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Holey graphene interpenetrating networks for boosting high-capacitive Co₃O₄ electrodes via an electrophoretic deposition process

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ABSTRACT

A composite of Co₃O₄/holey graphene (Co₃O₄/HG) was prepared via a facile hydrothermal route, and was then processed into an electrode by an electrophoretic deposition process. Holey graphene (HG) wrapped Co₃O₄ to form a 3D skeleton network, thereby providing high electrical conductivity, and the holes in HG could further shorten the electrolyte ion diffusion pathway. Therefore, by adjusting the mass ratio of Co₃O₄ to HG, the Co₃O₄/ HG composite afforded an enhanced capacitance of 2714 F g^{-1} (at a current density of 1 A g^{-1}), which is 20 times higher than that of pure Co₃O₄. To further explore the practical applications of Co₃O₄/HG, a symmetric supercapacitor employing Co₃O₄/HG was fabricated. The supercapacitor functioned stably at potentials up to 1.2 V, with an enhanced energy density of 165 Wh kg⁻¹ and a high power density of 0.6 kW kg⁻¹ at 1 A g⁻¹.

1. Introduction

With the increasing demand for large-scale energy storage applications, supercapacitors have become one of the dominant power sources that meet the requirements and challenges for high capacitance with a long lifetime. For an outstanding supercapacitor, the electrode material is the core that determines the upper limit of the capacitance and electrochemical performance. Therefore, thousands of prospective active materials have been investigated, including carbon materials, transition metal oxides, and polymers. Among them, Co₃O₄, owing to its ultrahigh theoretical capacitance of 3560 F g^{-1} , has emerged as a promising electrode candidate [1]. However, this high theoretical capacitance does not make Co₃O₄ a perfect active material in practical applications because the inferior intrinsic electronic conductivity and large volume changes of Co₃O₄ during the charge/discharge processes hinder its capacitance, deteriorating its rate capability and cycling stability [2,3].

Recently, to improve the performance of Co₃O₄-based electrodes, researchers have developed Co₃O₄ nanoparticles with sizes of a few nanometers to expose more active sites and enhance the capacitance [4]. Another strategy is to integrate Co₃O₄ with conductive carbon materials to enhance the electrical conductivity of the electrode [5,6]. For example, graphene, which has excellent flexibility, fast electron mobility (2000 S cm^{-1}), and a high theoretical specific surface area (>2630 m² g⁻¹), is regarded as the most appealing conductive carbon additive for integration with Co₃O₄ [7,8]. Currently, multiple methods for forming composites of graphene with Co₃O₄ have been developed, such as the microwave-assisted polyol [9], plasma-treatment [10], electrospray [11], and vacuum kinetic spray [12] techniques. Among them, the hydrothermal process is an effective synthesis method, in which Co₃O₄ nanoparticles are synthesized in situ on the surface of reduced graphene oxide (RGO) flakes or in the pores of graphene aerogels [13,14]. With the help of graphene, the conductivity is effectively improved, and the porous structure of the aerogels is beneficial for accommodating the electrolyte. However, the tight encapsulation of Co₃O₄ by graphene lengthens the ion transport pathway [15], which deteriorates the rate performance of Co₃O₄. Therefore, to fully utilize the potential capacitance of Co₃O₄, abundant exposed active sites and unobstructed ion transport pathways should be meticulously designed in

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the Co₃O₄/graphene composite electrode.

Moreover, the synthesis protocols and electrode assembly processes should be industrially viable as crucial factors for the practical application of Co_3O_4 electrodes. The electrophoretic deposition (EPD) technique can meet the extreme requirements of numerous substrates and has many advantages over other electrode fabrication techniques such as moldability, uniform and controllable thickness, and a smooth surface of the deposited species [16]. For example, Hui et al. prepared NiO@graphene composite electrodes by the EPD process for supercapacitors [17]. Zhang et al. achieved MnO₂-coated CNTs deposited on graphite sheets using the EPD process, as a flexible electrode for supercapacitors [18]. These reports demonstrate that EPD is an efficient technique for preparing supercapacitor electrodes with good electrode morphology and electrochemical performance.

Based on the above considerations, in this study a binder-free $Co_3O_4/$ holey graphene (Co_3O_4/HG) interpenetrating network was developed via hydrothermal assembly followed by an EPD process. The self-assembled HG porous network provides an interconnected scaffold for electron conduction, and the holes in the HG sheets facilitate rapid electrolyte ion diffusion. By controlling the mass ratio of Co_3O_4 to HG, charge transport in the interconnected architecture was optimized to deliver a high specific capacitance and a desirable rate capability. As a result, the Co_3O_4/HG based supercapacitor exhibited high energy and power densities.

2. Materials and methods

2.1. Synthesis of Co₃O₄

First, 0.996 g of $Co(Ac)_2$ ·4H₂O (99.5%, Macklin Co.) and 0.200 g of NaOH (98%, Aladdin Co.) were dissolved in 10 mL deionized (DI) water to obtain the $Co(Ac)_2$ and NaOH solutions. The NaOH solution was added dropwise to the $Co(Ac)_2$ solution under constant stirring for 30 min. Afterward, 1.2 g of sodium dodecyl benzene sulfonate (SDBS, 95%, Aladdin Co.) was added to the above solution with vigorous stirring for 2 h until the SDBS was evenly dispersed. The as-prepared dispersion was sealed in a 100 mL Teflon-lined stainless steel autoclave and maintained at 160 °C for 36 h. After cooling to room temperature, the dispersion was centrifuged at 9500 rpm, and the precipitate was re-dispersed in DI water. The centrifugation and re-dispersion processes were repeated five times to rinse the precipitate, and the precipitate was dried in an oven at 80 °C to obtain black powders.

2.2. Synthesis of HG and RGO

HG was prepared by adding a graphene oxide (GO) suspension (20 mL, 2 mg mL⁻¹, Global Graphene Group) and H₂O₂ solution (30 wt%, 0.1 mL, Aladdin Co.) to a 50 mL Teflon-lined steel autoclave, followed by curing at 180 °C for 6 h. The above solution was then purified by filtration (membrane pore size, $0.2 \,\mu$ m). The precipitate (0.001 g) was added to 10 mL of DI water to form a 1 mg mL⁻¹ HG solution. The function of H₂O₂ is to create holes in the graphene nanosheets [15,19], and the hydrothermal process reduces the GO [20]. RGO without holes was prepared using the same procedure, but without adding H₂O₂.

2.3. Synthesis of Co₃O₄/HG and Co₃O₄/RGO

First, 80 mg of Co_3O_4 was dispersed in 19 mL of DI water, after which 10 mL HG (1 mg mL⁻¹) solution was added dropwise under stirring for 2 h. Thereafter, 1 mL of HI (\geq 47%, Macklin Co.) was added to the above mixture, which was then transferred to a 50 mL Teflon-lined steel autoclave and kept at 180 °C for 12 h. The resulting solution was purified by filtration (membrane pore size, 0.2 µm) and washed with DI water several times until the pH of the solution was equal to 7, to remove the residual HI. Other Co₃O₄/HG composites were also prepared by adjusting the mass ratio of Co₃O₄ to HG, which were named as Co₃O₄/

Table 1

Components used for synthesizing Co3O4/110 and Co3O4/1100	Components used	l for synthesizing	Co ₃ O ₄ /HG and	Co_3O_4/RGO_4
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	Co ₃ O ₄ /mg	HG/RGO/mg	HI/mL
Co ₃ O ₄ /HG-1	80	10	1
Co ₃ O ₄ /HG-2	160	10	1
Co ₃ O ₄ /HG-3	240	10	1
Co ₃ O ₄ /RGO	160	10 (RGO)	1

HG-1, 2, and 3, as shown in Table 1. As a reference, Co_3O_4/RGO was prepared using the same procedure.

2.4. Electrode preparation

The EPD process was used to fabricate active electrodes, including Co_3O_4 , Co_3O_4/RGO , and $Co_3O_4/HG-1$, 2, and 3. In brief, 0.064 g of electrode material dispersed in 40 mL acetone with 0.04 g of I₂ (99.8%, Macklin Co.) was used as the electrolyte for EPD. A 2×1 cm² nickel foil was used as the negative electrode for the EPD, while a Pt plate was used as the counter positive electrode. Using a dc power source, 30 V was applied between the two electrodes for 1 min, after which the nickel foil was removed and dried in a vacuum oven at 80 °C for 2 h. The weight of the active materials of each electrode was weighed for electrochemical characterization. The average areal deposition loading is ~0.5 mg cm⁻².

2.5. Characterization

The morphology and microstructure of the samples were observed by scanning electron microscopy (SEM, HITACHI SU-8010) and transmission microscopy (TEM, FEI Tecnai G2 F20). The elemental energy spectrum was acquired using energy dispersive spectroscopy (EDS, AMETEK EDAX). The crystalline structures were evaluated by X-ray diffraction (XRD, Ultima IV) in the 20 range of 5–90°. Raman spectra were recorded on a Horiba Scientific LabRAM HR Evolution system with a laser operating at 532 nm. The surface area was measured using the BET method from nitrogen gas adsorption–desorption isotherms at 77 K.

2.6. Electrochemical measurements

All electrochemical tests were performed using an electrochemical workstation (Bio-Logic, VSP-300) in a 2 M KOH aqueous electrolyte. In the three-electrode system, an Ag/AgCl electrode and a Pt plate were used as the reference and counter electrodes, respectively. The symmetric supercapacitor was assembled using two as-prepared electrodes with the same mass loading, and a glass fiber member was used as the separator. The specific gravimetric capacitances (C_m , F g⁻¹) and areal capacitance (C_A , mF cm⁻²) from the galvanostatic charge/discharge (GCD) curves and cyclic voltammetry (CV) were calculated using the following equations:

$$C_{m(GCD)} = \frac{It}{\Delta Vm}$$

$$C_{m(CV)} = \int IdV / 2m\Delta Vv$$

$$C_{A(GCD)} = \frac{It}{\Delta VA}$$

$$C_{A(CV)} = \int IdV / 2A\Delta Vv$$

where *I* is the discharge current, *t* is the discharge time, ΔV is the potential change during discharging, *m* is the mass loading of the working electrode, *A* is the area of the working electrode, $\int IdV$ is the integrated area of the enclosed CV curves, and *v* is the scan rate.

The energy density (E, Wh kg⁻¹) and power density (P, W kg⁻¹) of



Fig. 1. Schematic illustration of synthesis and reaction mechanism of Co₃O₄/RGO and Co₃O₄/HG.



Fig. 2. TEM images of HG (a) and RGO (b); SEM images of Co₃O₄ (c), Co₃O₄/HG-1 (d), Co₃O₄/HG-2 (e), Co₃O₄/HG-3 (f), and Co₃O₄/RGO (g).

the symmetric supercapacitors were calculated from the GCD curves using the following equations:

3. Results and discussion

3.1. Synthetic route and morphology characteristics

The synthesis scheme and reaction mechanism of the Co_3O_4/RGO and Co_3O_4/HG composites are illustrated in Fig. 1. The difference

 $P = E \times 3600/t$



Fig. 3. (a) XRD patterns of HG, Co₃O₄, Co₃O₄/RGO, and Co₃O₄/HG-2. (b) Raman spectra of GO, RGO, HG, Co₃O₄, Co₃O₄/RGO, and Co₃O₄/HG-2.

between Co₃O₄/RGO and Co₃O₄/HG during synthesis is the usage of H₂O₂, which is used as an etchant to create holes on the graphene flakes. As shown in Fig. 2a and Fig. S1, holes with a size of ~20 nm were successfully etched in the graphene flakes by H₂O₂. Undoubtedly, no holes were observed in RGO (Fig. 2b and Fig. S1). The ensuing hydrothermal treatment with HI further reduced HG and RGO [21]. The graphene flakes assembled during the hydrothermal treatment to form an interconnected 3D skeleton structure and wrap the cubic-shaped Co₃O₄/HG and Co₃O₄/RGO powders were fabricated into electrodes using the EPD process without any binder. As shown in Fig. 2d–g, Co₃O₄ was wrapped inside the network, and the amount of Co₃O₄ particles also clearly increased when the mass ratio of Co₃O₄/HG-1, 2, and 3 increased from 8:1 to 24:1. The thickness of the Co₃O₄/HG-2 is ~5 µm, as obtained

from the cross-sectional SEM in Fig. S2. The wrapping of Co_3O_4 was further confirmed by EDS analysis. As illustrated in Fig. S3, Co was detected throughout the sample, indicating that the Co_3O_4 particles were successfully and uniformly loaded.

3.2. Structural characteristics

The crystal structures of HG, Co_3O_4 , Co_3O_4/RGO , and $Co_3O_4/HG-2$ were characterized by XRD and Raman spectroscopy. HG is RGO with holes, in which the crystallinity of RGO was unchanged. Therefore, the XRD pattern of HG showed two peaks at 24.8° and 42.7° (Fig. 3a), corresponding to the (002) and (100) planes of the RGO sheets, respectively. In addition, seven sharp diffraction peaks at 19.0°, 31.2°, 36.8°, 44.8°, 55.6°, 59.3°, and 65.2° were observed in the XRD patterns



Fig. 4. Electrochemical properties of Co_3O_4 , RGO, HG, Co_3O_4 /RGO, and Co_3O_4 /HG-1, 2, 3 electrodes. (a) CV curves at a scan rate of 10 mV s⁻¹. (b) GCD curves at current density of 1 A g⁻¹. (c) Specific gravimetric capacitances depending on various current densities. (d) Nyquist plots of the electrodes.



Fig. 5. Electrochemical performance of Co_3O_4 /HG-2-based symmetric supercapacitors. (a) CV curves at various scan rates. (b) GCD curves at various current densities. (c) Specific capacitances depending on various scan rates and current densities. (d) Ragone plots for Co_3O_4 /HG-2-based symmetric supercapacitor compared with other reported supercapacitors [4,14,29,32–36].

of Co₃O₄, Co₃O₄/RGO, and Co₃O₄/HG-2, respectively, which were perfectly indexed to the (111), (220), (311), (400), (422), (511), and (440) crystal planes of cubic spinel Co₃O₄ (JCPDS 42–1467), indicating the high purity of Co₃O₄. Because of the low mass ratio of HG/RGO to Co₃O₄, the diffraction peak of RGO could barely be observed in the case of Co₃O₄/RGO and Co₃O₄/HG-2.

The Raman spectra in Fig. 3b show two peaks at 1355 and 1590 cm⁻¹, commonly denoted as the D and G peaks, for GO, RGO, and HG, which arise from the disordered structure and bond-stretching motion of sp²-hybridized carbon, respectively. After reduction, the D peak to G peak intensity ratio (I_D/I_G) of RGO decreased slightly. However, owing to the defects induced by the holes in the HG nanosheets, the I_D/I_G ratio increased in the case of HG. Three characteristic peaks of Co₃O₄ centered at 481, 520, and 687 cm⁻¹ were clearly observed in the Raman spectra of Co₃O₄, Co₃O₄/RGO, and Co₃O₄/HG-2, which can be assigned to the E_g, F_{2g}, and A_{1g} modes of the lattice vibration of Co₃O₄/HG-2 because of the low mass ratio of RGO and HG.

3.3. Electrochemical characterization

The electrochemical properties of Co_3O_4 , RGO, HG, Co_3O_4 /RGO, and Co_3O_4 /HG-1, 2, and 3 were analyzed with an electrochemical station in a three-electrode system using a KOH aqueous electrolyte. First, CV tests were carried out at a scan rate of 10 mV s⁻¹ for all electrodes. As plotted in Fig. 4a, perfectly reversible redox peaks were observed, indicating the pseudocapacitive characteristics of the Co_3O_4 -based materials. The reversible redox reactions among the valence states of $Co^{2+}/Co^{3+}/Co^{4+}$ can be described by the following electrochemical equations [22,23]:

$$Co_3O_4 + OH + H_2O \rightleftharpoons 3CoOOH + e$$

 $CoOOH + OH = CoO_2 + H_2O + e^{-1}$

From the above equations, the change from Co₃O₄ to CoO₂ occurs via two steps; however, only one peak was observed in Fig. 4a. Literature reports indicate that the redox reactions take place intensely during the CV test, and thus the two-step reaction occurs almost simultaneously, which appears as two close peaks that cannot be distinguished [4,24]. The specific capacitance (SC) of Co₃O₄, RGO, and HG was calculated as 134, 81, and 97 F g^{-1} , respectively. Upon forming the composite with RGO, the SC of the resulting Co₃O₄/RGO was improved 3.5 times and reached 476 F g^{-1} . Compared with pure Co₃O₄, RGO in Co₃O₄/RGO can greatly enhance the electrical conductivity, thereby improving the SC of the composite electrode. However, the abundant holes in HG can provide channels for ions in the electrolyte to access Co₃O₄ efficiently; therefore, Co₃O₄/HG-1, 2, and 3 have better porous structures than Co₃O₄/RGO (Fig. 2d-f and 2g). Furthermore, the BET surface area in Fig. S4a confirms that Co₃O₄/HG-2 provides a higher specific surface area of 26.0 m² g⁻¹ than that of Co₃O₄/RGO (9.2 m² g⁻¹), while the pure Co_3O_4 has the lowest specific surface area of 8.4 m² g⁻¹. As shown in Fig. S4b, the pore sizes of Co₃O₄/HG-2 are mainly distributed ranging from 1 to 20 nm which can be ascribed to the holes in HG. As a result, the SC was significantly enhanced by utilizing HG; the SC of the Co₃O₄/HG-1, 2, 3 electrodes reached 751, 2538, and 1456 F g⁻¹, respectively. Among them, Co₃O₄/HG-2 shows the highest SC, which can be ascribed to the appropriate mass ratio of Co₃O₄ to HG, which takes full advantage of Co3O4 and HG. HG provides a scaffold with optimal porosity and conductivity [15,19,25,26], thereby retaining the high capacitance of Co₃O₄.

Fig. 4b illustrates the GCD performance of the electrodes at a current density of 1 A g^{-1} . Co₃O₄/HG-2 achieved the best SC of 2714 F g^{-1} , while Co₃O₄, RGO, HG, Co₃O₄/RGO, Co₃O₄/HG-1, and Co₃O₄/HG-3 provided SCs of 131, 128, 170, 491, 729, and 1498 F g^{-1} , respectively.

reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ceramint.2021.06.143.

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depending on the current density (Figs. S5–S11), are shown in Figs. 4c and S12a, respectively. Co_3O_4 /HG-2 showed the highest SC and desirable rate capability, with 78% capacity retention at current densities from 1 to 10 A g⁻¹, while Co_3O_4 only exhibited a retention of 66%. Further comparison was made between Co_3O_4 /HG-2 and other reported Co_3O_4 -based materials to demonstrate the excellent electrochemical performance of Co_3O_4 /HG-2. As shown in Fig. S13 and Table S1, Co_3O_4 /HG-2 in our work delivers the highest SC, with excellent rate capability [27–32].

The specific gravimetric and areal capacitances of these composites,

Electrochemical impedance spectroscopy was used to investigate the kinetic features of ion diffusion. The Nyquist plots obtained in the frequency range of 300 kHz to 10 mHz are shown in Fig. 4d. Wrapped by RGO/HG, the equivalent series resistance of the Co_3O_4 electrode decreased obviously, indicating enhancement of the electrical conductivity by the addition of RGO/HG. The plots show nearly vertical lines for Co_3O_4 /HG-1, 2, and 3, revealing better ion diffusion behavior compared to that of Co_3O_4 /RGO and pure Co_3O_4 . This can be ascribed to the holes in HG that shorten the ion diffusion pathway.

To further explore the practical applications of Co₃O₄/HG-2, symmetric supercapacitors were assembled by employing the Co₃O₄/HG-2 electrodes with 2 M KOH as the electrolyte. In the case of symmetric supercapacitors, the electrodes can work stably in a higher potential window than in the three-electrode system, and thus, the CV and GCD tests were conducted at a potential of 1.2 V at different scan rates and current densities, as shown in Fig. 5a and b, respectively. The welldefined curve without any polarization confirms the capability of the Co₃O₄/HG-2 supercapacitor to work at a high potential. Accordingly, the SC of the Co₃O₄/HG-2 supercapacitor was calculated from the CV and GCD data. High SCs of 743 F g^{-1} (371.5 mF cm⁻²) at a scan rate of 10 mV s $^{-1}$ and 825 F g $^{-1}$ (412.5 mF cm $^{-2})$ at a current density of 1 A g $^{-1}$ was achieved, as shown in Figs. 5c and S12b. Notably, the supercapacitor shows outstanding rate capability, with a capacitance retention of 78% when the scan rate was increased from 10 to 150 mV s⁻¹, and 70% when the current density was increased from 1 to 10 A g^{-1} .

The practical applications of supercapacitors are related to their stability and energy restoration capability. Therefore, as shown in Fig. S14, a cyclic test was conducted over 10,000 cycles, in which 92% of the initial capacitance remained, indicating the superior stability of the Co₃O₄/HG-2-based supercapacitor. Ragone plots (Fig. 5d) were constructed to compare the Co₃O₄/HG-2-based supercapacitor with other reported Co₃O₄-based supercapacitors [4,14,29,32–36]. Impressively, our work illustrates both higher energy density (165 Wh kg⁻¹ at 1 A g⁻¹, 115 Wh kg⁻¹ at 10 A g⁻¹) and power density (0.6 kW kg⁻¹ at 1 A g⁻¹, 6 kW kg⁻¹ at 10 A g⁻¹) than the other reported works, suggesting great potential application of the Co₃O₄/HG-2 supercapacitor.

4. Conclusions

In this study, a high-capacitive Co_3O_4/HG electrode was developed using a one-step hydrothermal assembly and EPD process. In this electrode, HG provides a good scaffold for high electrical conductivity; the abundant holes in HG provide a shortened ion pathway; the Co_3O_4 nanoparticles wrapped in the HG network provide high capacitance. As a result, the Co_3O_4/HG electrode shows excellent electrochemical performance compared to pure Co_3O_4 and Co_3O_4/RGO electrodes. Upon further optimizing the mass ratio of Co_3O_4 to HG, the $Co_3O_4/HG-2$ based supercapacitor afforded a high SC of up to 825 F g⁻¹ at a current density of 1 A g⁻¹ with superior rate capacity. Moreover, the desirable cyclic ability and superior energy and power densities make the $Co_3O_4/HG-2$ electrode a promising candidate for energy storage devices.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work

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