RESEARCH PAPER



Hydrothermal Synthesis of CuCo₂S₄ Nano-structure and N-Doped Graphene for High-Performance Aqueous Asymmetric Supercapacitors

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Recently, transition metal sulfides have drawn a lot of attention due to their potential application in energy and environmental fields. In this paper, we present a simple and facile method for preparing $CuCo_2S_4$ nanoparticles as high performance supercapacitor electrode materials. Electrochemical measurements exhibit that the $CuCo_2S_4$ nanoparticles electrode has a high specific capacitance of (190 C g⁻¹ at 1A g⁻¹), relatively high rate capability (46 % capacitance retention at 10A g⁻¹) and good cycling stability (77 % of the initial specific capacitance can be maintained after 3000 cycles at 4A g⁻¹). When fabricated as aqueous asymmetric supercapacitor by using $CuCo_2S_4$ nanoparticles and N-doped graphene (NG) composites as the positive electrode and the negative electrode, respectively. The assembled device exhibits a high energy density of 32.7 Wh kg⁻¹ at a power density of 794 W kg⁻¹. And it still operates at a high power density of 6.4 kW kg⁻¹ with an energy density of 19.5 Wh kg⁻¹. Moreover, after 6000 consecutive GCD cycles at a current density of 4 A g⁻¹, 78.0 % of the initial capacitance value can be maintained. These attractive results manifest that $CuCo_2S_4/NG$ hold a great potential for practical applications in the field of energy storage system.

Keywords: Transition metal sulfides; Electrode material; Aqueous asymmetric supercapacitors; Assembled device

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1. Introduction

With continuous increase in the demand for fossil fuels and the consumption of non-renewable energy and global warming challenge, there is an urgent demand for developing cleaner and more efficient energy storage systems, such as fuel cells, lithium-ion batteries and supercapacitors (SCs).¹⁻³ Among them, supercapacitors have been considered as one of the most promising energy storage devices due to their relatively higher power density, quicker charge/discharge capability and longer recyclability compared with conventional rechargeable such as lithium-ion batteries.45 SCs can be divided into two types by different energy storage mechanisms: electrical double-layer capacitors and faradaic redox reaction pseudo capacitors.⁶ However, supercapacitor has low potential window and an order of magnitude lower energy density compared with batteries in practical application. Recently, battery-type faradaic electrodes are emerging as possible solution to over come the lagging status with respect to energy density by taking advantage of enhanced charge storage originating from deep surface faradaic processes. In order to improve the performance of battery-type capacitor, a sequence of transition metal oxides have been investigated as electrodes materials, such as mixed or ternary metal oxides with two different metal cations. For example, NiCo₂O₄,⁷ CuCo₂O₄,⁸ and

MnCo2O4,9 and have attracted numerous attentions in energy storage fields due to their high erelectroactivity and charge capacity. Unfortunately the applications of these materials are mainly restricted by various aspects as low energy capacity and poor cycle life. Meanwhile, a number of researchers have been engaged in developing transition metal sulfides, which have been considered as notable electrode materials for battery-type faradaic electrodes since they exhibit lower electronegativity, higher specific capacitance and richer redox reactions compared with corresponding oxides.¹⁰ As a kind of the most significant transition metal sulfides, CuCo2S4 sparked worldwide interest as an attractive battery-type faradaic electrode to fabricate advanced capacitor devices for the presence of Cu⁺/Cu²⁺ and Co²⁺/Co³⁺ redox couples in the spinel structure." What are markable that the addition of Co can largely facilitate electron transport. Significantly, CuCo₂S₄ has also been used in many other fields such as water oxidation and Li ion batteries.12 The excellent performance in the fields of lithium and oxygen reduction confirms that CuCo₂S₄ has enormous potential in the application of electrochemical reactions. Graphene has received significant attention because of its extraordinary electrical conductivity, high surface area, and good mechanical properties. Compared with other carbonaceous materials, including carbon nanotubes, activated carbons, and carbide derived carbons, graphene with hierarchical nanosheets structures can achieve superior electrochemical properties due to their large specific surface area, superior elasticity, chemical stability, and excellent electrical conductivity. But the capacitance of pure graphene is fundamentally limited by its electrical double layer capacitance mechanism. Recently, researchers reported that the introducing of N-element could improve the electrochemical performance of graphene flakes, such as specific capacitance, cycle

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stability and son on.¹³ S. Suresh Balaji¹⁴ reported that two-dimensional N-doped graphene flakes possessed high specific capacitance and good cycle stability. Sun¹⁵ fabricated nitrogen-doped graphene, which facilitated the rapid transport of the electrolyte. Herein, we demonstrate a strategy with aspartic acid as a nitrogen source to prepared coiled flake nitrogen-doped graphene. Coiled flakeare important for enhancing exposed surface area and facilitating electrolyte ion transport for energy storage.

How to design and synthesize advance delectrode materialsin inexpensive raw material and easy fabrication processes for battery-type supercapacitor, which can enhance power density due to its high electrochemical reactivity caused by fast redox reaction remains challenges. In the past year, various studies have been carried out to address these challenges. Different nanostructures have been developed such as nanorods,¹⁶ nanowires,¹² nanocubes,¹⁷ microspheres,¹⁸ nanosheets¹⁹ and core-shell hybrid nanostructures.²⁰ Despite these developments, there are still more space to improve the morphological structure through easier process and use of inexpensive materials.

Present work aims to enchance the electrochemical performance of battery-type capacitor to further improve the morphological structure of electrode material. Polyvinyl pyrrolidone (PVP), as a growth modifier and surface stabilizer, was used to synthesize CuCo₂S₄ nanoparticles by hydrothermal method. And a novel asymmetric supercapacitor was fabricated using CuCo₂S₄ and NG as the anode electrode and the cathode electrode, respecitively. The rational design of the asymmetric device afforded outstanding electrochemical performance with a high energy density of 32.7 Wh kg⁻¹ at a power density of 794 W kg⁻¹ and a high power density of 6.4 kW kg⁻¹ with an energy density of 19.5 W h kg⁻¹. Furthermore, the CuCo₂S₄/NG maintains 78.0 % initial capacitance after 6000 cycles at current density of 4 A g⁻¹. These attractive results show that CuCo₂S₄/NG is inspired in the energy storage system for practical applications.

2. Experimental section

All the chemicals were of analytical grade and used without further purification.

2.1 Synthesis of CuCo₂S₄ Nanoparticles

In a typical synthesis procedure, 2.5 mmol Cu(NO₃)₂ • 6H₂O, 5mmol CoCl₂ • 2H₂O, 15 mmol HMT(C₆H₁₂N₄) and 1g PVP were dissolved in 70 mL distilled water. Then the mixed suspension was transferred into a 100 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and subjected to heat treatment at 95 °C for 10 h. After being cooled to room temperature naturally, the product was carefully cleaned with deionized water and absolute ethanol. Then the obtained hydroxides were annealed in air at 350 °C for 3 h with a heating rate of 1 °C min⁻¹. Finally, the CuCo₂S₄ were fabricated by placing hydroxide nanoparticles in a Teflon-lined stainless steel autoclave kept at 160 °C for 8h containing 25 mmol Na₂S • 9H₂O aqueous solution and the final product was cleaned with distilled water and dried in vacuum then dried at 60 °C overnight.

2.2 Synthesis of N-doped Graphene (NG) Aerogel

Graphene oxide (GO) was prepared by a modified Hummers method in our previous paper.²¹ N-doped graphene aerogel (NG) was synthesized as following: 150 mg aspartic acid was suspended in 30 mL of GO aqueous dispersion (2mg mL⁻¹) and thoroughly dispersed with ultrasonic treatment for 15 min. The solution was transferred to a 50 ml Teflonlined autoclave and kept at 160 °C for 3 h. Then the resulting products were collected, washed with deionized water for several times and freeze-dried.

2.3 Materials Characterization

The phase composition and chemical valence states of the obtained materials were investigated by X-ray diffraction (XRD, Bruker D8, Cu-K α radiation λ =1.5406 Å) and X-ray photoelectron spectroscopy (XPS) were performed on an ESCALAB 250Xi electron spectrometer (Thermo Fisher Scientific) using an Al-K α radiation. The morphology and microstructure of synthesized materials were characterized by scanning electron microscopy (SEM, S-4800, Japan) equipped with an electron dispersive spectroscopy (EDS) and transmission electron microscopy (TEM, JEM-2100F, Japan).

2.4 Electrochemical Characterization

All the electrochemical performance was conducted using a threeelectrode system in 3M aqueous KOH electrolyte with Pt as the counter electrode and Hg/HgO as the reference electrode, respectively. For preparation of the working electrode, the as-synthesized samples were mixed with acetylene black and poly-(tetrauoroethylene) in a mass ratio of 8:1:1 by adding a small quantity of ethanol. The mixture was stirred adequately to form a homogeneous slurry, and then coated and pressed onto a nickel foam $(1 \times 1 \text{ cm}^2)$ current collector and dried at 60 °C under vacuum. The mass loading of the active material was about 3.0 mg. All of the electrochemical performance of electrodes were carried out by a CHI 760E electrochemical workstation. The specific capacitance of the battery-type electrode was calculated from the charge-discharge curve based on the following equation:²²

$$Cs = \frac{1000 \times i \times t}{3600 \times m} \times 3.6 \tag{1}$$

where Cs, *i*, t, m represents the specific capacity (C g^{-1}), the current applied (A), the discharge time (s), and the mass of active materials, respectively. Energy density (E, Wh kg⁻¹) and power density (P, W kg⁻¹) of the device can be evaluated according to the following equations²⁵:

$$\mathbf{E} = \frac{\int I \times V(t) dt}{1000 \times 3600} \tag{2}$$

$$P = \frac{E \times 3600}{\Delta t}$$
(3)

where I (A g⁻¹) is the current density, V(t) (V) is the cell voltage, dt (s) is the time differential and Δt (s) is the discharge time.

3. Resultand Discussion

3.1 Synthesis and Characterization

X-ray diffraction(XRD) patterns of CuCo_2S_4 and CuCo_2O_4 were shown in Fig.1a. The diffraction peaks located at 16.1°, 26.6°, 31.2°, 37.9°, 46.9°, 49.9°, 54.8°, 57.6°, 64.4°, 68.5° correspond to the respective (111), (220), (311), (400), (422), (511), (440), (531), (533) and (444) planes of CuCo_2S_4 (JCPDS card no.09-0425). All reflection peaks of the CuCo_2O_4 (Fig. 1a) also can be indexed to the cubic phase CuCo_2O_4 , in good accordance with there ported values from the JCPDS card (no. 01-1155). Note that, there are no extra peaks detected afterwards, implying the purity of all synthesized samples.

To identify elemental composition and electronic structure of the samples, the characterization of X-ray photoelectron spectroscopy (XPS) was carried out. Fig. 1 (b) is the survey spectrum of the sample, wherein the attributions of all the peaks have been marked. Evidently,

all the peaks can be ascribed to the elements Cu, Co, O, C, and S. The C (as reference) elements can be attributed to the exposure of air. So, the chemical composition in the near-surface range of the product is Cu, Co, S and O, which is in good agreement with our experiment. The Cu 2p, Co 2p, and S 2p high-resolution XPS spectra were fitted by gaussian fitting method considering two spin-orbit doublets and shakeup satellites (marked as "Sat."). As regards the Cu 2p XPS spectrum, the binding energies at 932.2 eV in Cu 2p₃₂ and 952.1 eV in Cu $2p_{1/2}$ are characteristic of Cu⁺²⁴. In Fig.1(c), the binding energies of 778.76 eV and 796.35 eV of the Co 2p peaks are assigned to Co^{3+} and the binding energies²⁵ of 782.32 eV and 797.70 eV to Co²⁺. For the Co 2p spectrum, two distinguished doublets are shown at low-energy (Co 2p₃₂) and high energy bands (Co 2p₁₂). Moreover, the spin-energy separation value of Co $2p_{\scriptscriptstyle 1/2}$ and Co $2p_{\scriptscriptstyle 3/2}$ is over 15 eV, indicating the coexistence²⁶ of Co^{2+} and Co^{3+} . In the Fig. 1(d), the core-level spectrum of S 2p region and the binding energy of 161.8 eV are corresponding to S 2p_{3/2}. The peak centered at about 162.98 eV is consistent with the binding energies of metal-sulfur bonding (Ni-S and Co-S bonding)²⁷. The binding energy of 169.06 eV is attributed to shakeup satellites

(indicated as "Sat."). In addition, the detailed O 1s spectrum was presented in Fig. 1(f), exhibits three oxygen bonding features. The peak of O1 at 529.53 eV is a typical metal-oxygen bond,²⁸ while the peak of O2 at 531.13 eV are corresponding to a high number of defect sites with low oxygen coordination in the material with a small particle size.²⁹ And the peak of O3 at 532.93 eV can be ascribed to physically and chemically adsorbed water on the surface.¹³ According to the XPS analysis, the near-surface composition of the CuCo₂S₄ sample is composed of Co²⁺, Co³⁺, Cu²⁺ and S²⁻, ^{12, 15, 30} which match well with the molecular formula of CuCo₂S₄.

The morphologies of the as-synthesized CuCo_2S_4 and CuCo_2O_4 were characterized by SEM (Fig. 2). It is obvious that the assynthesized CuCo_2S_4 is composed of nanoparticles. In the first step of the hydrothermal process, the OH ions gradually were released by the hydrolysis of hexamethylenetetramine (HMT) at high temperature, facilitating the formation and uniform assembly $\text{CuCo}(\text{OH})_x$ nanoparticles. Then the $\text{CuCo}(\text{OH})_x$ releases OH via high temperature calcinationto obtain CuCo_2O_4 nanoparticles.³¹ After sulfidation reaction, it can be clearly seen (Fig. 2a and b) that the CuCo_2S_4 emerge a



Fig. 1 Crystallography and chemical states of copper, cobalt-based examples: (a) XRD patterns of $CuCo_2S_4$ and $CuCo_2O_4$, (b) XPS survey spectrum and high resolution XPS spectra of (c) Cu 2p, (d) Co2p, (e) S 2p, and (f) O 1s for Cu-Co oxysulfide.

relatively uniform nanoparticles morphology and are homogeneously distributed. And the surfaces of nanoparticles are smooth and there are no obvious defects, which are benefitting for faradaic reactions. Instead, for $CuCo_2O_4$ (Fig. 2c and d), the edges of nanoparticles are dimmed, and the top surface is not smooth any more instead of being full with desultory nanoparticles after calcination. Bulk materials usually possess limited electrochemical active sites and will increase the conduction resistance of ion/electrons, hence resulting in unsatisfactory electrochemical performance.

The detailed microstructures of $CuCo_2S_4$ and $CuCo_2O_4$ were characterized by TEM and HRTEM. TEM images of $CuCo_2S_4$ with different magnifications are shown in Fig. 3a-b. It can be observed that

the CuCo₂S₄ sample contains numerous nanoparticles with the diameter about 50-60 nm, confirmed to the SEM tests. The nanoparticles structure effectively pushes up the amount of electroactive sites and can greatly increase the electrode/electrolyte contact interface and enhance ion and electron diffusion. Fig. 3d-e are typical TEM images of CuCo₂O₄ with different magnifications. The Fig. 3d clearly illustrates a large number of disordered CuCo₂S₄ nanoparticles which are interconnected with each other in the range of 3-6 nm. And these nanoparticles with very small gap could facilitate rapid redox reactions and increase the contact area between the electrode and electrolyte. From the HRTEM of Fig. 3f, the crystal lattices with d-spacing of ~0.32 and ~0.405 nm correspond to the (511) and (731) planes of CuCo₂S₄,



Fig. 2 SEM images of CuCo₂S₄(a,b) and CuCo₂O₄(c,d) at different magnifications.



Fig.3 TEM and HRTEM images of (a-c)CuCo₂S₄, (d-f) CuCo₂O₄.



Fig. 4 Dark-field STEM elemental mapping analysis of the $CuCo_2S_4$ nanoparticles (a) selected area and corresponding elemental mapping of (b) cobalt, (c) copper, (d) sulfur, and (e) STEM-EDS elemental line mapping images of $CuCo_2S_4$ nanoparticles.



Fig. 5 Electrochemical performances using a three-electrode mode in 3 KOH aqueous electrolyte. CV curves of (a) $CuCo_2S_4$ (b) $CuCo_2O_4$ electrode at various scanrates ranging from 1-20 mV s⁻¹. GCD curves of (c) $CuCo_2S_4$ (d) $CuCo_2O_4$ electrode at various current densities in the voltage range of 0-0.45 V. (e) Comparative of specific capacitance of $CuCo_2S_4$ and $CuCo_2O_4$ at various current densities in 3 M KOH aqueous solution. (f) Cycling stability of $CuCo_2S_4$ and $CuCo_2O_4$ at current densities in 3 M KOH aqueous solution. (f) Cycling stability of $CuCo_2S_4$ and $CuCo_2O_4$ at current densities in 3 M KOH aqueous solution.

while the d-spacings of 0.305 and 0.409 nm correspond to the (422) and (533) planes of the CuCo₂O₄ crystal (Fig. 3c), respectively, which are well consistent with the XRD result. Furthermore, The SAED pattern of image (Fig. S1[†]) further demonstrates that CuCo₂S₄ nanoparticles are single-crystal structure.

The elemental distribution and composition of $CuCo_2S_4$ nanoparticles were further investigated by STEM with energy dispersive X-ray spectroscopy (EDS) analysis. The dark-field STEM images as well as the corresponding cobalt, copper and sulfur mappings are shown in Fig. 4. The EDS mapping showed that cobalt, copper, and sulfur were well dispersed, which is consistent with the TEM results. The STEM-EDS line mapping (Fig. 4g) clearly revealed that the synthesized $CuCo_2S_4$ nanoparticles consist of Co, S, and Cu. Meanwhile, the elemental distribution and composition of $CuCo_2O_4$ nanoparticles were also investigated by STEM with energy dispersive X-ray spectroscopy (EDS) in the Fig.S2[†].

To verify the superiority of the $CuCo_2S_4$ after sulfurization, the electrochemical performance of $CuCo_2S_4$ and $CuCo_2O_4$ were investigated, respectively. As shown in Fig. 5a-b, the CV curves of $CuCo_2S_4$ and $CuCo_2O_4$ reveal the faradic nature attributed to M-S/M-S-

OH of the battery-type electrodes, where M represents both Cu and Co ions.12 Notably, the CV curves of samples show adistinct pair of redox peaks. Moreover, the redox peaks of CuCo2O4 represent more obvious than CuCo₂S₄ indicating more faradic reaction occurred. Fig. 5c-d shows the GCD tests that were performed within the voltage range of 0-0.45 V. From the GCD plots, the CuCo₂S₄ exhibited specific capacities of ~190, 167, 152, 129, 103, and 88.3 C g^{-1} , at 1, 2, 3, 5, 8, and 10 A g^{-1} . In contrast, the CuCo₂O₄ delivers good capacities of ~82, 75, 67, 57, 43 and 35 C g⁻¹ under the same series of current densities (seen from Fig. 5d). Compared with $CuCo_2O_4$, the straight line of $CuCo_2S_4$ is nearly perpendicular to the real axis, indicating higher capacitive behavior. In addition, cycling stability of CuCo₂S₄ and CuCo₂O₄ were also evaluated by the long-term cycling performance at the constant current density of 4A g⁻¹ and the results were shown in Fig. 5f. 71% of the initial specific capacity can be maintained after 3000 cycles. However, specific capacity of the CuCo₂S₄ still remains 77 % of the initial specific capacity retention. The comparison of the electrochemical performance of the $CuCo_{3}S_{4}$ between this work and other studies reported in the literature were listed in the form of a table (Table S1[†]in Supporting Information). These results suggest that the CuCo₂S₄ with unique structure exhibits a



Fig. 6 (a) CV curves of $CuCo_2S_4/NG$ cell at different voltage windows in a 3 M KOH electrolyte at a current density of $5mV s^{-1}$. (b) CV curves measured between 0 and 1.6 V with different scan rates from 2 to 50 mV s⁻¹. (c) GCD curves of $CuCo_2S_4/NG$ at various current densities in the voltage range of 0-0.45 V. (d) Specific capacitance versus current density curves. (e) Ragone plot of the ASC device for comparison. (f) Cycling performance of the $CuCo_2S_4/NG$ at a current density of 4A g⁻¹.

good long-term stability than that of CuCo2O4.

To further evaluate the $CuCo_2S_4$ electrode for practical applications, a novel ASC as developed using CuCo₂S₄ and NG as the cathode and anode electrodes, respectively. A series of CV and the GCD curves of the NG at various scan rates ranging from 2 to 50 mV s⁻¹ in a 3 M KOH aqueous electrolyte were shown in Fig. S2[†]of SI[†]. Fig. 6a shows the CV curves of the asymmetric supercapacitor cell at different voltage windows in a 3 M KOH electrolyte at a scan rate of 5 mV s⁻¹. It is noted that the stable electrochemical window of the asymmetric supercapacitor cell voltage can be extended to 1.6 V. Fig. 6b presents the CV curves of $CuCo_2S_4$ //NG ASC at different scan rates from 2 to 50 mV s⁻¹ within a 0-1.6 V potential window. The ASC device shows a relatively quasi-rectangular CV shape with weak redox peaks, which indicates CuCo2S4/NG exhibiting good capacitive behavior with the combination of EDLC and pseudocapacitance. With the increase of scan rate from 2 to 50 mV s⁻¹, the shapes of the CV curves of the device do not change, implying the desirable rapid charge/discharge characteristic for supercapacitors. Fig. 6c shows the GCD curves of CuCo₂S₄//NG ASC with cell voltage as high as 1.6 V at various current densities from 1 to 8 A g⁻¹. During the charge/discharge procedure, the charge curves of CuCo₂S₄//NG ASC are almost symmetrical to its corresponding discharge counterpart, confirming the excellent electrochemical reversibility. The Cs of the CuCo_2S_4/NG ASC based on the total mass of the device was calculated from the charge/discharge curves according to eq. (1). The values of Cs are 148, 131, 117, 109, and 88 C g^{-1} at current densities of 1, 2, 3, 5, 8 A g⁻¹, as shown in Fig. 6c. The energy and power densities are calculated according to eq. (2) and (3) to further demonstrate the electrochemical performance of the supercapacitors, as shown in Fig. 6e. Remarkably, the present device displays a high energy density about 32.7 Wh kg⁻¹ at a power density of 794 W kg⁻¹, which confirms the superiority of our device compared to the other reported ASC. For example, NiMoO₄//NGO (30.3 W h kg⁻¹ at 187 W kg⁻¹),³² NiCo₂S₄//RGO (31.5 W h kg⁻¹ at 156.6 W kg⁻¹),³³ CuCo₂O₄//AC (18 W h $kg^{\text{-1}}$ at 259 W $kg^{\text{-1}}),^{\text{34}}$ and CuS//AC (15.06 Whkg^{\text{-1}} at 392.9 W $kg^{\text{-1}}).^{\text{35}}$ The cycling performance of the CuCo2S4/NG ASC is also tested (Fig. 6f). After 6000 consecutive GCD cycles at acurrent density of 4 A g⁻¹, 78 % of the initial specific capacitance can be maintained. This reveals that CuCo₂S₄ nanoparticles are a class of promising electrode materials for supercapacitors.

4. Conclusions

In conclusion, $CuCo_2S_4$ nano-structure was successfully synthesized through a facile hydrothermal method for electrochemical energy storage. The efficient and low-cost fabrication method involves the hydrothermal method and anion-exchange reaction. $CuCo_2S_4$ delivers a high specific capacity of 190 C g⁻¹ at 1 A g⁻¹, as well as good rate capability and long cycle stability, which are mainly owing to good mechanical and electrical contact with electrolyte ions and electrons, low crystallinity and good wettability without an annealing process, rich redox reactions, as well as high conductivity and transport rate. An asymmetric supercapacitor cell was fabricated with $CuCo_2S_4$ nanoparticles and NG as anode and cathode electrode, respectively, which exhibits a high energy density of 32.7 Wh kg⁻¹ at a power density of 794 W kg⁻¹. Our results suggest that $CuCo_2S_4$ nanoparticles can hold great promise for application in energy storage devices.

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