# Self-templating thermolysis synthesis of $Cu_{2-x}S@M$ (M = C, TiO<sub>2</sub>, MoS<sub>2</sub>) hollow spheres and their application in rechargeable lithium batteries

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### ABSTRACT

Owing to their unique structural stability and impressive long-term cycling performance, coated hollow structures are highly attractive for energy storage systems, especially batteries. Many efforts have been devoted and various strategies have been proposed to prepare such materials. In the present work, we propose a self-templating thermolysis strategy, different from traditional wet processing methods, to fabricate cuprous sulfide hollow spheres coated with different shells, by exploiting the thermal decomposition properties of the core (CuS) and the protection provided by the shell. To demonstrate the generality of this synthetic approach, three different coating materials (carbon, TiO<sub>2</sub>, MoS<sub>2</sub>) have been chosen to prepare Cu<sub>2-x</sub>S@C, Cu<sub>2-x</sub>S@TiO<sub>2</sub> and Cu<sub>2-x</sub>S@MoS<sub>2</sub> hollow spheres. All synthesized composite materials were then assembled as electrodes and tested in lithium batteries, showing excellent cycling stability. In particular, the electrochemical properties of Cu<sub>2-x</sub>S@C were thoroughly investigated. The results of this work provide an alternative route to prepare coated metal sulfide hollow spheres for energy storage applications.

# 1 Introduction

Lithium ion batteries (LIBs) have dominated the portable electronic device market since the 1990s, owing to attractive properties such as long-term cycle life and

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high specific energy [1, 2]. In recent years, the largescale application of LIBs in electric vehicles (EV), hybrid electric vehicles (HEV), and plug-in hybrid electric vehicles (PHEV) has led to an increasing demand for high-power and safe materials.  $Li_4Ti_5O_{12}$  has been

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widely studied and applied in high-power storage systems, owing to its negligible volume change during (de)lithiation that ensures high structural stability and relatively high (dis)charge plateaus (~1.5 V) and avoids dendritic plating of lithium, guaranteeing high safety in battery applications [3, 4]. However, the low theoretical specific capacity (175 mAh·g<sup>-1</sup>) of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> has prevented its further application in high-performance batteries [5]. Therefore, numerous attempts have been made to develop new types of advanced electrode materials with higher energy density [6-10]. Among them, Li<sub>3</sub>VO<sub>4</sub> has attracted increasing attention, owing to their high theoretical capacity (394 mAh·g<sup>-1</sup>) and ionic conductivity [11]. Nevertheless, additional efforts such as the fabrication of nanostructures or coatings are needed to improve their very poor electronic conductivity [12]. Moreover, the vanadium-based raw materials used to prepare Li<sub>3</sub>VO<sub>4</sub> are not fully environmentally friendly. As another potentially promising type of anode materials, transition metal sulfides are also drawing significant attention owing to their high specific capacity, excellent electronic conductivity, and environmental friendliness [13, 14]. Among these materials, copper and cuprous sulfides have attracted great attention because of high capacity (~ 337 and ~560 mAh·g<sup>-1</sup> for Cu<sub>2</sub>S and CuS, respectively), low cost, good electrical conductivity (10<sup>-3</sup> S·cm<sup>-1</sup>), and favorable electrochemical properties with voltage plateaus similar with Ti-based materials [15, 16]. Unlike materials based on intercalation reactions (such as LiCoO<sub>2</sub>, Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>, etc.) and phase transitions (LiFePO<sub>4</sub>), which exhibit relatively high structural stability during (de)lithiation, the most severe problem hindering further application of conversion reaction-based materials in LIBs is the poor cyclability associated with their volume expansion and lattice distortion [17–20]. In addition, the loss of electroactive species is another critical factor that negatively affects the cyclability, because of the dissolution of sulfide species during cycling [21]. Several strategies have been proposed to address these issues, in order to improve the electrochemical performances.

Coating is a common and effective approach to enhance the electrochemical performances of different materials [22, 23]. Hwa et al. synthesized Li<sub>2</sub>S@C spheres for Li/S cells, exhibiting a low capacity decay rate of 0.046% per cycle over 1,500 cycles at 2 C [24]. Zhang et al. obtained MoS<sub>2</sub>@C nanorods with a reversible discharge capacity of 621 mAh·g<sup>-1</sup> after 80 cycles at 200 mA·g<sup>-1</sup> [25]. Cao et al. prepared a carbon-coated LiCoO<sub>2</sub> composite and applied it in lithium ion batteries. Compared with the uncoated LiCoO<sub>2</sub>, a lower charge transfer resistance and higher lithium diffusion coefficient were observed in the case of the coated LiCoO<sub>2</sub> electrode [26]. Likewise, Wang et al. obtained a TiO<sub>2</sub>/C composite exhibiting significantly improved electrochemical performances, such as the higher rate capability. The enhanced lithium storage properties of TiO<sub>2</sub>/C are ascribed to the introduction of the carbon coating layer, which significantly improves electron transport in the electrodes [27]. Seh and coworkers prepared sulfur@TiO<sub>2</sub> yolk shell structure for Li/S batteries, displaying outstanding cycl performance. The composite released an initial capacity of 1,030 mAh·g<sup>-1</sup> at 0.5 C and its capacity decay rate was 0.033% per cycle over 1,000 cycles [28]. This enhanced cyclability was ascribed to the physical and chemical stability of the coating layer, which is beneficial to maintain the morphology of well-designed nanostructures and reduces the loss of active species during long-term cycling [28, 29]. The fabrication of a hollow structure is another strategy used to improve the electrochemical properties of a material. Qian et al. prepared MoS<sub>2</sub>@C hollow nanotubes with a capacity of 1,058 mAh·g<sup>-1</sup> over 300 cycles at 0.5 C [30]. Similarly, Liu et al. synthesized hollow cobalt sulfide nanoparticles embedded in carbonaceous nanocages, with a residual discharge capacity of 365 mAh·g<sup>-1</sup> after 150 cycles at 1 C [31]. The superior electrochemical properties of these materials were attributed to their high specific area that allows a higher amount of electrolyte to interact with the active material, and to their internal void space that can effectively accommodate large volume changes [32]. Different methods have been developed to synthesize hollow structures. These approaches can be classified as: 1) hard templating, 2) soft templating, 3) sacrificial templating, and 4) Ostwald ripening methods. Comprehensive reviews summarizing these approaches are available [33, 34]. Although the hard/soft and sacrificial templating methods are attractive and

widely used to prepare sulfides and oxides, several factors such as the compatibility between templates and targeted materials and the etching conditions may significantly limit their broader applicability. The template-free Ostwald ripening, based on a recrystallization process, is an alternative method to prepare hollow materials, which has been applied to synthesize sulfides and oxides with a hollow structure. However, obtaining uniform and monodisperse particles is not easy, because the recrystallization process is difficult to control [35, 36]. Therefore, alternative approaches based on simple and general procedures need to be developed in order to meet these requirements for application in LIBs.

In this work, we propose a universal self-templating thermolysis method for the rational synthesis of  $Cu_{2-r}S@M$  (M = C, TiO<sub>2</sub>, and MoS<sub>2</sub>) composites with a hollow spherical structure, based on the thermal decomposition of CuS. At high temperature and under inert atmosphere, the inner CuS core is thermally decomposed to cuprous sulfides and elemental sulfur. At the same time, the outer layer is formed via carbonization (forming carbon) or calcination (forming TiO<sub>2</sub> and MoS<sub>2</sub>). The protection provided by the shell prevents the calcination of the CuS core and maintains its spherical shape, whereas the uncoated CuS spheres are sintered to micro-sized bulk materials. At the same time, elemental sulfur sublimates and is carried away by the flowing gas, leaving internal void spaces and completing the preparation of Cu2-xS@C, Cu2-xS@TiO2, and Cu2-xS@MoS2 hollow spheres. In the case of the  $Cu_{2-r}S@C$  system, the thickness of the carbon shell can be controlled by altering the amount of glucose added as carbon source, in such a way to obtain Cu2-xS@1.2C and Cu<sub>2-x</sub>S@1.6C compositions. The electrochemical performances of the Cu<sub>2-x</sub>S@M composites were tested by assembling them as electrodes for lithium batteries. In particular, the properties of the Cu<sub>2-x</sub>S@C hollow spheres were thoroughly investigated, including their rate capability and electrochemical impedance. We believe that the present template-free thermolysis strategy can represent an effective alternative to prepare coated metal sulfide hollow spheres for energy storage applications.

# 2 Experimental

#### 2.1 Materials synthesis

#### 2.1.1 CuS spheres

The CuS spheres were prepared by a modified microwave-assisted method [37]. Typically, 0.005 mol CuSO<sub>4</sub>· $5H_2O$  and 0.005 mol Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>· $5H_2O$  were sequentially added to 50 mL deionized water and evenly mixed under magnetic stirring followed by cyclic microwave irradiation (6 s on and 24 s off, 650 W) for 30 min to obtain CuS spheres. The products were washed by deionized water and absolute alcohol several times and then dried at 60 °C under vacuum overnight.

#### 2.1.2 $Cu_{2-x}S@C$ spheres

The as-prepared CuS spheres (0.8 g) and specific amounts (1.2 and 1.6 g) of glucose were added to 50 mL deionized water under magnetic stirring for 20 min. The mixture was transferred to a 100 mL Teflon-lined stainless steel autoclave, which was heated to 190 °C for 12 h and then naturally cooled down to room temperature. The resulting precipitate was filtered and then washed several times with deionized water and absolute alcohol. The obtained CuS@C was dried at 60 °C for 10 h under vacuum. The CuS@C was calcined at 500 °C for 8 h in Ar gas to obtain Cu<sub>2-x</sub>S@C hollow spheres. The final products are denoted as Cu<sub>2-x</sub>S@1.2C and Cu<sub>2-x</sub>S@1.6C in the following, according to the initial amount of added glucose.

#### 2.1.3 *Cu*<sub>2-x</sub>S@TiO<sub>2</sub>

The CuS spheres (0.5 g) and 0.25 g tetrabutyl titanate were added to 50 mL absolute alcohol, followed by magnetic stirring and heating at 70 °C until all alcohol was evaporated. The dried precursor was calcined at 500 °C for 6 h in Ar gas to obtain the Cu<sub>2-x</sub>S@TiO<sub>2</sub> hollow spheres.

#### 2.1.4 $Cu_{2-x}S@MoS_2$

The CuS spheres (0.5 g), 0.5 mmol Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O, 0.5 mmol Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O, and 2.5 mmol sulfur powder were added to 50 mL deionized water, followed by magnetic stirring for 0.5 h. The mixture was transferred to a 100 mL Teflon-lined stainless steel autoclave,

which was heated to 200 °C for 12 h and then naturally cooled down to room temperature. The precursor was washed using deionized water and absolute alcohol and then dried at 60 °C under vacuum overnight, followed by calcination at 500 °C for 6 h in Ar gas to obtain the  $Cu_{2-x}S@MoS_2$  hollow spheres.

2.1.5  $Cu_{2-x}S$ 

A 0.5 g amount of CuS spheres was directly calcined under the same conditions as those employed to prepare  $Cu_{2-x}S@C$ , and the final product is denoted as  $Cu_{2-x}S$  in the following.

#### 2.2 Structure characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Mini Flex 600 diffractometer with Cu Ka  $(\lambda = 1.5418 \text{ Å})$  radiation. The operating voltage and current were 40 kV and 15 mA, respectively. The morphologies and elemental distributions of the materials were characterized by field-emission scanning electron microscopy (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, JEOL JEM-2100). Thermogravimetric analysis (TGA) was performed on a SDT Q600 (TA Instruments) analyzer; the TGA measurements were carried out under air flow from room temperature to 800 °C, at a heating rate of 10 °C·min<sup>-1</sup>. The specific surface area was measured by the Brunauer-Emmett-Teller (BET) method, using N<sub>2</sub> adsorption and desorption isotherms obtained with a Micromeritics ASAP 2020 analyzer.

# 2.3 Cell fabrication and electrochemical characterization

The electrodes were fabricated according to the following procedure: The slurry (a mixture of 70 wt.%

 $Cu_{2-x}S@M$  as active material, 15 wt.% acetylene black as the conductive agent, and 15 wt.% polyvinylidene difluoride as the binder in N-methyl-2-pyrrolidinone solvent) was coated on a copper foil current collector. The electrode was dried at 60 °C for 12 h under vacuum. The mass loading of the electrodes ranged from 1.2 to 1.8 mg·cm<sup>-2</sup>. CR 2016-type coin cells were assembled in an argon-filled glove box with Celgard 2400 as the separator and lithium foil as the counter electrode. The electrolyte employed was 1 M bis(trifluoromethane)sulfonimide lithium salt (LiTFSI, J&K Chemical) dissolved in 1,3-dioxolane and dimethyl ether (1:1 v/v, Aladdin). Galvanostatic charge/discharge measurements were conducted in the 1.0-3.0 V voltage range (versus Li<sup>+</sup>/Li) on a Land CT2001A battery testing system. Cyclic voltammetry (CV) measurements were performed between 1.0 and 3.0 V, with a scan rate of 0.2 mV·s<sup>-1</sup> on a electrochemical workstation (CH Instruments Inc., CHI1030C). Electrochemical impedance spectroscopy (EIS) measurements were performed in the 10<sup>-1</sup>–10<sup>5</sup> Hz frequency range on a Solartron Modulab 1287/1260 system. All electrochemical tests were conducted at room temperature. The capacity of Cu<sub>2-x</sub>S@1.2C and Cu<sub>2-x</sub>S@1.6C was calculated according to the mass of copper sulfide, whereas the specific capacity of Cu2-xS@TiO2 and Cu2-xS@MoS2 was calculated according to the total mass of active material.

# 3 Results and discussion

# 3.1 Synthesis and structural characterization of $Cu_{2-x}S@M$ (M = C, TiO<sub>2</sub>, MoS<sub>2</sub>) hollow spheres

The synthetic scheme used to prepare the  $Cu_{2-x}S@M$ 

hollow spheres is illustrated in Fig. 1. CuS spheres

 $Coating \qquad Coating \qquad Calcination \qquad Calcinat$ 

Figure 1 Schematic illustration of the preparation of  $Cu_{2-x}S@C$  hollow spheres.

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were firstly synthesized under microwave irradiation, followed by the application of different coatings. CuS was chosen because it has been reported that it can thermally decompose to cuprous sulfides (Cu<sub>1.8</sub>S and Cu<sub>2</sub>S) and elemental sulfur under inert atmosphere at high temperature [38, 39]. At 500 °C, sulfur sublimates and is carried away by the flowing gas, leaving void spaces inside the particles. Considering the preparing process and requirement of application in batteries, the coating material should meet the requirements: 1) high thermal stability to maintain the morphology of precursors during calcination, 2) inert chemical reactivity with copper and cuprous sulfides, 3) high mechanical strength to guarantee structure stability during lithiation/delithiation processes. As we know, carbonaceous materials are widely used as the coating material since they exhibits physical and chemical advantages [29]. Besides, coating materials as well as contributing extra capacities are welcomed. Among these, TiO<sub>2</sub> is regarded as a favourable coating layer, applied in modifying cathode and anode materials because of its chemical safety and structural stability [40, 41]. The two-dimensional layered MoS<sub>2</sub> also displays high structural stability above 1.0 V because only insertion reactions will take place to form Li<sub>x</sub>MoS<sub>2</sub>, barely inducing structural stress [42]. Thus, uniform and monodispersed Cu<sub>2-x</sub>S@M hollow spheres were successfully prepared via the self-templating thermolysis route. The XRD pattern of CuS is shown in Fig. S1(a) (in the Electronic Supplementary Material (ESM)). The diffraction peaks of CuS are indexed to the standard card (JCPDS: 078-0876) and no other impurity phases can be observed. After calcination, the pattern (Fig. S2(c) in the ESM) has changed and the peaks correspond to the standard patterns of Cu<sub>2</sub>S (JCPDS: 072-1071) and Cu<sub>1.8</sub>S (JCPDS: 023-0962). It is well known that there are various sulfides, especially for cuprous sulfides composed of chalcocite, djurleite and so on [43]. In order to simplify the denotation here,  $Cu_{2-x}S$  is used to represent the calcined CuS product without any coating. For Cu<sub>2-x</sub>S@1.2C and Cu<sub>2-x</sub>S@1.6C, both XRD patterns (Figs. 2(a) and 2(b)) indicate that they have totally transformed into cuprous sulfides. The characteristic peaks of  $Cu_{2-x}S@TiO_2$  (Fig. 2(c)) can be well indexed to Cu<sub>1.8</sub>S and Cu<sub>2</sub>S, in which the weak peak at  $25.8^{\circ}$  is ascribed to TiO<sub>2</sub> (JCPDS: 065-2448). The relatively low intensity of the  $TiO_2$  peak may be ascribed to the small added amount of tetrabutyl titanate and to the low crystallinity. Similarly, the pattern of  $Cu_{2-x}S@MoS_2$  (Fig. 2(d)) matches well with the standard reference cards of  $Cu_{1.8}S$  and  $Cu_2S$ , except for the broad peak around 14.2°, indexed to the (002) plane of MoS<sub>2</sub> (JCPDS 065-0160) [44]. The XRD patterns discussed above thus suggest that the coating layer does not affect the materials composing the core ( $Cu_2S$ and  $Cu_{1.8}S$ ) after calcination.

Figure 3(a) shows that the synthetic CuS precursors are uniform spherical particles with a size of about 800 nm. The magnified image in the inset shows that the surface of the CuS spheres is rough and populated by a large number of nanocrystals. Upon calcination, the uncoated CuS spheres turn into micro-sized bulk materials, losing their spherical morphology (Fig. 3(b)). On the other hand, after coating with carbon, both CuS@1.2C (Fig. S2 in the ESM) and CuS@1.6C (Figs. 2(c) and 2(d)) retain their morphology. The insets reveal that their surface becomes smoother after coating. The morphologies of Cu2-3S@TiO2 and Cu2-3S@MoS2 are also well preserved after calcination. Notably, numerous nanosheets cover the surface of the Cu<sub>2-x</sub>S@MoS<sub>2</sub> spheres (see the inset in Fig. 3(h)), which can be ascribed to the formation of MoS<sub>2</sub> nanosheets [45]. The four cases discussed above demonstrate that the coating layer can play a key role in maintaining the morphology of the substrate, because its high



**Figure 2** XRD patterns of (a)  $Cu_{2-x}S@1.2C$ , (b)  $Cu_{2-x}S@1.6C$ , (c)  $Cu_{2-x}S@TiO_2$ , and (d)  $Cu_{2-x}S@MoS_2$ , along with the standard reference patterns of (e)  $Cu_{1.8}S$  and (f)  $Cu_2S$ .



**Figure 3** SEM images of (a) CuS, (b)  $Cu_{2-x}S$ , (c) and (d)  $Cu_{2-x}S@1.6C$ , (e) and (f)  $Cu_{2-x}S@TiO_2$ , and (g) and (h)  $Cu_{2-x}S@MoS_2$ . The scale bars of the insets in (a), (d), (f), and (h) are 500 nm, whereas the scale bar in (b) is 4 µm.

mechanical strength and elasticity act as a solid barrier to prevent rapid size growth and morphology degradation during calcination.

Elemental mapping analysis was conducted (Fig. 4) to investigate the elemental distribution in higher detail. The analysis indicates that Cu, S and C elements are homogeneously distributed over the whole structure of Cu<sub>2-x</sub>S@1.2C and Cu<sub>2-x</sub>S@1.6C. Similarly, Cu, S, Ti, O and Cu, S, Mo elements also homogenously distributed in Cu<sub>2-x</sub>S@TiO<sub>2</sub> and Cu<sub>2-x</sub>S@MoS<sub>2</sub>, respectively. TGA was used to determine the carbon content of Cu<sub>2-x</sub>S@1.2C and Cu<sub>2-x</sub>S@1.6C, as shown in Fig. S3 in the ESM. The mass uptake from 300 to 500 °C can be ascribed to the Cu<sub>2</sub>S + 1.5O<sub>2</sub>  $\rightarrow$  Cu<sub>2</sub>O + SO<sub>2</sub> and Cu<sub>2</sub>O + O<sub>2</sub> + SO<sub>2</sub>  $\rightarrow$  CuO·CuSO<sub>4</sub> reactions. The mass loss observed between 600 and 750 °C corresponds to the loss of carbon, due to the decomposition of CuO·CuSO<sub>4</sub>

and CuO. The residual weights of Cu<sub>2-r</sub>S@1.2C and Cu<sub>2-r</sub>S@1.6C (82.1% and 76.2%, respectively) correspond to carbon contents of 8.8% and 15.3%, respectively. TEM analysis was applied to further examine the interfacial structures. Figure 5(a) shows that the surface of the CuS spheres exhibits a rugged morphology, which can be observed more clearly in the highresolution TEM (HRTEM) image in Fig. 5(b). In the case of the Cu<sub>2-x</sub>S@1.2C material (Fig. 5(d)), a noncontiguous layer with a thickness of about 10 nm can be distinguished through its different contrast, indicating the presence of a coating layer on the surface. On the other hand, a 20 nm-thick and contiguous outer coating layer integrally wrapping up the core can be observed in the case of Cu<sub>2-x</sub>S@1.6C (Fig. 5(f)). No coating layer could be observed for  $Cu_{2-x}S@TiO_2$  (Figs. 5(g) and 5(h)), which may be due to the small amount of TiO<sub>2</sub> and to the close contact between TiO<sub>2</sub> and the sulfide sphere. In the case of  $Cu_{2-x}S@MoS_2$  (Figs. 5(i) and 5(j)), a large number of nanosheets can be observed on the surface region of the sphere. It should be noted that, at variance with other similar studies [23, 31, 46], the hollow structure could not be easily observed for the present materials. This may be ascribed to the fact that the electron beam could not penetrate the relatively thick outer coating shell and the inner cuprous sulfide layer, which can be seen in the insets of Fig. S4 in the ESM. Figures S4(a) and S4(b) in the ESM clearly highlight the presence of several broken Cu2-xS@C spheres and also show that the thickness of the double shell is about 100 nm. Broken spheres can be also observed in the case of Cu<sub>2-x</sub>S@TiO<sub>2</sub> and Cu<sub>2-x</sub>S@MoS<sub>2</sub>. The hollow structure of the present materials was demonstrated using nitrogen adsorption-desorption isotherm analysis, as shown in Fig. 6. The specific surface areas of CuS,  $Cu_{2-x}S@1.2C$ , Cu<sub>2-x</sub>S@1.6C, Cu<sub>2-x</sub>S@TiO<sub>2</sub>, and Cu<sub>2-x</sub>S@MoS<sub>2</sub> are 1.63, 10.4, 14.4, 1.76, and 4.90 m<sup>2</sup>·g<sup>-1</sup>. As shown in Fig. S4 in the ESM, some broken spheres can be observed in all cases; therefore, the increasing surface area in the above sequence can be ascribed to the exposed coating layer of the broken spheres and to the inner surface, especially for the carbon coating spheres. In fact, the carbon layer, with a thickness of less than 20 nm, exhibits a large surface area, similar to the case of reduced graphene oxide (rGO), whereas the TiO<sub>2</sub> layer

(a)



(c)

(b)

@1.2C

Figure 4 Elemental mapping images of (a)–(d)  $Cu_{2-x}S@1.2C$ , (e)–(h)  $Cu_{2-x}S@1.6C$ , (i)–(m)  $Cu_{2-x}S@TiO_2$ , and (o)–(r)  $Cu_{2-x}S@MoS_2$ .



Figure 5 TEM images of (a) and (b) CuS, (c) and (d)  $Cu_{2-x}S@1.2C$ , (e) and (f)  $Cu_{2-x}S@1.6C$ , (g) and (h)  $Cu_{2-x}S@TiO_2$ , and (i) and (j)  $Cu_{2-x}S@MoS_2$ .

does not provide an equally large area [47]. In the case of the  $Cu_{2-x}S@MoS_2$  material, the coating layer is composed of many  $MoS_2$  nanosheets (Fig. 3(h) and Fig. S4(d) in the ESM), which provide a larger surface area compared with TiO<sub>2</sub>.

#### 3.2 Electrochemical properties

In the initial discharge process, the electrochemical reactions only take place on the surface of the  $Cu_{2-x}S$  material because the bulk material is so compact that the solvated lithium ions could not penetrate in the

internal regions, leading to high polarization and lower utilization of the active material. After activation, the material utilization is improved, so that the capacity can be restored and the typical charge/discharge curves emerge again. A residual reversible capacity of less than 220 mAh·g<sup>-1</sup> remains after 200 cycles. In the case of the Cu<sub>2-x</sub>S@1.2C and Cu<sub>2-x</sub>S@1.6C materials, a high polarization is avoided and the initial discharge capacities are about 345 and 353 mAh·g<sup>-1</sup>, respectively. Two plateaus at around 2.1 and 1.7 V are observed in the initial discharge process, as shown in Figs. 7(b)



**Figure 6** N<sub>2</sub> adsorption–desorption isotherms analysis of (a) CuS, (b)  $Cu_{2-x}S@1.2C$ , (c)  $Cu_{2-x}S@1.6C$ , (d)  $Cu_{2-x}S@TiO_2$ , and (e)  $Cu_{2-x}S@MoS_2$ .

and 7(c), which are attributed to the reduction of sulfur species and copper ions, respectively. The electrochemical reactions corresponding to the discharge plateaus at 2.2 and 1.7 V are the following [21, 48–51]

$$2Cu_{2-x}S + 2xLi \rightarrow xLi_2S + (2-x)Cu_2S$$
(1)

$$Cu_2S + 2Li \rightarrow Li_2S + 2Cu \tag{2}$$

Turning to the charging processes, the width of the plateau at ~ 2.3 V continuously decreases while that of the plateau at ~ 1.9 V keeps increasing, which is consistent with other reports [21, 48]. After 200 cycles, only a single discharge plateau (~ 1.7 V) and a charge plateau at ~ 1.9 V are left in all cases, highlighting the high reversibility of the electrochemical reaction (2) [16, 51]. Figure S5(a) in the ESM displays the charge/ discharge curves of  $Cu_{2-x}S@TiO_2$  and  $Cu_{2-x}S@MoS_2$ , respectively. Since the charge and discharge plateaus



**Figure 7** Charge/discharge curves of (a)  $Cu_{2-x}S$ , (b)  $Cu_{2-x}S@1.2C$ , and (c)  $Cu_{2-x}S@1.6C$  at 400 mA·g<sup>-1</sup>; (d) cycling performances at 400 and 800 mA·g<sup>-1</sup>; (e) long-term cycling performance of  $Cu_{2-x}S@1.2C$  and  $Cu_{2-x}S@1.6C$  at 800 mA·g<sup>-1</sup>.

of TiO<sub>2</sub> are close to those of the cuprous sulfides, the charge and discharge curves of Cu<sub>2-x</sub>S@TiO<sub>2</sub> are also very similar to those of the cuprous sulfides [52]. At variance with TiO<sub>2</sub>, MoS<sub>2</sub> undergoes more complicated electrochemical reactions. Above 1.1 V, lithium insertion reactions (MoS<sub>2</sub> + xLi<sup>+</sup> +  $xe^- \rightarrow Li_x$ MoS<sub>2</sub>) take place, leading to a sloping plateau and higher specific capacity of Cu<sub>2-x</sub>S@MoS<sub>2</sub> (Fig. S5(b) in the ESM) [53, 54].

Cycling tests were conducted at different current densities. Cu<sub>2-x</sub>S@1.2C (Fig. 7(d)) showed discharge capacities of 285 and 276 mAh·g<sup>-1</sup> after 200 cycles at 400 and 800 mA·g<sup>-1</sup>, respectively. Reversible discharge capacities of 274 and 263 mAh·g<sup>-1</sup> remained for  $Cu_{2-x}S@1.6C$ , whereas the pristine  $Cu_{2-x}S$  electrodes delivered 218 and 194 mAh·g<sup>-1</sup>, respectively. Figure 7(e) shows the results of the long-term cycling tests for both systems at a current density of 800 mAh·g<sup>-1</sup>. In the case of the Cu<sub>2-x</sub>S@1.2C electrode, a specific capacity of 245 mAh·g<sup>-1</sup> is maintained over 1,000 cycles, while a reversible capacity of 278 mAh·g<sup>-1</sup> is still retained for the Cu<sub>2-x</sub>S@1.6C electrode. The superior cycling stability of Cu<sub>2-x</sub>S@1.6C is presumably due to the synergistic effect of the carbon coating layer and to the hollow structure. The carbonaceous layer helps to balance the loss of active material, substantially improving the cyclability [22, 24, 55]. The internal hollow space can effectively buffer the volume change, which is a common strategy used to enhance the structural stability during cycling [28, 33, 56]. It is interesting to observe that the discharging capacity of Cu<sub>2-x</sub>S@1.6C is restored and starts to increasing after 350 cycles. The capacity recovery is usually observed in metal sulfides/oxides, especially sulfide/oxide and carbon composites, and is ascribed to the interfacial storage of lithium ions and self-reconstruction of the active material [57-59]. As discussed above, the outstanding cycling performance of Cu<sub>2-x</sub>S@C is ascribed to its unique hollow structure and to the effective protection provided by carbon shell. However, no capacity recovery was observed in the case of  $Cu_{2-r}S@1.2C$ , probably due to the thickness of the carbon layer. As observed in Fig. 5(d),  $Cu_{2-y}S@1.2C$ exhibits an non-contiguous coating layer with a thickness of about 10 nm, which is not enough to protect the inner  $Cu_{2-x}S$  core. During long-term cycling, the active species will be lost, leading to capacity degradation.

Although some capacity recovery may also take place, the loss of capacity is more prominent, which leads to the overall capacity decrease observed for Cu<sub>2-x</sub>S@1.2C. The cycling performances of Cu<sub>2-x</sub>S@TiO<sub>2</sub> and  $Cu_{2-x}S@MoS_2$  were also tested at 400 mA·g<sup>-1</sup>. The initial discharge capacity of Cu<sub>2-x</sub>S@TiO<sub>2</sub> is around  $252 \text{ mAh} \cdot \text{g}^{-1}$  (Fig. S5(c) in the ESM). After 200 cycles, the reversible capacity decreases to 204 mAh·g<sup>-1</sup> and the Coulombic efficiency is close to 100%. We note that the reversible capacities of the Cu<sub>2-x</sub>S@TiO<sub>2</sub> electrode are inferior to those of the pristine  $Cu_{2-x}S$ . This can be ascribed to the following reasons: 1) The calculation of the specific capacity of  $Cu_{2-r}S@TiO_2$  is based on the total Cu<sub>2-r</sub>S@TiO<sub>2</sub> mass. The theoretical specific capacity of TiO<sub>2</sub> is about 175 mAh·g<sup>-1</sup>, leading to a lower specific capacity for the  $Cu_{2-r}S@TiO_2$  composite. 2) The poor electronic conductivity of TiO<sub>2</sub> may have a negative impact on the electrochemical properties of the cuprous sulfides. Nevertheless, Cu<sub>2-x</sub>S@TiO<sub>2</sub> displays superior cycling performance to pristine  $Cu_{2-r}S$ . The capacity retention of the former is 80.9% after 200 cycles, whereas that of  $Cu_{2-x}S$  (measured from the 2nd to the 200th cycle) is 76.0%. TiO<sub>2</sub>, owing to its high mechanical strength, can also be applied as host for Li-S batteries, in which it can effectively accommodate the volume expansion and inhibit loss of sulfur species [28]. Moreover, the hydrophilic Ti–O bonds favorably bind polysulfide anions, preventing the gradual loss of the active material [60]. The initial discharge capacity of the Cu2-xS@MoS2 composite (Fig. S5(d) in the ESM) is 381 mAh·g<sup>-1</sup>, and its reversible capacity is 361 mAh·g<sup>-1</sup>, which also denote impressive cycling performances. We note that the initial discharge capacity of Cu<sub>2-x</sub>S@MoS<sub>2</sub> is higher and the capacity is restored after 100 cycles. This may be due to the special electrochemical properties of MoS<sub>2</sub>. In the first discharge process (discussed above), Li<sup>+</sup> ions will insert into MoS<sub>2</sub> to form Li<sub>e</sub>MoS<sub>2</sub>, which contributes extra capacity and also induces irreversible structural expansion and deformation [42, 53]. Upon subsequent cycling, Li<sub>1</sub>MoS<sub>2</sub> decomposes to Mo and Li<sub>2</sub>S, with the latter contributing additional capacity. These effects explain the capacity restoration capability observed for Cu<sub>2-x</sub>S@MoS<sub>2</sub>. The data discussed above indicates that the  $Cu_{2-x}S@M$  (M = C, TiO<sub>2</sub>, and MoS<sub>2</sub>) hollow spheres prepared by the present self-templating

thermolysis strategy also exhibit excellent cycling capability.

The impressive long-term cycling performances of Cu<sub>2-x</sub>S@C (Fig. 7(e) in the ESM) prompted us to perform additional electrochemical tests to investigate the properties of Cu<sub>2-7</sub>S@1.2C and Cu<sub>2-7</sub>S@1.6C. Figure 8(a) shows the rate capability of  $Cu_{2-x}S$ ,  $Cu_{2-x}S@1.2C$ , and Cu<sub>2-x</sub>S@1.6C electrodes. The average discharge capacities of Cu<sub>2-x</sub>S@1.6C are 321, 314, 310, 304, 299, 298, and 286 mAh·g<sup>-1</sup> at 200, 400, 800, 1,600, 2,400, 3,200, and  $6,400 \text{ mA} \cdot \text{g}^{-1}$ , respectively. Under the same conditions, Cu<sub>2-x</sub>S@1.2C shows discharge capacities of 297, 284, 277, 271, 267, 265, and 260 mAh·g<sup>-1</sup>, respectively, whereas the  $Cu_{2-r}S$  electrode delivers capacities of 282, 275, 273, 270, 268, 266, and 246 mAh·g<sup>-1</sup>. Figure 8(b) compares the average discharge capacities of the three materials. The Cu<sub>2-x</sub>S@1.6C delivers the highest capacity at each different current density, whereas  $Cu_{2-x}S$  exhibits the lowest reversible capacities. The corresponding charge/discharge curves at 6,400 mA·g<sup>-1</sup> are shown in Fig. S6 in the ESM. The gap between the charge and discharge plateaus of pristine Cu<sub>2-x</sub>S is 37 mV, which is larger than the gaps measured for the carbon-coated sulfides (34 and 31 mV for Cu2-xS@1.2C and Cu<sub>2-x</sub>S@1.6C, respectively). These results indicate that the carbon coating layer, with its excellent electronic conductivity, can reduce the electrochemical polarization and enhance the rate capability of the active materials, especially in the case of  $Cu_{2-x}S@1.6C$  [29, 46].

Because the cycle performance and rate capability are highly correlated with the lithium ion diffusion and interfacial charge transfer properties, EIS measurements were performed to explore the reaction kinetics of the electrodes before cycling and after 100 cycles, as shown in Figs. 8(c) and 8(d). An equivalent circuit was used to fit the Nyquist plots. In Fig. 8,  $R_s$ stands for the bulk resistance corresponding to the ohmic resistance of electrolyte, electrodes, and cell hardware,  $R_{\rm ct}$  represents the charge-transfer resistance, and  $W_{0}$  is associated with the Li<sup>+</sup> diffusion process [61, 62]. The Nyquist plots before cycling and after 100 cycles consist of a semicircle at high frequency and a sloping line in the low-frequency region, corresponding to  $R_{ct}$  and Li<sup>+</sup> diffusion process, respectively. The impedance parameters are listed in Table 1. On one hand, the  $R_{\rm ct}$  values after 100 cycles are much smaller than before cycling, reflecting the activation of the active materials. The  $R_{ct}$  values of  $Cu_{2-x}S@1.2C$  and  $Cu_{2-x}S@1.6C$  are 6.60 and 3.82  $\Omega_{r}$ respectively, which are both smaller than the  $R_{ct}$  of



**Figure 8** (a) Rate capability and (b) reversible capacities of  $Cu_{2-x}S$ ,  $Cu_{2-x}S@1.2C$ , and  $Cu_{2-x}S@1.6C$  electrodes; EIS spectra before cycling (c) and after 100 cycles (d), both under fully charged conditions.

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Table 1Impedance parameters before cycling and after 100 cyclesat 400 mA·g $^{-1}$ 

Before cycling					
	$R_{\rm s}\left(\Omega ight)$	Error (%)	$R_{\rm ct}\left(\Omega\right)$	Error (%)	
Cu <sub>2-x</sub> S	2.12	2.14	40.4	1.77	
$Cu_{2-x}S@1.2C$	1.61	2.97	48.1	1.90	
Cu <sub>2-x</sub> S@1.6C	1.39	6.62	59.5	3.10	
	After 100 cycles				
	Aft	er 100 cycles			
	Aft $R_{\rm s}\left(\Omega\right)$	er 100 cycles Error (%)	$R_{\rm ct}\left(\Omega\right)$	Error (%)	
Cu <sub>2-x</sub> S	After $R_{\rm s}(\Omega)$ 9.82	er 100 cycles Error (%) 0.312	$R_{\rm ct}(\Omega)$ 11.5	Error (%) 0.665	
Cu <sub>2-x</sub> S Cu <sub>2-x</sub> S@1.2C	After $R_{\rm s}(\Omega)$ 9.82 3.08	er 100 cycles Error (%) 0.312 2.24	$R_{\rm ct}(\Omega)$ 11.5 6.60	Error (%) 0.665 2.00	

pristine  $Cu_{2-x}S(11.5 \Omega)$ , demonstrating that the carbon coating can effectively reduce the polarization and improve the electrical activity of the materials. On the other hand, the increased  $R_s$  values indicate that the bulk resistance of the cell becomes larger, mostly due to the resistance of the electrolyte. It has been reported that sustained side reactions between sulfides and electrolytes will dry out the electrolyte, leading to an increase in its resistance [61]. According to this interpretation, side reactions take place between the uncoated  $Cu_{2-x}S$  and the electrolyte. In contrast, the side reactions are substantially reduced for both Cu2-xS@C composites. The EIS results confirm that the carbon layer can effectively protect the inner active material, which also explains the superior cycling stability of  $Cu_{2-x}S@C$  compared with pristine  $Cu_{2-x}S$ .

#### 4 Conclusions

In summary, different  $Cu_{2-x}S@M$  (M = C, TiO<sub>2</sub>, and  $MoS_2$ ) hollow spheres were fabricated by a selftemplating thermolysis strategy, taking advantage of the thermal properties of CuS. At variance with the conventional wet processes, the proposed strategy is based on the pyrolysis of the precursors. Following this method, uniform and monodisperse coated hollow spheres of cuprous sulfide were successfully prepared. The performance of the prepared  $Cu_{2-x}S@M$  in lithium ion batteries were also tested. All electrodes, and especially the  $Cu_{2-x}S@C$ -based one, showed superior electrochemical performances compared with the uncoated  $Cu_{2-x}S$  electrode. The present results demonstrate the general applicability of the proposed strategy for the preparation of coated hollow spheres; the materials prepared by this approach also exhibit excellent electrochemical properties. In addition, different core precursors (as long as they possess thermolysis properties) and coating layers can be employed. We believe that the approach introduced in this work provides an effective alternative route to prepare coated hollow-structured materials for energy storage applications.

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**Electronic Supplementary Material**: Supplementary material (XRD patterns of CuS and Cu<sub>2-x</sub>S, SEM and TEM images of Cu<sub>2-x</sub>S@C, Cu<sub>2-x</sub>S@TiO<sub>2</sub> and Cu<sub>2-x</sub>S@MoS<sub>2</sub>, TGA curves, charge/discharge profiles and cycle performances of Cu<sub>2-x</sub>S@TiO<sub>2</sub> and Cu<sub>2-x</sub>S@MoS<sub>2</sub>, and charge/discharge profiles of Cu<sub>2-x</sub>S and Cu<sub>2-x</sub>S@C at the high rate) is available in the online version of this article at https://doi.org/10.1007/s12274-017-1693-1.

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