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Clustered-microcapsule-shaped Microporous Carbon Coated Sulfur Composite Synthesized via In-situ Oxidation

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KEYWORDS: clustered microcapsule structure, microporous carbon coated sulfur composite, high sulfur content, in-situ oxidation preparation, clustered ZnS precursor

ABSTRACT

Hollow materials as sulfur hosts, have been intensively investigated to address the poor cycling stabilities of Li-S batteries. Herein, we report an enhanced hollow framework to improve its applicability of the sulfur confinement. A clustered-microcapsule-shaped microporous carbon...
encapsulating sulfur (CM-S@MPC) composite, is prepared from the clustered zinc sulfide (C-ZnS) precursor, through an in-situ oxidation process. The high specific surface area and the in-situ preparation guarantee the uniform distribution of sulfur inside the carbon microcapsule, even under a higher sulfur content of 83 wt%. In addition, the interconnected frame constructed by the stacking of carbon microcapsules also mitigates the LPSs loss by setting interlayered hurdles on their pathway along the out-ward diffusion. Hence, these enable a fully demonstration of excellent cycling stability, compared to control sample obtained via physical sulfur infiltration. The outstanding decay rate of 0.039 % per cycle is achieved during 700 cycles at 1 C, even under high sulfur loading.

INTRODUCTION

As promising materials widely applied in the fields of catalysis,\textsuperscript{1-4} gas sensor,\textsuperscript{5-8} energy storage and conversion,\textsuperscript{9-15} hollow materials have also been researched as the hosts of sulfur in Li-S batteries for years, due to their special structures and functional characteristics.\textsuperscript{16-18} In the previous reports, Li-S battery is regarded as one of the prospective alternatives to the commercial Li-ion batteries, owing to its high theoretical energy density, cost-effective and environmental benignity.\textsuperscript{19-21} However, it is still plagued by three serious problems which are;\textsuperscript{22-24} (i) insulation of sulfur, (ii) volumetric change during cycling, and (iii) the dissolution of the intermediates. Hollow materials seem to be the right solution to the menaces. The inner void space can be employed to store the active sulfur and accommodate the large volumetric expansion (80 %) in the discharge process. And the considerable specific surface area provides full contact between the hollow host and the sulfur, enhancing the electron conductivity of sulfur and the discharge
end-product Li₂S. More notably, the shells are functionalized to block the dissolved intermediates of lithium polysulfides (LPSs) spreading out and shuttling to the anode, not only by space barrier, but also by chemical trap. The commonly researched hollow materials are; hollow carbon spheres,²⁵-³² hollow carbon nanofibers/tubes,¹⁶,³³-³⁴ various hollow oxides,¹⁹,³⁵-³⁸ and their hybrids.³⁹-⁴³ The introduction of these hollow hosts overcomes the shortcomings of the sulfur cathode, which significantly improves the cycling stabilities of the Li-S batteries. It is hoped that sulfur is better to be loaded inside the hollow cavity rather than in the micro/meso-pores on the outer shell.²⁷,²⁸ Only in this way, the hollow cavity can be fully used as the buffer pool to accommodate volumetric expansion, and the micro/meso-pores on the outer shell can take their positive roles of lithium-ion transmission and LPSs blockage. Remorsefully, it has been shown that the hollow materials have insufficient internal surface areas, leading to failed deposition of sulfur and Li₂S.²⁹ Hence, the shortage needs to be supplemented by micro/meso-pores in the outer shell, which will enable free flow of dissolved LPSs. Furthermore, the loading position of sulfur is difficult to control by the existing method that involves filling sulfur by capillary adsorption in the gaseous or liquid state.²⁷ This causes the distribution of the sulfur both inside and outside shell. In most cases, it also lead to the presence of sulfur at the micro and meso-pores of the outer-shell, which may results in the easy outflow of the LPSs.

To solve these aforementioned issues, Loose and clustered ZnS (C-ZnS) was skillfully synthesized to be the self-sacrificial template and sulfur source, followed by microporous carbon coating to form clustered microporous carbon coated ZnS (C-ZnS@MPC) with core-shell structure. Then, the clustered-microcapsule shaped microporous carbon coated sulfur (CM-S@MPC) composite was prepared via in-situ oxidation of the obtained C-ZnS@MPC. In the preparation process, the loose and clustered structure of C-ZnS, facilitated the carbon source to
access the interior of the C-ZnS and wrap each small ZnS particle homogeneously, forming the inter-connected carbon frame. Then, for the characteristic adsorption, iodine was easily distributed on the microporous carbon backbones, and served as the oxidizing agent to ensure in-situ oxidation of the ZnS inside the carbon microcapsule. This approach guaranteed the generated sulfur to be precisely deposited on the inwall of the carbon microcapsule.\textsuperscript{44,45}

Therefore, compared with the original hollow configuration, our improvement endowed the CM-S@MPC composite with particular features: (i) Larger specific surface area provided possibility for accommodation of more sulfur and discharge end-product; (ii) The sulfur preparation of in-situ oxidation enabled the sulfur to be deposited homogeneously inside every single carbon microcapsule, even under a higher sulfur content; (iii) The inter-connected carbon frame constructed by the clustered microcapsules, functioning as interlayered spatial barriers, effectively mitigated the out-ward diffusion of LPSs.

RESULTS AND DISCUSSION
Figure 1. Schematic illustration of the synthesis of the CM-S@MPC composite.

Figure 1 schematically illustrates the preparation process of CM-S@MPC. The loose and clustered ZnS (C-ZnS) precursor is synthesized through solvothermal reaction. In the preparation, the simultaneous additions of the two surfactants suppress the growth of the ZnS nanoparticles, and provide the primary particle with high surface energy that makes them aggregated to form a cluster shape, follow the principle of minimum energy. Resorcinol formaldehyde (RF) resin is employed as the carbon source precursor to coat the prepared C-ZnS. It is exactly the loose structure of the C-ZnS that enables the RF to access the interior and wrap every primary ZnS particle. RF resin is transformed to be the carbon layer, coating outside of every primary particle, after a calcination at 750 °C. The microporous carbon coated clustered
ZnS (C-ZnS@MPC) is obtained. And then, ZnS is oxidized inside every carbon microcapsule by the iodine that is enriched on the carbon shell. The generated sulfur is homogeneously oriented-deposited on the inwall of every carbon microcapsule, forming a single layer of sulfur. Hence, each microcapsule demonstrates double-hollow-sphere structure of sulfur and carbon. The whole structure looks like numerous microcapsules gathering together to form a cluster, so we name it clustered-microcapsule-shaped microporous carbon coated sulfur composite (CM-S@MPC).

![Figure 2](image-url)

**Figure 2.** TEM image of (a) overall, and (b) a single sphere of CM-S@MPC. (c) HRTEM image of CM-S@MPC. (d) Pore size distribution of CM-HCS, C-ZnS@MPC and CM-S@MPC. The STEM element mappings of (e) HAADF, (f) carbon, (g) sulfur, and (h) overlaying of the three.

In order to verify whether the micro-morphologies of the prepared materials are consistent with the designs, SEM and TEM are performed. Figure S1a shows that the obtained C-ZnS is monodispersed, with a particle distribution of 162±30 nm. The cluster structure can be observed clearly to be formed by the accumulation of large amount of ZnS primary particles in the TEM image (Figure S2a). The HRTEM in Figure S2b reveals that interplanar d-spacings is 0.312 nm,
corresponding to that of (0,0,60) lattice plane of the trigonal-type ZnS (JCPDS No. 01-089-2192). This result matches up with the strongest peak located at 28.55° in the XRD pattern (Figure S3). C-ZnS@MPC basically conserves the outline structure of C-ZnS, just slightly grows in size (Figure S1b and S2c). Every ZnS primary particle can be observed to be coated with a 2 nm thick carbon layer outside, in Figure S2d. The crystal type of ZnS is changed after the carbonization process (Figure S2d and S3). The CM-S@MPC composite, obtained via in-situ oxidation, maintains the original appearance and intact carbon configuration (Figure S1c and Figure 2a). Compared with C-ZnS@MPC precursor, the dimension of CM-S@MPC becomes smaller. The TEM image of CM-S@MPC demonstrates a spherical shape stacked by numerous hollow capsules (Figure 2b), which is in agreement with our material structure design. In comparison, without the use of the two surfactants, the ZnS ball gets bigger and closed packed, which enables the carbon source precursors only to coat outside (Figure S4a), rather than enter the interior. So, the different morphology of sulfur/carbon composite is achieved (Figure S4b). The HRTEM and STEM element mappings (Figure 2c and e-h) indicate that the distribution of sulfur is consistent with that of carbon, and the sulfur is homogeneously distributed without obvious aggregations, even under a sulfur content of higher than 80 wt% (Figure 3a). The HRTEM in Figure 2c shows that the average inner diameter of the microcapsule unit is approximate 12 nm. It is in highly agreement with the dominant pore size distribution at around 12 nm of CM-HCS (Figure 2d), which is obtained by removing the ZnS nano-particles in C-ZnS@MPC. Besides, the steep rises at P=P° in the isothermal curves (Figure S5) and the sharp peaks distributed in the micropore region (Figure 2d) of both CM-HCS and C-ZnS@MPC indicate the distribution of micropores on the carbon shells of microcapsules.42, 43 In the CM-S@MPC composite, sulfur has occupied part of the micropores of the CM-HCS, as well as part
of mesopores, which can be observed from the pore size distribution (Figure 2d). According to the discussion aforementioned, the sulfur is verified to be distributed inside of the CM-S@MPC composite. The micropore volume ($V_{\text{<2 nm}}$) of 0.23 cm$^3$ g$^{-1}$ (Figure S6) can be calculated to accommodate only 8.09 wt% of sulfur. Thereby, more than 74.91 wt% of sulfur could be deduced to be loaded on the inwall of carbon host, occupying the space of the hollow cavity. That is why the mesopore volume significantly decreases. In addition, the $V_{\text{<2 nm}}$ of 0.23 cm$^3$ g$^{-1}$ represents a relative small value, guaranteeing the suppression to the out-ward diffusion of LPSs.

It can be calculated that the mesopore volume provided by the microcapsules is 1.4 times the volume that 83 wt% sulfur (Figure 3a) needed, based on the sulfur density of 2.07 g cm$^3$ and $V_{\text{<2 nm}}$ of 3.38 cm$^3$ g$^{-1}$. This suggests the volume inside the microcapsule is fairly enough for the sulfur storage. In a similar way, the total pore volume of 4.36 cm$^3$ g$^{-1}$ can be calculated to be large enough to accommodate the corresponding Li$_2$S, based on the Li$_2$S density of 1.66 g cm$^3$. 
Figure 3. (a) TGA, (b) XRD patterns, (c) Raman, and (d) XPS of CM-S@MPC and S/CM-HCS.

The visualization discharge experiments of (e) CM-S@MPC, and (f) S/CM-HCS.

CM-HCS is employed as the host to be loaded with sulfur through melt-diffusion method, to obtain the S/CM-HCS composite (Figure S7). S/CM-HCS serves as the control sample, and is compared with CM-S@MPC using various techniques, to examine the structural characteristics of the CM-S@MPC composite and the advantages of in-situ oxidation approach. The TGA results in Figure 3a show that the weight loss temperature of S/CM-HCS is approximately 50 °C earlier than that of CM-S@MPC, under the similar sulfur content (about 82 wt.%), indicating
that the sulfur loaded in the same CM-HCS frame by the traditional physical method is easier to be lost than by the in-situ oxidation approach.\textsuperscript{33,46} The XRD pattern of S/CM-HCS displays obvious peaks mainly located at 23.12°, 25.94° and 26.78°, respectively, which matches up with the characteristic peaks of S\textsubscript{8} (JCPDS No.01-074-1465). The sulfur prepared directly from the oxidation of C-ZnS, also shows characteristic peaks of S\textsubscript{8}, suggesting that the sulfur synthesized via this approach is crystalline. While, no obvious sulfur characteristic peak appears in the XRD spectra of CM-S@MPC (Figure 3b), revealing that the sulfur introduced via in-situ oxidation method, is likely to attain uniform distribution, and does not exist outside the CM-HCS host.\textsuperscript{19,47} In the Raman spectra (Figure 3c), the characteristic peaks distributed at 472.0, 219.5, 155.6 and 85.5 cm\textsuperscript{-1} of S/CM-HCS indicate the presence of sulfur on the surface of CM-HCS host, further suggesting that it is difficult to load sulfur into the microporous carbon frame by the traditional melt-diffusion method.\textsuperscript{26} Comparatively, the much lower intensities of the sulfur characteristic peaks in the Raman spectra of CM-S@MPC also explain well confinement of sulfur in the CM-HCS host. Additionally, the lower I\textsubscript{D}/I\textsubscript{G} ratios of 0.85 and 0.90 show the relative higher graphitization extents, suggesting the superior electric conductivity of the carbon matrix. The surface of carbon frame may be oxidized partly by the iodic acid, resulting in the decreased graphitization degree of CM-S@MPC. That is why CM-S@MPC exhibits relative higher I\textsubscript{D}/I\textsubscript{G} ratio. This can be also verified by the higher oxygen atomic concentration of CM-S@MPC in the XPS results, compared with S/CM-HCS (Figure 3d). The characteristic peaks of O 1s, C1s, S2s and S2p can be observed in the XPS pattern of Figure 3d. Therein, the inset table exhibits that the sulfur atomic concentration of CM-S@MPC is 7.86\%, much lower than that of S/CM-HCS, which exhibits less sulfur content on the surface of CM-S@MPC. This is consistence with the aforementioned test results. An off-line visualization experiment is
performed under 0.5 current rate (based on the sulfur quantity on cathode). The cathode with CM-S@MPC as the active material demonstrates slight color change of the electrolyte during discharge (Figure 3e), explaining excellent LPSs confinement of the microporous walled carbon microcapsules. In contrast, the electrolyte color of S/CM-HCS becomes darker with time, which only indicates that the sulfur is not fully loaded inside the CM-HCS frames. From these results, it can be concluded that: in the CM-S@MPC, sulfur is well confined in the carbon microcapsule; and during the discharge process, CM-S@MPC also demonstrates superior space restriction to the dissolved LPSs. By comparison, it is difficult to infiltrate sulfur into the microporous CM-HCS host. Therefore, in the case of outside-in sulfur loading approach, the sulfur confinement effect of microporous carbon shell and the accommodation function of the hollow space in the CM-HCS frame cannot be well realized.
Figure 4. (a) Rate performance of CM-S@MPC and S/CM-HCS, (b) charge/discharge voltage profiles of CM-S@MPC in rate test. (c) Cycling performances at current rate of 0.2 C, and (d) 0.5 C of the two sulfur/carbon composites. (e) Long-term cycling capacity and coulombic efficiency of CM-S@MPC at 1 C.

The electrochemical performance of CM-S@MPC is evaluated to verify the sulfur confinement effect of the particular frame on the practical perspective. This is done based on a coin cell configuration with S/CM-HCS as the control sample. Figure 4a displays the discharge specific
capacities and coulombic efficiencies under different current rates. The average capacities of CM-S@MPC reaches 1148, 940, 880, 831 and 758 mAh g\(^{-1}\) at 0.2, 0.4, 0.6, 0.8 and 1 C, respectively, even under the sulfur loading of 3.5 mg cm\(^{-2}\). Moreover, the capacity of 955 mAh g\(^{-1}\) is recovered when the current density switches back to 0.4 C, a little higher than that of before, suggesting excellent reversible rate cycling performance. In the S/CM-HCS composite, part of sulfur is inevitably loaded on the outside of the carbon frame, where the mass transmission is better than inside. That is why it delivers the higher discharge capacities at the 0.2 C and 0.4 C. However, this part of sulfur is easy to loss, thereby, S/CM-HCS exhibits faster decreased specific capacities in the following rate cycles. The charge/discharge profile of CM-S@MPC is provided in Figure 4b. On the discharge curve of 0.2 C (Figure 4b), there is a small discharge voltage plateau at the low potential, which is the unique discharge manifestation of the microporous materials.\(^{26,30,48}\) The sulfur generated by in-situ oxidation is tightly anchored on the inwall of the carbon microcapsule with uniform distribution, enabling the fast electron transfer. This is also reflected by the relative smaller charge transfer resistance (R\(_{ct}\)) and ohmic impedance in EIS results (Figure S8). That is why the superior rate capability of CM-S@MPC is achieved.

On account of the rate results, the galvanostatic cycling tests are performed at 0.1 C for activation,\(^{48-50}\) followed by 0.2 C and 0.5 C, respectively. The results are displayed in Figure 4c and d. The initial capacity of 882 mAh g\(^{-1}\) and retained capacity of 830 mAh g\(^{-1}\) are obtained by CM-S@MPC after 100 cycles at 0.2 C, corresponding to the capacity retention of 94 %. The control sample only delivers a capacity retention of 70 %, which is much lower than that of CM-S@MPC. During the 0.5 C cycling (Figure 4d), the CM-S@MPC expresses an initial capacity of 859 mAh g\(^{-1}\) and the capacity retention of 72 % after 200 cycles. While, only 285 mAh g\(^{-1}\) is maintained by S/CM-HCS after 200 cycles. Then, the long-term cycling of CM-S@MPC is
carried out under 1 C-rate and sulfur loading of 3.03 mg cm$^{-2}$. It delivers an initial peak capacity of 657 mAh g$^{-1}$ and a capacity retention of 73 % after 300 cycles. The capacity is remained almost unchanged between 300 to 700 cycles. The calculated degradation ratio during the whole 700 cycles is 0.039 % per cycle. It is noted that such a long-term stability is a very attractive result for the cathode materials with similar frameworks (Table S1). The outstanding cycling stability is attributed to the special clustered-microcapsule structure that is stacked by a number of nano-scale double-hollow-spheres of carbon and sulfur. Every single microcapsule, as a miniature of hollow structure, possesses a hollow space for accommodating the volumetric expansion, and a microporous shell to serve as the LPSs hindrance. These are considered as the most prominent merits of hollow construction. Furthermore, it demonstrates several new advantages. Firstly, the relative thinner carbon walls facilitate fast transmission of lithium ions. Secondly, the larger specific surface area provides the higher content of sulfur with enough redeposition active sites. Thirdly, the big sphere after stacking not only improves the bulk density for easier process, but also sets multiple space hurdles on the diffusion path of LPSs, which significantly mitigates the loss of the active sulfur. Additionally, the intact microstructure is another cause to bring it high stabilities, which is confirmed by the STEM element mappings of CM-S@MPC after cycling (Figure S9). All of the abovementioned merits are beneficial to enhance the cycling stability at high sulfur areal loading.

CONCLUSION

In this work, a clustered-microcapsule-shaped microporous carbon coated sulfur (CM-S@MPC) composite with high sulfur content is synthesized through the in-situ oxidation of a loose clustered ZnS precursor. It is proved that the sulfur prepared by this approach is homogeneously
deposited on the inwall of every single microcapsule, even under the sulfur content of 83 wt%,
which is mainly attributed to: (i) The high specific surface area of 1668 m² g⁻¹, and pore volume
of 4.36 cm³ g⁻¹ of the CM-HCS host provide enough space for the deposition of sulfur and Li₂S;
(ii) The in-situ approach for loading sulfur enables accurate and reliable control of initial sulfur
deposition. Furthermore, in the visualization experiment, CM-S@MPC demonstrates a more
effective suppression to the out-ward diffusion of LPSs, compared with the control sample
obtained by physical sulfur infiltration. Therefore, it achieves satisfactory electrochemical
performance, with a remarkable low decay rate of 0.039 % per cycle during 700 cycles at 1C-rate,
under sulfur loading of 3.03 mg cm⁻². In short sentence, this work provides an innovative
preparation method and research strategy for the application of hollow materials in Li-S
secondary batteries.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the Internet at http://pubs.acs.org.
Material preparation, characterization and electrochemical measurements, SEM, TEM and
HRTEM images of the prepared materials, XRD patterns, N₂ adsorption/desorption isothermals,
pore volume analyses, EIS pattern, and the performance comparison table of hollow structure
cathode materials

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. ‡These authors contributed equally.

Notes

The authors declare no competing financial interest.

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