Uniform Yolk–Shell MoS\textsubscript{2}@Carbon Microsphere Anodes for High-Performance Lithium-Ion Batteries

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Abstract: As an electrode material for lithium-ion batteries (LIBs), MoS\textsubscript{2} has attracted much attention because of its high capacity and low cost. However, the rational design of a novel electrode structure with a high capacity, fast charge/discharge rate, and long cycling lifetime remains a great challenge. Herein, an environmentally friendly etching strategy is reported for the construction of monodisperse, inner void-controlled yolk–shell MoS\textsubscript{2}@carbon microspheres. The resulting anode reveals an initial discharge capacity up to 1813 mAh g\textsuperscript{−1}, a high reversible capacity (1016 mAh g\textsuperscript{−1}), excellent cycling stability (200 cycles), and superior rate performance. Such microspheres consist of nanosized MoS\textsubscript{2} yolk, porous carbon shells \((\approx 280 \text{ nm})\), and well-controlled internal voids in between, opening a new pathway for the optimization of the electrochemical properties of MoS\textsubscript{2}-based anodes without sacrificing their capacity. In addition, this etching strategy offers a new method for the development of functional, hollow MoS\textsubscript{2}-based composites.

Introduction

Molybdenum disulfide (MoS\textsubscript{2}) is a typical layered material that consists of 2D \(\text{S–Mo–S}\) layers stacked together through interlayer van der Waals interactions.\textsuperscript{[1–3]} Owing to the high theoretical capacity (669 mAh g\textsuperscript{−1}) and the four-electron-transfer conversion mechanism, it has been studied widely as an anode material for lithium-ion batteries (LIBs).\textsuperscript{[4–7]} Nonetheless, the practical application of MoS\textsubscript{2} still suffers from some limits caused by its poor electronic/ionic conductivities and substantial volume expansion, which causes electrode pulverization and active material/current collector detachment; the latter results in fast capacity fading and rate performance deterioration during cycling.\textsuperscript{[8, 9]} Two strategies have been proposed to address these issues and optimize the electrochemical performance of MoS\textsubscript{2}-based electrodes. One of these is to tune the shape and morphology of MoS\textsubscript{2} on the nanoscale (e.g., nanosheets,\textsuperscript{[10]} nanospheres,\textsuperscript{[11]} nanoflowers,\textsuperscript{[12]} nanotubes\textsuperscript{[13]}, with the aim of relaxing the volume-change-induced mechanical strain and facilitating lithium intercalation during charge/discharge. The other is to construct hybrid structures through combination with conductive materials that can enhance the electrical conductivity and structural stability, as achieved with MoS\textsubscript{2}/graphene,\textsuperscript{[14, 15]} MoS\textsubscript{2}/CNTs,\textsuperscript{[16, 17]} MoS\textsubscript{2}/carbon,\textsuperscript{[18, 19]} and MoS\textsubscript{2}/conductive polymers.\textsuperscript{[7, 20]} In this regard, hollow nanostructures are of great interest because of their structural advantages and functionalities. The hierarchical hollow particles, for example, assembled from nano-building blocks, provide a promising solution to the above challenges by (a) the void space accommodating the substantial volume expansion upon lithium intercalation,\textsuperscript{[21]} (b) preventing the aggregation of nanoparticles,\textsuperscript{[22]} (c) providing more electrode/electrolyte interfaces for Li storage,\textsuperscript{[23]} and (d) shortening the diffusion pathway of Li ions.\textsuperscript{[5]}

Previous studies have shown that hollow MoS\textsubscript{2}-based nanostructures are effective in improving the electrochemical performance of LIBs.\textsuperscript{[8, 24–26]} Nevertheless, the lowered tap densities, compared with their solid counterparts, inevitably compromise the volumetric energy/power densities of the electrodes.\textsuperscript{[27]} In terms of making full use of the inner void space, yolk–shell structures have attracted great interest because the core can increase the weight fraction of active components.\textsuperscript{[25, 28]} Thus far, a wide range of yolk–shell metal oxides have been studied and applied in many fields.\textsuperscript{[28, 29]} However, studies involving yolk–shell metal sulfides as anode materials for LIBs are quite limited. Template-based spray pyrolysis has been used to synthesize different yolk–shell metal sulfide particles, including Co\textsubscript{9}S\textsubscript{8},\textsuperscript{[30]} SnS\textsubscript{2},\textsuperscript{[29]} Zn-Fe-S,\textsuperscript{[31]} and MoS\textsubscript{2}.\textsuperscript{[32]} For example, the yolk–shell MoS\textsubscript{2}@void@MoS\textsubscript{2} sphere structures deliver a discharge capacity of 687 mAh g\textsuperscript{−1} after 100 cycles at 1 A g\textsuperscript{−1} and an enhanced rate performance.\textsuperscript{[12]} However, its lithium storage still suffers from the drawbacks of poor conductivity, wide particle size distribution, and non-ideal inner cavity structures.

We here propose a novel design and synthesis strategy for the preparation of highly uniform, interstitial void-controlled yolk–shell MoS\textsubscript{2}@C microspheres. This unique structure consists of MoS\textsubscript{2} particles (as yolks) and carbon shells, and reveals...
some advantages: a) yolk–shell MoS$_2$@C microspheres are monodisperse with a narrow particle size distribution, b) the interstitial void space of microspheres can be tailored in a controlled manner, and c) the carbon shells serve as conductive and buffer layers, which improve the charge transfer within the whole anode and accommodate the volumetric expansion/shrinkage during charge/discharge. These features endow the resulting LiB anode with superior reversible capacity and rate performance.

**Experimental Section**

**Chemicals**

Tris(hydroxymethyl) aminomethane, dopamine hydrochloride (DOP), ammonium molybdate tetrahydrate (NiH$_4$MoO$_4$), and molybdenum trioxide (MoO$_3$) were purchased from Aladdin. Thiourea, ethylene glycol (C$_2$H$_4$O$_2$), hydrogen peroxide (H$_2$O$_2$), sublimed sulfur (S), and hydrochloric acid (HCl) were purchased from Sinopharm Chemical Reagent Co. Ltd. All reagents were of analytical grade and used without purification.

**Preparation of yolk–shell MoS$_2$@C microspheres**

**Synthesis of MoS$_2$ microspheres:** Typically, S (12 mmol) and MoO$_3$ (5 mmol) were first dissolved in ethylene glycol (300 mL) to form a solution. The solution was then transferred to a Teflon-lined stainless steel autoclave and heated in an oven at 200 °C for 12 h. After cooling to room temperature, the black product was separated by centrifugation, and washed several times with deionized water and ethanol, respectively. Finally, the obtained product was dried in a vacuum oven at 60 °C overnight.

**Synthesis of MoS$_2$@PDA core–shell microspheres:** MoS$_2$ microspheres (800 mg) and dopamine hydrochloride (200 mg) were dispersed in Tris-buffer solution (200 mL, 10 mM, pH 8.5) with magnetic stirring for 12 h. The collected product was washed several times with water and ethanol, respectively, then dried in an oven at 60 °C overnight.

**Synthesis of yolk–shell MoS$_2$@C microspheres:** The as-synthesized MoS$_2$@PDA core–shell microspheres were annealed at 800 °C for 2 h in N$_2$ with a heating rate of 5 °C·min$^{-1}$, which translated them into MoS$_2$@C core–shell microspheres. Next, the annealed product (200 mg) was dispersed in different volume concentrations of H$_2$O$_2$ solutions (50 mL: 0.2, 0.4, 0.6, and 1.0 vol%) with vigorous stirring for 1 h; these were denoted as MoS$_2$@C-0.2%, MoS$_2$@C-0.4%, MoS$_2$@C-0.6%, respectively. This is an etching process, controlled by adjusting the concentration of H$_2$O$_2$. Subsequently, the etched products were harvested through centrifugation, washed repeatedly with ethanol, and vacuum dried at 60 °C overnight. For further improvement of the crystallization of MoS$_2$, MoS$_2$ was annealed at 800 °C for 2 h in N$_2$ with a heating rate of 5 °C·min$^{-1}$.

**Characterization**

Field-emission scanning electron microscopy (FESEM, Ultra 55) and transmission electron microscopy (TEM, Tecnai G2 F20 TWIN, operating at 200 kV) were used to observe the morphology of the samples. Powder X-ray diffraction (XRD) of the samples was conducted using PANalytical X’Pert PRO with CuK$_\alpha$ radiation (\(\lambda = 1.54 \) A) at a voltage of 40 kV and a current of 40 mA. Raman characterization was performed with a Raman spectroscope (excitation wavelength 532 nm, XploRA, HORIBA JobinYvon). Thermogravimetric analysis (TGA) was performed under air flow with a temperature ramp of 10 °C·min$^{-1}$. The specific surface areas of the samples were determined with an Automated Surface Area and Pore Size Analyzer (Quatasorb evo). X-ray photoelectron spectroscopy (XPS) was performed using an AXIS Ultra DLD spectrometer (Kratos Analytical Ltd.) and PHI 500 (PerkinElmer).

**Results and Discussion**

Our etching strategy for the fabrication of yolk–shell MoS$_2$@C microspheres is illustrated in Figure 1a. The interstitial space is tailored by controlling the concentration of H$_2$O$_2$ solution. We first synthesized highly uniform MoS$_2$ microspheres through a solvothermal method, using molybdenum trioxide (MoO$_3$) as the Mo precursor and sublimed sulfur (S) as the S precursor in ethylene glycol solution. The MoS$_2$ microspheres obtained were coated with dopamine (PDA) to form MoS$_2$@PDA core–shell microspheres (denoted as MoS$_2$@PDA), which were subsequently carbonized to yield MoS$_2$@carbon core–shell microspheres (MoS$_2$@C-0) by annealing. Subsequently, hydrogen peroxide (H$_2$O$_2$) solution was used to etch the MoS$_2$ core. Different concentrations (0.2, 0.4, and 0.6 vol%) of H$_2$O$_2$ solution resulted in the formation of different sizes of the interstitial space in the yolk–shell MoS$_2$@C microspheres, denoted as MoS$_2$@C-0.2%, MoS$_2$@C-0.4%, and MoS$_2$@C-0.6%, respectively. The etching mechanism can be described by the chemical reaction given in Equation (1),

\[
\text{MoS}_2 + 9\text{H}_2\text{O}_2 \rightarrow \text{MoO}_2^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ + 8\text{H}_2\text{O}
\]

As shown in Figure 1b, the three yolk–shell MoS$_2$@C microspheres anodes reveal different electrochemical behaviors during the lithiation process. First, the controlled interstitial space of MoS$_2$@C-0.4% between the MoS$_2$ core and the carbon shell can effectively accommodate the volume expansion upon lithium intercalation without excess empty space; the latter could decrease the tap density and compromise the overall capacity, as in the MoS$_2$@C-0.6% anode. In contrast, the carbon shell of MoS$_2$@C-0.2%, possessing a limited interstitial space, could be broken owing to the volume expansion upon lithia-
tion. Secondly, the carbon shells MoS$_2$@C-0.4% and MoS$_2$@C-0.6%, acting as self-supporting frameworks, allow the formation of stable solid electrolyte interphase (SEI) layers on the surface of the carbon shells.\cite{34, 35} However, the carbon shell of MoS$_2$@C-0.2% could exhibit persistent rupture and reformation of the SEI layer during cycling, causing low Coulombic efficiency, high ion transport resistance, and low electronic conductivity.\cite{34} Thirdly, the nanosized MoS$_2$ cores can effectively shorten the diffusion length of Li ions, thus improving the rate performance. Finally, the carbon shells are both electronically and ionically conducting, which is beneficial for the desired electrochemical kinetics.

The as-synthesized MoS$_2$ microspheres were characterized by FESEM at different magnifications. The representative images clearly show that the microspheres obtained are monodisperse, with an average diameter of approximately 280 nm and quite smooth surfaces (Figure 2). For investigation of the crystal structure of the MoS$_2$ particles, X-ray diffraction (XRD) studies were conducted. As shown in Figure S1 (Supporting Information), the XRD pattern of the MoS$_2$ microspheres shows only the (101) diffraction peak, indicating an imperfect lattice structure. After annealing at 800 °C in N$_2$ for two hours, the annealed MoS$_2$ microspheres reveal three dominant diffraction peaks at 2θ = 33.36, 39.35, and 59.04°, corresponding to the (101), (103), and (110) planes of MoS$_2$, respectively. This implies that the annealing process facilitates the perfecting of the MoS$_2$ lattice structure. Notably, the (002) diffraction peak is hardly observed in the XRD patterns after annealing, indicating that no order stacking exists along the c-axis direction. The rel-

Figure 1. a) Schematic illustration of construction of MoS$_2$@C microspheres with different H$_2$O$_2$ contents; b) schematic lithiation processes in yolk-shell MoS$_2$@C-0.2%, MoS$_2$@C-0.4%, and MoS$_2$@C-0.6% microsphere anodes.

Figure 2. a, b) FESEM images of MoS$_2$ microspheres; c) FESEM, and d) TEM images of MoS$_2$@PDA core–shell microspheres.
ative contents in the product were determined through ICP-AES analysis as 35.76% S and 59.10% Mo. The calculated Mo/S atomic ratio of the product was 1.82, which is close to the stoichiometric value of MoS$_2$. The coating of polydopamine was conducted by self-polymerization of dopamine on the surface of the MoS$_2$ microspheres in the buffer solution (pH 8.5) in air (see Experimental Section). This coating method enables the thickness of the polydopamine coating to be controlled well by adjusting the concentration of monomer, and subsequently, the polydopamine formed can be transformed into a highly conformal and effective carbon coating by thermal treatment.[36] The FESEM and TEM images show that uniform and smooth PDA layers were coated onto the surface of the MoS$_2$ microspheres (Figure 2c), with a PDA thickness of around 30 nm (Figure 2d).

Figure 3 shows the morphologies of MoS$_2$@C microspheres with and without H$_2$O$_2$ etching. Figure 3a–d presents the FESEM and TEM images of MoS$_2$@C-0, in which the PDA layers were carbonized into carbon layers by annealing at 800°C for 2 h in N$_2$. The thickness of the carbon layers is approximately 25 nm, as shown in the TEM images. No obvious cavities are observed between the carbon shells and the MoS$_2$ cores, indicating that the carbon shells were anchored on the surface of the MoS$_2$ microspheres. The homogeneous carbon coatings are crucial for yolk–shell structures because they should be able to prevent the electrolyte from ingress, so that the SEI forms only on the outside surface of the shell.[34] In our study, the as-obtained MoS$_2$@C yolk–shell microspheres revealed well-controlled interior voids, which arise from the etching effect of different concentrations of H$_2$O$_2$ solutions. Such structure-controlled yolk–shell microspheres are important for accommodating the volume expansion of the MoS$_2$ cores. As shown in Figure 3g and h, after etching with 0.2 vol% H$_2$O$_2$ solution, a visible cavity appears between the carbon shell and the MoS$_2$ core. For MoS$_2$@C-0.4% and MoS$_2$@C-0.6%, the cavity sizes increase gradually (Figure 3k, l, o, p), along with decreasing MoS$_2$ core sizes from 225 (−0.2%), to 190 (−0.4%), to 100 nm (−0.6%; Figure 3d, h, l). In addition, slight collapse of the carbon shells is observed after etching, as shown in the FESEM images (Figure 3e, f, i, j, m, n), and the MoS$_2$ cores almost disappear in MoS$_2$@C-1.0% (Figure S2, Supporting Information). This implies that such an etching strategy can also be used as a hard-template synthesis method for the fabrication of hollow carbon microspheres, in particular those with large, open carbon shells.

Raman spectroscopy was performed to characterize MoS$_2$@C-0, MoS$_2$@C-0.2%, MoS$_2$@C-0.4%, and MoS$_2$@C-0.6%. All four curves show two characteristic peaks at 381 and
405 cm\(^{-1}\), which correspond to the \(E_{2g}^1\) and \(A_{1g}^1\) vibration modes of MoS\(_2\) respectively (Figure 4). The \(E_{2g}^1\) mode reflects the in-plane displacement of Mo and S atoms, whereas the \(A_{1g}^1\) vibration mode involves the out-of-plane symmetric displacement of S atoms along the \(c\) axis.\(^{[2, 37, 38]}\) Note that H\(_2\)O\(_2\) etching significantly reduces the intensity of the two peaks because of the decreased MoS\(_2\) contents. Additionally, the Raman spectra of all four curves display two similar broad peaks around 1371 (D-band) and 1608 cm\(^{-1}\) (G-band), two typical characteristics of carbon materials.\(^{[39]}\) Given that the relative intensity ratio \(I_{D}/I_{G}\) reflects the number of defects in carbon materials,\(^{[40, 41]}\) an \(I_{D}/I_{G}\) of around 1.0 suggests that the pyrolytic product of PDA contains graphitic carbon atoms (despite the presence of defects), which is beneficial for improving the electrical conductivity of anodes.

X-ray photoelectron spectroscopy (XPS) was used to analyze the surface and chemical state of the MoS\(_2\)-based materials. As shown in Figure 5, the high-resolution spectra of the four MoS\(_2\)-based composites (MoS\(_2\)@C-0%, MoS\(_2\)@C-0.2%, MoS\(_2\)@C-0.4%, and MoS\(_2\)@C-0.6%, corresponding to decreasing MoS\(_2\) contents, see Table S2, Supporting Information) have a couple of doublet peaks of Mo3d\(_{5/2}\) and Mo3d\(_{3/2}\) corresponding to Mo\(^{4+}\) in MoS\(_2\), and the other doublet peaks at higher energies corresponding to Mo\(^{6+}\) in MoO\(_2\)\(^{2+}\) or MoO\(_3\). The intensity of the Mo\(^{6+}\) peak increases with decreasing MoS\(_2\) content, indicating the formation of MoO\(_2\)\(^{2+}\) through the chemical reaction given in Equation (1). In addition, there is a minor peak around 226.6 eV corresponding to S\(_2\). All four samples present two distinct peaks (S2p\(_{3/2}\) and S2p\(_{1/2}\)), suggesting that sulfur exists in the form of S\(^2-\) ions. Note that two S2p peaks (S2p\(_{3/2}\) and S2p\(_{1/2}\)) shift slightly to higher binding energies, probably owing to the increased contamination of SO\(_4\)\(^{2-}\) ions. They all show one strong peak at 284.6 eV for C–C, and two weak peaks for C–N and C=O.\(^{[42]}\) In the high-resolution spectra of O1s, the intensity of C–O increases with strengthening H\(_2\)O\(_2\) etching, because of the presence of oxygen functional groups (hydroxyl and epoxy) introduced by H\(_2\)O\(_2\) etching.\(^{[43]}\) In agreement with the Mo3d spectra, the intensity of Mo\(^{5+}\) 3p also increases with decreasing MoS\(_2\) content, further confirming the formation of MoO\(_2\)\(^{2+}\). There is a distinct peak at around 398.7 eV corresponding to N\(_\infty\), with a nitrogen content of about 1.93% in the carbon. Such N doping in the carbon shell is beneficial for...
Li$^+$ storage given the contribution to the electrical conductivity of carbon shells and the charge transfer at the interface.$^{[46]}$

The XRD patterns (Figure 6) show all the characteristic diffractions of MoS$_2@C$ microspheres, which can be assigned to hexagonal MoS$_2$ (PDF #37-1492) without detectable impurity peaks. In agreement with the annealing MoS$_2$, no (002) diffraction peak is observed in MoS$_2@C$. However, the (002) diffraction peak is discernible in MoS$_2@C-0.2\%$, MoS$_2@C-0.4\%$, and MoS$_2@C-0.6\%$, but shifts to a lower angle (13.8°). This suggests an increased interlayer distance ($\approx 0.65$ nm) of the (002) plane, attributed to exfoliation and restacking of MoS$_2$ nanosheets,$^{[33]}$ which can facilitate the ionic diffusion and alleviate the volumetric expansion during lithiation.

The TGA curves give the MoS$_2$ contents in these MoS$_2@C$ microspheres, as shown in Figure 7. Upon heating in air, the carbon was completely removed, and MoS$_2$ reacted with oxygen at approximately 350°C to form MoO$_3$, resulting in different residual weights for MoS$_2$ (91.3%), MoS$_2@C-0$ (77.0%), MoS$_2@C-0.2\%$ (73.7%), MoS$_2@C-0.4\%$ (61.0%), and MoS$_2@C-0.6\%$ (50.2%). This implies that the weight fractions of MoS$_2$ in MoS$_2@C-0$, MoS$_2@C-0.2\%$, MoS$_2@C-0.4\%$, and MoS$_2@C-0.6\%$ are 85.4%, 80.7%, 66.8%, and 55.0%, respectively.

The Brunauer–Emmett–Teller (BET) surface areas of MoS$_2@C$-0, MoS$_2@C-0.2\%$, MoS$_2@C-0.4\%$, and MoS$_2@C-0.6\%$ were calculated to be 22, 135, 225, and 408 m$^2$ g$^{-1}$, respectively (Figure 8). Apparently, H$_2$O$_2$ etching significantly enhanced the surface area of the MoS$_2@C$ microspheres, owing to the exfoliation of MoS$_2$ and the formation of porous carbon shells; this is expected to improve the power/energy density of LIBs.$^{[14]}

Figures 9a and 9b (Supporting Information) show cyclic voltammetry curves (CVs) of MoS$_2@C$-0, MoS$_2@C-0.2\%$, MoS$_2@C-0.4\%$, and MoS$_2@C-0.6\%$ electrodes for the first, second, third, fourth, and fifth cycles at 0.5 mV s$^{-1}$ (voltage range 0.01–3.0 V vs. Li/Li$^+$). All four curves have the same redox peaks but different specific capacities. Two reduction peaks (at $\approx 0.99$ and 0.42 V) are observed in the first cathodic scan. The peak at around 0.99 V arises from the insertion of Li$^+$ ions into the interlayer space of MoS$_2$ to form Li$_x$MoS$_2$ [Eq. (2)], along with the transformation from the 2H to 1T phase; the peak at approximately 0.42 V is attributed to the decomposition of Li$_x$MoS$_2$ into Li$_2$S and Mo nanoparticles [Eq. (3)].$^{[44-46]}$ Although diminished in the subsequent cathodic scan, a dominant cathodic peak appeared at 1.88 V, which is assigned to the formation of Li$_2$S [Eq. (3)]. In the reverse anodic scan, a pronounced peak at around 2.41 V is attributed to the conversion of Li$_2$S to S [Eq. (4)], and is somewhat similar to that of Li-S batteries. Because the Li$_2$S generated cannot effectively react with the metal at low voltages (<2.0 V), it is finally oxidized to sulfur at a high voltage (2.41 V) during the delithiation process.$^{[3,14,47]}$ The CVs show good overlap after the first cycle, indicating excellent reversibility and capacity retention. Additionally, the lithium storage mechanism in these MoS$_2@C$ yolk–shell composites is verified by their discharge/charge voltage profiles (Figure S4, Supporting Information).

\begin{align}
\text{MoS}_2 + x \text{Li}^+ + x \text{e}^- & \rightarrow \text{Li}_x\text{MoS}_2 \\
\text{Li}_x\text{MoS}_2 + (4-x) \text{Li}^+ + (4-x) \text{e}^- & \rightarrow \text{Mo} + 2 \text{Li}_2\text{S} \\
\text{Li}_2\text{S} + 2 \text{Li}^+ + 2 \text{e}^- & \rightarrow 2 \text{Li}_2\text{S}
\end{align}

The discharge/charge cycling performance of these MoS$_2@C$ particles was evaluated in the potential window 0.01–3.0 V at 200 mA g$^{-1}$, as shown in Figure 9b. They exhibit very different initial discharge capacities of 887.4, 1184, 1813.2, and 1498.2 mAh g$^{-1}$ for MoS$_2@C-0$, MoS$_2@C-0.2\%$, MoS$_2@C-0.4\%$, and MoS$_2@C-0.6\%$, respectively, with corresponding initial Cou-

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lombic efficiencies of 87.3%, 72.6%, 63.9%, and 67.6%, respectively. The capacity loss of the initial cycle is caused mainly by the irreversible decomposition of the electrolyte and the formation of the SEI film.\[24\] Apparently, MoS$_2$@C-0.4% reveals an optimal initial discharge capacity. After the second cycle, MoS$_2$@C-0.4% exhibits Coulombic efficiencies higher than 96%. Notably, MoS$_2$@C-0.4% delivers a discharge capacity up to 1015.8 mAh g$^{-1}$ after 50 cycles, and a reversible discharge capacity of 879.7 mAh g$^{-1}$ even after 200 cycles at 200 mA g$^{-1}$, which is the highest value among these four yolk–shell MoS$_2$@C microspheres electrodes and approximately 75.4% of the discharge capacity in the second cycle. MoS$_2$@C-0 and MoS$_2$@C-0.2% delivered lower discharge capacities, probably because of squeezing or fracturing of the carbon shells, continual formation of the SEI, and insufficient utilization of the MoS$_2$ cores during discharge/charge. Compared with the MoS$_2$@C-0.4% anode, the discharge capacity of MoS$_2$@C-0.6% is significantly lower. This is attributed to the redundant void space and smaller MoS$_2$ cores, which give rise to longer ion diffusion distances, compromising the discharge capacity. Remarkably, MoS$_2$@C-0.4% still delivered a capacity up to 781.3 mAh g$^{-1}$ at 500 mA g$^{-1}$ after 150 cycles (Figure 9c), and 665.2 mAh g$^{-1}$ at 1 A g$^{-1}$ after 250 cycles (Figure S5, Supporting Information). These results are among the highest values in MoS$_2$-based hollow-structure anode materials (Table S1, Supporting Information). For example, in a recent study, the MoS$_2$ anode, which consists of ultrathin sheets on hollow carbon shells, showed a high specific capacity of around 952 mAh g$^{-1}$.\[24\] However, such an architecture involves a relatively large invalid volume (0.455 $\mu$m$^3$/$\mu$m$^3$ per particle), which is not beneficial for improving the volumetric energy/power densities of electrodes. In this study, all the samples exhibit specific capacities higher than the theoretical capacity (669 mAh g$^{-1}$; Table S2, Supporting Information), which may arise from two factors: a) the synergy between MoS$_2$ and carbon contributes to the total electrode capacity, but the contribution of carbon nanostructures cannot be captured by the standard rules of mixtures; and b) the element sulfur (theoretical capacity 1675 mAh g$^{-1}$) also has a contribution to the electrode capacity, given the degradation of MoS$_2$ during lithiation. The degradation makes sulfur an electrochemically active material, and the nanostructured Mo particles serve as physical adsorption sites for Li$^+$ storage.\[3, 40\]

The rate capacities of the MoS$_2$@C anodes were evaluated at different current densities ranging from 0.1 to 5 A g$^{-1}$ (Figure 9d). MoS$_2$@C-0.4% exhibits average specific capacities of 1110, 985, 830, 725, 600, 450, and 950 mAh g$^{-1}$ at 0.1, 0.2, 0.5, 1, 2, 5, and 0.1 A g$^{-1}$, respectively. Upon returning the current density to 0.1 A g$^{-1}$ after cycling, a capacity of 950 mAh g$^{-1}$ was recovered; this demonstrated particularly long cycling capacity (over 92.7% reversible capacity retention after 100 cycles, as shown in Figure S6, Supporting Information), indicating its superior structural stability and reversibility. Moreover, a capacity (450 mAh g$^{-1}$) far higher than that of graphite can still be delivered even at 5 A g$^{-1}$. By comparison, MoS$_2$@C-0, MoS$_2$@C-0.2%, and MoS$_2$@C-0.6% exhibit much lower capacities: 630, 825, and 870 mAh g$^{-1}$, respectively, at 0.2 A g$^{-1}$, and poor rate capacities: 168, 313, and 325 mAh g$^{-1}$, respectively, at 5 A g$^{-1}$. As shown in Figure S7 (Supporting Information), the MoS$_2$ cores of all four electrodes suffer from great structural degradation: the carbon shells of MoS$_2$@C-0 and MoS$_2$@C-0.2% crack out, whereas the MoS$_2$@C-0.4% and MoS$_2$@C-0.6% stay intact after cycling at various current rates. These results demonstrate the great structural advantages of such yolk–shell microspheres.
For further investigation of the contribution of carbon to the capacity of the MoS$_2$@C electrodes, MoS$_2$@C-1.0% (carbon hollow spheres) was tested as an anode material. As shown in Figure S8a (Supporting Information), the MoS$_2$@C-1.0% (carbon hollow spheres) exhibits an initial discharge capacity of 1707.1 mAh g$^{-1}$ and an initial Coulombic efficiency of 49.3%, which is the lowest among all the MoS$_2$@C electrodes (MoS$_2$@C-0 87.3%, MoS$_2$@C-0.2% 72.6%, MoS$_2$@C-0.4% 63.9%, and MoS$_2$@C-0.6% 67.6%). This endorses the formation of an SEI layer owing to the increased specific surface area (SSA) in MoS$_2$@C-1.0% (etching effect of H$_2$O$_2$). MoS$_2$@C-1.0% delivers a discharge capacity of approximately 830 mAh g$^{-1}$ at 200 mAg$^{-1}$, which can be assigned to its porous nanostructure and high SSA; the latter shortens the ion transport length and increases electrode/electrolyte interfaces. In addition, N-doped, defect-free carbon nanostructures afford more active sites for Li$^+$ adsorption and improve the capacity for Li$^+$ storage.$^{[10]}$ MoS$_2$@C-1.0% exhibits rate capacities of 1000, 840, 670, 570, 480, 365, and 850 mAh g$^{-1}$ at 0.1, 0.2, 0.5, 1, 2, 5, and 0.1 Ag$^{-1}$, respectively, as shown in Figure S8b (Supporting Information). Given their different SSAs (different H$_2$O$_2$ etching conditions), the contribution of carbon to the capacity of each MoS$_2$@C electrode may be different, and further study is necessary.

The enhanced lithium-storage performance of MoS$_2$@C-0.4% probably arises from its advantageous structural features. The N-doped carbon shells can act not only as conductive frameworks, but also as electrolyte blocking layers that enable SEI formation on the outside surface of the shells. The optimized interstitial space in MoS$_2$@C-0.4% effectively alleviates the stress caused by the volume expansion of the MoS$_2$ cores during charge/discharge. Meanwhile, the small MoS$_2$ yolk and high SSAs contribute to shortening the diffusion distance of electrons and ions, thus significantly improving the rate capacity.

In addition, the electrochemical impedance spectra (EIS) in Figure 10 show that the diameter of the high-frequency semicircle (corresponding to the charge-transfer resistance between active materials and liquid electrolyte) decreases greatly with increasing H$_2$O$_2$ concentration, indicating a reduced solid-state interface layer resistance. This can be attributed to sufficient wetting of the electrolyte on the solid surface and enhanced Li$^+$ diffusion kinetics. Such an etching strategy for MoS$_2$@C microspheres opens a new avenue for the optimization of the electronic/ion conductivities and electrochemical performances of MoS$_2$-based anodes.

**Conclusions**

We have designed and synthesized highly uniform yolk–shell MoS$_2$@C microspheres for enhanced LIB anodes. The inner cavity between the carbon shells and MoS$_2$ cores can be tailored easily by a novel etching strategy. The rationally designed void space of MoS$_2$@C-0.4% allows the expansion of the MoS$_2$ cores without redundant inner space, thus preventing the deformation of the carbon shells or disruption of the SEI layers on the outside. Impressively, the yolk–shell MoS$_2$@C-0.4% microspheres anode exhibits a high reversible capacity of 1016 mAh g$^{-1}$ at a current density of 200 mAg$^{-1}$, excellent cycling stability (200 cycles), and superior rate performance. Additionally, the etching MoS$_2$@C core–shell microspheres strategy developed in this study may open up a new approach for the preparation of other carbon-based hollow nanostructures.

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**Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** electrochemistry • lithium-ion batteries • microspheres • nanostructures • MoS$_2$


