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Facile hydrothermal synthesis of NiS hollow microspheres with mesoporous shells for high-performance supercapacitors

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Nickel sulfide (NiS) hollow microspheres with mesoporous shells have been successfully synthesized via a facile hydrothermal route using nickel chloride hexahydrate (NCH) as nickel source and thiosemicarbazide (TSC) as sulfur source. The NH₂-NH- group in TSC molecule plays a crucial role in the formation of hollow microspheres. Ostwald ripening mechanism was suggested to explain the formation of NiS hollow microspheres with mesoporous shells. The resulting NiS hollow microspheres were further used as the electrode material for supercapacitors and found to exhibit a high specific capacitance of 1848.0 F/g at a discharge current density of 1 A/g. About 74.3% of capacity was retained as the current density increased from 1 to 10 A/g. Furthermore, NiS hollow microspheres electrode also presented excellent cycle stability at a scan rate of 50 mV/s. The results indicate that the as-prepared NiS hollow microsphere with mesoporous shells is a promising electrode material for supercapacitors.

1. Introduction

Recently, with the rapidly consumption of fossil fuels and everincreasing demand for energy, the effort to optimize the utilization of present energy sources and search for advanced energy storage devices has intensified dramatically¹⁻³. Supercapacitors, also known as electrochemical capacitors or ultracapacitors have received increasing attention due to their many advantages including high power density, faster charge/discharge process, long cycle lifetime, small size, and relatively low cost⁴⁻⁶. Based on the energy storage mechanisms, supercapacitors can be classified into electrical double layer capacitors and pseudocapacitors^{4, 7}. In electrical double layer capacitors, capacitance arises from the charge separation at the electrode/electrolyte interface, whereas in pseudocapacitors, charge is stored and released in faradaic processes at/or near the electrode surface^{8, 9}. Pseudocapacitors usually offer much higher specific capacitances than electric double layer capacitors^{10, 11}.

It is well accepted that electrode materials play a vital role to improve the performance of supercapacitors^{12, 13}. And capability of an electrode material is significantly influenced by its morphology. An electrode material with uniform, and ordered structure is expected to exhibit superior performance for supercapacitors¹⁴⁻¹⁷. Among various micro/nanomaterials for supercapacitors, hollow structured materials with low densities and high surface areas have attracted much attention¹⁸⁻²⁰. Hollow structured materials have been proved to be an optimized architecture for boosting the capacitive performance due to their high surface areas, short

diffusion paths for ions and electrons, resulting in reduced internal resistance and improved high power capability^{6, 21-23}. Until now, many methods have been developed to synthesize hollow structures for supercapacitors, such as chemical precipitation^{24, 25}, electrospining³, template^{26, 27}, layer-by-layer self-assembly⁵, solvothermal and hydrothermal methods^{19, 21}. For example, Shao et al. have reported that graphene hollow spheres with a specific capacitance of 273 F/g at discharge current density of 0.5 A/g using polystyrene spheres as templates²⁸. Hollow V₂O₅ spheres were synthesized by a solvothermal process, which exhibited a high capacitance of 479 F/g at 5 mV/s¹⁸.

As a new kind of electrode material, NiS has been extensively applied in supercapacitors due to its low cost, high capacity and electronic conduction, and environmental sustainability. For example, Lou's group has obtained hierarchical NiS hollow spheres with specific capacitances of 927 F/g at a current density of 4.08 A/g by a template-engaged conversion method²⁹. Yang et al. reported a hierarchical flower-like β -NiS architecture synthesized via solvothermal method with specific capacitances of 857.76 F/ g at 2 A/g and 512.96 F/g at 5 A/g.

Although a great deal of effort has been made and some successes have been achieved^{13, 29-32}, the realization of high capacitance with good rate performance and long cycle lifetime for nickel sulfide still remains a significant challenge. Herein, we applied a simple and efficient one-step hydrothermal route for the synthesis of NiS hollow microspheres using nickel chloride hexahydrate as nickel source and thiosemicarbazide (TSC) as sulfur source. Neither surfactant nor template was used in our reaction system. The substituent group in the sulfur source plays an important role in the formation of NiS hollow microspheres. Ostwald ripening mechanism is proposed to account for the formation of NiS hollow microspheres show impressive electrochemical properties with high specific



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New Journal of Chemistry

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2. Experimental Section

and excellent cycling performance.

2.1. Materials

ARTICLE

Nickel chloride hexahydrate (NCH), thiosemicarbazide (TSC), thiourea (TU), thioacetamide (TAA) and other reagents used were purchased from Sinopharm Chemical Reagent Co. Ltd. and used without further purification. The water used throughout the experiments was distilled water.

2.2. Synthesis of nickel sulfide hollow microspheres

Nickel sulfide hollow microspheres were synthesized by a facile hydrothermal route. In a typical process, 1.0 mmol nickel chloride hexahydrate was dissolved in 15.0 mL distilled water, followed by addition of 2.0 mmol thiosemicarbazide. After stirring vigorously, the mixture was transferred to a 25 mL Teflon-lined pressure vessel, stainless steel autoclave. The autoclave was sealed and heated in an oven at 180°C for 24 h. The pressure vessel was cooled to room temperature naturally after reaction time. The precipitate was collected by centrifugation and washed with distilled water and ethanol for several times. Then the precipitate was dried at 60°C for 12 h under vacuum condition.

2.3. Characterization

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 advance diffractometer with Cu $K\alpha$ radiation. Morphology observations were done on Tecnai-12 transmission electron microscopy (TEM) and HITACHI-3400s scanning electron microscopy (SEM). Samples for TEM experiments were deposited on copper grids. High-resolution TEM (HRTEM) characterization was performed with a FEI G2 F30 S-TWIN field emission transmission electron microscopy operating at an accelerating voltage of 300 kV. N₂ adsorption-desorption isotherm was tested using a Quadrasorb SI analyzer.

2.4. Electrochemical measurements

The working electrodes were prepared by mixing nickel sulfide, acetylene black and polytetrafluoroethylene (PTFE) in a weight ratio of 80:10:10. The loading mass of hollow NiS microspheres is about 2~3 mg. Isopropanol was added to the mixture to produce a homogeneous paste, which was subsequently brush-coated onto nickel foam and then dried at 60°C for 12 h in a vacuum oven. All electrochemical tests were conducted on a CHI 660C electrochemical workstation in 2.0 mol·L⁻¹ KOH solution with a three electrode cell where a platinum foil serves as the counter electrode and a standard calomel electrode (SCE) as the reference electrode, respectively.

3. Results and discussion

3.1. Morphology and structure of NiS hollow microspheres

The phase and composition of as-prepared hollow microspheres were examined by X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS), as shown in Fig. 1a and 1b. Four diffraction peaks were observed at $2\theta = 30.2^{\circ}$, 34.7° , 45.9° , and 53.6° , which

can be perfectly indexed to the (100), (101), (102), and (110) reflections of hexagonal NiS with lattice constants a = 3.41 Å, b = 3.41 Å, c = 5.317 Å (JCPDS No. 02-1280)^{13, 33, 34}. In addition, energy dispersive spectrum (EDS) was also employed to determine the chemical composition. Both the peaks of the elements Ni and S were detected, which further confirmed that the as-prepared hollow microspheres were composed of NiS. Morphology of the resulting NiS was investigated by SEM and TEM. Some holes are found on the surfaces of NiS spherical particles in Fig. S1, clearly demonstrating the hollow structure of NiS microspheres. Fig.1 c shows a representative TEM image of NiS hollow microspheres. As shown in Fig. 1c, hollow spheres with the diameter of about 2 µm are observed. From the inset in Fig. 1c, we can see clearly that there are numerous gaps in the surface of hollow microspheres. And the different brightness in TEM image can illuminate the hollow structure of NiS microspheres. The TEM image shows that the microsphere consists of particles leading to textural pores. For further insight into the crystal structure of NiS hollow microspheres, structural analyses were performed by HRTEM and fast Fourier transform (FFT) pattern. Fig. 1d shows a typical HRTEM image of NiS hollow microsphere. Lattice planes can be seen from Fig. 1d and a d spacing of 0.256 nm for adjacent lattice planes corresponds to the (101) planes of hexagonal NiS. Meanwhile, the FFT was carried out, shown as inset in Fig. 1d. The spot pattern implies that the asprepared NiS hollow microsphere is single crystal in nature.



Fig.1 (a) XRD pattern; (b) EDS pattern; (c) TEM images; (d) HRTEM image and inset FFT pattern; (e) N_2 adsorption-desorption isotherm; and (f) pore diameter distribution of NiS hollow microspheres.

New Journal of Chemistry Accepted Manuscrip

2 | J. Name., 2012, 00, 1-3

capacitance of 1848.0 F/g at a discharge current density of 1 A/g

Journal Name

The pore size and specific surface area are very important for the electrode materials in supercapacitors³⁵. Fig. 1e presents the N_2 adsorption-desorption isotherm of NiS hollow microspheres. There is a separation between adsorption branch and desorption branch at a relative pressure in the range of 0.3-1.0, suggesting the existence of mesoporous. The specific surface area of NiS hollow microspheres is 5.3 m²/g. The low specific surface area may be ascribed to the fact that the diameter of NiS microsphere is very large. The pore diameter distribution obtained from desorption branch based on the NLDFT equilibrium model is shown in Fig. 1f. The pore diameter mainly locates at 3.9 nm, 4.6 nm, and 13.3 nm. The unique hollow structure with mesoporous shells of NiS hollow microspheres can provide fast ion and electron transport, leading to the excellent electrochemical capacitive properties.



Fig. 2 XRD patterns prepared at various molar ratios of NCH to TSC.



Fig. 3 TEM images obtained at various molar ratios of NCH to TSC. (a) 1:1; (b) 1:3; (c) 1:4 and (d) 1:5.

3.2 Effect of synthesis conditions on the morphology evolution

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ARTICLE

To investigate the morphology evolution of NiS microstructures, the influences of reaction parameters such as molar ratio of reactants, reaction temperature and reaction time were studied, respectively. Considering that morphology of the final product is usually affected by the molar ratio of reactants in hydrothermal process. In the present case, the influence of molar ratios of NCH to TSC on the final product was investigated systematically. The evolutions of compositions and morphologies were examined by XRD and TEM. Fig. 2a represents the XRD patterns of products prepared at the molar ratio of NCH/TSC ranging from 1:1 to 1:5. All diffraction peaks agree well with the reported value (JCPDS No. 02-1280) when the molar ratio of NCH/TSC is in the range of 1:1-1:4. No characteristic peak due to impurity is detected, indicating that the as-prepared products consist of a single phase of hexagonal NiS. It's worth noting that the crystallinity becomes poorer and poorer as the molar ratio of NCH to TSC decreased from 1:1 to 1:4. However, when the molar ratio of TSC to NCH was increased to 5:1, the peaks of NiS₂ (JCPDS No. 65-3325) were found in the XRD pattern. Therefore, the molar ratio of NCH to TSC is an important factor for the formation of NiS hollow microspheres with high purity.

Fig. 3 shows the TEM images of the products obtained at the corresponding molar ratios. NiS hollow microspheres about 1.5-2.3 μ m in diameter were obtained when the molar ratio is in the range of 1:1-1:4 (Fig. 3a-c). However, when the experiment was carried out at the molar ratio of 1:5, only fragments of broken NiS hollow microspheres were observed in Fig. 3d. In the present paper, we choose the molar ratio of NCH to TSC is 1:2 in the subsequent experiments.

Fig. 4 represents the XRD patterns of products prepared at 120-200°C when the molar ratio of NCH/TSC was 1:2. When the experiment was conducted at 120°C or 140°C, amorphous NiS was obtained. When the reaction temperature was increased to 160°C, a diffraction peak at 2θ = 53.6° emerged in XRD pattern, which is in accordance with the (110) reflection of hexagonal NiS (JCPDS No.02-1280). There are four diffraction peaks observed at 2θ = 30.2°, 34.7°, 45.9°, and 53.6° when the temperature is raised to 200°C, which are in accordance with the (100), (101), (102), and (110) reflections of hexagonal NiS (JCPDS No. 02-1280).



Fig. 4 XRD patterns of products obtained at different temperatures.

ARTICLE

Fig. 5 shows the corresponding TEM images of samples obtained at various reaction temperatures. When the experiment was conducted at 120°C or 140°C, solid NiS microspheres could be produced (Fig. 5a and 5b). As shown in Fig. 5c, NiS particles with rough surfaces were obtained when the reaction was carried out at 160°C. When the reaction temperature was raised to 180°C or 200°C, significant change in the product shapes occurred. The final products in Fig.1c and Fig.5d generally comprised NiS hollow microspheres with diameters of 1.5-2.5 μ m. The difference of NiS morphology is just because of the reaction temperature, which may be ascribed to the different growth ratio of NiS at different reaction temperature. Hence, reaction temperature has direct effect on the morphology of NiS samples. In this case, we chose 180°C as the reaction temperature. In order to investigate the evolutions of NiS hollow microspheres, a series of time-dependent experiments were carried out. The evolutions of structures and morphologies were examined by XRD and TEM, as shown in Fig. 6 and Fig. 7. At the initial stage of reaction (1 h), solid spherical particles with amorphous structure were obtained (Fig. 6 and 7a). After hydrothermal treatment is prolonged to 4 h, (110) reflection of hexagonal NiS (JCPDS No.02-1280) emerged in the XRD pattern. Fig. 7b shows that the sample collected at 4 h exhibits immature spherical morphology, and it is integrated by masses of tiny thorns. This could be explained by that the newly formed nuclei with a high surface energy preferred to aggregate driven by the minimization of surface energy and self-assembly controlled by the intrinsic crystal orientation³⁶. After 8 h hydrothermal treatment, all XRD peaks were well consistent with those of the final product obtained at 24 h. In addition, the degree of crystallinity was enhanced with the hydrothermal treatment time (shown in Fig. 6). When hydrothermal treatment time was prolonged to 8 h, NiS hollow microspheres were obtained as shown in Fig. 7c. The diameter of NiS hollow microsphere was increased with the longer reaction time in Fig. 7d.



Fig. 5 TEM images of products obtained at different temperatures. Temperature (°C): (a) 120; (b) 140; (c) 160; (d) 200.



Fig. 6 XRD patterns of products obtained at different reaction time.



Fig. 7 TEM images of products obtained at different reaction time. Reaction time (h): (a) 1; (b) 4; (c) 8; (d) 16.



Fig. 8 XRD patterns of products obtained with TU and TAA.

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It is clear that the growth process was neither surfactant-assisted nor template-directed, because no surfactant or template was used in our reaction system. On the basis of the characterization results from condition-dependent experiments, the growth process of NiS hollow microspheres could be explained in terms of Ostwald ripening process^{37, 38}. This process is associated with a progressive redistribution of matter from the interior to exterior. In the initial stage, NiS crystal nuclei are produced and aggregate to solid aggregates to decrease the surface energy. During the course of reaction, the concentration of reactants in the solution decrease so that supersaturation falls over time and a chemical equilibrium between the solid-liquid interfaces is established. Compared with the large and well-crystallized particles on the exteriors of the spheres, the inner amorphous small crystallites have a higher surface energy, which offers drive force for the Ostwald ripening process³⁹. Then, the inner crystallites tend to dissolve, resulting in an interior void space. The exterior crystals will serve as starting points to attract the smaller metastable crystals under the surface layers, which is confirmed by the fact that the diameters of NiS microspheres increase with the reaction time. As a consequence, NiS hollow microspheres are formed.

In addition, we found the substituent group in the S source plays an important role in formation of NiS hollow microspheres. If the NH₂-NH- group was replaced by NH₂- or CH₃-, no hollow microstructures were found at the same conditions except the S source. As shown in Fig. 8, when TU was used as S source, the product was composed of NiS (JCPDS No. 02-1280) and Ni₃S₄ (JCPDS No.43-1469). Rod-like structures were obtained (Fig. 9a). If S source was replaced by TAA, the mixture of NiS (JCPDS No. 02-1280), NiS (JCPDS No. 12-0041) and Ni₃S₄ (JCPDS No. 43-1469) was achieved at the same experimental conditions (Fig. 9b). And morphology of the product was irregular particles. It is well accepted that H₂S and N₂H₄ released gradually as the decomposition of thiosemicarbazide with the increasing of temperature. Then, N₂H₄ may adopt a complexant to bind nickel ions 32 , forming Ni(N_2H_4)_3Cl_2 complex. Ni(N_2H_4)_3Cl_2 complex and H₂S reacted to form NiS original nuclei, which can be expressed as follows:

| $\mathrm{NH_2CSNHNH_2} + \mathrm{H_2O} \rightarrow \mathrm{H_2S} + \mathrm{N_2H_4} + \mathrm{CO_2} + \mathrm{NH_3}$ | (1) |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| $Ni^{2+} + 3N_2H_4 \rightarrow [Ni(N_2H_4)_3]^{2+}$ | (2) |
| $[\operatorname{Ni}(\operatorname{N}_2\operatorname{H}_4)_3]^{2+} + \operatorname{H}_2\operatorname{S} \rightarrow \operatorname{Ni}\operatorname{S} + 2[\operatorname{N}_2\operatorname{H}_5]^+ + \operatorname{N}_2\operatorname{H}_4$ | (3) |



Fig. 9 TEM images of products obtained with different S sources. S sources: (a) TU; (b) TAA.



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ARTICLE

Fig. 10 (a) CV curves and (b) the dependence of capacitance loss on the scan rate; (c) charge/discharge curves and (d) specific capacitance at various current densities.

3.3 Electrochemical properties of NiS hollow microspheres

NiS hollow microspheres were further evaluated as an electrode material for supercapacitors by cyclic voltammograms (CV) and galvanostatic charge/discharge (GCD) techniques using a three electrode system. Typical cyclic voltammograms at various scan rates (2-40 mV/s) are shown in Fig. 10a. Each cyclic voltammogram curve presents a pair of distinct redox peaks, which is different from the rectangular shape for conventional electric double-layer capacitor⁴⁰. This result indicates that the energy storage of NiS hollow microspheres were mainly ascribed to pseudocapacitance due to the following redox reaction^{41, 42, 29}.

$$+ OH^{-} \leftrightarrow NiSOH + e^{-}$$
 (4)

The voltammetric charge integrated from a positive or negative scan of cyclic voltammogram can be used as an effective signal in determining the pseudocapacitance. Accordingly, the average specific capacitance (C_s) of the sample was calculated by the following equation⁴³⁻⁴⁵.

NiS

$$C_{\rm s} = \frac{q}{\Delta Vm} = \frac{1}{mv\Delta V} \int i(V) dV$$
 (5)

Where, *m* is the mass of NiS hollow microspheres and *v* is scan rate, ΔV represents the potential window. The dependence of specific capacitance loss on the scan rate from 2 to 40 mV/s is illustrated in Fig. 10b. Increasing scan rate has a direct impact on the diffusion of OH⁻ into NiS hollow microspheres matrix⁴⁶. At low scan rate, OH⁻ can easily diffuse into the electrode. However, at high scan rate, OH⁻ will only approach the outer surface of the electrode, and the effective interaction between OH⁻ and the electrode is greatly reduced. The material located in the inner has little contribution to the capacitance.

The rate capability of electrode material is a significant consideration for practical applications of supercapacitor⁴⁷. Fig. 10c provides the GCD curves at different current densities in the voltage range between 0 and 0.4 V (*vs.* SCE). Obviously, there are voltage plateaus in all discharge curves, further supporting its typical Faradaic redox pseudocapacitance^{31,48}. The specific capacitance can be calculated according to Equation 6⁵.

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$$C_s = \frac{C}{m} = \frac{i \times \Delta t}{m \times \Delta V}$$
(6)

Where, C_s is the specific capacitance, *i* is the discharge current, Δt is the discharge time, ΔV represents the potential drop during discharge, and m is the mass of the active material within the electrode. NiS hollow microspheres electrode delivers high specific capacitance values of 1848.0, 1636.4, 1507.6, 1449.6, 1404.7, and 1372.9 F/g at the discharge current densities of 1, 2, 4, 6, 8 and 10 A/g, respectively (Fig. 10d), which are more competitive than NiS with various morphologies, such as 927 $F{\cdot}g^{{\cdot}1}$ for NiS hollow spheres $^{29}\!\!,\,857.76\,\,\text{F}\cdot\text{g}^{\text{-1}}$ for flower-like NiS $^{30}\!\!,\,$ and 893 $\text{F}\cdot\text{g}^{\text{-1}}$ for NiS nanoparticles⁴⁹. The specific capacitance gradually decreased with the increase of current density due to the incremental IR drop and insufficient active material involved in redox reaction at higher current densities^{50, 51}. Besides, at higher current densities, OH ions on the electrode decrease with the increase of current, whereas OH⁻ ions in the solution diffuse too slowly to meet the need of ions near the interface during charge/discharge process^{52,53}. 74.3% of the specific capacitance was still retained when the discharge rate increased from 1 to 10 A/g. Therefore, NiS hollow microspheres electrode not only exhibits large specific capacitance but also maintains them well at higher current densities. The outstanding electrochemical performance of NiS hollow microspheres electrode could be attributed to its unique structure.

Electrochemical impedance spectroscopy (EIS) was conducted to evaluate the charge transfer and electrolyte diffusion in the electrode/electrolyte interface and the corresponding Nyquist plots are shown in Fig. 11. Obviously, the EIS of NiS hollow microspheres electrode was composed of a semicircle in the high frequency region and a straight line in the low frequency region. The internal resistance (R_b) can be obtained from the intercept of the plot with the real axis in the high frequency region. After 1000 cycles R_b value increased from 1.23 Ω to 1.26 $\Omega.$ The small semicircle corresponds to the low charge transfer resistance (R_{ct}) of the electrodes. The low R_{ct} leads to better rate capability because R_{ct} acts a limiting factor for fast charge and discharge of supercapacitor⁵⁴. The R_{ct} value became larger after 1000 cycles. The increase of R_b and R_{ct} values may be attributed to the collapse of hollow microspheres. At low frequency region, the straight line represents the diffusive resistance (Warburg impedance). NiS hollow microspheres electrode exhibits very low Warburg impedance before 1000 cycles, which will facilitate the diffusion of OH⁻ ions into the electrode. Therefore, NiS hollow microspheres with an impressive electrochemical capacitive property could be achieved.

Long cycle lifetime is another critical requirement for practical applications of supercapacitors^{55,56}. Cycle stability of NiS hollow microspheres electrodes was examined by CV measurement. Specific capacitance retention of NiS hollow microspheres electrode over 1000 times of continuous cycling at a scan rate of 50 mV/s is shown in Fig. 12. The specific capacitance is 480.3 F/g and 493.8 F/g for the 1st cycle and 1000th cycle, respectively. Continuous CV characterization indicates that NiS hollow microspheres electrode has excellent electrochemical cycle stability.

In order to highlight the superiority of hollow microspheres, the electrochemical properties of NiS solid microspheres were also performed by CV and GCD measurements (Fig. 13). Compared to NiS hollow microspheres, the similar figures are obtained for NiS

solid microspheres. However, the specific capacitances are only 85.2% and 82.5% of those for NiS hollow microspheres at scan rate of 2 mV/s and discharge current density at 1 A/g, respectively. This result may be attributed to the unique hollow and mesoporous structure of NiS hollow microspheres.



Fig. 11 Nyquist plots of NiS hollow microspheres electrode.



Fig. 12 Electrochemical cycle stability of NiS hollow microspheres electrode at scan rate of 50 mV/s.



Fig. 13 (a) CV curves and (b) the dependence of capacitance loss on the scan rate; (c) charge/discharge curves and (d) specific capacitance at various current densities of NiS solid microspheres.

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4. Conclusions

In summary, NiS hollow microspheres with mesoporous shells were successfully synthesized through a facile hydrothermal route using nickel chloride hexahydrate as nickel source and thiosemicarbazide as sulfur source, respectively. The NH₂-NH- group in the thiosemicarbazide molecule plays a vital role for the formation of NiS hollow microstructures. Ostwald ripening mechanism was proposed to explain the formation of NiS hollow microspheres. When tested in electrodes for supercapacitors, NiS hollow microspheres with mesoporous shells exhibit a high specific capacitance and excellent cycle stability, which suggests that the NiS hollow microspheres with mesoporous shells could be a promising candidate electrode material for supercapacitors.

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Graphical Abstract



NiS hollow microspheres with excellent capacitive performance were prepared by a

facile hydrothermal route without any surfactant or template.