintained at 2000 rpm for 20 s. The film was dried naturally overnight. The electropolymerization of aniline onto the as-treated ITO glass or formed MnFe2O4 film was performed on an electrochemical working station VersaSTAT 4 potentiostat (Princeton Applied Research). A typical three electrode electrochemical cell was employed, in which a saturated calomel electrode (SCE) served as the reference electrode, a platinum (Pt) wire served as the counter electrode and the MnFe2O4 coated ITO glass or bare ITO glass slide with an effective area of 4.0 cm2 served as the working electrode. A long path length home-made spectrophotometric cell with a Teflon cell body with front and rear windows clamped with two steel plates was used when the ITO glass slide was used as the working electrode. A long path length home-made spectrophotometric cell with a Teflon cell body with front and rear windows clamped with two steel plates was used when the ITO glass slide was used as the working electrode for optical characterization. A typical electrochemical polymerization was performed for 10 cycles scanned back and forth from 0 to +1.2 V vs. SCE at a scan rate of 50 mV s-1 in 0.5 M H2SO4 aqueous solution containing 0.1 M aniline.

2.3 Characterization

The morphologies of the thin films grown on the ITO glass slides were characterized using a scanning electron microscope (SEM, Hitachi S4300). An FT-IR spectrometer coupled with an ATR accessory (Bruker Inc. Vector 22) was used to characterize the surface functionality of the thin films grown on the ITO glass slides in the range of 2000 to 700 cm-1 at a resolution of...
The electrochemical behaviors of the pure MnFe2O4 film, pristine PANI film, and PANI/MnFe2O4 nanocomposite film were investigated by CV scanned from −0.2 to 0.8 V vs. SCE at a series of scan rates and galvanostatic charge–discharge measurements with different current densities in 1.0 M H2SO4 aqueous solution. Electrochemical impedance spectroscopy (EIS) was carried out in the frequency range from 100 000 to 0.01 Hz at a 5 mV amplitude referring to the open circuit potential (OCP). The spectroelectrochemistry measurements were performed on a Jasco V-670 spectrophotometer coupled with a potentiostat for applying electrochemical potentials. In situ chronocoulometry (CC) was conducted under square-wave voltages of 0.8 and −0.2 V with a pulse width of 20 s. The electrolyte concentration and temperature effects on the supercapacitive behaviors were investigated by varying the H2SO4 concentration from 0.5 to 2.0 M and applying different temperatures of 2, 22 and 50 °C using the same measurements as CV, galvanostatic charge–discharge and EIS.

### 3. Results and discussion

#### 3.1 Materials characterization

The cyclic voltammetry (CV) curves obtained during the potentiodynamic electropolymerization growth of PANI onto the bare MnFe2O4 coated ITO glass slides are shown in Fig. S1(A and B).† The pristine PANI and PANI/MnFe2O4 nanocomposite films are prepared by sweeping the potential between 0 and 1.2 V at a scan rate of 50 mV s⁻¹ in 0.5 M H2SO4 solution containing 0.1 M aniline. The film growth can be verified by the monotonously increased current with increasing the CV cycle. Similar CV patterns except lower anodic current peaks are observed for the PANI/MnFe2O4 nanocomposite film growth, which is probably attributed to the increased resistance due to the introduction of the MnFe2O4 film on the ITO glass slide. In addition, it is observed that the anodic irreversible peaks started at around +0.9 V for both pristine PANI and PANI/MnFe2O4 nanocomposite films, indicating the oxidation of aniline monomers and the initiation of the electropolymerization of PANI.

The mass of monomers electropolymerized onto the substrate can be roughly estimated from the total faradic charge consumed in electropolymerization assuming an average of 2.5 electrons per aniline monomer in emeraldine.

\[
m = \frac{CM_an}{2.5F}
\]

where \(m\) is the mass of PANI polymerized onto the substrate, in grams (g); \(C\) is the total faradic charge consumed in electropolymerization, in coulomb (C), \(M_an\) is the molecular mass of aniline monomers (93.13 g mol⁻¹), and \(F\) is the Faraday constant (96 485 C mol⁻¹). About 0.032 and 0.029 µg polymers were calculated for the pristine PANI film and PANI/MnFe2O4 nanocomposite film, respectively. The lower amount of PANI in the PANI/MnFe2O4 nanocomposite film further confirms the increased resistance caused by the introduced MnFe2O4.

Fig. 1(A) displays the FT-IR spectra of the pristine PANI and PANI/MnFe2O4 nanocomposite films in the region of 2000–700 cm⁻¹. For the pristine PANI thin film onto ITO, Fig. 1(A)(a), the peaks at 1559 and 1483 cm⁻¹ correspond to the characteristic C=C stretching mode of the quinoid and benzenoid rings, respectively. The peaks at 1299 and 1234 cm⁻¹ are attributed to the C–N and C≡N stretching modes. The peaks at 1126 and 796 cm⁻¹ are assigned to the in-plane and out-of-plane bending of the C–H. For the PANI/MnFe2O4 nanocomposite film, Fig. 1(A)(b), the characteristic peaks of PANI are mainly observed due to the dominant PANI. However, it is noticed that all the characteristic peaks corresponding to PANI in the PANI/MnFe2O4 nanocomposite film are shifting to higher wave-numbers compared with those of the pristine PANI film, indicating the interactions between MnFe2O4 and PANI due to the π–π stacking and electrostatic interactions as well as hydrogen bonding between MnFe2O4 and the –NH group of PANI.

Fig. 1(B) represents the UV-visible spectra of the pure MnFe2O4, pristine PANI and MnFe2O4/PANI nanocomposite

![FT-IR spectra](image)

Fig. 1 (A) FT-IR spectra of the (a) pristine PANI film and (b) PANI/MnFe2O4 nanocomposite film, and (B) UV-visible absorption spectra of the (a) pure MnFe2O4 film, (b) pristine PANI film, and (c) PANI/MnFe2O4 nanocomposite film, respectively.
films in the wavelength range of 200–800 nm. The FT-IR spectrum of MnFe₂O₄ (Fig. 1[B][a]) displays characteristic peaks of ferrite at around ~568 cm⁻¹, corresponding to the stretching vibration of tetrahedral group complexes.⁴¹ For the pristine PANI films, Fig. 1[B][b], two distinct absorption bands located at around 300 and 600 nm are assigned to the excitation of amine (π–π* electronic transition of the benzenoid ring) and imine (electron transition from the benzenoid to quinoid ring) of polymer chains.⁴²⁴³ A similar absorption spectrum is observed in the PANI/MnFe₂O₄ nanocomposites, Fig. 1[B][c], implying the dominant role of PANI.⁴⁴ However, a considerable red shift from 253 to 267 nm with a higher intensity is observed in the MnFe₂O₄/PANI nanocomposite films due to the formed guest–host band between the –NH groups in the PANI chains and O-metal part in MnFe₂O₄.⁴⁶

SEM characterization was also employed to investigate the morphology variation of the composite films. Fig. 2(a–c) show the SEM images of pure MnFe₂O₄, pristine PANI and MnFe₂O₄/PANI nanocomposite films deposited on ITO, respectively. For the pure MnFe₂O₄ film, Fig. 2(a), MnFe₂O₄ particles exhibit a roughly spherical-like morphology on the ITO glass slide, confirming the successful spin coating of MnFe₂O₄ on the ITO glass. Fig. 2(b) shows the SEM image of the pristine PANI film on the ITO coated glass slide; the short fiber-like PANI is successfully formed on the ITO glass slide through the electropolymerization method. For the PANI/MnFe₂O₄ nanocomposite film, Fig. 2(c), the morphology of the film is roughly similar to that of pristine PANI; it is clearly seen that the PANI polymer is coated on the surface of MnFe₂O₄ particles during the in situ polymerization process. A hydrogen bonding model has been employed to explain this wrap behavior of polymers on metal oxides.⁴⁶ PANI chains are first formed due to the inner hydrogen bonding which further leads to a PANI network structure; furthermore, the bonds between PANI and the oxygen atoms in MnFe₂O₄ also facilitate the embedment of the MnFe₂O₄ particles in the PANI matrix thus forming a stable structure. This pattern has been confirmed by similar morphologies observed in the PANI/TiO₂, PANI/SnO₂ and PANI/Fe₃O₄ composites.⁵⁶⁶⁶⁶⁷

### 3.2 Electrochromic behaviors

Fig. 3(a) and (b) show the UV-vis transmission spectra of the pristine PANI and PANI/MnFe₂O₄ nanocomposite films at different potentials in 1.0 M H₂SO₄, respectively. For both films from 0.8 to −0.2 V, similar UV-vis spectra are clearly observed as the transmittance decreases monotonously when increasing the potential, indicating increasingly oxidized PANI. Furthermore, the small absorbance band at around 700 nm is characteristic of the emeraldine base form of PANI due to the π–π* transition in the quinoid ring,⁴⁸ which implies the dominant role of PANI in the hybrid PANI/MnFe₂O₄ film. Correspondingly, varying colors of the nanocomposite film are obtained upon applying different potentials. Fig. 4 shows the digital photograph of color switching at different potentials in 1.0 M H₂SO₄. The photos were taken after applying different potentials on the film for 20 s. The PANI/MnFe₂O₄ film displayed light yellow at −0.2 V (reduced state), light green at 0.5 V, blue at 0.8 V (partially oxidized state), and finally dark blue at 1.0 V (fully oxidized state). The corresponding mechanism is also illustrated at the bottom of Fig. 4.

The coloration switching responses of the pristine PANI and PANI/MnFe₂O₄ nanocomposite films are studied by applying potential steps of 0.8 and −0.2 V with a pulse width of 20 s. Fig. 5(a–d) show the transmittance–time (on the left) and the corresponding charge density–time curves (on the right) at 633 nm of pristine PANI (a & b) and PANI/MnFe₂O₄ nanocomposite film (b & d). The transmittance modulations (transmittance difference in the bleached and colored states in the electrochromic materials) of 16.2 and 35.2% are calculated for the pristine PANI and PANI/MnFe₂O₄ nanocomposite films, respectively. The coloration time (τ₁) and bleaching time (τ₂) are defined as the time required for a 90% change in the full transmittance modulation, respectively.⁴⁹ For the pristine PANI film, Fig. 5(a), τ₁ is found to be 9.52 s and τ₂ is 7.47 s from the cycles in the transmittance–time curve. However, it is obtained from Fig. 5(c) that the PANI/MnFe₂O₄ nanocomposite film exhibits a much faster τ₂ of 4.79 s and a slightly slower coloration time of 9.61 s than the pristine PANI film. Even though larger electrical resistance observed in the composite film than that in the pure PANI film due to the introduction of MnFe₂O₄ might not be good for the redox reactions during the color switching, a faster switching response observed in the composite film can be explained by the differed morphology from that of the pure PANI film. In the composites, the MnFe₂O₄ particles embedded in the PANI matrix facilitate H⁺ intercalation/deintercalation; the unique donor–acceptor electronic structure occurring in the composite film also contributes to faster color switching.⁷⁶⁷⁷

Coloration efficiency (CE or η) is an important consideration of electrochromic materials for practical application in display and window devices. It is defined as the change in optical density (OD) per unit charge (Q) inserted into (or extracted from) the electrochromic films, i.e., the amount of energy to affect a color change. The CE is calculated from eqn (2) and (3).²⁷
where ΔOD is the change in optical density, λ is the dominant wavelength of the material, \( Q_d \) is the charge density (injected/ejected charges per unit electrode area), \( T_{\text{bleached}} \) refers to the transmittance of the film in the bleached state, and \( T_{\text{colored}} \) refers to the varying transmittance of the film during the coloring process. Fig. 6 depicts the plots of the calculated ΔOD obtained from the second cycle in the transmittance–time curve at a wavelength of 633 nm, Fig. 5(a) and (c), versus the corresponding inserted charge density obtained from the charge density–time curve, Fig. 5(b) and (d). \( \eta \) is extracted as the slope of the line fitting to the linear region of the curve. The values of \( \eta \) are found to be 80.13 and 92.31 cm² C⁻¹ for the pristine PANI film and the PANI/MnFe₂O₄ nanocomposite film, respectively. The enhanced CE for the nanocomposite film indicates an improved color switching response ability as fewer charges injected can contribute to a greater optical density change than that observed in the pristine PANI film. The \( \eta \) value of the PANI/MnFe₂O₄ nanocomposite film (92.31 cm² C⁻¹) is also comparable with those of a lot of excellent reported films such as the NiO microflake film (146.9 cm² C⁻¹), WO₃/graphene film (96.1 cm² C⁻¹), PANI/WO₃ film (98.4 cm² C⁻¹) and PEDOT:PSS/WO₃ film (117.7 cm² C⁻¹), which enables its promising applications in EC devices. Finally, it is clearly seen that the transmittance vs. time and charge density vs. time curves of the PANI/MnFe₂O₄ nanocomposite film are more stable than those of the pristine PANI film, which indicates a stable response after the introduction of inner MnFe₂O₄ layer.

### 3.3 Capacitive energy storage performances

Fig. 7(a)–(c) depict the CV curves of the pristine PANI, PANI/MnFe₂O₄ and MnFe₂O₄ films grown on the ITO coated glass slides in 1.0 M H₂SO₄ aqueous solution at a scan rate of 5 mV s⁻¹ from −0.2 to 0.8 V. For the pristine PANI film, Fig. 7(a), two
typical redox pairs as A/A' at 0.20/0 V corresponding to the transition between the leucoemeraldine and emeraldine states of PANI, and B/B' at 0.50/0.40 V corresponding to the exchange between the emeraldine and pernigraniline states are clearly observed, indicating the typical pseudocapacitive characteristics of PANI.\textsuperscript{77,78} For the PANI/MnFe\textsubscript{2}O\textsubscript{4} nanocomposite film, Fig. 7(b), the same characteristic peaks of PANI are also obtained due to the dominant PANI in the hybrid PANI/MnFe\textsubscript{2}O\textsubscript{4} film. In addition, it is worth noting that the potential ranges between the typical redox peaks as A/A' and B/B' in the PANI/MnFe\textsubscript{2}O\textsubscript{4} nanocomposite film are larger than those of the pristine PANI. The wide potential range implies more difficult oxidation/reduction processes in the hybrid PANI/MnFe\textsubscript{2}O\textsubscript{4} film compared with that of the pristine PANI film, which is probably due to the increased resistance in the PANI/MnFe\textsubscript{2}O\textsubscript{4} nanocomposite film. However, for the bare MnFe\textsubscript{2}O\textsubscript{4} film in Fig. 7(c), no obvious peaks are observed, indicating a negligible supercapacitive activity of MnFe\textsubscript{2}O\textsubscript{4} arising from its small amount.

EIS as a powerful technique that gives a wealth of information regarding the internal resistance of the electrode materials as well as the resistance between the electrode and the electrolyte was also employed, Fig. 8(a)(c). The Nyquist plots of the pure MnFe\textsubscript{2}O\textsubscript{4} film, pristine PANI film and PANI/MnFe\textsubscript{2}O\textsubscript{4} nanocomposite film onto the ITO glass were obtained at the OCP in the frequency range from 100 kHz to 0.01 Hz with an AC-voltage amplitude of 5 mV, respectively. The Nyquist plot is divided into two regions as the high-frequency region and the low-frequency region. In the high-frequency range, the intercept of the curve

Fig. 5  \textit{In situ} transmittance and the corresponding chronocoulometry curves of (a & b) pristine PANI and (c & d) PANI/MnFe\textsubscript{2}O\textsubscript{4} nanocomposite films onto ITO glass at 633 nm in 1.0 M H\textsubscript{2}SO\textsubscript{4} aqueous solution. The tests were conducted under square-wave voltages of 0.8 and –0.2 V with a pulse width of 20 s.

Fig. 6  The plot of \textit{in situ} optical density (\Delta O/D) versus charge density of the (a) pristine PANI film and (b) PANI/MnFe\textsubscript{2}O\textsubscript{4} nanocomposite film. The optical density was measured at 633 nm at 0.8 V in 1.0 M H\textsubscript{2}SO\textsubscript{4} aqueous solution.
with the real axis represents the equivalent series resistance (ESR), which mainly arises from the electrolyte resistance, the intrinsic resistance of the active material, and the contact resistance at the active material/current collector interface. The ESR values are approximately 140, 170 and 176 Ω for the pure MnFe₂O₄, pristine PANI, and PANI/MnFe₂O₄ nanocomposite films, respectively. Even though the pure MnFe₂O₄ film exhibits the lowest ESR value due to a small amount of MnFe₂O₄, it displays much larger resistance throughout the whole frequency range. The increased ESR values observed for the pristine PANI and PANI/MnFe₂O₄ nanocomposite films are due to the added PANI material. In addition, the increased ESR value of the PANI/MnFe₂O₄ nanocomposite film compared with that of the pristine PANI film confirms again that the underlayered MnFe₂O₄ film has increased the total resistance. However, the almost overlap of the two lines in the low-frequency region implies an approximately equal migration of the ions regardless of the effect of MnFe₂O₄. Another important parameter is the diameter of the semicircles in the high-frequency to mid-frequency region, which represents the charge transfer resistance (Rct) between the electrode and the electrolyte interface. The observed equivalent semicircles for both the pristine PANI and PANI/MnFe₂O₄ films indicate that Rct mainly arises from PANI in the PANI/MnFe₂O₄ nanocomposite film. Furthermore, for the pristine PANI and PANI/MnFe₂O₄ nanocomposite films, the slope of the straight lines is much sharper compared with that of the pure MnFe₂O₄ film, indicating the ideal capacitive properties of these two films.

The areal capacitance of the films, which is perceived as a better indicator to evaluate the performance of thin film-based supercapacitors for application in small scale electronic devices and stationary energy storage devices, is calculated from the CV curves at different scan rates from −0.2 to 0.8 V in 1.0 M H₂SO₄ aqueous solution using eqn (4):

\[
C_s = \frac{(\int i dV) / (2S \times \Delta V \times \nu)}{C_0}
\]  

where \(C_s\) is the areal capacitance in F cm⁻², \(\int i dV\) is the integrated area of the CV curve, \(S\) is the surface area of active materials in the single electrode in cm², \(\Delta V\) is the scanned potential window in V, and \(\nu\) is the scan rate in mV s⁻¹.

The CV curves (on the left) and the corresponding capacitance dependence on the scan rate plots (on the right) of the pristine PANI and PANI/MnFe₂O₄ nanocomposite films are provided in Fig. S2(a and b), respectively. It is clearly seen that the cathodic peaks shift negatively and the anodic peaks shift positively when increasing the scan rate from 5 to 100 mV s⁻¹, which is probably due to the internal resistance of the electrode. Increased areal capacitance values with decreasing scan rate are observed for both the pristine PANI and PANI/MnFe₂O₄ nanocomposite films as indicated in the capacitance vs. scan rate plots. The linear increase in the capacitance with decreasing scan rate suggests a good rate producing ability of these films. The direct impact of increasing scan rate is on the diffusion of H⁺ into the PANI matrix; H⁺ is unable to approach the inner surface of the electrode at higher scan rates and the materials deep within the pores contribute little to the reaction thus resulting in decreased capacitance values. However, the relatively slow diffusion speeds at lower scan rates are able to ensure that the ions in the electrolyte diffuse near the electrode–electrolyte interface to get full access to the inner MnFe₂O₄ electrode materials and contribute to the increased capacitance values. It is clear that the capacitance values of the pristine PANI (2.38 and 3.13 mF cm⁻²) are higher than those of the PANI/MnFe₂O₄ nanocomposite film (1.88 and 2.74 mF cm⁻²) at higher scan rates of 100 and 50 mV s⁻¹. Since the upper layer PANI largely contributes to the capacitance at higher scan rates, the larger PANI amount confirmed by the CV synthesis results mainly accounts for the increased capacitance of the pristine PANI film. In contrast, the areal capacitance values of the PANI/MnFe₂O₄ nanocomposite film are larger than those of the pristine PANI film (4.05 and 4.46 mF cm⁻² vs. 3.87 and 3.95 mF cm⁻² at 10 and 5 mV s⁻¹, respectively).
Since the MnFe$_2$O$_4$ particles are largely covered by the PANI matrix, they are negligible in contributing to the capacitance at high scan rates. However, their capacitances will be increasingly exploited with decreasing the scan rate as more and more electrode materials will be accessible by the ions and contribute to increased capacitance.\textsuperscript{85-87} The PANI/MnFe$_2$O$_4$ nanocomposite film retains 42.13% of the capacitance at higher scan rates, compared to 69.3% for the pristine PANI film, indicating worse ion diffusion in the former at higher scan rates due to the inner layered MnFe$_2$O$_4$ film.

The galvanostatic charge–discharge measurements by chronopotentiometry (CP) are also carried out on the films in 1.0 M H$_2$SO$_4$ aqueous solution in order to evaluate the areal capacitance using eqn (5).\textsuperscript{82}

$$C_a = (i \times t)/(S \times \Delta V)$$

where $C_a$ is the areal capacitance in F cm$^{-2}$, $i$ is the discharge current in A, $t$ is the discharge time in s, $S$ is the surface area of the active materials in the single electrode in cm$^2$, and $\Delta V$ is the scanned potential window (excluding the IR drop in the beginning of the discharge) in V.

Fig. S3(a and b)† show the potential responses of the pristine PANI and PANI/MnFe$_2$O$_4$ nanocomposite films at different currents (on the left) and the corresponding plots of current density vs. areal capacitance (on the right). Typical pseudo-capacitive galvanostatic charge–discharge curves are presented, which are not ideal straight lines, indicating that the reactions are faradic processes. In addition, the IR drop is found to decrease with increasing the charge–discharge current density due to the increased exposure of electrode materials. For the corresponding capacitance variation, the areal capacitance of each film is observed to increase with decreasing current density due to the better ion diffusion and improved electrode access. A negligible capacitance difference between the two films is observed at 0.32 mA cm$^{-2}$ due to the less deposited PANI and the increased film resistance in the PANI/MnFe$_2$O$_4$ nanocomposite film. The capacitance values of the PANI/MnFe$_2$O$_4$ nanocomposite film gradually exceed those of the pristine PANI film due to the increasingly available MnFe$_2$O$_4$ layer at 0.04 and 0.08 mA cm$^{-2}$. It is noticeable that the areal capacitance of the PANI/MnFe$_2$O$_4$ nanocomposites is enhanced to 4.10 mF cm$^{-2}$ compared with that of the pristine PANI film (3.67 mF cm$^{-2}$) at 0.04 mA cm$^{-2}$, which is also consistent with the capacitance variation trend obtained from the CV results. Even though the capacitance of this PANI/MnFe$_2$O$_4$ nanocomposite film can be directly enhanced through increasing PANI sweeping cycles, the 10 cycles produced 4.10 mF cm$^{-2}$ at 0.04 mA cm$^{-2}$ is still comparable with a lot of reported values such as 5.83 mF cm$^{-2}$ of the CNFs/PANI/RGO film at 0.0043 mA cm$^{-2}$,\textsuperscript{88} 4.1 mF cm$^{-2}$ of the PANI/WO$_3$ film at a current density of 0.02 mA cm$^{-2}$ and 6.3 mF cm$^{-2}$ for the PANI/GO film at 0.16 mA cm$^{-2}$.\textsuperscript{89} However, the mass capacitance of this hybrid film can reach an extraordinary level (>1000 mF g$^{-1}$) due to the ultra-small amount of active materials. The cycling performance is also evaluated using galvanostatic charge–discharge measurements for 800 cycles at a current density of 0.08 mA cm$^{-2}$.

Fig. S4.† The PANI/MnFe$_2$O$_4$ nanocomposite film exhibits a slightly declined stability due to the instability of MnFe$_2$O$_4$ in H$_2$SO$_4$ solution; however, the comparable cycling stability and enhanced electrochromic and supercapacitive properties still enable PANI/MnFe$_2$O$_4$ to be superior for applications.

### 3.4 H$_2$SO$_4$ concentration effect on electrochemical behavior

The electrolyte, known as the “blood” for supercapacitors, plays an important role in governing the rate capability and energy density of supercapacitors. Investigating the concentration effect of H$_2$SO$_4$, a common electrolyte used in PANI-based supercapacitors, is of great significance for practical usage.\textsuperscript{91} Three concentrations of 0.5, 1.0 and 2.0 M are selected to study the concentration effect on the pristine PANI and PANI/MnFe$_2$O$_4$ nanocomposite films. Characterization techniques such as CV, galvanostatic charge–discharge and EIS are employed to investigate the H$_2$SO$_4$ concentration effect on the supercapacitive behaviors, Fig. 9. The CV curves of the pristine PANI and PANI/MnFe$_2$O$_4$ nanocomposite films are obtained at 20 mV s$^{-1}$ in the corresponding electrolytes, Fig. 9(a) and (b). Similar CV curves with a clear area decrease are obtained, indicating the negative role of increasing the H$_2$SO$_4$ concentration on the capacitance; the capacitance values of the PANI/MnFe$_2$O$_4$ nanocomposite film are calculated to decrease from 4.51, 4.23, to 3.76 mF cm$^{-2}$ for 0.5, 1.0 and 2.0 M H$_2$SO$_4$, respectively. In addition, it is clearly seen from Fig. 9(a) and (b) that the typical redox pair peaks shift, widening the potential differences between the redox peaks, indicating a worse reversibility with increasing the H$_2$SO$_4$ concentration. Fig. 9(c) and (d) depict the galvanostatic charge–discharge curves of the pristine PANI and PANI/MnFe$_2$O$_4$ nanocomposite films at a current density of 0.08 mA cm$^{-2}$, respectively. Similar decreased discharging times are also observed for both films with increasing the H$_2$SO$_4$ concentration, which are consistent with the CV results. In addition, the increased IR drop observed in Fig. 9(c) and (d) also suggests deteriorated performances, which would be explained by the corresponding EIS Nyquist impedance plots, Fig. 9(e) and (f), obtained in the frequency range of 100 000 to 0.01 Hz with a 5 mV amplitude referring to the OCP. Similar curves are obtained for both PANI and PANI/MnFe$_2$O$_4$ films, \textit{i.e.}, small semicircles in the high frequency range and the following tail in the low frequency range for all the H$_2$SO$_4$ concentrations. The same trends as the decreased ESR and increased $R_{ct}$ values are simultaneously observed for both films with increasing the H$_2$SO$_4$ concentration. Since the electrolyte resistance is usually predominant in determining the ESR,\textsuperscript{92} it is deduced that the increasingly available H$^+$ ions would mainly account for the decreased ESR values. However, the increased $R_{ct}$ values determined from the increased diameter of semicircles clearly indicate harder charge transfer process with increasing the H$_2$SO$_4$ concentration, which would mainly account for the deteriorated performances. The ion diffusion coefficient ($D$) was also calculated according to eqn S1† and is provided in Fig. S5† as 0.5 M (1.51 × 10$^{-12}$ cm$^2$ s$^{-1}$) > 1.0 M (3.29 × 10$^{-13}$ cm$^2$ s$^{-1}$) > 2.0 M (7.31 × 10$^{-14}$ cm$^2$ s$^{-1}$) for pristine PANI and 0.5 M (3.28 × 10$^{-13}$ cm$^2$ s$^{-1}$) > 1.0 M (9.51 ×
10^{-14} \text{ cm}^2 \text{ s}^{-1}) > 2.0 \text{ M} (2.18 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1})$ for the PANI/MnFe$_2$O$_4$ nanocomposite film, which is consistent with the CV and galvanostatic charge–discharge results.

### 3.5 Temperature effect on electrochemical behavior

According to the above experimental results, the 0.5 M H$_2$SO$_4$ electrolyte was selected to study the effect of temperature on the supercapacitive properties of the pristine PANI and PANI/MnFe$_2$O$_4$ nanocomposite films. Three temperatures of 2, 22 and 50 °C representing cold, normal, and hot weather were selected to evaluate the temperature effect using CV, galvanostatic charge–discharge, and EIS characterization as the same logic. Fig. 10(a)–(f) display the CV, galvanostatic charge–discharge, and EIS characterization of the pristine PANI film (a, c and e) and PANI/MnFe$_2$O$_4$ nanocomposite film (b, d and f), respectively. For the CV curves, Fig. 10(a) and (b), they were conducted at a scan rate of 20 mV s$^{-1}$ at different temperatures. The small area increase is first observed for both the pristine PANI and PANI/MnFe$_2$O$_4$ films with increasing the temperature from 2 to...
suggesting a positive role of temperature in enhancing the supercapacitive properties due to the greatly enhanced ion mobility. However, a clear area decrease is observed as the temperature is increased to 50 °C. The degradation of the pristine PANI and PANI/MnFe₂O₄ nanocomposite films at high temperatures is mainly responsible for the worse performance, which is demonstrated by the first 6 and 3 CV cycles at 50 °C as shown in Fig. S7(a and b).† For the galvanostatic charge–discharge curves with a current density of 0.08 mA cm⁻². (c & d) Galvanostatic charge–discharge curves with a current density of 0.08 mA cm⁻². (e & f) EIS performed from 100 kHz to 0.01 Hz with an amplitude of 5 mV at the open potential.

Fig. 10 Temperature effect (2, 22 and 50 °C) on the supercapacitive behavior of the pristine PANI film (a, c and e) and PANI/MnFe₂O₄ nanocomposite film (b, d, and f) in 0.5 M H₂SO₄. (a & b) CV conducted at a scan rate of 20 mV s⁻¹ from −0.2 to 0.8 V. (c & d) Galvanostatic charge–discharge curves with a current density of 0.08 mA cm⁻². (e & f) EIS performed from 100 kHz to 0.01 Hz with an amplitude of 5 mV at the open potential.

22 °C, suggesting a positive role of temperature in enhancing the supercapacitive properties due to the greatly enhanced ion mobility. However, a clear area decrease is observed as the temperature is increased to 50 °C. The degradation of the pristine PANI and PANI/MnFe₂O₄ nanocomposite films at high temperatures is mainly responsible for the worse performance, which is demonstrated by the first 6 and 3 CV cycles at 50 °C as shown in Fig. S7(a and b).† For the galvanostatic charge–discharge curves with a current density of 0.08 mA cm⁻². (c & d) Galvanostatic charge–discharge curves with a current density of 0.08 mA cm⁻². (e & f) EIS performed from 100 kHz to 0.01 Hz with an amplitude of 5 mV at the open potential.
functions of EC and energy storage. It is clearly seen from Fig. 10(e) and (f) that the ESR values of both the films follow an order as ESR (2 °C) < ESR (22 °C) due to the enhanced mobility of ions when increasing the temperature, which is also consistent with the calculated $D$ values of 2 °C ($4.23 \times 10^{-13}$ cm$^2$ s$^{-1}$) < 22 °C ($4.23 \times 10^{-13}$ cm$^2$ s$^{-1}$) for pristine PANI and 2 °C ($4.23 \times 10^{-13}$ cm$^2$ s$^{-1}$) < 22 °C ($6.68 \times 10^{-13}$ cm$^2$ s$^{-1}$) for the PANI/MnFe$_2$O$_4$ nanocomposite film in Fig. S6.† However, the increased ESR and $R_\text{ct}$ values in the pristine film and the disappeared semicircle in the PANI/MnFe$_2$O$_4$ nanocomposite films at 50 °C are subsequently observed and attributed to the destruction effect of high temperature on the PANI structure, demonstrated by the decreased $D$ values of pristine PANI ($3.31 \times 10^{-13}$ cm$^2$ s$^{-1}$) and PANI/MnFe$_2$O$_4$ nanocomposites ($5.22 \times 10^{-13}$ cm$^2$ s$^{-1}$) at 50 °C.

### 4. Conclusions

A PANI matrix embedded with MnFe$_2$O$_4$ particle have been successfully prepared by electrodeposition of aniline monomers onto MnFe$_2$O$_4$ coated ITO glass slides. A multi-color electrochromic phenomenon displayed at different potentials has been observed in this nanocomposite film due to the dominant PANI component in the composites. A higher coloration efficiency and a faster switching response than those of the pristine PANI film are obtained due to the inner interactions between the PANI matrix and the MnFe$_2$O$_4$ particles as well as the resulting rougher morphology. The PANI/MnFe$_2$O$_4$ nanocomposite film also exhibits an enhanced areal capacitance compared to the pristine PANI film at low scan rates due to the capacitive role of MnFe$_2$O$_4$. A negative role of increasing H$_2$SO$_4$ concentration on the supercapacitive behaviors of the pristine PANI and PANI/MnFe$_2$O$_4$ nanocomposite films has been demonstrated by the increased $R_\text{ct}$ values. The positive role of increasing the temperature in the relatively low temperature range can enhance the discharge curves, Fig. 10(c) and (d), similar trends to those of the CV results are observed, demonstrating that increasing temperature in the low temperature range can enhance the performance but the PANI structure will be destroyed when the temperature is continuously increased. In order to further investigate the operating temperature effect on the kinetics transfer process, EIS tests were performed under open circuit conditions in a frequency range from 100 kHz to 0.01 Hz with an AC-voltage amplitude of 5 mV. It is greatly facilitated mobility of ions. However, fast degradation of both pristine PANI and PANI/MnFe$_2$O$_4$ nanocomposite film structures has been observed implying the destructive role of the relatively high temperatures. These novel PANI/MnFe$_2$O$_4$ nanocomposite films, that can be easily produced, have demonstrated considerable electrochromic and capacitive behaviors, which make them suitable for application in devices integrating the functions of EC and energy storage.

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