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Electrochemical performance and complex impedance properties of reduced-graphene oxide/polypyrrole nanofiber nanocomposite

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Abstract

Reduced-graphene oxide/polypyrrole nanofiber (RGO/PPy-Nf) nanocomposite has been prepared as the electrode material of the supercapacitor. This nanocomposite was prepared via a facile two-step process, including exfoliation and reduction of graphene oxide by microwave irradiation (MRGO) and in situ polymerization pyrrole onto it. The morphological, structural, and porosity characterizations of this nanocomposite were shown the proper formation of RGO/PPy-Nf composite with a mesoporous structure. The high specific capacitance of 277 F g⁻¹ was obtained for the RGO/PPy-Nf nanocomposite at a constant current density of 1 A g⁻¹ in a 1 M H₂SO₄ solution electrolyte. This nanocomposite revealed the highest energy density of 38.5 Wh kg⁻¹ with a corresponding power density of 500 W kg⁻¹, and the capacitor response time revealed that the dominant mechanism in pristine PPy and MRGO is faradaic reactions and electrical double-layer capacitance (EDLC), respectively, and both mechanisms play a role in the RGO/PPy-Nf nanocomposite. Also, the relaxation time investigation revealed this nanocomposite exhibit an ideal capacitive behavior at very low frequency.

Keywords Reduced graphene oxide \cdot Polypyrrole nanofiber \cdot Supercapacitor \cdot Microwave-assisted method \cdot In situ chemical polymerization \cdot Electrochemical measurements

Introduction

Renewable energy productions and energy storage systems have recently developed due to the growing interest in clean and portable devices [1–3]. Among them, supercapacitors have become of great interest due to their superior properties, such as rapid charge/discharge process, high power density, and long cycle life. However, they have low energy density

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compared to batteries [2, 4, 5]. Supercapacitors in terms of charge storage mechanisms are classified as (i) EDLCs where electrolyte ions are adsorbed onto the surface of an electrode and (ii) pseudocapacitors where the charges are stored by fast and reversible faradaic reactions [2, 6].

Specific surface area, porosity, electrical conductivity, and stability are essential factors in the electrode material of a supercapacitor [7, 8]. Typically, the electrode materials of supercapacitors can be classified into: (i) carbon materials and their derivatives, which are as an EDLC [5, 9, 10]; (ii) transition metal oxides (nitrates or sulfides) [11–13] and conducting polymers [14, 15], which are as a pseudocapacitor [1]. Among carbon-based materials, graphene with a 2-dimensional carbon atom structure with an sp²-hybridized has a high theoretical specific surface area and excellent electrical properties [16-18]. It exhibits a good EDLC, but the agglomeration and weak mechanical stability of graphene sheets limit the energy density and cycling stability of supercapacitors [19]. To overcome these problems, some graphene-based composite electrodes have been recently proposed [15, 20-24]. Conductive polymers (such as polypyrrole (PPy), polyaniline (PAni), and poly(3,4-ethylene dioxythiophene) (PEDOT)), due to their rapid faradaic reactions and high theoretical capacitance, are an ideal candidate for it [1, 25-27]. Among them, PPy is one of the most extensively developed cases due to its good redox properties, flexibility, high conductivity, availability of initial monomers, and environmental stability [1]. Various composites of graphene and PPv have been studied in terms of capacitive performance, which often show the improvement of ion diffusion rate and surface area [28-34]. Zhang et al. directly coated PEDOT, PPy, and PAni on the reduced graphene oxide and achieved a specific capacitance of 102, 204, and 323 F g^{-1} , respectively, at a current density of 1 A g^{-1} [14]. By a pulsed electropolymerization technique, Davies et al. reported a graphene-polypyrrole composite film. They obtained a specific capacitance of 237 F g⁻¹, an energy density of 33 Wh kg⁻¹, and a power density of 1184 W kg⁻¹, at a scan rate of 10 mV s⁻¹ [35]. In these electrochemical systems, investigation of charge kinetic and behavior of each component is essential that can be evaluated by electrochemical impedance spectroscopy (EIS). Impedance analysis can be used to determine resistance and capacitance properties of each cell component, such as electrode, electrolyte, and collector. Furthermore, the frequency dependence of the electrode behavior can be utilized to study capacitive and resistive behavior in different frequency regions [36, 37].

In this study, the RGO/PPy-Nf nanocomposite has been prepared as the supercapacitor electrode material. This nanocomposite is prepared using a facile two-step method, including exfoliation and reduction of graphene oxide (GO) by microwave irradiation and in situ oxidative polymerization pyrrole onto it. The characterization of this nanocomposite in terms of morphology, structure, and porosity has demonstrated the proper formation of RGO/PPy-Nf mesoporous nanocomposite. It has exhibited a maximum specific capacitance of 277 F g^{-1} and a high energy density of 38.5 Wh kg⁻¹ at 1 A g^{-1} , which can be attributed to the improvement of pseudocapacitance properties. In evaluating the samples by EIS, the obtained values of capacitor response time reveal that the dominant mechanism in pristine PPy and MRGO is faradaic reactions and EDLC, respectively, and both mechanisms play a role in the RGO/PPy-Nf nanocomposite. Also, relaxation time measurement shows that this nanocomposite exhibits an ideal capacitive behavior at very low frequency.

Experiment

Preparation of the samples

The RGO/PPy-Nf nanocomposite was prepared via in situ oxidative polymerization of pyrrole onto MRGO nanosheets. The weight ratio of pyrrole to MRGO was selected as 10:1. It was found that this ratio show the maximum conductivity [30]. Briefly, 0.2 g of MRGO was dispersed in 80 mL of ethanol with ultrasonication (SCENTZ-IID Ultrasonic Homogenizer) for 30 min at the power of 500 W. The mixture was stirred and cooled in an ice bath under an N2 atmosphere, and the freshly distilled pyrrole monomer was added to it. Then, 4.9 g of iron (III) chloride hexahydrate (\geq 99%) was dissolved in 0.1 M hydrochloric acid, and the product solution was slowly injected into the suspension with stirring. The mixture was allowed to proceed at 0-5 °C for 24 h. Finally, the suspension was filtrated, washed subsequently with DI water and ethanol several times, and dried overnight under a vacuum at 60 °C. The pure PPy was also prepared by using the identical method. As-prepared, the samples were kept in a cool place for followed characterizations.

Measurements and characterizations

The morphological and structural characterizations of the samples were studied by the transmission electron microscopy (TEM), field emission gun scanning electron microscopy (FE-SEM), Fourier transform infrared (FTIR), Raman spectroscopy, X-ray powder diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) at room temperature. The thermal stability was analyzed using thermogravimetric analysis (TGA) under a nitrogen atmosphere. The porous textural properties were evaluated using the BET method at 77 K. Specifications of these devices are given in the Supporting Information.

The electrochemical properties of the synthesized samples were determined by using a CHI660E Electrochemical Workstation system (Shanghai, China) at ambient temperature. In this system, the counter and reference electrodes were platinum foil and Ag/AgCl, respectively. For the working electrodes, the mixture was prepared by 80 wt% of the activated material (MRGO, PPy, or RGO/PPy-Nf nanocomposite), 10 wt% of polyvinylidene fluoride, and 10 wt% of activated carbon, which were dispersed in 1-methyl-2pyrrolidinone. The obtained slurry was cast onto the glassy carbon electrode by a micropipette and dried at 60 °C for 24 h. All the measurements were carried out in a solution of 1 M H₂SO₄ as the electrolyte. It is the common aqueous acid electrolyte bearing the merits of easy handling in an open environment and has a low ionic resistivity.

Cyclic voltammetry (CV) was done at the different voltage scan rates in the potential window of -0.2 to +0.8 V (vs. Ag/AgCl). Also, galvanostatic charge/discharge (GCD) measurements were carried out at the different applied current in the potential range of -0.2 to +0.8 V. The specific capacitance

 $(C_s^{dis} \text{ in F g}^{-1})$ is calculated by the following expression from the discharge part of GCD curves [39, 40]:

$$C_s^{dis} = \frac{I}{m \frac{\Delta V}{\Delta t}} \tag{1}$$

where *I* is the applied current, ΔV , Δt , and *m* are the potential window (in V), the discharge time (in s), and the mass of active electrode material (in g), respectively. EIS measurements were done at an open circuit potential of 0.4 V in the frequency range from 10^{-2} to 10^{5} Hz.

Results and discussion

The preparation process of RGO/PPy-Nf nanocomposite is schematically illustrated in Fig. 1. The optical images of GO powders before and after microwave irradiation (MWI) demonstrate the reduction and expansion of GO under MWI. The FE-SEM image of MRGO exhibits a good exfoliation of MRGO nanosheet after MWI. Also, the TEM image of RGO/PPy-Nf nanocomposite clearly illustrates polypyrrole nanofibers' formation onto the MRGO sheets.

XRD pattern of GO, MRGO, PPy, and RGO/PPy-Nf nanocomposite is presented in Fig. 2a. The feature diffraction peaks at $2\theta = 10.56^{\circ}$ and 42.36° are corresponded to (001) and (100) planes of GO, respectively. The diffraction peak at $2\theta = 26.50^{\circ}$ related to (002) planes of MRGO, implied that the GO had been reduced to MRGO after microwave [41]. Also, it can be seen that a broad diffraction peak at $2\theta = 22.14^{\circ}$ for pristine PPy, which arises from its amorphous structure [42]. This peak overlaps with the (002) peak of MRGO for the RGO/PPy-Nf composite sample, and they generate a new broad peak at $2\theta = 26.36^{\circ}$.

The XPS survey spectra of the RGO/PPy-Nf nanocomposite, shown in Fig. 2b, exhibit characteristic peaks of C 1 s, N 1 s, and O 1 s orbitals at the binding energies of 285.0, 400.2, and 533.2 eV, respectively. It clearly illustrates the presence of carbon, nitrogen, and oxygen elements in this nanocomposite. In Fig. 2c, the high-resolution deconvolution of C 1 s corelevel spectra exhibits the characteristic peaks at binding energies of 285.1, 286.5, 287.2, and 288.3 eV, which assign to C– C/C=C, C–N, C–O, and C=O bonds, respectively [43]. The decomposed N 1 s core-level spectrum has been shown in Fig. 2d. The peaks of the N 1 s signal at 396.7 and 399.3 eV correspond to the imine (-N=) and amine (-NH-) nitrogen atoms, respectively [14, 44]. Two characteristic peaks at the



Fig. 1 The schematic illustration of the preparation of RGO/PPy-Nf nanocomposite. The optical images of GO and MRGO powders before and after MWI, FE-SEM image of MRGO powders, and TEM images of RGO/PPy-Nf nanocomposite



Fig. 2 a XRD patterns of the synthesized samples, b the XPS survey spectra, and the deconvolution of c C 1 s and d N 1 s core-level spectra of the RGO/ PPy-Nf nanocomposite

higher energy of 400.0 and 403.3 eV can be attributed to protonated nitrogen atoms or high oxidation states of the nitrogen atoms (N_{I}^{+} and N_{II}^{+}) [44, 45].

FTIR spectra of MRGO, PPy, and RGO/PPy-Nf nanocomposite have been presented in Fig. 3a. The active band at 3425 cm⁻¹ in the spectrum of PPy is assigned to the N–H stretching. The peak at 1532 cm⁻¹ corresponds to the asymmetric ring-stretching vibration [46], and the bands at 1288, 1160, and 980 cm⁻¹ are assigned to the in-plane vibration of = C–H, stretching vibration of –C–N, and –C–H, respectively [47]. Also, the band at 1033 cm⁻¹ can be assigned to some residue oxide groups such as –C–O [32]. The peaks at 3425, 1532, 1288, 1033, and 980 cm⁻¹ significantly are observed in the spectrum of RGO/PPy-Nf nanocomposite, which proves a strong interaction between PPy and MRGO. As shown in Fig. 2b, the bands at 1532 and 1033 cm⁻¹ in the spectrum of RGO/PPy-Nf nanocomposite have stronger peak intensities than

PPy, due to overlap with intensive peaks of MRGO at 1605 and 1118 cm⁻¹, respectively. Also, the peak at 1160 cm⁻¹ corresponding to the PPy compound shifts to a lower wavenumber at 1147 cm⁻¹ for RGO/PPy-Nf nanocomposite, which can be attributed to the interaction of the N–H group in PPy with the –OH group of MRGO through hydrogen bonding.

Raman spectroscopy of the samples has been shown in Fig. 3b. Two observed characteristic bands at the wavenumber of 1588 and 1350 cm⁻¹ in the spectrum of MRGO are related to the G- and D-bands of carbonaceous materials, respectively [47]. The G-band is attributed to E_{2g} mode from the in-plane vibration of sp² carbon, while D-band corresponds to A_{1g} phonons of sp³ carbon atoms in disordered graphite [48, 49]. The characteristic peaks at 1568, 1042, and 977 cm⁻¹ in the Raman spectrum of PPy are attributed to the C=C stretching vibration, C–H in-plane deformation vibration, and the pyrrole ring deformation, respectively [47]. As shown in Fig. 3b,



Fig. 3 a FTIR and b Raman spectra, and c TGA plots of MRGO, PPy, and RGO/PPy-Nf nanocomposite. d The N₂ adsorption-desorption isotherms and pore size distribution (inset) of RGO/PPy-Nf nanocomposite

the peaks at 977, 1042, and 1350 cm⁻¹ are presented in RGO/ PPy-Nf nanocomposite spectrum, and the G-band has been shifted to 1562 cm⁻¹. This small red-shift can be attributed to the π - π interaction of PPy chains with MRGO sheets, suggesting the formation of RGO/PPy-Nf nanocomposite [50]. The ratio of D-band to G-band intensity (I_D/I_G), which can be related to the density of defects and the graphitization degree of carbonaceous materials, is 0.900 for MRGO, while this value increases to 0.922 for RGO/PPy-Nf nanocomposite, indicating a decrement in the sizes of in-plane sp² domains and the higher defects in it [46, 48].

The thermal stability of the samples is investigated by using TGA curves (Fig. 3c). The theoretical weight loss for RGO/PPy-Nf nanocomposite, according to the initial weight ratio of polymer to graphene (10:1) is calculated to be about 44.6% at 800 °C. In comparison, its experimental value

obtains 32.3%, which might be due to pyrrole monomers' interaction and reduced graphene oxide sheets.

To study the specific textural properties, the N₂ adsorptiondesorption isotherms (using the BET method) and Barrett-Joyner-Halenda (BJH) pore size distribution are investigated for RGO/PPy-Nf nanocomposite, and their results are shown in Fig. 3d. The nitrogen adsorption-desorption isotherm plot with clear hysteresis loop in the range of 0.45–1 PP₀⁻¹, classified as typical type-IV isotherm, indicates the mesoporous nature of material [51]. The BJH pore size distribution of RGO/PPy-Nf nanocomposite is shown in the inset of Fig. 3d. The BET-specific surface areas and BJH average pore diameter of the RGO/PPy-Nf nanocomposite are calculated as 12.03 m² g⁻¹ and 24.30 nm, respectively. The efficient transport of charge carriers into the RGO/PPy-Nf nanocomposite electrode material leads to high electrochemical performance because of their high surface area and mesoporous structure.

The cyclic voltammetry analyses were done for all the samples at scan rates of 5, 10, 20, 50, and 100 mV s⁻¹. The CV plot of RGO/PPy-Nf nanocomposite has been shown in Fig. 4a. The CV plots of MRGO and pristine PPy have been shown in Figs. S1 and S2, respectively. The CV curve of RGO/PPy-Nf nanocomposite demonstrates a near-rectangular shape with a broad redox peak, suggesting pseudocapacitance behavior [4]. As can be seen in Fig. 4a, the area of the closed CV loop of RGO/PPy-Nf nanocomposite electrode increases, and its redox peak shifts to higher potential with increasing the scan rates, indicating a good ion response and rate capability [14, 52]. Figure 4b presents the CV plots of the samples at a scan rate of 5 mV s⁻¹. It can be seen that the current density and the closed-loop area of RGO/PPy-Nf nanocomposite have dramatically increased than both

PPy and MRGO at the same scan rate. It reveals that the specific capacitance of RGO/PPy-Nf nanocomposite significantly increases, which can be due to the efficient combination and the synergistic effects between this nanocomposite components.

The current peak in the CV curve is related to the potential scan rate following a power law: $I_p = a \ \vartheta^b$, where I_p is the current peak intensity, a and b are fitting coefficients, and ϑ is the scan rate [4, 53]. This dependence is used to determine the rate-limiting step and kinetic information of an electrochemical reaction [54, 55]. It was found that b has values between 0.5 and 1, where it is ≈ 0.5 for a redox reaction limited by semi-infinite diffusion and ≈ 1 for a capacitive process (which is attributed to the battery and capacitive behavior, respectively) [4]. Come et al. showed that $b \approx 0.5$ for LiFePO₄, which is used as a Li-ion battery material [55], while it was obtained ≈ 1 for Nb₂O₂, which was used as a capacitor



Fig. 4 The CV plots of **a** RGO/PPy-Nf nanocomposite at different scan rates, and **b** the samples at a 5 mV s⁻¹. **c** The current peak behavior versus scan rates for the samples

material by Augustyn et al. [54]. The behavior of the current peaks (I_p) versus the potential scan rate has been shown in Fig. 4c for MRGO, PPy, and RGO/PPy-Nf nanocomposite. The solid lines in Fig. 4c show the best fitting of this power law equation to the experimental data. The obtained *b* value is 0.82 and 0.52 for the MRGO and PPy, respectively. It reveals that the pristine PPy exhibits a battery-type behavior, and redox reactions play a prominent role in the storage mechanism. In contrast, the MRGO exhibits a capacitive-type behavior. The *b* parameter increases to 0.90 for RGO/PPy-Nf nanocomposite. It can be attributed to a decrease in the redox reactions in RGO/PPy-Nf nanocomposite due to π - π interactions between PPy chains and MRGO sheets. Thus, RGO/PPy-Nf nanocomposite exhibits capacitance behavior.

The electrochemical performance can be evaluated by GCD measurements under current-controlled conditions. Figure 5 a illustrates the GCD curves of RGO/PPy-Nf nanocomposite at a current density of 1, 2, 3, 5, and 10 A g^{-1} at the potential range of -0.2 to 0.8 V for the first cycle. The GCD plot of RGO/PPy-Nf nanocomposite represents a deviated triangular symmetry, revealing pseudocapacitive behavior. It agrees with the obtained results by the current peaks (I_n) in Fig. 4c. The GCD curves of MRGO and PPy have been shown in SI (Figs. S3 and S4). The GCD plots of the samples have been shown in Fig. 5b at 1 A g^{-1} . The longer discharge time of RGO/PPy-Nf nanocomposite indicates a higher specific capacitance. The specific capacitance values were calculated using Eq. (1), and their results are shown in Fig. 5c. The maximum obtained specific capacitance is 48.4, 36.8, and 277.0 F g⁻¹ for MRGO, PPy, and RGO/PPy-Nf nanocomposite at 1 A g^{-1} respectively. The theoretical specific capacitance of RGO/PPy-Nf nanocomposite can be calculated by $C_{S_{RGO/PPy-Nf}} = R_{MRGO} C_{S_{MRGO}} + R_{PPy} C_{S_{PPy}}$, where R_{MRGO} and R_{PPv} are weight percentage of MRGO and PPy, respectively, and $C_{S_{MRGO}}$ and $C_{S_{PPv}}$ are the specific capacitance of MRGO and polypyrrole, respectively. The theoretical specific capacitance of RGO/PPy-Nf nanocomposite is obtained 37.8 F g^{-1} . It reveals that the specific capacitance of RGO/PPy-Nf nanocomposite has increased by seven times than its components, which can be assigned to the synergistic effects between this nanocomposite components. The specific capacitance of MRGO, PPy, and RGO/PPy-Nf nanocomposite decreases to 29.1, 8.2, and 177.6 F g^{-1} with increasing current density to 10 A g^{-1} . It can be attributed to the inability of ions to the whole diffusion into the internal sites of electrode material that results in a decrease of specific capacitance with increasing current [42]. This specific capacitance value is higher than both the reported specific capacitance value for RGO/PPy nanocomposite by Zhang et al. (204 F g^{-1} at 1 A g^{-1} , in a similar preparation method) [14] and by Zhu et al. (223.5 F g^{-1} at 1.6 A g^{-1} in 3 M KCl electrolyte, prepared using chemical reduction of GO) [56].

The Ragone plot, which is the relationship between the energy density (E) and power density (P), is illustrated in Fig. 5d for RGO/PPy-Nf nanocomposite. The specific energy density is given by the equation of $E = C_s^{dis} V^2/2$, where C_s^{dis} and V are the GCD specific capacitance (in F g^{-1}) and potential window (in V), and the power density is given by P = E/t, where t is discharge time (in s). The RGO/PPy-Nf nanocomposite exhibits a maximum energy density of 38.5 Wh kg⁻¹ with a power density of 500 W kg^{-1} at a current density of 1 A g^{-1} . Such high energy density can be ascribed by the ability of the electrolyte ions to diffuse throughout the porosity of the electrode material and the presence of proper pseudocapacitance behavior due to synergistic effects [57]. This nanocomposite at a high power density of 5000 W kg⁻ at 10 A g^{-1} , still has a high energy density of 24.6 Wh kg⁻¹. The decreasing energy density, at this high current density, can be due to time deficiency of ion diffusion to the electrode material [57].

The retention of specific capacitance of RGO/PPy-Nf nanocomposite was evaluated in a first 1000-cycle GCD configuration at a current density of 1 A g⁻¹. As can be seen in Fig. 5e, the specific capacitance decreases to 267 F g⁻¹ (\approx 96.4%) for the first 100 cycles, which may be due to the activation process and broken-off nanocomposite structure. After 1000 cycles, the specific capacitance has still maintained 263 F g⁻¹, which is \approx 95% of the first cycle. This excellent long-term stability is comparable to 81% reported for RGO/PPy nanocomposite by Zhang et al. [14] and 90% reported for graphene/PPy nanocomposite by Bose et al. [58].

The frequency-dependent electrochemical properties of the samples were evaluated by the electrochemical impedance spectra. The results of EIS measurements have been shown in Fig. 6a-d for the samples. Nyquist plots, which can illustrate the frequency response of the electrode/electrolyte system, have been shown in Fig. 6a in the frequency range of 10^{-2} -10⁵ Hz. The solid lines in Fig. 6a are the results of the best fitting with an equivalent circuit, shown in Fig. 6b. The combination of electrolyte resistance, intrinsic resistance of active electrode material, and active-material/collector contact resistance, called R_s , is determined from the intercept of the real impedance axis at very high frequencies [57, 59]. R_{ct} is charge-transfer resistance between electroactive material and electrolyte in the electrochemical process. The equivalent circuit of Fig. 6b consists of a modified Randles circuit cell [36], as R_{ct} is in series with a Warberg impedance (Z_w) and both in parallel with a constant phase element (CPE). Also, C_F and R_L are the faradaic capacitance and limit resistance, respectively [60]. The obtained values of parameters based upon the best fitting of the equivalent circuit to the experimental data are presented in Table S1. R_{ct} value is 1.99, 46.57, and 5.21 Ω for MRGO, pristine PPy, and RGO/PPy-Nf nanocomposite, respectively. The lower R_{ct} of MRGO can be attributed to the electrical conductivity of MRGO sheets. It is also found that



Fig. 5 The GCD plots of a RGO/PPy-Nf nanocomposite at different current density, and **b** the samples at 1 A g^{-1} . **c** The behavior of specific capacitance versus current density for the samples. **d** Ragone plot and **e** specific capacitance behavior versus cycle numbers for RGO/PPy-Nf nanocomposite

the charge transfer resistance in RGO/PPy-Nf nanocomposite is much lower than for pristine PPy. The equivalent series resistance (*ESR*) of the system is evaluated with R_s , R_{ct} , and R_L . The obtained ESR value is 13.64 and 17.77 Ω for MRGO



Fig. 6 a The Nyquist plots for the samples and their fitted lines, and magnified part of it at the high-frequency region of the inset, **b** represents the electrical equivalent circuit. **c** The magnitude of complex resistance

and the phase angle, and **d** the real (C') and imaginary (C'') parts of complex specific capacitance versus log(ω) for the samples

and RGO/PPy-Nf nanocomposite, respectively, which agrees with the obtained value CPE-n = 0.58 for RGO/PPy-Nf nanocomposite. However, the obtained high capacitance of $C_{\rm F} = 0.018$ F for RGO/PPy-Nf nanocomposite (rather than 0.002 F for MRGO and 3.05×10^{-6} F for PPy) indicates an improvement of charge storage that arises from the pseudocapacitance mechanism.

The magnitude of complex resistance $(\log |Z(\omega)|)$, and the phase angle $\Phi(\omega)$, (Bode plots) has been shown in Fig. 6c as a function of frequency (log ω) for the samples, where ω is the angular frequency. The Bode plots can be divided into the

frequency dependence into low-, medium-, and highfrequency regions. The low-frequency region can be considered the near – 1 slope in log |Z| plot and phase angle between – 45° and – 90°. The regions where the frequency dependence of the |Z| is weak, and the phase angle is close to zero, can be regarded as the high-frequency regions [61, 62]. The lowfrequency region is below 8.94 and 1.6 Hz for the MRGO and RGO/PPy-Nf nanocomposite, respectively. As shown in Fig. 6c, the low-frequency regions for PPy is between 0.16 and 4.76 Hz. At these low-frequency regions, the samples indicate capacitive behavior. Besides, the corresponding frequency $\Phi = -45^{\circ}$, shown by dash lines in Fig. 6c, can be related to the frequency response to the ideally capacitive behavior [61, 62]. The obtained response time of the capacitor is 0.11, 6.2, and 0.62 s for MRGO, PPy, and RGO/PPy-Nf nanocomposite, respectively. The longer response time of PPy and shorter response time of MRGO can be attributed to faradaic reaction and EDLC mechanism, respectively, supported by obtained results from the current peak (I_P) in Fig. 4c.

Supercapacitors exhibit a capacitance behavior at low frequencies, a resistance behavior at high frequencies, and their combination at medium frequencies. The frequency dependence of complex capacitance, $C(\omega)$, can be used to study capacitive and resistive behavior. The real (C') and imaginary (C'') part of complex specific capacitance can be inferred from the complex impedance from the following equations [37]:

$$C'(\omega) = \frac{-Z^{\dagger}(\omega)}{m\omega|Z(\omega)|^2}$$
(2)

$$C^{\dagger}(\omega) = \frac{Z'(\omega)}{m\omega|Z(\omega)|^2}$$
(3)

C' and C'' correspond to the charges in available stored energy and energy dissipation process as a function of frequency, respectively. C' and C'' have been illustrated as a function of frequency in Fig. 6d for the samples. The characteristic frequency of f_0 can divide the electrode behavior predominantly into capacitive and resistive behavior. The f_0 can be determined from the peak frequency of C'' [63]. The relaxation time constant, $\tau_0 \left(= \frac{1}{f_0} \right)$, which is a minimum time needed to discharge all of the stored energy from electrode material, can be deduced from the complex capacitance plots. The obtained f_0 value was 3.83, 0.018, and 1.00 Hz for MRGO, PPy, and RGO/PPy-Nf nanocomposite, respectively. It reveals that MRGO exhibits a capacitive behavior on a broader frequency range, which can be attributed to the more electrical conductivity of MRGO, supported by obtained results from their ERS values.

Conclusion

The RGO/PPy-Nf nanocomposite was prepared as an electrode material of a supercapacitor. The results of FE-SEM and TEM images, XRD patterns, FTIR and Raman spectroscopy, XPS, and BET analysis confirmed the formation of RGO/PPy-Nf nanocomposite with a mesoporous structure. The high specific capacitance of 277 F g⁻¹ was obtained for the RGO/PPy-Nf nanocomposite at a constant current density of 1 A g⁻¹ in a 1 M H₂SO₄ solution electrolyte. This nanocomposite revealed the highest energy density of 38.5 Wh kg⁻¹ with a corresponding power density of 500 W kg⁻¹. The capacitive retention of 95% after 1000 cycle

demonstrated excellent cyclic stability of this nanocomposite. In evaluating the samples by electrochemical impedance spectroscopy, the values of capacitor response time revealed that the dominant mechanism in pristine PPy and MRGO is faradaic reactions and electrical double-layer capacitance, respectively, and both mechanisms play a role in the RGO/PPy-Nf nanocomposite. These good capacitive properties can be assigned to the synergetic effect of both EDLC and pseudocapacitance in this nanocomposite. Also, relaxation time investigation revealed that this nanocomposite exhibits an ideal capacitive behavior at very low frequency.

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