Self-assembled Co$_9$S$_8$/RGO-CNT interconnected architecture as composite electrode for supercapacitors†

Wen Chen, Ye Li, Xiao Han, Xiaoran Zhao and Yan Zhao*

Co$_9$S$_8$ nanoparticles are dispersed homogeneously on the backbone of self-assembled RGO-CNT by using hydrothermal and vacuum filtration method. The interconnected structure of Co$_9$S$_8$/RGO-CNT generates a profound impact on the electrode, resulting from the addition of CNTs into RGO/Co$_9$S$_8$, forming a 3D intertwined structure. The composite electrode shows a high specific capacitance of 1376.78 F g$^{-1}$, which is much higher than that of graphene or Co$_9$S$_8$ as electrode material, and excellent cycling stability at the scan rate of 5 mV s$^{-1}$. In addition, the composite electrode exhibits brilliant long-term stability with the specific capacitance of 894.9 F g$^{-1}$ after 500 charge/discharge cycles. The Co$_9$S$_8$/RGO-CNT composite with interconnected architecture is a promising electrode candidate for supercapacitors.

1 Introduction

Supercapacitors have been widely researched because of their increasing applications not only in computers, cameras and other small power devices, but also in the trigger devices of automobiles and large wind power plants.$^{1-3}$ Supercapacitors have higher power density, faster charge–discharge ability, longer life cycle and higher efficiency compared with traditional batteries.$^{4-7}$ However, the energy density of supercapacitors is low, which can restrict their applications. It is reported that high energy density can be achieved by pseudocapacitive reactions, such as those using RuO$_2$, MnO$_2$, Co$_9$O$_4$, V$_2$O$_5$, NiO, etc.$^{8-12}$ In addition, metal sulfide-based supercapacitors of the same element group have also been studied.$^1$ Wang and co-workers showed that the CoS$_2$-based supercapacitor electrode achieved 314 F g$^{-1}$ at the current density of 0.5 A g$^{-1}$.$^1$ Similarly, Ranga Rao synthesized hierarchical structured Co$_9$O$_4$ with high porosity, and charge–discharge measurement results indicated that this electrode material can attain 548 F g$^{-1}$ at the current density of 8 A g$^{-1}$. However, such specific capacitances are still relatively low in the application of electrical devices. Thus, it is essential to hybridize supercapacitors with pseudocapacitive materials to achieve high specific capacitance and high energy density.

Graphene has been regarded as a promising electrode material for supercapacitor application because of its ultrathin surface area and excellent electrical conductivity.$^{13-16}$ However, monolayer graphene units often stack into multilayers, which can cause a great loss to surface area of graphene. Thus, graphene supercapacitors have low capacitance caused by the stacking of graphene. It is worth noting that metal oxide or sulfide nanoparticles, such as Co$_3$O$_4$/RGO, MnO$_2$/GNS, and Co$_9$S$_8$/RGO, may be used as spacers to prevent graphene mono-layers from stacking.$^{17,18}$ In addition, inserting some conductive carbons materials, such as carbon nanotubes (CNT), between graphene sheets can link graphene sheets into a stable network, which can effectively prevent the stacking of graphene sheets.$^{17,18}$ Niu and coworkers synthesized the graphene/CNT interconnected network for lithium sulfur batteries with an initial capacity of 1008 mAh g$^{-1}$ at 0.3C and capacity retention of 70% after 100 cycles.$^{17}$ Many recent research studies reported that cobalt sulfide exhibits great performance as an electrode material for supercapacitors, which results from its various nanostructures.$^{19,20}$

Herein, we report Co$_9$S$_8$ with graphene and CNT-based materials. On the one hand, the large specific surface of graphene can benefit the loading of Co$_9$S$_8$ nanoparticles;$^{21}$ on the other hand, CNTs link the graphene sheets and form a intertwined, connected structure, which can make more paths for electrons and ions.

2 Experimental

2.1 Materials

Natural flake graphite and cobaltous sulfate heptahydrate (CoSO$_4$·7H$_2$O) were purchased from GuoYao Group Chemical Reagent Co., Ltd, China. Multiwalled carbon nanotubes (MWCNTs) were purchased from Beijing TianNai Co., Ltd, China. Sulphuric acid, potassium permanganate, hydrogen peroxide, thiourea, potassium nitrate, ammonia and glucose were purchased from Beijing Chemical Factory; all these reagents were of analytical grade.

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2.2 Synthesis of Co$_9$S$_8$/RGO-CNT composites

GO was prepared by modified Hummers’ method, and MWCNTs were acid-treated with concentrated H$_2$SO$_4$ (60 mL) and KNO$_3$ (1.5 g) at 70 °C for 7 h. As for Co$_9$S$_8$/RGO-CNT composite synthesis, about 1.2 g CoSO$_4$·7H$_2$O was dissolved in 30 mL of ethylene glycol (EG) and 10 mL of deionized water under stirring, then about 0.6 g thiourea was dispersed into this scarlet-red solution. About 65 mg of GO was dissolved in the aforementioned scarlet-red solution through sonication for 1 h. Then, 2 mL ammonia and 0.1 g glucose were added into the mixed solution, which was then transferred into a 50 mL Teflon-lined stainless-steel autoclave and heated in an oven at 170 °C for 10 h. After cooling to room temperature naturally, Co$_9$S$_8$/RGO powder was finally obtained by centrifugation, washing thoroughly with DI water and ethanol repeatedly, and drying at 60 °C for 7 h in a vacuum oven. Next, CNTs were added into the Co$_9$S$_8$/RGO aqueous solution through vacuum filtration and sonication. For self-assembly of the Co$_9$S$_8$/RGO-CNT composite, Co$_9$S$_8$/RGO and surface-modified CNTs (Co$_9$S$_8$/RGO : CNTs = 3 : 1 wt ratio) were dispersed evenly with the addition of 3 mg CTAB in 100 mL of DI water under sonication for 2 h. Then, the solution was vacuum-filtered with a polytetrafluoroethylene (PTFE) membrane, pore size = 0.2 μm, and self-assembled Co$_9$S$_8$/RGO-CNT film was formed during the filtration process and designated as 30% CNT. Two other Co$_9$S$_8$/RGO-CNT composites were prepared by changing the amount of CNTs (10 wt% and 50 wt%), and the samples were designated as 10% CNT and 50% CNT, respectively. For comparison, pure Co$_9$S$_8$/RGO was also prepared following the same procedure in the absence of CNTs.

2.3 Characterization

The physical properties of the Co$_9$S$_8$/RGO-CNT were examined with X-ray diffraction (XRD), cold cathode analytical field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and X-ray photo-electron spectroscopy (XPS).

XRD analysis was obtained with a Rigaku D/max-2200 with Cu Kα radiation as X-ray source. The SEM images were taken via a JSM-7500F for morphological analysis. TEM images were obtained with a Tecnai G² F20 microscope. The chemical state and composition of the composites were measured by XPS via an ESCALab 220i-XL spectrometer with a monochromated Al K radiation (1486.6 eV).

2.4 Electrochemical measurements

The electrochemical performance of the Co$_9$S$_8$/RGO-CNT electrode was analyzed in a three-electrode cell including a Pt wire as the counter electrode, saturated calomel electrode (SCE) as the reference electrode, a 1 M KOH aqueous solution as the electrolyte, and the Co$_9$S$_8$/RGO-CNT film loaded on Ni foam (1.0 cm × 1.0 cm) as the working electrode.

Herein, cyclic voltammetry (CV) experiments, electrochemical impedance spectroscopy (EIS) and galvanostatic charge–discharge curves were performed using a CHI 660E electrochemical workstation. CV measurements were conducted at a scan rate of 10 mV s$^{-1}$ with the voltage range of $-0.1 \text{ V to } 0.6 \text{ V}$. EIS tests were performed at open-circuit potential in the frequency range between 100 kHz and 0.01 Hz under a perturbation amplitude of 5 mV. Galvanostatic charge–discharge analysis was carried out at various current densities with the voltage range of $-0.1 \text{ V to } 0.3 \text{ V}$. All electrochemically characterized data for each composite given in the report were obtained under identical conditions at room temperature.

The specific capacitance ($C$) of the electrode can be calculated according to the following equation,

$$C = \frac{\int I dV}{\text{nm} V},$$

where $C$ (F g$^{-1}$) is the specific capacitance of the electrode based on the mass of the active materials, $I$ (A) is the current, $V$ (V) is the potential during the discharge and charge process, and $m$ (g) is the mass of the active materials (Fig. 1).

3 Results and discussion

3.1 Structural and morphological characterization of Co$_9$S$_8$/RGO-CNT

The composition and purity of the obtained Co$_9$S$_8$ sample is shown in Fig. 2a–c. All of the diffraction peaks in this pattern
can be readily indexed to face-centered cubic Co$_9$S$_8$ (JCPDS card no. 65-6801). The crystal structure of Co$_9$S$_8$ is shown in Fig. 2c, where the S atoms are arranged through cubic close-packing, 8/9Co atoms are surrounded by a tetrahedron of atoms, and 1/9Co atoms are surrounded by an octahedron of S atoms. Comparing the diffraction peaks of the Co$_9$S$_8$ and Co$_9$S$_8$/RGO samples, there are some differences shown in Fig. 2b; the diffraction peaks of the plane (222) between two samples are different from 2θ and the peak’s value, which may be caused by the addition of graphene, and which may prove that there might be some kinds of molecular forces between Co$_9$S$_8$ and RGO sheets. The crystal size grown on the surface of the RGO could be calculated by the Scherrer equation:

$$D = \frac{0.89\lambda}{\beta \cos \theta}, \quad (2)$$

where $D$ is crystal dimension, $\lambda$ is wavelength, $\beta$ is the full-width-half-maxima of peaks and $\theta$ is diffraction angle. According to the Scherrer equation, the crystalline sizes of Co$_9$S$_8$ were found to be about 25 nm.

More detailed elemental analysis of the Co$_9$S$_8$/RGO sample was done by XPS. Fig. 3a and b shows the core level spectra of the Co 2p and S 2p region. The Co 2p spectrum, including Co 2p$_{3/2}$ and Co 2p$_{1/2}$, suggest the two spin–orbit doubles characteristic of Co$^{2+}$ and Co$^{3+}$. The S 2p peak at 161.9 eV is the binding energy of Co–S. The Co 2p and S 2p peaks in the XPS patterns are characteristic of Co$_9$S$_8$. The microstructures and morphologies of the Co$_9$S$_8$/RGO-CNT composite were investigated by SEM. As shown in Fig. 4a, the Co$_9$S$_8$ nanoparticles were scattered evenly with a size of about 50 nm on the RGO sheets, and the Co$_9$S$_8$ particles are microspheres; it is noteworthy that the particles are uniformly anchored on RGO sheets. The small size and homogenous distribution of Co$_9$S$_8$ particles in the Co$_9$S$_8$/RGO composite could be attributed to the functional groups on RGO acting as the nucleation sites for Co$_9$S$_8$ particles. Fig. 4b–d present SEM images of Co$_9$S$_8$/RGO composite with different contents of CNTs. It can been seen easily that Co$_9$S$_8$/RGO is well dispersed in the CNT network in Fig. 4c, while in Fig. 4b, part of the Co$_9$S$_8$/RGO is out of the CNT network, and in Fig. 4d, lots of CNTs are intertwined together, thus resulting in aggregation. To sum up, it is concluded that proper CNTs added into the Co$_9$S$_8$/RGO composite are extremely significant. With Co$_9$S$_8$/RGO evenly scattered in the highly conductive CNT network, the 3D hierarchical structure can provide a robust electrical connection within the entire electrode framework, enable the contact with the liquid electrolyte readily, and even maintain such features during the cycling process because of the 3D wrapping effect of the CNTs.

Further microstructures of the Co$_9$S$_8$/RGO-CNT composite were characterized by TEM. From Fig. 5a and b, it can be observed that Co$_9$S$_8$ particles are well dispersed on the RGO sheets, while aggregation occurred in a portion of the area. Fig. 5c is the high-resolution TEM (HRTEM) image of Co$_9$S$_8$/RGO, and it indicates Co$_9$S$_8$ particles with a $d$-spacing of 0.350 nm, 0.299 nm and 0.220 nm, which correspond to the (220), (311) and (420) planes of Co$_9$S$_8$, respectively. As for the TEM image of the Co$_9$S$_8$/RGO-CNT composite in Fig. 5d, it is obvious that the CNTs are well interconnected, which could enhance the conduction of the composite. The XRD pattern of Co$_9$S$_8$/RGO sample was done by XPS. Fig. 3a and b shows the core level spectra of the Co 2p and S 2p region. The Co 2p spectrum, including Co 2p$_{3/2}$ and Co 2p$_{1/2}$, suggest the two spin–orbit doubles characteristic of Co$^{2+}$ and Co$^{3+}$. The S 2p peak at 161.9 eV is the binding energy of Co–S. The Co 2p and S 2p peaks in the XPS patterns are characteristic of Co$_9$S$_8$. The microstructures and morphologies of the Co$_9$S$_8$/RGO-CNT composite were investigated by SEM. As shown in Fig. 4a, the Co$_9$S$_8$ nanoparticles were scattered evenly with a size of about 50 nm on the RGO sheets, and the Co$_9$S$_8$ particles are microspheres; it is noteworthy that the particles are uniformly anchored on RGO sheets. The small size and homogenous distribution of Co$_9$S$_8$ particles in the Co$_9$S$_8$/RGO composite could be attributed to the functional groups on RGO acting as the nucleation sites for Co$_9$S$_8$ particles. Fig. 4b–d present SEM images of Co$_9$S$_8$/RGO composite with different contents of CNTs. It can been seen easily that Co$_9$S$_8$/RGO is well dispersed in the CNT network in Fig. 4c, while in Fig. 4b, part of the Co$_9$S$_8$/RGO is out of the CNT network, and in Fig. 4d, lots of CNTs are intertwined together, thus resulting in aggregation. To sum up, it is concluded that proper CNTs added into the Co$_9$S$_8$/RGO composite are extremely significant. With Co$_9$S$_8$/RGO evenly scattered in the highly conductive CNT network, the 3D hierarchical structure can provide a robust electrical connection within the entire electrode framework, enable the contact with the liquid electrolyte readily, and even maintain such features during the cycling process because of the 3D wrapping effect of the CNTs.

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noteworthy that Co$_9$S$_8$/RGO groups are connected to each other by CNTs. The results indicate that with the unique structural properties of RGO and highly conductive nature of uniformly interconnected CNT network, such continuous interconnected network finally can render well-developed porous structures, high mechanical strength, and superior flexibility of the Co$_9$S$_8$/RGO-CNT composites, and hence can be considered as an ideal electrode material in supercapacitors.\textsuperscript{35,36}

### 3.2 Electrochemical characterization of Co$_9$S$_8$/RGO-CNT

The capacitive properties of the composite materials were assessed by CV, galvanostatic charge–discharge and EIS measurements.

Fig. 6a–d shows the CV curves of pure Co$_9$S$_8$/RGO and Co$_9$S$_8$/RGO-CNT with the voltage range of $-0.1$ V to 0.6 V and various scan rates ranging from 5 mV s$^{-1}$ to 50 mV s$^{-1}$. The CV curves of

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**Fig. 4** SEM images of Co$_9$S$_8$/RGO (a), Co$_9$S$_8$/RGO-10% CNT (b), Co$_9$S$_8$/RGO-30% CNT (c) and Co$_9$S$_8$/RGO-50% CNT (d). CNT and graphene sheets intertwine and form an interconnected structure.

**Fig. 5** (a) TEM image of Co$_9$S$_8$/RGO, (b) Co$_9$S$_8$ nanoparticle distribution diagram, with the average size of Co$_9$S$_8$ particles of 28 nm, (c) HR-TEM image of Co$_9$S$_8$/RGO, d-spacing of 0.350 nm, 299 nm and 0.220 nm correspond to the (220), (311) and (420) planes of Co$_9$S$_8$, respectively, and (d) TEM image of Co$_9$S$_8$/RGO-CNT.
Co$_9$S$_8$ and Co$_9$S$_8$/RGO-CNT have two nearly reversible and symmetrical redox peaks, indicating good capacitive behavior. Though there is no unified conclusion explaining the reaction mechanism of Co$_9$S$_8$, it is reported that Co$_9$S$_8$ may react with the form between Co$^{2+}$, Co$^{3+}$ and Co$^{4+}$, and it can be described as the following reaction:

$$37Co_9S_8 + OH^- \rightarrow Co_9S_7OH + e^-$$  \hspace{1cm} (3)

$$Co_9S_7OH + OH^- \rightarrow Co_9S_6(OH)_2 + e^-$$  \hspace{1cm} (4)

The specific capacitance of Co$_9$S$_8$/RGO was calculated by CV curves using a standard equation as stated in the Experimental section. The highest specific capacitance of RGO, Co$_9$S$_8$ and Co$_9$S$_8$/RGO was found to be 243.99 F g$^{-1}$, 541.99 F g$^{-1}$ and 709.25 F g$^{-1}$, respectively, while that of Co$_9$S$_8$/RGO-CNT is

\[ \text{Fig. 6} \] CV curves of pure RGO (a), Co$_9$S$_8$ (b), Co$_9$S$_8$/RGO (c) and Co$_9$S$_8$/RGO-CNT (d) at different scan rates in a three-electrode system.

\[ \text{Fig. 7} \] The galvanostatic charge–discharge curves of pure RGO (a), Co$_9$S$_8$ (b), Co$_9$S$_8$/RGO (c) and Co$_9$S$_8$/RGO-CNT (d) at various current densities in the three-electrode system.
have a unique 3D structure caused by graphene and CNTs interconnected together. Moreover, the excellent electrochemical performance of Co$_9$S$_8$/RGO-CNT composites is attributed to the conductive 3D interconnected network composed by interconnected graphene sheets and CNTs, which provide a fast and continuous highway for electron and ion transfer and accommodate the load of Co$_9$S$_8$ particles during charge/discharge cycling. The unique structure can guarantee a better specific capacitance as well as charge-discharge and long-term stability, which shows a good prospect for the future. The highest specific capacitance of Co$_9$S$_8$/RGO-CNT is 1376.78 F g$^{-1}$ at the scan rate of 5 mV s$^{-1}$, and the specific capacitance of Co$_9$S$_8$/RGO-CNT is 894.9 F g$^{-1}$ after 500 cycles. The outstanding electrochemical properties of Co$_9$S$_8$/RGO-CNT suggest that it is a promising electrode material for supercapacitors.

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**Notes and references**