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One-step alkaline hydrothermal strategy was developed to fabricate the strongly coupled Co$_3$O$_4$ NSs-rGO hybrid with large specific capacitance and high electrochemical utilization at high rates towards advanced supercapacitors.
One-step hydrothermal fabrication of strongly coupled Co$_3$O$_4$ nanosheets-reduced graphene oxide towards electrochemical capacitors

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Abstract

In the work, we developed one-step synthetic strategy to prepare the strongly coupled Co$_3$O$_4$ nanosheets-reduced graphene oxide (Co$_3$O$_4$ NSs-rGO) hybrid, and further utilized it as a promising electroactive material for electrochemical capacitors (ECs). During the hydrothermal procedure, the GO was reduced and Co$_3$O$_4$ NSs were in situ grown onto the rGO sheets simultaneously due to the electrostatic interaction between the Co$^{2+}$ and GO sheets. Electrochemical characteristics indicated that the Co$_3$O$_4$ NSs-rGO hybrid with ~7.2 wt.% Co$_3$O$_4$ loading delivered a specific capacitance (SC) of 187 F g$^{-1}$ at 1.2 A g$^{-1}$. Furthermore, the SC degradations of the
hybrid were ~6 and 9% at constant current densities of 1.2 and 5 A g\(^{-1}\) after 1000 continuously charge-discharge cycles, demonstrating its desirable electrochemical stability. The synergetic effect of nanoscale size and good redox activity of the Co\(_3\)O\(_4\) NSs combined with high electronic conductivity of the rGO resulted in the enhanced electrochemical utilization at high rates. In addition, an activated carbon/Co\(_3\)O\(_4\) NSs-rGO asymmetric EC was further fabricated, and exhibited a specific energy density of ~13.4 Wh kg\(^{-1}\), specific power density of ~2166 W kg\(^{-1}\) and striking electrochemical stability with ~11% SC degradation after 1000 cycles.

**Key words:** Co\(_3\)O\(_4\) nanosheets; Reduced graphene oxide; Hydrothermal synthesis; Electrochemical capacitors

1. Introduction

Most recently, electrochemical capacitors (ECs), as a promising intermediate system between dielectric capacitors and conventional batteries, have drawn wide attention, due to their outstanding characteristics of fast energy delivery, short charging time, high power capability, long cycling life, and environment-friendly features.\(^{1-3}\) It is such promising properties that make them intriguing energy-storage devices in a wide range of applications, including electric vehicles (EVs), HEVs, mobile electronic devices, memory backup systems, and so on. In general, ECs can be categorized into electrical double-layer capacitors (EDLCs) and pseudo-capacitors, depending upon the different charge storage mechanisms as well as the electroactive...
materials used. As both of the two have pluses and minuses, accordingly, enormous efforts were greatly stimulated to couple pseudo-capacitive materials with double-layer capacitive materials together for maximizing electrochemical performance in targeting high power and energy delivery capabilities meanwhile as a result of the synergetic mechanism both of EDLC and pseudo-capacitors.

Of particular note, cobalt oxide (Co$_3$O$_4$) has been investigated well as a typical electroactive material among these Faradaic pseudo-capacitive transition metal oxides (TMOs), considering its low cost, natural abundance, environmental safety, et al. Unfortunately, relatively poor electronic conductivity of the Co$_3$O$_4$ itself commonly results in modest specific capacitance (SC) and ineffective electrochemical utilization for ECs application. Various carbonaceous electrode materials, such as, carbon fibers, carbon nanotubes, and otherwise, are thereby anticipated to enhance the electrochemical performance of the electroactive Co$_3$O$_4$ phase, thanks to their highly accessible surface area, good electronic conductivity, and superior chemical stability. On the other hand, it is worthy of noting that the reduced graphene oxide (rGO) is extensively considered as a fascinating “wonder land” perfect for integrating functional pseudocapacitive Co$_3$O$_4$ with special microstructure and morphologies. Nevertheless, a troublesome two-step method, particularly annealing at high temperature, is commonly necessary to grow nanosized and well-dispersed Co$_3$O$_4$ upon the rGO surface. Therefore, it is still challenging and imperative to explore more efficient yet even simpler ways to synthesize nanoscale Co$_3$O$_4$-rGO hybrid with improved electrochemical capacitance for advanced ECs.
Herein, we develop a facile but efficient strategy to fabricate strongly coupled Co$_3$O$_4$ nanosheets-rGO (donated as Co$_3$O$_4$ NSs-rGO hereafter) for ECs application via a simple one-step hydrothermal route. In essence, the method proposed here utilizes a facile one-pot hydrothermal route, yet it distinguishes itself from other conventional routes where the two-step process, even including high-temperature calcination, was generally applied. Afterwards, electrochemical performance of the hybrid Co$_3$O$_4$ NSs-rGO electrode is evaluated for high-performance ECs in a three-electrode system at room temperature (RT). And the as-prepared Co$_3$O$_4$ NSs-rGO hybrid exhibits striking SCs and good cycling stability at high rates in a 2 M KOH aqueous electrolyte. Furthermore, an asymmetric EC was fabricated, where activated carbon (AC) and Co$_3$O$_4$ NSs-rGO were used as the negative and positive electrodes, respectively, and delivered an excellent specific power density, attractive energy density and electrochemical stability.

2. Experimental

2.1. Synthesis of the hybrid Co$_3$O$_4$ NSs-rGO

All the chemicals were of analytical grade and directly used without further purification. Graphene oxide (GO) was prepared from natural graphite by a modified Hummers method as described elsewhere. The as-synthesized GO was suspended in water to give a brown dispersion, which was then subjected to dialysis to completely remove residual salts and acids. In a typical synthesis of the hybrid Co$_3$O$_4$ NSs-rGO, firstly, 27 mg of GO and 7.5 mg of Co(NO$_3$)$_2$·6H$_2$O were dispersed into 32 mL de-ionized (DI) water by ultrasonication for 2 h to form uniform GO
solution. Secondly, 18 mL of NH$_3$·H$_2$O was added into the mixed solution under stirring for 10 min. The reaction mixture was then transferred to a Teflon-lined autoclave and hydrothermally treated at 100 ºC for 15 h. After cooled to RT, the solid product was obtained by filtering and washing with DI water and absolute ethanol for several times. For comparison, 5, 12.5 and 15 mg of Co(NO$_3$)$_2$·6H$_2$O was added during synthetic process to prepare another Co$_3$O$_4$-rGO hybrids, which were denoted as Co$_3$O$_4$-rGO-1, Co$_3$O$_4$-rGO-2 and Co$_3$O$_4$-rGO-3, respectively. Furthermore, without the addition of the Co species in the synthetic procedure, the rGO was also fabricated accordingly.

2.2. Materials characterization

The samples were examined by powder X-ray diffraction (XRD) (Max 18 XCE, Japan) using a Cu Ka source ($\lambda = 0.154056$ nm) at a scanning speed of 3° min$^{-1}$ over a 2$\theta$ range of 10 – 80°. The morphologies and structures were observed with field-emission scanning electron microscopy (FESEM, JEOL-6300F, 15 kV) and transmission electron microscope (TEM) and high-resolution TEM (HRTEM) (JEOL JEM 2100 system operating at 200 kV).

2.3. Electrochemical tests

The working electrode was prepared by mixing 85 wt.% of the hybrid Co$_3$O$_4$ NSs-rGO, 5 wt.% of acetylene black (AB) and 10 wt.% of poly(tetrafluoroethylene) (PTFE), and then pressing the mixture onto a nickel grid (1 cm$^2$). The electrolyte used here was 2 M KOH aqueous solution. Electrochemical performance of the samples was evaluated at RT by cyclic voltammetry (CV) and chronopotentiometry (CP) tests.
with an IVIUM electrochemical workstation (the Netherlands). The typical loading of the electroactive Co$_3$O$_4$ NSs-rGO hybrid is 5 mg cm$^{-2}$. The activated carbon (AC, Chenming Co., China) electrode was prepared by the same method as that of hybrid Co$_3$O$_4$ NSs-rGO electrode. All experiments were carried out in a three-electrode system with a working electrode, a platinum plate counter electrode (1 cm$^2$) and a saturated calomel electrode (SCE) reference electrode. And the cycling performance was carried out with a CT2001D tester (Wuhan, China). The SC of the hybrid Co$_3$O$_4$ NSs-rGO, and AC electrodes was calculated from the CP curves based on the following equation:

$$C = \frac{It}{\Delta V}$$

(1)

where $C$, $I$, $t$ and $\Delta V$ are the SC (F g$^{-1}$) of the electrodes, the discharging current density (A g$^{-1}$), the discharging time (s) and the discharging potential range (V), respectively.

An asymmetric quasi-capacitor was further fabricated by using 5 mg of AC as negative electrode and 7 mg of the Co$_3$O$_4$ NSs-rGO hybrid as positive electrode face to face in 2 M KOH aqueous solution. And the specific energy density ($E$) and power density ($P$) of the asymmetric EC can be calculated by using the equation:

$$E = Pr = \frac{1}{2}C(\Delta V)^2$$

(2)

3. Results and discussion

3.1. Characteristics of the resulting Co$_3$O$_4$ NSs-rGO sample

Fig. 1a presents the typical XRD pattern of the as-obtained GO product. As
evident, an intense and sharp peak is observed at $2\theta = 11.3^{\circ}$, corresponding to the characteristic (001) diffraction peak of the GO. The interlayer spacing of 0.78 nm is much larger than that of natural graphite (~0.34 nm), due to the introduction of the oxygen-containing function groups on the graphite sheets.\textsuperscript{25, 26} And the wide-angle XRD pattern of the hybrid Co$_3$O$_4$ NSs-rGO product, in which ~7.2 wt.% Co$_3$O$_4$ loading is delivered on the condition that the Co species is wholly converted into the Co$_3$O$_4$ phase, is shown in Fig. 1b. Attractively, the sharp peak at $2\theta = 11.3^{\circ}$ disappears after alkaline hydrothermal treatment at 100 $^{\circ}$C for 15 h, which confirms that the GO has been successfully reduced, and the rGO is formed accordingly. In addition, other nine peaks at 18.8 $^{\circ}$, 31.2 $^{\circ}$, 36.7 $^{\circ}$, 44.7 $^{\circ}$, 55.6 $^{\circ}$, 59.3 $^{\circ}$, 65.2 $^{\circ}$, 74.8 $^{\circ}$, 78.9 $^{\circ}$ fully correspond to the typical reflections from (111), (220), (311), (400), (422), (551), (440), (620) and (622) crystal planes of the well-crystallized Co$_3$O$_4$ with a face-centered cubic structure (JCPDS Card No. 43-1003), respectively. Moreover, the low and broad diffraction peaks indicated the small size of the as-synthesized Co$_3$O$_4$ phase. These XRD data obviously presents the unambiguous fact that the hybrid Co$_3$O$_4$-rGO can be fabricated via such one-step facile alkaline hydrothermal route. Evidently, the alkaline hydrothermal treatment applied here not only facilitates the reduction of the GO\textsuperscript{7, 27, 28} but also renders the formation of the Co$_3$O$_4$ phase.

Fig. 2a shows the representative low-magnification TEM image of the resulting Co$_3$O$_4$ NSs-rGO sample. The unique hybrid possesses a typical NS micro-structure with rippled silk morphology, owing to its ultrathin feature. In addition, as observed in the higher-magnification TEM image (Fig. 2b), some Co$_3$O$_4$ NSs with dark color, as
marked by the red circles, are dispersed well upon the light-colored RGO surface. It is due to the electrostatic interaction between the Co\textsuperscript{2+} and GO sheets\textsuperscript{21, 29} that the strongly coupled Co\textsubscript{3}O\textsubscript{4} NSs-rGO hybrid was obtained. The HRTEM image taken from the dark regions is demonstrated in Fig. 2c. As evident, crystal fringes are clearly displayed, and the \(d\)-spacing is derived to be ~0.21 nm, corresponding to the spacing between (220) planes of the nanoscale Co\textsubscript{3}O\textsubscript{4}. And when 5 mg of Co(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O was applied for preparing the Co\textsubscript{3}O\textsubscript{4}-rGO-1 product (~4.8 wt.% Co\textsubscript{3}O\textsubscript{4} loading), even less Co\textsubscript{3}O\textsubscript{4} NSs are observed upon the rGO surface (Fig. 3a). More interestingly, when the amount of Co(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O used in the synthetic process is up to 12.5 mg, another distinct morphology is thus presented for the Co\textsubscript{3}O\textsubscript{4}-rGO-2 sample (~11.5 wt.% Co\textsubscript{3}O\textsubscript{4} loading), as shown in Fig. 3b. Clearly, some spherical Co\textsubscript{3}O\textsubscript{4} nanoparticles (NPs) of ~200 – 300 nm and even some Co\textsubscript{3}O\textsubscript{4} NPs aggregations with the size range of ~600 – 800 nm are obviously located upon the rGO surface. Thereby, it is easy to conclude that the concentration of the Co\textsuperscript{2+} applied here plays a significant role in the elegant formation of the strongly coupled Co\textsubscript{3}O\textsubscript{4} NSs-rGO hybrid.

3.2 Electrochemical behavior of the hybrid Co\textsubscript{3}O\textsubscript{4} NSs-rGO electrode

The as-synthesized Co\textsubscript{3}O\textsubscript{4}-rGO hybrids are further fabricated as ECs electrodes, and first characterized with the CV technique in a three-electrode system with a 2 M KOH aqueous electrolyte. Representative CV curves of the hybrid Co\textsubscript{3}O\textsubscript{4} NSs-rGO at various scan rates ranged from 5 to 50 mV s\textsuperscript{-1} are demonstrated in Fig. 4a. Obviously, a pair of well-defined redox peaks within the electrochemical window of 0.0 – 0.5 V
(vs. SCE) is found over the entire range of scan rates as indicated, suggesting that the
distinguished capacitive characteristics are mainly governed by Faradaic redox
reactions taking place on and/or near the electroactive surface of the unique Co$_3$O$_4$
NSs-rGO hybrid electrode, which is greatly distinct from the common EDLC characterized by nearly rectangular CV shapes. Notably, the electrochemical current subsequently increases while the CV shape almost keeps the same with the increase of the scan rates, suggesting good electrochemical capacitance of the unique hybrid electrode. Impressively, the peak potential shifts only ~50 mV for a 10-time increase in the scan rate, revealing the low polarization of the coupled Co$_3$O$_4$ NSs-rGO electrode. Also, the typical redox peaks observed here should be attributed to the electrochemical inter-transition of multi-valence Co species, *i.e.*, two sequential redox reactions taking place according to the following two expressions (3 and 4).

\[
\begin{align*}
\text{Co}_3\text{O}_4 + \text{OH}^- + \text{H}_2\text{O} & \leftrightarrow 3\text{CoOOH} + e^- \quad (3) \\
\text{CoOOH} + \text{OH}^- & \leftrightarrow \text{CoO}_2 + \text{H}_2\text{O} + e^- \quad (4)
\end{align*}
\]

Of particular note, both the electrochemical cathodic and anodic peak currents vary linearly with the sweep rates, as seen from the Fig. 4b. This demonstrates that the unique Co$_3$O$_4$ NSs-rGO hybrid electrode owns excellent power property, and the typical capacitive behavior is not diffusion controlled.

Fig. 5a shows galvanostatic charge-discharge curves of the hybrid Co$_3$O$_4$
NSs-rGO electrode in a three-electrode system. The nonlinear CP curves further verify the typical pseudo-capacitive feature of the hybrid electrode, which is in good
agreement with the CV analysis mentioned above. Based on the CP plots presented in 
Fig. 5a, the SCs are calculated, and then depicted in Fig. 5b. Evidently, the SCs of the 
hybrid electrode at 1.2, 1.5, 2, 3, 4 and 5 A g$^{-1}$ are 187, 182, 177, 169, 162 and 152 F 
g$^{-1}$, respectively, much higher than that of 163.8 F g$^{-1}$ (at 1 A g$^{-1}$) for the Co$_3$O$_4$-rGO 
scrolls in recent report.\textsuperscript{35} And ~81% of the SC is also retained with the current density 
increases from 1.2 to 5 A g$^{-1}$, showing its appealing rate performance. In particular, as 
for other Co$_3$O$_4$-rGO hybrid electrodes with even more Co$_3$O$_4$ loadings, as seen in the 
inset in Fig. 5b, the Co$_3$O$_4$-rGO-2 and Co$_3$O$_4$-rGO-3 (~13.3 wt.% Co$_3$O$_4$ loading) 
samples just deliver a SC of 135 and 142 F g$^{-1}$ at a current density of 1.2 A g$^{-1}$, and 
~72% and 67% of SC retention are observed for the Co$_3$O$_4$-rGO-2 and Co$_3$O$_4$-rGO-3 
products the when the current density increases up to 5 from 1.2 A g$^{-1}$, the reasons for 
which should be related to the larger size of the Co$_3$O$_4$ NPs and the second 
aggregation of Co$_3$O$_4$ NPs in these hybrids. And for the hybrid Co$_3$O$_4$-rGO-1, a SC of 
156 F g$^{-1}$ was obtained at a current density of 1.2 A g$^{-1}$, less than that of the strongly 
coupled Co$_3$O$_4$ NSs-rGO, due to the less loading of electroactive Co$_3$O$_4$. And the SC 
value is even higher than those of the Co$_3$O$_4$-rGO-2 and Co$_3$O$_4$-rGO-3 samples with 
much more Co$_3$O$_4$ loadings, for which the much larger naked electrochemical surface 
area of the Co$_3$O$_4$-rGO-1 should be responsible. More importantly, in such 
electrochemically working window, a modest SC of ~11 F g$^{-1}$ is for the rGO at 2 A g$^{-1}$ 
(Fig. S1, ESI†), similar to the reported before.\textsuperscript{7, 20} As a consequence, the SCs 
calculated here for the Co$_3$O$_4$ NSs-rGO hybrid is mainly contributed by the 
pseudo-capacitive Co$_3$O$_4$ NSs, and the SCs of the Co$_3$O$_4$ NSs thus can be estimated as
~2300 F g\(^{-1}\) at a current density of 2 A g\(^{-1}\), considering ~7.2 wt.% of the Co\(_3\)O\(_4\) loading in the hybrid Co\(_3\)O\(_4\) NSs-rGO. These data mentioned above strongly support the fact that the hybrid Co\(_3\)O\(_4\) NSs-rGO is a promising electrode for ECs application due to its striking ability to deliver large SCs and high electrochemical utilization at high charge-discharge rate, which might be related to the striking structural features of the present hybrid electrode. Firstly, the rGO exiting in the unique hybrid enhances the electronic conductivity of the hybrid, prevents the agglomeration of the Co\(_3\)O\(_4\) NSs, and increases the effective interfacial area between the Co\(_3\)O\(_4\) NSs and the electrolyte during the electrochemical reaction. Secondly, the nanoscale size of the obtained Co\(_3\)O\(_4\) NSs can reduce the diffusion length over which the OH\(^{-}\) must transfer during the charge-discharge process. It is the synergetic interaction between the rGO and Co\(_3\)O\(_4\) NSs that renders its improved electrochemical capacitance even at large current densities.

The cycling stability of the strongly coupled Co\(_3\)O\(_4\) NSs-rGO hybrid electrode is further evaluated by the repeated charging-discharging measurement at current densities of 1.2 and 5 A g\(^{-1}\) in a 2 M KOH aqueous solution, respectively, as shown in Fig. 6. Obviously, the SC is around 186 F g\(^{-1}\) in the first cycle and it gradually decreases to 175 F g\(^{-1}\) after cycling for 1000 times at a current density of 1.2 A g\(^{-1}\), corresponding to a SC loss of only ~6%. And of particular note, the SC retention of 9% even can be achieved at a large current density of 5 A g\(^{-1}\), which is good among TMOs-based nanostructure electrode materials.

3.3 Electrochemical performance of the AC/Co\(_3\)O\(_4\) NSs-rGO asymmetric EC
To further highlight its application as a promising positive electrode for ECs, we fabricated an asymmetric EC by using AC with electrical double-layer capacitance as negative electrode (Fig. S2, ESI†) and the as-synthesized Co$_3$O$_4$ NSs-rGO as positive electrode, respectively. The typical I-E response of the asymmetric EC is presented in Fig. 7a, and shows well-defined mirror shape with the respect to the zero-current line and rapid current response on voltage reversal at each potential. Moreover, the upper voltage limit of the CV curves can be extended to 1.45 V, which is of great significance to the enhancement of specific energy density and practical commercial interest. Fig. 7b demonstrates the galvanostatic CP plots of the AC/Co$_3$O$_4$ NSs-rGO asymmetric EC at a current density of 1 A g$^{-1}$ in the potential range from 0 to 1.45 V. In addition, a nearly linear variation of the voltage is observed during the charge-discharge process, proving appealing capacitive behavior of the asymmetric EC. And a SC is calculated as ~42 F g$^{-1}$ for such asymmetric EC according to the data shown in Fig. 7b. In addition, when the current density is up to 3 A g$^{-1}$ (Fig. S3, ESI†), a SC of 33 F g$^{-1}$ is still obtained, and a maximum SC of 46 F g$^{-1}$ can be delivered at a current density of 0.25 A g$^{-1}$.

Furthermore, the Ragone plot of the AC/Co$_3$O$_4$ NSs-rGO asymmetric EC is shown in Fig. 8a, and illustrates the corresponding energy/power densities. The data of Fig. 8a clearly demonstrates that the asymmetric EC possesses good specific energy density and power density. Strikingly, the asymmetric EC is capable of delivering a high energy density of ~13.4 Wh kg$^{-1}$ and an appealing power density of ~2166 W kg$^{-1}$, which is even comparable to other systems. The long-term
cyclability is of great significance for EC application. Accordingly, the cycling behavior of the symmetric EC during charge-discharge process at 1 A g\(^{-1}\) for continuous 1000 cycles without relaxation is performed within the electrochemical window from 0.0 to 1.45 V. As shown in Fig. 8b, the SC of the symmetric EC decreases with the growth of the cycle number, and after continuous 1000 cycles, the capacitance value remains ~89% of that of the first cycle. The capacitance attenuation of ~11% suggests the good electrochemical stability of the symmetric EC.

4. Conclusions

In summary, an efficient one-pot hydrothermal strategy was proposed to fabricate the strongly coupled Co\(_3\)O\(_4\) NSs-rGO hybrid. During the hydrothermal reaction, the GO was reduced, and the Co\(_3\)O\(_4\) NSs were in situ grown onto the rGO NSs simultaneously due to the electrostatic interaction between the Co\(^{2+}\) and GO NSs. When further utilized as high-performance positive material for ECs, the hybrid Co\(_3\)O\(_4\) NSs-rGO with ~7.2 wt.% of the Co\(_3\)O\(_4\) NSs loading delivered a SC of 187 F g\(^{-1}\) at 1.2 A g\(^{-1}\), and 151 F g\(^{-1}\) even at a large current density of 5 A g\(^{-1}\). Appealing, the SC retention of the hybrid are ~94 and 91% after continuously cycling for 1000 times at 1.2 and 5 A g\(^{-1}\), respectively, strongly revealing its striking electrochemical stability. The existence of rGO in the hybrid was anticipated to prevent the agglomeration of the Co\(_3\)O\(_4\) NSs, enhance the electronic conductivity of the hybrid electrode, and increase the contact surface between the Co\(_3\)O\(_4\) NSs and the electrolyte during the electrochemical reaction, which synergistically contributed to the enhanced electrochemical utilization of the unique Co\(_3\)O\(_4\) NSs-rGO electrode even at high rates.
Furthermore, an AC/Co$_3$O$_4$ NSs-rGO asymmetric EC exhibited an attractive specific energy density, high power density and desirable cycling performance.

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3, 904.


Captions and Figures

**Fig. 1.** Wide-angle XRD patterns of (a) the GO and (b) as-fabricated Co$_3$O$_4$ NSs-rGO product

**Fig. 2.** (a) TEM and (b) HRTEM images of the strongly coupled Co$_3$O$_4$ NSs-rGO sample

**Fig. 3.** (a) TEM image of the Co$_3$O$_4$-rGO-1 sample and (b) FESEM image of the Co$_3$O$_4$-rGO-2 sample

**Fig. 4.** (a) CV curves at various scan rates and (b) the relationship between peak current ($i_p$) and the sweep rate ($v$) of the resulting hybrid Co$_3$O$_4$ NSs-rGO

**Fig. 5.** (a) Charge-discharge curves (E vs. time) and (b) calculated SC as a function of current density for the Co$_3$O$_4$ NSs-rGO hybrid sample. The inset for the SC via current density for other Co$_3$O$_4$-rGO hybrids as indicated

**Fig. 6.** Cycling performance of the hybrid Co$_3$O$_4$ NSs-rGO sample at different current densities as indicated

**Fig. 7.** (a) CV curves (10 mV s$^{-1}$) and (b) charge-discharge plots (1 A g$^{-1}$) of the AC/Co$_3$O$_4$ NSs-rGO asymmetric EC

**Fig. 8.** (a) Ragone plot and (b) cycling behavior (1 A g$^{-1}$) of the AC/Co$_3$O$_4$ NSs-rGO asymmetric EC
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Figure 4 by Changzhou Yuan, et al.
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Figure 7 by Changzhou Yuan, et al.
Figure 8 by Changzhou Yuan, et al.