Electropolymerized Polypyrrole Nanocomposites with Cobalt Oxide Coated on Carbon

Paper for Electrochemical Energy Storage

Huige Wei ^{a,b}, Cuizhu He ^c, Jiurong Liu ^{c,*}, Hongbo Gu, ^d Yiran Wang ^a, Xingru Yan ^a,
Jiang Guo ^a, Daowei Ding ^b, Nancy Z Shen ^b, Xuefeng Wang ^d, Suying Wei ^{b, e,*}
and Zhanhu Guo ^{a,*}

^a Integrated Composites Laboratory (ICL), Department of Chemical and Biomolecular Engineering, The University of Tennessee, Knoxville, TN 37996 USA

^b Dan F. Smith Department of Chemical Engineering
Lamar University, Beaumont, TX 77710 USA

^c Key Laboratory for Liquid-Solid Structural Evolution and Processing of Materials, Ministry of Education and School of Materials Science and Engineering, Shandong University, Jinan, Shandong 250061 China

^d Department of Chemistry, Key Laboratory of Yangtze River Water Environment, Ministry of Education, Tongji University, Shanghai 200092 China

^e Department of Chemistry and Biochemistry, Lamar University, Beaumont, TX 77710 USA

*Authors to whom correspondence should be addressed.

E-mail: zguo10@utk.edu (Z. G.); jrlu@sdu.edu.cn (J. L.); swei@lamar.edu (S.W.)

ABSTRACT

Polypyrrole (PPy)/cobalt oxide (Co_3O_4)/carbon paper (CP) ternary composites prepared by potentiodynamic electropolymerization of pyrrole monomers onto flower-like Co_3O_4 (f- Co_3O_4) nanoparticles coated on CP (PPy/f- Co_3O_4 /CP) were studied serving as electrode materials for supercapacitor applications. The f- Co_3O_4 with unique porous morphology on CP was first obtained by drop casting Co_3O_4 ethanol suspensions onto CP. Ball-like Co_3O_4 (b- Co_3O_4) with dense structure was also prepared for comparison. The electrochemical results including cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) in 2.0 M KOH aqueous solution revealed that the PPy/ Co_3O_4 /CP ternary composites exhibited superior supercapacitive performances than both f- Co_3O_4 /CP and b- Co_3O_4 /CP. Specifically, a specific capacitance of 398.4 F/g was obtained for the PPy/f- Co_3O_4 /CP, much higher than that of 40.9 and 22.0 F/g for f- Co_3O_4 /CP and b- Co_3O_4 /CP, respectively. The electrochemical impedance spectroscopy studies suggested that better capacitive properties in PPy/f- Co_3O_4 /CP were attributed to the pseudocapacitive contributions from the PPy nanocoating and greatly reduced charge transfer resistance in the composites. PPy/f- Co_3O_4 /CP also displayed an excellent cycling stability with negligible capacitance loss after 1000 cycles.

Keywords: Cobalt oxide; Polypyrrole; Carbon paper; Composites; Supercapacitor

1. Introduction

Conductive polymers and their composites have emerged as new materials of great potential considering their cost-effective processability, lightweight, tunable mechanical and magnetic properties, and environmental friendliness [1,2]. Versatile applications for electrocatalysts [3], sensors [4,5], anticorrosion [6], carbon dioxide captures [7], nanofiltration membranes for separating organic mixtures [8], light emitting diodes [9], electrochromic devices [10], batteries [11], and electrochemical capacitors [12,13] have been explored till now. Among the conductive polymers including polyaniline (PANI) [14–16], polythiophenes and their derivatives [17], poly(DNTD) [18,19], polypyrrole (PPy) has received more attention for the easy oxidation, water solubility, and commercial availability of pyrrole monomers [20]. Recently, PPy composites used for supercapacitors have been intensively studied due to their fast electrochemical switching, good redox reversibility, and high pseudocapacitance values [21]. For example, carbon materials such as graphene [22], carbon nanotubes [23] and carbon nanofibers [24] were introduced to PPy matrix for improving the electrical conductivity and rate capability of the electrode. Our previous work has also demonstrated the feasibility of preparing uniform PPy nanocoatings on carbon paper (CP) using potentiodynamic electropolymerization technique at lower scan rates. However, the improvement of the supercapacitive performance is limited due to low capacitances and energy densities of the carbons [25]. Therefore, PPy incorporated with materials of higher capacitances has been investigated, for example, transition metal oxides including RuO_2 [26], MnO_2 [27], CoO [28], V_2O_5 [29], and MoO_3 [30], as well as conductive polymers such as PANI [31]. Of all the transition metal oxides, Co_3O_4 is considered as a promising candidate in view of its relatively low cost, high theoretical capacitance of 3560 F/g [32], and excellent redox activities. Via the reversible faradic redox reactions, Co_3O_4 exhibits excellent electrochemical

behavior with its ability to interact with electrolyte ions not only at the surface, but also throughout the bulk in alkaline solutions [33]. The other advantage of Co_3O_4 is its controllable size and shape, tunable surface, and structural properties. Nanoparticles [34], nanorods [35], and nanowires [36] have been synthesized through the hydro-thermal/solvothermal route. A proper morphology and optimized microstructure will endow Co_3O_4 based electrodes with high specific surface areas and facilitated electrolyte ion transport [37]. For example, Dong et al. reported chemical oxidative polymerization of pyrrole monomers in the presence of Co_3O_4 particles to form PPy and Co_3O_4 power composites, and then prepared stable films for the immobilization of hemoglobin and glucose oxidase by dissolving the composites in ionic liquids [38]. Liu et al. also studied the reduced graphene oxide-PPy- Co_3O_4 ternary composites for microwave absorption [39]. Yet, to couple Co_3O_4 with PPy for energy storage applications, to the best of our knowledge, has rarely been reported.

Herein, PPy ternary composites via electropolymerization of pyrrole monomers onto carbon paper (CP) modified with Co_3O_4 were prepared for supercapacitor applications. Two different structured cobalt oxides, i.e., flower-like cobalt oxide (f- Co_3O_4) and ball-like cobalt oxide (b- Co_3O_4) were first synthesized through a facile solvothermal method. The structure and morphology of the cobalt oxides were examined by X-ray powder diffraction (XRD) and field emission scanning electron microscope (FE-SEM). The f- Co_3O_4 /CP and b- Co_3O_4 /CP electrodes were prepared by drop casting the two structured cobalt oxide ethanol suspensions onto CP, respectively. PPy/f- Co_3O_4 /CP ternary composites were fabricated by electropolymerization of pyrrole monomers on the pre-obtained f- Co_3O_4 /CP. Supercapacitive performances of the f- Co_3O_4 /CP, b- Co_3O_4 /CP, and PPy/f- Co_3O_4 /CP were evaluated using cyclic voltammetry (CV),

galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy measurements.

2. Experimental

2.1 Materials

The carbon paper (CP, thickness: 0.010 ± 0.001 inch, density: 0.46 g/cm^3 , mean pore diameter: $30 \text{ }\mu\text{m}$, electrical resistivity: $2 \text{ }\Omega/\text{cm}$) was provided by Fuel Cell Store. Cobalt acetate tetrahydrate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, analytical grade), methanol (analytical grade) and polyvinylpyrrolidone (PVP, K30 with average Mw 40,000) were purchased from Sinopharm Chemical Reagent Co., Ltd. All the chemicals were used as received without any further treatment.

2.2 Preparation of *f*- Co_3O_4 and *b*- Co_3O_4

The cobalt oxides were synthesized through a facile solvothermal method. Specifically, for *f*- Co_3O_4 , 2 mmol cobalt acetate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) and 1.0 g polyvinyl-pyrrolidone (PVP, K30) were dissolved in 40 mL methanol under magnetic stirring. The resulting red solution was transferred into a 100 mL Teflon-lined stainless steel autoclave, sealed, and subsequently heated in an oven at 453 K for 3 h. The intermediate precursor of $\text{Co}(\text{OH})_2$ was centrifuged and washed using deionized water and ethanol for five times, respectively, and dried in vacuum. The as-prepared precursor was then annealed at 623 K for 3 h to give the final *f*- Co_3O_4 product. In the case of the synthesis of *b*- Co_3O_4 , 2 mmol cobalt acetate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$), 4 mmol urea and 0.5 g polyvinyl-pyrrolidone (PVP, K30) were dissolved in 40 mL methanol under magnetic stirring. The solution was transferred into a 100 mL Teflon-lined stainless steel autoclave, sealed,

and then heated in an oven at 473 K for 6 h. The precursor of $\text{Co}(\text{OH})_2$ was centrifuged and washed using deionized water and ethanol for five times, respectively, and then dried in vacuum. The as-prepared precursor was subject to annealing at 773 K for 2 h to yield the final b- Co_3O_4 product.

2.3 Fabrication of $\text{Co}_3\text{O}_4/\text{CP}$ and $\text{PPy}/\text{f-Co}_3\text{O}_4/\text{CP}$ electrodes

To obtain the $\text{Co}_3\text{O}_4/\text{CP}$ composite electrode, f- Co_3O_4 or b- Co_3O_4 was dispersed in ethanol (1 mg cobalt oxide per 1 mL ethanol) by sonication, and then the dispersion was drop-casted onto the CP (1 cm $\times$ 1 cm) and dried in air. The mass of the Co_3O_4 on CP was controlled to be around 1 mg. The polypyrrole modified electrode was prepared by potentiodynamic electropolymerization of pyrrole monomers onto the f- $\text{Co}_3\text{O}_4/\text{CP}$ composite performed on an electrochemical working station VersaSTAT 4 potentiostat (Princeton Applied Research) at room temperature. A typical electrochemical polymerization was performed using $\text{Co}_3\text{O}_4/\text{CP}$ as the working electrode, saturated calomel electrode (SCE) as the reference electrode, and a platinum (Pt) wire as the counter electrode. The electropolymerization was scanned back and forth from 0 to +1.2 V vs. SCE at a scan rate of 50 mV/s for two cycles in aqueous solution containing 0.05 M pyrrole monomers and 0.1 M KNO_3 .

2.4 Characterizations

X-ray powder diffraction (XRD) pattern of the cobalt oxides was obtained by a Rigaku D/Max RC X-ray diffractometer with Ni filtered $\text{Cu K}\alpha$ radiation ($V=40$ kV, $I=50$ mA) at a scanning rate of $4^\circ/\text{min}$. Correspondingly, their microstructures were examined using a JSM-6700F field emission scanning electron microscope (FE-SEM) at an accelerating voltage of 20 kV and electric current of 1.0×10^{-10} A, and a JEOL JEM-2100 high-resolution TEM (HR-TEM)

operated at 200 kV. Fourier transform infrared spectrometer (FT-IR) was recorded on a VERTEX-70 FT-IR spectrometer.

The specific Brunauer-Emmett-Teller (BET) surface areas and pore-size distributions of the cobalt oxides were measured on a Quantachrome Nova 2200e by nitrogen adsorption at 77.4 K. Prior to each measurement, samples were degassed at 300 °C for 8 h under high vacuum (<0.01 mbar). The mesopore-size distribution was calculated using the Barrett-Joyner-Halenda (BJH) method from the desorption isotherm. Optical properties of cobalt oxides were carried out on a UV-VIS-NIR spectrophotometer (Jasco V-670) by dispersing the powders by sonication in ethanol to obtain dilute solutions.

The electrochemical measurements of the $\text{Co}_3\text{O}_4/\text{CP}$ and $\text{PPy}/\text{f-Co}_3\text{O}_4/\text{CP}$ composites were carried out on the VersaSTAT 4 potentiostat in 2.0 M KOH aqueous solution in a three-electrode setup with the $\text{Co}_3\text{O}_4/\text{CP}$ or $\text{PPy}/\text{f-Co}_3\text{O}_4/\text{CP}$ electrode serving as the working electrode, SCE as the reference electrode, and Pt wire as the counter electrode. The cyclic voltammetry (CV) was scanned from -0.1 to 0.5 V vs. SCE at a series of scan rates ranging from 200 to 10 mV/s. The galvanostatic charge-discharge (GCD) was performed at current densities from 50 to 10 A/g. Electrochemical impedance spectroscopy (EIS) was carried out in the frequency range of 100,000 to 0.01 Hz at a 5 mV amplitude referring to the open circuit potential. All the characterizations were carried out at room temperature in air.

3. Results and discussions

3.1 Synthesis and characterization of f- Co_3O_4 and b- Co_3O_4

Fig. 1. XRD patterns of (a) f- and (b) b- Co_3O_4 .

To examine the crystalline structure of the cobalt oxides obtained, XRD patterns of both samples were collected, Fig. 1. All diffraction peaks could be indexed to Co_3O_4 (JCPDS card No.43-1003) [40], and no peak of other phases was detected, indicative of the high purity of the cubic Co_3O_4 phase obtained in the present work.

Fig. 2. SEM and HRTEM images of f-Co₃O₄ at lower (a), (c), and (b), (d) higher magnifications, respectively; (e) lattice resolved HRTEM image of a single f-Co₃O₄ nanocrystal and (f) the selected area electron diffraction (SAED) pattern obtained by the converge beam; SEM images of b-Co₃O₄ at lower (g) and (h) higher magnifications.

Morphology plays a critical role in determining the supercapacitive performances of the electrode material, where a proper morphology and optimized microstructure will enable electrodes with high specific surface areas and facilitate electrolyte ion transport [41]. Therefore, SEM and TEM were utilized to characterize the morphology and structure of the cobalt oxides, Fig. 2. The SEM image reveals flower-like structure with a diameter of approximately 4-5 μm for the monodispersed f- Co_3O_4 , Fig. 2a. A higher magnification SEM image, Fig. 2b, shows that the flower-like structure is composed of two-dimensional petaloid nanosheets, from which a lot of pores are observed. To obtain further information on the porous structures, HR-TEM images of the f- Co_3O_4 are present in Fig. 2c. The apparent contrast between the white part and the black ligaments also confirms the nanoporous wormhole-like characteristic of the pores, Fig. 2d, and the pore size is measured ca. 5-10 nm. From the HRTEM image, Fig. 2e, the typical lattice fringe spacing is measured to be 0.243 nm, corresponding to the (311) crystal plane of cubic Co_3O_4 [42]. The corresponding selected area electron diffraction (SAED) pattern, Fig. 2f, indicates a polycrystalline structure of the porous structures. Differed from f- Co_3O_4 , b- Co_3O_4 displays a dense microsphere structure with a diameter of approximately 1-2 μm , Fig. 2g. The microspheres are built of nanorods about 100-300 nm in length at a higher magnification, Fig. 2h. The nanoporous structure in f- Co_3O_4 is expected to be more favorable for the access of ions to the electrode material and help achieve more desirable supercapacitive performances.

BET gas-sorption measurements were carried out to investigate the specific surface area and pore size distributions of the two cobalt oxides. Desirable electrode materials are proposed to be featured with macropores (>50 nm) serving as ion reservoirs to reduce ion diffusion distances to the interior surfaces, mesopores (between 2 and 50 nm) providing low-resistive pathways for ions through the porous particles, and micropores (<2 nm) to enhance electric double layer

capacitance [43]. Fig. 3 shows the nitrogen adsorption-desorption isotherms of the cobalt oxide samples and the corresponding Barrett-Joyner-Halenda (BJH) pore size distribution obtained from the desorption branch in the insets. The f-Co₃O₄ exhibits a typical IV type curve of the mesoporous structure [37], which can be further confirmed by the BJH pore size distribution plot, Fig. 3a. The uptake of N₂ at higher relative pressure ($P/P_0 > 0.9$) in the BET isotherm suggests the existence of macropores in the sample [44]. The pore size distribution plot also verifies the presence of micro- and meso pores in the material with a pore size distribution maxima centered at ~6 nm. A BET specific surface area of around 44.31 m²/g and a total pore volume of 0.17 cm³/g are also determined for the f-Co₃O₄. In the case of b-Co₃O₄, a similar nitrogen adsorption-desorption isotherm with a larger pore size distribution maxima centered at ~26 nm is obtained, Fig. 3b. Compared to f-Co₃O₄, b-Co₃O₄ possesses much lower specific surface area and total pore volume, 3.62 m²/g and a 0.05 cm³/g, respectively. The superior physiochemical properties of f-Co₃O₄ than those of b-Co₃O₄ render the former more suitable for supercapacitor electrodes than the latter.

Fig. 3. BET isotherms of (a) f- and (b) b- Co_3O_4 . The inset is the corresponding BJH pore size distribution profile.

3.2 Electronic Property from Optical Test

Optical band gaps have been found correlated with the electrical conductivity of the electrode materials, which affects the supercapacitive performances [45]. The optical properties of the dilute cobalt oxide solutions in ethanol were characterized by UV/Vis/NIR spectroscopy. The bandgap of the cobalt oxide, a p-typed semiconductor, was influenced by the particle size, shape, and dimensions. Fig. 4 shows the UV-Vis absorbance spectrum of the cobalt oxides. Three absorption bands (276, 481, and 778 nm for f- Co_3O_4 , 279, 490, and 780 nm for b- Co_3O_4 , respectively) are in agreement with the Co_3O_4 band structure [46]. The optical band gap was determined using Tauc plot using Eq. (1) [47]:

$$\alpha h\nu = (h\nu - E_g)^n \quad (1)$$

where α , h , ν , and E_g is the absorbance coefficient, planck constant, photon frequency, and photonic energy band gap, respectively. The parameter n is a number associated with different types of electronic transitions: n is 1/2 for direct-allowed (the minimum energy level of the

lowest conduction band positioned directly under the maximum of the highest valence band in k space) and is 2 for indirect-allowed (the minimum energy level of the lowest conduction band shifted relative to the maximum of the highest valence band, and the lowest-energy interband transition must then be accompanied by phonon excitation) [48]. The value of the optical band-gap can be obtained by extrapolating the linear portion of the curve. The best fitting gives $n=1/2$, indicating a direct allowed transition for the Co_3O_4 samples. Two optical transitions, 0.62 and 2.68 eV for f- Co_3O_4 , 0.73 and 2.72 eV for b- Co_3O_4 , respectively, are observed in the Tauc plot. The lower and higher band gap values are assigned to $\text{O}^{2-} \rightarrow \text{Co}^{3+}$ and $\text{O}^{2-} \rightarrow \text{Co}^{2+}$ charge transfer process, respectively [49]. Generally, the band gap energy increases as the crystallite size is decreased, and vice versa [50]. The slightly smaller band gap values of f- Co_3O_4 compared to those of b- Co_3O_4 are consistent with the bigger particle size for the former as confirmed by the TEM analysis. Meanwhile, the smaller band gaps also suggest a better electrical conductivity of f- Co_3O_4 than b- Co_3O_4 .

Fig. 4. UV-Vis absorbance spectrum of (a) f- Co_3O_4 and (b) b- Co_3O_4 . The inset is the corresponding Tauc plot.

3.3 Electrochemical Analysis

To study capacitive properties and ion diffusion kinetics of Co₃O₄/CP electrodes, cyclic voltammetry (CV) curves at different scan rates (0.2, 0.1, 0.05, 0.02, and 0.01 V/s) within a potential range of -0.1 to 0.5 V vs. SCE in 2 M KOH aqueous solution were plotted in Fig. 5a&b. Pure CP exhibits negligible current densities as demonstrated in our previous study and therefore not shown here. For cobalt oxide based electrode materials, there are usually two redox transitions, around ~0.2 and 0.3 V, respectively [51], corresponding to the oxidation/reduction of Co₃O₄ as follows [52]:

In the present study, the two oxidation and reduction peaks overlap with each other, leaving only one oxidation peak A and one reduction peak A', which are also reported in the mesoporous cobalt oxide nanowires electrode materials [53,54]. A positive shift in the anodic peak potential is observed with increasing the scan rate, taken f-Co₃O₄/CP for example, 0.386 V at 0.01 V/s and 0.407 V at 0.2 V/s. This phenomenon is explained by the scan rate dependent diffusion of OH⁻ ions to the electrode material, where both the outer- and inner-pore surfaces are utilized at lower scan rates and only the outer pores will be accessed by the OH⁻ ions at higher scan rates [55]. For both f-Co₃O₄/CP and b-Co₃O₄/CP, an almost linear/quasi-linear relationship is established between the anodic peak current density and the applied scan rate, insets of Fig. 5a&b, indicating the surface redox reactions occurring in the cobalt oxides/CP electrodes during the redox reactions [37].

Fig. 5. (a) CV comparison at a scan rate of 0.2 V/s in 2.0 M KOH aqueous solution and CV curves of (b) f-Co₃O₄/CP, (c) b-Co₃O₄/CP, and (d) PPY/f-Co₃O₄/CP electrodes at different scan rates.

In comparison, the f-Co₃O₄/CP demonstrates better defined redox peaks and higher current densities than the b-Co₃O₄/CP, For example at 0.2 V/s, [Fig. 5c](#), indicating more energy stored in the latter [\[56\]](#). This phenomenon is mainly due to higher specific surface area and pore volume of the unique porous morphology of f-Co₃O₄, which facilitate the accessibility of the OH⁻ ions to the electrode materials for faster redox reactions whereas the condensed b-Co₃O₄ does not favor

the OH⁻ ions diffusion. The conclusion is confirmed by the much higher ion diffusion coefficient D in the former (5.2×10^{-11} vs. 7.0×10^{-12} cm²/s) according to Randles–Servcik in Eq. (2) [57]:

$$i_p = 2.72 \times 10^5 n^{3/2} D^{1/2} C_o \nu^{1/2} \quad (2)$$

where D is the diffusion coefficient (cm²/s), C_o is the concentration of the active ion in solution (mol/cm³), ν is the sweep rate (V/s), n is the number of electrons, here is 1, and i_p is the peak current density (A/cm²).

Considering the aforementioned better physicochemical properties of f-Co₃O₄ than b-Co₃O₄, f-Co₃O₄ is incorporated with PPy to prepare composites for electrochemical capacitor applications. PPy was potentiodynamically electropolymerized on f-Co₃O₄/CP to fabricate PPy/Co₃O₄/CP ternary composites at a scan rate of 0.05 V/s for 2 cycles in an aqueous solution containing 0.05 M pyrrole monomers and 0.1 M KNO₃. The growth of PPy on f-Co₃O₄/CP is shown in Fig. 6.

Fig. 6. Electropolymerization of polypyrrole onto on f-Co₃O₄/CP for 2 cycles at a scan rate of 0.05 V/s in the aqueous solution containing 0.05 M pyrrole and 0.1 M KNO₃.

The mass and thickness of the PPy polymer on the composite films can be estimated from Eqs. (3&4) [58]:

$$m = \frac{Q}{F} \cdot \frac{M_m + \gamma M_d}{2 + \gamma} \quad (3)$$

$$d = \frac{m}{2\rho A} \quad (4)$$

where Q is the total Faradic charges consumed in the electropolymerization, F is Faraday constant (96485 C/mol), γ is the doping density (0.33 for polypyrrole) [59], M_m and M_d are the molar weight of the monomer (67.09 g/mol for pyrrole) and the dopant (62.00 g/mol for NO_3^-), respectively, d is the thickness of the PPy thin film on the carbon paper, ρ is the density of the PPy (1.5 g/cm³) [60], and A is the surface area of the composite film. The mass is calculated to be 6.58×10^{-8} g and the thickness is around 7.3 nm. The PPy nanocoating can also be convinced by the SEM images, Fig. S1. The f-Co₃O₄ particles are apparently observed uniformly distributed on the CP, Fig. S1a, and became less obvious after the PPy coating, Fig. S1b, suggesting the formation of PPy network on the f-Co₃O₄/CP.

Even the mass of PPy is negligible, the effect of PPy on enhancing the current densities is significant. Compared to f-Co₃O₄/CP, PPy/f-Co₃O₄/CP exhibits much higher current densities in addition to the redox peaks (A/A') ascribed to cobalt oxide, indicating the Faradic current contribution from the PPy thin film. To study the PPy nanocoating effect on the ion diffusion kinetics, CV curves of PPy/f-Co₃O₄/CP at different scan rates were also obtained, Fig. 5d. Interestingly, a linear relationship between the square root of scan rate and the peak current density is found for PPy/f-Co₃O₄/CP, suggesting a diffusion-limited redox process, which is

usually observed in the polymer thin film electrodes [61,62]. The varied ion diffusion behaviors imply the morphology difference brought by the PPy coating on the cobalt oxide.

Galvanostatic charge-discharge (GCD) measurements at a current density of 50 A/g and other different current densities (40, 20, and 10 A/g) were further carried out to investigate the supercapacitive properties of f-Co₃O₄/CP and PPy/f-Co₃O₄/CP in 2.0 M KOH aqueous solution from -0.1 to 0.5 V vs. SCE using Eq. (5) [45]:

$$C_s = (i \times t) / (m \times \Delta V) \quad (5)$$

where C_s is the specific capacitance in F/g, i is the discharge current in A, t is the discharge time in s, m is the mass of the active materials (the mass of cobalt oxides in view of little PPy electropolymerized) in the electrode in g, ΔV is the scanned potential window (excluding IR drop arising from the internal resistance of the cell at the beginning of the discharge process) in V. Fig. 7 shows the typical potential responses of the samples at a current density of 50 A/g, Fig. 7a, and the specific capacitances of the electrode materials at different current densities, Fig. 7b. In consistence with the CV results, the non-linear and asymmetric GCD curves suggest a pseudocapacitance behavior of the electrode materials. The results show that the b-Co₃O₄/CP displays the highest IR drop whereas the f-Co₃O₄/CP and PPy/f-Co₃O₄/CP show similar IR drop, Fig. 7a, indicating the highest resistance in the former. The PPy/f-Co₃O₄/CP displays the longest discharge time, followed by the f-Co₃O₄/CP, and then b-Co₃O₄/CP. The specific capacitance of the electrode materials against the current density is plotted in Fig. 7b. The specific capacitance values of f-Co₃O₄/CP and b-Co₃O₄/CP is 40.9 and 22.0 F/g, respectively, at a high current density of 10 A/g, comparable to those reported for cobalt oxide nanotubes (70 F/g) and hexagonal plates (15 F/g) at a much lower current density of 1.0 A/g [63]. As aforementioned,

the porous nanosheet structure of the f-Co₃O₄/CP is capable of providing faster ion and electron transfer and larger reaction surface area, giving rise to better electrochemical performances than the b-Co₃O₄/CP. It's noteworthy that the corresponding specific capacitance is significantly increased to 398.4 F/g for the PPy/f-Co₃O₄/CP. The value is much higher than the reported 150 F/g for porous cobalt oxide at a much lower current density of 1.0 A/g [64]. The pseudocapacitance contributions from PPy, as confirmed by the CV result, is mainly attributed to the improved capacitive performances.

Fig. 7. (a) Charge-discharge curves f-Co₃O₄/CP, b-Co₃O₄/CP, and PPy/f-Co₃O₄/CP electrodes at 50 A/g, and (b) current density dependent specific capacitance in potential range from -0.1 to 0.5 V in 2.0 M KOH aqueous solution. The inset is the magnified view of the specific capacitance for f-Co₃O₄/CP and b-Co₃O₄/CP.

The energy density, E , and the power density, P of the electrode materials were calculated from Eqs. (6&7) [65]:

$$E = \frac{C_s \Delta V^2}{7.2} \quad (6)$$

$$P = \frac{3600E}{t} \quad (7)$$

where E is the energy density in Wh/kg, P is the power density in kW/kg. C_s is the specific capacitance in F/g, ΔV is the scanned potential window (excluding IR drop at the beginning of the discharge) in V, t is the discharge time in s.

Fig. 8. Ragone plots of f-Co₃O₄/CP, b-Co₃O₄/CP, and PPy/f-Co₃O₄/CP composite electrodes.

Fig. 8 shows the corresponding Ragone plots of the f-Co₃O₄/CP, b-Co₃O₄/CP, and PPy/f-Co₃O₄/CP obtained from the GCD measurements. The f-Co₃O₄/CP and PPy/f-Co₃O₄/CP show both higher power and energy densities than the b-Co₃O₄/CP benefitting from the less IR drop and higher specific capacitances [66]. Meanwhile, the PPy/f-Co₃O₄/CP has much improved energy densities compared to f-Co₃O₄/CP. For example, at a high current density of 50 A/g, the corresponding energy densities are 1.7, 1.2, and 0.5 Wh/kg at a power densities 12.6, 12.6, 11.3 kW/kg for PPy/f-Co₃O₄/CP, f-Co₃O₄/CP and b-Co₃O₄/CP, respectively. The energy density is increased to 18.4, 1.9, and 0.9 Wh/kg at a lower power densities of 2.9, 2.9, and 2.5 kW/kg.

To obtain a further fundamental understanding of the properties of the electrode materials, EIS was employed. Fig. 9 shows the corresponding Nyquist plots. The equivalent series

resistances (R_s , arising from the ohmic resistance of the electrolyte, the internal resistance of the electrode materials, and contact resistance between electrodes and current collectors) can be obtained from the first intercept in the real axis [13]. A semicircle, the diameter of which represents the charge transfer resistance at the electrode/electrolyte interface, was observed in both electrodes in the high frequency region. The PPy/f-Co₃O₄/CP exhibits much smaller R_{ct} than f-Co₃O₄/CP cobalt oxide, indicating a facilitated charge transfer upon the introduction of the PPy film. The Warburg resistance observed in the lower frequency of the electrodes is related to the frequency dependent ion diffusion/transport in the electrolyte [14]. An equivalent circuit consisting of R_s , R_{ct} , and CPE is proposed using ZsimpWin electrochemical software. CPE, as defined in Eq. (8) [67], is a constant phase element that is employed considering the deviation of from ideal capacitor behaviors due to inhomogeneity and roughness of the electrodes

$$Z_{CPE} = T_{CPE} (j\omega)^{-n} \quad (8)$$

where Z_{CPE} is the complex impedance of CPE, T_{CPE} and n are frequency-independent constants, and ω is the angular frequency ($\omega=2\pi f$, f is the frequency). n is related to the roughness of the electrode surface and ranges from 0 to 1 for an CPE. n is 0 for a resistor, 1 for an ideal capacitor, and 0.5 for a Warburg impedance (mass transfer impedance). Table 1 gives the fitting values of the elements. The R_s of PPy/f-Co₃O₄/CP is around 2.62 Ω , lower than that (3.06 Ω) of f-Co₃O₄. The difference in n indicates a morphology change by the induction of PPy nanocoating on the f-Co₃O₄. Meanwhile, the R_{ct} of PPy/f-Co₃O₄/CP is 152.4 Ω , which is much lower than that (513.9 Ω) of f-Co₃O₄/CP. The remarkably reduced R_{ct} is inferred to contribute to improved electrochemical properties. The higher value of CPE, 0.002377 in PPy/f-Co₃O₄/CP compared with 0.001682 in f-Co₃O₄/CP, is in good agreement with the CV and GCD results. Meanwhile,

the slightly larger mass transfer resistance Z_w witnessed in PPy/f-Co₃O₄/CP than f-Co₃O₄/CP (0.03 vs. 0.06 Ω), further confirms the diffusion-limited behaviors in the CV measurements.

Fig. 9. Complex-plane plots of f-Co₃O₄/CP and PPy/f-Co₃O₄/CP. The inset is an expanded view of the Nyquist plot at the high frequency region and the equivalent circuit of the electrodes.

Table 1

Fitting parameters of f-Co₃O₄/CP and PPy/f-Co₃O₄/CP in the equivalent circuit model.

	f-Co ₃ O ₄ /CP	PPy/f-Co ₃ O ₄ /CP
R_s (Ω)	3.06	2.62
CPE (F)	0.001682	0.002377
n	0.8699	0.8472
R_{ct} (Ω)	513.9	152.4
Z_w (Ω)	0.03	0.06

The long-term charge-discharge cycling stability of f-Co₃O₄/CP and PPy/f-Co₃O₄/CP is investigated at a current density of 50 A/g after 1000 cycles, Fig. 10. The increased capacitance retention over 100% is caused by the activation of the electrodes [68], which is usually observed in the cobalt oxide based electrode materials. In the case of PPy/f-Co₃O₄/CP, the capacitance retention is around 100.0%, indicating a good cycling stability of the ternary composite electrode.

Fig. 10. Capacitance retention of f-Co₃O₄/CP and PPy/f-Co₃O₄/CP at 50 A/g in 2.0 M KOH aqueous solution after 1000 cycles.

4. Conclusions

Flower-like Co₃O₄ nanostructures have been successfully synthesized by a facile solvothermal method and used for fabricating PPy/f-Co₃O₄/CP ternary composites for electrochemical supercapacitor applications. The ball-like Co₃O₄ (b-Co₃O₄) was also prepared for comparison. The PPy/f-Co₃O₄/CP ternary composites exhibit superior supercapacitive performances as compared with f-Co₃O₄/CP and b-Co₃O₄/CP. The pseudocapacitance from PPy and remarkably reduced charge transfer resistance are inferred to be responsible for the enhanced electrochemical properties. The study shows a promising potential to fabricate stable, cost-effective, and high performance PPy/metal oxide/carbon composites for supercapacitor applications.

Acknowledgments

The project is financially supported by the National Science Foundation (NSF) USA-Nanoscale Interdisciplinary Research Team, and Materials Processing and Manufacturing (CMMI 10-30755) and nanomanufacturing (CMMI 13-14486).

References

- [1] Skotheim TA, Reynolds JR, editors. Handbook of conducting polymers. 3rd ed. Boca Raton: CRC Press; 2007.
- [2] Gu H, Guo J, Wei H, Zhang X, Zhu J, Shao L, et al. Polymer 2014;55:944–50.
- [3] Ding K, Jia H, Wei S, Guo Z. Ind Eng Chem Res 2011;50:7077–82.
- [4] Xue K, Zhou S, Shi H, Feng X, Xin H, Song W. Sens Actuators B Chem 2014;203:412–6.
- [5] Guo J, Gu H, Wei H, Zhang Q, Haldolaarachchige N, Li Y, et al. J Phys Chem C 2013;117:10191–202.
- [6] Deshpande PP, Jadhav NG, Gelling VJ, Sazou D. J Coat Technol Res 2014;11:473–94.
- [7] Sevilla M, Valle-Vigón P, Fuertes AB. Adv Funct Mater 2011;21:2781–7.
- [8] Shao L, Cheng X, Wang Z, Ma J, Guo Z. J Membr Sci 2014;452:82–9.
- [9] Gao J, Heeger AJ, Lee JY, Kim CY. Synth Met 1996;82:221–3.
- [10] Takagi S, Makuta S, Veamatahau A, Otsuka Y, Tachibana Y. J Mater Chem 2012;22:22181–9.
- [11] Seh ZW, Wang H, Hsu P-C, Zhang Q, Li W, Zheng G, et al. Energy Environ Sci 2014;7:672.
- [12] Shi Y, Pan L, Liu B, Wang Y, Cui Y, Bao Z, et al. J Mater Chem A 2014;2:6086–91.
- [13] Gu H, Wei H, Guo J, Haldolaarachchige N, Young DP, Wei S, et al. Polymer 2013;54:5974–85.
- [14] Wei H, Zhu J, Wu S, Wei S, Guo Z. Polymer 2013;54:1820–31.
- [15] Wei H, Gu H, Guo J, Wei S, Guo Z. J Electrochem Soc 2013;160:G3038–45.
- [16] Wei H, Yan X, Wu S, Luo Z, Wei S, Guo Z. J Phys Chem C 2012;116:25052–64.
- [17] Patil BH, Jagdale AD, Lokhande CD. Synth Met 2012;162:1400–5.
- [18] Wei H, Yan X, Li Y, Gu H, Wu S, Ding K, et al. J Phys Chem C 2012;116:16286–93.
- [19] Wei H, Yan X, Li Y, Wu S, Wang A, Wei S, et al. J Phys Chem C 2012;116:4500–10.
- [20] Sabouraud G, Sadki S, Brodie N. Chem Soc Rev 2000;29:283–93.
- [21] Tao J, Liu N, Li L, Su J, Gao Y. Nanoscale 2014;6:2922–8.
- [22] Zhao Y, Liu J, Hu Y, Cheng H, Hu C, Jiang C, et al. Adv Mater 2013;25:591–5.
- [23] Lu X, Dou H, Yuan C, Yang S, Hao L, Zhang F, et al. J Power Sources 2012;197:319–24.
- [24] Wang J-G, Yang Y, Huang Z-H, Kang F. J Mater Chem 2012;22:16943–9.
- [25] Zhang LL, Zhao XS. Chem Soc Rev 2009;38:2520–31.
- [26] Zang J, Bao S-J, Li CM, Bian H, Cui X, Bao Q, et al. J Phys Chem C 2008;112:14843–7.
- [27] Sharma RK, Rastogi AC, Desu SB. Electrochimica Acta 2008;53:7690–5.
- [28] Zhou C, Zhang Y, Li Y, Liu J. Nano Lett 2013;13:2078–85.
- [29] Qu Q, Zhu Y, Gao X, Wu Y. Adv Energy Mater 2012;2:950–5.
- [30] Liu Y, Zhang B, Yang Y, Chang Z, Wen Z, Wu Y. J Mater Chem A 2013;1:13582–7.
- [31] Mi H, Zhang X, Ye X, Yang S. J Power Sources 2008;176:403–9.
- [32] Rakhi RB, Chen W, Cha D, Alshareef HN. Nano Lett 2012;12:2559–67.
- [33] Lang J, Yan X, Xue Q. J Power Sources 2011;196:7841–6.
- [34] Vijayakumar S, Ponnalagi AK, Nagamuthu S, Muralidharan G. Electrochimica Acta 2013;106:500–5.
- [35] Wang G, Shen X, Horvat J, Wang B, Liu H, Wexler D, et al. J Phys Chem C 2009;113:4357–61.
- [36] Xia X, Tu J, Mai Y, Wang X, Gu C, Zhao X. J Mater Chem 2011;21:9319–25.

- [37] Meher SK, Rao GR. *J Phys Chem C* 2011;115:15646–54.
- [38] Dong S, Peng L, Liu D, Yang Q, Huang T. *Bioelectrochemistry* 2014;98:87–93.
- [39] Liu P, Huang Y. *RSC Adv* 2013;3:19033–9.
- [40] Ma J, Manthiram A. *RSC Adv* 2012;2:3187–9.
- [41] Meher SK, Rao GR. *J Phys Chem C* 2011;115:15646–54.
- [42] Shan Y, Gao L. *Mater Chem Phys* 2007;103:206–10.
- [43] Lv Y, Gan L, Liu M, Xiong W, Xu Z, Zhu D, et al. *J Power Sources* 2012;209:152–7.
- [44] Rouquerol F. *Adsorption by powders and porous solids: principles, methodology and applications*. 2014.
- [45] Wei H, Gu H, Guo J, Wei S, Guo Z. *ECS J Solid State Sci Technol* 2013;2:M3008–14.
- [46] Wang G, Shen X, Horvat J, Wang B, Liu H, Wexler D, et al. *J Phys Chem C* 2009;113:4357–61.
- [47] Xi L, Tran PD, Chiam SY, Bassi PS, Mak WF, Mulmudi HK, et al. *J Phys Chem C* 2012;116:13884–9.
- [48] Wei H, Ding D, Yan X, Guo J, Shao L, Chen H, et al. *Electrochimica Acta* 2014;132:58–66.
- [49] Li H, Wang J, Chu Q, Wang Z, Zhang F, Wang S. *J Power Sources* 2009;190:578–86.
- [50] Wang X, Chen X, Gao L, Zheng H, Zhang Z, Qian Y. *J Phys Chem B* 2004;108:16401–4.
- [51] Park S, Kim S. *Electrochimica Acta* 2013;89:516–22.
- [52] Wang D, Wang Q, Wang T. *Inorg Chem* 2011;50:6482–92.
- [53] Xiao Y, Zhang A, Liu S, Zhao J, Fang S, Jia D, et al. *J Power Sources* 2012;219:140–6.
- [54] Rakhi RB, Chen W, Cha D, Alshareef HN. *Nano Lett* 2012;12:2559–67.
- [55] Meher SK, Justin P, Ranga Rao G. *Nanoscale* 2011;3:683–92.
- [56] Shen J, Liu A, Tu Y, Foo G, Yeo C, Chan-Park MB, et al. *Energy Environ Sci* 2011;4:4220–9.
- [57] Wei H, Yan X, Wang Q, Wu S, Mao Y, Luo Z, et al. *Energy Environ Focus* 2013;2:112–20.
- [58] Arcila-Velez MR, Roberts ME. *Chem Mater* 2014;26:1601–7.
- [59] Waltman RJ, Bargon J. *Can J Chem* 1986;64:76–95.
- [60] Qi Z, Pickup PG. *Chem Mater* 1997;9:2934–9.
- [61] Roberts ME, Wheeler DR, McKenzie BB, Bunker BC. *J Mater Chem* 2009;19:6977–9.
- [62] Yue G, Wu J, Xiao Y, Lin J, Huang M, Lan Z. *J Phys Chem C* 2012;116:18057–63.
- [63] Frackowiak E, Béguin F. *Carbon* 2001;39:937–50.
- [64] Meng F, Fang Z, Li Z, Xu W, Wang M, Liu Y, et al. *J Mater Chem A* 2013;1:7235–41.
- [65] Liu J, Jiang J, Bosman M, Fan HJ. *J Mater Chem* 2012;22:2419–26.
- [66] Conway BE. *Electrochemical supercapacitors: scientific fundamentals and technological applications*. New York: Plenum Press; 1999.
- [67] Orazem ME. *Electrochemical impedance spectroscopy*. Hoboken, N.J: Wiley; 2008.
- [68] Du W, Liu R, Jiang Y, Lu Q, Fan Y, Gao F. *J Power Sources* 2013;227:101–5.

Graphical Abstract