


One-pot synthesis of flake $\text{Cu}_{1.81}\text{S}/\text{C}$ composite for high-performance supercapacitors electrodes

Haihua Hu, Yanwei Sui , Yaoyao Zhou, Jiqiu Qi, Fuxiang Wei, Yezeng He, Qingkun Meng, Zhi Sun, Yulong Zhao

School of Materials Science and Engineering, China University of Mining and Technology, Xuzhou 221116, People's Republic of China

✉ E-mail: wyds123456@outlook.com

Published in Micro & Nano Letters; Received on 10th June 2016; Revised on 2nd October 2016; Accepted on 11th October 2016

One-pot fabrication of flake $\text{Cu}_{1.81}\text{S}/\text{C}$ composite with size of 300 nm was successfully demonstrated in this work. As the supercapacitor electrode material, the obtained $\text{Cu}_{1.81}\text{S}/\text{C}$ composite sample displayed good cycling stability of 83.6% capacitance retention after 1000 cycles and high specific capacitance of 617 F g^{-1} at current density of 0.5 A g^{-1} . The excellent electrochemical performance is mainly attributed to flake nanostructure, which provides large electrode-electrolyte contact area and facilitates an easy access of electrolyte ions to the electrode surface. This result provides a new pathway for the fabrication of high-performance electrode material for supercapacitors.

1. Introduction: Supercapacitors (SCs), with high specific power density and long cycle lives represent a unique sort of energy storage device, which have attracted extensive attention in recent years [1–3].

Pseudocapacitors, one type of SCs, store charges through rapid and reversible electrochemical redox reactions from electrodes such as metal oxides/hydroxides, metal sulphides and conducting polymers which are able to provide high specific capacitance and energy density [4–7]. Recently, metal sulphides have been widely proposed for the SCs because of the excellent electroactive abilities [8–11]. As important metal sulphides, copper sulphides exhibit many different stoichiometric composition in a wide range from Cu_2S at the copper-rich side to CuS_2 at the copper-deficient side [12], including CuS nanowire arrays (305 F g^{-1} at 0.6 mA cm^{-2}) [13], $\text{Cu}_{7.2}\text{S}_4$ sub-microspheres (491.5 F g^{-1} at 1 A g^{-1}) [14]. However, up to now there exist no reports about the electrochemical properties of $\text{Cu}_{1.81}\text{S}$ electrode, and no doubt, $\text{Cu}_{1.81}\text{S}/\text{C}$ composite is possible to have been used in SCs.

In this work, a one-pot method was developed to synthesise $\text{Cu}_{1.81}\text{S}/\text{C}$ composite with novel flake nanostructure. What's more, the obtained sample showed excellent cycling stability and high specific capacitance, due to nanoflake structure providing a large contact area with electrolyte.

2. Experimental

2.1. Chemical and synthesis: All the reagents were analytical grade and used without any further purification. The $\text{Cu}_{1.81}\text{S}/\text{C}$ composite was prepared by a one-step sulphidation method. In a typical process, 1.5 g copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) and 3.0 g benzene-1,3,5-tricarboxylic acid ($\text{C}_6\text{H}_3(\text{COOH})_3$) were dissolved in a 5 ml and 55 ml methanol under ultrasonication for 1.5 h, respectively. Then, the two solutions were mixed vigorously for 10 s. and the solution was placed at room temperature for 12 h until blue precipitation finished. Finally, we collected the precipitation with centrifugal machine and dried in vacuum at 70°C for 12 h. During the final sulphidation process, 0.2 g precipitation and 0.08 g sublimed sulphur were put into a combustion boat and then heated to 650°C at the rate of 2°C min^{-1} and kept at 650°C for 2 h under an argon flow in a tube furnace.

2.2. Characterisation of materials: The crystal structures and morphologies of the as-prepared product was characterised by

X-ray diffraction (XRD, D8 Advance, Bruker, Germany), Hitachi SU-70 scanning electron microscopy (SEM), FEI Tecnai G2 F20 transmission electron microscopy (TEM) and selected area electron diffraction (SAED).

2.3. Electrochemical measurements: The electrochemical measurements were all conducted on a CHI 660E electrochemical workstation (Shanghai, Chenhua) in a three-electrode arrangement with a Pt plate as counter electrode and a Hg/HgO electrode as reference electrode, with 1 M KOH as the electrolyte. The working electrodes were prepared by mixing by active materials ($\text{Cu}_{1.81}\text{S}/\text{C}$), carbon black and polyvinylidene difluoride in a weight ratio of 8:1:1 to form viscous slurry. Afterwards, the slurry was spread onto a piece of $1.0 \times 2.0 \text{ cm}$ nickel foam, and then dried under vacuum at 70°C for 3 h. The electrochemical properties of the supercapacitor electrodes were characterised by cyclic voltammetry (CV), galvanostatic charge–discharge. The specific capacitance C can be calculated according to the following equation [15]

$$C = \frac{I\Delta t}{m\Delta V} \quad (1)$$

where I is the discharge current, Δt is total discharge time, and m

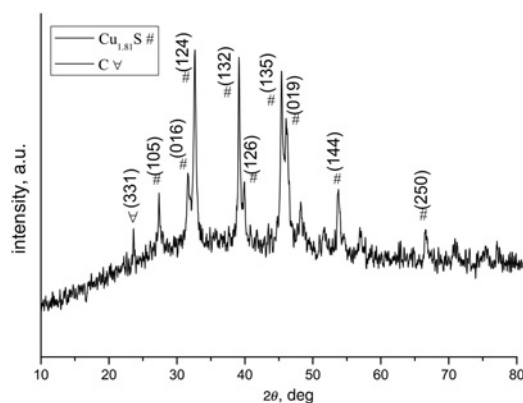


Fig. 1 XRD pattern of $\text{Cu}_{1.81}\text{S}/\text{C}$ composite

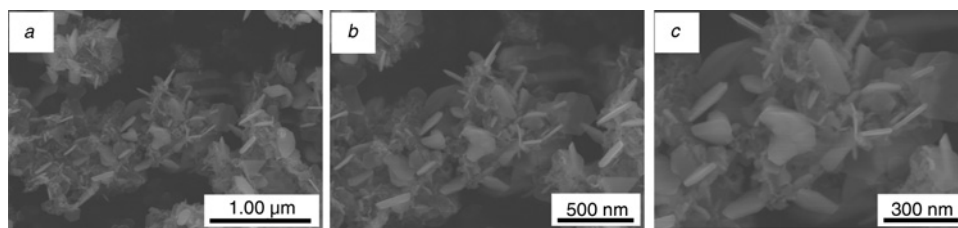


Fig. 2 a–c SEM images of flake $\text{Cu}_{1.81}\text{S}/\text{C}$ nanoparticles with different magnification

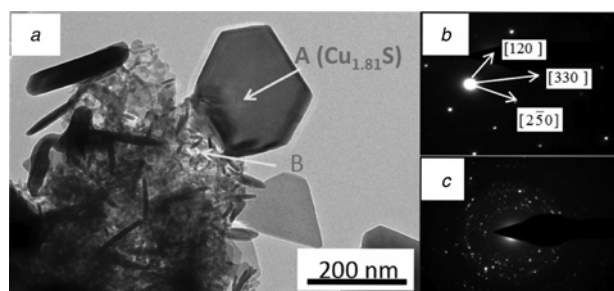


Fig. 3 a TEM image of heart-shaped flake particle in Fig. 2c, b SAED image of A particle in a, and c SAED image of B particle in a

and ΔV represent the weight of the active materials and total potential difference, respectively.

3. Results and discussion: The XRD pattern of the obtained sample are shown in Fig. 1. All diffraction pattern present peaks that can be successfully indexed to those phase of $\text{Cu}_{1.81}\text{S}$ (JCPDS Card No. 41-0959) except the diffraction peak around 27.4° which corresponds to the (331) diffraction peak of C

(JCPDS Card No. 44-0558) could be found in the pattern, indicating that the as-prepared sample was $\text{Cu}_{1.81}\text{S}/\text{C}$ composite.

The morphology and structure of the as-prepared sample were investigated by SEM and TEM technique. As shown in Figs. 2a–c, we can clearly observe that the sample is mainly composed by irregular flake nanoparticles with an average size of about 300 nm. The TEM image in Fig. 3a further confirm that the sample is composed of nanoflake particles, which is consistent with the above SEM results. To further confirm the component of the sample, SAED patterns (Figs. 3b and c) are taken from the marked area A and B in Fig. 3a, respectively. Fig. 3b indicates the single crystalline nature of the flake area A, corresponding well to the (250) plane of flake $\text{Cu}_{1.81}\text{S}$. Fig. 3c illustrates the polycrystalline nature of $\text{Cu}_{1.81}\text{S}/\text{C}$ sample, however, the image is not characteristic due to irregular placement of flake particles.

The CV is regarded as a perfect technique to investigate the capacitive behaviour of electrode materials. The CV curves displayed in Fig. 4a were achieved at scan rates ranging from 10 to 100 mV s^{-1} in a potential window from -0.6 to 0.4 V (against Hg/HgO). Obviously, one pair of well-defined redox peaks was exhibited in the CV curves, indicating that the capacitance characteristics were mainly governed by Faradaic redox reactions. It should be noted that the current density generated by the nickel foam is very low based on the CV areas, as compared with that of the

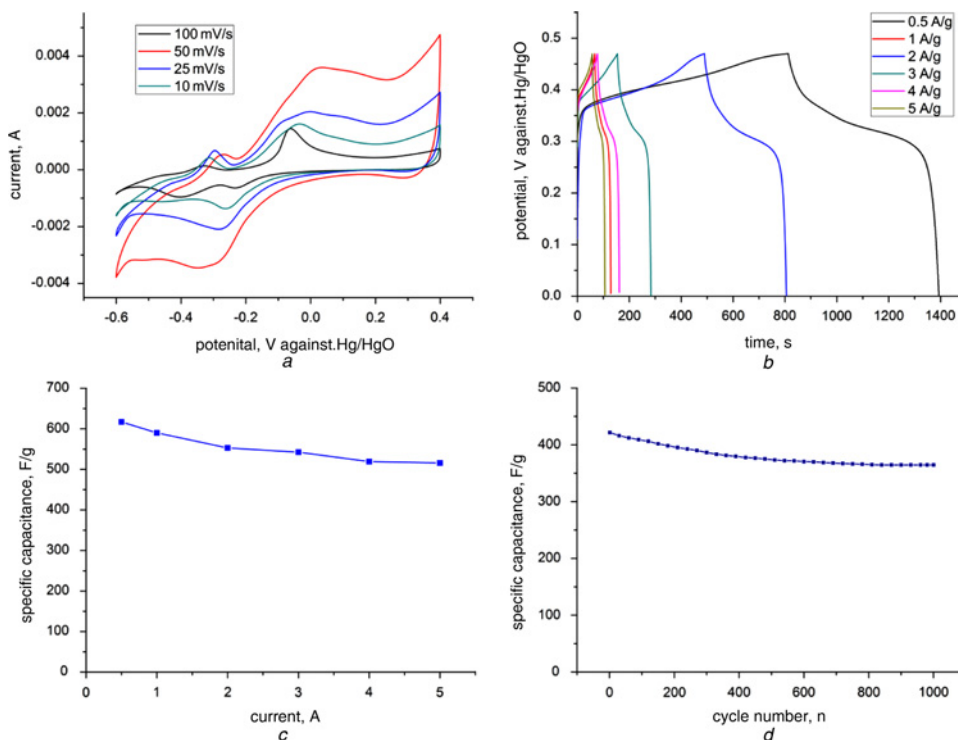
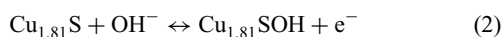


Fig. 4 a CV curves of $\text{Cu}_{1.81}\text{S}/\text{C}$ electrode, b Galvanostatic charge/discharge curves of $\text{Cu}_{1.81}\text{S}/\text{C}$ composites at different current densities, c Specific capacitance as a function of current density, and d Cyclic performance of $\text{Cu}_{1.81}\text{S}/\text{C}$ at 10 A g^{-1}

active material [16]. Therefore, the capacitance is mainly attributed to the Cu_{1.81}S/C composite. The redox peaks corresponding to the reversible redox reaction could be expressed as



Moreover, the shape of the CV curves is not changed with the increase of scan rate, suggesting that the as-prepared nanoparticle favours fast redox reactions.

To further evaluate the electrochemical properties of Cu_{1.81}S/C electrode, galvanostatic charge/discharge measurements were conducted at various current densities (against Hg/HgO) and the results are displayed in Fig. 4b. The flake Cu_{1.81}S/C composite exhibited a specific capacitance of 617 F g⁻¹ at 0.5 A g⁻¹ and 516 F g⁻¹ at 5 A g⁻¹, and it was higher than some previous works which reported some other copper sulphides of CuS nanowire arrays (305 F g⁻¹ at 0.6 mA cm⁻¹), Cu_{1.96}S/C octahedra (200 F g⁻¹ at 0.5 A g⁻¹) [17], and CuS/polypyrrole composites (427 F g⁻¹ at 1 A g⁻¹) [18].

The specific capacitance of the sample can be calculated based on the charge–discharge curves and the results are illustrated in Fig. 4c. The specific capacitances are as high as 617, 590, 553, 542.6, 519.2 and 516 F g⁻¹ at discharge current densities of 0.5, 1, 2, 3, 4 and 5 A g⁻¹, respectively. The sample exhibited approximately a 83.6% specific capacitance retention with the current density increasing from 0.5 to 5 A g⁻¹, suggesting a good rate capability.

To get more information of the electrochemical stability of the Cu_{1.81}S/C electrode, the cycling stability of the Cu_{1.81}S/C electrode was conducted at a current density of 10 A g⁻¹ for 1000 cycles, as shown in Fig. 4d. Although the specific capacitance decreased gradually with increasing cycle number, it remained at over 86.4% relative to the initial capacitance after 1000 cycles. Electrochemical properties suggest that the as-obtained Cu_{1.81}S/C nanoparticles are potential material for high-performance SCs.

4. Conclusion: In summary, a one-pot method has first been used to synthesise Cu_{1.81}S/C composite which has novel nanoflake structure. The as-prepared flake Cu_{1.81}S/C composites electrode displayed excellent cycling stability and outstanding electrochemical properties with high specific capacitance of 617 F g⁻¹ at 0.5 A g⁻¹, which is attributed to its nanostructure providing a large contact area between electrode and electrolyte. The facile synthesis method and excellent electrochemical performance ensure such Cu_{1.81}S/C nanoparticles significant potential to be further exploited in high-performance SCs.

5. Acknowledgment: This work was supported by National Natural Science Foundation of China (grant nos. 51671214 and 51601220) and Science and Technology Projects of Jiangsu Province (grant no. BY2016026-05). We also appreciate Colleges Students' Innovative Project (grant no. 201610290048).

6 References

- [1] Tang J.H., Ge Y.C., Shen J.F., *ET AL.*: 'Facile synthesis of CuCo₂S₄ as a novel electrode material for ultrahigh supercapacitor performance', *Chem. Commun.*, 2016, **52**, pp. 1509–1512
- [2] Yu Z., Tetard L., Zhai L., *ET AL.*: 'Supercapacitor electrode materials: nanostructures from 0 to 3 dimensions', *Science*, 2015, **8**, pp. 702–730
- [3] Wang R., Qi J.Q., Sui Y.W., *ET AL.*: 'Fabrication of nanosheets Co₃O₄ by oxidation-assisted dealloying method for high capacity supercapacitors', *Mater. Lett.*, 2016, **184**, pp. 181–184
- [4] Rauda I., Augustyn V., Dunn B., *ET AL.*: 'Enhancing pseudocapacitive charge storage in polymer templated mesoporous materials', *Acc. Chem. Res.*, 2013, **46**, pp. 1113–1124
- [5] Xia X., Zhu C., Luo J., *ET AL.*: 'Synthesis of free-standing metal sulfide nanoarrays via anion exchange reaction and their electrochemical energy storage application', *Small*, 2014, **10**, pp. 766–773
- [6] Chen H., Hu L., Yan Y., *ET AL.*: 'One-step fabrication of ultrathin porous nickel hydroxide-manganese dioxide hybrid nanosheets for supercapacitor electrodes with excellent capacitive performance', *Adv. Energy Mater.*, 2013, **3**, pp. 1636–1646
- [7] Yan J., Sumboja A., Wang X., *ET AL.*: 'Insights on the fundamental capacitive behavior: a case study of MnO₂', *Small*, 2014, **10**, pp. 3568–3578
- [8] Li Y., Ye K., Cheng K., *ET AL.*: 'Electrodeposition of nickel sulfide on graphene-covered make-up cotton as a flexible electrode material for high-performance supercapacitors', *J. Power Sources*, 2015, **274**, pp. 943–950
- [9] Wang J., Chao D., Liu J., *ET AL.*: 'Ni₃S₂ @ MoS₂ core/shell nanorod arrays on Ni foam for high-performance electrochemical energy storage', *Nano Energy*, 2014, **7**, pp. 151–160
- [10] Rodriguez-Moreno J., Navarrete-Astorga E., Dalchiale E., *ET AL.*: 'Vertically aligned ZnO @ CuS @ PEDOT core @ shell nanorod arrays decorated with MnO₂ nanoparticles for a high-performance and semi-transparent supercapacitor electrode', *Chem. Commun.*, 2014, **50**, pp. 5652–5655
- [11] Zhang Q., Xu C., Lu B.: 'Super-Long life supercapacitors based on the construction of Ni foam/graphene/Co₃S₄ composite film hybrid electrodes', *Electrochim. Acta*, 2014, **132**, pp. 180–185
- [12] Roy P., Srivastava S.: 'Nanostructured copper sulfides: synthesis, properties and applications', *CrystEngComm*, 2015, **17**, pp. 7801–7815
- [13] Hsu Y., Chen Y., Lin Y.: 'Synthesis of copper sulfide nanowire arrays for high-performance supercapacitors', *Electrochim. Acta*, 2014, **139**, pp. 401–407
- [14] Zhou K.Y., Liang J.C., Liu J., *ET AL.*: 'Synthesis of porous Cu_{7.2}S₄ sub-microspheres by an ion exchange method for high-performance supercapacitors', *RSC Adv.*, 2016, **6**, pp. 16832–16837
- [15] Hwang Y.H., Lee S.M., Kim Y.J., *ET AL.*: 'A new approach of structural and chemical modification on graphene electrodes for high-performance supercapacitors', *Carbon*, 2016, **100**, pp. 7–15
- [16] Peng S.J., Li L.L., Tan H.T., *ET AL.*: 'MS₂ (M=Co and Ni) hollow spheres with tunable interiors for high-performance supercapacitors and photovoltaics', *Adv. Funct. Mater.*, 2014, **24**, pp. 2155–2162
- [17] Wu R.B., Wang D.P., Kumar V., *ET AL.*: 'MOFs-derived copper sulfides embedded within porous carbon octahedra for electrochemical capacitor applications', *Chem. Commun.*, 2015, **51**, pp. 3109–3112
- [18] Ma G., Peng H., Mu J., *ET AL.*: 'In situ intercalative polymerization of pyrrole in grapheme analogue of MoS₂ as advanced electrode material in supercapacitor', *J. Power Source*, 2013, **229**, pp. 72–78