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

Rongfang Zhao,ab Yue Han,c Wenlong Li,c Jinhua Li,ab Ming Chenb,ac and Lingxin Chenb,ad

Nanocage-structured materials – heterogeneous binary metal sulfides (MoS$_2$ and Co$_9$S$_8$) in carbon nanocages (Co$_9$S$_8$/MoS$_2$@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$_x$X$_y$) 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$_2$, FeS$_2$, MoS$_2$, WS$_2$, 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,$^{15-19}$ 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. MoS$_2$ embedded in CNCs as anchorage provided the growth site for Co$_9$S$_8$ vulcanized from ZIF-67, achieving the nanocage-structured Co$_9$S$_8$/MoS$_2$@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 Co$_9$S$_8$/MoS$_2$@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 MoS$_2$ nanosheets first undergo confined growth in the CNCs to form nanocage-structured MoS$_2$@CNCs. A few MoS$_2$ 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 MoS$_2$@CNCs to form ZIF-67/MoS$_2$@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 Co$_9$S$_8$ nanoparticles, which are anchored on the surface of the MoS$_2$ nanosheets to fabricate the heterogeneous binary metal sulfide Co$_9$S$_8$/MoS$_2$@CNCs (Fig. S3, ESI†), displaying a specific surface area of about 110.34 m$^2$ 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 MoS$_2$. Meanwhile, the lattice distance of 0.275 nm corresponds to the (222) lattice plane of...
was estimated to be 70 wt%. Co₉S₈@CNCs as a control sample was synthesized by the vulcanization of ZIF-67@CNCs (Fig. S5, ESI†). MoS₂@CNCs are formed, which enhances the electrical conductivity of the electrode materials. The weight fraction of carbon nanocages is present on the carbon shell meaning that N-doped pyridinic N being the largest. The N-doped carbon shell should be able to enhance the performance of lithium storage.

The cyclic voltammetry (CV) curve of Co₉S₈@CNCs displays two cathodic peaks at potentials of 1.55 and 1.18 V in the first cycle (Fig. S8, ESI†), corresponding to the multistep conversion of Mo₆S₁₆ into MoS₂. The double peaks at 407.1 cm⁻¹ were assigned to MoS₂, which indicates the formation of the binary metal sulfides.

XPS survey spectra of Co₉S₈/MoS₂@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 Mo⁶⁺, Mo⁴⁺ 3d₃/₂, Mo⁴⁺ 3d₅/₂, and Mo⁻⁴, whereas the Mo⁶⁺ comes from MoO₄.²⁻. It is most fantastic that the binding energies of Mo⁴⁺ 3d₃/₂ and 3d₅/₂ in Co₉S₈/MoS₂@CNCs are lower than those in MoS₂/MoS₂@CNCs (at 232.8 and 229.7 eV), which indicates some kind of interfacial effect leading to the energy decline of Mo⁴⁺. As shown in Fig. 2D(a), the binding energies of 781.6, 786.9, 797.7, and 802.9 eV correspond to Mo–S, Co–S, C–S, and S–O, respectively. The peaks at 283.9, 285.5, and 286.7 eV can be assigned to Co²⁺ 2p₃/₂ and 2p₁/₂, and those at 785.7 and 802.0 eV can be assigned to Co²⁺ 2p₃/₂ and 2p₁/₂ (Fig. 2D(b)), respectively. Compared with Co₉S₈@CNCs, the total curve of Co 2p in Co₉S₈/MoS₂@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 MoS₂ nanosheets and Co₉S₈ nanoparticles. In the S 2p XPS spectrum (Fig. 2E), three distinct peaks at 161.3, 162.5, and 168.7 eV correspond to S²⁻ and S²⁻, 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 was deconvoluted into three types of graphitic N being the largest. The N-doped carbon shell should be able to enhance the performance of lithium storage.
formation of Li$_x$Co$_9$S$_8$ ($\text{Co}_9\text{S}_8 + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{Co}_9\text{S}_8$) and Li$_3$S ($\text{Li}_3\text{Co}_9\text{S}_8 + (16-x)\text{Li}^+ + (16-x)e^- \rightarrow 9\text{Co} + 8\text{Li}_2\text{S}$), 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$_9$S$_8$. 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$_x$S and the formation of Co$_9$S$_8$. 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$_x$MoS$_2$ and the conversion formation of Li$_2$S. 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$_2$S.

As shown in Fig. 3C, the strong peak at ~0.88 V (the first cycle) can be ascribed to the conversion reduction of Co$_9$S$_8$/MoS$_2$ and the insertion of Li$^+$ to form metallic Co/Mo and Li$_2$S. 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$_9$S$_8$ in accordance with the CV curve of Co$_9$S$_8$@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 Co$_9$S$_8$/MoS$_2$@CNC electrodes. 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$_9$S$_8$@CNCs, MoS$_2$@CNCs, and Co$_9$S$_8$/MoS$_2$@CNCs at 0.2 A g$^{-1}$ are shown in Fig. 3D–F. The first discharge and charge capacities of nanocage-structured Co$_9$S$_8$/MoS$_2$@CNCs are 1324.26 and 1151.30 mA h g$^{-1}$, higher than those of Co$_9$S$_8$@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 Co$_9$S$_8$/MoS$_2$@CNCs of 86.94% is higher than those of Co$_9$S$_8$@CNCs (77.13%) and MoS$_2$@CNCs (75.31%). During the 2nd cycle, the discharge and charge capacities of Co$_9$S$_8$/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 Co$_9$S$_8$/MoS$_2$@CNCs display the highest discharge/charge capacities compared to those of Co$_9$S$_8$@CNCs and MoS$_2$@CNCs, which is attributed to the high filling rate of Co$_9$S$_8$ and MoS$_2$ in the NCNs.

The nanocage-structured Co$_9$S$_8$/MoS$_2$@CNCs exhibited excellent rate performances, clearly shown in Fig. 4A. The reversible capacities of Co$_9$S$_8$/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$_9$S$_8$@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 Co$_9$S$_8$/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$_9$S$_8$@CNCs (691.6 mA h g$^{-1}$) and CNCs (194.1 mA h g$^{-1}$) (Fig. S11 and S12, ESI†).

Impressively, Co$_9$S$_8$/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$_9$S$_8$@CNCs and MoS$_2$@CNCs slightly decrease to 527 and 570 mA h g$^{-1}$ after 1000 cycles. In Co$_9$S$_8$/MoS$_2$@CNCs, MoS$_2$ nanosheets are used as linkers to connect Co$_9$S$_8$ nanoparticles and CNCs, which ultimately form the interconnected 3D conductive
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 CoS8 nanoparticles due to the partition effect of the MoS2 nanosheets. After multiple cycles, the structure of CoS8/MoS2@CNCs is shown in Fig. S13 (ESI†). It is clear that the structural integrity of the CNCs remains unchanged. However, CoS8 and MoS2 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 (Rct), whereas the slope line represents the Li+ diffusion process in the electrode materials. As shown in Fig. 4D, CoS8/MoS2@CNCs exhibit the smallest Rct value compared to those of CoS8@CNCs and MoS2@CNCs, indicating a fast reaction kinetics of CoS8/MoS2@CNCs during the intercalation/de-intercalation of lithium. Meanwhile, CoS8/MoS2@CNCs display the largest Dli, as shown in Fig. S14 and Table S1 (ESI†), revealing that CoS8/MoS2@CNCs have excellent Li+ diffusion properties.

A comparison of the electrochemical performances of various CoS8-based or MoS2-based anodes is shown in Table S2 (ESI†). The nanostructure-nanocage structured CoS8/MoS2@CNCs display superior electrochemical performances, which should be attributed to the following points: (1) the unique nanoporous 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 CoS8 and MoS2.

In summary, we have reported a novel strategy to design nanostructure-nanocage structured CoS8/MoS2@CNCs by two-step confined growth in CNCs, in which CoS8 nanoparticles are anchored on the surface of MoS2 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 nanostructure, which have potential applications in the energy storage and conversion fields.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

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