# **RESEARCH ARTICLE**



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# Yolk-shell nanoarchitecture for stabilizing a Ce<sub>2</sub>S<sub>3</sub> anode HPSTAR 1203-2021 Kanglong Hui<sup>1,2</sup> | Jipeng Fu<sup>1,3</sup> $\square$ | Jie Liu<sup>1</sup> | Yongjin Chen<sup>1</sup> | Xiang Gao<sup>1</sup> |

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## Abstract

Rare-earth sulfides are of research interest for lithium-ion batteries (LIBs) due to their abundant lithium intercalation sites and low redox voltage. However, their electrochemical performances are not satisfactory because of poor conductivity and volume change upon electrochemical cycling. Herein, nanoarchitectures of  $\gamma$ -Ce<sub>2</sub>S<sub>3</sub> encapsulated in a hollow mesoporous carbon nanosphere (Ce<sub>2</sub>S<sub>3</sub>@HMCS) are fabricated using the self-template strategy combined with the in-sphere sulfuration method and tested as an LIB anode. The void space between the Ce<sub>2</sub>S<sub>3</sub> core and the outer layer of the carbon nanosphere has been properly designed and modulated to achieve excellent electrochemical performance in terms of electronic conductivity, reversibility, and rate capability. The reversible capacity of Ce<sub>2</sub>S<sub>3</sub>@HMCS is 2.6 times that of the pure Ce<sub>2</sub>S<sub>3</sub> anode, which can gradually increase and maintain a capacity of  $282 \text{ mAh} \cdot \text{g}^{-1}$  at a current density of  $1 \text{ A} \cdot \text{g}^{-1}$ , and a high Coulombic efficiency (~100%) can be achieved even after 1000 cycles. This good performance is attributed to the unique yolk-shell nanostructure with a highly crystallized and stable Ce<sub>3</sub>S<sub>2</sub> core and volume expansion buffer space upon lithiation/ delithiation. Ex situ X-ray diffraction and nuclear magnetic resonance results indicate that the lithiation of Ce<sub>2</sub>S<sub>3</sub>@HMCS is an intercalation process. This study represents an important advancement in precise structural design with in-sphere sulfuration and sheds light on a potential direction for highperformance lithium storage.

# **KEYWORDS**

Ce<sub>2</sub>S<sub>3</sub> anode, intercalation mechanism, lithium ion batteries, structure stabilizing, yolk-shell nanoarchitecture

#### **INTRODUCTION** 1

Because of their high safety, long cycling life, and high energy density, lithium-ion batteries (LIBs) have been widely used as energy storage materials in portable electronic devices and electric vehicles.<sup>1–4</sup> With the rapid \_\_\_\_\_

development of high techniques, the demand for energy storage remains and is becoming increasingly more intensive. To meet the ever-increasing demand for LIBs, considerable effort has been dedicated toward developing more efficient anode materials. Some promising substitutes for LIB anode materials have been reported, such

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as carbon materials,<sup>3,5-8</sup> metal sulfides,<sup>9-13</sup> and metal oxides.<sup>14-19</sup> Rare-earth elements have been widely introduced into the battery community, such as the  $CeO_2$ in-laid Li-rich cathode,<sup>20</sup> and Ce-based anodes.<sup>21,22</sup> The combination of sulfur and rare-earth elements is expected to produce unpredicated properties due to multiple oxidation states of sulfur. Ce<sub>2</sub>S<sub>3</sub> displays three typical crystal structures: a,  $\beta$ , and  $\gamma$ .  $\gamma$ -Ce<sub>2</sub>S<sub>3</sub> usually shows a cubic structure of Th<sub>3</sub>P<sub>4</sub> with internal defects, and its chemical formula can be written as  $Ce_{3-x} \square_x S_4$  ( $\square$  represents vacancy,  $0 \le x \le 1/3$ ; therefore, Ce contains both +3 and +4 states. Due to abundant lithium intercalation sites and suitable voltage,<sup>23</sup> some studies used Ce<sub>2</sub>S<sub>3</sub> as anodes in addition to transition-metal sulfides:  $\text{SnS}_{x}^{24,25}$  FeS<sub>2</sub>,<sup>26</sup> NiS<sub>x</sub>,<sup>11</sup> MoS<sub>2</sub>,<sup>10,23</sup> and VS<sub>2</sub>.<sup>13</sup> Hou et al.<sup>27</sup> used the solid-state method to obtain a-Ce<sub>2</sub>S<sub>3</sub>-MoS<sub>2</sub> composites and investigated their electrochemical properties; however, the origin of capacity was not clearly identified, as to whether it was from Ce<sub>2</sub>S<sub>3</sub> or MoS<sub>2</sub>. The theoretical capacity of  $Ce_2S_3$  material is 428 mAh·g<sup>-1</sup>, which is higher than that of graphite material  $(372 \text{ mAh} \cdot \text{g}^{-1})$ . Although Ce<sub>2</sub>S<sub>3</sub>-based materials have low redox voltages, theoretical prediction shows that their poor electronic conductivity and volume instability upon cycling would further result in pulverization and structural collapse. Thus, electrochemical investigations of Ce<sub>2</sub>S<sub>3</sub> have rarely been conducted. In addition, the diameter of Ce<sub>2</sub>S<sub>3</sub> particles was not well controlled because of grain growth under high temperatures during sulfuration, which hinders fast intercalation/extraction of Li<sup>+</sup>. Nano-sized structures can effectively shorten the transport path of lithium ions and electrons during the process of charge and discharge.

To tackle the above challenges, relevant efforts have been made to enhance the electrochemical performance of sulfide-based anode materials.<sup>9–12,28</sup> Carbon-coated core–shell architecture appears to be an effective strategy and facilitates rapid electron diffusion,<sup>10,11,28,29</sup> resulting in improved electronic conductivity. Additionally, the core–shell structure provides spatial confinement, which prevents the pulverization and aggregation of sulfide. However, this strategy does not provide sufficient void space to buffer the volume expansion of sulfide compounds during Li<sup>+</sup> intercalation/deintercalation; therefore, stress fracture and exfoliation are usually observed for the anode upon cycling. The fabrication of the yolk-shell nanoarchitecture with tunable void space has been proven to be a new and attractive strategy to prevent damage of the architecture due to the reservation of the volume space for internal expansion. MoS<sub>2</sub> nanosheets inside hollow mesoporous carbon spheres were prepared for enhanced capacity and rate performance of LIBs.28 Ultrathin WS2 nanosheets were vertically embedded in hollow mesoporous carbon spheres (HMCSs) to form hierarchical triple-shelled (WS2-C-WS2) hollow nanospheres, leading to improved performance of LIBs and electrocatalysts.<sup>30</sup> NiS<sub>x</sub> was restricted in yolk-shell microboxes to avoid particle collapse and thus increase cycling stability.<sup>11</sup> Besides the aforementioned hollow confined structure for LIBs, the strategy is also extended to sodiumion batteries with various metals, sulfide, and oxide. FeS<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>, SnS, and FeS<sub>2</sub> nanoparticles were encapsulated into hollow carbon nanospheres to optimize the anode for sodium-ion batteries.<sup>17,31–33</sup> There is few report about rareearth sulfides confined into hollow carbon spheres with synergistic effects of enhancing electronic conductivity, structure stability, and shortening Li ion diffusion paths.

Herein,  $\gamma$ -Ce<sub>2</sub>S<sub>3</sub> nanoparticles encapsulated in hollow mesoporous carbon nanospheres were successfully designed using the self-template strategy combined with the in-sphere sulfuration method. The interfacial voids between carbon and nano Ce<sub>2</sub>S<sub>3</sub> were further modulated to form carbon tightly coated Ce<sub>2</sub>S<sub>3</sub> (Ce<sub>2</sub>S<sub>3</sub>@C) and yolk-shell Ce<sub>2</sub>S<sub>3</sub> (Ce<sub>2</sub>S<sub>3</sub>@HMCS). Enhanced capacity and stability are obtained for the well-constructed yolk-shell Ce<sub>2</sub>S<sub>3</sub>@HMCS when compared with the untreated Ce<sub>2</sub>S<sub>3</sub>. The unique and novel architecture provides not only conductive channels for the transport of Li<sup>+</sup> and electrons but also spatial void to buffer volume change during cycling. The procedure of fabricating Ce<sub>2</sub>S<sub>3</sub>@HMCS is demonstrated in Schematic 1. The lithium intercalation process mechanism of rare-earth sulfide was first proposed using ex situ X-ray diffraction



**SCHEME 1** Illustration diagram of fabricating Ce<sub>2</sub>S<sub>3</sub>@HMCS nanospheres. HMCS, hollow mesoporous carbon sphere; RF, resorcinol-formaldehyde

(XRD) and nuclear magnetic resonance (NMR), demonstrating the feasibility of the three-dimensional nanostructure strategy of rare-earth sulfide for potential application. First, uniform CeO<sub>2</sub> nanospheres were synthesized by the improved solvothermal method and used as subsequent templates.<sup>34</sup> Second, a layer of SiO<sub>2</sub> was coated on the surface of CeO<sub>2</sub> using the sol-gel method. The prepared CeO<sub>2</sub>@SiO<sub>2</sub> was dissolved in deionized water, and the resorcinol-formaldehyde (RF) was coated to obtain the core-shell structure of CeO<sub>2</sub>@SiO<sub>2</sub>@RF nanospheres. Third, the CeO<sub>2</sub>@void@C of the yolk-shell structure was obtained by annealing and etching. Finally, uniform Ce<sub>2</sub>S<sub>3</sub>@HMCS yolk-shell nanospheres were obtained by further reacting CeO<sub>2</sub>@void@C and CS<sub>2</sub>.

# 2 | EXPERIMENTAL SECTION

# 2.1 | Materials

Cerium nitrate hexahydrate ( $Ce_2(CO_3)_3 \cdot 6H_2O$ ), ethylene glycol, ethanol, deionized water, glacial acetic acid, sodium citrate, tetraethylorthosilicate (TEOS), ammonia solution (28 wt%), ethylenediamine, resorcinol, formaldehyde, sodium carbonate anhydrous, sodium hydroxide solution, and carbon disulfide were purchased from Macklin and used as starting materials. All chemicals were analytical grade and used without further purification.

# 2.2 | Sample preparation

# 2.2.1 | The precursor $CeO_2$

CeO<sub>2</sub> nanospheres were synthesized using the solvothermal method. Typically, 1 g of Ce<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was dissolved in 1 mL of deionized water, followed by the addition of 1 mL of glacial acetic acid, 0.1 g of sodium citrate, and 30 mL of glycol. The above mixture was stirred for 30 min under magnetic force and was then transferred to a Teflon-lined stainless-steel autoclave, followed by heating at 180°C for 4 h. The product was washed with ethanol and deionized water, and dried at 60°C for 12 h to obtain well-dispersed CeO<sub>2</sub> nanospheres.

# 2.2.2 | Synthesis of $CeO_2@SiO_2@RF$

Hundred milligrams of precursor  $CeO_2$  nanospheres were dispersed in a mixture of 40 mL deionized of water and 160 mL of ethanol, and the mixture was continuously for 30 min; 3 mL of ammonia solution (28 wt%) and 0.5 mL of TEOS solution were then added successively, followed by stirring for 6 h at room temperature. The products were separated by centrifugation, washed with ethanol and deionized water, and dried under 60°C for 12 h to obtain pure  $CeO_2@SiO_2$  nanospheres; 100 mg of  $CeO_2@SiO_2$  nanospheres were added to 20 mL of deionized water and 80 mL of ethanol, 3 mL of ammonia solution (28 wt%) was added,

ARBON ENERGY-WILEY-

spheres were added to 20 mL of deionized water and 80 mL of ethanol, 3 mL of ammonia solution (28 wt%) was added, and the mixture was stirred for 30 min. Then, 100 mg of resorcinol and 0.14 mL of formaldehyde solution were added to the above mixture, with further stirring for 24 h at room temperature. The reaction products were centrifuged and washed with water and ethanol. The final product was further dried at 60°C for 12 h to obtain  $CeO_2@SiO_2@RF$  nanospheres.

# 2.2.3 | Synthesis of $Ce_2S_3$ @HMCS

CeO<sub>2</sub>@SiO<sub>2</sub>@RF nanospheres were annealed at 600°C in an N<sub>2</sub> atmosphere for 4 h to obtain CeO<sub>2</sub>@SiO<sub>2</sub>@C, which was then stirred in NaOH solution at 80°C for 24 h to etch the SiO<sub>2</sub> layer to form CeO<sub>2</sub>@void@C. The above-obtained CeO<sub>2</sub>@void@C was mixed with anhydrous Na<sub>2</sub>CO<sub>3</sub> in a molar ratio of Na/Ce = 0.2. Then, the mixture was loaded into a porcelain boat and placed in a furnace at 800°C for 2 h under an N<sub>2</sub> atmosphere. When the furnace temperature increased to 500°C, CS<sub>2</sub> liquid was bubbled into the furnace with N<sub>2</sub> gas to form the final product Ce<sub>2</sub>S<sub>3</sub>@void@C (Ce<sub>2</sub>S<sub>3</sub>@HMCS).

# 2.2.4 | Synthesis of $Ce_2S_3@C$

Hundred milligrams of precursor CeO<sub>2</sub> nanospheres was dispersed in a mixture of 20 mL of deionized water and 80 mL of ethanol. Then, 1 mL of ammonia solution (28 wt%) was added, and the mixture was stirred for 30 min; 100 mg of resorcinol and 0.14 mL of formaldehyde solution were then added and stirred for 24 h at room temperature. The products were separated by centrifugation, washed with water and ethanol, and dried under 60°C for 12 h to obtain CeO<sub>2</sub>@RF nanospheres, which were annealed at 600°C under an N<sub>2</sub> atmosphere for 4 h to form CeO<sub>2</sub>@C. CeO<sub>2</sub>@C and anhydrous Na<sub>2</sub>CO<sub>3</sub> were mixed according to the molar ratio of Na/Ce = 0.2 and then the mixture was loaded into a porcelain boat and heated at 800°C for 2 h. When the furnace temperature increased to 500°C, the CS<sub>2</sub> liquid was bubbled into the furnace with N<sub>2</sub> gas to produce Ce<sub>2</sub>S<sub>3</sub>@C.

# 2.3 | Structure and morphology characterization

The morphologies were characterized by field emission scanning electron microscopy (FE-SEM; JSM-7900F) and

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field emission transmission electron microscopy (FE-TEM; Tecnai G2 F20 S-Twin). An X-ray diffractometer (PANalytical Empyrean) was used to determine the crystal structure. Thermogravimetric analysis (TGA) was performed on a thermal analyzer (TG, Netzsch STA449 F5/F3 Jupiter) at a heating rate of  $10^{\circ}$ C·min<sup>-1</sup>. The Raman spectra were carried out using a Renishaw inVia Reflex spectrometer. The specific surface area and pore size of the samples were measured using a physical adsorption analyzer (ASAP 2460). The chemical states of the samples were studied by X-ray photoelectron spectroscopy (XPS) (Thermo ESCALAB 250Xi). <sup>7</sup>Li magic-angle-spinning (MAS) NMR experiments were performed on a Bruker Avance spectrometer in a 9.2 T magnetic field with a <sup>7</sup>Li Larmor frequency of 155.5 MHz. All electrodes were packed into 4.0 mm rotors in an Ar glovebox and spun at a rate of 8 kHz. The recycle delay was set as 5.0 s and the 90° pulse length was  $2.4 \,\mu s$ . <sup>7</sup>Li chemical shifts were referenced by the 1 M LiCl solution with shifts at 0 ppm.

### 2.4 **Electrochemical performance**

The active material pure Ce<sub>2</sub>S<sub>3</sub> or Ce<sub>2</sub>S<sub>3</sub>@C or Ce<sub>2</sub>S<sub>3</sub>@HMCS, conductive carbon (Super P), and polyvinylidene fluoride were mixed and dispersed in an Nmethyl-2-pyrrolidine solvent at 8:1:1 by weight ratio to obtain a homogeneous slurry, which was coated on a copper foil. The active material loading of the copper foil is  $1.4 \text{ mg} \cdot \text{cm}^{-2}$ . The coated sheet was dried at  $120^{\circ}\text{C}$  for 12 h under vacuum, and the cut electrode was then assembled into a 2032 coin cell in an argon-filled glovebox. Lithium metal sheet was used as the counter electrode, and 1 M LiPF<sub>6</sub> in ethylene carbonate/dimethyl carbonate (EC:DMC = 1:1 in volume) solvent was used as the electrolyte. The electrochemical performances were carried out on a Lanthe CT2001A/B battery tester. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out on an SP-150 electrochemical workstation (Bio-Logic). All current density and specific capacity calculations were based on the total mass of the composite.

#### 3 **RESULTS AND DISCUSSION**

The cubic fluorite precursor CeO<sub>2</sub> nanospheres were successfully synthesized using the solvothermal method as proved by XRD patterns (Figure 1). The coated CeO<sub>2</sub>@SiO<sub>2</sub>, CeO<sub>2</sub>@SiO<sub>2</sub>@RF, and CeO<sub>2</sub>@void@C retained their original cubic structure patterns, except for slight broadening of CeO<sub>2</sub>@SiO<sub>2</sub> and CeO<sub>2</sub>@SiO<sub>2</sub>@RF (Figure 1). This is likely

due to the influence of SiO<sub>2</sub>. The obtained CeO<sub>2</sub>@void@C was further reacted with CS2 gas at 800°C under the protection of an N2 atmosphere to form y-Ce2S3@void@C (hereinafter called Ce<sub>2</sub>S<sub>3</sub>@HMCS), which is revealed by XRD with the reference of JCPDS: No.50-0851 (Figure 1). The peaks of Ce<sub>2</sub>S<sub>3</sub>@HMCS are much sharper when compared with these CeO<sub>2</sub>-based materials. This is mainly due to the difference between the synthetic methods of these two materials, which lead to different degrees of crystallization. However, the materials synthesized by the high-temperature annealing method have a higher degree of crystallinity. XRD measurements were also carried out for CeO2, CeO2@C, and their sulfured products (Ce<sub>2</sub>S<sub>3</sub>, Ce<sub>2</sub>S<sub>3</sub>@C), which are well in agreement with the standard patterns as shown in Figures S1 and S2.

The SEM and TEM morphologies of Ce<sub>2</sub>S<sub>3</sub>@HMCS and Ce<sub>2</sub>S<sub>3</sub>@C are shown in Figure 2. The particle sizes of Ce<sub>2</sub>S<sub>3</sub>@C and Ce<sub>2</sub>S<sub>3</sub>@HMCS are, respectively, distributed in the range of around 180 and 200 nm, with an outer carbon shell of 20 nm in thickness. The Ce<sub>2</sub>S<sub>3</sub>@HMCS shows an obvious void between the Ce<sub>2</sub>S<sub>3</sub> core and the carbon shell, whereas no void was observed for Ce<sub>2</sub>S<sub>3</sub>@C (Figure 2A,B,E,F). The high-resolution transmission electron microscopy (HRTEM) images in Figures 2C and 2G show that the lattice fringe d spacing of each sample is in good agreement with the XRD patterns. The results of energy-dispersive X-ray spectrum elemental mappings indicate that Ce and S are homogeneously distributed in the core regions of Ce<sub>2</sub>S<sub>3</sub>@C and Ce<sub>2</sub>S<sub>3</sub>@HMCS, which reveals that the carbon shell prevents reunion during the sulfuration process of CeO<sub>2</sub>



FIGURE 1 X-ray diffraction patterns of CeO<sub>2</sub>, CeO<sub>2</sub>@SiO<sub>2</sub>, CeO2@SiO2@RF, CeO2@void@C, and Ce2S3@HMCS. HMCS, hollow mesoporous carbon sphere; RF, resorcinol-formaldehyde



**FIGURE 2** Scanning electron microscopy images (A,E), transmission electron microscopy images (B,F), high-resolution transmission electron microscopy images (C,G), and energy-dispersive X-ray spectrum elemental mappings (D,H) of  $Ce_2S_3@HMCS$  and  $Ce_2S_3@C$ , respectively

(Figure 2A,B). However, the vulcanized products of  $CeO_2$  nanoparticles without a carbon shell were intensively agglomerated (Figure S4).

Figure 3A shows the Raman spectra of Ce<sub>2</sub>S<sub>3</sub>@HMCS, CeO<sub>2</sub>@void@C, and Ce<sub>2</sub>S<sub>3</sub>@C. Two broad peaks at 1350 and 1590 cm<sup>-1</sup>, corresponding to the D band (disorder induction) and the G band (graphite), are detected for all three samples.35 Ce<sub>2</sub>S<sub>3</sub>@C and Ce<sub>2</sub>S<sub>3</sub>@HMCS have similar intensity ratios of the D/G band, which show high graphitization and electronic conductivity.<sup>28,36</sup> Compared with CeO<sub>2</sub>@void@C, the D/G band ratios of Ce2S3@C and Ce2S3@HMCS decreased slightly, which may be caused by the continuous sulfuration under high temperatures.

The TGA curve of the Ce<sub>2</sub>S<sub>3</sub>@HMCS sample is shown in Figure 3B. The slight weight loss below 200°C is attributed to the vaporization of the adsorbed water. The weight evolution between 350°C and 650°C is the result of two contributions: on the one hand, cerium sulfide reacts with oxygen to form sulfur oxide, with oxygen absorption for weight gain, and this corresponds to the exothermic peak observed at 517°C;<sup>37</sup> on the other hand, carbon is oxidized by weight loss, and this corresponds to the exothermic peak observed at 365°C. The rapid weight loss in the range of 650°C and 900°C is attributed to a deeper oxidation reaction of the previously formed sulfur oxide to produce and release SO<sub>2</sub> gas.<sup>38</sup> By subtracting the adsorbed water from the system, the carbon content in the Ce<sub>2</sub>S<sub>3</sub>@HMCS is around 18% according to the equation shown in the Supporting Information.

The pore structures of Ce<sub>2</sub>S<sub>3</sub>, Ce<sub>2</sub>S<sub>3</sub>@C, and Ce<sub>2</sub>S<sub>3</sub>@HMCS were measured by the N<sub>2</sub> adsorption/ desorption technique (Figure 3C). Obviously, the N<sub>2</sub> adsorption/desorption isotherms of pure Ce<sub>2</sub>S<sub>3</sub> is small, with a specific surface area of 26.13 m<sup>2</sup>·g<sup>-1</sup>. Ce<sub>2</sub>S<sub>3</sub>@C and Ce<sub>2</sub>S<sub>3</sub>@HMCS present a type IV adsorption/desorption isotherm, being a typical characteristic of mesoporous materials. The specific surface areas of Ce<sub>2</sub>S<sub>3</sub>@C and Ce<sub>2</sub>S<sub>3</sub>@HMCS are determined to be 73.00 and 169.95 m<sup>2</sup>·g<sup>-1</sup>, respectively. The large specific surface area of Ce<sub>2</sub>S<sub>3</sub>@HMCS is mainly due to the hollow carbon nanoshells. The adsorption pore sizes of Ce<sub>2</sub>S<sub>3</sub>@HMCS are mainly concentrated at 3.9 nm (Figure 3D), while those of Ce<sub>2</sub>S<sub>3</sub>@C are 3.6 nm. This derivation is possibly due to mesoporous carbon shells.

The element states of Ce<sub>2</sub>S<sub>3</sub>@HMCS were analyzed by XPS. All signals of Ce, S, and C are present in the full survey (Figure 4A). Figure 4B shows the high-resolution XPS of Ce. The peaks located at 885.5 and 904.3 eV are assigned to Ce  $3d_{5/2}$  and Ce  $3d_{3/2}$  in Ce<sub>2</sub>S<sub>3</sub>, respectively.<sup>39</sup> The Ce 4d peak in the full survey also belongs to Ce<sub>2</sub>S<sub>3</sub>, proving the existence of Ce<sup>4+</sup> in Ce<sub>2</sub>S<sub>3</sub>. The three components at 284.8, 285.7, and 288.7 eV in the C 1s spectrum (Figure 4C) are C–C, C–O, and C=O, respectively.<sup>28,40</sup> The peaks at 163.9 and 164.4 eV correspond to S  $2p_{3/2}$  and S  $2p_{1/2}$  of S<sup>2–</sup> in Ce<sub>2</sub>S<sub>3</sub> (Figure 4D). The signal at 165.2 eV reflects the formation of the C–S bond, which indicates that S atoms are likely introduced into the carbon shell during the sulfuration process. The peak at 168.7 eV is related to SO<sub>x</sub> caused by the oxidation of sulfur in the air.<sup>36</sup>



FIGURE 3 (A) Raman spectra of  $Ce_2S_3@C$ ,  $CeO_2@void@C$ , and  $Ce_2S_3@HMCS$ . (B) TGA curve of  $Ce_2S_3@HMCS$ . (C) Nitrogen adsorption-desorption isotherms and (D) pore size distributions of  $Ce_2S_3@C$ ,  $CeO_2@void@C$ , and  $Ce_2S_3@HMCS$ . HMCS, hollow mesoporous carbon sphere; TGA, thermogravimetric analysis

To determine the electrochemical property, the CV experiment was first carried out for Ce<sub>2</sub>S<sub>3</sub>@HMCS. Ce<sub>2</sub>S<sub>3</sub>@HMCS and metallic lithium were used as counter electrodes and carbonate-based electrolytes were used for the determination of electrochemical performance. Figure 5A shows the CV curve of the Ce<sub>2</sub>S<sub>3</sub>@HMCS electrode in the first four cycles in the range of 0.01-3 V. The first cycle of the sample is partially irreversible because of side reactions such as electrolyte decomposition and the formation of a solid-electrolyte interface (SEI) film.<sup>41</sup> The capacity quickly becomes stable and the discharge-charge curves almost overlap with each other, indicating that the electrochemical reactions are highly reversible for the Ce<sub>2</sub>S<sub>3</sub>@HMCS electrode. The CV curves of Ce<sub>2</sub>S<sub>3</sub> and Ce<sub>2</sub>S<sub>3</sub>@C are similar to that of Ce<sub>2</sub>S<sub>3</sub>@HMCS, except that they show worse performance (Figure S5). The capacity of the pure  $Ce_2S_3$  can only be obtained below 1.5 V. Figure 5B shows the first five cycles of Ce<sub>2</sub>S<sub>3</sub>@HMCS at a current density of 100 mA $\cdot$ g<sup>-1</sup>, with capacities of 612 and  $367 \text{ mAh} \cdot \text{g}^{-1}$  upon first discharge and charge. A decayed capacity of  $367 \text{ mAh} \cdot \text{g}^{-1}$ 

was observed during the second discharge, which originated from an irreversible reaction. The Coulombic efficiency increases from 60% to 96% during the first five cycles. In comparison, the discharge capacities of the pure Ce<sub>2</sub>S<sub>3</sub> and Ce<sub>2</sub>S<sub>3</sub>@C remained 129 and 139 mAh·g<sup>-1</sup>, respectively, for the fifth cycle (Figure S5). After 100 cycles at  $100 \text{ mA} \cdot \text{g}^{-1}$  current density, the Coulombic efficiency of  $Ce_2S_3$ @HMCS is almost 100%, while the discharge capacity is maintained at  $320 \text{ mAh} \cdot \text{g}^{-1}$  (Figure 5C). As an LIB anode, the performance of Ce<sub>2</sub>S<sub>3</sub>@HMCS is comparable to those of other sulfide-based materials (Table S1). Under the same cycling conditions, the discharge capacities of the pure Ce<sub>2</sub>S<sub>3</sub> and Ce<sub>2</sub>S<sub>3</sub>@C are maintained at 124 and 153 mAh·g<sup>-1</sup>, respectively. A higher current density of  $1000 \text{ mA} \cdot \text{g}^{-1}$  was used to cycle the afore-mentioned Ce<sub>2</sub>S<sub>3</sub>, Ce<sub>2</sub>S<sub>3</sub>@C, and Ce<sub>2</sub>S<sub>3</sub>@HMCS as demonstrated in Figure 5D. Specific capacities in the range of  $80-90 \text{ mA} \cdot \text{g}^{-1}$ are obtained for pure Ce<sub>2</sub>S<sub>3</sub> during the first 100 cycles, which is lower than the ones of  $\sim 120 \text{ mA} \cdot \text{g}^{-1}$  obtained under a current density of  $100 \text{ mA} \cdot \text{g}^{-1}$  (Figure 5C). Carbon-coated Ce2S3@C shows a higher capacity of



FIGURE 4 (A) Full XPS spectrum of  $Ce_2S_3$ @HMCS. High-resolution XPS spectra of (B) Ce 3d, (C) C 1s, and (D) S 2p for  $Ce_2S_3$ @HMCS. HMCS, hollow mesoporous carbon sphere; XPS, X-ray photoelectron spectroscopy

~110 mA·g<sup>-1</sup> when compared with pure Ce<sub>2</sub>S<sub>3</sub>. There was a reduction of about  $20 \text{ mA} \cdot \text{g}^{-1}$  for Ce<sub>2</sub>S<sub>3</sub>@C when the current density increased from 100 to  $1000 \text{ mA} \cdot \text{g}^{-1}$  during the first 100 cycles. Ce<sub>2</sub>S<sub>3</sub>@HMCS showed improved capacities in the range of  $145-230 \text{ mA} \cdot \text{g}^{-1}$  compared with Ce<sub>2</sub>S<sub>3</sub> and Ce<sub>2</sub>S<sub>3</sub>@C. On further cycling up to 1000 cycles, slowly increased capacities were observed for the three materials: 120, 130, and 282 mA $\cdot$ g<sup>-1</sup> are achieved for Ce<sub>2</sub>S<sub>3</sub>, Ce<sub>2</sub>S<sub>3</sub>@C, and Ce<sub>2</sub>S<sub>3</sub>@HMCS in the 1000th cycle, respectively. The increase in the capacity of the activation process may be due to the gap between the core and the shell, which delayed the full infiltration of the electrolyte into the shell in a short period of time. This gap can be adjusted to a proper volume in future work. In addition, similar to the previous reports of metal sulfides/oxides with similar structures, a common activation phenomenon in metal sulfides/oxides for alkali-metal-ion storage was observed after prolonged cycling.<sup>26</sup> These results highlight the efficient lithium storage properties of Ce<sub>2</sub>S<sub>3</sub>@HMCS, which may be attributed to the distinct stability effect of rareearth elements.<sup>17</sup> Obviously, Ce<sub>2</sub>S<sub>3</sub>@HMCS with a

yolk-shell structure provides higher specific capacity and Coulombic efficiency.

Discharge capacities of 121, 105, 67, 45, and  $20 \text{ mAh} \cdot \text{g}^{-1}$  are, respectively, obtained for pure Ce<sub>2</sub>S<sub>3</sub> at various current densities of 0.1, 0.2, 1, 2, and  $5 \text{ A} \cdot \text{g}^{-1}$ (Figure 5E). Slightly increased capacities of 143, 127, 100, 92, and 67 mA $\cdot$ g<sup>-1</sup> are determined for the carbon-coated Ce<sub>2</sub>S<sub>3</sub>@C under the corresponding current densities. For Ce<sub>2</sub>S<sub>3</sub>@HMCS, the capacities significantly increased to 320, 264, 210, 195, and  $150 \text{ mA} \cdot \text{g}^{-1}$ , respectively. All three materials showed slightly increased capacities when the current density was reverted from  $5 \text{ A} \cdot \text{g}^{-1}$  back to  $1 \operatorname{A} \cdot g^{-1}$ , indicating good reversibility with an activation procedure. Obviously, the rate performance and cycling stability of Ce<sub>2</sub>S<sub>3</sub>@HMCS with the yolk-shell structure are much better than those of pure Ce<sub>2</sub>S<sub>3</sub> and Ce<sub>2</sub>S<sub>3</sub>@C. The designed voids within Ce<sub>2</sub>S<sub>3</sub>@HMCS effectively buffer the volume change upon an electrochemical reaction. Figure S6 shows the TEM images of Ce<sub>2</sub>S<sub>3</sub>@HMCS and Ce<sub>2</sub>S<sub>3</sub>@C after 100 charge-discharge cycles at a current density of  $1000 \text{ mA} \cdot \text{g}^{-1}$ . The cores of



**FIGURE 5** (A) Cyclic voltammetry of the Ce<sub>2</sub>S<sub>3</sub>@HMCS electrode at a scan rate of  $0.1 \text{ mV} \cdot \text{s}^{-1}$  between 0.01 and 3.0 V at room temperature. (B) Galvanostatic charge–discharge curves of Ce<sub>2</sub>S<sub>3</sub>@HMCS at a current density of 100 mA·g<sup>-1</sup>. Cycling performance of pure Ce<sub>2</sub>S<sub>3</sub>, Ce<sub>2</sub>S<sub>3</sub>@C, and Ce<sub>2</sub>S<sub>3</sub>@HMCS at current densities of (C) 100 mA·g<sup>-1</sup> and (D) 1000 mA·g<sup>-1</sup>. (E) Rate capability of pure Ce<sub>2</sub>S<sub>3</sub>, Ce<sub>2</sub>S<sub>3</sub>@C, and Ce<sub>2</sub>S<sub>3</sub>@HMCS at different current densities. The full circles and open boxes represent capacities obtained from discharge and charge, respectively. The open circles represent the Coulombic efficiencies. (F) Nyquist impedance curve for pure Ce<sub>2</sub>S<sub>3</sub>, Ce<sub>2</sub>S<sub>3</sub>@HMCS. HMCS, hollow mesoporous carbon sphere

 $Ce_2S_3$ @HMCS did not reunite and maintained a good yolk-shell morphology (Figure S6b) after cycling. However, the carbon directly coated  $Ce_2S_3$ @C without voids obviously reunited, and the carbon shell showed the carbon shell shows an intensive loss after cycling (Figure S6d). EIS was performed to determine the resistance and diffusion behavior (Figure 5F). The

8

semicircle in the high-frequency region corresponds to the SEI film resistance ( $R_s$ ) and the charge-transfer resistance ( $R_{ct}$ ).<sup>42,43</sup> The semicircular shape of Ce<sub>2</sub>S<sub>3</sub>@HMCS is smaller than that of pure Ce<sub>2</sub>S<sub>3</sub> and Ce<sub>2</sub>S<sub>3</sub>@C (Figure 5F). Based on the equivalent circuit model, the charge-transfer resistance  $R_{ct}$  of Ce<sub>2</sub>S<sub>3</sub>@HMCS is calculated to be 74.3  $\Omega$ , which is lower than that of pure  $Ce_2S_3$  (151.3  $\Omega$ ) and  $Ce_2S_3@C$  (116.2  $\Omega$ ). The straight line in the low-frequency region represents the Warburg impedance (Zw) of the Li<sup>+</sup> ion diffusion process in the electrode. The slopes of  $Ce_2S_3@HMCS$  and  $Ce_2S_3@C$  are similar in the low-frequency region, but both are larger than that of pure  $Ce_2S_3$ , indicating that Li<sup>+</sup> diffuses faster in  $Ce_2S_3@HMCS$  and  $Ce_2S_3@C$ . As shown in Figure S7, with increasing number of cycles, the resistance decreased and Li<sup>+</sup> diffusion increased according to the change of the slope. The evolution of both resistance and diffusion is the source of gradual activation of the electrode material with the increase of the number of cycles.

To further unravel the electrochemical mechanism of the  $Ce_2S_3$ @HMCS anode, CV curves were measured at different rates. As shown in Figure 6A, by changing the scan rate, the CV curves maintain similar configurations with a slight shift for the redox peak, indicating that a reversible reaction and rapid charge transfer occur. The storage capacity of lithium is governed by two mechanisms: diffusion-controlled charge process and pseudocapacitance-controlled charge storage. According to the CV curves at different rates, the storage mechanism of lithium can be estimated using the following equations<sup>44,45</sup>:

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$$i = av^b, \tag{1}$$

$$\log(i) = b \times \log(v) + \log(a), \tag{2}$$

where *i* is the peak current, *v* is the scan rate, and *a* and *b* are adjustable parameters. When the *b* value is 0.5, the process is completely controlled by ion diffusion; when *b* equals 1, the mechanism is controlled by the capacitance effect. As shown in Figure 6B, *b* values of 0.906, 0.739, and 0.914 are, respectively, determined for peak 1, peak 2, and peak 3, indicating that the lithium storage reaction



**FIGURE 6** (A) Cyclic voltammetry curves from 0.1 to  $1.2 \text{ mV} \cdot \text{s}^{-1}$  of the Ce<sub>2</sub>S<sub>3</sub>@HMCS electrode. (B) Linear relationship of the peak current ( $i_p$ ) and the square root of the scan rate ( $\nu^{1/2}$ ). (C) Pseudo-capacitive contribution of Ce<sub>2</sub>S<sub>3</sub>@HMCS to the total charge storage at  $1 \text{ mV} \cdot \text{s}^{-1}$ . (D) Contribution ratio of the pseudo-capacitive and diffusion-controlled capacities at different scan rates of Ce<sub>2</sub>S<sub>3</sub>@HMCS. HMCS, hollow mesoporous carbon sphere

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of  $Ce_2S_3$ @HMCS is mainly controlled by pseudocapacitance behavior, together with the small fraction of ion diffusion. According to the following equation, the capacitance contribution of the  $Ce_2S_3$ @HMCS electrode is further quantitatively estimated:

$$i(v) = k_1 v + k_2 v^{1/2},$$
 (3)

where  $k_1 v$  is the contribution of pseudo-capacitance and  $k_2 v^{1/2}$  is the diffusion-controlled reaction. Figure 6C shows that the current contribution of pseudocapacitance control of the Ce2S3@HMCS electrode reaches 76% at the scan rate of  $1 \text{ mV} \cdot \text{s}^{-1}$ . As shown in Figure 6D, the pseudo-capacitance contributions are 50.4%, 59.4%, 68.1%, 73.5%, 76.4%, and 77.9% at scanning rates of 0.1, 0.2, 0.5, 0.8, 1.0, and  $1.2 \text{ mV} \cdot \text{s}^{-1}$ , respectively. The results show that the pseudo-capacitance control behavior plays an important role in the total charging capacity and its contribution increases with the increase of the scan rate. Cycling stability is a key premise of obtaining high pseudo-capacitance. The voids between the Ce<sub>2</sub>S<sub>3</sub> core and the carbon shell buffer the volume expansion of Ce<sub>2</sub>S<sub>3</sub> during lithium intercalation, which offers structural stability with good cycling performance. In addition, the configuration of the porous carbon layer and nano-sized Ce<sub>2</sub>S<sub>3</sub> is conducive to the rapid transfer of Li<sup>+</sup> and electrons in the electrode, resulting in excellent rate performance.

Ex situ XRD investigation during the first cycle was carried out to track the evolution of Ce<sub>2</sub>S<sub>3</sub>@HMCS. The data points were chosen as marked to the right of Figure 7. Upon discharge, the reflection peaks of (211), (310), and (321) planes in the cubic structure shift to lower values of  $2\theta$  because of cell volume expansion during lithiation. In the subsequent charge process, these reflection peaks revert to larger  $2\theta$  values, which is due to the extraction of Li ions. The peak positions of the sample at the end of charge are still slightly lower than those of the pristine material, which is possibly attributed to the irreversible reaction. No new phase was detected in the whole charge–discharge process. Therefore, the electrochemical cycling of the Ce<sub>2</sub>S<sub>3</sub>@HMCS electrode is an intercalation/extraction reaction process.

Solid-state <sup>7</sup>Li MAS NMR spectra of Li<sub>x</sub>Ce<sub>2</sub>S<sub>3</sub>@HMCS electrodes at different cycling states were investigated. For better analysis and discussion, only the isotropic resonances are simulated and displayed in Figure 8. In fact, all spectra show broad spinning-side-bands (SSBs) covering up to 800 ppm (-400 to 400 ppm) because of the hyperfine interaction between the unpaired electron of Ce<sup>3+,4+</sup> and the measured lithium nuclei as shown in Figure S8.<sup>46-48</sup> The electrode discharged to 0.9 V (Figure 8A) shows a narrow symmetric <sup>7</sup>Li resonance at -0.7 ppm. Upon further lithia-tion to 0.3 V, the isotropic peak becomes broader with a shift





FIGURE 7 Ex situ X-ray diffraction of Ce<sub>2</sub>S<sub>3</sub>@HMCS at various cycling states. HMCS, hollow mesoporous carbon sphere



**FIGURE 8** Ex situ solid-state <sup>7</sup>Li nuclear magnetic resonance spectra of lithiated  $Ce_2S_3@HMCS$  at different cycling states. (A–C)  $Ce_2S_3@HMCS$  electrodes were discharged to 0.9, 0.3, and 0.01 V, respectively. (D) and (E) the lithiated  $Ce_2S_3@HMCS$  electrodes were charged to 1.5 and 3.0 V. The corresponding electrochemical curve is plotted on the right. Blue and red-dashed spectra show the signals obtained from the experiment and deconvolution, respectively. The shift position and relative occupancy are listed next to each simulated peak. HMCS, hollow mesoporous carbon sphere

to a low field (Figure 8B). At the end of discharge to 0.01 V, an additional resonance shifts further to ~8.5 ppm (Figure 8C). Reversible evolution was observed for the peak position when delithiation/charge takes place (Figure 8D,E). The evolution from NMR is in good agreement with the above-mentioned XRD analysis. Despite various chemical environments and distribution, simulation is attempted to perform only on the isotropic resonances rather than all SSBs (Figure S8). For the electrode discharged to 0.3 V, an additional peak at 4 ppm with 70% occupancy appears in addition to the first peak at -0.7 ppm, which accounts only for 30% as shown in Figure 8B. Further discharge to 0.01 V

produces an extra signal at even downfield to 8.5 ppm (Figure 8C). These shifts are mainly caused by the change of Fermi contact along the Ce–S–Li bond, as the electron cloud varies due to the reduction of  $Ce^{4+}$  to  $Ce^{3+}$  upon discharge, or different sites/vacancies are occupied by the intercalated  $Li^{+}.^{49-51}$ 

# 4 | CONCLUSIONS

In summary, yolk-shell structured  $\gamma$ -phase Ce<sub>2</sub>S<sub>3</sub>@HMCS was synthesized using the in-shell sulfuration method and tested as an anode for LIBs. Ce<sub>2</sub>S<sub>3</sub>@HMCS provides not only good electronic conductivity but also a buffering space for the volume change during cycling of the Ce<sub>2</sub>S<sub>3</sub> core. The nano-sized Ce<sub>2</sub>S<sub>3</sub>@HMCS enhances capacity and presents excellent structural stability. Fast charge transfer and longterm cycling stability result in a high pseudo-capacitance contribution for Ce<sub>2</sub>S<sub>3</sub>@HMCS. Ex situ XRD and NMR analyses reveal that the intercalation process dominates the reaction for the Ce<sub>2</sub>S<sub>3</sub>@HMCS anode. The structural property correlation represents a promising strategy of fabricating a nano-sized Ce<sub>2</sub>S<sub>3</sub> core and carbon shell with adjustable voids, which show efficient lithium storage properties. This study may inspire the design and construction of advanced hybrid materials for energy storage.

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# **CONFLICT OF INTERESTS**

The authors declare that there are no conflict of interests.

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# SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

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