

Short Communication

## Flower-like CuS/reduced Graphene Oxide Composite as Anode Materials for Lithium Ion Batteries

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We developed a liquid phase method to synthesize flower-like CuS/reduced graphene oxide (rGO) composite for lithium ion batteries. The as-obtained products were characterized by XRD, Raman spectra, FESEM and TEM. The CuS nanoflowers are uniformly distributed onto the surface of rGO or wrapped in the rGO. The electrochemical performance of CuS/rGO composite was measured by galvanostatic charge/discharge cycling, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The results show that CuS/rGO composite presents superior lithium ion batteries with large reversible capacity and good cycle performance. The first discharge and charge capacities are 1236 and 658 mAh g<sup>-1</sup>, respectively. After 50 cycles, the reversible discharge capacity is still maintained at 399 mAh g<sup>-1</sup>. The excellent electrochemical performance is ascribed to the unique architecture of CuS nanoflowers/rGO composite. The rGO sheets effectively prevent the agglomeration of CuS nanoflowers and act as an excellent conductive agent to provide a highway for electron transport. In turn, The CuS nanoflowers grown on rGO effectively keep the neighboring graphene sheets separated.

**Keywords:** CuS, graphene, anode materials, lithium ion batteries

### 1. INTRODUCTION

Lithium ion batteries with high-energy density, long cycle life, cost-effective and environment friendly are strongly desired for rapid growing portable electronic devices, mobile communication devices and electric/hybrid vehicles [1, 2]. Graphite is currently used as the anode materials for lithium ion batteries, but it has a low theoretical capacity of 372 mAh g<sup>-1</sup>, so many efforts have been devoted to studying cheap and safe anode materials with large reversible capacity, long cycle life, desirable rate capability, and good compatibility with electrolyte [3, 4]. Metal sulfides have been widely investigated

owing to their high specific capacity and low cost. For example, Bozheyev et al. applied  $\text{MoS}_2$  nanopowder as the anode material for Lithium ion batteries[5]. Yin et al. studied the lithium storage property of  $\text{SnS}_2$  at room temperature[6]. However, most of the metal sulfides undergo poor electronic conductivity and large volume variation during charge/discharge process, leading to severe mechanical strains and rapid capacity decay[7, 8]. To solve these issues, one of the most effective way is to design and prepare composite with carbon matrix which acts as a buffer layer and electrically connecting media for volume change.

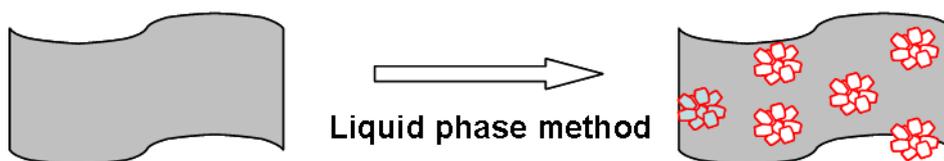
Graphene-based materials such as  $\text{MoS}_2$ /graphene[9],  $\text{CoS}_2$ /graphene[10],  $\text{NiS}$ /graphene[11],  $\text{FeS}$ /graphene[12] and  $\text{MnS}$ /graphene[13] have been synthesized to exhibit excellent electrochemical performance due to large specific surface area, high electronic conductivity and high mechanical strength of graphene. Among these composite,  $\text{CuS}$ /graphene composite has also been fabricated via a hydrothermal or solvothermal reaction and it exhibits high specific capacities[1, 14, 15]. However, the production of hydrothermal/solvothermal method is less, which restricts the application of composite materials.

In this paper, we have designed a novel and facile liquid phase method to obtain well organized flower-like  $\text{CuS}$ /reduced graphene oxide (rGO) composite. The resultant  $\text{CuS}$ /rGO composite possesses highly reversible capacity and good cycle performance, which can be employed as superior anode materials for high performance lithium ion batteries.

## 2. EXPERIMENTAL

### 2.1 Synthesis of flower-like $\text{CuS}$ /rGO composite

Graphene oxide was synthesized from the natural graphite via modified Hummers method[16]. rGO was obtained by reduction graphene oxide using ascorbic acid. Flower-like  $\text{CuS}$ /rGO composite was prepared by a liquid phase method, as shown in Fig.1. In a typical synthetic procedure, 0.17 g of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and 0.01g of sodium dodecyl benzene sulfonate (SDBS) were first put into a beaker with a capacity of 100 ml at room temperature, and 50 ml of deionized water was added to the above beaker for completely dissolving and mixing into a solution A. Then, 0.225 g of thioacetamide and 0.1g of rGO were placed into another beaker, and adding to 25 ml of deionized water, stirring to completely dissolve and blending into solution B. Then, the solution B was quickly added into the solution A under the magnetic stirring and reacted for 4 h at 50 °C. Finally, the as-prepared sample was centrifuged and washed with ethanol, which was followed by drying at 60 °C.



**Figure 1.** Schematic illustration of the fabrication of  $\text{CuS}$ /rGO composite.

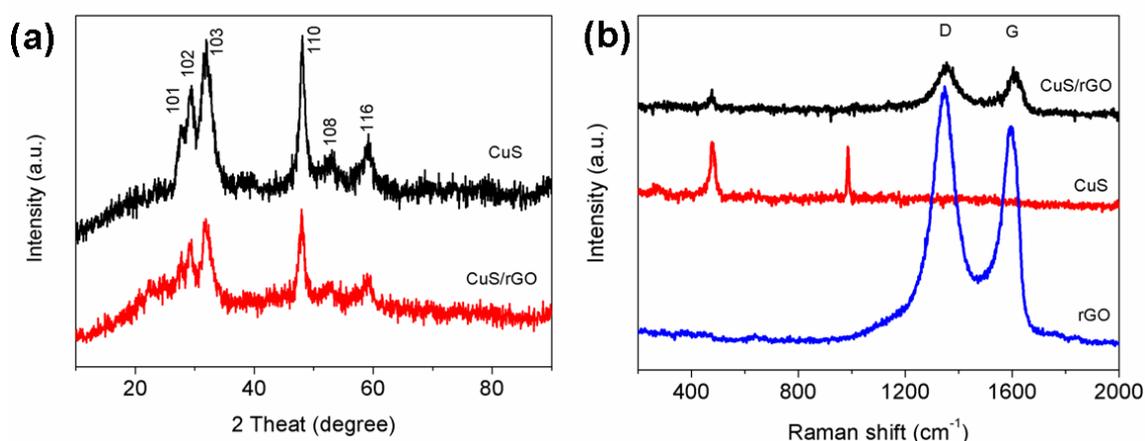
### 2.2 Characterization

The crystallographic structure of the as-synthesized products was investigated by means of X-ray diffraction (XRD) analysis using a TD-3500X X-ray diffractometer with a Cu K $\alpha$  X-ray radiation ( $\lambda=1.54056 \text{ \AA}$ ) at a scanning rate of  $0.07^\circ \text{ s}^{-1}$  between  $10^\circ$  and  $90^\circ$  (2 theta). The Raman spectra were collected by a micro-Raman spectrometer (LabRAM HR800) with wavelength of 633 nm (1.96 eV) at room temperature. The morphology and microstructure were analysed using field emission scanning electron microscopy (FESEM, FEI Quanta 250) and transmission electron microscopy (TEM, Tecnai G2 F20).

### 2.3. Electrochemical measurements

The electrochemical properties of as-obtained samples were tested by CR2032-type coin cells. Working electrodes were prepared by mixing active materials (bare CuS, CuS/rGO composite), acetylene black and polyvinylidene fluoride (PVDF) at the weight ratio of 80:10:10 in N-methyl-2-pyrrolidone (NMP). Lithium metal was used as both the counter electrode and the reference electrode. The electrolyte was 1 M LiPF $_6$  (1.0 M) in ethylene carbonate (EC) and dimethyl carbonate (DMC) mixture with a volume ratio of 1:1. The polypropylene membrane (Celgard2400) was used as the separator to electronically separate the two electrodes. All the CR2032-type coin cells were fabricated in an Ar-filled glove box. Galvanostatically cycling measurements were performed on a Neware battery test system (BTS-610) at a current density of  $100 \text{ mA g}^{-1}$  in the voltage range between 0 and 3.0 V. The cyclic voltammetry (CV) curves were collected at  $0.2 \text{ mV/s}$  at the range of 0–3.0 V and Electrochemical impedance spectroscopy (EIS) was carried out in the frequency range of 0.1 Hz to 100 kHz using an electrochemical workstation (CHI760E).

## 3. RESULTS AND DISCUSSION

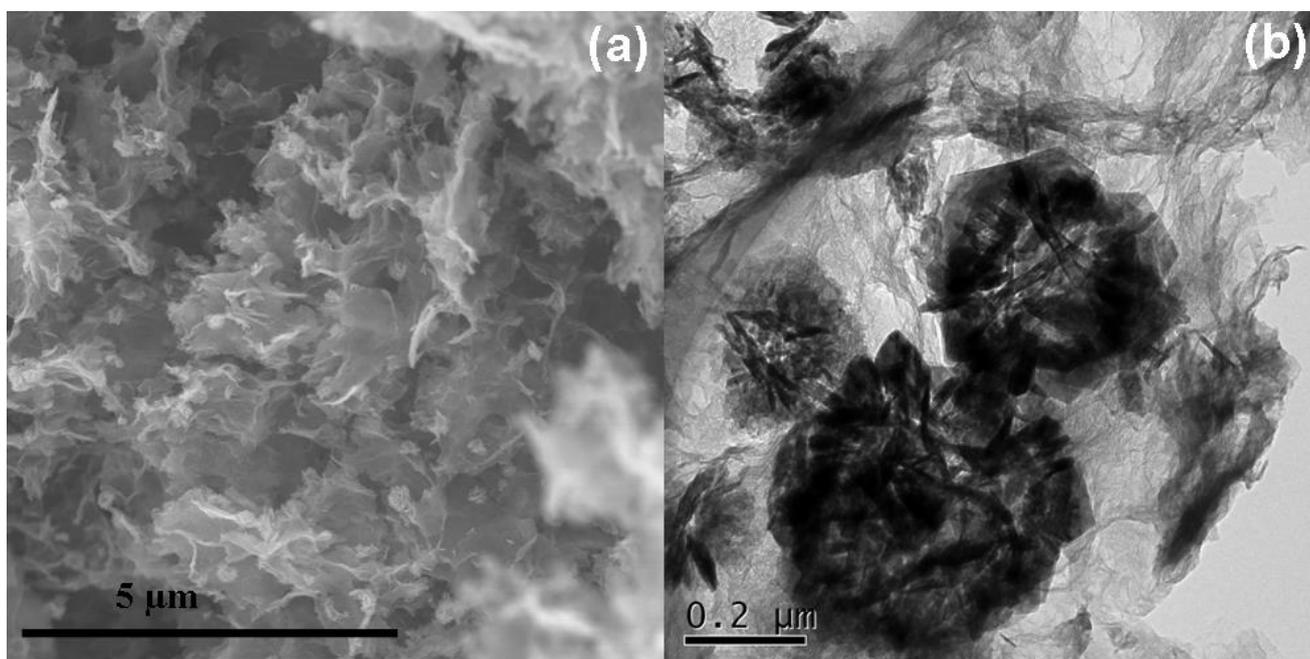


**Figure 2.** (a) X-ray diffraction patterns of CuS and CuS/rGO composite, (b) Raman spectra of RGO, CuS and CuS/rGO composite.

The crystalline structures of bare CuS and CuS/rGO composite were investigated by XRD analysis. As shown in Fig. 1a, both of these two samples (as-obtained CuS and CuS/rGO composite)

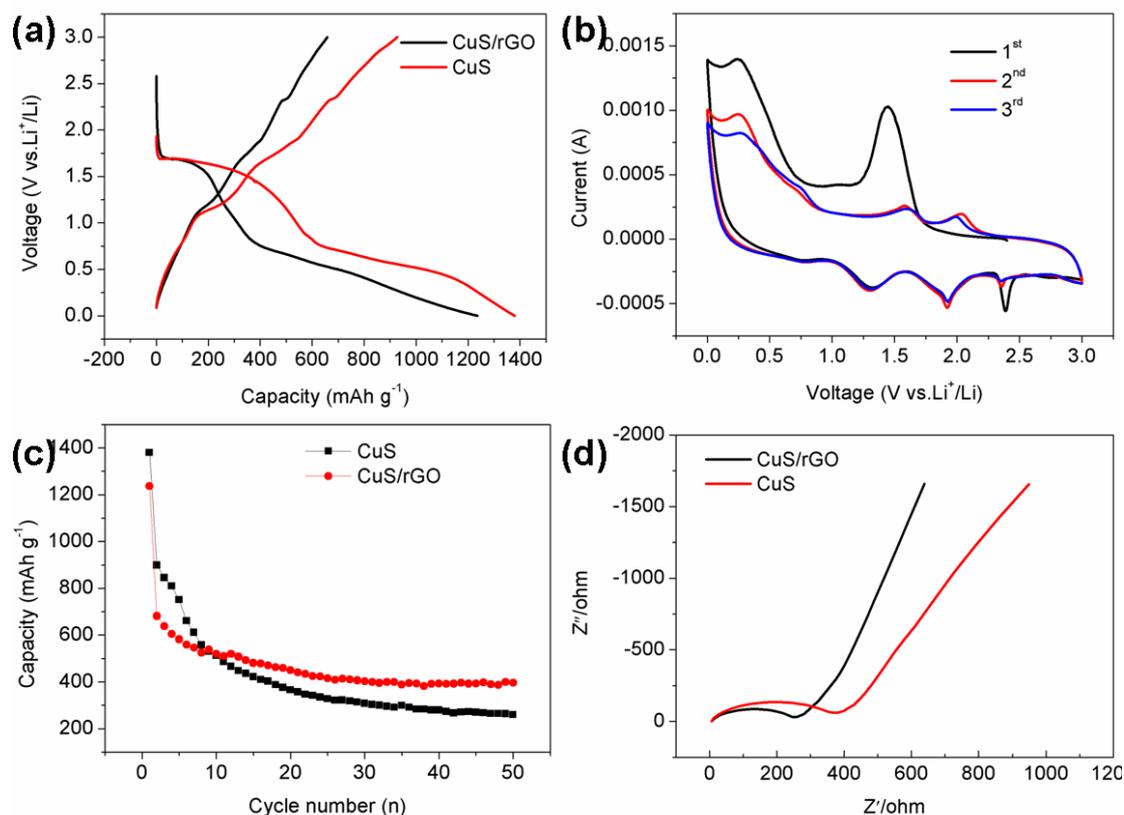
display similar diffraction peaks, which can be attributed to (101), (102), (103), (110), (108) and (116) crystal planes of CuS (JCPDS 06-0464). These results indicate that the crystal structures and the excellent crystallinity of CuS in CuS/rGO composite are well-preserved during the liquid phase synthesis processes. From the XRD pattern there is no diffraction peak of rGO can be observed, it may be due to its low amount and low diffraction intensity.

Fig. 1b shows the Raman spectra of rGO, CuS and the CuS/rGO composite. Two characteristic peaks of the D band and G band from rGO and CuS/rGO composite are observed at about 1350  $\text{cm}^{-1}$  and 1586  $\text{cm}^{-1}$  [2]. One characteristic peak from CuS at 471  $\text{cm}^{-1}$  is detected in the spectrum of the CuS/rGO composite, it can be ascribed to the S-S stretching mode of  $A_{1g}$  symmetry of CuS molecules, which is similar to the previous reports [17]. Apparently, the intensity ratio of the D and G band ( $I_D/I_G$ ) for CuS/rGO increases to 1.49 from 1.17 in comparison with that of rGO, as reported before [18], it indicating the formation of new graphitic domains in the reaction. Both XRD and Raman spectra measurements confirm the successful integration of rGO and CuS.



**Figure 3.** Morphology images of CuS/rGO composite (a) SEM, (b) TEM.

The morphology and structure of CuS/rGO composite were examined by SEM and TEM, as shown in Fig. 3. Fig. 3a displays the SEM image of CuS/rGO, graphene sheets can be observed, and they present a curly and wrinkled appearance. The CuS nanoflowers are uniformly distributed onto the surface of rGO or wrapped in the rGO. TEM image of CuS/rGO composite are shown in Fig. 3b. The CuS nanoflowers are formed by self-assembly of nanosheets and the size of CuS nanoflowers is 200-400 nm, graphene sheets can be also observed from the background.



**Figure 4.** (a) Discharge and charge profiles of CuS and CuS/rGO composite for the first cycle, (b) CV of CuS/rGO composite, (c) Cycling performance for CuS and CuS/rGO composite, and (d) EIS of CuS and CuS/rGO composite.

The electrochemical properties of CuS/rGO composite and bare CuS are evaluated by galvanostatic charge–discharge cycling at the current density of 100 mA g<sup>-1</sup> in the voltage range from 0–3.0 V. The initial charge/discharge curves of CuS/rGO composite and bare CuS are similar (Fig. 4a), indicating that CuS is the main contributor for lithium storage in the composite. The charge and discharge capacities of CuS/rGO composite are lower than those of CuS, and the CuS/rGO composite delivers the initial discharge and charge capacities of 1236 and 658 mA h g<sup>-1</sup>, with coulombic efficiency of 53.2%.

The electrochemical reactivity of CuS/rGO composite as anode materials in lithium ion batteries is estimated by CV. As can be seen from Fig. 4b, in the first cycle, there is a strong cathodic peak at 2.35 V, which can be attributed to the formation of solid electrolyte interface (SEI) film. The cathodic peaks at about 1.9 and 1.25 V in the first cycle, which are ascribed to lithium ions intercalation into the CuS lattices and the decomposition of CuS into metallic Cu and Li<sub>2</sub>S, respectively[1, 19]. Two anodic peaks at 0.3 and 1.45 V can be observed, which represent the reversible process related with the cathodic reaction.

Fig. 4c shows the cycling stabilities of bare CuS and CuS/rGO composite in the voltage of 0–3.0 V at the current density of 100 mA g<sup>-1</sup>. The CuS/rGO composite exhibits a reversible capacity of 399 mAh g<sup>-1</sup> after 50 cycles with coulombic efficiency of 98%. The bare CuS has a reversible capacity

of only 259 mAh g<sup>-1</sup> after 50 cycles. It is known that the cyclic performance of the flower-like CuS/rGO composite is far superior to the previous research results from table 1. This improvement is attributed to the unique architecture of CuS nanoflowers/rGO composite. The rGO sheets effectively prevent the agglomeration of CuS nanoflowers and act as an excellent conductive agent to provide a highway for electron transport for improving the accessible capacity. In turn, The CuS nanoflowers grown on rGO effectively keep the neighboring graphene sheets separated.

**Table 1.** Comparison with electrochemical capacity of previous CuS

Materials	Current density (mA g <sup>-1</sup> )	Cycle number (n)	Reversible capacity (mA h g <sup>-1</sup> )	References
Flower-like CuS/rGO	100	50	399	This work
Sphere-like CuS	100	10	80	[20]
CuS nanospheres	10	30	90	[21]
CuS/graphene	50	25	296	[3]

Fig.4d presents the EIS spectra of CuS/rGO composite and bare CuS. The EIS spectra are combinations of a semicircle in high frequencies and a straight line in low frequencies. For the LIBs, the charge transfer resistance is a measure of the charge transfer kinetics, and the charge transfer process determines the rate of transfer reaction. The diameter of the semicircle is assigned to the charge transfer resistance. The incline in the low frequency region indicates the Li<sup>+</sup> diffusion within the as-prepared electrode. The smaller semicircle for CuS/rGO composite indicates a lower electrochemical resistance than that of bare CuS. The slope of the impedance of CuS/rGO composite is bigger than that of bare CuS, indicating that the superior Li<sup>+</sup> diffusion speed of CuS/rGO composite. These results also confirm that rGO can significantly improve the electronic conductivity of electrode.

#### 4. CONCLUSIONS

In summary, we have developed a facile and effective strategy to prepare novel flower-like CuS/rGO composite by liquid phase method. The CuS nanoflowers are uniformly distributed onto the surface of rGO or wrapped in the rGO. As an anode electrode for lithium ion batteries, it is found that the CuS/rGO composite presents higher reversible capacity and longer cycle life than the bare CuS. The excellent electrochemical performance is ascribed to rGO, rGO not only provides a highway for electron transport but also offers a large contact surface for individual dispersion of CuS nanoflowers to prevent the agglomeration of CuS. So as to CuS/rGO composite maintains the structural integrity of the electrode after large volume changes during the charge/discharge process.

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## References

1. C. Ding, D. Su, W. Ma, Y. Zhao, D. Yan, J. Li, H. Jin, *Appl. Surf. Sci.*, 403 (2017) 1.
2. H. Liu, Z. Hu, Y. Su, H. Ruan, R. Hu, L. Zhang, *App. Surf. Sci.*, 392 (2017) 777.
3. H.-C. Tao, X.-L. Yang, L.-L. Zhang, S.-B. Ni, *J. Phys. Chem. Solids*, 75 (2014) 1205.
4. H. Liu, J. Huang, X. Li, J. Liu, Y. Zhang, K. Du, *Appl. Surf. Sci.*, 258 (2012) 4917.
5. F. Bozheyev, A. Zhexembekova, S. Zhumagali, A. Molkenova, Z. Bakenov, *Mater. Today- Proceedings*, 4 (2017) 4567.
6. L. Yin, S. Chai, J. Ma, J. Huang, X. Kong, P. Bai, Y. Liu, *J. Alloy. Comp.*, 698 (2017) 828.
7. Q. Wang, L. Jiao, Y. Han, H. Du, W. Peng, Q. Huan, D. Song, Y. Si, Y. Wang, H. Yuan, *J. Phys. Chem. C*, 115 (2011) 8300.
8. C. Xing, D. Zhang, K. Cao, S. Zhao, X. Wang, H. Qin, J. Liu, Y. Jiang, L. Meng, *J. Mater. Chem. A*, 3 (2015) 8742.
9. P. He, K. Zhao, B. Huang, B. Zhang, Q. Huang, T. Chen, Q. Zhang, *J. Mater. Sci.*, 53 (2018) 4482.
10. S. Tao, W. Huang, H. Xie, J. Zhang, Z. Wang, W. Chu, B. Qian, L. Song, *Rsc Adv.*, 7 (2017) 39427.
11. H.-C. Tao, X.-L. Yang, L.-L. Zhang, S.-B. Ni, *J. Electroanal. Chem.*, 739 (2015) 36.
12. J. He, Q. Li, Y. Chen, C. Xu, K. Zhou, X. Wang, W. Zhang, Y. Li, *Carbon*, 114 (2017) 111.
13. Y. Hao, C. Chen, X. Yang, G. Xiao, B. Zou, J. Yang, C. Wang, *J. Power Sources*, 338 (2017) 9.
14. K.-J. Huang, J.-Z. Zhang, Y. Liu, Y.-M. Liu, *Int. J. Hydrogen Energy*, 40 (2015) 10158.
15. Z. He, Y. Zhu, Z. Xing, Z. Wang, *J. Electron. Mater.*, 45 (2016) 285.
16. W.S. Hummers, R.E. Offeman, *J. Am. Chem. Soc.*, 80 (1958) 1339.
17. B. MincevaSukarova, M. Najdoski, I. Grozdanov, C.J. Chunnillall, *J. Mol. Struct.*, 410 (1997) 267.
18. X.-S. Hu, Y. Shen, Y.-T. Zhang, H.-F. Zhang, L.-H. Xu, Y.-J. Xing, *J. Alloy. Comp.*, 695 (2017) 1778.
19. C. Feng, L. Zhang, Z. Wang, X. Song, K. Sun, F. Wu, G. Liu, *J. Power Sources*, 269 (2014) 550-555.
20. Y. Han, Y. Wang, W. Gao, Y. Wang, L. Jiao, H. Yuan, S. Liu, *Powder Technology*, 212 (2011) 64.
21. Q. Li, Y. Xue, Y. Zhu, Y. Qian, *J. Nanosci. Nanotechno.*, 13 (2013) 1265

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