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## COMMUNICATION

# Bowl-like sulfur particles wrapped by graphene oxide as cathode material of lithium-sulfur batteries

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**We successfully synthesized sulfur particles with a bowl-like structure and wrapped those by graphene oxide (GO) via a simple method. The GO-wrapped bowl-like sulfur composite (GO-BS) with void space inside was used as cathode material of Li-S batteries, which realized the protection of active material and tolerance of volumetric expansion.**

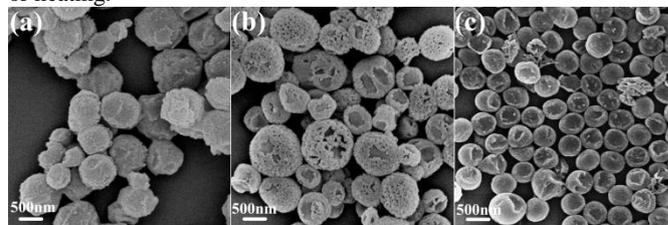
There has been a growing demand for high-performance and long-lifespan rechargeable batteries since the rapid development of portable electronics, electrical vehicles and grid-scale stationary energy storage.<sup>1–5</sup> Lithium ion batteries have been widely researched due to their advantages of high voltage, high capacity, and long usage lifetime.<sup>6,7</sup> However, traditional lithium ion batteries based on lithium metal oxide (such as  $\text{LiCoO}_2$  and  $\text{Li}_2\text{FeSiO}_4$ ) cathodes and carbon anodes cannot meet the need of high-energy storage quite well.<sup>4,8–10</sup> People hunger for higher capacity electrode materials to achieve enormous improvement of rechargeable batteries.

Sulfur (S) is an exciting candidate used as cathode due to its high theoretical capacity of 1,673 mAh/g as well as large abundance, low toxicity, low cost and environmental-friendly.<sup>11,12</sup> However, there are multiple problems impeding the application of Li-S batteries. The rapid capacity decay of S cathode is due to three major causes, including the large volume expansion (up to 80% change) of sulfur during lithiation, dissolution of intermediate lithium polysulfides ( $\text{Li}_2\text{S}_x$ ,  $4 \leq x \leq 8$ ) in the electrolyte, and low ionic/electronic conductivity of both S and  $\text{Li}_2\text{S}$ .

Over the years, various materials, such as carbon nanostructures and conductive polymers, have been used as matrix to hold sulfur and trap polysulfides within the frameworks.<sup>13–22</sup> These methods helped to protect the cathode, reduce the loss of active substance, and improve the conductivity of the electrode so that the property of the batteries could be better. Many researchers used the melt-diffusion method to fill sulfur into matrix. For example, Kai Zhang and his coworkers have prepared a composite, in which sulfur is infiltrated into porous hollow carbon spheres via a melt-diffusion process. The composite has realized high initial discharge capacity (1450 mAh/g) and good stability.<sup>23</sup> Another way is the so-called bottom-up approach, which can do better in protecting inner active component. Sulfur particles have been coated by conductive polymers and carbon materials. For instance, Jiepeng Rong and his

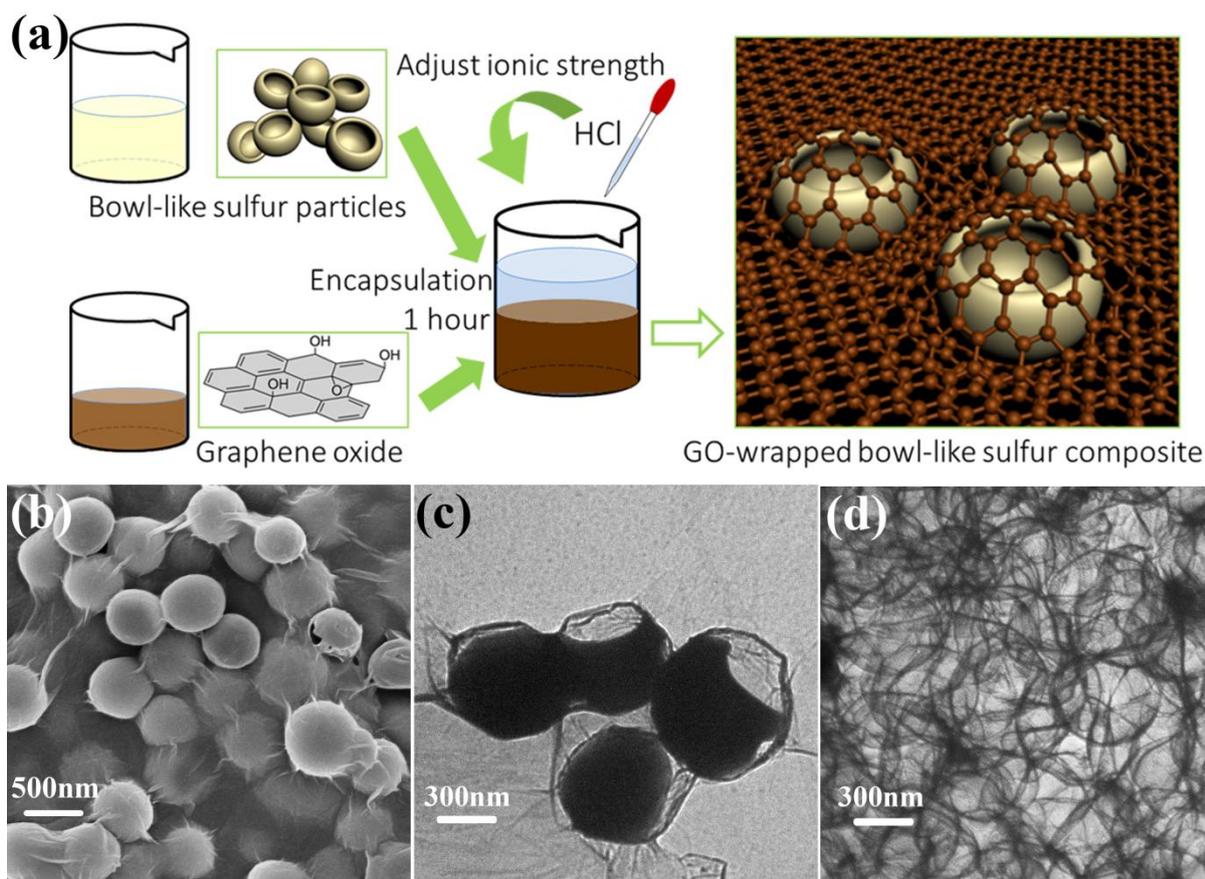
co-workers introduced a method to coat GO on various functional particles via solution ionic strength engineering and produced GO/sulfur particles with good electrochemical performance.<sup>24</sup> Furthermore, in order to overcome the volume expansion, nanostructures with internal void space have been prepared, using coating approach followed by a heating process or treated with toluene.<sup>25,26</sup> Besides, Ning Ding and his co-workers have synthesized S@C yolk-shell particles and such particle based 3D interconnected nanostructures through a novel method.<sup>27</sup>

Herein, we introduce a simple and efficient method to prepare GO-wrapped bowl-like sulfur composite (GO-BS) with void space inside used as cathode material of Li-S batteries. In this research, bowl-like sulfur particles were synthesized by controlling the amount of surfactant, and were wrapped in graphene oxide by adjusting ionic strength of the solution. (see detail in ESI<sup>†</sup>) The GO-BS used as cathode material for Li-S batteries showed good electrochemical properties with a specific capacity of 836 mAh/g at 0.2 A/g, and remaining 310 mAh/g after 500 cycles at 1 A/g. This method realized the structure with void space inside the GO shell by adjusting the shape of sulfur particles, without treating with toluene or heating.



**Fig. 1** SEM images of sulfur particles prepared with different amount of PVP: (a)  $2 \times 10^{-4}$  g, (b)  $2 \times 10^{-3}$  g, (c) 0.2 g.

Fig. 1 shows the morphology of sulfur particles with different shapes. In our experiment, we use PVP to modulate the shape of sulfur particles which is an important factor for the final internal void space of composite. PVP worked as surfactant, with hydrophilic group and hydrophobic group located respectively in the opposite sides of one molecule, making the concave structure possible.<sup>26</sup> Too little PVP made the particles solid as shown in Fig. 1(a). The ratio of concave structure on the particles became higher with larger amount of PVP. Fig. 1(c) shows the prepared bowl-like sulfur particles. The



**Fig. 2** (a) Schematic of the synthesis for GO-wrapped bowl-like sulfur composite. (b) SEM image, (c) TEM image of GO-BS. (d) TEM image of the composite after heat treatment.

average diameter was about 500 nm. Another SEM image of bowl-like sulfur particles could be found in Fig. S1, ESI<sup>†</sup>.

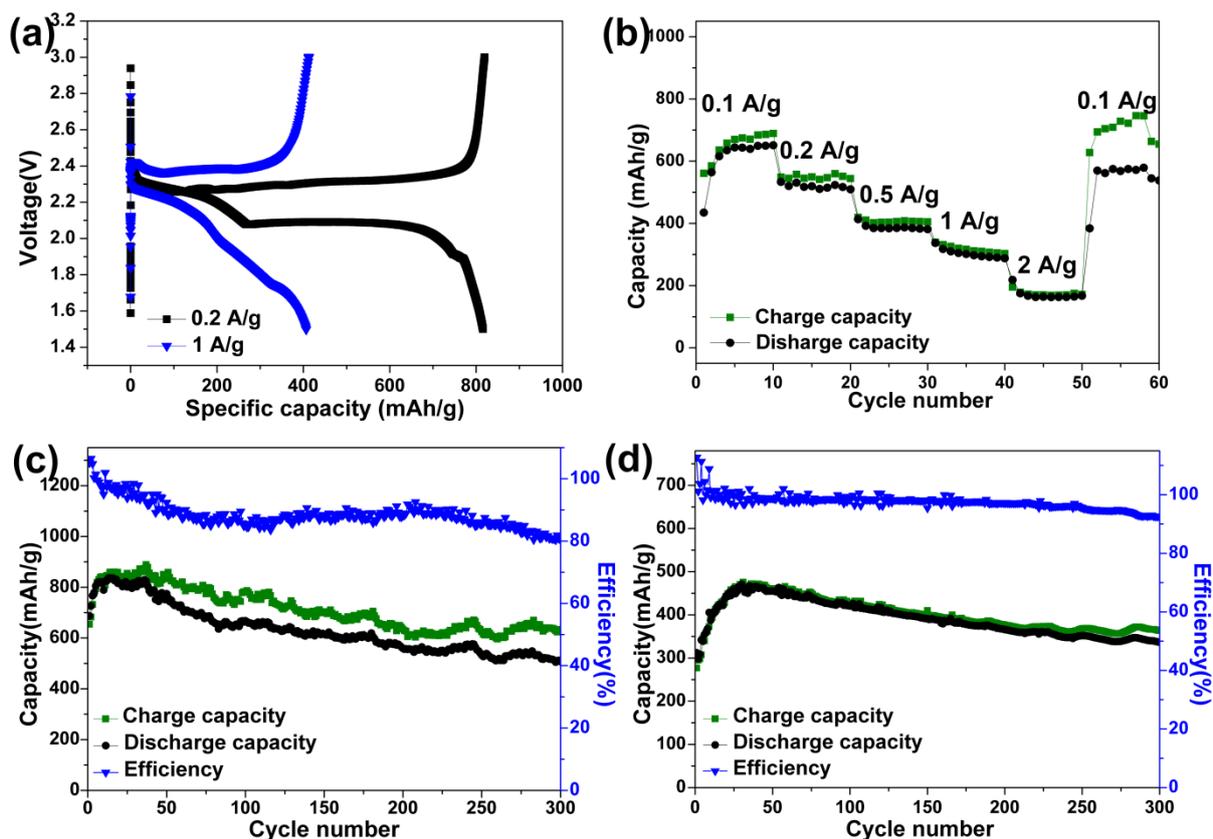
Fig. 2(a) is the schematic diagram of preparing the composite with internal void space. Owing to the special structure of sulfur particles, the method we used was very simple. GO solution was mixed with sulfur particles to form a suspension. Some HCl was dropped into the mixture. Large amount of brown floccule appeared. After washing and drying processes, GO-BS composite was collected. The SEM image of the composite was shown in Fig. 2(b). Sulfur particles were wrapped tightly by the GO layer. The TEM result in Fig. 2(c) proves that there was some void space inside the shell due to the bowl-like structure of sulfur particles. More SEM and TEM images of GO-BS can be found in supplementary information (Fig. S2, ESI<sup>†</sup>). The mechanism of encapsulation was explained by researchers that there are lots of groups such as hydroxyl and carboxylic located on GO. When dispersed in water, ionization of the groups caused GO to be negatively charged, which made it stable. The addition of HCl changed the surface charge (Zeta potential) of GO, forcing it to crinkle and coat on sulfur particles.<sup>24</sup> However, it can be observed from the picture that the shell was very thin and there were a few small holes existing on the surface. Thermal gravimetric analysis results (Fig. S3, ESI<sup>†</sup>) indicated that the weight fraction of sulfur in the composite is about 95 wt%. The structure results after heat treatment is exhibited in Fig. 2(d). When sulfur had been sublimed, a mass of shells were left alone.

To test electrochemical performance, 2032-type coin cells were fabricated using a Li foil as the anode. The results are shown in Fig. 3. Fig. 3(a) exhibits the typical discharge-charge voltage curves of

GO-wrapped sulfur composite at 0.2 A/g and 1A/g between 1.5 and 3.0 V. The curves showed several sequential steps corresponding to the charge and discharge processes. Two discharge plateaus exist at 2.3 V and 2.1 V, which can be assigned to the two-step reaction, corresponding to the formation of high-order polysulfides and low-order polysulfides respectively.<sup>21</sup>

When cycling under various C-rates, the performance of GO-BS was shown in Fig. 3(b). The cathode material was tested from 0.1 A/g to 2 A/g, 10 cycles at each current rate. The specific capacity reached 651 mAh/g, 533 mAh/g, 384 mAh/g, 301 mAh/g and 163 mAh/g at 0.1 A/g, 0.2 A/g, 0.5 A/g, 1 A/g and 2 A/g respectively. When the current density was sequentially decreased to 0.1 A/g, the specific capacity increased back to 574 mAh/g. Rate properties of GO-BS was much better than that of pure sulfur particles (Fig. S4(a), ESI<sup>†</sup>) which dropped sharply.

Fig. 3(c) shows the cycling performance of the battery made from GO-BS at 0.2 A/g for 300 cycles. The initial discharge specific capacity was 674 mAh/g. After more than ten cycles, a discharge specific capacity of 836 mAh/g was measured. When continued the charge-discharge processes, the capacity started to decrease little by little. After 300 cycles, a discharge specific capacity of 507 mAh/g was retained. The results were similar for cycling at 1 A/g, shown in Fig. 3(d), better than that of GO-wrapped solid sulfur composite (Fig. S4(b), ESI<sup>†</sup>), which reflected the importance of bowl-like structure of sulfur. Within the preliminary cycles, the specific capacity increased to 471 mAh/g. When continued the processes, the capacity began to decay slowly. After 300 cycles, the capacity remained 336 mAh/g.



**Fig. 3** Electrochemical characterization of GO-BS composite: (a) Typical discharge-charge voltage curves. (b) Rate properties at various rates. (c) Cycling performance at rates of 0.2 A/g and (d) 1 A/g.

In summary, the GO-BS composite showed a good electrochemical performance. This mainly derived from the protective function of GO shell, which means GO wrapped the sulfur particles tightly, preventing the polysulfide from escaping out of the structure during charge-discharge processes. What's more, the void space from the bowl-like sulfur particles helped to accommodate volume expansion generated during the charge-discharge processes, which protected the GO shell from breaking. As a result, the capacity could be retained to a great extent after hundreds of cycles.

However, different from most S-based cathode material, the discharge capacity didn't decay from the beginning, but increased for the first dozens of cycles. This phenomenon was mainly because the electrode made from GO-BS composite needed sometime to be activated. Most sulfur were encapsulated by GO, separated from the electrolyte. At the beginning of the charge-discharge procedure, the electrolyte permeated through the shell gradually and the specific capacity increased correspondingly. After the electrode was activated thoroughly and reached the maximum capacity, the value began to decrease. Furthermore, we also noticed that the coulombic efficiency was not very high, and dropped quickly. We attribute this result to the imperfection of structure. As shown in SEM image of the GO-BS composite (Fig. 2b), there were some scattering broken parts on the shell. The broken holes were large enough for polysulfide to come out, which caused much loss of the active material, resulting in the decrease of coulombic efficiency.

## Conclusions

In all, we successfully prepared bowl-like sulfur particles by controlling the amount of PVP addition, and GO-wrapped bowl-like sulfur composite was achieved via ionic strength engineering. It is indicated under SEM and TEM that the bowl-like sulfur particles were wrapped tightly by GO shell. The encapsulation structure as well as the inner void space resulted in a good electrochemical performance. Nevertheless, there still remained some problems such as decay of the capacity and coulombic efficiency. In the future, it is expected to improve its properties by further optimizing the structure. For example, we can attempt to thicken the shell, or to use other conductive materials to wrap the bowl-like sulfur. Especially, a strategy to develop graphene or reduced GO-wrapped sulfur should be considered in our near future study. And maybe this method could be widely used in preparing cathode material of Li-S batteries.

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## Notes and references

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