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Construction of nanocage-structured heterogeneous binary metal sulfides *via* step-by-step confined growth for boosted lithium storage properties†

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Nanocage-structured materials – heterogeneous binary metal sulfides (MoS₂ and Co₉S₈) in carbon nanocages (Co₉S₈/MoS₂@CNCs) – obtained *via* step-by-step confined growth display superior Li-storage performance, profiting from the synergistic effect of the bimetallic sulfides, high filling rate of active materials and free interspace in the nanocage structure for volume expansion.

Transition metal dichalcogenides (M_xX_y) are an emerging class of anode materials for lithium-ion batteries (LIBs), where M denotes a transition metal (*e.g.*, Co, Mo, W, *etc.*) and X represents a chalcogen (*e.g.*, S or Se),^{1–6} due to their high capacity and good electrochemical reversibility. Various metal sulfides, such as CoS_x, FeS_x, MoS₂, WS₂, *etc.*,^{7–12} have been reported for lithium storage. However, the poor conductivity and large volume changes restrict their rate and cycling performance.^{13,14} So far, two strategies are generally adopted to overcome the aforementioned problems. One method is constructing composites with other materials, such as carbon,^{15–18} to enhance the conductivity of electrode materials and accommodate the volume changes. Furthermore, the cage materials structured with a controlled and tunable space enable powerful applications as battery materials due to their ability to accommodate the volume changes, receiving considerable interest.¹⁹ Traditional preparation methods for the production of cage-structured materials were generally from bottom to top—starting from the core to the shell, then by selective etching or using a sacrificial template, limiting the application of the approach.^{20–22} Hence, it is urgent to develop a simple and feasible strategy for fabricating cage-structured nanomaterials.

In our previous work, carbon nanocages (CNCs) as desirable nanoreactors were found to confine the growth of transition metal sulfides and phosphides displaying superior performances in LIBs,^{23–27} providing enough interspace needed for the conversion and improving the electrical conductivity of the composite. Nevertheless, the low single component filling ratio causes the volume waste to hardly improve the lithium storage. Herein, we report a strategy to realize binary metal sulfide filling into CNCs *via* step-by-step confined growth. MoS₂ embedded in CNCs as anchorage provided the growth site for Co₉S₈ vulcanized from ZIF-67, achieving the nanocage-structured Co₉S₈/MoS₂@CNCs. It was observed that the CNCs buffer the expansion of active materials during the lithium intercalation/deintercalation process, which confirms the outstanding rate performance and long cycling stability. The synergistic effect of binary metal sulfides contributed greatly to the lithium storage properties.

The fabrication of nanocage-structured bimetallic sulfide Co₉S₈/MoS₂@CNCs *via* step-by-step confined growth is illustrated in Fig. 1A. CNCs as nanoreactors with ~35 nm shells were formed according to the previously reported studies (Fig. S1, ESI†). Fig. 1B shows that the MoS₂ nanosheets first undergo confined growth in the CNCs to form nanocage-structured MoS₂@CNCs. A few MoS₂ nanosheets are randomly distributed in the CNCs, where they reserve some free space for the growth of ZIF-67. Subsequently, the size of ZIF-67 grown in MoS₂@CNCs to form ZIF-67/MoS₂@CNCs is 50–100 nm, which is obviously smaller than that of ZIF-67 grown without the constraint of CNCs (Fig. 1C and Fig. S2, ESI†). After sulfuration, ZIF-67 *in situ* vulcanized to form 20–50 nm Co₉S₈ nanoparticles, which are anchored on the surface of the MoS₂ nanosheets to fabricate the heterogeneous binary metal sulfide Co₉S₈/MoS₂@CNCs (Fig. S3, ESI†), displaying a specific surface area of about 110.34 m² g^{−1} and the main pore size distribution centered at 4 nm (Fig. 1D–F and Fig. S4, ESI†). The interplanar distances of 0.662 and 0.272 nm are consistent with the (002) and (100) planes of hexagonal MoS₂. Meanwhile, the lattice distance of 0.275 nm corresponds to the (222) lattice plane of

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Fig. 1 (A) Schematic illustration for synthesizing nanocage-structured $\text{Co}_9\text{S}_8/\text{MoS}_2/\text{CNCs}$; TEM images of (B) MoS_2/CNCs , (C) $\text{ZIF-67}/\text{MoS}_2/\text{CNCs}$, and (D and E) $\text{Co}_9\text{S}_8/\text{MoS}_2/\text{CNCs}$; (F and G) HRTEM images, (H) SAED patterns, (I) HAADF-STEM images and elemental mapping images of (J) Mo, (K) Co, (L) S, (M) C, and (N) N of $\text{Co}_9\text{S}_8/\text{MoS}_2/\text{CNCs}$.

cubic phase Co_9S_8 , as shown in Fig. 1G. It could be deduced that the crystal growth of Co_9S_8 nanoparticles occurred on the (100) lattice plane of MoS_2 , which provides the anchorage site for the growth of Co_9S_8 . The Debye-Scherrer ring patterns of (002) and (110) planes shown in Fig. 1H were indexed to MoS_2 , while the ring patterns of (331) and (222) planes were indexed to Co_9S_8 , which confirms the existence of the binary metal sulfides.

Fig. 1J–N show the distribution of Mo, Co, S, C and N elements of $\text{Co}_9\text{S}_8/\text{MoS}_2/\text{CNCs}$. It is worth noticing that Co and Mo show the same distribution area, which evidences the interfacial anchoring effect between Co_9S_8 nanoparticles and MoS_2 nanosheets. Moreover, the N element from the organic ligands of ZIF-67 is present on the carbon shell meaning that N-doped carbon nanocages are formed, which enhances the electrical conductivity of the electrode materials. The weight fraction of Co_9S_8 and MoS_2 as active components in $\text{Co}_9\text{S}_8/\text{MoS}_2/\text{CNCs}$ was estimated to be 70 wt%. $\text{Co}_9\text{S}_8/\text{CNCs}$ as a control sample was synthesized by the vulcanization of $\text{ZIF-67}/\text{CNCs}$ (Fig. S5, ESI†). MoS_2 content in MoS_2/CNCs and Co_9S_8 content in $\text{Co}_9\text{S}_8/\text{CNCs}$ were only about 23 and 47 wt %, respectively (Fig. S6 and S7, ESI†). Obviously, the confined step-by-step growth of MoS_2 and Co_9S_8 improves the filling rate of the active materials and the volume energy density of the electrode material, which will efficiently enhance the lithium storage capacity.

The XRD patterns of $\text{Co}_9\text{S}_8/\text{MoS}_2/\text{CNCs}$ (Fig. 2A) confirm the two-phase coexistence, *i.e.* the hexagonal phase of MoS_2 and the cubic phase of Co_9S_8 . The crystal structures of MoS_2 and Co_9S_8 are shown in Fig. 2B. In the Raman spectra (Fig. S8, ESI†), the peak at 678.2 cm^{-1} corresponds to Co_9S_8 , and the distinctive peaks at 1345 and 1580 cm^{-1} are attributed to the D band and

Fig. 2 (A) XRD patterns of $\text{Co}_9\text{S}_8/\text{CNCs}$ and $\text{Co}_9\text{S}_8/\text{MoS}_2/\text{CNCs}$; (B) crystal structure of MoS_2 and Co_9S_8 ; high-resolution XPS spectra of (C) Mo 3d for $\text{Co}_9\text{S}_8/\text{MoS}_2/\text{CNCs}$, (D) Co 2p for (a) $\text{Co}_9\text{S}_8/\text{CNCs}$ and (b) $\text{Co}_9\text{S}_8/\text{MoS}_2/\text{CNCs}$, and (E) S, (F) N1s, and (G) C1s for $\text{Co}_9\text{S}_8/\text{MoS}_2/\text{CNCs}$.

the G band, respectively. The value of I_D/I_G is close to 1:1, indicating that the carbon displays high graphitization.^{28,29} In addition, for $\text{Co}_9\text{S}_8/\text{MoS}_2/\text{CNCs}$ (Fig. S8, ESI†), the double peaks at 407.1 cm^{-1} were assigned to MoS_2 , which indicates the formation of the binary metal sulfides.

XPS survey spectra of $\text{Co}_9\text{S}_8/\text{MoS}_2/\text{CNCs}$ indicate the existence of Mo, Co, S, C, and N, as shown in Fig. S9 (ESI†). Four peaks at 235.0, 231.6, 228.6, and 225.8 eV, as shown in Fig. 2C, were assigned to Mo^{6+} , $\text{Mo}^{4+} 3d_{3/2}$, $\text{Mo}^{4+} 3d_{5/2}$, and Mo–S, wherein the Mo^{6+} comes from MoO_4 .^{2–30} It is most fantastic that the binding energies of $\text{Mo}^{4+} 3d_{3/2}$ and $3d_{5/2}$ in $\text{Co}_9\text{S}_8/\text{MoS}_2/\text{CNCs}$ are lower than those in MoS_2/CNCs (at 232.8 and 229.7 eV²⁰), which indicates some kind of interfacial effect leading to the energy decline of Mo^{4+} . As shown in Fig. 2D(a), the binding energies of 781.6, 786.9, 797.7, and 802.9 eV assigned to $\text{Co}^{3+} 2p_{3/2}$, $\text{Co}^{2+} 2p_{3/2}$, $\text{Co}^{3+} 2p_{1/2}$, and $\text{Co}^{2+} 2p_{1/2}$ are characteristic of Co^{2+} and Co^{3+} .³¹ In the spectrum of $\text{Co}_9\text{S}_8/\text{CNCs}$, the peaks at 780.4 and 796.1 eV can be attributed to $\text{Co}^{3+} 2p_{3/2}$ and $2p_{1/2}$, and those at 785.7 and 802.0 eV can be assigned to $\text{Co}^{2+} 2p_{3/2}$ and $2p_{1/2}$ (Fig. 2D(b)), respectively. Compared with $\text{Co}_9\text{S}_8/\text{CNCs}$, the total curve of Co 2p in $\text{Co}_9\text{S}_8/\text{MoS}_2/\text{CNCs}$ shifts to the high binding energy direction with the gap at about 1 eV, which further confirms the existence of a heterogeneous interface between MoS_2 nanosheets and Co_9S_8 nanoparticles. In the S 2p XPS spectrum (Fig. 2E), three distinct peaks at 161.3, 162.5, and 168.7 eV correspond to $2p_{1/2}$ and $2p_{3/2}$ of S^{2-} , and SO_3 .^{2–32} The peaks at 283.9, 285.5, 286.7, and 288.4 eV were ascribed to C–C, C–N, C–O, and C=O, respectively (Fig. 2F). In Fig. 3G, the N 1s XPS spectrum is deconvoluted into three types of graphitic N (401.8 eV), pyrrolic N (400.2 eV), and pyridinic N (397.5 eV), the proportion of pyridinic N being the largest. The N-doped carbon shell should be able to enhance the performance of lithium storage due to its good electrical conductivity and ion transmission rate.³³

The cyclic voltammetry (CV) curve of $\text{Co}_9\text{S}_8/\text{CNCs}$ displays two cathodic peaks at potentials of 1.55 and 1.18 V in the first cycle (Fig. 3A), corresponding to the multistep conversion

Fig. 3 Cyclic voltammograms and charge/discharge voltage profiles of (A and D) Co_9S_8 @CNCs, (B and E) MoS_2 @CNCs and (C and F) $\text{Co}_9\text{S}_8/\text{MoS}_2$ @CNCs.

formation of $\text{Li}_x\text{Co}_9\text{S}_8$ ($\text{Co}_9\text{S}_8 + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{Co}_9\text{S}_8$) and Li_2S ($\text{Li}_x\text{Co}_9\text{S}_8 + (16-x)\text{Li}^+ + (16-x)e^- \rightarrow 9\text{Co} + 8\text{Li}_2\text{S}$), respectively. The cathodic peak at 0.63 V corresponds to the formation of a solid electrolyte interface (SEI) layer. Two anodic peaks located at 1.30 and 2.02 V should be attributed to the oxidation of metallic Co to Co_9S_8 . In the subsequent curves, the cathodic peaks at 1.30 V correspond to the insertion of Li^+ , and the anodic peaks shift to 2.06 V, which is assigned to the Li^+ de-intercalation of Li_2S and the formation of Co_9S_8 . In Fig. 3B, the two peaks at 1.03 and 0.29 V in the first cathodic sweep are related to the Li^+ intercalating into the MoS_2 lattice to form Li_xMoS_2 and the conversion formation of Li_2S . During the following two cathodic scans, two new cathodic peaks appear at 1.94 and 1.12 V, corresponding to the reduction of S and the intercalation of Li^+ . The obvious anodic peak at 2.33 V is attributed to the delithiation of Li_2S .

As shown in Fig. 3C, the strong peak at ~ 0.88 V (the first cycle) can be ascribed to the conversion reduction of $\text{Co}_9\text{S}_8/\text{MoS}_2$ and the insertion of Li^+ to form metallic Co/Mo and Li_2S . The cathodic peak at 0.42 V should be attributed to the formation of the solid electrolyte interface (SEI) layer. In the subsequent curves, one peak at 1.85 V corresponds to the Li^+ insertion of S, and the other peak at 1.30 V is attributed to the conversion reaction of metallic sulfide. In the anode scan, two peaks at 1.38 and 2.05 V are attributed to the oxidation of metallic Co to Co_9S_8 in accordance with the CV curve of Co_9S_8 @CNCs. The other two anodic peaks at 1.00 and 2.32 V can be assigned to the oxidation of metallic Mo to form MoS_2 , which further confirms the formation of binary metal sulfides. In the following cycles, the overlapped CV curves show the good reversibility and high stability for the Li^+ insertion/extraction of $\text{Co}_9\text{S}_8/\text{MoS}_2$ @CNC electrodes.^{34,35} Every metal sulfide has its own charging and discharging potential. When one metal sulfide is undergoing an intercalation reaction, the other can buffer the volume changes from the former reaction. Meanwhile, the reduced elemental metals, *i.e.* Co and Mo, will be used as a conductive matrix to improve the electrochemistry reaction between them due to the different charging/discharging plateaus.

The galvanostatic charge/discharge profiles of Co_9S_8 @CNCs, MoS_2 @CNCs, and $\text{Co}_9\text{S}_8/\text{MoS}_2$ @CNCs at 0.2 A g^{-1} are shown

in Fig. 3D–F. The first discharge and charge capacities of nanocage-structured $\text{Co}_9\text{S}_8/\text{MoS}_2$ @CNCs are 1324.26 and 1151.30 mA h g^{-1} , higher than those of Co_9S_8 @CNCs (1205.86 and 960.03 mA h g^{-1}) and MoS_2 @CNCs (1167.12 and 878.93 mA h g^{-1}). This further reveals that the 1st cycle Coulombic efficiency (CE) for $\text{Co}_9\text{S}_8/\text{MoS}_2$ @CNCs of 86.94% is higher than those of Co_9S_8 @CNCs (77.13%) and MoS_2 @CNCs (75.31%). During the 2nd cycle, the discharge and charge capacities of $\text{Co}_9\text{S}_8/\text{MoS}_2$ @CNCs are 1206 and 1177 mA h g^{-1} , giving rise to a high CE of 98%. From the 1st to 3rd cycle, nanocage-structured $\text{Co}_9\text{S}_8/\text{MoS}_2$ @CNCs display the highest discharge/charge capacities compared to those of Co_9S_8 @CNCs and MoS_2 @CNCs, which is attributed to the high filling rate of Co_9S_8 and MoS_2 in the CNCs.

The nanocage-structured $\text{Co}_9\text{S}_8/\text{MoS}_2$ @CNCs exhibited excellent rate performances, clearly shown in Fig. 4A. The reversible capacities of $\text{Co}_9\text{S}_8/\text{MoS}_2$ @CNCs are 1095.7, 1054.6, 974.6, 869.6, 774.7, 550.5, 845.1, and 1004.5 mA h g^{-1} at 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 0.5, and 0.1 A g^{-1} . At the same current densities, the discharge capacities of Co_9S_8 @CNCs are only 822.7, 770.7, 688.9, 596.3, 533.8, 384.2, 683.2 and 786.1 mA h g^{-1} . Meanwhile, the discharge capacities of MoS_2 @CNCs are 1012.0, 878.9, 771.9, 664.3, 581.8, 484.2, 774.3 and 995.2 mA h g^{-1} , respectively. Furthermore, the nanocage-structured $\text{Co}_9\text{S}_8/\text{MoS}_2$ @CNCs still deliver a reversible specific capacity of around 1014.0 mA h g^{-1} after the 500th cycle at 0.2 A g^{-1} (Fig. 4B), which is higher than that of Co_9S_8 @CNCs (691.6 mA h g^{-1}) and CNCs (194.1 mA h g^{-1}) (Fig. S11 and S12, ESI†).

Impressively, $\text{Co}_9\text{S}_8/\text{MoS}_2$ @CNCs show a superior cycling performance, retaining 731 mA h g^{-1} at a high current density of 2 A g^{-1} after 1000 cycles, which is shown in Fig. 4C. For comparison, the capacities of Co_9S_8 @CNCs and MoS_2 @CNCs slightly decrease to 527 and 570 mA h g^{-1} after 1000 cycles. In $\text{Co}_9\text{S}_8/\text{MoS}_2$ @CNCs, MoS_2 nanosheets are used as linkers to connect Co_9S_8 nanoparticles and CNCs, which ultimately form the interconnected 3D conductive

Fig. 4 (A) Cycling performance at different current densities of $\text{Co}_9\text{S}_8/\text{MoS}_2$ @CNCs, Co_9S_8 @CNCs and MoS_2 @CNCs; (B) cycling performance of $\text{Co}_9\text{S}_8/\text{MoS}_2$ @CNCs at 0.2 A g^{-1} , (C) cycling performance and Coulombic efficiency at 2 A g^{-1} , and (D) Nyquist plots of $\text{Co}_9\text{S}_8/\text{MoS}_2$ @CNCs, Co_9S_8 @CNCs and MoS_2 @CNCs.

network. The step-by-step confined growth of binary metal sulfides in CNCs effectively reduces the size of active substances and avoids the aggregation of Co_9S_8 nanoparticles due to the partition effect of the MoS_2 nanosheets. After multiple cycles, the structure of $\text{Co}_9\text{S}_8/\text{MoS}_2@\text{CNCs}$ is shown in Fig. S13 (ESI[†]). It is clear that the structural integrity of the CNCs remains unchanged. However, Co_9S_8 and MoS_2 are powdered and still confined inside the CNCs. The CNCs effectively prevent small nanoparticles from escaping and improve the reversibility and cycling stability. Electrochemical impedance spectroscopy (EIS) measurement further demonstrated the surface film impedance and charge transfer resistance (R_{ct}), whereas the slope line represents the Li^+ diffusion process in the electrode materials. As shown in Fig. 4D, $\text{Co}_9\text{S}_8/\text{MoS}_2@\text{CNCs}$ exhibit the smallest R_{ct} value compared to those of $\text{Co}_9\text{S}_8@\text{CNCs}$ and $\text{MoS}_2@\text{CNCs}$, indicating a fast reaction kinetics of $\text{Co}_9\text{S}_8/\text{MoS}_2@\text{CNCs}$ during the intercalation/de-intercalation of lithium. Meanwhile, $\text{Co}_9\text{S}_8/\text{MoS}_2@\text{CNCs}$ display the largest D_{Li} , as shown in Fig. S14 and Table S1 (ESI[†]), revealing that $\text{Co}_9\text{S}_8/\text{MoS}_2@\text{CNCs}$ have excellent Li-ion diffusion properties.

A comparison of the electrochemical performances of various Co_9S_8 -based or MoS_2 -based anodes is shown in Table S2 (ESI[†]). The nanocage-structured $\text{Co}_9\text{S}_8/\text{MoS}_2@\text{CNCs}$ display superior electrochemical performances, which should be attributed to the following points: (1) the unique nanocage structure with an internal void alleviates the volume effect during the charging/discharging process; (2) the introduction of binary metal sulfides increases the filling rate of the active component, effectively enhancing the specific capacity and volume energy density of the electrode material; (3) the rate performance and excellent cycle stability can be attributed to the outstanding synergistic lithium storage effect and the interfacial anchoring effect between Co_9S_8 and MoS_2 .

In summary, we have reported a novel strategy to design nanocage-structured $\text{Co}_9\text{S}_8/\text{MoS}_2@\text{CNCs}$ by two-step confined growth in CNCs, in which Co_9S_8 nanoparticles are anchored on the surface of MoS_2 nanosheets to form a heterogeneous interface, displaying super reversibility and cycling stability. Therefore, the step-by-step confined growth of binary metal sulfides in carbon nanocages provides a new method to design metal binary sulphides/phosphides/selenides with nanocage structures, which have potential applications in the energy storage and conversion fields.

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Conflicts of interest

There are no conflicts to declare.

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