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# Realizing high reversible capacity: 3D intertwined CNTs inherently conductive network for CuS as an anode for lithium ion batteries



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## GRAPHICAL ABSTRACT



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## ABSTRACT

CuS nanospheres interconnected by the carbon nanotubes (CNTs) have been successfully prepared via a facile one-step microwave-assisted method. The component and microstructure of CuS/CNTs hybrid materials are well characterized by X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HR-TEM). Assembled as electrodes and tested in lithium ion batteries, the composites show impressive electrochemical performances. After 450 cycles, the CuS/0.1 CNT and CuS/0.5 CNT release more than 437 and 569 mAh  $g^{-1}$ , respectively, at 400 mA  $g^{-1}$ , which are superior to those of contrast experiments (pristine CuS and CuS mechanically mixing with CNTs). Even at the high current density of 6400 mA  $g^{-1}$ , the CuS/0.5 CNT still displays the reversible capacity of about 400 mAh  $g^{-1}$ . The improved performances can be ascribed to the inherently CNTs conducting network, boosting the interior electron transport and reaction kinetics, so that a significantly enhanced reversible capacities and rate capability can be realized. Furthermore, the surface properties and reaction kinetics of electrodes are also investigated via cyclic

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Received 7 June 2017; Received in revised form 7 September 2017; Accepted 10 September 2017 Available online 11 September 2017 1385-8947/ © 2017 Elsevier B.V. All rights reserved. voltammetry (CV) and galvanostatic intermittence titration (GITT) measurements, proving the enhanced lithium storage properties.

#### 1. Introduction

Both high energy density and power density are necessary for nextgeneration rechargeable batteries to meet the increasing requirement in electric vehicle and large scale storage systems [1,2]. The electrode material is one of the key components deciding the capability of batteries, which leads to substantial investigations in electrode materials [3,4]. In recent years, as one of anode material candidates, conversion reaction-based metal sulfides (MSs) have attracted great attention due to their high specific capacities compared to the commercial graphitebased and Ti-based anodes [5-7]. Among these, CuS has been paid much attention and investigated in lithium batteries due to the high theoretical capacity ( $\sim$  560 mAh g<sup>-1</sup>), flat charge/discharge plateaus and good electronic conductivity [8-11]. However, the biggest problem hindering its further application is the rapid capacity fading in the first several cycles, leading to the infeasibility of its high capacity [12–14]. The main reasons can be ascribed to difficultly in complete re-oxidation of electrochemically inactive discharge product-Li<sub>2</sub>S and the large volume expansion in (de)lithiation processes [5,15]. To address these issues, many strategies have been proposed, such as constructing nanostructures to reduce dimensions of materials, complexing with carbon matrix to improve electric conductivity and buffer the volume change [12,16-18]. Although improved long-term cycling performances are truly realized, the problem of severe capacity fading in the first several cycles still exists. Besides, the nano-sized particles intend to cluster, deteriorating the battery performances. And in most cases, the carbon matrix just provides an external conductive framework, which is too feeble to solve the problem of fully re-oxidation of Li2S.

As a feasible choice, introducing 3D interior conducting network can effectively improve the electrochemical properties, which has been a common strategy in architecting metal oxides with poor electronic conductivity. For example, CuxO/SnOx@CNT and CuxO/SnOx@SnO2/ CNT composites showed excellent cycling performances [19]. More than 580 and 800 mAh  $g^{-1}$  could be obtained over 70 cycles for  $\mbox{Cu}_{x}\mbox{O}/$ SnO<sub>x</sub>@CNT and Cu<sub>x</sub>O/SnO<sub>x</sub>@SnO<sub>2</sub>/CNT. Mao and co-workers successfully prepared MnO<sub>2</sub>@CNT microsphere composites [20]. The composite showed the reversible capacity of more than 800 mAh  $g^{-1}$  at  $0.1~{\rm A~g^{-1}}$  over 70 cycles, whereas the pristine  ${\rm MnO}_2$  released less than  $200 \mbox{ mAh g}^{-1}.$  The initial coulombic efficiency of  $MnO_2@CNT$  was 71.1%, which is much higher than that (37.8%) of MnO<sub>2</sub>. Wang et al. synthesized mesoporous CNT@TiO2-C composite [21]. The composite released highly reversible capacities of 187 and 122 mAh g<sup>-1</sup> at 5 C and 50 C over 2000 cycles, showing extremely impressive cycling performance and rate capability. The enhanced performances above are mainly ascribed to the internal 3D CNT network, which not only acts as an electronically conducting network to connect primary particles with each other, but also serves as an elastic host to buffer the large volume change. Therefore, to achieve excellent electrochemical performances for CuS, introducing an internal 3D conductive network may be an alternative strategy.

In this work, CuS/CNT composites are prepared via a facile one-pot microwave-assisted method. Under the microwave irradiation, CuS nanoparticles are rapidly nucleated on CNTs, guaranteeing intimate connection between each other. Besides, the surface of CuS nanospheres is partially covered and connected by CNTs. Thus, the intertwined CNTs provide a 3D electron transporting network both in and on CuS nanospheres and play an important role in buffering the volume change during (de)lithiation. Benefiting from the unique hybrid structure, the large initial capacity loss in the first several cycles is significantly mitigated and the reaction kinetic is greatly boosted, resulting in the realization of high reversible capacities and admirable rate capability.

### 2. Experimental section

#### 2.1. Synthesis

 $CuSO_4$ :5H<sub>2</sub>O and  $Na_2S_2O_3$ :5H<sub>2</sub>O were purchased from Shanghai Sinopharm Reagent Chemical Co. Ltd. Carbon nanotubes were purchased from Chengdu Organic Chemicals Co., Ltd. (Chinese Academy of Sciences). All reagents were directly used without further purification.

A modified microwave-assisted method was adopted [11]. For CuS, 50 mL 0.1 M  $CuSO_4$ ·5H<sub>2</sub>O and 50 mL 0.1 M  $Na_2S_2O_3$ ·5H<sub>2</sub>O were mixed, followed by magnetic stirring for 10 min. The mixture was then transferred to a microwave reactor (Model: LWMC-201, microwave frequency: 2450 MHz, output power: 650 W) and treated by cyclic irradiation (9 s on, 21 s off) for 20 min. The dark blue precipitation was collected by filtration and washed with deionized water and absolute alcohol several times, then dried at 60 °C under vacuum overnight.

For CuS/CNTs composites, a certain amount (0.1 g and 0.5 g) of CNTs suspension liquid (10 wt%) was added into 100 mL deionized water and under ultrasonic for 20 min. 50 mL 0.1 M CuSO<sub>4</sub>:5H<sub>2</sub>O and 50 mL 0.1 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>:5H<sub>2</sub>O were added to the 100 mL mixture, followed by magnetic stirring for 10 min. The mixture was then transferred to a microwave reactor and treated by cyclic irradiation (9 s on, 21 s off) for 20 min. The product was collected by filtration and washed with deionized water and absolute alcohol several times, then dried at 60 °C under vacuum overnight. The samples are denoted as CuS/0.1 CNT and CuS/0.5 CNT, respectively, according to the adding mount of CNTs suspension.

For CuS/CNTs mixtures, a certain amount (2.5 wt% and 12 wt%) CNTs powders and CuS powders were mixed via hand-milling with an agate mortar for 30 min. The samples are designated as CuS/2.5% CNT and CuS/12% CNT, respectively.

#### 2.2. Materials characterization

The crystalline phases were ascertained by X-ray diffraction (XRD, Rigaku mini Flex 600 with Cu K $\alpha$  radiation) operated at 40 kV and 15 mA. The morphologies were characterized by scanning electron microscopy (SEM, HITACHI S-4800) and transmission electron microscopy (TEM, JEOL-2100). Raman spectra were collected on a Raman spectroscope (HORIBA Xplora) with the 532 nm Ar-ion laser. Thermogravimetric analysis (TGA) was taken on the SDTQ600 (TAInstruments) under air flow (RT to 800 °C, 10 °C min<sup>-1</sup>). The Cu/S ratios were determined by ICP-AES (NCS Testing Technology Co., Ltd., Plasma 1000).

#### 2.3. Cell assembly and testing

The electrode slurry was prepared by mixing the synthetic material, acetylene black (AB) as the conductive agent and polyvinylidene difluoride (PVDF) as the binder in the N-methyl-2-pyrrolidinone (NMP) solvent at the weight ratio of 80:10:10, which was coated on a Cu foil using a doctor blade and dried in a vacuum oven at 60 °C for 12 h. The electrode was punched to circular discs. The mass loading of active material ranges from 1.6 to 2.00 mg cm<sup>-2</sup>. The CR2016 coin-type cells were assembled in an argon-filled glove box with the lithium as a counter electrode, the Celgard 2400 as a separator and the 1 M lithium bis(trifluoromethanesulfon)imide (LiTFSI, J & K Chemical) dissolved in 1, 3-dioxolane and dimethyl ether (1: 1, v/v, Aladdin) as a electrolyte.

The charging/discharging tests were conducted on the Neware battery program-control system from 1.0 to 3.0 V. Cyclic voltammetry (CV) data were collected by using CHI 660D electrochemical workstation (Chenhua, Shanghai) at the scan rate of  $0.2 \text{ mV s}^{-1}$  and the Metrohm Autolab PGSTAT 302N electrochemical workstation at different scan rates from 0.2 to  $3.0 \text{ mV s}^{-1}$ . For the galvanostatic intermittence titration (GITT) tests, the cells (after 30 cycles at 400 mA g<sup>-1</sup>) were discharged at 15 µA for 10 min, followed by a relaxation process under open circuit for 600 min. Electrochemical impedance spectroscopies (EIS) were performed on the Solartron Modulab 1287A/1260 in the frequency of  $10^{-1}$  Hz to  $10^{5}$  Hz. The specific capacity is calculated based on the mass of CuS for all cases.

#### 3. Results and discussions

Fig. 1 shows the synthetic scheme of CuS/CNT composite. The microwave synthesis is well known as a rapid and efficient method to prepare different kinds of inorganic materials, which is adopted in this work to obtain hybrid materials [22]. Under the microwave irradiation, the CNTs are heated faster than the water solvent, which can be seen as hotpots and provide nucleation sites [23,24]. With the rapidly increasing temperature,  $S_2O_3^{2-}$  decomposes to HS- and HSO<sub>4</sub><sup>-</sup>, where HS<sup>-</sup> will react with Cu<sup>2+</sup> to form CuS spheres [11]. Since there are many nucleation sites around, CuS particles will intend to nucleate on the hotpots. Thus, the 3D hybrid material, CuS spheres threaded by intertwined CNTs, has been successfully prepared.

Fig. 2a shows the XRD patterns of synthetic CuS/0.1 CNT and CuS/ 0.5 CNT. Diffraction peaks of both are well indexed to the standard card of hexagonal phase CuS (JCPDS No. 065-3588). The characteristic peaks of CNT (Fig. S1a) cannot be observed for both cases, which are consistent with other reports [20,25]. Fig. S1a (Supplementary material) shows that the diffraction peaks of as-prepared CuS are the same as those of CuS/CNT composites and exclusively ascribed to the standard card, indicating that adding CNTs makes no difference in purity of products. To demonstrate the existence of CNTs and further investigate the structural feature, Raman spectroscopy is used as shown in Fig. 2b. From the curves, peaks at 266, 476, 928, 1377 and 1588  $\text{cm}^{-1}$  can be observed for the cases of CuS/0.1CNT and CuS/0.5CNT. The Raman peaks at 1377 and 1588 cm<sup>-1</sup> correspond to D band and G band of carbon, respectively [26,27]. The strong peak at 476  $\text{cm}^{-1}$  is identified as the S-S stretching mode [28]. The sharp peak indicates that the lattice atoms are periodically aligned in the crystal [29].

The bands at 266 cm<sup>-1</sup> and 928 cm<sup>-1</sup> are also ascribed to CuS phase, which can be clearly observed from the Raman curve of pristine CuS [29,30]. Scanning electron microscopy is used to characterize the morphology. The prepared CuS particles without adding CNTs (Fig. S1b, Supplementary material) are uniform spheres with the average size of 700 nm. After adding CNTs, the obtained CuS particles (Fig. 2c-f) are also spherical with sizes of 400–600 nm. The CNTs threading through and distributing on CuS nanospheres (insets in Fig. 2d and f) form an

interconnected network. The interconnected hybrid structure is further ascertained by TEM as shown in Fig. 2g and h. The substance with dark contrast is supposed to be CuS. The long and curving tubes with a diameter of about 50 nm are supposed to be CNTs, threading through the CuS nanospheres. The lattice fringes can be observed from highresolution TEM (HRTEM) (Fig. 2h and j). The lattice spacings of CuS/ 0.1 CNT and CuS/0.5 CNT are 0.329 and 0.302 nm, respectively, corresponding to those from (1 0 0) and (1 0 2) planes of CuS. Fig. 3a-h display the energy dispersive spectroscopy (EDX) mapping images of CuS/CNTs composites, showing the homogeneously distribution of elemental S, Cu and C. The signal of C is relatively weak compared to S and Cu, indicating the relatively low content of carbon. To determine the content of carbon, elemental analysis is applied. The TGA curves of CuS, CuS/0.1 CNT and CuS/0.5 CNT are shown in Fig. S1c. Calculated from the weight percentage above 750 °C, it can be known that the carbon contents of CuS/0.1CNT and CuS/0.5CNT are 2.65 wt% and 13.1 wt%, meaning that the contents of CuS are 97.4 wt% and 86.9 wt %, respectively. Furthermore, the chemical compositions of pristine CuS, CuS/0.1CNT and CuS/0.5CNT are determined by ICP-AES. As shown in Fig. S2, the Cu/S ratios of CuS, CuS/0.1CNT and CuS/0.5CNT are 1.20, 1.18 and 0.96.

Coin cells are assembled to test the electrochemical properties of CuS/CNTs composites. To make a better comparison, the electrochemical performances of the pristine CuS nanospheres and the CuS mechanically mixed with CNTs of definite amount (denoted as CuS/ 2.5% CNT and CuS/12% CNT, respectively, according to the adding mount of CNTs) are also investigated. Fig. 4a and b show the CV profiles in the 1st and 5th cycle. In the 1st cycle, two strong cathodic peaks (around 1.9 V and 1.5 V) and a strong anodic peat at 2.3 V emerge. After 5 cycles, the cathodic peaks shift positively and the anodic peaks shift negatively, indicating the improving reaction reversibility. In particular, the redox peak gap of CuS/0.5 CNT is the smallest (from 0.80 V to 0.38 V), indicating the lowest polarization. Fig. 4c and d show the charge/discharge profiles of CuS/CNTs composites at the current density of 400 mA  $g^{-1}$  (the specific capacity is calculated based on the mass of CuS). Two discharge plateaus at 1.95 V and 1.62 V are observed in the first cycle, corresponding to the following electrochemical reactions [10,31-33]:

$$2CuS + 2Li \rightarrow Cu_2 S + Li_2S \tag{1}$$

$$Cu_2 S + 2Li \rightarrow 2Cu + Li_2S$$
 (2)

During the charging process, a temporary plateau at 2.28 V emerges, which goes down in the following cycles. According to other reports and our previous researches, it can be ascribed to the initial voltage barrier, relating to formation of the polysulfide intermediates [8,32,34]. Regarding to the charge mechanism of CuS, Kalimuldina and Taniguchi studied it thoroughly via ex-situ XRD analysis. It is reported that Cu and Li<sub>2</sub>S will be re-oxidized to Cu<sub>1.96</sub>S when using the copper foil as the current collector. It means that CuS will turn to cuprous



Fig. 1. Schematic illustration of preparing CuS/CNT composite.



Fig. 2. (a) XRD patterns and (b) Raman spectra of CuS/0.1 CNT and CuS/0.5 CNT. SEM images of (c, d) CuS/0.1 CNT and (e, f) CuS/0.5 CNT. TEM images of (g, h) CuS/0.1 CNT and (i, j) CuS/0.5 CNT. The scale bars of insets in (d) and (f) are 600 nm.



Fig. 3. Element mapping of (a-d) CuS/0.1 CNT and (e-h) CuS/0.5 CNT.

sulfides with subsequent cycling and this phenomenon also explains why the higher discharge plateau at 1.95 V keeps shrinking [13]. The CV curves and (dis)charge curves of CuS/0.1CNT and CuS/0.5CNT (Fig. S3) shows that with subsequent cycling, CuS may totally change to Cu<sub>2-x</sub>S and the electrochemical reaction becomes more reversible, which accords with the above-mentioned mechanism.

Fig. 4e shows the long-life cycling performances at 400 mA g<sup>-1</sup>. The initial discharge capacities of CuS, CuS/2.5% CNT and CuS/12% CNT, CuS/0.1 CNT and CuS/0.5 CNT are 404, 495, 513, 464 and 512 mAh g<sup>-1</sup>, respectively. Over 300 cycles, the capacity fading can be observed in the case of pristine CuS, whereas the discharge capacities of

CuS/2.5% CNT and CuS/12% CNT stay steady. For the CuS/0.1 CNT and CuS/0.5 CNT, the capacity recovery can be observed after 100 cycles, which will be illustrated later. After 450 cycles, the releasing capacities of CuS, CuS/2.5% CNT and CuS/12% CNT, CuS/0.1 CNT and CuS/0.5 CNT are 295, 352, 362, 437 and 558 mAh g<sup>-1</sup>, respectively. The cycling performances in other reports are listed in Table 1, from which it can be known that nanostructured construction or providing exterior network (reduced graphene oxide) has played a limited role in improving the reversible capacity of CuS. By contrast, simply providing an interior electronic conductive network can boost the cycling performance, especially in the case of CuS/0.5 CNT composites. According



Fig. 4. (a, b) CV profiles of CuS, CuS/2.5% CNT, CuS/12% CNT, CuS/0.1 CNT and CuS/0.5 CNT in the 1st and 5th cycles. Charge-discharge curves of (c) CuS/0.1 CNT and (d) CuS/0.5 CNT in the first three cycles. (e) Long-term cycling performance tests at 400 mA  $g^{-1}$ , (f) discharge capacities in the first 10 cycles, (g) rate capability and (h) reversible discharge capacities in different current densities. The specific capacity is calculated based on the mass of CuS.

Comparison of cycling performance in different reports.

Materials	Current density (mA g <sup>-1</sup> )	Voltage Range (V)	Cycles	Retained capacity (mAh g <sup>-1</sup> )	Ref.
CuS nanorod CuS coated on a Cu foil with a carbon fiber paper interlayer	112 560	0.01–3.0 1.2–3.0	250 200	~ 390 ~ 360	[12] [13]
CuS sphere-like hierarchical structure	100	0.01–3.0	10	~50	[14]
CuS nanowire bundle	112 2240	0.02–2.7	95	~518 ~200	[16]
CuS/rGO	100 500	1.0-3.0	70 200	~ 421 ~ 390	[17]
CuS nanoflake	560 1120	1.2–3.0	100 100	~ 395 ~ 386	[47]
CuS nanoflake microsphere microflower nanowire	27	1.8–2.7	50	~5 ~90 ~54 ~52	[48]
CuS/0.1 CNT CuS/0.5 CNT	400 400	1.0–3.0	450 450	~ 437 ~ 558	This work

to analysis, we find that the capacity fading in the first several cycles (normally less than 5 cycles) has a major impact in the reversible capacity (Fig. 4f). After 4 cycles, the releasing capacity levels off in all cases and capacity retentions of CuS, CuS/2.5% CNT and CuS/12% CNT are 74.3%, 64.3% and 60.6%, respectively. The significant capacity drop can be observed from other reports [13,16,17]. This may be related to the loss of CuS since CuS suffers from great volume change in the first cycles due to electrochemical re-construction, forming the electronic and ionic insulting Li<sub>2</sub>S [5]. Some Li<sub>2</sub>S will detach and cannot turn back to CuS if there is no suitable conductive and buffering network, which is blamed for main irreversible capacity. The cells of CuS, CuS/0.1CNT and CuS/0.5CNT after 150 cycles were disassembled and the electrodes were characterized by SEM, as shown in Fig. S4. In the case of CuS, the spherical morphology tends to be bulk-like materials. For the CuS/0.1CNT and CuS/0.5CNT, the morphologies are not maintained and particles with nano-size as well as carbon nanotubes can be observed. The CuS/0.1CNT and CuS/0.5CNT electrodes still display excellent cycling performances while the pristine morphologies are destroyed. We suppose that the CNTs conductive network here plays a significant role in the enhanced performances. Although both composites turn to nano-particles, the homogenously distributed CNTs still provides an effective electron transport conductive network for the active material. On the contrary, suffering from the electrochemical reorganization, some Li<sub>2</sub>S particles detaching from the matrix may not



Fig. 5. Schematically illustration of difference between pristine CuS and CuS/CNT.



Fig. 6. (a) EIS spectra of CuS/0.1 CNT and CuS/0.5 CNT before cycling and after 50 cycles, CV plots of (b) CuS/0.1 CNT and (c) CuS/0.5 CNT at different scan rates, (d) relation between reduction peak currents and the square root of scan rates, (e) GITT curves of CuS/0.1 CNT and CuS/0.5 CNT, (f) the calculated Li chemical diffusion coefficients as a function of stoichiometry from GITT.

Table 2					
The Li <sup>+</sup>	diffusion	coefficients	obtained	by CV	tests.

	CuS	CuS/2.5% CNT	CuS/12% CNT	CuS/0.1 CNT	CuS/0.5 CNT
$D(10^{-11} \text{ cm}^2 \text{ s}^{-1})$	5.79	6.76	8.82	6.40	11.0
$R^2$	0.997	0.996	0.998	0.998	0.995

obtain electrons in the case of pristine CuS, hence leading to loss of active materials and capacity fading. This data also proves the significance of introducing the internal conductive network. Nevertheless, even if external conductive and buffering networks such as reduced graphene oxide (rGO) are introduced (2.5%CNT and 12%CNT in our case), they cannot provide enough inherent electronic conductive pathway and the problem is not yet well addressed [18,35]. On the contrary, the CuS/0.1 CNT and CuS/0.5 CNT possessing internal electronic conductive skeleton suffer from less capacity loss in the first several cycles, the corresponding capacity retentions (4th cycle) are 79.4% and 83.1%, respectively. The strategy providing internal conductive skeleton to enhance the electrochemical properties also works for other materials like MnO<sub>2</sub>, TiO<sub>2</sub>, Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> and FeS<sub>2</sub> [20,21,36,37]. In addition, the reversible capacities of CuS/0.1 CNT and CuS/0.5 CNT recover after 100 cycles. The similar phenomenon occurred in cobalt sulfides is also reported by other groups [38]. It is ascribed to the reversible growth/dissolution of a polymeric gel-like polymer and enhanced faradic pseudocapacity-behavior occurred on the re-constructed surface of active materials [39-41]. For pristine CuS, CuS/2.5% CNT and CuS/12% CNT, the capacity recovery does not emerge and it is supposed that the sustaining loss of active materials is predominant, whereas the capacity loss is well inhibited in the case of CuS/0.1 CNT and CuS/0.5 CNT. The rate capability is investigated at different current densities ranging from 200 to 6400 mA  $g^{-1}$ . It can be known from the Fig. 4g and h that the rate performances of CuS/0.1 CNT and CuS/0.5 CNT are better than others. The reversible capacities of CuS/0.1 CNT are 376, 374, 370, 362, 349 and 324 mAh  $g^{-1}$ , while those of CuS/0.5 CNT are 454, 441, 431, 421, 408 and 386 mAh  $g^{-1}$  at 200, 400, 800, 1600, 3200 and 6400 mA  $g^{-1}$ , respectively. When the current density turns back to 200 mA  $g^{-1}$ , capacities of 396 and 459 mAh  $g^{-1}$  can be regained, respectively. Voltage gaps between charge/discharge plateaus at 6400 mA g<sup>-1</sup> are shown in Fig. S5 (Supplementary material). The smaller gap is attributed to better reaction kinetics [42]. That is to say, the gap of CuS/0.5 CNT is 431 mV, showing the best reaction kinetics. From the data above, it can be concluded that higher reversible capacity and better rate capability can be achieved in the case of CuS/CNTs. To illustrate the reason, a model representing the utilization degree of CuS is proposed as shown in Fig. 5. For the pristine CuS, the utilization in the interior is low, since the Li<sub>2</sub>S is electronic and ionic insulator. When the battery is recharged, Li<sub>2</sub>S on the surface of particles is easily oxidized to CuS, whereas that in the interior cannot acquire enough electrons, leading to low utilization of active material. By contrast, the internal electronic conductive network has been constructed for the CuS/CNT. The network guarantees effective electron transfer between the current collector and the interior of active materials, resulting in the high utilization of CuS. Therefore, superior electrochemical properties can be achieved by the CuS/CNTs composite.

Surface properties and reaction kinetics are of great importance, so EIS and chemical Li<sup>+</sup> ion diffusion coefficients are well investigated then. Fig. 6a shows the EIS profiles of CuS/0.1 CNT and CuS/0.5 CNT before cycling and after 50 cycles. The profiles are consisted of a depressed semi-circle and a sloped line, in which the semi-circle refers to the cell reaction resistance (ohmic surface layer resistance and chargetransfer resistance) and the sloped line corresponds to the diffusion of Li<sup>+</sup> ions in the electrode [43]. Before cycling, both contain a large semicircle. After 50 cycles, the circle becomes smaller, indicating decreasing reaction resistance. The decreasing resistance can be ascribed to the activation of active materials, which is consistent with the results of CV tests. Next, the chemical Li<sup>+</sup> ion diffusion coefficients (D) are obtained by the CV tests with different scan rates. Based on the Randles-Sevcik equation, the D can be calculated as follow [44,45]:

$$i_p = 0.4463nFAC \left(\frac{nFvD}{RT}\right)^{\frac{1}{2}}$$
(1)

where the i<sub>p</sub> refers to the redox peak current, F is the Faraday constant, n indicates the number of transferred electrons, A stands for the working electrode area, C is the concentration of lithium ions,  $\nu$  represents the scan rate, T is the temperature, R is the gas constant and D stands for the diffusion coefficient. As the scan rate increases, the intensity of peak current also becomes strong, accompanied by redox peak shifting (Figs. 6b and c, S6a-4c, Supplementary material). According to the Eq. (1), the redox peaks current exhibits a linear relationship with the square root of the scan rates (Fig. 6d), where the D is proportional to the slope of the line. The calculated D of CuS, CuS/2.5% CNT and CuS/12% CNT, CuS/0.1 CNT and CuS/0.5 CNT are shown in Table 2. Overall, adding CNTs is beneficial to promote the lithium ion diffusion coefficient, and higher coefficients can be obtained as increasing amount of CNTs. Compared to the CuS/12% CNT, the coefficient of CuS/0.5 CNT is higher, demonstrating the distinctly enhanced lithium ion diffusion due to the interior conductive network.

GITT measurements are also implemented (Figs.6e and S6d–4f, Supplementary material). Assuming the  $Li^+$  ion transfer satisfies the Fick's second law, the diffusion coefficients can be calculated based on the Eq. (2) as follow [45,46]:

$$D_{Li} = \frac{4}{\pi\tau} \left[ \left( \frac{m_B V_m}{A M_B} \right) \frac{\Delta E_s}{\Delta E_t} \right]^2 \left( \tau < \frac{L^2}{D_{Li}} \right)$$
(2)

where  $\tau$  represents the constant current titration time,  $V_m$  refers to the molar volume of active materials,  $m_B$  and  $M_B$  are the weight and molecular weight of active materials, A is the electrode surface area,  $\Delta E_s$  and  $\Delta E_t$  stand for the steady-state voltage change after a current disturbance and voltage change during the constant current titration, L is

the diffusion length. Observed from Fig. 5f, the diffusion coefficients of CuS/0.5 CNT ( $5.05 \times 10^{-8} \sim 3.15 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ ) are obviously higher than those of others ( $2.18 \times 10^{-10} \sim 2.05 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ ). From the results above, it can be concluded that the introducing internal electronic conductive network can actually enhance the electrochemical reaction kinetics, realizing the improved rate capability for CuS.

#### 4. Conclusion

In summary, CuS/CNT composites are successfully prepared via a one-pot microwave-assisted method. Under the microwave irradiation, CuS spheres are nucleated on the CNTs, in which the CNTs provide an intertwined and inherently conductive network. Contrast experiments are also set with the pristine CuS and the CuS mechanically mixed with CNTs (2.5%wt and 12%wt). Based on different electrochemical measurements, it can be concluded that the severe capacity fading is well inhibited via the CuS/CNTs hybrid materials designed, which show superior electrochemical performances (over 450 cycles, the CuS/0.5 CNT releases more than 569 mAh g<sup>-1</sup> at 400 mA g<sup>-1</sup> and the reversible capacity of 394 mAh g<sup>-1</sup> can be obtained even at the high current density of 6400 mA g<sup>-1</sup>.). Through GITT and CV tests, it can be proved that the hybrid structure (CuS/0.5 CNT) can boosts the Li<sup>+</sup> diffusion coefficient, which insures favorable cycling performance and outstanding rate capability. Thus, the facilely obtained CuS/CNT hybrid materials can be a hopeful anode candidate for high-performance energy storage systems.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2017.09.070.

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