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One-step Synthesis of Ni₃S₂ Nanoplatelets on Graphene for High Performance Supercapacitors

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Here, we present a one-step hydrogen reduction synthesis of Ni₃S₂ nanoplatelets on graphene surface by using NiSO₄·3N₂H₄/GO as precursor. In this process, we have demonstrated that hydrazine molecule, which can coordinate with NiSO₄ in the form of pink precipitation, not only contributes to the formation of Ni₃S₂ nanoplatelets structure, but also enhances the efficiency of SO₄²⁻ to S₂⁴⁻ conversion compared with NiSO₄/GO. Supercapacitors made from the obtained Ni₃S₂/rGO composite exhibits a specific capacitance of 912.2 F g⁻¹ at 2 mV s⁻¹ scanning rate, and 875.6 F g⁻¹ at galvanostatic discharge current density of 1 A g⁻¹, along with exceptional rate capability of 83.2 % at discharge current density from 1 A g⁻¹ to 10 A g⁻¹ as well as good cycling stability. We attribute the excellent performance from the improved contact between graphene and the planar Ni₃S₂ structure, which strengthens the synergistic effect with graphene as conductive support and Ni₃S₂ nanoplatelets as the pseudocapacitive materials. This method allows the direct and efficient preparation of Ni₃S₂, and provides a simple route to integrate them with graphene for energy storage applications.

Introduction

Transition metal oxides and chalcogenides have been intensively studied because of their broad application such as energy storage and catalyst.¹⁻³ Among transition metal chalcogenides (TMCs), recently, Ni₃S₂ has attracted tremendous attention ascribed to their superior performance in energy storage. For example, it was reported that Ni₃S₂ nanorods prepared via hydrothermal method exhibits a specific capacitance of 1277 F g⁻¹ at 2 mV s⁻¹ scanning rate.⁴ Similar method is used to produce Ni_xCo_{3-x}S₄ hollow nanoprisms, which also perform enhanced pseudocapacitive behavior.⁵ However, those methods relies on wet chemistry through the sulfidation of Ni using H₂S decomposed from sulfur-containing molecules like thioacetamide (TAA) or thiourea that used in work mentioned above. Other methods like CVD method have also been reported, but the process involve many different steps thus are less efficient.⁶

On the other hand, due to the semiconducting property of TMCs, conductive materials like carbon materials are commonly used to combine with TMCs to improve their electron conductivity in order to fully exploit their pseudocapacitive capacity for energy storage application. However, to composite TMCs with carbon

materials through wet chemistry is not efficient since transition metal nanoparticles should be integrated with the desired carbon materials firstly. Previously, we have developed a two-step method to prepare graphene supported droplet-shape structure of hollow Ni₃S₂/rGO and core-shell Ni@Ni₃S₂/rGO for supercapacitors application.⁷ Although enhanced pseudocapacitance has been achieved, the process is still not easy enough.

In this work, we have further developed a direct method to prepare Ni₃S₂ nanoplatelets through H₂ reduction of NiSO₄-hydrazine complex (NiSO₄·3N₂H₄). In addition, this method allows the convenient integration of Ni₃S₂ nanoplatelets with graphene through one-step H₂ reduction of NiSO₄·3N₂H₄/GO. Compared with wet chemistry through the sulfidation of transition metals adopted elsewhere, this presented method shows several obvious advantages. Firstly, Ni₃S₂ are reduced directly from NiSO₄·3N₂H₄, with no need to prepare nickel nanoparticles in advance as common methods. Secondly, Ni₃S₂ prepared from this method can be easily integrated with carbon materials like graphene avoiding the prior preparation of nickel/carbon material composites. Moreover, because of the interaction between Ni²⁺ and oxygen-containing groups on graphene oxide, the prepared Ni₃S₂ nanoplatelets have good contact with graphene, enabling charge transfer between them. After made into electrodes and tested for supercapacitors, a specific capacitance of 912.2 F g⁻¹ at scanning rate of 2 mV s⁻¹ and 875.6 F g⁻¹ at 1 A g⁻¹ galvanostatic discharge current density are obtained for Ni₃S₂/rGO composite reduced from NiSO₄·3N₂H₄/GO. Compared with the two-step method we developed before,⁷ the main advantage of this presented method is the simple process but comparable performance.

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† Electronic supplementary information (ESI) available: The calculation method for specific capacitance, XRD, XPS, Raman, TEM and electrochemical test results.

Results and discussion

We have firstly investigated the hydrogen reduction of NiSO_4 and $\text{NiSO}_4 \cdot 3\text{N}_2\text{H}_4$, respectively. Here, $\text{NiSO}_4 \cdot 3\text{N}_2\text{H}_4$ is prepared according to previous reported method,⁸ and the corresponding XRD result is shown in Fig. S1. During hydrogen reduction process, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 3\text{N}_2\text{H}_4$ are separately loaded into a furnace under 200 sccm Ar and 20 sccm H_2 at 400 °C for 2 h. After hydrogen reduction, as shown in XRD results in Fig. S2, peaks at 21.8° (101), 31.2° (110), 37.9° (003), 44.5° (202), 49.7° (211), 55.3° (300) of Ni_3S_2 (JCPDS no. 44-1418) are identified for both $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 3\text{N}_2\text{H}_4$, suggesting the formation of Ni_3S_2 and the successful conversion of SO_4^{2-} into S_2^{4-} , and peaks at 51.9° (200), 76.5° (220) of Ni (JCPDS no. 04-0850) indicates partial reduction of Ni ions in NiSO_4 or Ni_3S_2 under H_2 environment. In a control experiment without introduction of H_2 , after loading $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ into furnace annealed under argon at 400 °C for 2h, only peaks for NiSO_4 are observed (Fig. S3), indicating that H_2 is a crucial reactant in this conversion. X-ray photoelectron spectroscopy (XPS) is then used to demonstrate the state change of sulphur element. From high resolution S2p XPS spectrum, after H_2 reduction of $\text{NiSO}_4 \cdot 3\text{N}_2\text{H}_4$, peak at range of 167 eV ~ 172 eV corresponding to SO_4^{2-} has been almost vanished along with the appearance of a new peak for S_2^{4-} at range of 160.5 eV ~ 163.5 eV in Figure 1,^{9,10} indicating a complete conversion of SO_4^{2-} into S_2^{4-} . While using $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ as precursor, besides the new peak for S_2^{4-} , high intensity SO_4^{2-} peak at range of 167 eV ~ 172 eV (Fig. S4) is still observed. Compared with $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, it can be concluded that N_2H_4 indeed enhances the conversion of SO_4^{2-} to S_2^{4-} in $\text{NiSO}_4 \cdot 3\text{N}_2\text{H}_4$. Previous methods to realize such conversion relies on the use of sulphate-reducing bacteria (SRB), a type of anaerobic microorganisms, for sulphate degradation,¹¹ however, hydrogen reduction of transition metal sulphate or transition metal sulphate-hydrazine complex has not been reported before. At current stage, the conversion mechanism of NiSO_4 and $\text{NiSO}_4 \cdot 3\text{N}_2\text{H}_4$ into Ni_3S_2 is not clear. A possible explanation is that under H_2 environment at 400 °C, Ni^{2+} and SO_4^{2-} will be reduced to Ni and $\text{H}_2\text{S}/\text{SO}_2$, respectively, followed by reaction between them to form Ni_3S_2 .^{7,12,13} Since the precursor NiSO_4 is water-soluble, the method we have developed here makes the

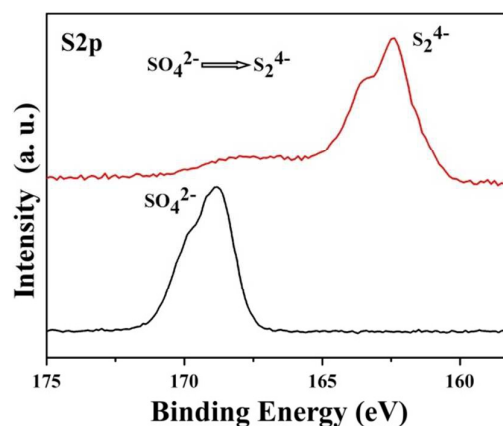


Figure 1. High-resolution S2p XPS spectrum of pure NiSO_4 (black line) and Ni_3S_2 reduced from $\text{NiSO}_4 \cdot 3\text{N}_2\text{H}_4$ by H_2 (red line).

convenient integration of Ni_3S_2 with carbon materials possible.

To integrate Ni_3S_2 with graphene for supercapacitors application, Figure 2 displays the scheme for the preparation of $\text{Ni}_3\text{S}_2/\text{rGO}$ from $\text{NiSO}_4 \cdot 3\text{N}_2\text{H}_4/\text{GO}$. In detail, firstly, NiSO_4/GO (Figure 2a) is prepared by simply mixing NiSO_4 solution with graphene oxide (GO) dispersion. After the observation of well mixing of NiSO_4 with GO, excess N_2H_4 solution is added dropwise. The key reason we use N_2H_4 here is that it can precipitate NiSO_4 in the form of $\text{NiSO}_4 \cdot 3\text{N}_2\text{H}_4$. Ascribed to electrostatic interaction between Ni^{2+} and oxygen-containing group on GO, the formed $\text{NiSO}_4 \cdot 3\text{N}_2\text{H}_4$ is supposed to sedimentate *in situ* and attach tightly onto graphene surface as shown in Figure 2b. After that, through one-step H_2 reduction of $\text{NiSO}_4 \cdot 3\text{N}_2\text{H}_4/\text{GO}$, $\text{Ni}_3\text{S}_2/\text{rGO}$ are obtained and denoted as $\text{Ni}_3\text{S}_2/\text{rGO-2}$ (Figure 2c), and the XPS result is shown in Fig. S5, in which N element is detected due to the usage of N_2H_4 . In another experiment, $\text{Ni}_3\text{S}_2/\text{rGO}$ reduced directly from NiSO_4/GO by H_2 is denoted as $\text{Ni}_3\text{S}_2/\text{rGO-1}$. Figure 3 shows the XRD results of $\text{Ni}_3\text{S}_2/\text{rGO-1}$ and $\text{Ni}_3\text{S}_2/\text{rGO-2}$. Besides peaks for Ni_3S_2 , graphene peak C(002) is also identified, confirming the

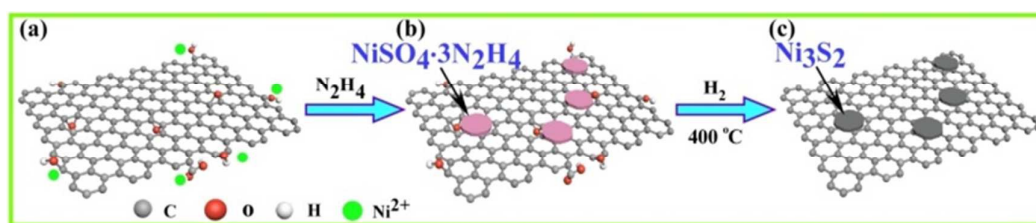


Figure 2. Schematic illustration for the synthesis of $\text{Ni}_3\text{S}_2/\text{rGO}$. (a) graphene oxide (GO) and Ni^{2+} aqueous solution. (b) NiSO_4 precipitates in the form of $\text{NiSO}_4 \cdot 3\text{N}_2\text{H}_4$ on GO after the introduction of hydrazine. (c) Ni_3S_2 nanoplatelets formed *in situ* on graphene surface after H_2 reduction, accompanied with the reduction of GO into rGO.

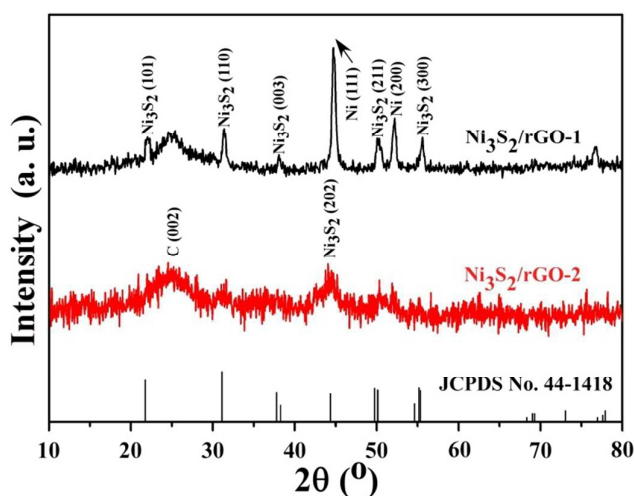


Figure 3. XRD spectrum of $\text{Ni}_3\text{S}_2/\text{rGO-1}$ reduced by H_2 from NiSO_4/GO and $\text{Ni}_3\text{S}_2/\text{rGO-2}$ reduced from $\text{NiSO}_4 \cdot 3\text{N}_2\text{H}_4/\text{GO}$, respectively.

successful integration of Ni_3S_2 with rGO. The lack of strong Ni_3S_2 diffraction peaks in sample $\text{Ni}_3\text{S}_2/\text{rGO-2}$ results from the well dispersion of Ni_3S_2 nanoplatelets on graphene surface as well as the small thickness of obtained Ni_3S_2 nanoplatelets, as confirmed by TEM results (shown later in Figure 4). Fig. S6 shows the Raman spectrum of GO in comparison with reduced graphene oxide in $\text{Ni}_3\text{S}_2/\text{rGO-1}$ and $\text{Ni}_3\text{S}_2/\text{rGO-2}$. The increase of I_D/I_G ratio from 0.733 (GO) to 1.051 for $\text{Ni}_3\text{S}_2/\text{rGO-1}$ and 1.066 for $\text{Ni}_3\text{S}_2/\text{rGO-2}$ indicates the reduction of GO.

Morphology of $\text{Ni}_3\text{S}_2/\text{rGO}$ is characterized by transmission electron microscopy (TEM), and shown in Figure 4, for $\text{Ni}_3\text{S}_2/\text{rGO-2}$ (*i.e.* reduced from $\text{NiSO}_4 \cdot 3\text{N}_2\text{H}_4/\text{GO}$). We can see small nanoplatelets with uniform size are distributed on the graphene surface without obvious aggregation. In contrast, TEM images of $\text{Ni}_3\text{S}_2/\text{rGO-1}$ (*i.e.* reduced from NiSO_4/GO) show round and irregular nanoparticles with broad diameter distribution, as depicted in Fig. S7. The morphology difference observed should be resulted from the different precipitation process. In NiSO_4/GO , NiSO_4 deposits from solution and randomly anchors on the graphene surface during the drying-recrystallization process. On the contrary, for $\text{NiSO}_4 \cdot 3\text{N}_2\text{H}_4/\text{GO}$, with the aid of N_2H_4 , NiSO_4 is precipitated in the form of $\text{NiSO}_4 \cdot 3\text{N}_2\text{H}_4$ and tightly fixed on the graphene surface due to the interaction between Ni^{2+} and oxygen-containing groups, similar to previous work for the preparation of $\text{NiO}/\text{Ni}(\text{OH})_2$ nanosheets/nanoplates.^{14,15} During the following H_2 reduction of $\text{NiSO}_4 \cdot 3\text{N}_2\text{H}_4/\text{GO}$, Ni_3S_2 will be prepared *in situ* to form $\text{Ni}_3\text{S}_2/\text{rGO}$, while Ni_3S_2 is more likely to aggregate into different morphology and size in $\text{Ni}_3\text{S}_2/\text{rGO-1}$ (*i.e.* reduced from NiSO_4/GO). From the particle size analysis histogram in Figure 4b, the average size of these Ni_3S_2 nanoplatelets is about 29.6 nm for $\text{Ni}_3\text{S}_2/\text{rGO-2}$. High resolution TEM image in Figure 4c

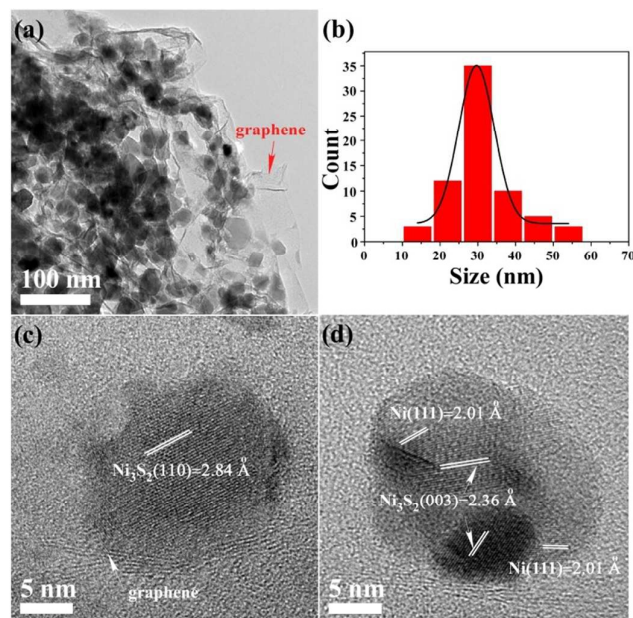


Figure 4. TEM results of $\text{Ni}_3\text{S}_2/\text{rGO}$ reduced from $\text{NiSO}_4 \cdot 3\text{N}_2\text{H}_4/\text{GO}$. (a) Ni_3S_2 nanoplatelets with uniform size distributed on graphene surface. (b) Particle size analysis histogram of Ni_3S_2 nanoplatelets (mean: 29.6 nm, standard deviation: 9.4 nm). (c) and (d) High resolution TEM of Ni_3S_2 nanoplatelets on graphene surface.

shows the crystal structure, and plane spacing of 2.84 Å corresponds to Ni_3S_2 (300). More importantly, these Ni_3S_2 nanoplatelets are in good contact with graphene as pointed out by white arrow in Figure 4c, in agreement with our previous analysis. In addition, Ni domains from partial reduction of Ni ions in $\text{NiSO}_4/\text{Ni}_3\text{S}_2$ can be detected in some particles as illustrated in Figure 4d, consistent with XRD results stated before.

To demonstrate their potential application in energy storage, we further use electrochemical methods to investigate capacitive property of $\text{Ni}_3\text{S}_2/\text{rGO-1}$ (*i.e.* reduced from NiSO_4/GO) and $\text{Ni}_3\text{S}_2/\text{rGO-2}$ (*i.e.* reduced from $\text{NiSO}_4 \cdot 3\text{N}_2\text{H}_4/\text{GO}$), respectively. The electrochemical tests of those synthesized materials are carried out in a three-electrode setup, where Pt works as the counter electrode, Hg/HgO as the reference electrode and 2 M KOH as the electrolyte solution. Electrochemical results are shown in Figure 5, in which cyclic voltammetry (CV) test is conducted between 0.1 V and 0.6 V, and galvanostatic charge/discharge test range is from 0.1 V to 0.55 V. Figure 5a shows the CV curves for $\text{Ni}_3\text{S}_2/\text{rGO-1}$ and $\text{Ni}_3\text{S}_2/\text{rGO-2}$ at scanning rate of 2 mV s^{-1} , and both of these two composites show a pair of reversible redox peaks at the range between 0.25 V and 0.5 V, demonstrating their pseudocapacitive properties. And a specific capacitance of 360 F g^{-1} for $\text{Ni}_3\text{S}_2/\text{rGO-1}$ and 912.2 F g^{-1} for $\text{Ni}_3\text{S}_2/\text{rGO-2}$ can be calculated from these CV curves (for detailed calculation see the Supporting Information). CV

results at different scanning rate from 2 mV s⁻¹ to 50 mV s⁻¹ are presented in Fig. S8a and Fig. S8c for Ni₃S₂/rGO-1 and Ni₃S₂/rGO-2, respectively. Figure 5b displays the galvanostatic discharge curves at 1 A g⁻¹, and a specific capacitance of 140.0 F g⁻¹ for Ni₃S₂/rGO-1 and 875.6 F g⁻¹ for Ni₃S₂/rGO-2 are obtained (see the Supporting Information for calculation method). The significantly increased performance for Ni₃S₂/rGO-2 is possibly due to several reasons. Firstly, with the aid of N₂H₄, the conversion of SO₄²⁻ into S₂⁴⁻ is more complete, as confirmed with XPS result. Thus after H₂ reduction, NiSO₄·3N₂H₄/GO leads to higher ratio of Ni₃S₂ active materials than that of NiSO₄/GO. Secondly, the Ni₃S₂ nanoplatelets in Ni₃S₂/rGO-2 have better contact with graphene substrate than round/irregular shape Ni₃S₂ nanoparticles with non-uniform size randomly deposited on graphene in Ni₃S₂/rGO-1. Thirdly, due to its highly reductive property, hydrazine can help reduce GO into rGO, contributing to improved electronic conductivity. Ni₃S₂/rGO-2 also delivers better rate capability than Ni₃S₂/rGO-1 as plotted in Figure 5c. By increasing galvanostatic charge/discharge current density from 1 A g⁻¹ to 10 A g⁻¹, the calculated specific capacitance for Ni₃S₂/rGO-2 varies from 875.6 F g⁻¹ to 728.5 F g⁻¹, equal to 83.2 % capacitance is retained. While for Ni₃S₂/rGO-1, specific capacitance decreases rapidly from 140 F g⁻¹ to 42.2 F g⁻¹, only 30.1 % capacitance maintained. Fig. S8b and Fig. S8d present the galvanostatic discharge curves for these two composites at different current density from 1 A g⁻¹ to 10 A g⁻¹. The CV and galvanostatic discharge curves for pure Ni₃S₂-2 reduced from NiSO₄·3N₂H₄ and pure rGO are presented in Fig. S9, and a capacitance value

of 333.8 F g⁻¹ for Ni₃S₂-2 and 78.2 F g⁻¹ for rGO are obtained at 1 A g⁻¹ discharge current density. Taking into account the rGO weight percentage of 55.6%, the faradic capacitance is 832.1 F g⁻¹ for Ni₃S₂/rGO-2 at 1 A g⁻¹ current density. Electrochemical impedance spectroscopy (EIS) is also employed to measure the ion diffusion and charge transfer process at the frequency from 100 kHz to 10 mHz with amplitude of 5 mV, and results are shown in Nyquist plots in Figure 5d, with inset equivalent circuit, where *R_s* is the ohmic resistance accounting for the intrinsic resistance of electrode, contact resistance between current collector and electrode materials as well as the electrolyte resistance, *C_{DL}* is the double layer capacitance, *R_{CT}* is the charge transfer resistance, *W* is the Warburg diffusion element and *C_F* is the faradic capacitance.^{7,16} The Nyquist plots fit well with the equivalent circuit by the equation:¹⁶

$$Z = R_s + \frac{1}{j\omega C_{DL} + \frac{1}{R_{CT} + W}} - \frac{j}{\omega C_F}$$

The lower *R_s* of 0.53 Ω for Ni₃S₂/rGO-2 than Ni₃S₂/rGO-1 (0.78 Ω) should be mainly resulted from its better conductivity due to the introduction of N₂H₄. The *R_{CT}* for Ni₃S₂/rGO-1 and Ni₃S₂/rGO-2 are 1.23 Ω and 1.01 Ω, respectively. Smaller *R_{CT}* value for Ni₃S₂/rGO-2 indicates better charge transfer, attributed to the good contact of Ni₃S₂ nanoplatelets with graphene. At last, we have conducted the cycling performance test for Ni₃S₂/rGO-2 (*i.e.* reduced from NiSO₄·3N₂H₄/GO) at current density of 5 A g⁻¹, as shown in Fig. S10. After 1000 cycles at this current density, 91.3 % capacitance is maintained, demonstrating its good cycling stability.

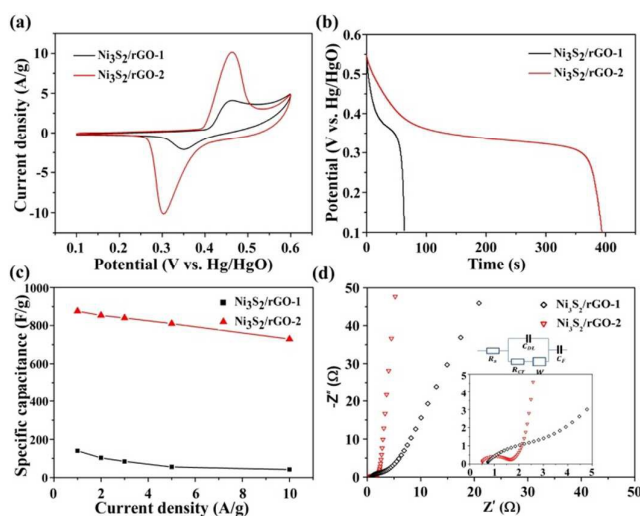


Figure 5. Electrochemical results of Ni₃S₂/rGO. (a) CV at scanning rate of 2 mV s⁻¹ for Ni₃S₂/rGO reduced from NiSO₄/GO (Ni₃S₂/rGO-1) and NiSO₄·3N₂H₄/GO (Ni₃S₂/rGO-2) respectively. (b) Corresponding galvanostatic discharge results at 1 A g⁻¹ for Ni₃S₂/rGO-1 and Ni₃S₂/rGO-2. (c) Rate capability comparison of Ni₃S₂/rGO-1 and Ni₃S₂/rGO-2 at discharge current density from 1 A g⁻¹ to 10 A g⁻¹. (d) Nyquist plots at amplitude of 5 mV over frequency range from 100 kHz to 0.01 Hz. Inset are the equivalent circuit and high frequency part zoomed in.

Experimental

Chemicals

Graphite (Grafguard 160-50N with the average particle size of 350 μm) was expanded by microwave before use. K₂S₂O₈, P₂O₅, H₂SO₄, KMnO₄, H₂O₂, NiSO₄·7H₂O, N₂H₄ (35 wt% in water) and poly(vinylidene fluoride)(PVDF) were all purchased from Sigma-Aldrich with analytical grade and used without further purification.

Preparation of graphene oxide (GO)

Graphene oxide (GO) is prepared through modified Hummers method.^{17,18} In brief, firstly, 30 mL concentrated sulfuric acid is added into a flask containing 1 g graphite, 5 g K₂S₂O₈ and 5 g P₂O₅, reacted at 90 °C for 4.5 h. Then filtrate the product through a 0.2 micron Nylon Millipore filter and wash the sample with excess DI until the pH is around 5.5. Secondly, after drying the sample at 60 °C, 150 mL concentrated sulfuric acid and 30 g KMnO₄ are added in sequential slowly and reacted at 35 °C for another 4 h. Thirdly, the mixture product is added to 1 L DI water and stirred for 2 h, followed by the addition of 50 mL 30 % H₂O₂ until the solution turns into bright yellow. After stirred for another 2 h, settle down the solution for 24 h. Finally, discard the supernatant and use 1 L of 10 %

HCl solution and excess DI to wash the product until the pH \sim 7.

Preparation of $\text{NiSO}_4 \cdot 3\text{N}_2\text{H}_4$ complex

To 2 ml 0.1 M NiSO_4 solution, 1 mL hydrazine solution (35 wt. % in H_2O) is added and stirred for 10 mins. After filtration and drying the pink precipitate, $\text{NiSO}_4 \cdot 3\text{N}_2\text{H}_4$ is obtained.

Preparation of NiSO_4/GO and $\text{NiSO}_4 \cdot 3\text{N}_2\text{H}_4/\text{GO}$ composites

To 20 ml 1 mg/mL GO solution, 2 mL 0.1 M NiSO_4 is added slowly under vigorous stirring, and then stirred for another 1 h. After freeze-drying the mixture solution, NiSO_4/GO composite is obtained. To prepare $\text{NiSO}_4 \cdot 3\text{N}_2\text{H}_4/\text{GO}$ composite, 1 mL hydrazine solution (35 wt. % in H_2O) is added into the above NiSO_4/GO solution. After filtration and drying the product, $\text{NiSO}_4 \cdot 3\text{N}_2\text{H}_4/\text{GO}$ composite is obtained.

Preparation of $\text{Ni}_3\text{S}_2/\text{rGO}$ composites

Load the prepared NiSO_4/GO and $\text{NiSO}_4 \cdot 3\text{N}_2\text{H}_4/\text{GO}$ composite into a furnace under 200 sccm Ar and 20 sccm H_2 at 400 °C for 2h, respectively. After cooling down to room temperature, the products are collected. rGO and Ni_3S_2 are prepared separately through a procedure similar to the preparation of $\text{Ni}_3\text{S}_2/\text{rGO}$, apart from the absence of NiSO_4 and GO respectively. The mass ratio of Ni_3S_2 in $\text{Ni}_3\text{S}_2/\text{rGO}$ -1 and $\text{Ni}_3\text{S}_2/\text{rGO}$ -2 are 63.1% and 55.6%, respectively.

Crystal structure and morphology characterization:

All the characterization tests are done in Materials Characterization and Preparation Facility (MCPF) in Hong Kong University of Science and Technology (HKUST). XRD (PW1830, Philips) with Cu K α radiation ($\lambda=1.5406$ Å) is used to test the phase structure. The state change of sulphur is checked with XPS (VG Micro Tech ESCA 2000). And transmission electron microscope (TEM, JEOL 2010) is used to characterize the morphology and crystal structure.

Electrode preparation and electrochemical measurement:

90 wt% electrode materials and 10 wt% PVDF as the binder are put into an agate mortar to make slurry. Then coat the slurry onto Ni foam with area of 1 cm² uniformly. After drying at 80 °C for 12 h under vacuum environment, the prepared electrodes are pressed tightly under 10 MPa. Three-electrode system is employed here to measure the electrochemical properties of the electrodes. In this system, the prepared electrode is used as the working electrode, platinum plate as counter electrode and Hg/HgO as reference electrode. The electrolyte used here is 2 M KOH. Before the electrochemical test, the electrodes are dipped into the electrolyte for 6 h. The electrochemical test is carried out on an electrochemical workstation (CHI 660). Cyclic voltammetry test and galvanostatic charge/discharge test are conducted at the range from 0.1 V to 0.6 V and 0.1 V to 0.55 V, respectively. The electrochemical impedance spectroscopy (EIS) is done at the

frequency range from 100 kHz to 0.01 Hz under amplitude of 5 mV.

Conclusions

In summary, we have synthesized Ni_3S_2 directly from NiSO_4 -hydrazine complex ($\text{NiSO}_4 \cdot 3\text{N}_2\text{H}_4$) through H_2 reduction, and integrated these Ni_3S_2 nanoplatelets with graphene for supercapacitors application. As a result, $\text{Ni}_3\text{S}_2/\text{rGO}$ reduced from $\text{NiSO}_4 \cdot 3\text{N}_2\text{H}_4/\text{GO}$ shows a specific capacitance of 912.2 F g⁻¹ at scanning rate of 2 mV s⁻¹ and 875.6 F g⁻¹ at 1 A g⁻¹ discharge current density. We believe that hydrazine molecule introduced in $\text{NiSO}_4 \cdot 3\text{N}_2\text{H}_4$ contributes to the enhancement of conversion of SO_4^{2-} into S_2^{4-} , and also allows the formation of Ni_3S_2 nanoplatelets, ensuring better contact with the underlying graphene. The method presented here provides a new simple route for the preparation of Ni_3S_2 as well as $\text{Ni}_3\text{S}_2/\text{rGO}$ composite for energy storage.

Acknowledgements

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One-step Synthesis of Ni₃S₂ Nanoplatelets on Graphene for High Performance Supercapacitors

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A one-step hydrogen reduction synthesis of Ni₃S₂ nanoplatelets on graphene surface has been developed for supercapacitors application.

