

Free-standing RGO-Co₃O₄-Polypyrrole composite films as electrodes for supercapacitors

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Abstract

Supercapacitors are of great importance for energy storage and have been the subject of intensive research in recent years, in which conductive polymers have been used to make flexible and free-standing electrodes. However, their insufficient access to the electrolytes and the low chemical stability of these conductive polymers have led to their poor performance. To solve these issues, we demonstrate here that a facile method can be used to synthesize free-standing composite film electrodes of reduced graphene oxide-cobalt oxide-polypyrrole

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(RGO-Co₃O₄-PPy) as supercapacitors. They exhibit high specific capacitance of 532 F g⁻¹ and nearly no degradation after 700 cycles of charging and discharging. We determine that the synergistic effect of Co₃O₄, RGO, and PPy is responsible for the superior property. The three-phase composite electrode utilizes a reduced graphene oxide nanosheet as a substrate to provide a large surface area for loading Co₃O₄ nanoparticles and also to enhance the electron transfer. Furthermore, the deposition of PPy largely reduces the resistivity of the RGO-Co₃O₄-PPy and the introduction of Co₃O₄ nanoparticles significantly improves the cycle stability.

Key words: graphene; cobalt oxide; polypyrrole; supercapacitor; free-standing electrode.

Introduction

Supercapacitors have attracted extensive attention for energy storage due to their fast charge-discharge characteristics and high power density.^[1] They are used along with batteries to provide the additional power required in many applications, such as in the automotive industry and in transportation systems. Supercapacitors can also partially replace the lithium-ion cells.^[2] According to the energy storage mechanism, namely electrical double-layer capacitance (EDLC) and pseudocapacitance, electrode materials play a significant role in the electrochemical properties of supercapacitors. For decades, conductive polymers such as polyaniline (PANi) and polypyrrole (PPy) have quite often been chosen as electrode materials and have been widely applied in the production of functional supercapacitors.^[3] However, the utilization of these conductive polymers is usually limited by their two major drawbacks: (i) insufficient access to the electrolytes due to their normal bulk structure leading to low specific capacity; and (ii) low chemical stability during the

electrochemical process and poor cycling performance. ^[4]

To overcome the first drawback, graphene sheets with large surface areas have been used together with the conductive polymers to obtain composite electrode materials that exhibit increased contact with electrolytes. Zhao *et al.*^[5] directly coated reduced graphene oxide (RGO) sheets with conductive polymers and obtained RGO-poly(3,4-ethylenedioxythiophene) (PEDOT), RGO-PANi, and RGO-PPy composites. The RGO sheets were found to provide both large surface area and mechanical support for conductive polymers. The results showed that these RGO/conductive polymers have good electrochemical properties. Besides the large surface area, other unique properties of graphene, including its high electrical and thermal conductivity, can also improve the electrochemical properties of the composite flexible electrodes for supercapacitors.^[6] Shu *et al.* ^[7] developed a free-standing RGO-PPy hybrid paper via the electropolymerization process. The results proved that this hybrid paper delivers an enhanced areal capacitance of 440 mF cm⁻² at 0.5 A g⁻¹ and retains 81% of its initial capacitance after 5,000 cycles.

To overcome the second drawback, metal oxides have been incorporated to form composite electrode materials with further enhanced electrochemical performance. Tang *et al.*^[4a] developed a solution-based approach to grow PPy films on 2D MoS₂ monolayers in order to obtain MoS₂/PPy composites. Their results showed the record high specific capacitance of MoS₂/PPy composites, as well as improved stability. In our previous study, we also investigated the incorporation of a metal oxide (TiO₂) and found that the stability of RGO/PPy composite electrode materials was improved. We used a direct heating process to incorporate TiO₂ into RGO-PPy sheets to produce free-standing and flexible RGO-TiO₂-PPy composite electrode materials for supercapacitors. We found that RGO-TiO₂-PPy retained ~76.5% capacitance after 100 charge-discharge cycles, much higher than the ~26% retained in

RGO-PPy (G-PPy).^[8] Recently, Co_3O_4 nanoparticles have been considered to be a promising material because of their high theoretical capacitance (3,560 F/g) and good electrochemical performance, as well as being environmentally friendly.^[9] Hai *et al.*^[10] produced a PANi/ Co_3O_4 nanocomposite electrode for supercapacitors, which exhibited a high specific capacitance and good cycle stability, *e.g.*, 84.9% of its capacitance was retained after 1,000 cycles.

In this work, we report that a free-standing three-phase RGO- Co_3O_4 -PPy (named G- Co_3O_4 -PPy) composite film was synthesized in a facile manner for use as an electrode material in supercapacitor applications. The electrochemical properties were tested and indicate very good performance with 532.8 F g⁻¹ capacitance, higher than that of either RGO- Co_3O_4 or RGO-PPy. The cycling test demonstrated almost 100% retention after 700 cycles. The mechanisms for the high performance of the composite film were further investigated, along with the reasons for the long-term stability.

Results and discussion

The typical wrinkled structure of RGO, denoted as G, is demonstrated by SEM as shown in Fig. 1a. Figure 1b confirms the abundance of Co_3O_4 nanoparticles decorating the G films. The Co_3O_4 nanoparticles seem to be distributed evenly, as shown by the TEM image in the inset of Fig. 1b. The typical spherical morphology of the G- Co_3O_4 -PPy composite is seen in Fig. 1c, which indicates successful PPy coating on the surface of the G- Co_3O_4 film.^[11] The Fourier-transform infrared spectroscopy (FTIR) spectrum (Fig. S1) also confirms the successful deposition of PPy on the surface. In addition, the XRD spectrum (Fig. 1d) also confirms the presence of Co_3O_4 nanoparticles, exhibiting the characteristic peaks of 31.34°, 36.93°, 59.51°, and 65.4°, for the (220), (311), (511), and (440) crystallographic planes of

Co_3O_4 (JCPDS No. 027498), respectively.

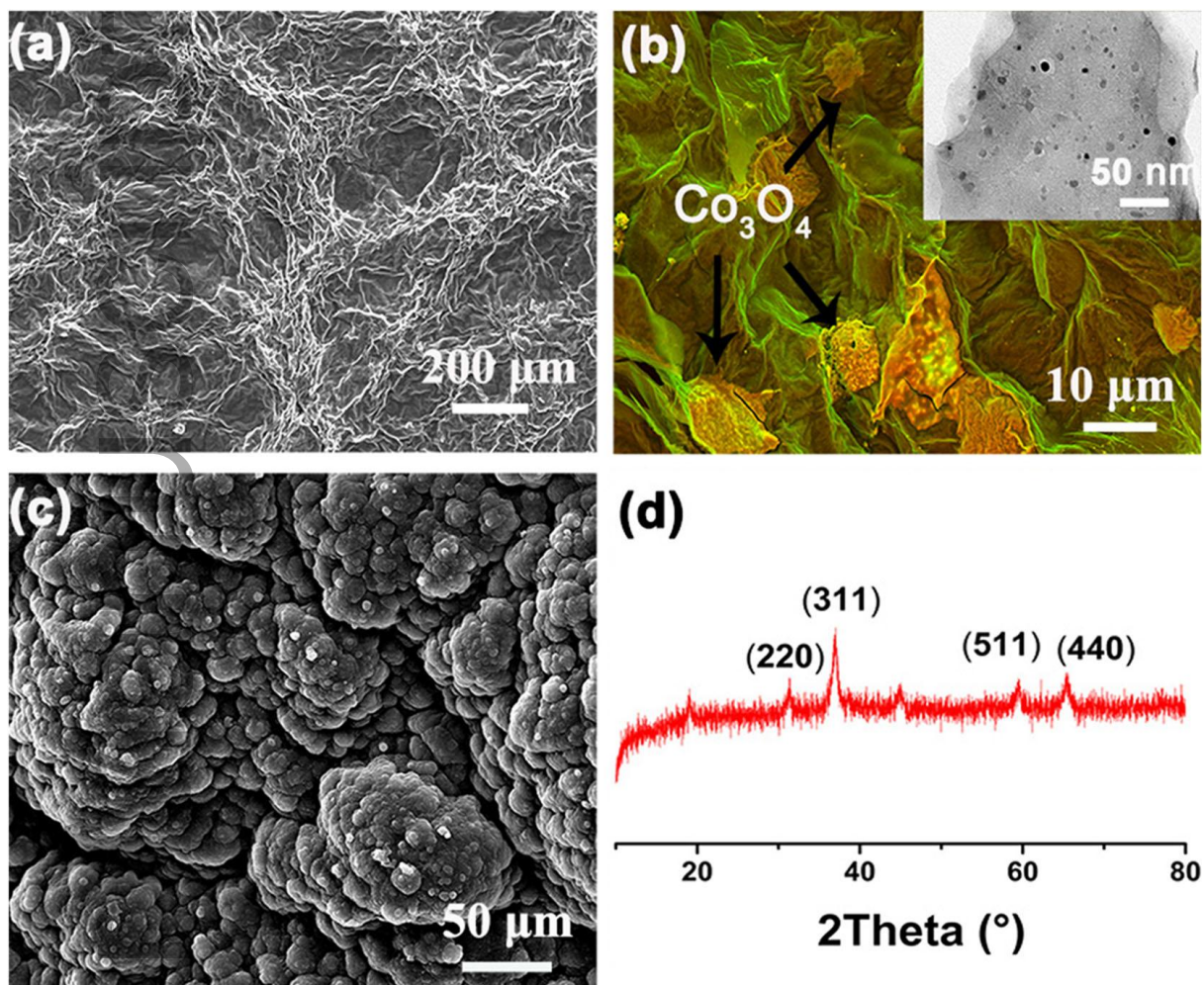


Figure 1. (a) SEM image of G film; (b) the morphology of G- Co_3O_4 (inset: TEM image of G- Co_3O_4); (c) the morphology of G- Co_3O_4 -PPy; and (d) XRD spectrum of Co_3O_4 obtained at 250 °C.

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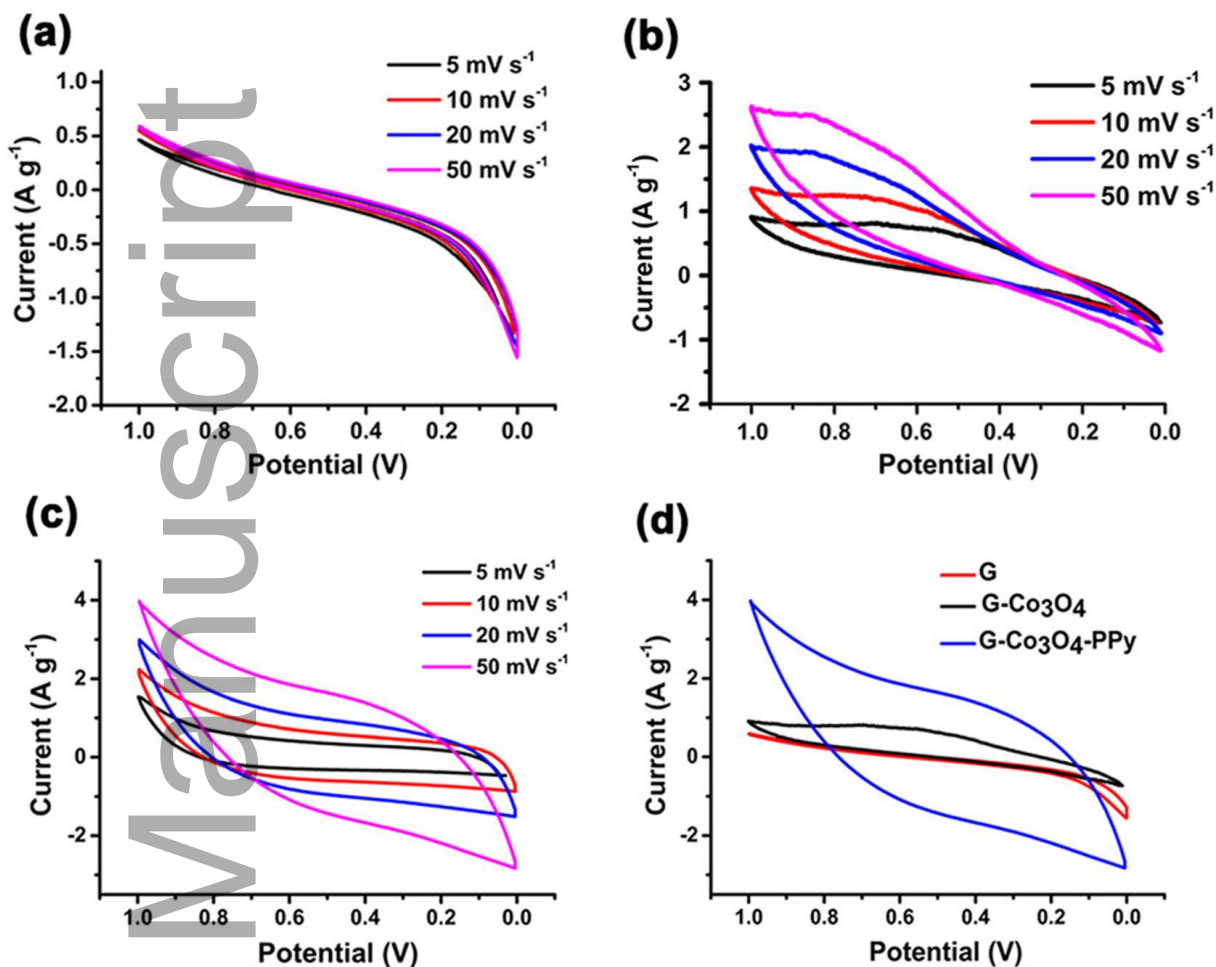


Figure 2. The CV profiles of various electrodes at a series of scan rates: (a) G; (b) G-Co₃O₄; and (c) G-Co₃O₄-PPy. (d) The CV profile of each sample at the scan rate of 5 mV s⁻¹.

The cyclic voltammetry (CV) profiles of the three electrodes with scan rates from 5 to 50 mV s⁻¹ are depicted in Fig. 2. The CV curves of G exhibit behavior typical of an electric double-layer capacitor (EDLC) (Fig. 2a). After incorporating Co₃O₄, the CV curves of G-Co₃O₄ present an additional pseudocapacitance due to the reversible redox reaction of Co₃O₄ (Fig. 2b).^[12] The reactions between different oxidation states and the electrolyte are as follows:





The CV profile of G-Co₃O₄ shows the anodic peak at about 0.8 V, corresponding to the redox equation. After the deposition of PPy, the CV profiles of G-Co₃O₄-PPy display a nearly taper shape with very slight redox peaks, indicating both EDLC and pseudocapacitor behaviors (Fig. 5c). These CV profiles maintain similar shapes at different scan rates, although they show an increased leaning angle to the voltage-axis with increasing scan rate. This phenomenon demonstrates that the electrodes have low equivalent series resistance and that ions can efficiently diffuse between the electrolyte and the electrodes.^[13] As shown in Fig. 2d, the CV profiles of each sample at the scan rate of 5 mV s⁻¹ reveal their significant difference. G-Co₃O₄-PPy achieves the highest integrated area, indicating the highest capacitance. Moreover, G-Co₃O₄-PPy also has the highest current density, which may be due to the synergistic contribution of PPy and reduced graphene oxide. With the presence of both PPy and RGO, the conductivity of the composite films is improved while the diffusion and migration lengths for electrons are reduced. The specific capacitance of these as-prepared electrodes was estimated (Fig. 2d). The highest capacitance of G-Co₃O₄-PPy is about 532.8 F g⁻¹, which is higher than that of G-Co₃O₄ (230.5 F g⁻¹) and G (131.5 F g⁻¹). These results clearly show that incorporation of Co₃O₄ nanoparticles and PPy significantly improve the capacitance of free-standing RGO-based composite electrodes for supercapacitors. This synergistic effect can be summarized as: (i) the pseudocapacitance effect of Co₃O₄ and PPy; (ii) the same conductive mechanism based on the sp² hybridized structure of RGO and PPy, which facilitates the electron transfer among different phases of the composite films; and (iii) RGO acting as a bridge, enhancing the electron transfer among Co₃O₄ nanoparticles as well as between Co₃O₄ nanoparticles and PPy.

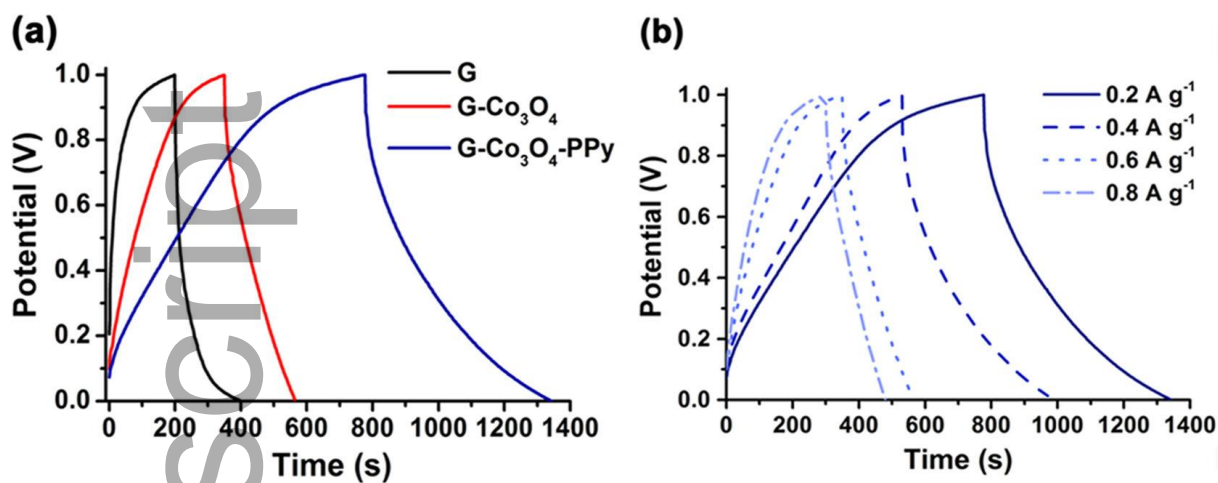


Figure 3. (a) Galvanostatic charge-discharge curves of three electrodes at a current of 0.2 A g⁻¹; and (b) Galvanostatic charge-discharge curves of as-prepared G-Co₃O₄-PPy electrodes at different current densities in 6M KOH.

Galvanostatic charge and discharge curves of the as-prepared electrodes are shown in Fig. 3. G-Co₃O₄-PPy has the longest discharge time, which again reflects its highest capacitance among these three samples (Fig. 3a). As shown in Fig. 3b, the specific capacitance of G-Co₃O₄-PPy decreases with increasing current density. The capacity retention of 55.1% at 0.8 A g⁻¹ proves the good rate performance of this free-standing and flexible electrode.

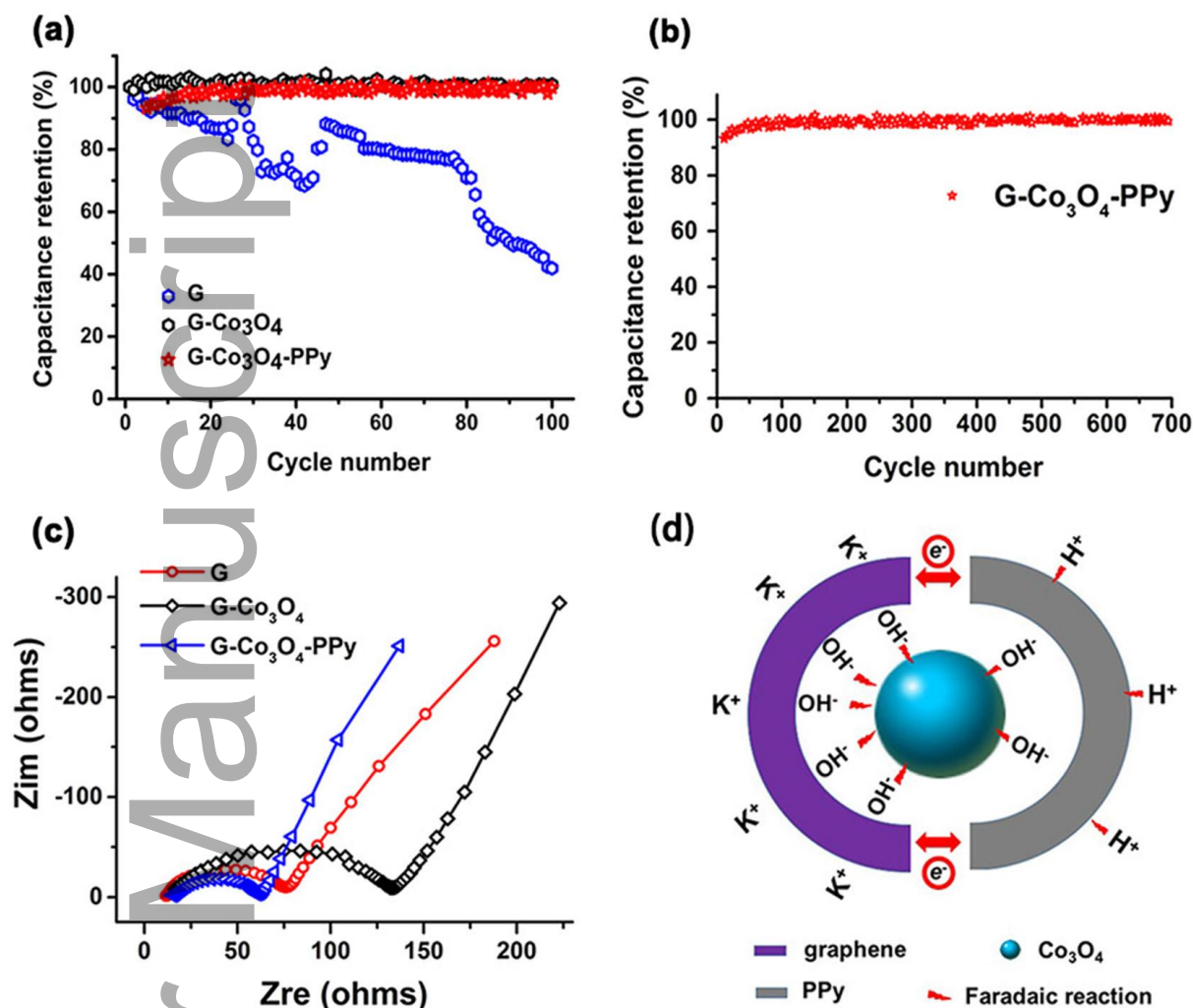


Figure 4. (a) Cycle stability of three as-prepared RGO-based electrodes at a current of 0.2 A g^{-1} ; (b) stability of G-Co₃O₄-PPy up to 700 cycles; (c) Nyquist plots for the samples at a direct current bias of 0 V with a sinusoidal signal of 20 mV over the frequency range of 200 kHz to 0.01 Hz; and (d) schematic representation of the electrochemical behavior of G-Co₃O₄-PPy.

As shown in Fig. 4a, the cycle stability of the three as-prepared RGO-based electrodes was obtained. For G film, 41.8% of the capacitance was retained after 100 charge-discharge cycles. G-PPy has the lowest stability with only 23.8% of the primary capacitance retained (Fig. S2). On the other hand, G-Co₃O₄ and G-Co₃O₄-PPy films both display very good cycle

stability performance, with nearly no decrease of capacitance after the first 100 cycles. Several previous studies have proven that graphene-incorporated metal oxides could greatly enhance the electrochemical cycle stability. Bao *et al.*^[14] produced a three-dimensional graphene and Co_3O_4 composite by the thermal explosion method. Their results showed that ~93% capacitance was maintained after 5,000 cycles. He *et al.*^[15] fabricated Co_3O_4 flakes and graphene composite paper by the self-assembly method, with 87% of capacitance remaining after 1,000 cycles. To further prove the contribution of RGO and Co_3O_4 to the cycle stability performance of G- Co_3O_4 -PPy, testing was continued for an additional 600 cycles. The results indicate outstanding cycle stability performance of G- Co_3O_4 -PPy (Fig. 4b). The low stability of G-PPy may be due to the film structure, which not only gives PPy sufficient access to the electrolytes, increasing the specific capacitance, but also further enhances the fade pace of the PPy molecular structure during the electrochemical process. Moreover, the introduction of Co_3O_4 nanoparticles significantly improves the cycle stability of G- Co_3O_4 and G- Co_3O_4 -PPy composite films in comparison with the samples without the nanoparticles.

Electrochemical impedance spectroscopy (EIS) was then employed to understand the effects of Co_3O_4 nanoparticles and PPy on the conductivity of graphene-based samples. Figure 4c shows the Nyquist plots of all of the graphene-based samples. These curves demonstrate that the introduction of Co_3O_4 and PPy have different effects on the resistivity of graphene-based free-standing electrodes. After incorporation with Co_3O_4 nanoparticles, the resistivity of G- Co_3O_4 increases because Co_3O_4 is a semiconductor material with a low conductivity. However, coating with conducting PPy largely reduces the overall resistivity of the G- Co_3O_4 -PPy to achieve better performance.

Based on the above results, the excellent cycle stability performance of G- Co_3O_4 -PPy can be attributed to three aspects: (i) The EDLC behavior and the pseudocapacitance have a

synergistic effect. On one hand, reduced graphene oxide layers behave as an EDLC during the electrochemical process. In the electrolyte of KOH, the K^+ and OH^- ions form the electrical double layers on the RGO side as shown in Figure 4d. According to Eq. (1), OH^- is the key ion for the pseudocapacitance behavior of Co_3O_4 nanoparticles. Hence, the pseudocapacitance behavior of Co_3O_4 nanoparticles could be enhanced due to the structure in which they are distributed on the surface of, or wrapped by, RGO. On the other hand, the adsorption and desorption of H^+ contributes to the pseudocapacitance behavior of PPy, which also causes the PPy molecular structure collapse. However, the reaction of Co_3O_4 and OH^- inhibits the Faradaic reaction efficiency of PPy and H^+ , which may support the outstanding cycle stability performance of G- Co_3O_4 -PPy. (ii) Graphene and PPy both have very good conductivity (Fig. 4c), which is important during the electrochemical process^[16]. Moreover, they have the same conductive mechanism based on the sp^2 hybridized structure, which makes electron transport between graphene and PPy easy and rapid, facilitating the whole Faradaic reaction process and leading to the higher electrochemical performance and long-term cycle stability.^[17] (iii) The electrolyte also influences the electrochemical performance of the as-prepared electrodes. The concentration of H^+ in an alkaline electrolyte is limited. This may also affect the cycle stability of PPy. Although less H^+ may influence the pseudocapacitance of PPy, the higher transport of ions in PPy still plays a significant role in improving the electrochemical performance and long-term cycle stability performance of G- Co_3O_4 -PPy.

Conclusion

Free-standing G- Co_3O_4 -PPy composite electrodes for use as supercapacitors were made and their electrochemical properties were studied. It was clearly shown that introduction of Co_3O_4

nanoparticles and RGO sheets remarkably enhance the capacitance and electrochemical stability of G-Co₃O₄-PPy composite electrodes. The capacitance of G-Co₃O₄-PPy reaches 532.8 F g⁻¹ with no degradation showing after 700 charge-discharge cycles, which is due to the synergistic effects of Co₃O₄, RGO, and PPy. Meanwhile, the interconnected structure of all of the phases contributes to the enhancement of the capacitance and the electrochemical cycle stability.

Materials and Methods

Synthesis of Graphene Oxide (GO) and Reduced Graphene Oxide (RGO) Films. RGO films were prepared through reducing GO films by a thermal reduction process (900 °C). GO solution and GO films were synthesized using a modified Hummer's method and a direct heating process at 70 °C for 12 h, respectively. The details have been reported previously.^[8, 13a, 18]

Preparation of Co₃O₄ Nanoparticles. Co₃O₄ nanoparticles were fabricated by a hydrothermal process. Briefly, 6 g Co(NO₃)·6H₂O and 20.5 g sodium citrate (Na₃C₆H₅O₇·2H₂O) were dissolved in 300 ml deionized water. The solution was then injected with 50 ml NaBH₄ (37.8 g L⁻¹) and stirred for 2 h, followed by adding 30 mg sodium dodecylsulfate (SDS) and 50 ml NaOH solution (12 g L⁻¹). The hydrothermal process was carried out at 45 °C for 24 h to obtain the cobalt-containing precursor. Subsequently, the Co₃O₄ nanoparticles were obtained through 250 °C thermal treatment for 4 h, followed by washing and grinding.

Preparation of G-Co₃O₄-PPy composite films. Figure S3 shows the procedures for preparing RGO-Co₃O₄-PPy composite films. In detail, 0.05 g Co₃O₄ nanoparticles and 0.02 g of SDS were mixed with 50 mL homogeneous GO dispersions (5 mg mL⁻¹). The free-standing

and flexible G-Co₃O₄ composite films were obtained by a direct heating and thermal reduction process. Electrochemical deposition of PPy on G-Co₃O₄ films was then conducted at room temperature using a electrochemical workstation (PARSTAT 4000, AMETEK, USA). The as-prepared G-Co₃O₄ film acted as the working electrode. Following the electrochemical process, PPy was evenly deposited on the surface of the G-Co₃O₄ films, and the free-standing G-Co₃O₄-PPy was then obtained (Fig. S3).

Characterizations. A scanning electron microscope (SEM; INSPECT-F, FEI, The Netherlands) was employed to characterize the morphology and composition of RGO-based composite films. Transmission electron microscopy (TEM, Tecnai G2 F20 S-TWIN) with an acceleration voltage of 200 kV was used to check the morphology of the samples. The crystalline phase of the Co₃O₄ nanoparticles was determined by an X-ray diffractometer (XRD; X²pert pro-MPD, PANalytical, The Netherlands). The XRD measurements were performed using a Cu K α (wavelength, 1.5056 Å) X-ray source with a step rate of 0.02° s⁻¹.

An electrochemical analytical system (PARSTAT 4000, AMETEK, USA) was used to measure the electrochemical properties of the composites. The cyclic voltammetry was conducted at room temperature within the potential range from 0 to 1 V in the electrolyte of 6 M KOH. The scanning rate of cyclic voltammetry (CV) was set at 5, 10, 20, and 50 mV s⁻¹. The galvanostatic charge-discharge testing was also performed within the potential range from 0 to 1 V in 6 M KOH. The gravimetric specific capacitance C_{sp} (F g⁻¹) of the as-prepared films was calculated from each CV profile according to the following equation:

$$C_{sp} = \frac{1}{mV_V} \int_{v_-}^{v_+} i(v)dv = \frac{S}{mV_V} \quad (3)$$

where V_V is the width of the voltage window, v is the scan rate, $i(v)$ is the current, m is the mass of the prepared sample, C_{sp} is the capacitance of the electrode, and S is the integrated

area of the CV profile.

Acknowledgements

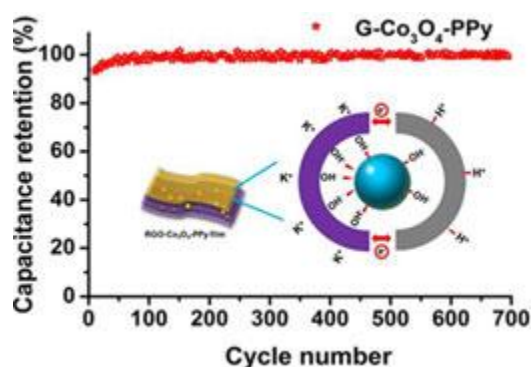
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References

- [1] a) E. Frackowiak, *Phys. Chem. Chem. Phys.* **2007**, *9*, 1774; b) G. Wang, L. Zhang, *Chem. Soc. Rev.* **2012**, *41*, 797-828.
- [2] a) Z. Yu, L. Tetard, *Energy Environ. Sci.* **2015**, *8*, 702-730; b) D. P. Dubal, O. Ayyad, *Chem. Soc. Rev.* **2015**, *44*, 1777-1790; c) N. Choudhary, C. Li, *Adv. Mater.* **2017**, *29*.
- [3] a) Y. Shi, L. Peng, *Chem. Soc. Rev.* **2015**, *44*, 6684-6696; b) Y. Shi, G. Yu, *Chem. Mater.* **2016**, *28*, 2466-2477; c) Q. Kang, J. Zhao, *Nano Energy* **2017**, *32*, 201-208; d) K. Guo, N. Yu, *J. Phys. Chem. A* **2016**, *5*; e) A. K. Mishra, S. Ramaprabhu, *J. Phys. Chem. C* **2011**, *115*, 14006-14013; f) H. Hu, H. Cheng, *Nano Lett.* **2015**, *15*, 5116-5123.
- [4] a) H. Tang, J. Wang, *Adv. Mater.* **2015**, *27*, 1117-1123; b) L. Nyholm, G. Nyström, *Adv. Mater.* **2011**, *23*, 3751-3769; c) Y. Zhang, H. Feng, *Int. J. Hydrogen Energy* **2009**, *34*, 4889-4899; d) S. A. Ansari, H. Fouad, *J. Colloid Interface Sci.* **2017**, *504*, 276-282; e) X. Liu, N. Wen, *ACS Sustainable Chem. Eng.* **2015**, *3*, 475-482.
- [5] J. Zhang, X. S. Zhao, *J. Phys. Chem. C* **2012**, *116*, 5420-5426.
- [6] a) W. K. Chee, H. N. Lim, *J. Phys. Chem. C* **2016**, *8*, 4153-4172; b) R. R. Salunkhe, Y. H. Lee, *Chemistry* **2014**, *20*, 13838; c) C. Y. Li, J. Patra, *ACS Sustainable Chem. Eng.* **2017**, *5*, 8269-8276.
- [7] K. Shu, C. Wang, *Electrochim. Acta* **2016**, *212*, 561-571.
- [8] L. Jiang, X. Lu, *J. Phys. Chem. C* **2015**, *119*, 3903-3910.
- [9] a) R. B. Rakhi, W. Chen, *Nano Lett.* **2012**, *12*, 2559; b) G. Wang, X. Shen, *J. Phys. Chem. C* **2009**, *113*, 4357-4361; c) X. Lin, Y. Shang, *ACS Sustainable Chem. Eng.* **2015**, *3*, 903-908.
- [10] Z. Hai, L. Gao, *Appl. Surf. Sci.* **2016**, *361*, 57-62.
- [11] a) J. Sun, Y. Huang, *Nano Energy* **2016**, *27*, 230-237; b) X. Zuo, Y. Zhang, *J. Alloys Compd.* **2016**, *688*, 140-148.

- [12] a) M. Liao, Y. Liu, *J. Alloys Compd.* **2013**, 562, 106-110; b) Z. Gao, C. Chen, *Electrochim. Acta* **2018**, 260, 932-943.
- [13] a) L. Jiang, X. Lu, *J. Mater. Sci. - Mater. Electron.* **2015**, 26, 747-754; b) S. Bose, T. Kuila, *J. Mater. Chem.* **2011**, 22, 767-784.
- [14] L. Bao, T. Li, *Small* **2017**, 13.
- [15] C. He, Y. Liang, *Composites Part B* **2017**, 121, 68-74.
- [16] a) T. Liu, L. Finn, *Nano Lett.* **2014**, 14, 2522-2527; b) G. Lota, K. Fic, *J. Mater. Chem.* **2011**, 4, 1592-1605.
- [17] a) Q. Zhu, K. Liu, *Chem. Eng. J.* **2017**, 321, 554-563; b) L. Han, P. Tang, *Nano Energy*. **2014**, 7, 42-51.
- [18] a) L. Jiang, X. Lu, *J. Mater. Sci. - Mater. Electron.* **2014**, 25, 174-180; b) D. Luo, F. Wang, *Proc. Nat. Acad. Sci.* **2016**, 113, 7711-7716; c) D. Luo, F. Wang, *Carbon* **2018**, 126, 105-110; d) D. Luo, F. Wang, *Chem. Mater.* **2017**, 29, 3454-3460.

TOC:



Synopsis: In this study, new composite electrode materials were made and studied for use as supercapacitors in energy storage applications.