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Abstract

Layered MoS₂ has attracted much attention as a promising anode material for lithium ion batteries. The intrinsically poor electrical/ionic conductivity, volume expansion and pulverization, stress accumulation and unstable solid-electrolyte interface formation within MoS₂ electrodes during the lithiation-delithiation process significantly result in their fast capacity fading, poor rate capability and cycle life. To address these critical issues, a novel nanobowl structure for MoS₂ with a carbon coating (MoS₂@C-400, 500, 600) is successfully fabricated by a facile solvothermal method, followed by a post-annealing process. The fabricated MoS₂@C-600 and MoS₂@C-500 exhibited high reversible capacities of 1164.4 and 1076.4 mA h g⁻¹ at 0.2C, and maintained high capacity retention of 72.1% and 78.4% over 150 cycles, respectively. Such remarkable lithium storage properties are attributed to the unique nanobowl structure, which provides a large accessible surface area and high pore volume, and flexible carbon film coating, allowing for easy diffusion of electrolyte, alleviation of volume expansion, formation of stable solid electrolyte interfaces and fast diffusion of lithium ions.

Keywords

mos2, c, nanobowls, growth, lithium, material, ion, battery, anode

Disciplines

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Growth of MoS₂@C nanobowls as a lithium-ion battery anode material†

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Layered MoS₂ has attracted much attention as a promising anode material for lithium ion batteries. The intrinsically poor electrical/ionic conductivity, volume expansion and pulverization, stress accumulation and unstable solid–electrolyte interface formation within MoS₂ electrodes during the lithiation–delithiation process significantly result in their fast capacity fading, poor rate capability and cycle life. To address these critical issues, a novel nanobowl structure for MoS₂ with a carbon coating (MoS₂@C-400, 500, 600) is successfully fabricated by a facile solvothermal method, followed by a post-annealing process. The fabricated MoS₂@C-600 and MoS₂@C-500 exhibited high reversible capacities of 1164.4 and 1076.4 mA h g^{−1} at 0.2C, and maintained high capacity retention of 72.1% and 78.4% over 150 cycles, respectively. Such remarkable lithium storage properties are attributed to the unique nanobowl structure, which provides a large accessible surface area and high pore volume, and flexible carbon film coating, allowing for easy diffusion of electrolyte, alleviation of volume expansion, formation of stable solid electrolyte interfaces and fast diffusion of lithium ions.

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1. Introduction

Lithium-ion batteries (LIBs) have attracted increasing research interest and become one of the main power supplies for smart electronic devices and electric vehicles (EVs) and hybrid EVs (HEVs) due to their advantages of high power/energy density, long cycling life, and environmental friendliness.¹ In order to acquire even higher energy density of LIBs, the development of high-energy electrode materials is the key to success.² In the commercial market, graphite as an anode material has been commonly used in LIBs for the past two decades owing to its rich natural resources, low cost, and good cycling stability. Its low theoretical capacity (~372 mA h g^{−1}), poor rate performance and plating (deposition) of metallic Li at ~0.05 V (vs. Li⁺/Li), however, limit its further application in high-energy EVs and HEVs. Graphene, a crystalline allotrope of carbon with 2-dimensional (2D) properties, has been widely investigated for energy conversion/storage applications due to its unique physical and chemical properties.³ In terms of its application as anode for LIBs, graphene exhibited much higher capacity and rate capability than graphite because of its larger surface area, higher electronic conductivity, and remarkable thermal and mechanical stability.⁴

Analogue to graphene, two-dimensional transition-metal layered transition-metal dichalcogenides have also been widely investigated as anode materials in reversible storage of Li to replace the graphite, as well as graphene.⁵ MoS₂, one of the MX₂-type (M = Ti, Nb, Mo, Ta; X = S, Se, Te) compounds, possesses a layered crystal structure that is stacked layer-by-layer in the order of ‘S–Mo–S’, in which the S–S layers are supported by van der Waals forces and Mo atoms are sandwiched in the center between S–S layers.⁶ These structural features provide strong molecular bonds within a single layer but weak interlayer bonds, and thus facilitate the insertion/extraction of Li⁺ ions, leading to a high theoretical capacity of ~670 mA h g^{−1} based on 4 Li⁺ ions reacted with every MoS₂ molecule. Owing to its high theoretical capacity, as well as its rich natural resources, MoS₂ has been extensively demonstrated to be an ideal anode material for LIBs.⁷

To date, intrinsically poor electrical/ionic conductivity, volume expansion and pulverization, stress accumulation and unstable solid–electrolyte interface formation within MoS₂ electrode during the lithiation–delithiation process significantly result fast capacity fading, poor rate capability and cycle life. To solve these critical issues, many efforts have been made, including morphology control,^{8–13} hybridizing MoS₂ nanostructures with more conductive materials (e.g., porous carbon, carbon nanotubes, and graphene),^{8–18} and enlarging the lattice in the *c*-direction between S–S layers.¹⁹ Among these efforts, nanostructure engineering and hybridization with more conductive materials of MoS₂ have been proven to be an effective method. Typically, hollow structures for electrode materials have been widely demonstrated to be beneficial to enhance electrical/ionic

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conductivity and buffer volume expansion. The hollow structures not only provide free spaces to alleviate the structural strain during the lithium insertion/extraction process, but also facilitate the fast diffusion of lithium ions in large accessible areas and by short diffusion paths, leading to improved rate capability and cycling stability. Despite the structural advantages of hierarchical hollow MoS₂,^{12,17} as well as MoS₂ microspheres,⁸ MoS₂/polyaniline nanowires,¹⁰ MoS₂/carbon nanoflake,^{13,18} honeycomb-like MoS₂,¹¹ and MoS₂/graphene nanoflowers, the further enhancement of the capacity, rate capability and cycling stability of MoS₂ is still highly desirable.

Here, for the first time, we synthesized novel nanobowl structures for MoS₂@C by a facial solvothermal method, followed by an annealing process. Apart from the structural advantages of hollow spheres or other closed hollow structures, the bowl-like nanostructure of MoS₂@C with open interior and exterior surfaces provides extra excellent/enhanced characteristics to further enhance the electrochemical performance. For example, it includes: (i) higher accessible specific surface area and surface to volume ratio than the hollow structure, offering more accessible areas from the interfacial contact areas to facilitate the quick penetration of electrolyte and more lithium ion storage; (ii) amorphous carbon films coated on not only the exterior, but also the interior surfaces of MoS₂ to protect electrodes from pulverization and enhance the conductivity of MoS₂, enabling fast electron transportation across the interface of the MoS₂ and the carbon sheets; and (iii) a 'sandwich-like' amorphous carbon coating to enhance the mechanical flexibility and maintain the structural integrity of MoS₂, as well as alleviating its volume changes. Therefore, by integrating these advantages of both nanostructure engineering and hybridization, we found that the MoS₂@C-600 exhibited the high initial capacity of 1558.3 mA h g⁻¹ at 0.1C and 1164.4 mA h g⁻¹ at 0.2C while MoS₂@C-500 maintained a high reversible capacity of 846 mA h g⁻¹ at 0.2C over 150 cycles, corresponding to an initial capacity retention of 78.4%. The capacity and cycle stability was considerably enhanced compared to MoS₂-graphene (808 mA h g⁻¹ retained after 100 cycles, 100 mA g⁻¹),¹⁶ and MoS₂-C (698 mA h g⁻¹ retained after 60 cycles, 100 mA g⁻¹).¹⁴

2. Experimental section

2.1 Synthesis of MoS₂

Firstly, sodium molybdate and thioacetamide were dissolved in deionized water and *N*-methyl pyrrolidone (NMP) with continuous stirring for 30 minutes. Secondly, the obtained mixture was transferred into a 50 mL Teflon-lined stainless steel autoclave and maintained at 200 °C for 24 h. Thirdly, the reaction system was naturally cooled down to room temperature. Finally, the obtained products were collected by centrifugation, washed with distilled water and ethanol, and dried at 60 °C under vacuum.

2.2 Synthesis of MoS₂@C

Firstly, 0.1 g of the as-prepared MoS₂ and 5 mL oleic acid were mixed, and the mixture was kept under stirring for 24 h in a 40°

thermostatic water bath. Secondly, the obtained mixture was collected by centrifugation and washed with ethanol, which was followed by an annealing process in Ar atmosphere at a heating rate of 3° min⁻¹ at temperatures of 400°, 500°, and 600° for 2 h, and finally, naturally cooling to room temperature.

2.3 Materials characterizations

The morphologies and structures of the as-prepared samples were characterized by scanning electron microscopy (SEM) on a Hitachi S-4800, with both transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) on a JEOL2010. The phase of the as-prepared samples was identified by X-ray diffraction (XRD) using a Rigaku D max-2500. Raman spectra were collected on a Lab RAM HR 800 Raman spectrometer. X-ray photoelectron spectra (XPS) were acquired on an ESCALAB 250. The Brunauer–Emmett–Teller (BET) measurements were carried out using a Micromeritics ASAP 2020 system. Pore size distribution (PSD) curves were obtained from N₂ adsorption data by the density functional theory (DFT) method (Micromeritics). Thermogravimetric analysis (TGA, Setaram018124) was performed at a heating rate of 10 °C min⁻¹ in air.

2.4 Electrochemical measurements

The electrodes were fabricated by blending the MoS₂, MoS₂@C-400, MoS₂@C-500, or MoS₂@C-600 with acetylene black carbon and polyvinylidene difluoride (PVDF), in a weight ratio of 8 : 1 : 1, respectively. *N*-Methyl-2-pyrrolidone (NMP) was used as the blending solvents for the mixture. The obtained slurry was coated on Cu foil, dried at 90°C for 12 h, and cut into electrodes. The obtained electrodes were dried again at 90°C for 12 h in vacuum. CR 2032 coin-type cells were assembled using the as-prepared electrode as the working electrode, Li foil as the counter electrode and reference electrode, porous polypropylene film as the separator, and 1 M LiPF₆ in a 1 : 1 : 1 (v/v/v) mixture of ethylene carbonate (EC), ethylene carbonate (EC), and diethyl carbonate (DEC) as the electrolyte. The performance of the cells was measured using an automatic battery tester system (Land®, China) and galvanostatically charged and discharged at various current densities in the voltage range of 0.02–3.0 V, with 1C = 500 mA g⁻¹. Cyclic voltammograms (CV) and electrochemical impedance spectra (EIS) were collected using a CHI 760C (CH Instruments, USA) electrochemical workstation over a frequency range of 50 mHz to 1 MHz. Owing to the low amount of carbon, only ~5 wt%, the capacity contribution from carbon was neglected. Moreover, the specific capacity and C-rates of MoS₂@C were calculated based on the total mass of MoS₂@C.

3. Results and discussion

The fabrication process of MoS₂@C nanobowls is simply illustrated in Fig. 1. The MoS₂ nanobowls were initially synthesized by a solvothermal reaction using sodium molybdate (SM) and thioacetamide (TAA) in *N*-methyl pyrrolidone (NMP)/H₂O at 200 °C for 24 h. To explore the influence of synthesis conditions on the morphology and structure of MoS₂, a series of MoS₂

Fig. 1 Schematic illustration of the formation mechanism of the MoS₂@C nanobowls (OA: oleic acid).

prepared by using different volume ratios of solvents (NMP/H₂O, 0 : 4, 1 : 3, 2 : 2, 3 : 1 and 4 : 0) and mass ratios of solutes (SM/TAA, 1 : 1, 1 : 1.5, 1 : 2, 2 : 2, 4 : 4) are compared in Experimental section (ESI, Table S1†). Based on the optimal synthesis condition, the formation mechanism of MoS₂ nanobowls is proposed. Initially, the growth in the [001] or [002] direction of MoS₂ is strongly hindered because of the blocking effect of -OH on the crystal planes (*e.g.*, (001) or (002)), leading to the formation of MoS₂ monolayers.²⁰ In the following step, the adjacent MoS₂ monolayers that bonded by van der Waals forces self-assemble to form nanoflakes, then the MoS₂ nanoflakes stack and form the sheet structure that is thinner at the edge and thicker in the middle.²¹ Driven by ever-growing thermodynamic forces, the thinner edges of the MoS₂ sheets become curled up to make the 2D architectures more stable, and the lamellar structures at the edge gradually grow upwards. Simultaneously, the thicker middle of the MoS₂ sheets forms as the bottom of a sphere-shaped bowl. Since the surface energy of MoS₂ reaches a fixed value with MoS₂ ever growing, the unique nanobowl structure of the MoS₂ remains stable. In order to further enhance the anode performance of MoS₂, a series of the as-synthesized MoS₂ nanobowls with carbon coating (MoS₂@C) are prepared by annealing mixtures of MoS₂/oleic acid (OA) at 400 °C, 500 °C, and 600 °C. During this annealing process, the OA is expected to be carbonized to a thin carbon film that uniformly coated inner and outer surfaces of the MoS₂ nanobowls. More details of the synthesis procedure are presented in the Experimental section. The obtained MoS₂@C annealed at 400 °C, 500 °C and 600 °C were denoted as MoS₂@C-400, MoS₂@C-500, and MoS₂@C-600, respectively.

The morphologies and structures of the as-prepared MoS₂ and MoS₂@C samples are systematically investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As can be seen, Fig. 2a–d displays that all MoS₂, MoS₂@C-400, MoS₂@C-500 and MoS₂@C-600 are composed of the nanobowls with a uniform size of ~50 nm in diameter. As expected, there were no distinct morphology changes for MoS₂ and MoS₂@C, indicating the excellent

structural stability of MoS₂ nanobowls after annealing. The detailed structures and sizes of MoS₂ and MoS₂@C nanobowls were also further confirmed by TEM (Fig. 2e–h) and high-resolution TEM (HR-TEM) (Fig. 2i–l). As shown in Fig. 2i, MoS₂ was composed of a ring-like structure with 3–7 lamellar layers. The ring-like structures have a lattice spacing of 0.68 nm between lamellar layers corresponding to a distance between (002) planes of MoS₂. After pyrolysis of the carbon precursor, the lattice spacing of MoS₂@C was slightly decreased from 0.68 to 0.62 nm. The decreased lattice spacing could be ascribed to recrystallization and removal of structural defects of MoS₂.^{8,13,15,16}

Fig. 3a displays the XRD patterns of MoS₂, MoS₂@C-400, MoS₂@C-500, and MoS₂@C-600. As shown in Fig. 3a, MoS₂ exhibits four distinct peaks at 9.0°, 17.8°, 32.5°, and 57.5°. Two broadened peaks in the high-angle regions (32.5° and 57.0°) correspond to the (100) and (110) planes, respectively. The peak at 17.8° is indexed to the reflection of (002) plane while the peak at 9.0° is assigned to the (001) plane.¹⁴ After the annealing process, all the XRD peaks of MoS₂@C-400, MoS₂@C-500, and MoS₂@C-600 are well indexed to hexagonal MoS₂ (JCPDS card no. 73-1508), including a 14.9° main peak, which can be assigned to the (002) plane. As can be seen, the presence of the peak at 14.9° but disappearance of two peaks at 9° and 17.8° are due to the removal of structural defects and recrystallization of MoS₂ after the annealing process, leading to the decrease in the layer-by-layer lattice spacing.¹⁷ These results are consistent with the HRTEM results (Fig. 2i–l). Raman spectroscopy (Fig. 3b) reveals the MoS₂ structure with the appearance of two characteristic peaks at 379 cm⁻¹ and 403 cm⁻¹, corresponding to the E_{2g}¹ and A_{1g}¹ modes, respectively.¹⁷ As expected, MoS₂@C composites all display typical E_{2g}¹ and A_{1g}¹ modes in the same region. In addition, the characteristic D band (a defect/disorder peak) at 1370 cm⁻¹ and G band (a graphitic peak) at 1580 cm⁻¹ further confirm the presence of carbon in the MoS₂@C. The intensity ratio of I_D/I_G decreased from MoS₂@C-400, MoS₂@C-500, to MoS₂@C-600. It is mainly due to higher degree of carbonization of carbon nanosheets at higher annealing temperature. As expected, the high crystallization of carbon is

Fig. 2 Morphologies of the MoS₂@C nanobowls. (a–d) SEM images, (e–h) TEM images, and (i–l) HRTEM images of MoS₂ (a, e and i), MoS₂@C-400 (b, f and j), MoS₂@C-500 (c, g and k) and MoS₂@C-600 (d, h and l).

beneficial to improve electrical conductivity of MoS₂@C.²² FT-IR spectroscopy was employed to explore the chemical functional groups of MoS₂@C composites (especially, uniform carbon coating film on the surfaces), as shown in Fig. 3c. The peaks of the FT-IR spectra represent various functional groups. As expected, MoS₂@C-600 displays various functional groups, including, the O–H bond at 3403 cm^{−1}, C–H bond at 2918 cm^{−1}, C=C bond at 1587 cm^{−1} and C–O bond at 1147 cm^{−1}. Compared to MoS₂@C-400 and MoS₂@C-500, the more sharp peaks with high intensities for MoS₂@C-600 further reveal that oleic acid are highly carbonized on the surfaces of MoS₂ at higher annealing temperatures.²³ In order to determine the carbon content in the MoS₂@C, thermogravimetric analysis (TGA) was adopted. As shown in Fig. 3d and S3,† the carbon content of MoS₂@C-400, MoS₂@C-500, and MoS₂@C-600 was estimated to be 15.67, 13.44, and 15.11 wt%, respectively. Apart from the confirmation by HRTEM (Fig. 2j), an additional exothermic peak in the differential thermogravimetric (DTG) curve for MoS₂@C-400 (Fig. S3b†) also further confirms the lower crystallization of carbon coating for MoS₂@C-400.

To investigate the chemical states of Mo, S, and C of the MoS₂ and MoS₂@C, high resolution X-ray photoelectron spectroscopy (XPS) measurements were carried out. As shown in

Fig. 3e, the individual doublet peaks with binding energies at 162 and 163.2 eV in the S 2p spectrum are exactly assigned to the S^{2−} ions of MoS₂, whereas two main peaks with binding energies of 232.5 eV (Mo 3d_{3/2}) and 232.5 eV (Mo 3d_{5/2}) in the Mo 3d (Fig. 3f) spectrum are well indexed to Mo⁴⁺ of MoS₂.¹² As expected, the Mo and S XPS peaks Fig. S4,† and likewise, the MoS₂@C-500 (Fig. S4d and e†) and MoS₂@C-600 (Fig. S4g and h†) peaks are well matched with those of MoS₂. In addition, the presence of carbon in the MoS₂@C composites is also further confirmed by distinct XPS C1s peaks at around 285 eV in each C1s spectrum (Fig. S4c, f, and i†).

Brunauer–Emmett–Teller (BET) analysis was employed to further investigate the pore size distribution and specific surface area of MoS₂ and MoS₂@C. As shown in Fig. 4, a typical hysteresis loop indicating a mesoporous structure is observed in both the MoS₂ sample and the MoS₂@C samples. MoS₂, MoS₂@C-400, MoS₂@C-500, and MoS₂@C-600 exhibit specific surface areas of 88.21, 44.86, 49.65, and 72.75 m² g^{−1}, respectively. Owing to the higher degree of carbonization at higher annealing temperature, more mesopore structures can be obtained from the carbon layer, so the MoS₂@C composites at higher annealing temperature feature higher BET specific surface areas and total pore volumes, as well as a wider pore size

Fig. 3 (a) XRD patterns, (b) Raman spectra, and (d) TGA curves of MoS₂, MoS₂@C-400, MoS₂@C-500, and MoS₂@C-600; (c) FT-IR spectra of MoS₂@C-400, MoS₂@C-500, and MoS₂@C-600; high resolution XPS peaks of (e) Mo 3d, and (f) S 2p of MoS₂.

distribution (insets of Fig. 4b–d). Besides, due to the carbon coating for inner-sides of MoS₂, the void volume of MoS₂ is partially occupied, leading to lower surface areas for the MoS₂@C than MoS₂. Nevertheless, the carbon film coated on the surfaces of MoS₂@C nanobowls can provide more favorable paths for electrons fast transportation, protect the electrode pulverization and enhance the mechanical properties of composites during the lithiation–delithiation process.

Fig. S5a–d† presents typical CV curves of the MoS₂, MoS₂@C-400, MoS₂@C-500, and MoS₂@C-600 cells at 0.2 mV s⁻¹ in the voltage range of 0.02–3.0 V, respectively. As shown in Fig. S5a,† MoS₂ displays two reduction peaks at 1.1 and 0.3 V in the first cathodic process. The peak at 1.1 V can be attributed to insertion of Li ions into the interlayers of MoS₂ (formation of Li_xMoS₂), which change from trigonal prisms to octahedra in the MoS₂ structure. The weak reduction peak at 1.1 V indicates the poor ionic conductivity for MoS₂. The peak at 0.3 V is indicative of the conversion of Li_xMoS₂ into metallic Mo and Li₂S.¹⁰ In the following anodic process, an oxidation peak is observed at ~1.85 V (A1) that is attributed to the oxidation of Mo to MoS₂, followed by another oxidation peak at ~2.39 V (A2) associated

with the oxidation of Li₂S. In the following cathodic process, the peaks at 1.1 and 0.3 V disappear, and two new peaks at about 1.9 (C1) and 1.3 V (C2) emerge, which can be ascribed to the conversion of S to Li₂S and the association of Li⁺ ions with Mo, respectively.¹⁶ After the first anodic–cathodic cycle, highly overlapping and distinct pairs of redox peaks (A1–C2 and A2–C1) appeared in the subsequent CV curves of MoS₂, indicating the good reversibility of MoS₂. For the MoS₂@C composites, take MoS₂@C-600 (Fig. 5a or S5d†) as example, it displays three distinct reduction peaks at approximately 0.95, 0.45, and 0.05 V. Compared to MoS₂, the clear peak at 0.95 V is associated with insertion of Li⁺ ions, while the peak at 0.45 V is indicative of the conversion process, and the formation of solid electrolyte interphase (SEI), another clear peak at 0.05 V is related to the lithium ion storage of the amorphous carbon layers. Due to the contribution of the carbon layers, extra Li⁺ ions can be inserted in for MoS₂@C composites, so the MoS₂ CV curves (Fig. S5a†) show weaker reduction peaks at 1.1 V than MoS₂@C (Fig. S5b–d†). Similarly, highly overlapped CV curves in the subsequent cycles further support the high reversibility of MoS₂@C. It should be noted that the oxidation peaks at ~1.85 V in all three

Fig. 4 BET nitrogen adsorption and desorption isotherms of (a) MoS_2 , (b) $\text{MoS}_2\text{@C-400}$, (c) $\text{MoS}_2\text{@C-500}$, and (d) $\text{MoS}_2\text{@C-600}$. Inset of each plot: pore size distribution of the corresponding sample.

anodic processes and the reduction peak at 1.1 V in the second and third cathodic processes are extremely weak for all $\text{MoS}_2\text{@C}$ composites compared with that of MoS_2 . This is probably due to the strong interaction between lithium ions and carbon nano-sheets, overlapping the oxidation peaks of Mo.

Fig. 5b presents the first discharge-charge profiles for the MoS_2 , $\text{MoS}_2\text{@C-400}$, $\text{MoS}_2\text{@C-500}$, and $\text{MoS}_2\text{@C-600}$ at 0.1C in the voltage range of 0.02–3 V. As can be seen, the discharge-charge electrochemical behavior of MoS_2 and $\text{MoS}_2\text{@C}$ were almost consistent with the cyclic voltammetry (CV) measurements. Along with the discharge-charge profiles of MoS_2 and $\text{MoS}_2\text{@C}$ at 0.1C, the discharge-charge profiles of $\text{MoS}_2\text{@C-600}$ at various C-rates from 0.2 to 10C are also presented in Fig. 5c. The electrochemical behaviors of MoS_2 and $\text{MoS}_2\text{@C}$ agree well with previous reports.^{15,24}

To compare the rate capability of MoS_2 and $\text{MoS}_2\text{@C}$, we charged and discharged the cells for 60 cycles in the voltage range of 0.02–3 V at current densities from 0.2C to 10C (Fig. 5d). As shown in Fig. 5d, the initial discharge capacities of the MoS_2 , $\text{MoS}_2\text{@C-400}$, $\text{MoS}_2\text{@C-500}$, and $\text{MoS}_2\text{@C-600}$ are 1461.5, 1405.3, 1478.1 and 1558.3 mA h g^{-1} at 0.1C (assume 1C = 500 mA g^{-1}), with initial coulombic efficiencies of 67.8%, 71.6%, 74.6%, and 75.6%, respectively. When the C rate is increased from 0.2 to 10C and changes back to 0.1C, the $\text{MoS}_2\text{@C-600}$ exhibits the higher average charge capacities of 958.6 (0.2C), 792.5 (0.5C), 657.6 (1C), 504 (2C), 363.3 (5C), and 171.5 (10C) mA h g^{-1} , followed by the $\text{MoS}_2\text{@C-500}$, than $\text{MoS}_2\text{@C-400}$ and MoS_2 . When the charge/discharge current density changes from 10C back to 0.1C, the specific capacity of all these four samples can be well restored, indicating extraordinarily high cycling stabilities. The detailed numerical results are listed in Table 1.

To further compare their rate capabilities, the capacity retention vs. C-rates of MoS_2 and $\text{MoS}_2\text{@C}$ composites is presented in Fig. S6a,† obviously $\text{MoS}_2\text{@C-500}$ and $\text{MoS}_2\text{@C-600}$ present higher capacity retention (as a function of C-rate) than MoS_2 or $\text{MoS}_2\text{@C-400}$. The improved rate capability is attributed to the carbon coating film, resulting the improved conductivity and enhanced mechanical properties of $\text{MoS}_2\text{@C-500}$ or $\text{MoS}_2\text{@C-600}$ during the discharge-charge process. Although a thin carbon film was also coated on the surface of $\text{MoS}_2\text{@C-400}$, $\text{MoS}_2\text{@C-400}$ presented poorer rate capability than $\text{MoS}_2\text{@C-500}$ or $\text{MoS}_2\text{@C-600}$ because of its lower degree of carbonization at 400 °C.

Fig. 5e presents the relatively long-term cycling performances of the MoS_2 and $\text{MoS}_2\text{@C}$ at 0.2C. As can be seen, the MoS_2 , $\text{MoS}_2\text{@C-400}$, $\text{MoS}_2\text{@C-500}$, and $\text{MoS}_2\text{@C-600}$ exhibited initial discharge capacities of 928.8, 898.3, 1076.4, and 1164.4 mA h g^{-1} , with an initial coulombic efficiency of 69.9%, 73.5%, 76.9%, and 79.1%, respectively. After 150 cycles, the MoS_2 , $\text{MoS}_2\text{@C-400}$, $\text{MoS}_2\text{@C-500}$, and $\text{MoS}_2\text{@C-600}$ cells can maintain discharge capacities of 621.6, 605.1, 846.0, and 839.3 mA h g^{-1} with initial capacity retention of 66.9%, 67.4%, 78.6%, and 72.1%, respectively. Despite the different capacities and capacity retention, MoS_2 and $\text{MoS}_2\text{@C}$ all present average coulombic efficiencies of $\sim 99\%$, further indicating their highly stable structures during the lithiation-delithiation processes. Furthermore, the long-term cycling performances of MoS_2 , $\text{MoS}_2\text{@C-400}$, $\text{MoS}_2\text{@C-500}$, and $\text{MoS}_2\text{@C-600}$ at the higher C-rate of 1C are also compared in Fig. 5e and S7.† As can be seen, $\text{MoS}_2\text{@C-600}$ delivered a higher discharge capacity of 858.2 mA h g^{-1} compared with the other three samples (Fig. S7†). After 150 cycles, $\text{MoS}_2\text{@C-500}$ maintained higher

Fig. 5 (a) CV curves of $\text{MoS}_2\text{@C-600}$ for the first 3 cycles at 0.2 mV s^{-1} ; (b) discharge-charge profiles at 0.1C (assume $1\text{C} = 0.5 \text{ A g}^{-1}$) of MoS_2 , $\text{MoS}_2\text{@C-400}$, $\text{MoS}_2\text{@C-500}$, and $\text{MoS}_2\text{@C-600}$; (c) discharge-charge profiles of $\text{MoS}_2\text{@C-600}$ at various C-rates from 0.1 – 10C ; (d) rate capability measurements of MoS_2 , $\text{MoS}_2\text{@C-400}$, $\text{MoS}_2\text{@C-500}$, and $\text{MoS}_2\text{@C-600}$; and (e) long-term cycling performance for 150 cycles of MoS_2 , $\text{MoS}_2\text{@C-400}$, $\text{MoS}_2\text{@C-500}$, and $\text{MoS}_2\text{@C-600}$.

Table 1 The detailed rate capability numerical results of MoS_2 , $\text{MoS}_2\text{@C-400}$, $\text{MoS}_2\text{@C-500}$, and $\text{MoS}_2\text{@C-600}$ when the C rate is increased from 0.2 to 10C and changes back to 0.1C

	0.2C	0.5C	1C	2C	5C	10C	0.1C
MoS_2	850.9	659.9	537.5	270.1	99.6	51.0	910.5
$\text{MoS}_2\text{@C-400}$	546.7	344.2	221.1	140.9	69.4	67.3	642.6
$\text{MoS}_2\text{@C-500}$	892.5	737.1	679.1	482.6	353.9	185.3	988.4
$\text{MoS}_2\text{@C-600}$	958.6	792.5	657.6	504.0	363.3	171.5	1024.9

initial capacity retention of 58.5% compared with $\text{MoS}_2\text{@C-600}$ (48.3%) over the 150 cycles, although $\text{MoS}_2\text{@C-600}$ delivered a higher capacity than $\text{MoS}_2\text{@C-500}$ in the initial cycles. The higher initial capacity retention at 1C indicates the excellent anode performance of $\text{MoS}_2\text{@C-500}$ at higher C-rate. This is mainly associated with the moderate degree of crystallization of the carbon film of $\text{MoS}_2\text{@C-500}$, which could provide good mechanical properties during the repeated discharge-charge cycles at higher C-rates, leading to the enhanced cycling stability.

To investigate the kinetics of MoS_2 and $\text{MoS}_2\text{@C}$ nanobowls, electrochemical impedance spectra (EIS) were conducted on the cells before cycling, after rate capability measurements, and

after long-term cycling measurements at 0.2C , over the frequency range from 1 MHz to 0.05 Hz . As shown in Fig. 6a–c, all the spectra include a depressed semicircle in the high- and medium-frequency regions, which could be assigned to the resistance associated with lithium-ion diffusion through the solid electrolyte interphase (SEI) film (R_s) and the charge transfer resistance (R_{ct}), respectively, and a clear $\sim 45^\circ$ inclined line in the low-frequency region, which could be considered to be Warburg impedance (W).²⁵ The R_{ct} is a key indicator for the kinetics of the electrode material. The R_{ct} was calculated by using the equivalent circuit model shown in the inset of Fig. 6a. The fabricated model also includes electrolyte resistance (R_e), a constant phase element (CPE-1), and a non-ideal constant phase element (CPE-2). Compared with the fresh cells before cycling (Fig. 6a), all the corresponding cells after rate measurements (Fig. 6b) or long-term cycling measurements (Fig. 6c) at 0.2C apparently show decreased R_{ct} of the electrode materials. This is mainly due to the electrode-electrolyte activation after deep discharge-charge cycles. As estimated from the fabricated model (inset of Fig. 6a), the relatively low R_{ct} (less than 100Ω) of the electrodes after rate capability measurements and long-term cycling measurements further indicate the excellent structural and chemical stability of the electrode

Fig. 6 Electrochemical impedance spectra (EIS) of MoS_2 , $\text{MoS}_2\text{@C-400}$, $\text{MoS}_2\text{@C-500}$, and $\text{MoS}_2\text{@C-600}$: (a) before cycling, (b) after rate capability measurements (shown in Fig. 3d) and (c) after long-term cycling measurements (shown in Fig. 3e) at 0.2C. Inset of (a): equivalent circuit model.

materials, facilitating ions fast transportation. The R_{ct} values of MoS_2 and $\text{MoS}_2\text{@C}$ before and after cycling increase in the order of $\text{MoS}_2\text{@C-600} < \text{MoS}_2\text{@C-500} < \text{MoS}_2\text{@C-400} < \text{MoS}_2$ (before rate measurements) and $\text{MoS}_2\text{@C-500} < \text{MoS}_2\text{@C-600} < \text{MoS}_2\text{@C-400} < \text{MoS}_2$ (after rate measurements), indicating highest kinetics of $\text{MoS}_2\text{@C-600}$ or $\text{MoS}_2\text{@C-600}$ among the series electrodes. These results are almost consistent with their electrochemical performance.

4. Conclusion

In summary, we have successfully fabricated the MoS_2 and $\text{MoS}_2\text{@C}$ composites with high uniformity and a well-defined nanobowl structure through a facial solvothermal method, followed by an annealing process. Compared to MoS_2 , the $\text{MoS}_2\text{@C}$ presented the excellent electrochemical performance for LIBs. The $\text{MoS}_2\text{@C-500}$ maintained a high reversible capacity of 846 mA h g^{-1} at 0.2C over 150 cycles, corresponding to an initial capacity retention of 78.4%. The excellent electrochemical performance of $\text{MoS}_2\text{@C-500}$ nanobowls is attributed to their unique nanobowl structure. The nanobowl structure provides large accessible surface areas and pore volumes for easy electrolyte penetration and rapid Li^+ diffusion, as well as the accommodation of volume variation during the repeated charge-discharge cycles, thus leading to enhanced capacity and rate capability. The $\text{MoS}_2\text{@C}$ nanobowls are expected to be an ideal anode material for high-energy LIBs in future.

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