



# Synthesis of copper tin sulfide/reduced graphene oxide composites and their electrochemical properties for lithium ion batteries



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## ABSTRACT

Copper tin sulfide/reduced graphene oxide (CTS/RGO) composites are facile synthesized via a simple one-pot hydrothermal route using ethylenediamine tetraacetic acid disodium salt (EDTA- $\text{Na}_2$ ) as a chelating agent. The results of Raman spectra and Fourier transform infrared (FTIR) spectra demonstrate that graphite oxide (GO) sheets are *in situ* reduced to a certain extent. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) observations indicate that CTS microspheres, with an average diameter of 450 nm around, are anchored on RGO sheets. Electrochemical tests show the CTS/RGO composites exhibit an extraordinary capacity of  $1514.6 \text{ mAh g}^{-1}$  with a higher initial coulombic efficiency, excellent cycling stability and better rate capability compared to  $\text{Cu}_2\text{SnS}_3$  hollow microspheres (CTS-HMSs) prepared by a similar route in the absence of GO. The enhancement in the electrochemical performance can be attributed to the introduction of RGO sheets that not only accommodate the volume changes and therefore bring the structural integrity of electrode materials, but also provide a highly conductive network for rapid electron transport in electrode during electrochemical reaction.

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## 1. Introduction

During the past decades, metal sulfides, ranging from binary sulfides ( $\text{FeS}_2$  [1],  $\text{SnS}_x$  [2–5],  $\text{MoS}_2$  [6] and  $\text{Bi}_2\text{S}_3$  [7]) to more compositional complex ternary and quaternary sulfides such as,  $\text{CoSbS}$  [8],  $\text{Cu}_2\text{ZnSnS}_4$  [9] and  $\text{CuInZnS}$  [10], with potential applications as anodes or cathodes for lithium ion batteries, have attracted great attention due to their high theoretical capacity. Nevertheless, for most of metal sulfides, the reversible specific capacity undergo a fast fading during cycling, which can be partly attributed to the problems of low electrical conductivity and volume expansion during cycling that confines the further application in the lithium ion batteries [7,11]. In order to overcome these drawbacks, various strategies have been proposed to improve electrochemical properties, one of most effective way is to design composites with a matrix such as carbon which can act as a buffer layer for the volume expansion during charge-discharge processes [11–13].

Recently, graphene nanosheets, a new two dimensional carbon material, due to their extraordinary electronic transport properties, large surface area and mechanical flexibility [14], have been considered as a matrix material to improve electrochemical performance of metal sulfides. Chen et al. [15] synthesized

$\text{MoS}_2$ /graphene composites by an L-cysteine-assisted solution-phase method and found that the  $\text{MoS}_2/\text{G}(1:2)$  electrodes exhibited a high reversible capacity of  $1187 \text{ mAh g}^{-1}$  after 100 cycles. In addition, other graphene-based hybrids such as  $\text{SnS}_2$ @graphene [16],  $\text{CoS}_x$ /graphene nanosheets [17] and  $\text{NiS}_x/\text{N-G}$  [18,19] have been reported to exhibit extraordinarily excellent electrochemical performance as well.

Copper tin sulfide ( $\text{Cu}_2\text{SnS}_3$ , CTS), which is belonging to an important category of I-V-VI ternary chalcogenides materials, has received ever increasing attention as a potential anode material in lithium ion batteries for the good electrical conductivity of copper-based multicomponent chalcogenide and the interlayer spaces and tunnels in CTS which can be effective in facilitating the  $\text{Li}^+$  diffusion through its crystal structure [9,10,20]. Later on, CTS cabbage-like nanostructures and mesoporous spheres synthesized via solvothermal methods by Wang and co-workers [21,22] are also utilized as active electrode materials in lithium ion batteries, which show large initial discharge capacities of  $1021 \text{ mAh g}^{-1}$  and  $913 \text{ mAh g}^{-1}$ , respectively. However, on the one hand, many reports on the preparation of CTS are based on solvothermal route, which use complicated organic solvents as reaction agents and some of them are usually expensive and toxic [21–23]. On the other hand, synthesis of multicomponent sulfides in water is very difficult due to the different reaction kinetics of metal cations with sulfur [24,25]. Therefore, the construction of pure CTS materials by a facile hydrothermal method is still a big challenge. Moreover, to

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the best of our knowledge, ternary CTS microspheres have never been *in situ* combined with graphene or graphene derivatives (e.g. GO and RGO), which may contribute to a better cycling stability and rate capability when they are applied in lithium ion batteries.

Herein, sphere-like CTS was *in situ* anchored on reduced oxide graphene nanosheets (CTS/RGO) via facile hydrothermal method, which ethylenediamine tetraacetic acid disodium salt (EDTA- $\text{Na}_2$ ) was ingeniously introduced to balance the reaction velocity between metal cations and sulfur. The unique composites were then employed as activity electrode materials for lithium ion batteries, they exhibited excellent electrochemical properties with a high specific capacity, enhanced cycling performance and better rate capability compared to bare  $\text{Cu}_2\text{SnS}_3$  hollow microspheres (CTS-HMSs).

## 2. Experimental

### 2.1. Synthesis CTS/RGO composites

All reagents used in this experiment were of analytical grade without further purification. Typically, the CTS/RGO composites were synthesized by a one-pot hydrothermal route. First, the Graphene oxide (GO) was prepared by a modified Hummers method [26], and a  $1 \text{ mg ml}^{-1}$  homogeneous GO dispersion was achieved by ultrasonication of 45 mg of GO in 45 ml of ultrapure water for 1 h. Then, 2 mmol of  $\text{CuCl}_2$ , 1 mmol of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  and 3 mmol of  $\text{EDTA-Na}_2$  were added into the above dispersion successively. After stirring for several minutes to form a purplish blue suspension, 3 mmol of L-cysteine was introduced as sulfur resource. Followed by ultrasonic processing and stirring for another 0.5 h, the reaction mixture was immediately transferred into a 60 ml Teflon-lined stainless steel autoclave and then heated in an electric oven at  $180^\circ\text{C}$  for 24 h. Finally, the autoclave was allowed to cool down to room temperature naturally. The resulting black precipitate was collected by centrifugation, washed several times with ultrapure water and absolute ethanol, and dried at  $60^\circ\text{C}$  in vacuum overnight. In a controlled experimental, CTS-HMSs were also prepared under the same conditions by just recommending ultrapure water without GO as solvent.

### 2.2. Material Characterization

X-Ray diffraction (XRD) analysis with  $\text{Cu K}\alpha$  radiation (Rigaku D/max Diffraction System,  $\lambda = 1.5406 \text{ \AA}$ ) was used to determine the phase and the crystallinity. The morphology and microstructure of the samples were observed under scanning electron microscope (SEM, Quanta FEG 250) and transmission electron microscopy (TEM, Tecnai G2 F20 S-TWIX). The composition of the sample was analyzed using energy-dispersive X-ray (EDX) spectroscopy (INCA energy). The Raman spectra were obtained on a Jobin-Yvon LabRAM HR-800 spectrometer with excitation from an argon ion laser ( $514 \text{ nm}$ ). Fourier transform infrared (FTIR) spectra were recorded with Nicolet 6700 spectrometer ranging from  $500$  to  $4000 \text{ cm}^{-1}$ .

### 2.3. Electrochemical measurement

For an electrochemical evaluation of CTS/RGO composites and CTS-HMSs, the electrodes consisted of active materials (80 wt. %), carbon black (Super P, 10 wt. %) as a conducting agent and polyvinylidene fluoride (PVdF, 10 wt. %) dissolved in N-methyl pyrrolidinone (NMP) as a binder. Prepared slurries were coated on the copper foil substrates, pressed and dried at  $100^\circ\text{C}$  for 8 h under vacuum. The electrodes were assembled into CR2025 coin-type cells with Li electrode and electrolyte (1 M  $\text{LiPF}_6$  in EC: EMC: DMC = 1: 1: 1 in volume) in an Ar-filled glove box. Cyclic voltammetry (CV) tests were performed on an electrochemical Workstation

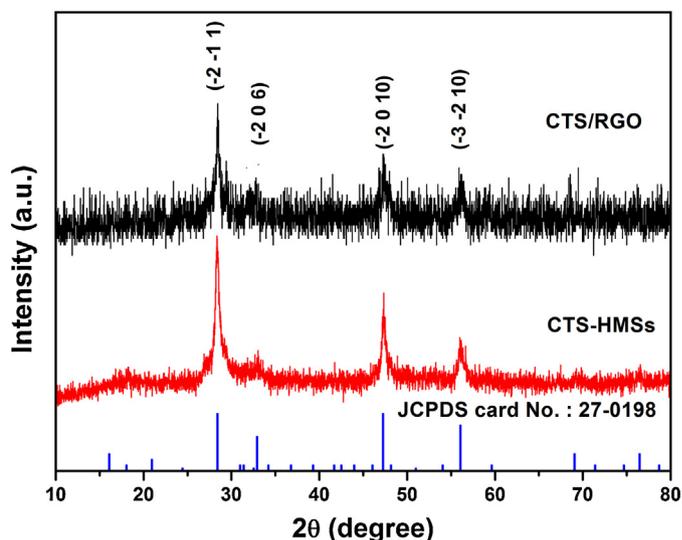


Fig. 1. XRD patterns of as-prepared CTS/RGO composites and CTS-HMSs.

(1470e cell test system) between 0.01 V and 3.00 V at a scanning rate of  $0.2 \text{ mV s}^{-1}$ . Charge-discharge measurements were performed with a Land CT2001A battery test system between 0.01 V and 3.0 V vs.  $\text{Li}^+/\text{Li}$  at a current density of  $100 \text{ mA g}^{-1}$ . It should be noted that the specific capacity was calculated on the basis of total mass of the CTS/RGO composites. Electrochemical impedance spectra (EIS, cell test system) were obtained by applying a sine wave with amplitude of 5.0 mV over the frequency range from 100 kHz to 10 mHz. All the electrochemical measurements were performed at room temperature.

## 3. Results and discussion

It is shown in Fig. 1 that the XRD pattern of as-prepared CTS-HMSs exhibits very sharp diffraction peaks, which can all be indexed to triclinic copper tin sulfide (CTS, JCPDS card No.: 27-0198, space group:  $P1(1)$ ,  $a = 0.664 \text{ nm}$ ,  $b = 1.151 \text{ nm}$ ,  $c = 1.993 \text{ nm}$ ). This is in accordance with Tiwari et al.'s report [27]. The sharp diffraction peaks, especially for  $(-2 -1 1)$  plane of the CTS, indicate that the products are highly crystalline. The obtained CTS/RGO composites display a similar XRD pattern to pure CTS samples, implying that the introduction of GO does not influence the fabrication of CTS samples. However, it is noteworthy that the diffraction peaks of the CTS-HMSs are slightly sharper than that of CTS/RGO, indicating that the crystals in CTS/RGO composites are smaller than that in the CTS-HMSs, which is similar with the report of CIZS@Graphene [10]. In addition, characteristic diffraction peaks of GO are not detected in the CTS/RGO composites may due to its low amount and relatively low diffraction intensity. And according to the element analyses, The RGO content in the as prepared CTS/RGO composites is estimated to be about 10.38 wt. % (Fig. S1) (Supplementary Materials).

The Raman spectra of GO and CTS/RGO are shown in Fig. 2a. There are two characteristic peaks of the D and G bands from GO and CTS/RGO composites are observed at about  $1350 \text{ cm}^{-1}$  and  $1580 \text{ cm}^{-1}$  respectively. The intensity ratio ( $I_{\text{D}}/I_{\text{G}}$ ) of the D band to G band for graphene oxide is about 0.84. Compared to GO,  $I_{\text{D}}/I_{\text{G}}$  for CTS/RGO composites increase to 1.05 due to decrease in the average size of the  $\text{SP}^2$  domains with increase of the quantity for these domains. The change of  $I_{\text{D}}/I_{\text{G}}$  generally indicates the GO has been *in situ* reduced, which was also supported by reported works [28,29]. Moreover, it can be deduced that the L-cysteine could act as reductant by releasing hydrogen sulfide ( $\text{H}_2\text{S}$ ) during hydrothermal reaction, which have been reported in previous reports [7,15]. Furthermore, Fig. 2b shows the FTIR spectra

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