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One-step synthesis of Ni$_3$S$_2$ nanorod@Ni(OH)$_2$ nanosheet core–shell nanostructures on a three-dimensional graphene network for high-performance supercapacitors†

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A three-dimensional graphene network (3DGN) grown on nickel foam is an excellent template for the synthesis of graphene-based composite electrodes for use in supercapacitors. Ni(OH)$_2$ nanosheets coated onto single-crystal Ni$_3$S$_2$ nanorods grown on the surface of the 3DGN (referred to as the Ni$_3$S$_2@$Ni(OH)$_2$/3DGN) are synthesized using a one-step hydrothermal reaction. SEM, TEM, XRD and Raman spectroscopy are used to investigate the morphological and structural evolution of the Ni$_3$S$_2@$Ni(OH)$_2$/3DGN. Detailed electrochemical characterization shows that the Ni$_3$S$_2@$Ni(OH)$_2$/3DGN exhibits high specific capacitance (1277 F g$^{-1}$ at 2 mV s$^{-1}$ and 1037.5 F g$^{-1}$ at 5.1 A g$^{-1}$) and areal capacitance (4.7 F cm$^{-2}$ at 2 mV s$^{-1}$ and 3.85 F cm$^{-2}$ at 19.1 mA cm$^{-2}$) with good cycling performance (99.1% capacitance retention after 2000 cycles).

Introduction

The increasing demand for energy and environmental protection has stimulated intensive research into energy storage and conversion from alternative energy sources. Currently, the supercapacitor is one of the most ideal candidates for green energy storage because of its high power density, super-high cycling life and safe operation. Based on the charge–storage mechanism, supercapacitors are generally divided into two types: electrical double-layer capacitors (EDLCs) that use carbon-active materials and pseudocapacitors that use redox-active materials. Among the numerous pseudocapacitor materials, transition metal oxides and hydroxides have been found to be excellent active materials, because of the variety of oxidation states they possess for charge transfer. Nickel hydroxide is an especially attractive candidate for pseudocapacitors due to its layered structure, with large interlayer spacing and high theoretical specific capacitance. However, these types of pseudocapacitors are often confronted with a compromised rate capability and reversibility, which rely on the Faradic redox reaction. Recently, metal sulfides, another kind of active material, have attracted increasing interest due to their good performance in energy storage applications including supercapacitors.

Two-dimensional (2D) graphene has attracted much attention due to its high surface area, high flexibility and electrical conductivity. Graphene and graphene-based materials are widely used in electrochemical applications, such as in graphene-based supercapacitors which have high specific capacitance. Since three-dimensional (3D) nanostructures with a short path for ion diffusion and large surface area provide more efficient contact between the ions of the electrolyte and the active materials, they are seen as promising electrode materials. For example, various 3D hybrid nanostructures, such as Co$_3$O$_4$@MnO$_2$, CoO@NiHON and MnO$_2$–NiO, have been used to significantly enhance both the capacitance and durability of supercapacitors.

Recently, a novel 3D graphene network (3DGN) with an enlarged void volume, large surface area and high electrical conductivity was reported. Our previous work showed that the 3DGN grown on nickel foam is an excellent template for a...
graphene-based composite electrode, which opened up a promising new strategy for the application of graphene-based materials in supercapacitors.\textsuperscript{25,27} Herein, we report the growth of a novel 3D hybrid structure, i.e. a Ni\(_3\)S\(_2\) nanorod@Ni(OH)\(_2\) nanosheet core–shell nanostructure grown on a 3DGN on nickel foam, referred to as a Ni\(_3\)S\(_2@\)Ni(OH)\(_2\)/3DGN, which has robust hierarchical porosity and a high specific surface area, using a simple one-step hydrothermal reaction. The composite and nanostructure of Ni\(_3\)S\(_2@\)Ni(OH)\(_2\)/3DGN can be controlled by varying the reaction time and the mass ratio of Ni foam to thioacetamide (TAA). Electrochemical measurements of this novel hybrid structure exhibited a high capacitance and good cycling performance.

Experimental section

Growth of the Ni\(_3\)S\(_2@\)Ni(OH)\(_2\)/3DGN hybrid structure

After the three-dimensional graphene network (3DGN) was grown on a nickel foam,\textsuperscript{23} Ni\(_3\)S\(_2@\)Ni(OH)\(_2\)/3DGN heterostructures were prepared using a simple one-step hydrothermal process. In a typical experiment, a piece of 3DGN on nickel foam was wrapped in Teflon tape with exposure area of \(\sim 1\) cm\(^2\), and immersed into a Teflon-lined stainless steel autoclave containing a 20 mL homogeneous solution of 25 mg thioacetamide (TAA, C\(_2\)H\(_5\)NS). The autoclave was then sealed for and the hydrothermal reaction was conducted at 180 °C for 6, 12 and 24 h in order to obtain Ni\(_3\)S\(_2\)/3DGN, Ni\(_3\)S\(_2@\)Ni(OH)\(_2\)/3DGN and Ni(OH)\(_2@\)3DGN, respectively. After the autoclave was cooled down to room temperature, the samples were rinsed with a copious amount of distilled water and then dried in an electric oven at 60 °C for 12 h. As a control experiment, the nickel foam without 3DGN was used to synthesize a Ni\(_3\)S\(_2\) nanorod@Ni(OH)\(_2\) nanosheet/nickel foam heterostructure, referred to as Ni\(_3\)S\(_2@\)Ni(OH)\(_2\)/Ni, at 180 °C for 12 h.

Characterization

Field emission scanning electron microscopy (FESEM, Model JSM-7600F, JEOL Ltd., Tokyo, Japan) was used to characterize the morphologies of the synthesized samples. Transmission electron microscopy (TEM) images were taken using a JOEL JEM 2100F microscope. The chemical composition was investigated by using energy dispersive X-ray spectroscopy (EDX). The X-ray powder diffraction (XRD) pattern of each sample was recorded on a Bruke D8 Advance powder X-ray diffractometer using Cu K\(_\alpha\) radiation (\(\lambda = 0.15406\) nm). Raman spectra were collected with a WITEC CRM200 Raman System (488 nm laser, 2.54 eV, WITec, Germany).

Electrochemical measurement

Cyclic voltammetry (CV) and galvanostatic charge–discharge were performed using a conventional three-electrode cell with 3 M KOH aqueous solution as the electrolyte and recorded on Solartron analytical equipment (Model 1470E, AMETEK, UK). The electrochemical impedance spectroscopy (EIS) test was performed using a conventional three-electrode system (CHI 660C, CH Instrument Inc., USA). The Ni\(_3\)S\(_2@\)Ni(OH)\(_2\)/3DGN on Ni foam substrate (1 cm\(^2\)), Ag/AgCl electrode (saturated KCl) and Pt wire were used as the working, reference and counter electrodes, respectively.

Results and discussion

SEM images of the obtained Ni\(_3\)S\(_2@\)Ni(OH)\(_2\)/3DGN (see the Experimental section for details) are shown in Fig. 1a–c. The 3DGN is covered by Ni\(_3\)S\(_2\) nanorods with a diameter of 0.5–1 \(\mu\)m and a length of 5–10 \(\mu\)m, which grew densely and almost vertically on the surface of the 3DGN. Magnified SEM images reveal that the Ni\(_3\)S\(_2\) nanorods are covered by Ni(OH)\(_2\) nanosheets (Fig. 1e). With such a unique hierarchical structure, the space between the Ni\(_3\)S\(_2\) nanorods in the array can be efficiently utilized, allowing the electrolyte ions easier access to the surface of the active material. The XRD spectrum of the as-grown Ni\(_3\)S\(_2@\)Ni(OH)\(_2\)/3DGN (Fig. 1d) shows peaks at \(2\theta = 21.7, 31.1, 37.8, 49.7\) and 55.2°, which correspond to the single crystalline Ni\(_3\)S\(_2\) (JCPDS no. 44-1418). It should be noted that two characteristic peaks for Ni at \(2\theta = 44.5\) and 51.8° in the XRD pattern arise from the Ni foam substrate (JCPDS no. 65-2865). A very small amount of NiS (JCPDS no. 21-0041) is also observed in the XRD pattern. While the presence of the Ni(OH)\(_2\) nanosheets was not confirmed by the XRD pattern, possibly due to there only being a tiny amount, it was confirmed from the HRTEM images and EDX (Fig. 2).

The nanostructures of the Ni(OH)\(_2\) nanosheets and Ni\(_3\)S\(_2\) nanorods were further investigated using TEM. Fig. 2a shows the typical TEM image of an individual Ni\(_3\)S\(_2\) nanorod covered by thin Ni(OH)\(_2\) nanosheets. The HRTEM image obtained from the white square area labelled (b) in Fig. 2a has a lattice spacing of 0.28 nm in the backbone area of the Ni\(_3\)S\(_2\) nanorod (Fig. 2b), which corresponds to the (110) interplanar spacing of Ni\(_3\)S\(_2\)
Ni3S2@Ni(OH)2 core–shell hierarchical structure.

Raman spectroscopy was used to further characterize the synthesized Ni3S2@Ni(OH)2/3DGN. Fig. 3 shows the typical G (~1580 cm⁻¹) and 2D (~2732 cm⁻¹) peaks that are characteristic of graphene in the 3DGN (curve a). The integrated peak area ratio of the 2D band to G band (~0.51) indicates that the 3D graphene network contains few-layer graphene.\(^{55,26}\) The typical G (~1563 cm⁻¹) and 2D (~2706 cm⁻¹) peaks shown in curve b of Fig. 3 indicate that the graphene still existed after the synthesis of Ni3S2@Ni(OH)2 on the 3DGN. In order to further confirm the presence of graphene, the Ni3S2@Ni(OH)2 and Ni foam in Ni3S2@Ni(OH)2/3DGN were removed by immersing Ni3S2@Ni(OH)2/3DGN in a 1 M HCl aqueous solution at 60 °C overnight followed by rinsing with DI water several times. Fig. S1 (ESI†) indicates the 3DGN remained and 3D structure was still preserved, however some pores were observed on the surface of the graphene. In addition, two characteristic Raman peaks at ~537.6 cm⁻¹ (longitudinal optical, LO) and ~1090.7 cm⁻¹ (phonon modes, 2LO) were attributed to Ni(OH)2 in Ni3S2@Ni(OH)2/3DGN.\(^{28,29}\)

To investigate the morphological and structural evolution of the Ni3S2@Ni(OH)2/3DGN, a series of experiments with different hydrothermal reaction times were conducted (Fig. 4a–c), which indicate the evolution of the structure from Ni3S2 nanorods to Ni3S2@Ni(OH)2, and then finally conversion to pure Ni(OH)2 nanosheets. After a hydrothermal reaction time of 6 h, Ni3S2 nanorods were obtained (Fig. 4a). The XRD pattern revealed that the nanorods were of the pure spinel Ni3S2 phase (Fig. 4d). However, if the hydrothermal reaction was carried out for 12 h, thin nanosheets were observed on the surface of the Ni3S2 nanorods (Fig. 4b), which were confirmed to be Ni(OH)2 using TEM, SAED patterns and the EDS spectrum as shown in Fig. 2. The Ni(OH)2 nanosheets are connected to each other, forming a highly porous morphology. At a longer reaction time of 24 h, structures composed of Ni(OH)2 nanosheets were observed (Fig. 4c) and the Ni3S2 nanorods had disappeared, which was also confirmed using TEM images (Fig. S2†). The absence of Ni3S2 nanorods and the existence of Ni(OH)2 (JCPDS no. 14–0117) peaks at 2θ = 33, 38.5 and 59° in the XRD spectrum (Fig. 4d) further confirmed that the Ni3S2 was transformed to Ni(OH)2 after long reaction times (e.g. 24 h). Therefore, the Ni3S2 nanorods can be used as a sacrificial template for synthesizing the Ni3S2@Ni(OH)2 hybrid structure using the hydrothermal reaction.

Based on the experimental results mentioned above, a possible growth mechanism for the Ni3S2@Ni(OH)2/3DGN is proposed (Fig. 4e). It has been reported that graphene oxide can be etched by hydrothermal steaming at 200 °C, forming porous structures.\(^{31}\) Therefore, we believe that the 3DGN can also be partially destroyed or etched during our hydrothermal process.
In this case, some of the Ni foam could be exposed. Therefore, during the hydrothermal process, the active species (S ions) released from thioacetamide (TAA) react with the exposed Ni foam to form small Ni$_3$S$_2$ particles on the surface of the 3DGN after a reaction time of 2 h (Fig. S3a and b†). The morphology obtained is different from the original 3DGN (Fig. S3c†). At longer reaction times (e.g. 6 h), the Ni$_3$S$_2$ nanorods grow on the surface of the 3DGN (step A in Fig. 4a and e). When the reaction time is increased to 12 h, the Ni$_3$S$_2$ nanorods are hydrolyzed under the hydrothermal conditions and the Ni$_3$S$_2$ nanorod@Ni(OH)$_2$ nanosheet core–shell heterostructure is formed (step B in Fig. 4b and e). Finally, after a reaction time of 24 h, the Ni$_3$S$_2$ nanorods are completely transformed into Ni(OH)$_2$ nanosheets (step C in Fig. 4c and e).

Fig. 5a shows the cyclic voltammogram (CV) curves of the Ni$_3$S$_2$@Ni(OH)$_2$/3DGN, Ni$_3$S$_2$/3DGN, Ni(OH)$_2$/3DGN and Ni$_3$S$_2$@Ni(OH)$_2$/Ni foam electrodes within the potential range of −0.15 to 0.55 V at a constant scan rate of 5 mV s$^{-1}$. The specific capacitance of the Ni$_3$S$_2$@Ni(OH)$_2$/3DGN, Ni(OH)$_2$/3DGN and Ni$_3$S$_2$/3DGN calculated from CV curves at 5 mV s$^{-1}$ were 1125, 981 and 340 F g$^{-1}$, respectively (for detailed calculations see the ESI†), which are higher than those of the composites directly grown on Ni foam without the 3DGN (i.e. Ni$_3$S$_2$@Ni(OH)$_2$/Ni, Ni$_3$S$_2$/Ni and Ni(OH)$_2$/Ni, Fig. S4†). This indicates that the 3DGN on the surface of the nickel foam plays an essential role in enhancing the supercapacitor performance. Importantly, the greatly enhanced electrochemical behavior of the Ni$_3$S$_2$@Ni(OH)$_2$/3DGN, compared with the Ni(OH)$_2$/3DGN and Ni$_3$S$_2$/3DGN, can be attributed to the synergistic effect resulting from the more active sites offered by the Ni(OH)$_2$ nanosheets and the quick electron transport of the highly crystalline Ni$_3$S$_2$ nanorods.$^{6,22}$ Fig. 5b shows the CV curves of the Ni$_3$S$_2$@Ni(OH)$_2$/3DGN at different scan rates. With the increase of scan rate, the current response increases accordingly and the shapes of CV curves are retained, indicating a good rate capability. The specific capacitance of the Ni$_3$S$_2$@Ni(OH)$_2$/3DGN calculated from CV curves at 5 mV s$^{-1}$ was 1125, 981 and 340 F g$^{-1}$, respectively (for detailed calculations see the ESI†), which are higher than those of the composites directly grown on Ni foam without the 3DGN (i.e. Ni$_3$S$_2$@Ni(OH)$_2$/Ni, Ni$_3$S$_2$/Ni and Ni(OH)$_2$/Ni, Fig. S4†). This indicates that the 3DGN on the surface of the nickel foam plays an essential role in enhancing the supercapacitor performance. Importantly, the greatly enhanced electrochemical behavior of the Ni$_3$S$_2$@Ni(OH)$_2$/3DGN, compared with the Ni(OH)$_2$/3DGN and Ni$_3$S$_2$/3DGN, can be attributed to the synergistic effect resulting from the more active sites offered by the Ni(OH)$_2$ nanosheets and the quick electron transport of the highly crystalline Ni$_3$S$_2$ nanorods.$^{6,22}$
capacitance of 398 F g\(^{-1}\)) was obtained (Fig. S5b†). It should be noted that the aforementioned capacitance values of the composite electrodes (e.g. the Ni\(_3\)S\(_2@\)Ni(OH)\(_2\)/3DGN and Ni\(_3\)S\(_2@\)Ni(OH)\(_2)/\)Ni) were calculated based on Ni\(_3\)S\(_2\) (for detailed calculations, see the ESI†), since the exact mass ratio of Ni\(_3\)S\(_2\) and Ni(OH)\(_2\)) is difficult to determine. Therefore, the actual capacitance value of the Ni\(_3\)S\(_2@\)Ni(OH)\(_2)/3DGN structure should be higher than the aforementioned value, e.g. 1724 F g\(^{-1}\) at 2 mV s\(^{-1}\) and 1402 F g\(^{-1}\) at 5.1 A g\(^{-1}\)) are calculated values based on Ni(OH)\(_2\)) (Fig. S5f).

The cycling performances of the Ni\(_3\)S\(_2@\)Ni(OH)\(_2)/3DGN, Ni(OH)\(_2)/3DGN and Ni\(_3\)S\(_2)/3DGN at a current density of 5.9 A g\(^{-1}\)) are shown in Fig. 5d. At this current density, the specific capacitance of 981 F g\(^{-1}\) (99.1% of the initial value of 1003 F g\(^{-1}\)), calculated based on the pure Ni\(_3\)S\(_2\), can be maintained after 2000 cycles. The shape of the last 20 charge–discharge curves (Fig. S6e) and the morphology of Ni\(_3\)S\(_2@\)Ni(OH)\(_2\)) after 2000 cycles (Fig. S6f) are nearly unchanged, indicating the excellent cyclability of the Ni\(_3\)S\(_2@\)Ni(OH)\(_2)/3DGN electrode. However, the Ni\(_3\)S\(_2/3DGN shows a relatively low specific capacitance of 177 F g\(^{-1}\)) for the first cycle. The specific capacitance increased slightly in subsequent cycles, possibly due to the formation of Ni(OH)\(_2\)) on the surface of the Ni\(_3\)S\(_2\) nanorods while in the alkaline solution.35,36 While the Ni(OH)\(_2)/3DGN possesses a specific capacitance of 903 F g\(^{-1}\) for the first charge–discharge cycle, its specific capacitance decreases to 704 F g\(^{-1}\) (78% of the initial value) after 1000 cycles. The relatively worse cycling performance of Ni(OH)\(_2\)) is similar to that seen in previous reports.29,30 Importantly, our Ni\(_3\)S\(_2@\)Ni(OH)\(_2)/3DGN electrode shows higher specific capacitance than many of the previously reported composite electrodes including CoO@NiHON (798.3 F g\(^{-1}\) at 1.67 A g\(^{-1}\), 95% maintained after 2000 cycles),9 NiS hollow sphere (927 F g\(^{-1}\) at 4.08 A g\(^{-1}\), 70% maintained after 3000 cycles)39 and NiO/3D graphene (745 F g\(^{-1}\) at 1.4 A g\(^{-1}\), 100% maintained after 2000 cycles)29 electrodes. In addition, electrochemical impedance spectroscopy (EIS) was also employed to characterize the composite electrodes (Fig. 5f). The equivalent series resistance (ESR) values of the Ni\(_3\)S\(_2/3DGN, Ni\(_3\)S\(_2@\)Ni(OH)\(_2)/3DGN and Ni(OH)\(_2)/3DGN are 1.07, 1.13 and 1.33 Ω, respectively, which are smaller than that reported for Ni(OH)\(_2\)-coated nickel foam electrodes with high capacitive performance.35 Compared to the aforementioned 3DGN-based composites, Ni\(_3\)S\(_2@\)Ni(OH)\(_2)/Ni has a higher ESR value (4.57 Ω), indicating that the 3DGN improved the charge transport properties of the composite electrodes (Fig. S4d†).

Fabrication of electrodes with high mass loading of active materials has practical significance in supercapacitor devices.36,37 However, the increase in loading density often results in a decrease of the performance of these electrochemical devices.38 Fortunately, our Ni\(_3\)S\(_2@\)Ni(OH)\(_2)/3DGN electrode with a high loading density (~3.7 mg cm\(^{-2}\)) still exhibits excellent supercapacitor performance as mentioned above. Moreover, the high areal capacitance of the Ni\(_3\)S\(_2@\)Ni(OH)\(_2)/3DGN is 4.7 F cm\(^{-2}\) at 2 mV s\(^{-1}\) and 3.85 F cm\(^{-2}\) at 19.1 mA cm\(^{-2}\)) (Fig. S5f), which is much better than the reported values for materials based on CoO\(_2@\)MnO\(_2\) (0.56 F cm\(^{-2}\) at 11.25 mA cm\(^{-2}\)),6 MnO\(_2/\)carbon nanotubes (2.8 F cm\(^{-2}\) at 0.05 mV s\(^{-1}\))9 and Co\(_3\)O\(_4/\)NiO (2.56 F cm\(^{-2}\) at 2 A g\(^{-1}\)).39 To further evaluate the performance of the Ni\(_3\)S\(_2@\)Ni(OH)\(_2)/3DGN electrode, the energy density (E) and power density (P) were calculated from the charge–discharge curves (see the ESI† for the details). The Ni\(_3\)S\(_2@\)Ni(OH)\(_2)/3DGN gave a high energy density of 70.6 Wh kg\(^{-1}\) at a power density of 1.3 kW kg\(^{-1}\)), and still retains a value of 27.1 Wh kg\(^{-1}\) at a power density of 5 kW kg\(^{-1}\) (Fig. S7†).

The aforementioned results reveal the high specific capacitance, remarkable rate capability as well as excellent cycling performance of the Ni\(_3\)S\(_2@\)Ni(OH)\(_2)/3DGN when used as high-performance electrochemical pseudocapacitors. Such superior performance of the Ni\(_3\)S\(_2@\)Ni(OH)\(_2)/3DGN can be attributed to the following factors. First, the CVD grown 3DGN on nickel foam with a high surface area and high electrical conductivity can effectively collect and transfer charges.35,37 Second, the Ni(OH)\(_2\) nanosheets possess a high contact area with the electrolyte, thus enabling fast and reversible redox reactions, which improve the specific capacitance.35,37 Third, the single-crystal Ni\(_3\)S\(_2\) nanorod array grown on the surface of the 3DGN provides large open spaces and a shorter ion diffusion path, which avoid the use of a polymer binder or conductive additive in the electrode materials.40 Importantly, Ni\(_3\)S\(_2\) has a hexagonal structure with short metal–metal distances in an approximately body-centred cubic sulphur lattice, which results in it having good electrical properties35 and enables the quick transport of electrons along the Ni\(_3\)S\(_2\) nanorods. In addition, the one-step synthesized Ni\(_3\)S\(_2@\)Ni(OH)\(_2\)) core–shell nanostructures on the 3DGN aids the electron transfer between the Ni(OH)\(_2\)), Ni\(_3\)S\(_2\) and 3DGN components due to the perfect interface connection between them.

Conclusions

In summary, the large-amount Ni\(_3\)S\(_2@\)Ni(OH)\(_2)/3DGN, i.e. Ni(OH)\(_2\)) nanosheets coated on the single-crystal Ni\(_3\)S\(_2\) nanorods grown on the surface of 3D graphene network, is synthesized by a simple one-step hydrothermal reaction. By controlling the reaction time, different composites and nanostructures, i.e., Ni\(_3\)S\(_2/3DGN, Ni\(_3\)S\(_2@\)Ni(OH)\(_2)/3DGN and Ni(OH)\(_2)/3DGN, are obtained. Detailed electrochemical characterization shows that the Ni\(_3\)S\(_2@\)Ni(OH)\(_2)/3DGN exhibits high specific capacitance (1277 F g\(^{-1}\) at 2 mV s\(^{-1}\)) and 1037.5 F g\(^{-1}\) at 5.1 A g\(^{-1}\) and areal capacitance (4.7 F cm\(^{-2}\) at 2 mV s\(^{-1}\) and 3.85 F cm\(^{-2}\) at 19.1 mA cm\(^{-2}\)) with good cycling performance (99.1% capacitance retention after 2000 cycles). The enhanced supercapacitor performance might arise from the synergistic effect between the Ni(OH)\(_2\)) nanosheets, Ni\(_3\)S\(_2\) nanorods and 3D graphene network.

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Notes and references