Controlled synthesis of three-phase $\text{Ni}_x\text{S}_y/\text{rGO}$ nanoflake electrodes for hybrid supercapacitors with high-energy and power density

Shuge Dai^{a,b,1}, Bote Zhao^{a,1}, Chong Qu^a, Dongchang Chen^a, Dai Dang^a, Bo Song^a,

Ben M. deGlee^a, Jianwei Fu^a, Chenguo Hu^{b,*}, Ching-Ping Wong^a, Meilin Liu^{a,*}

^a*School of Materials Science and Engineering, Georgia Institute of Technology, 771*

Ferst Drive, Atlanta, GA 30332-0245, United States

^b*Department of Applied Physics, Chongqing University, Chongqing 400044, P. R.*

China

*Corresponding author.

E-mail: meilin.liu@mse.gatech.edu (M.L.Liu)

¹These authors contributed equally to this work.

Abstract

Composition design and morphology control of electrode materials are effective strategies to enhancing the specific capacity, rate capability, and cycling life of electrochemical energy storage devices. Here we report our findings in the design and synthesis of a three-phase nickel sulfide ($\text{NiS-Ni}_3\text{S}_2\text{-Ni}_3\text{S}_4$, denoted as TP- Ni_xS_y) with 3D flower-like architecture assembled from interconnected nanoflakes, which delivers a specific capacity of 724 C g^{-1} at a current density of 1 A g^{-1} . When integrated with reduced graphene oxide (rGO), a TP- $\text{Ni}_x\text{S}_y/\text{rGO}$ composite nanoflake electrode, derived from a hydrothermal process, demonstrates not only higher specific capacity (807 C g^{-1} at 1 A g^{-1}) but also better rate capability ($\sim 72\%$ capacity retention as the current density was increased from 1 to 20 A g^{-1}). Moreover, a hybrid energy storage device, constructed from a TP- $\text{Ni}_x\text{S}_y/\text{rGO}$ positive electrode and a graphene-based negative electrode, shows a high energy density of 46 Wh kg^{-1} at a power density of 1.8 kW kg^{-1} . It retained an energy density of 32 Wh kg^{-1} at power density of 17.2 kW kg^{-1} , demonstrating its viability and potential for practical applications.

Keywords: graphene; composites; multiphase; supercapacitors; sulfides

1. Introduction

Transition metal sulfides such as cobalt sulfides (Co_3S_4 , Co_9S_8) [1,2], nickel sulfides (NiS , Ni_3S_2), [3,4] and ternary nickel cobalt sulfides (NiCo_2S_4 , $\text{Ni}_x\text{Co}_{3-x}\text{S}_4$) [5-7], have been extensively investigated as electrode materials for batteries and supercapacitors (SCs) because of their good electrical conductivity and high theoretical capacity. Among them, nickel sulfides have attracted much attention due to their excellent redox reversibility and relatively high theoretical capacity [7,8]. In recent years, many battery-type electrode materials (e.g., nickel-containing compounds that exhibit faradaic behavior) have been reported as pseudocapacitive materials, leading to some confusion for readers because the concept of capacitance (F) may not be applicable to purely faradaic behavior, where capacity (Coulomb, or mAh) is the most appropriate and meaningful metric to use [9-11]. As suggested by Gogosti et al. [10], it is inappropriate to describe nickel-based oxides, sulfides and hydroxides as pseudocapacitive electrode materials in alkaline aqueous electrolyte because they undergo faradaic reactions, in which their electrochemical signature is analogous to that of a battery-type material. However, those battery-type materials (e.g., nickel-based oxides, sulfides and hydroxides) with designed nanostructures could be combined with a capacitor-type negative electrode (e.g., carbon-based materials) to build a hybrid device with high energy and power density [8,11]. This hybrid device can widen the operation voltage window within the same aqueous electrolyte system, further increasing the energy density [8,12]. The attractive features of the hybrid SCs lie in the greatly improved specific capacity from the battery-type positive electrode (the rich redox reactions) and the wider operating voltage, which significantly increases the energy density [13]. To date, remarkable progress has been made in the development of the nickel-based positive electrode materials; however, the obtainable energy density of these devices is still low, more so at higher power delivery due to limited rate capability of the nickel oxides/sulfides. Accordingly, exploring novel nickel-based materials with high specific capacity while maintaining good rate capability and long cycle life still remains a great challenge.

It is well known that the electrochemical performance of energy storage devices depends sensitively on the structures and properties of electrode materials [13, 14]. Design and development of hybrid nanomaterials are seen as effective strategies for energy storage [11]. Recently, nickel sulfides have been extensively investigated as positive electrode materials for hybrid supercapacitors; for example, Li et al. [15] has demonstrated that the Ni_3S_2 - NiS hybrid nanostructure can deliver a high specific capacity (463 C g^{-1} at 2 A g^{-1}) when used as a positive electrode for hybrid SCs. Although the nickel sulfide materials usually exhibit a high specific capacity, its rate capability and cycling stability are relatively poor. To circumvent power/rate limitations, design of hybrid nanostructures through incorporation of highly conductive graphene into the nickel oxides/sulfides are effective solutions for energy

storage devices [8,16]. The presence of graphene in the hybrid electrode not only enhances the rate of electron transfer and current collection, but also improves the mechanical integrity of the whole electrode [17,18], thus greatly improving the electrochemical performance.

In this work, we report our findings in controlled synthesis and characterization of nickel sulfide nanostructures as battery-type electrode for hybrid energy storage device, where the phase structure and morphology is tuned by changing the initial $\text{NiCl}_2\text{:S}$ mole ratio and hydrothermal synthesis conditions. In particular, three-phase nickel sulfide ($\text{NiS-Ni}_3\text{S}_2\text{-Ni}_3\text{S}_4$, denoted as $\text{TP-Ni}_x\text{S}_y$) nanoflakes were successfully prepared, delivering a high specific capacity of 724 C g^{-1} at a current density of 1 A g^{-1} . Moreover, we further successfully prepared the $\text{TP-Ni}_x\text{S}_y/\text{rGO}$ nanoflakes by introducing GO, which demonstrated enhanced electrochemical performance compared to that of the $\text{TP-Ni}_x\text{S}_y$. This unique hybrid nanostructure is expected to offer a synergistic effect on redox reactions and render the desirable electronic conductivity for efficient energy storage. More importantly, a hybrid supercapacitor device was also fabricated, and the device demonstrated a high energy density (46 Wh kg^{-1}) and good cycling stability. Furthermore, two such devices connected in series could well power 37 commercial LEDs, revealing its great potential application in energy storage systems.

Fig. 1. Schematic of the preparation processes of nickel sulfide materials. The nickel sulfide nanomaterials are prepared by a controlled hydrothermal method. The phase structure and morphology is tuned by changing the initial $\text{NiCl}_2\text{:S}$ mole ratio and hydrothermal temperature.

2. Experimental Section

2.1. Synthesis of nickel sulfides

All the chemical reagents in this work were used as received without further purification. In a typical experiment, 1 mmol of $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ (AMRESCO, 99%), 2.5 mmol of sulfur powder (Sigma-Aldrich, 98%), and 53.6 mmol of KOH (Fisher Scientific, 87%) were first dissolved in 10 mL of deionized water in the Teflon containers, followed by addition of 2 mL of hydrazine monohydrate (N_2H_4 64-65 %, reagent grade, 98%, Sigma-Aldrich). Then the autoclave was sealed and maintained at a constant temperature (100, 150, or 200 °C) for 24 h. After natural cooling to room temperature, the samples were taken out, rinsed with deionized water until pH is close to 7, and dried under vacuum at 70 °C overnight. The $\text{NiS-Ni}_3\text{S}_4$ nanomaterials were obtained by changing the initial mole ratio of $\text{NiCl}_2\text{:S}$ from 1:2.5 to 1:5 while the other procedures remained the same.

2.2. Preparation of $\text{TP-Ni}_x\text{S}_y/\text{rGO}$ nanoflakes

Graphene oxide (GO) was prepared from natural graphite flakes using an improved Hummers' method [19]. The $\text{TP-Ni}_x\text{S}_y/\text{rGO}$ nanoflakes were synthesized using a hydrothermal process similar to the synthesis of Ni_xS_y . Briefly, 1 mmol of $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$, 2.5 mmol of sulfur powder, and 53.6 mmol of KOH were dissolved in 10 mL of GO solution (2 mg mL^{-1}) in the Teflon container, followed by adding 2 mL of hydrazine monohydrate and stirring for 15 min to form homogeneous solution. Then the autoclave was sealed and maintained at 150 °C for 24 h. After cooling down to room temperature naturally, the sample was taken out and rinsed with deionized water until pH is close to 7 and dried under vacuum at 70 °C overnight.

2.3. Preparation of negative electrode material

8 mL of GO solution (2 mg mL^{-1}) was first transferred into a 25 mL Teflon-lined stainless autoclave, followed by adding 8 mL of deionized water. Then the autoclave was sealed and maintained at 180 °C for 12 h. After cooling to room temperature naturally, the sample was taken out and rinsed with deionized water several times and dried under vacuum at 70 °C overnight.

2.4. Characterization

The phase structures of the samples were examined by X-ray diffraction (XRD) analysis (PAN'alytical X'Pert Alpha 1, using Cu K- α 1 X-rays). The microstructure and morphology of the products were observed using a scanning electron microscope (LEO 1530 field emission SEM) and a high resolution transmission electron microscope (JEOL 4000 EX). Surface characterization of elemental electronic states was measured by X-ray photoelectron spectroscopy (Thermo K-Alpha XPS, Thermo Fisher Scientific). The nitrogen adsorption–desorption isotherm measurement of the sample was performed using a Micromeritics ASAP 2020 analyzer. The specific surface area was obtained by the Brunauer-Emmett-Teller (BET) method. Raman spectra were obtained using a Renishaw RM 1000 spectromicroscopy system ($\sim 2\ \mu\text{m}$ spot size) equipped with a 20 $\times$ objective optical microscope.

2.5. Electrochemical measurement

Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) tests were carried out using a three-electrode configuration. For the working electrode, a mixture containing active electrode materials, Super P Li powders (TIMCAL Graphite & Carbon), and PTFE binder at a weight ratio of 8:1:1 was rolled with the assistance of ethanol to form a uniform film. The typical areal mass loading was approximately $4\ \text{mg cm}^{-2}$. The film electrode was then pressed between two nickel foams, and dried under vacuum at $80\ ^\circ\text{C}$ for 12 h. A platinum mesh and a Ag/AgCl electrode (prefilled with 4 M KCl aqueous solution saturated with AgCl) were used as the counter and the reference electrodes, respectively [20]. The cyclic voltammograms were acquired in a potential range of 0 ~ 0.5 V at different scan rates, and the charge-discharge processes were performed between 0 and 0.45 V at different current densities in a 2 M KOH aqueous electrolyte. The EIS was performed in the frequency range from 0.01 Hz to 100 kHz under the open-circuit condition. The specific capacity $Q\ (\text{C g}^{-1})$ of the battery-type electrodes was calculated as follows: [14].

$$Q = i_m Dt \quad (1)$$

where $i_m = I/m\ (\text{A g}^{-1})$ is the current density, m is the mass of the active electrode material, I is the current, and Δt is the discharge time.

The electrochemical measurements of the hybrid supercapacitor were carried out to evaluate the TP-Ni_xS_y/rGO nanoflakes for practical application in a two-electrode cell with a 2 M KOH aqueous electrolyte. The TP-Ni_xS_y/rGO film was used as the positive electrode and the graphene film served as the negative electrode. A graphene film electrode was composed of 90 wt% graphene and 10 wt% PTFE. Cyclic voltammograms and EIS were recorded on a Solartron electrochemical workstation (Solartron SI 1287 electrochemical interface and SI 1255 HF frequency response

analyzer). The galvanostatic charge/discharge measurements were performed using an Arbin testing system (BT-2143) at room temperature. The specific capacitance C (F g^{-1}) of the hybrid supercapacitor was calculated according to the following equation: [21].

$$C = \frac{2i_m \int V dt}{V^2} \bigg|_{V_i}^{V_f} \quad (2)$$

where V is the potential with initial and final values of V_i and V_f , respectively. $i_m = I/m$ (A g^{-1}) is the current density, I is the current and m is the active mass of the electrode [22].

Fig. 2. SEM images of as-synthesized nickel sulfide nanomaterials. (a,b) NiS nanoneedles-assembled microspheres. (c) NiS-Ni₃S₂ nanosheets. (d) NiS-Ni₃S₄ nanoparticles-assembled microspheres. (e,f) TP-Ni_xS_y nanoflakes.

3. Results and discussion

It is known that various polymorphs of nickel sulfides may be formed, depending sensitively on the hydrothermal reaction conditions, such as the ratio of precursors and the reaction temperature and time[15]. By tuning the initial mole ratio of reactants (NiCl₂, S) and reaction temperature, we have successfully synthesized nanostructured nickel sulfides of different compositions and controlled morphologies, as schematically illustrated in Figure 1. In particular, a three-phase nickel sulfide (TP-Ni_xS_y) nanoflake was produced. When the reaction temperature was maintained at 100 °C (the initial mole ratio of NiCl₂:S was 1:2.5), we obtained a single phase NiS (Fig. S1, Supporting information). The XRD patterns show four obvious characteristic peaks of NiS centered at $2\theta = 18.4^\circ$ (110), 32.2° (300), 35.7° (021) and 48.8° (131), and all the observed diffraction patterns are in good agreement with standard diffraction data (JCPDS-card no. 00-012-0041). When the reaction temperature was increased to 200 °C (the initial mole ratio of NiCl₂:S is 1:2.5), some additional characteristic peaks of Ni₃S₂ (Fig. S1) can be observed at $2\theta = 21.8^\circ$ (101), 31.1° (110), and 44.3° (202), which are in good agreement with the standard diffraction data for Ni₃S₂ (JCPDS-card no. 00-044-1418). When the initial mole ratio of NiCl₂:S was changed from 1:2.5 to 1:5 and the reaction temperature to 150 °C, we obtained a NiS-Ni₃S₄ composite because the characteristic peaks of Ni₃S₄ are observable in the XRD patterns (Fig. S1) of the as-synthesized sample, including the peaks at $2\theta = 16.2^\circ$ (111), 32.7° (222), and 58.3° (442) (JCPDS-card no. 04-003-2272). Finally, when the initial mole ratio of NiCl₂:S was 1:2.5 and the reaction temperature was kept at 150 °C, we obtained the TP-Ni_xS_y, as confirmed by X-ray diffraction analysis (Fig. S1, Supporting information). Further, X-ray photoelectron spectroscopy (XPS) was used to investigate the chemical composition of the TP-Ni_xS_y sample. The survey spectrum (Fig. S2a) indicates the presence of Ni and S. By using a Gaussian fitting method, the Ni 2p spectrum (Fig. 2Sb) was fitted with two spin-orbit doublets, characteristic of Ni²⁺ and Ni³⁺, and two shakeup satellites, indicating the existence of different phases of nickel sulfide in the TP-Ni_xS_y sample.

SEM was performed to investigate the microstructure and morphology of the as-synthesized samples. As shown in Fig. 2a, b, the morphology of the as-synthesized NiS is 0.5 ~ 1 μm flower-like microspheres composed of numerous nanoneedles. The morphology of the as-synthesized NiS-Ni₃S₂ is nanosheet, and numerous nanosheets overlap together to form irregular particles (Fig. 2c and Fig. S2c). Fig. 2d and Fig. S2d show that the morphology of the as-synthesized NiS-Ni₃S₄ is 0.8 ~ 1.5 μm

flower-like microspheres composed of numerous nanoparticles. SEM images (Fig. 2e, f) reveal that the morphology of the as-synthesized TP-Ni_xS_y is nanoflake, and these nanoflakes agglomerated to a porous 3D architecture. Notably, this porous structure is favorable for efficient and fast transport of the electrolyte to the surface of the active materials, thus improving the effective utilization of the active material [23,24].

The electrochemical performances of NiS nanoneedles-assembled microspheres, NiS-Ni₃S₂ nanosheets, NiS-Ni₃S₄ nanoparticles-assembled microspheres, and TP-Ni_xS_y nanoflakes were evaluated with a three-electrode configuration in a 2M KOH aqueous electrolyte. While we have tried to decouple the effect of the architecture from that of the phases, the attempt was unsuccessful because the architecture was intertwined with the phases (changes in architecture results in different phases). Some unique fabrication processes needs to be developed in order to independently control both the architecture and the phases, which is required to fully decouple the two effects. Fig. 3a shows the CV curves of these nanostructured materials at a scan rate of 5 mV s⁻¹. It is clear that the TP-Ni_xS_y nanoflakes show the higher current densities under the same conditions, suggesting the best electrochemical behavior among the samples tested. Fig. 3b displays the CV curves of the TP-Ni_xS_y nanoflakes at different scan rates; all the CV curves exhibit a pair of redox peaks, which are quite different from those of an electric double-layer capacitor. Moreover, Fig. S3(a, b) display that a linear relationship exists between the peak currents of the anodic and cathodic and the square root of the scan rates, respectively, revealing the dominance of diffusion-controlled electrode reaction, which indicates that the energy storage in our electrodes may depend on the Faradic reaction and these nickel sulfides appears to be battery-type materials. The corresponding CV curves of NiS nanoneedles-assembled microspheres, NiS-Ni₃S₂ nanosheets, NiS-Ni₃S₄ nanoparticles-assembled microspheres are also collected and shown in Fig. S5a-c. The GCD curves (Fig. 3c) further confirm the Faradic behavior of the TP-Ni_xS_y nanoflakes. It is clear that there are voltage plateaus at around 0.2 ~ 0.3 V, which correspond to the anodic and cathodic process.

Fig. 3. (a) CV curves of NiS nanoneedles-assembled microspheres, NiS- Ni_3S_2 nanosheets, NiS- Ni_3S_4 nanoparticles and TP- Ni_xS_y nanoflakes at scan rate of 5 mV s^{-1} . (b) CV curves of TP- Ni_xS_y nanoflakes at different scan rates. (c) GCD curves of TP- Ni_xS_y nanoflakes at different charging-discharging current densities. (d) The specific capacity of as-synthesized nickel sulfide samples.

The calculated specific capacity as a function of the discharge current density was plotted in Fig. 3d. The corresponding GCD curves of NiS nanoneedles-assembled microspheres, NiS- Ni_3S_2 nanosheets and NiS- Ni_3S_4 nanoparticles-assembled microspheres are shown in Fig. S5d-f. The NiS nanoneedles-assembled microspheres showed a specific capacity of 642 C g^{-1} at a current density of 1 A g^{-1} , but retained only 36% of the capacity when the current density was increased from 1 to 20 A g^{-1} . In comparison, both the NiS- Ni_3S_2 and the NiS- Ni_3S_4 hybrid electrodes showed higher capacity retention than the NiS nanoneedles-assembled microspheres. As shown in Fig. 3d, the NiS- Ni_3S_2 nanosheets and NiS- Ni_3S_4 nanoparticles-assembled microspheres retained around 43% (294 C g^{-1}) and 51% (336 C g^{-1}), respectively, as the current density was increased from 1 to 20 A g^{-1} . More remarkably, the TP- Ni_xS_y hybrid electrode displayed the best electrochemical performance, demonstrating a specific capacity of $\sim 723 \text{ C g}^{-1}$ (1825 F g^{-1}) at 1 A g^{-1} , and retained about 67% (484 C g^{-1}) of the capacity as the current density was increased from 1 to 20 A g^{-1} . In fact, the specific capacity of the TP- Ni_xS_y nanoflakes is much higher than those reported

previously for other electrodes based on binary nickel sulfides, including NiS/rGO (358 C g^{-1} , 716 F g^{-1} at 1 A g^{-1}) [17], $\text{Ni}_3\text{S}_2@\text{NiS}$ (258 C g^{-1} , 516 F g^{-1} at 0.5 A g^{-1}) [4], $\text{Ni}_3\text{S}_2@\beta\text{-NiS}$ (463 C g^{-1} , 1158 F g^{-1} at 2 A g^{-1}) [15], Cottons@Graphene nanosheets@NiS (310 C g^{-1} , 775 F g^{-1} at 0.5 A g^{-1}) [25], and $\beta\text{-NiS}$ (429 C g^{-1} , 858 F g^{-1} at 2 A g^{-1}) [26]. The excellent electrochemical performance of TP- Ni_xS_y nanoflakes may be attributed to its unique nanostructure or architecture. First, the TP- Ni_xS_y nanoflakes has relatively large specific surface area, greatly increasing the electrode/electrolyte contact area. As shown in Fig. S6a-d, the BET specific surface area of TP- Ni_xS_y nanoflakes is $28.1 \text{ m}^2 \text{ g}^{-1}$, which is higher than those of the NiS nanoneedles-assembled microspheres ($4.3 \text{ m}^2 \text{ g}^{-1}$), the NiS- Ni_3S_2 nanosheets ($7.5 \text{ m}^2 \text{ g}^{-1}$) and the NiS- Ni_3S_4 nanoparticles-assembled microspheres ($10.7 \text{ m}^2 \text{ g}^{-1}$). Its unique nanostructure facilitates the effective exposure of surface active sites for fast Faradic redox reaction, thereby enhancing the specific capacity [27]. Second, the formation of the three-phase TP- Ni_xS_y nanosheets offers more active crystal interfaces, thus may result in a great improvement in the specific capacity of the electrode. Additionally, the TP- Ni_xS_y offers rich redox reactions that enables multiple oxidation states of Ni ions, leading to higher electrochemical activity [14,27]. Third, the TP- Ni_xS_y nanoflakes agglomerated to form a porous 3D architecture, which reduces the mass-transfer resistances and enhances electrolyte penetration and ion diffusion. As shown in Fig. S6, the tails of the EIS at low frequencies for the TP- Ni_xS_y nanoflakes have a larger slope than those for the NiS nanoneedles-assembled microspheres, the NiS- Ni_3S_2 nanosheets, and the NiS- Ni_3S_4 nanoparticles-assembled microspheres, indicating a faster ion diffusion rate at the electrode/electrolyte interface, thus resulting in a significant increase in rate capability.

Fig. 4. (a) SEM image of TP-Ni_xS_y/rGO nanoflakes. (b) Low-magnification TEM image of TP-Ni_xS_y/rGO nanoflakes. (c) HRTEM image of TP-Ni_xS_y/rGO nanoflakes. (d) TEM-EDX mapping images of TP-Ni_xS_y/rGO nanoflakes. (e) XRD patterns of TP-Ni_xS_y/rGO nanoflakes. (f) XPS spectra of Ni 2p for TP-Ni_xS_y/rGO nanoflakes.

To further improve the electrochemical performance of the TP-Ni_xS_y, we also successfully synthesized the TP-Ni_xS_y/rGO nanoflakes. The content rGO the

TP-Ni_xS_y/rGO is about 8 wt% (for detailed information, see Fig.S7). As shown in Fig. 4a and Fig.S8a, The ultrathin rGO nanosheets were intertwined and intimately bound with the TP-Ni_xS_y nanoflakes, which was further confirmed by TEM analysis as shown in Fig. 4b. The TP-Ni_xS_y nanoflakes were well wrapped by the ultrathin rGO nanosheets, which exhibit a foldaway silk-like morphology, and the dark strips correspond to the folded edges or wrinkles of the nanosheets. The ultrathin rGO nanosheets not only enhance the charge transfer kinetics and current collection, but also facilitate local ion diffusion and maintain structural integrity of the electrodes during charge-discharge cycling as discussed below [27].

Fig. 5. (a) CV curves of TP-Ni_xS_y nanoflakes and TP-Ni_xS_y/rGO nanoflakes at a scan rate of 10 mV s⁻¹. (b) CV curves of TP-Ni_xS_y/rGO nanoflakes at different scan rates. (c) GCD curves of TP-Ni_xS_y/rGO nanoflakes at different charging-discharging current densities. (d) The specific capacity of TP-Ni_xS_y nanoflakes and TP-Ni_xS_y/rGO nanoflakes.

The high-resolution TEM images (Fig. 4c and Fig. S8b) show clear lattice fringes of 0.295 and 0.174 nm that corresponding to the spacing of the (101) and (401) planes of NiS, 0.408 and 0.287 nm that corresponding to the spacing of the (101) and (110) planes of Ni₃S₂, and 0.335 nm that corresponding to the spacing of the (220) plane of

Ni₃S₄, respectively. The TEM elemental mapping of the TP-Ni_xS_y/rGO nanoflakes is shown in Fig. 4(d), which clearly reveals that the TP-Ni_xS_y nanoflakes are distributed homogeneously in the rGO nanosheets. The phase of the TP-Ni_xS_y/rGO nanoflakes was confirmed by the X-ray diffraction as shown in Fig. 4e. Moreover, XPS was conducted to further investigate the chemical composition of the TP-Ni_xS_y/rGO nanoflakes. The survey spectrum (Fig. S8c.) indicates the presence of Ni, S and C. As shown in Fig. 4f, the Ni 2p spectrum was also fitted with two spin-orbit doublets, characteristic of Ni²⁺ and Ni³⁺, and two shakeup satellites, suggesting the existence of different phases of nickel sulfide in the TP-Ni_xS_y/rGO sample. The BET specific surface area of TP-Ni_xS_y/rGO nanoflakes is about 29.9 m² g⁻¹ (Fig. S8d).

Fig. 6. (a) illustration of assembling hybrid supercapacitor device. (b) CV curves of

the hybrid supercapacitor at various scan rates. (c) GCD curves of the hybrid supercapacitor at different charging-discharging current densities. (d) Ragone plots of the hybrid supercapacitor; the energy/power density was calculated based on the entire mass of active materials in negative and positive electrodes, which was used for quantitative comparison with those reported in literatures[30-34]. (e) Cycling performance of the hybrid supercapacitor. Inset shows the optical photograph of 37 LEDs lighted by two hybrid supercapacitors connected in series.

Presented in Fig. 5a are some typical CV curves of the TP-Ni_xS_y nanoflakes and the TP-Ni_xS_y/rGO nanoflakes at a scan rate of 10 mV s⁻¹. It is clear that the average area of the CV curve for the TP-Ni_xS_y/rGO nanoflakes is larger than that of TP-Ni_xS_y nanoflakes, implying that the TP-Ni_xS_y/rGO nanoflake electrode has a much higher specific capacity. The corresponding CV curves for the TP-Ni_xS_y/rGO nanoflakes at different scan rates are shown in Fig. 5b. The GCD curves for the TP-Ni_xS_y/rGO nanoflakes at various current densities are shown in Fig. 5c. It is clear that there are voltage plateaus at around 0.2~0.3V. The specific capacity of the TP-Ni_xS_y nanoflakes and TP-Ni_xS_y/rGO nanoflakes, calculated from the GCD curves, and the calculation of specific capacity based on the entire mass of TP-Ni_xS_y and rGO active materials. As shown in Fig. 5d, the TP-Ni_xS_y/rGO nanoflake electrode exhibits an excellent specific capacity of 807 C g⁻¹ (2074 F g⁻¹) at a current density of 1 A g⁻¹, which is higher than that of TP-Ni_xS_y nanoflakes (723 C g⁻¹ at 1 A g⁻¹). When the current density was increased from 1 to 20 A g⁻¹, it still retained ~72% (581 C g⁻¹) of the capacity. To the best of our knowledge, these electrochemical performances are far superior to those reported for any nickel sulfides based materials [17,25]. The excellent performance of the TP-Ni_xS_y/rGO nanoflakes can be attributed to the following factors: 1) the rGO is intertwined and intimately bound with the TP-Ni_xS_y nanosheets, greatly strengthening the mechanical integrity of the whole electrode. 2) the presence of rGO improves the electrical conductivity of the electrode, as shown in Fig. S9. The impedance loop at high frequencies for the TP-Ni_xS_y/rGO nanoflakes had smaller diameter, implying faster charge transfer kinetics. Similarly, the impedance tail at low frequencies for the TP-Ni_xS_y/rGO had larger slope than those for other Ni_xS_y nanostructures without rGO, suggesting faster ion diffusion near the electrode/electrolyte interface.

To further evaluate the viability of the TP-Ni_xS_y/rGO nanoflake electrode for practical application, we constructed a hybrid supercapacitor using the TP-Ni_xS_y/rGO nanoflakes as the positive electrode and a graphene-based electrode as the negative electrode (Fig. 6a). According to the CV studies of the individual TP-Ni_xS_y/rGO and the graphene electrode (Fig. S10, Supporting Information), the mass ratio of the negative electrode to the positive electrode is optimized to 3.5 to balance the charge between the two electrodes (for more information about the negative electrode, please see Fig. S11). To estimate the proper voltage window for the hybrid device, the hybrid supercapacitor was tested within different voltage windows with typical CV

curves shown in Fig. S12a. When the voltage windows increased to 0-1.6 V, the integral area increased, suggesting that higher capacitance was achieved. However, when the voltage window was extended to 0-1.8 V, water decomposition was observed. Thus, we use 1.6 V as the cutoff voltage. The CV curves at different scan rates demonstrate that the hybrid supercapacitor shows an excellent capacitive behavior in a voltage range of 0-1.6 V (Fig. 6b). GCD curves of the hybrid supercapacitor at various current densities are shown in Fig. 6c. The charging-discharging curves remain in good symmetry at cell voltage as high as 1.6V, revealing that the hybrid supercapacitor has excellent electrochemical reversibility and capacitive characteristics. Although the hybrid supercapacitor shows a lower Coulombic efficiency at the low charge-discharge current density (2 A g⁻¹), the efficiency improved with the number of cycles while maintaining the high specific capacitance (Fig. S12b, Supporting Information). The energy density (E) and power density (P), the two important parameters for practical application of SCs, are calculated from the GCD curves as follows:[28].

$$E = \frac{I \int V dt}{m} \quad (3)$$

$$P = \frac{E}{t} \quad (4)$$

where I is the charge-discharge current, V is the cell voltage, t is the discharging time and m is the whole effective mass of the active negative and positive electrode materials[14,29]. The calculation of energy/power density based on the entire mass of active materials in negative and positive electrodes was mainly used for quantitative comparison with those reported in literatures[30-34]. As shown in the Ragone plot (Fig. 6d), the hybrid supercapacitor can deliver a high energy density of 46 W h kg⁻¹ at a power density of 1.8 kW kg⁻¹. Even at a high power density of 17.2 kW kg⁻¹, it still retains an energy density of 32 W h kg⁻¹. The energy density is much higher than other previously reported hybrid supercapacitors with metal oxides or sulfides as active electrode material, including CoMoO₄@graphene//activated carbon (21.1 W h kg⁻¹ at a power density of 300 W kg⁻¹)[30], Ni-Co-S/G//carbon nanosheets (43.2 W h kg⁻¹ at a power density of 800 W kg⁻¹)[31], NiCo₂S₄//graphene (42.3 W h kg⁻¹ at a power density of 476 W kg⁻¹)[32], Co₃O₄//carbon (36 W h kg⁻¹ at a power density of 1600 W kg⁻¹)[33], and Ni(OH)₂//activated carbon (35.7 W h kg⁻¹ at a power density of 490 W kg⁻¹)[34]. In practical applications, SCs are often used at large current densities. The long-term cycle stability of electrode materials at high charge-discharge cycling rates is another critical requirement for practical applications [30]. As shown in Fig. 6e, the hybrid supercapacitor device still retained ~80% of the initial capacitance after 5,000 cycles at a high current density of 20 A g⁻¹, revealing its

excellent cycling stability. Furthermore, two such hybrid supercapacitors connected in series can power 37 commercial light-emitting diodes (LEDs) after being charged to 3.2 V (Fig. 6e, Inset), demonstrating its viability and potential in practical applications (for detailed information, see corresponding video in supporting information).

4. Conclusion

In summary, three-phase nickel sulfide with 3D flower-like architecture has been successfully prepared by a simple hydrothermal process. When tested in a capacitor, it exhibits a high specific capacity (724 C g^{-1} at 1 A g^{-1}) due to its unique morphology and structure. Moreover, we also successfully prepared the TP-Ni_xS_y/rGO nanoflakes electrode, and the presence of rGO greatly improves the specific capacity (807 C g^{-1} at 1 A g^{-1}) and rate capability ($\sim 72\%$ capacity retention when the current density was increased from 1 A g^{-1} to 20 A g^{-1}). More remarkably, a hybrid supercapacitor, constructed from a TP-Ni_xS_y/rGO nanoflakes positive electrode and a graphene-based negative electrode, demonstrated a high energy density of 46 Wh kg^{-1} at a power density of 1.8 kW kg^{-1} . Even at a high power density of 17.2 kW kg^{-1} , hybrid supercapacitor still retained high energy density of 32 Wh kg^{-1} , revealing its viability and potential for practical applications.

Acknowledgements

This work was supported by the US Department of Energy ARPA-E Program under award number DE-AR0000303 and by the US National Science Foundation under award number DMR-1410320. S. G. D. acknowledges the financial support of a scholarship from the China Scholarship Council (CSC).

References

- [1] J. Xu, Q.F. Wang, X.W. Wang, Q. Xiang, B. Liang, D. Chen, G.Z. Shen, *ACS Nano* 7 (2013) 5453-5462
- [2] D. Ghosh, C.K. Das, *ACS Appl. Mater. Interfaces* 7 (2015) 1122-1131.
- [3] W.J. Zhou, X.H. Cao, Z.Y. Zeng, W.H. Shi, Y.Y. Zhu, Q.Y. Yan, H. Liu, J.Y. Wang, H. Zhang, *Energy Environ. Sci.* 6 (2013) 2216-2221.
- [4] W.T. Wei, L.W. Mi, Y. Gao, Z. Zheng, W.H. Chen, X.X. Guan, *Chem. Mater.* 26 (2014) 3418-3426.

- [5] F. Lu, M. Zhou, W.R. Li, Q.H. Weng, C.L. Li, Y.M. Xue, X.F. Jiang, X.H. Zeng, Y.S. Bando, D. Golberg, *Nano Energy* 26 (2016) 313-323.
- [6] L.F. Shen, J. Wang, G.Y. Xu, H.S. Li, H. Dou, X.G. Zhang, *Adv. Energy Mater.* 5 (2015) 1400977.
- [7] L. Yu, L. Zhang, H.B. Wu, X.W. Lou, *Angew. Chem. Int. Ed.* 53 (2014) 3711-3714.
- [8] T. Brousse, D. Belanger, J.W. Long, *J. Electrochem. Soc.* 162 (2015) A5185-A5189.
- [9] P. Simon, Y. Gogotsi, B. Dunn, *Science* 343 (2014) 1210-1211.
- [10] Y. Gogotsi, P. Simon, *Science* 334 (2011) 917-918.
- [11] Y. Gogotsi, *ACS Nano* 8 (2014) 5369-5371.
- [12] X. Lu, M. Yu, G. Wang, T. Zhai, S. Xie, Y. Ling, Y. Tong, Y. Li, *Adv. Mater.* 25 (2013) 267-272.
- [13] S.J. Peng, L.L. Li, H.B. Wu, S. Madhavi, X.W. Lou, *Adv. Energy Mater.* 5 (2015) 1401172.
- [14] Q.B. Zhang, B.T. Zhao, J.X. Wang, C. Qu, H.B. Sun, K.L. Zhang, M.L. Liu, *Nano Energy* 28 (2016) 475-485.
- [15] W. Li, S.L. Wang, L.P. Xin, M. Wu, X.J. Lou, *J. Mater. Chem. A* 4 (2016) 7700-7709.
- [16] H. Chen, L.F. Hu, Y. Yan, R.C. Che, M. Chen, L.M. Wu, *Adv. Energy Mater.* 3 (2013) 1636-1646.
- [17] J.Q. Yang, X.C. Duan, W. Guo, D. Li, H.L. Zhang, W.J. Zheng, *Nano Energy* 5 (2014) 74-81.
- [18] H. Geng, S.F. Kong, Y. Wang, *J. Mater. Chem. A* 2 (2014) 15152-15158.
- [19] D.C. Marcano, D.V. Kosynkin, J.M. Berlin, A. Sinitskii, Z.Z. Sun, A. Slesarev, L.B. Alemany, W. Lu, J.M. Tour, *ACS Nano* 4 (2010) 4806-4814.
- [20] D. Dang, H.B. Zou, Z. Xiong, S.Y. Hou, T. Shu, H.X. Nan, X.Y. Zeng, J.H. Zeng, S.J. Liao, *ACS Catal.* 5 (2015) 4318-4324.
- [21] L.Q. Mai, A. Khan¹, X.C. Tian, K. M. Hercule, Y.L. Zhao, X. Lin, X. Xu, *Nat. Commun.* 4 (2013) 2923.

- [22] C. Qu, Y. Jiao, B.T. Zhao, D.C. Chen, R.Q. Zou, K. Walton, M.L. Liu, *Nano Energy* 26 (2016) 66-73.
- [23] L. Huang, D.C. Chen, Y. Ding, S. Feng, Z.L. Wang, M.L. Liu, *Nano Lett.* 13 (2013) 3135-3139.
- [24] J. Yang , C. Yu , X.M. Fan , J.S. Qiu, *Adv. Energy Mater.* 4 (2014) 1400761.
- [25] Y.J. Li, K. Ye, K. Cheng, J.L. Yin, D.X. Cao, G.L. Wang, *J. Power Sources* 274 (2015) 943-950.
- [26] J.Q. Yang, X.C. Duan, Q. Qin, W.J. Zheng, *J. Mater. Chem. A* 1 (2013) 7880-7884.
- [27] D.P. Dubal, P. Gomez-Romero, B.R. Sankapal, R. Holze, *Nano Energy* 11 (2015) 377-399.
- [28] X.X. Xiong, G. Waller, D. Ding, D.C. Chen, B. Rainwater, B.T. Zhao, Z.X. Wang, M.L. Liu, *Nano Energy* 16 (2015) 71-80.
- [29] S.G. Dai, W.N. Xu, Y. Xi, M.J. Ming, X. Gu, D.L. Guo, C.G. Hu, *Nano Energy* 19 (2016) 363-372.
- [30] X.Z. Yu, B.G. Lu, Z. Xu, *Adv. Mater.* 26 (2014) 1044-1051.
- [31] J. Yang, C. Yu, X. M. Fan, S.X. Liang, S.F. Li, H.W. Huang, Z. Ling, C. Hao, J.S. Qiu, *Energy Environ. Sci.* 9 (2016) 1299-1307.
- [32] L.F. Shen, L. Yu, H.B. Wu, X.Y. Yu, X.G. Zhang, X.W. Lou, *Nat. Commun.* 6 (2015) 6694.
- [33] R.R. Salunkhe, J. Tang, Y. Kamachi, T. Nakato, J.H. Kim, Y. Yamauchi, *ACS Nano* 9 (2015) 6288-6296.
- [34] H.B. Li, M.H. Yu, F.X. Wang, P. Liu, Y. Liang, J. Xiao, C.X. Wang, Y.X. Tong, G.W. Yang, *Nat. Commun.* 4 (2013) 1894.

Shuge Dai received his bachelor degree from the Department of Physics at Chongqing Normal University of China in 2012. He is currently a Ph.D. candidate at the Department of Applied Physics at Chongqing University of China. He joined Prof. Meilin Liu's group as a visiting student at School of Materials Science and Engineering, Georgia Institute of Technology in 2015. His research interests mainly focus on the efficient energy storage and conversion, including supercapacitors, nanogenerators, lithium ion batteries and fuel cells.

Bote Zhao is currently a postdoctoral fellow in the School of Materials Science and Engineering at Georgia Institute of Technology, USA. He received his B.S. And Ph.D. from Nanjing Tech University, China. His research experiences include binder-free films, nanostructured materials, and graphene-based materials for lithiumion batteries and supercapacitors, electrospinning synthesis of fibers, fabrication and water management of proton exchange membrane fuel cells, and hydrogen production from hydrous hydrazine. He is currently focusing on the synthesis and characterization of novel materials for batteries, fuel cells, and supercapacitors.

Chong Qu is currently a Ph.D. candidate under supervision of Prof. Ruqiang Zou, Peking University. He received his bachelor degree from School of Chemistry and Chemical Engineering at Nanjing University in 2013. He joined Prof. Meilin Liu's group as a GT-PKU joint program student at School of Materials Science and Engineering, Georgia Institute of Technology in 2014. His research interests include electrochemical materials based on crystalline porous frameworks for supercapacitors and Li-ion battery.

Dongchang Chen received his bachelor degree from department of chemical physics at University of Science and Technology of China in 2011. He is currently a Ph.D. candidate under supervision of Prof. Meilin Liu at School of Materials Science and Engineering, Georgia Institute of Technology. His research interests mainly focus on insitu spectroscopic study of solution-based electrochemical reactions.

Dai Dang is currently a Ph.D. candidate in South China University of Technology under supervision of Prof. Shijun Liao. He received his bachelor degree from South China University of Technology in 2011. He joined Prof. Meilin Liu's group as a joint

Ph.D. student in Georgia Institute of Technology in 2015. His research interests mainly focus on electrocatalysts for PEM fuel cells and intermediate temperature fuel cells.

Bo Song received his B.S.degree in Chemistry in 2013 from State University of New York at Binghamton. He is currently pursuing his Ph.D. degree at School of Chemistry and Biochemistry, Georgia Institute of Technology. He joined Prof. CP Wong's group in fall 2013. His research work includes fabrication of graphene-based materials for energy storage and conversion application, flexible and stretchable nanocomposite materials for electrical conductive adhesives and radio-frequency antennas.

Ben M. deGlee received his Bachelor's degree in Materials Science & Engineering from the University of Florida in 2012 and is currently a pursuing his PhD under the supervision of Prof. Meilin Liu at the Georgia Institute of Technology. His research focuses on the development of operando spectroscopy techniques for studying electrode surfaces, forming structure-property-performance relationships for novel catalyst coatings.

Jianwei Fu is currently an associate professor at School of Materials Science and Engineering, Zhengzhou University. He received his B.S. and M.S. degree from Zhengzhou University and Ph.D. degree from Shanghai Jiao Tong University, China. His research interests include rational design of nanostructured carbon materials for efficient energy storage and conversion, and synthesis of polymorphic polymer micro- and nanomaterials and their application in dye adsorption and catalysis.

Chenguo Hu is a professor of physics in Chongqing University and the director of Key Lab of Materials Physics of Chongqing Municipality. She received her Ph. D. in Materials from Chongqing University in 2003. Her research interests include methodology of synthesizing functional nanomaterials, investigation of morphology and size dependent physical and chemical properties of nanomaterials, and design and fabrication of electronic devices, such as nanogenerators and sensors.

Ching-Ping Wong is currently Dean of the Faculty of Engineering at the Chinese University of Hong Kong. He is on a no pay leave from Georgia Institute of Technology where he is a Regents' Professor and the Charles Smithgall Institute Endowed Chair at the School of Materials Science and Engineering. He received his B.S. Degree from Purdue University, and his Ph.D. degree from the Pennsylvania State University. His research interests lie in the fields of polymeric electronic materials, electronic, photonic and MEMS packaging and interconnect, interfacial adhesions, nano-functional material syntheses and characterizations, nanocomposites, lead-free alloys, flip chip underfill, ultra high-k capacitor composites and lotus effect coating materials.

Meilin Liu is a B. Mifflin Hood Chair, Regents' Professor, and Associate Chair of Materials Science and Engineering and Co-Director of the Center for Innovative Fuel Cell and Battery Technologies at Georgia Institute of Technology, Atlanta, Georgia, USA. He received his BS from South China University of Technology and both MS and Ph.D. from University of California at Berkeley. His research interests include insitu/operando characterization and multi-scale modeling of charge and mass transfer along surfaces, across interfaces, and in membranes, thin films, and nanostructured electrodes, aiming at achieving rational design of materials and structures with unique functionalities for efficient energy storage and conversion.

Graphical abstract

A three-phase nickel sulfide (NiS-Ni₃S₂-Ni₃S₄)/reduced graphene oxide was designed and successfully prepared, which delivered high specific capacity (807 C g⁻¹ at 1 A g⁻¹), and good rate capability. Importantly, a hybrid supercapacitor device was also fabricated based on the nickel sulfide/graphene positive electrode and graphene negative electrode, which demonstrated a high energy density and good cycling stability. Two such devices connected in series could well power 37 commercial LEDs, revealing its great potential application in energy storage systems.