

Study of the Electrochemical and Electrical Properties CoFe₂O₄@GO/PEDOT Magnetic Nanocomposite for Microsupercapacitor Applications

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The structural, electrical, and electrochemical properties of CoFe₂O₄, graphene oxide and poly (3,4-ethylenedioxythiophene) (CoFe₂O₄@GO/PEDOT) as stretchable nanocomposite based microsupercapacitor (MSC) were characterized in this study. The hydrothermal method was used for the preparation of nanocomposite, and then designed into an array of 3×3 microelectrode by printing sacrificial patterns and pen lithography. XRD and FESEM studies demonstrated the successful synthesis of CoFe₂O₄@GO/PEDOT. Results of the electrical property of samples using 4-point probe method showed that the GO had the higher conductivity value, and electrical conductivity was decreased with the addition of CoFe₂O₄ and PEDOT to the GO based nanocomposite. Electrochemical studies using EIS, CV and GCD indicated good electrolyte ion diffusion on the CoFe₂O₄@GO/PEDOT surface and ideal capacitive behavior with fast redox reactions. The areal specific capacitance, energy density and power density of CoFe₂O₄@GO/PEDOT nanocomposites based MSCs were obtained at 435F/g, 62Wh/kg and 0.9W/kg, respectively, at a current density of 2.5A/g in electrolyte of 100g/l PVA/H₂SO₄. The comparison between the results for CoFe₂O₄@GO/PEDOT nanocomposite-based MSC and reported MSCs showed that the better or comparable performance than other reported MSCs can be attributed to the synergetic effect of the CoFe₂O₄@GO composite and porous conductive polymer PEDOT which provide good electrical conductivity and large surface area, indicating an improvement in the areal specific capacitance and energy density value and a decrease in power density. After 1000 cycles, the cycling stability of CoFe₂O₄@GO/PEDOT nanocomposite based MSCs showed an amazing capacitance retention of about 96%, exhibiting good cycling stability of CoFe₂O₄@GO/PEDOT nanocomposite based MSCs.

Keywords: Microsupercapacitor; Gel electrolyte; Graphene magnetic nanocomposite; Electrical properties; Areal specific capacitance

1. INTRODUCTION

Today, the development and application of stretchable microscale electronics to miniaturize industrial, medical and energy harvesting devices such as cameras, mobile and personal entertainment

devices, calculators, exercise monitors, and wearable electronics such as electronic skins and healthcare monitoring systems causes significant competition in the market [1, 2]. More importantly, MSCs as flexible energy storage tools on-chip microscale devices have grown in popularity, and numerous studies have been conducted to discover suitable materials and electrode configurations in the development of MSC technology [3-6].

Accordingly, research has shown that most MSCs show good performance *in wave-like*, honeycomb kirigami, bridge-island, cellular, helical and textile fiber electrodes configurations [7-9]. Many studies have been conducted on, MnO_2RuO_2 , Ag@Ppy , V_2O_5 , VS_2 , MXene, PEDOT: PSS, porous carbon, graphene, and MWCNTs-based electrochemical [10-12]. Even so, application of the stretchable MSCs is faced with challenges due to poor mechanical stability and weak cycling and rate performance [13, 14]. Moreover, the manufacturing process of MSCs is also highly sensitive, and not only requires complicated and multistep processing involving expensive equipment but also need to work in a clean room [15-17].

As a result of the large market and increasing demand for MSCs, ongoing research is being conducted to overcome problems in design and development of fabrication methods with favorable materials to improve the capacity and stability of MSCs [18-20]. Therefore, this study presented the fabrication of $\text{CoFe}_2\text{O}_4\text{@GO/PEDOT}$ as a graphene based magnetic nanocomposite and the study of its structural and electrical properties and electrochemical characterizations for MSC applications.

2. EXPERIMENTAL

2.1. Synthesis of $\text{CoFe}_2\text{O}_4\text{@GO/PEDOT}$

The hydrothermal method was used for the preparation of a mixture of $\text{CoFe}_2\text{O}_4\text{@GO}$ [21]. GO (>95wt%, Xiamen Tob New Energy Technology Co., Ltd., China), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99%, Merck, Germany) aqueous solution, and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99%, Merck, Germany) aqueous solution were mixed in a molar ratio of 3:2:1 using magnetic stirring for 12 minutes. Then, the mixture was transferred to a Teflon-coated stainless steel autoclave and heated at 130°C for 12 hours. After cooling, the obtained black product was washed with ethanol three times, and dried at 55°C in the oven. 2g of The $\text{CoFe}_2\text{O}_4\text{@GO}$ was ultrasonically added in 10 mL of n-butyl acetate ($\geq 99.5\%$, Sigma-Aldrich) containing 50 $\mu\text{l/ml}$ of poly(3,4-ethylenedioxythiophene) (PEDOT, 97%, Sigma-Aldrich) to obtain the homogeneous nanocomposite ($\text{CoFe}_2\text{O}_4\text{@GO/PEDOT}$).

2.2. Preparation of microsupercapacitors of $\text{CoFe}_2\text{O}_4\text{@GO/PEDOT}$

For the preparation of an array of 3×3 microsupercapacitors (MSC), a pattern electrode was designed by printing sacrificial patterns using a commercial laser printer (DIY 2500w, Shenzhen Twotrees Technology Co., Ltd., China). The magnetic nanocomposite-based MSC was successfully fabricated on a transparent commercial polyethylene terephthalate (PET, Taizhou Shantai Packaging Co., China) film. Subsequently, the magnetic nanocomposite ink was loaded onto the substrate using a rollerball pen. Following that, 1 ml of 0.7 g/ml $\text{Fe}(\text{ClO}_4)_3$ (99%, Sigma-Aldrich) solution was

dropped directly onto the magnetic nanocomposite electrode and allowed to polymerize for 60 minutes at room temperature [22]. The resulted array was washed with absolute ethanol (99%, Shandong Baovi Energy Technology Co. Ltd., China) and deionized (DI) water thoroughly and then dried at room temperature for 40 minutes. The sample was carefully washed sequentially with acetone (99.5%, Shandong Baovi Energy Technology Co. Ltd., China) and DI water to remove the unwanted printer pattern and template from the substrate.

2.3. Fabrication of a GO/PEDOT nanocomposite-based MSC with a flexible microelectrode

The GO/PEDOT ink was synthesized by a mixture of GO, n-butyl acetate and 50 μ l/ml PEDOT in a volume ratio of 2:1:1. The mixture was sonicated for 60 minutes to achieve a homogeneous suspension [22], followed by the deposition of GO/PEDOT. For polymerization, 0.7 g/ml of Fe(ClO₄)₃ solution was slowly dropped on the GO/PEDOT electrode. After 60 minutes, the GO/PEDOT electrode was washed with a mixture of ethanol and DI water, and then dried at room temperature for 40 minutes. Afterwards, the silicone rubber coating (Aerol Formulations P. Ltd., India) was applied for the rubber coating of the surface of the GO/PEDOT electrode.

In order to assemble the flexible MSC, silver paste (Zhongshan Maxtor New Material Co., Ltd., China) was employed to meticulously connect each MSC to the GO/PEDOT electrode structure. Afterwards, the gel electrolyte was prepared by adding 2 g of polyvinyl alcohol (PVA, 99%, Jinzhou City Yicheng Cellulose Co., Ltd., China) into 2 g of H₂SO₄ (99.99%, Sigma-Aldrich) and 20 ml of DI water. The electrolyte was stirred at 85°C to obtain the transparent solution that it was spread onto the MSC arrays. The MSCs were dried at room temperature for 10 hours.

2.4. Structural and electrical characterizations

Field emission scanning electron microscopy (FESEM, SU8010, Hitachi Co., Tokyo, Japan) was used to study the morphological properties of nanocomposite. For crystal structure analysis, X-ray diffraction (XRD, Bruker Nanostar U) with Cu K α radiation ($\lambda = 0.1542$ nm) at 45 kV was applied. In order to study the electrical properties, electrical conductivity measurements were carried out using a pellet ($\Phi 20$ mm \times 0.5 mm) prepared from the synthesized nanocomposites with a pressure of 20 MPa, and 4-point probe method (ST2558B-F01, Suzhou Jingge Electronics Co., Ltd., China) was employed for the electrical conductivity of pressed pellets at room temperature under an applied current of 10 mA. Four electrical contacts were arranged in a line with uniform pin separation (1.5 mm) and placed on the surface of the sample.

2.5. Electrochemical studies

The electrochemical analyses of MSC arrays including cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge-discharge (GCD) were carried out in a potentiostat/galvanostat electrochemical workstation (Corrtest, Wuhan Corrtest Instruments Corp., Ltd., China) using both three-electrode and two-electrode systems. In the three-

electrode system, a prepared single microelectrode is used as a working electrode, a Pt wire as counter and a saturated calomel electrode (SCE) as a reference electrode. In the two-electrode system, two electrodes are employed as the working and the counter electrodes, respectively. An EIS was employed for a frequency range from 10^5 Hz to 10^{-2} Hz and sinusoidal amplitude of 10 mV. EIS data was fitted based on an equivalent electrical circuit model using ZSimpWin software. The areal specific capacitance (C_s) was calculated by the equation (1) [23, 24]:

$$C_s = I\Delta t/S\Delta V \quad (1)$$

Where I and Δt are the constant discharge current and the discharge time, respectively. ΔV is the applied potential interval, and S is the electrode area. The energy density (E) and power density (P) were calculated according to the following equations (2) and (3), respectively [25, 26]:

$$E = C \times (\Delta V)^2/7200 \quad (2)$$

$$P = E \times 3600/\Delta t \quad (3)$$

3. RESULTS AND DISCUSSION

3.1. Structural characterization

Figure 1 illustrates the XRD patterns of powders of GO nanosheets, CoFe_2O_4 , $\text{CoFe}_2\text{O}_4@\text{GO}$ and $\text{CoFe}_2\text{O}_4@\text{GO}/\text{PEDOT}$. The XRD pattern of powders of GO shows a sharp diffraction peak at $2\theta = 10.04^\circ$, which is related to the (001) plane [27]. The XRD pattern of CoFe_2O_4 shows the diffraction peaks at $2\theta = 18.27^\circ$, 30.21° , 35.56° , 37.34° , 43.14° , 53.69° , 56.98° , 62.72° and 74.28° , corresponding to the (111), (220), (311), (222), (400), (422), (511), (440) and (533) planes, respectively, which represent to crystal phase of CoFe_2O_4 with a spinel structure based on JCPDS card No. 00-022-108 [28, 29]. The XRD pattern of $\text{CoFe}_2\text{O}_4@\text{GO}$ exhibits all diffraction peaks of CoFe_2O_4 and GOES, indicating the successful synthesis of $\text{CoFe}_2\text{O}_4@\text{GO}$ nanocomposite. Moreover, the XRD pattern of the $\text{CoFe}_2\text{O}_4@\text{GO}/\text{PEDOT}$ shows all the diffraction peaks of $\text{CoFe}_2\text{O}_4@\text{GO}$ nanocomposite and an additional low intensity at $2\theta=26.18^\circ$ which is related to the intermolecular spacing of the polymer backbone that is assigned to the (020) reflection [30], demonstrating the successful synthesis of $\text{CoFe}_2\text{O}_4@\text{GO}/\text{PEDOT}$.

Figure 2 presents the FESEM images of GO, CoFe_2O_4 , $\text{CoFe}_2\text{O}_4@\text{GO}$ and $\text{CoFe}_2\text{O}_4@\text{GO}/\text{PEDOT}$. The FESEM image of GO in Figure 2a reveals agglomerated micro-sized nanosheets with an average thickness of 10nm. As observed from Figure 2b, $\text{CoFe}_2\text{O}_4@\text{GO}/\text{PEDOT}$ shows the presence of CoFe_2O_4 nanoparticles that are distributed on GO nanosheets and the coral-like morphology of PEDOT. Conjugated π -bonds are present in the PEDOT structure, and interactions between the PEDOT molecule and GO nanosheets can be strong due to π -stacking and the van der Waals force [31-33]. It can be seen that the polymerized nanocomposite ink of $\text{CoFe}_2\text{O}_4@\text{GO}/\text{PEDOT}$ provide the high porosity surface. Furthermore, CoFe_2O_4 nanoparticles have a synergistic effect on increasing effective surface area by reducing π - π interactions between sheets [34, 35], and the

electrostatic repulsion between the negatively charged $\text{CoFe}_2\text{O}_4@\text{GO}/\text{PEDOT}$ [36, 37]. In addition, the bonding of PEDOT with GO nanosheets enhances the surface roughness.

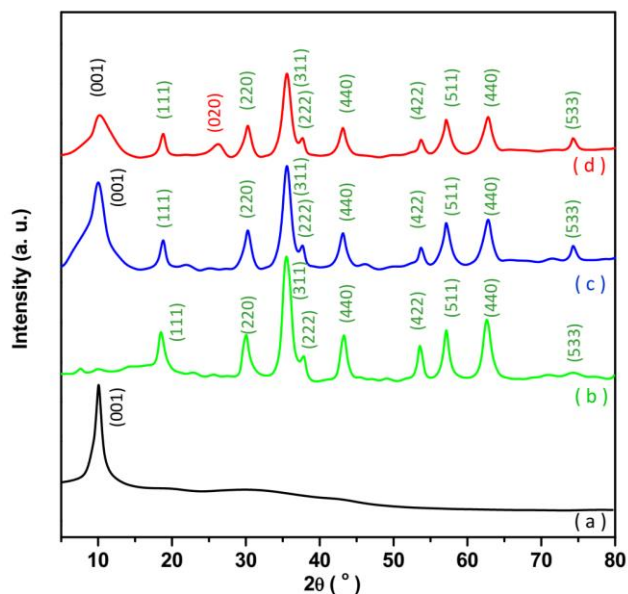


Figure 1. XRD patterns of powders of (a) GO nanosheets, (b) CoFe_2O_4 , (c) $\text{CoFe}_2\text{O}_4@\text{GO}$ and (d) $\text{CoFe}_2\text{O}_4@\text{GO}/\text{PEDOT}$.

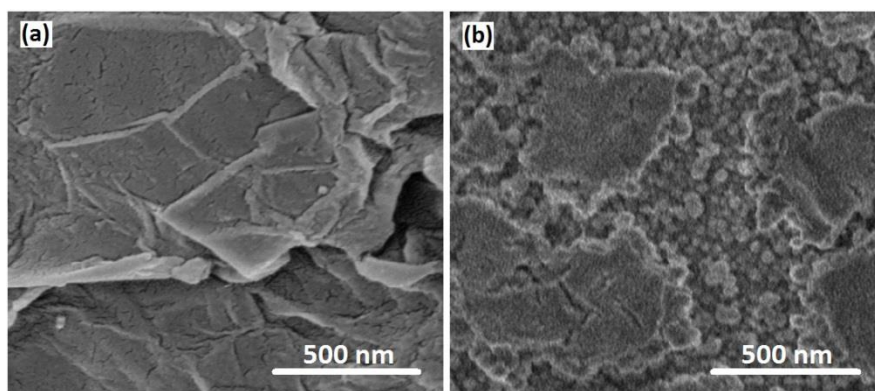


Figure 2. FESEM images of (a) GO, (b) CoFe_2O_4 , (c) $\text{CoFe}_2\text{O}_4@\text{GO}$ and (d) $\text{CoFe}_2\text{O}_4@\text{GO}/\text{PEDOT}$

3.2. Electrical characterizations

Table 1 presents the conductivity (σ) and resistivity (ρ) values of synthesized GO, CoFe_2O_4 , $\text{CoFe}_2\text{O}_4@\text{GO}$ and $\text{CoFe}_2\text{O}_4@\text{GO}/\text{PEDOT}$ nanocomposites. As observed from Table 1, the GO has the higher conductivity value, and electrical conductivity is decreased with the addition of the CoFe_2O_4 and PEDOT to the GO-based nanocomposite. CoFe_2O_4 also shows lower conductivity. The variation in electrical conductivity can be described in terms of percolation theory [38, 39]. Based on this theory,

the remarkable increase in conductivity occurs when the concentration of conductive filler exceeds its critical value. In composites containing conducting (ρ) and semiconducting (ρ_c) components, the relation between the electrical conductivity of the conducting-superconducting mixture of the percolation threshold is described by a simple power law $\sigma \sim (\rho - \rho_c)^t$, where the critical exponent t depends only on the dimensionality of the system [40, 41].

3.3. Electrochemical characterizations

EIS measurement was used to characterize the interface quality between the electrode and electrolyte, and study the capacitive and resistive behavior of samples. Generally, the Nyquist plot consists of three components: (i) a high-frequency intercept on the real Z' axis which mainly concerns the contribution of the electrolyte resistance, the intrinsic resistance of the active electrode material, and the contact resistance at the interface, (ii) a semicircle in the high-to-medium-frequency region which corresponds to the charge transfer reaction at the interface between the electrode and the electrolyte, and (iii) a straight line at the very low-frequency region associated with electrolyte ion diffusion [42]. Figure 3a exhibits the Nyquist plots for all samples in the frequency range from 10^5 Hz to 10^{-2} Hz with sinusoidal amplitude of 10 mV. As seen, there are no semicircles at the mid-frequency region for all the electrodes, implying to the possibility of electrochemical reactions related to the redox conversion of $\text{Fe}^{3+}/\text{Fe}^{2+}$ [43]. All samples show an EIS curve which is composed of a short arc and diagonal line with a slope of 45° (Warburg line), demonstrating good electrochemical capacitive behavior [44, 45]. Figure 3c depicts the resulting equivalent electrical circuit based on EIS data analyses, which includes series resistance (R_s), Warburg resistance (Z_W), and capacitance (CPE) [46]. The obtained parameters are shown in Table 1 which indicates the lowest R_s belonged to the $\text{CoFe}_2\text{O}_4@\text{GO}/\text{PEDOT}$ sample.

Figure 3b depicts the CV curves of GO, $\text{CoFe}_2\text{O}_4@\text{GO}$, $\text{CoFe}_2\text{O}_4/\text{PEDOT}$ and $\text{CoFe}_2\text{O}_4@\text{GO}/\text{PEDOT}$ nanocomposite based MSCs at a scan rate of 20 mV/s. As seen in the CV curves of $\text{CoFe}_2\text{O}_4@\text{GO}$, $\text{CoFe}_2\text{O}_4/\text{PEDOT}$ and $\text{CoFe}_2\text{O}_4@\text{GO}/\text{PEDOT}$, there are two pairs of redox peaks that result from the electrochemical reaction of the redox-active couples in the electrolyte: $\text{Fe}^{3+} + e^- \leftrightarrow \text{Fe}^{2+}$ [47]. The specific capacitance is proportional to the integral area of the CV curves as following equation [48-50]:

$$i_p = (2.687 \times 10^5) n^{3/2} A C D^{1/2} \nu^{1/2} C \quad (1)$$

Where i_p is the peak current and n corresponds to the count of transferred electrons. A represents the electrochemical active surface area (cm^2), D is diffusion coefficient, and ν and C denote the scan rate (V/s) and analytic amount, respectively. As seen, the surrounded area in the CV curve in $\text{CoFe}_2\text{O}_4@\text{GO}/\text{PEDOT}$ is larger than GO and $\text{CoFe}_2\text{O}_4@\text{GO}$. Thus, the large specific capacitance of $\text{CoFe}_2\text{O}_4@\text{GO}/\text{PEDOT}$ is derived from the CoFe_2O_4 phase instead of GO and PEDOT which may be related to the large availability of active sites of CoFe_2O_4 nanoparticles that decorated GO nanosheets and coral-like morphology of PEDOT [51], and synergistic effect in improving the electrical conductivity in $\text{CoFe}_2\text{O}_4@\text{GO}/\text{PEDOT}$ by mixing high conductive PEDOT and GO nanosheets [52].

Furthermore, the CV curves of CoFe₂O₄@GO/PEDOT are almost rectangular, which is associated with ideal capacitive behavior with fast redox reactions [53, 54].

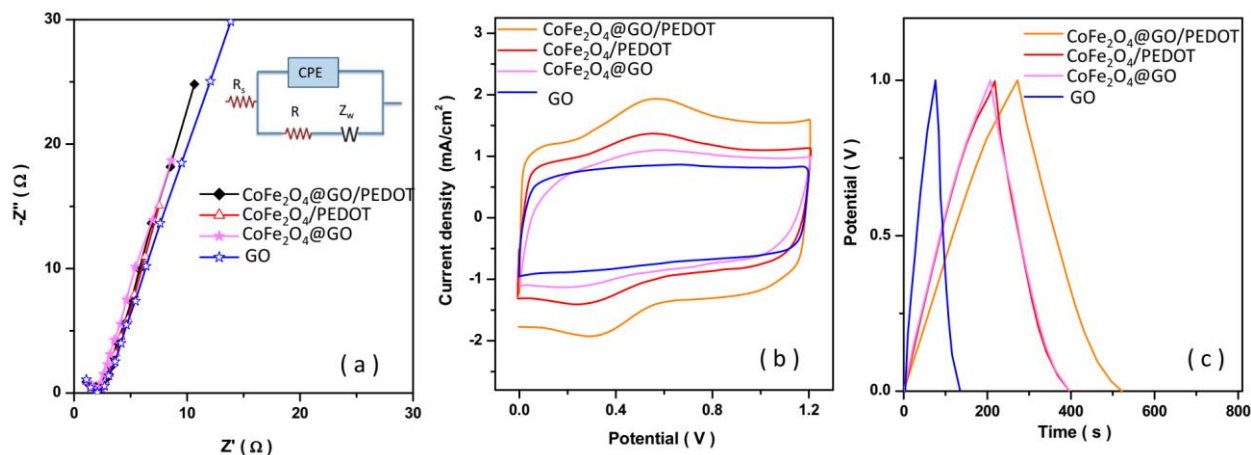


Figure 3. (a) Nyquist plots at 10 mV potential, (b) CV at 20 mV/s scan rate, (c) GCD curves at 2.5 A/g current density in potential range from 0 to 1.2 V for GO, CoFe₂O₄@GO, CoFe₂O₄/PEDOT and CoFe₂O₄@GO/PEDOT.

Table 1. The obtained values for C_s, E and P of GO, CoFe₂O₄@GO, CoFe₂O₄/PEDOT and CoFe₂O₄@GO/PEDOT nanocomposites based MSCs.

| Sample | R _s (Ω) | Z _w (Ω/S) | CPE (F) | σ (S/m) | ρ (Ω m) |
|--|--------------------|----------------------|---------|---------|-----------------------|
| GO | 1.31 | 0.049 | 0.025 | 18.33 | 5.44×10 ⁻² |
| CoFe ₂ O ₄ @GO | 1.29 | 0.144 | 0.085 | 15.80 | 6.61×10 ⁻² |
| CoFe ₂ O ₄ /PEDOT | 1.42 | 0.095 | 0.071 | 5.25 | 1.91×10 ⁻¹ |
| CoFe ₂ O ₄ @GO/PEDOT | 1.05 | 0.150 | 0.116 | 13.97 | 7.18×10 ⁻² |

Figure 3c displays the GCD curves of GO, CoFe₂O₄@GO, CoFe₂O₄/PEDOT and CoFe₂O₄@GO/PEDOT nanocomposites based MSCs obtained at a current density of 2.5 A/g. It can be observed that CoFe₂O₄/PEDOT and CoFe₂O₄@GO/PEDOT nanocomposites show a symmetric, triangle-shaped charge discharge profile in the GCD curve, implying good reversibility. There is a considerable enhancement in the charge storage capacity of CoFe₂O₄@GO/PEDOT nanocomposite based MSCs as compared to the other MSCs, and they also show significantly longer charging/discharging time as compared to other MSCs. The overwhelming long charge/discharge times are related to the pseudocapacitive characteristics of the CoFe₂O₄@GO/PEDOT electrode and the good charge storage property of the PEDOT in the energy storage systems [55-57]. The obtained values for C_s, E and P of GO, CoFe₂O₄@GO, CoFe₂O₄/PEDOT and CoFe₂O₄@GO/PEDOT nanocomposites based MSCs are presented in Table 2. It can be found that the synergistic effect of the GO and CoFe₂O₄ in the PEDOT matrix resulted in an improvement of the areal specific capacitance and energy density value and a decrease in the power density.

The increase in the capacitance in the $\text{CoFe}_2\text{O}_4@\text{GO}/\text{PEDOT}$ electrode is can be related to the change in the nanostructures, the high porosity between the CoFe_2O_4 nanoparticles, GO nanosheets with numerous edges and coral-like morphology of the PEDOT matrix can facilitate the penetration and movement of electrolyte ions into the inner region of the electrode. The resultant large surface area of the $\text{CoFe}_2\text{O}_4@\text{GO}/\text{PEDOT}$ nanocomposite gives more active sites for electrochemical reactions and enhances the charge transfer rate to the $\text{CoFe}_2\text{O}_4@\text{GO}/\text{PEDOT}$ [58-60]. PEDOT combined with GO nanosheets enhances the conductivity at reducing potentials, indicating better electrochemical performance of MSCs due to their good chemical and physical stability, wide tenability composition, and electrolyte compatibility [31]. Therefore, further electrochemical studies were conducted on the $\text{CoFe}_2\text{O}_4@\text{GO}/\text{PEDOT}$ electrode.

Table 2. The obtained values for C_s , E and P of GO, $\text{CoFe}_2\text{O}_4@\text{GO}$, $\text{CoFe}_2\text{O}_4/\text{PEDOT}$ and $\text{CoFe}_2\text{O}_4@\text{GO}/\text{PEDOT}$ nanocomposites based MSCs.

| Sample | Current density (A/g) | C_s (Fg^{-1}) | E (Whkg^{-1}) | P (Wkg^{-1}) |
|--|-----------------------|----------------------------|--------------------------|-------------------------|
| GO | 2.5 | 314 | 42 | 2.4 |
| $\text{CoFe}_2\text{O}_4@\text{GO}$ | 2.5 | 389 | 53 | 1 |
| $\text{CoFe}_2\text{O}_4/\text{PEDOT}$ | 2.5 | 315 | 43 | 0.9 |
| $\text{CoFe}_2\text{O}_4@\text{GO}/\text{PEDOT}$ | 2.5 | 435 | 62 | 0.9 |
| $\text{CoFe}_2\text{O}_4@\text{GO}/\text{PEDOT}$ | 5 | 398 | 54 | 1.5 |
| $\text{CoFe}_2\text{O}_4@\text{GO}/\text{PEDOT}$ | 10 | 365 | 49 | 3.2 |

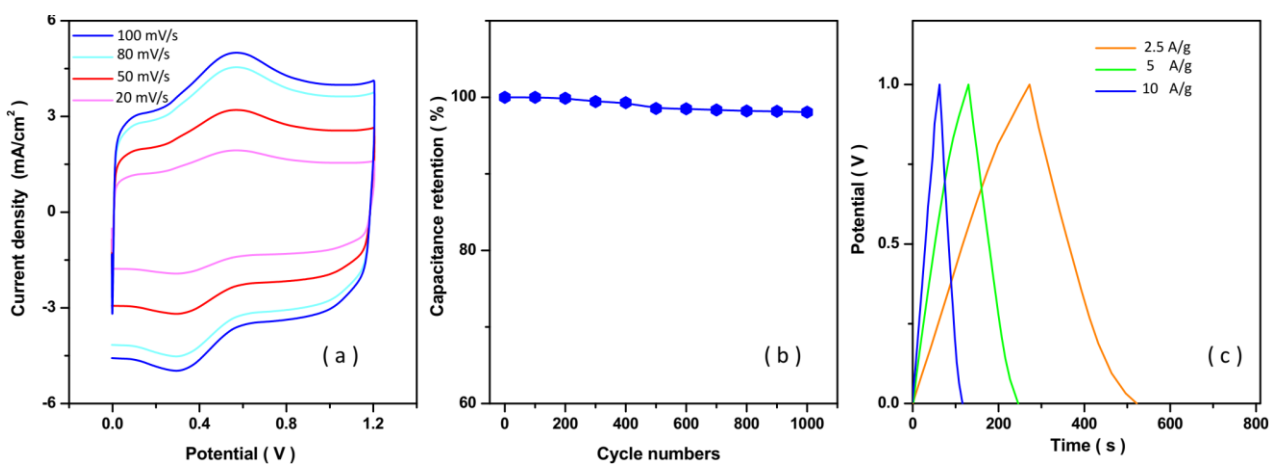


Figure 4. (a) CV at different scan rates from 20 to 100 mV/s, (b) GCD curves at current densities from 2.5 to 10 A/g of $\text{CoFe}_2\text{O}_4@\text{GO}/\text{PEDOT}$ in potential range from 0 to 1.2 V and (c) capacitance retention with respect to cycle numbers for $\text{CoFe}_2\text{O}_4@\text{GO}/\text{PEDOT}$.

Figure 4a indicates that the rectangular-like CV curve of $\text{CoFe}_2\text{O}_4@\text{GO}/\text{PEDOT}$ displays an increase in loop area with an increase in the scan rate from 5 to 100mV/s, demonstrating the increase in the current response and stability of $\text{CoFe}_2\text{O}_4@\text{GO}/\text{PEDOT}$ nanocomposite-based MSCs. Further

studies were conducted on the rate capability of the CoFe₂O₄@GO/PEDOT electrode through measurements of the GCD curves at current densities of 2.5, 5, and 10 A/g. Figure 4b depicts the resultant GCD profiles of the CoFe₂O₄@GO/PEDOT electrode which are symmetric, signifying excellent reversible charging-discharging performance. The obtained values for C_s, E and P of CoFe₂O₄@GO/PEDOT nanocomposite based MSC at current densities of 2.5, 5, and 10 A/g are presented in Table 1. It is observed that CoFe₂O₄@GO/PEDOT demonstrates excellent rate capability and high specific capacitance retention even at very high current densities. It exhibits specific capacitances of 398 and 365 Fg⁻¹ with 92% and 83% capacitance retention with increase the current density from 5 to 10 A/g, indicating the capacitance decreases with increasing current density because the diffusion and transfer of ions are limited at higher current densities [61, 62].

Table 3. Comparison between these results for CoFe₂O₄@GO/PEDOT nanocomposite based MSC and reported MSCs.

| Electrode material | Supporting electrolyte | C _s (F/g) | E (Wh/kg) | P (W/kg) | Current density (A/g) | Ref |
|---|--|-------------------------|--------------|-------------|--------------------------|-----------|
| Amorphous nickel hydroxide nanospheres | 1 M KOH | 153 | 35.7 | 490 | 4.3 | [63] |
| N/P co-doped ordered mesoporous carbon | 6 M KOH | 392 | 20.2 | 225 | 1 | [64] |
| nitrogen-doped active carbon/graphene | 6 M KOH | 378.9 | 13.1 | 12.5 | 2 | [65] |
| coffee grounds-derived/1T Reduced GO | 1 M H ₂ SO ₄ | 440 | 153.8 | 8750 | 0.5 | [66] |
| MoS ₂ /C | 1 M Na ₂ SO ₄ | 201.4 | -- | -- | 0.2 | [67] |
| Activated microwave exfoliated GO | 1-butyl-3-methyl-imidazolium Tetrafluoroborate/acetonitrile | 166 | 70 | 250 | 5.7 | [68] |
| Porous Activated Reduced GO | 1 M tetraethylammonium tetrafluoroborate/ acetonitrile | 120 | 26 | 500 | 10 | [69] |
| Activated microwave exfoliated GO | 1-ethyl-3-methylimidazolium bis-(trifluorosulfonyl)imide/ acetonitrile | 174 | 74 | 338 | 4.2 | [70] |
| PEDOT:PSS/CoFe ₂ O ₄ / Carbon Fiber Cloth | 1 M Na ₂ SO ₄ | 426 | 25.17 | 620.7 | 1 | [71] |
| rGO/CoFe ₂ O ₄ /PEDOT: PSS | 1 M KOH | 0.034 5 | 25.9 | 135.3 | 0.001 | [72] |
| CoFe ₂ O ₄ @GO/PEDOT | 100 g/l PVA/H ₂ SO ₄ | 435 | 62 | 0.9 | 2.5 | This work |
| | | 398 | 54 | 1.5 | 5 | |
| | | 365 | 48 | 3.2 | 10 | |

Figure 4c shows the results of the study on the cycling stability of CoFe₂O₄@GO/PEDOT nanocomposite based MSC as another important parameter of MSC. The cycling stability of the

sample was evaluated over 1000 continuous charge-discharge cycles at a scan rate of 50mV/s at room temperature. It can be found that the highly porous CoFe₂O₄@GO/PEDOT electrode displays outstanding capacitance retention of about 96% after 1000 cycles. There is a small decrease in specific capacitance after 500 cycles (~3 %). This decrease may be related to dissociation of the bimetal oxide ions during the redox process [73]. After 500 cycles, there is no significant change in specific capacitance value, demonstrating the good cycling stability of CoFe₂O₄@GO/PEDOT nanocomposite based MSCs.

Table 3 shows the comparison between these results for CoFe₂O₄@GO/PEDOT nanocomposite based MSC and reported MSCs. It can be observed that the developed nanocomposite-based MSC in this study shows better or comparable performance than other reported MSCs which can be attributed to synergetic effect of CoFe₂O₄@GO composite and porous conductive polymer PEDOT which provides good electrical conductivity and large surface area [71, 72].

4. CONCLUSION

This study focused on the fabrication of CoFe₂O₄@GO/PEDOT as stretchable nanocomposite based MSCs and studies of its structural and electrical properties and electrochemical characterization for MSCs applications. The hydrothermal method was used for the preparation of CoFe₂O₄@GO/PEDOT. Structural studies demonstrated the successful synthesis of CoFe₂O₄@GO/PEDOT, and synergistic effects of CoFe₂O₄ nanoparticles, GO nanosheets and coral-like morphology of PEDOT enhanced the effective surface area and provided the high porosity surface. Results of the study of the electrical properties of samples showed that the GO had the higher conductivity value, and electrical conductivity was decreased with the addition of CoFe₂O₄ and PEDOT to the GO-based nanocomposite. CoFe₂O₄ also showed the lower conductivity. Results of electrochemical studies indicated that the areal specific capacitance, energy density and power density of CoFe₂O₄@GO/PEDOT nanocomposites based MSCs were obtained at 435F/g, 62Wh/kg and 0.9W/kg, respectively, at a current density of 2.5A/g in electrolyte of 100g/l PVA/H₂SO₄. A comparison between the results for CoFe₂O₄@GO/PEDOT nanocomposite based MSC and reported MSCs showed the better or comparable performance than other reported MSCs. In the study, the cycling stability of developed MSC showed an outstanding capacitance retention of about 96% after 1000 cycles, demonstrating the good cycling stability of CoFe₂O₄@GO/PEDOT nanocomposite based MSCs.

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