

Spraying Coagulation-Assisted Hydrothermal Synthesis of MoS₂/Carbon/Graphene Composite Microspheres for Lithium-Ion Battery Applications

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Composite microspheres consisting of molybdenum disulfide, amorphous carbon, and reduced graphene oxide (named MoS₂-AC-RGO) were prepared by using a hydrothermal approach combined with the spraying coagulation process and calcinations step. Intercalation compound cellulose—MoS₂ was obtained after the spraying coagulation-assisted hydrothermal treatment, which then converts to MoS₂-AC-RGO after calcination. Graphene oxide and cellulose were utilized as the precursors of RGO and AC, respectively. Thiourea was adopted as both the species for cellulose dissolution and the sulfur precursor for MoS₂. The suspension of GO and sodium molybdate also played the role of the coagulation bath. The influence of cellulose on the structure, morphology, and electro-

1. Introduction

In recent years, with the emergence of Electric Vehicles (EV) and other portable electronic devices, there is a growing demand for clear, sustainable energy.^[1,2,3] Therefore, the research of a new generation of energy storage materials seems to be extremely urgent. Lithium ion batteries (LIBs) have drawn widespread attention due to its unique advantages such as high energy density, long cycle life, low self-discharge, environmentally friendly, no memory effect, etc.^[4,5,6] In order to further improve the performance of the current LIBs, lots of efforts

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chemical performance of the resultant MoS_2 -AC-RGO microspheres was investigated based on XRD, SEM, TEM, Raman spectra, TGA, and N₂ adsorption–desorption technique as well as electrochemical measurements. The composite microspheres show superior electrochemical properties as anode materials for lithium-ion batteries and exhibit a high reversible capacity of 910 mAhg⁻¹ at a current density of 200 mAg⁻¹, excellent rate capability, and superior cyclic stability with a capacity of 86% after 70 cycles. The roles of the graphene and the cellulose in improving the electrochemical properties of the MoS₂-AC-RGO composites are discussed based on the morphology, structure, phase, and electrochemical performance studies.

have been made to develop higher performance of electrode materials.

Molybdenum disulfide (MoS₂) is one of the typical layered transition-metal dichalcogenides (TMDS).^[7] As an analogue of graphene, MoS₂ exhibits unique chemical properties due to its layered structure: a graphite-like structure in which the Mo hexagonal layers are sandwiched by two S layers, and the interior of each layer is combined by strong covalent bonds (Mo-S) while the adjacent layers are linked together by weak van der Waals force.^[8] Because of the weak interlayer interaction, lithium ions can easily intercalated/extracted through MoS₂ layer without any apparent volume change.^[10,11] The theoretical specific capacity of MoS_2 (~670 mAh/g) is much higher than the commercial graphite anode (372 mAh/g) make them to be the promising alternative anode for LIB.^[1,12] However, the pure MoS₂ often suffer a lot from poor cycling stability and inferior rate capability because of its inherent low electronic conductivity and large volume change during constantly lithiation/delithiation process.^[13, 14, 15] In order to overcome these defects and further improve the electrode performance of MoS₂, fabrication of MoS₂/graphene composites is an efficient strategy.^[12, 16, 17, 18, 19] Graphene has high specific surface area and superior chemical stability and it can effective improve electron conductibility of MoS₂ and electron transfer for the composite electrode reaction.^[20,21] At the same time, graphene and MoS₂ can easily combine with each other because of their similar structure. In the previous researches, the emphasis of study has been played on either theoretical basis or the preparation and application of 2D structures.^[22, 23, 24, 25] Compared to 2D structure, 3D hierarchical structures possess more higher



surface area and improved reaction activity, and the 3D architectures can effectively alleviate the restacking of MoS_2 layers. $^{[16,26]}$

In this work, we report on a spraying coagulation process assisted hydrothermal approach to the preparation of flowerlike hierarchical structures of MoS₂ on amorphous carbon (AC)/ reduced graphene oxide (RGO) substrates (labeled as MoS₂-AC-RGO). As intermediate, intercalation of cellulose into MoS₂ has been obtained for the first time, which then is converted into the MoS₂-AC-RGO composites after calcinations. The novelty of this approach lies also in the two aspects: (1) natural cellulose is chosen as the precursor for amorphous carbon and thiourea is used as the active component for cellulose dissolution and also sulfur precursor for MoS_{2} ; (2) the suspension containing GO and sodium molybdate was exploited as coagulating bath for cellulose and also raw materials for the final products. In comparison with the traditional hydrothermal method, the reported approach can result composite microspheres with more unique properties such as uniform morphologies, improved electrochemical performance as an electrode material for LIBs and so on.

2. Results and Discussion

2.1. XRD

The crystallographic information and composition of the asprepared CL-MoS₂/RGO-X (X=0.05, 0.1 and 0.2) composites and pristine MoS₂/RGO composite obtained by the sprayingcoagulation-assisted solvothermal process have been investigated (see Figure S1). Interestingly, the XRD patterns of the CL-MoS₂/RGO-X show two low-angle diffraction peaks at 2 theta of 9 and 17°, respectively, which are completely different from that of typical MoS₂. Such a kind of XRD pattern has been ascribed to a characteristic of intercalation compounds of MoS₂.^[27] Obviously, the intensity of the low angle diffraction peaks increase with the increasing of cellulose content in the raw material. While, the pristine MoS₂/RGO composite shows an extra weak peak at 2 theta of 13°, which can be attributed to the (002) peak of pristine MoS₂. With the presence of cellulose, the peak at 2 theta of 13° disappears, meanwhile the peaks at 2 theta of 9 and 17° turn to obvious. Such a result points out the role of cellulose in the formation of the intercalation compound. The intense peak located at around 9° can be designated as the (002) plane of intercalation compound of MoS₂. In comparison with the pristine MoS₂ crystals, the (002) peak of the intercalation compound shifts to the low-angle region, demonstrating the expanding of the spacing between the MoS₂ layers (see Figure 1). A layer spacing of about 0.98 nm can then be calculated based on this peak. The formation mechanism of the cellulose-MoS₂ intercalation compound can be explained as due to the coordinating of thiourea with the cellulose chains during their dissolution, which then induces the encapsulation of cellulose between the MoS₂ layers during the hydrothermal growth process. A more detailed study on

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Figure 1. XRD patterns of the CL–MoS $_2$ /RGO-0.2 (A) and MoS $_2$ -AC-RGO-0.2 (B) samples.

the formation mechanism of the intercalation compounds and their application are still underway in our group.

The XRD patterns of these MoS₂-AC-RGO–X (X = 0.05, 0.1 and 0.2) composites and pristine MoS₂-RGO composite derived by calcining the corresponding CL–MoS₂/RGO–X precursors at 750 °C for 3 h are depicted in Figure S2. The four composites possess similar diffraction profile, and all the diffraction peaks showed in the patterns are consistent with hexagonal MoS₂ (JCPDS 37–1492), in which the diffraction peaks at 13.8, 33, 39 and 59.2° can be indexed to the (002), (100), (103) and (110) planes, respectively, of hexagonal MoS₂, indicating the intercalation compounds are decomposed and turned into pristine MoS₂ after calcinations.^[28] The prominent peak at around 13.8° corresponds to a spacing of 0.64 nm, demonstrating the existence of a well-stacked layered structure.^[29,30]

2.2. SEM and TEM Measurements

Figure 2 depicts the SEM images of the CL-MoS₂/RGO-X series composite microspheres consisting of MoS₂, RGO and cellulose



Figure 2. SEM images of pristine MoS $_2/RGO$ (A), CL–MoS $_2/RGO-0.05$ (B), CL–MoS $_2/RGO-0.1$ (C), and CL–MoS $_2/RGO-0.2$ (D).

with different ratios. It can be seen that the composite microspheres possess similar hierarchical flower-like structures with diameters in the range of 0.5–1 μ m. We can also see that with the addition of cellulose the resultant flower-like composite microspheres turn to uniform and fluffy. The influence of cellulose on the morphology of the resulted CL–MoS₂/RGO–X



composite spheres can be attributed to the sticky property of cellulose, which may tune the growth of the MoS_2 petals and induce the assembly of them.

The SEM images of MoS_2 -RGO and MoS_2 -AC-RGO–X nanoflowers derived from the MoS_2/RGO and $CL-MoS_2$ -RGO composites, respectively, by calcination process are presented in Figure 3. It can be seen that the calcined samples kept similar



Figure 3. SEM images of MoS_2 -RGO (A, a), MoS_2 -AC-RGO-0.05 (B, b), MoS_2 -AC-RGO-0.1 (C, c), and MoS_2 -AC-RGO-0.2 (D, d) with different magnifications.

can shorten the electrolyte access, lithium ion diffusion and insertion/extraction channels and alleviate the volume effect during the charge-discharge cycling.^[16,31,32] Figure 3D and Figure 3d reveal that when the addition amount of cellulose increase to 0.2 g, the composite spheres change to irregular and some dislocated sheets can be observed on the surface of the microspheres. From the high magnification image of Figure 3c we can see clearly that the distance between the adjoined sheets enlarged obviously.

To understand deeply the formation mechanism of the flower-like microspheres and the function of cellulose in the shape direction, SEM images of the intermediate solid formed during the spraying/coagulating process have been investigated. Images A and B of Figure 4 show the solids obtained



Figure 4. SEM images of the intermediate solid formed during the ultrasonic spray process.

morphologies as the corresponding MoS₂/RGO and CL-MoS₂/ RGO-X composites. Picture A shows the low magnification image of MoS₂-RGO composites, from the image one can see that the composites own spherical morphology on the whole but with some individual GO anchored on the surface of the microspheres. From the high magnification image (Picture a) it can be clearly observed further that some individual GO sheets were exposed outside of the spheres, and the MoS₂ sheets which composing of the flower-like structures were stacked closely together. Images B and b display that when the addition amount of cellulose reaches to 0.05 g, the resultant composite microspheres becomes more uniform and there are no individual GO outside of the composite spheres. However, it can also be seen from image b of Figure 3 that the nanosheets are still slightly stacked together. When the addition amount of cellulose is altered to 0.1 g, the morphology of the microspheres becomes more homogeneous and fluffier (Figure 3C and Figure 3c). The low magnification image of AC-MoS₂-RGO-0.1 composites (Figure 3C) demonstrates clearly the composites possess uniform spherical morphology with diameters in the range of 300-500 nm. No individual MoS₂ or graphene sheets could be observed from the SEM images, indicating that the MoS₂ nanosheets are anchored homogenously on the RGO substrates. EDS element mapping measurements have been carried out using the energy dispersive spectrometer attached on the SEM to recognize the RGO (see Figure S3). From the element mapping one can see the intense carbon signal, however due to the homogenous dispersion of amorphous carbon make it difficult to distinguish the C signal of RGO from AC. The close up view shown in Figure 3c reveal that the MoS₂-AC-RGO-0.1 composite possesses the hierarchical flowerlike structures, and each of the nanoflowers is built up with many curled ultrathin nanoplates. This special structure can provide abundant void space between the adjacent nanosheets which

after the spraying/coagulating process and were then dried by normal evaporation method and freezing dry method, respectively. From the images it can be seen that the solid derived by spraying/coagulating process consists of microspheres with size of a few hundred nanometers. The high magnification images as depicted in Figure 4C and Figure 4D reveal the cellulose microspheres are anchored on the surface of GO uniformly, and the curled GO layers are wrapped with numerous cellulose microspheres. Such a structure can be expected after the spraying/coagulating processes.

The cellulose droplets derived from the ultrasonic spraying process coagulated upon the contact with the coagulation bath containing sodium molybdate and graphene sheets, and some of the cellulose microspheres then anchored on the surface of the graphene sheets in-situ. Due to the coordinating effect between cellulose chains and thiourea molecules, the cellulose microspheres formed by the spraying/coagulating processes can then act as nuclear centers during the subsequent hydrothermal process, in which the thiourea hydrolyzed and reacted with sodium molybdate, generating molybdenum disulfide decorated RGO composite with nanoflower morphology (a detailed formation mechanism, please refer to Scheme 1).

TEM and HRTEM characterization was adopted to observe the microstructure of MoS_2 -AC-RGO-0.1 composites as shown in Figure 5. Picture a of Figure 5 shows a low-magnification TEM image of the sample, and it can be seen that some of the MoS_2 nanosheets are stacked together and curled due to their ultrathin character. The magnified TEM image demonstrates the uniform distribution of the MoS_2 sheets (Figure 5b). However, due to the morphology similarity between MoS_2 sheets and RGO layers, it is difficult to recognize RGO in the composite





Scheme 1. Illustration of the formation process of the MoS₂-AC-RGO composite microspheres.



Figure 5. TEM images of MoS₂-AC-RGO-0.1 under different magnifications.

spheres. As shown in Figure 5c, the high-magnification TEM image distinctly displays the well-stacked layered structures of the MoS_2 petals. The MoS_2 nanosheets consisting of about 9 staked layers with a lattice spacing between two adjacent lattice planes of about 0.64 nm have been observed. The observed spacing is slightly larger than that of MoS_2 bulk crystals (0.62 nm), and such an enlarged spacing will facilitate the insertion and desertion of Li-ion and improve the electrochemical performance of the MoS_2 -AC-RGO-0.1 composite.^[33,34,35]

2.3. Raman Spectra

Raman spectra of the MoS_2 -AC-RGO-0.1 composite were also investigated to confirm the carbon material and the MoS_2 structure (Figure 6). The spectrum exhibits obviously two



Figure 6. Raman spectra of the MoS₂-AC-RGO-0.1 composite.

prominent bands of MoS₂ species located at 378 and 406 cm⁻¹, which correspond to the E_{2q} and A_{1q} modes of hexagonal phase of MoS_{2} , respectively. The E_{2q} mode arises from the in-plane displacement of Mo and S atoms, whereas the $A_{1 \alpha} \mbox{ mode}$ is associated with the out-of-plane symmetric displacements of two S atoms along the c-axis.^[36, 37, 38, 39] In addition to the distinct peaks for MoS₂ species, the other two remarkable peaks around at the bands of 1349 and 1590 cm⁻¹ correspond to the D and G bands of carbon, respectively. It is well-known that the D band is indicative of the vibrations of carbon atoms with dangling bonds for the in-plane terminations of disordered graphite, while the G band is ascribed to the vibration of ordered sp² carbon atoms in a 2D hexagonal lattice. And the intensity ratio of band D and G (I_D/I_G) is a critical parameter to estimate the degree of graphitization of carbon materials.^[40] As shown in Figure 6, the calculated value of I_D/I_G for MoS₂-AC-RGO-0.1 sample is 1.2, which is slightly higher than the I_D/I_G of GO (0.81). The fact may be caused by the reduction of GO after the hydrothermal reduction process and the presence of amorphous carbon which was introduced by carbonization of the cellulose in the composite during the hydrothermal process and the following thermal treatment.

2.4. Thermal Analysis

To further determine the amount of MoS_2 in the two samples, the composites were also conducted by thermogravimetric analysis (TGA). Figure 7 shows the TGA profiles of MoS_2 -AC-



Figure 7. TGA profiles of the MoS₂-AC-RGO-0.1 and MoS₂-RGO composites.

RGO-0.1 and MoS₂-RGO composites, respectively. It can be seen that both the samples show a dramatic weight loss between 370 and 450 °C, which can be attributed to the oxidation of MoS₂, graphene and amorphous carbon. Based on the fact that the final product of MoO₃ after complete oxidation, then the mass fraction of MoS₂ in the MoS₂-AC-RGO-0.1 and MoS₂-RGO composites can be calculated to be about 85% and 91%, respectively.^[41]



2.5. Nitrogen Adsorption-Desorption Measurements

N₂ adsorption-desorption measurements were employed to investigate the specific surface area and the porosity of the MoS₂-AC-RGO-0.1 and the MoS₂-RGO composites. Figure 8 shows the nitrogen adsorption-desorption isotherms and the corresponding pore size distribution of these samples. As can be seen that both the isotherms of the MoS₂-AC-RGO-0.1 composite and the MoS₂-RGO composite show obvious hysteresis loops and capillary condensation steps. In comparison with the MoS₂-AC-RGO-0.1 composite, the MoS₂-RGO composite shows a narrow and irregular hysteresis loop at the high p/p₀ region, indicating a reduction of porosity.^[42] The BET surface areas for them are of 50.9 and 29.85 m²g⁻¹, respectively. The large specific surface area of the MoS₂-AC-RGO-0.1 composite can be contributed to the well integration of RGO sheets with the MoS₂ nanosheets under the adhesion of cellulose. The presence of cellulose can be beneficial for the mixture of the precursor, which then can result in more uniform nanoflower products with a high specific surface area. The average pore sizes of MoS₂-AC-RGO-0.1 composite and MoS₂-RGO composite were calculated to be 41 and 39 nm, respectively. The pores in the composites could enhance rapid Li⁺ transport during the lithium ion insertion/extraction and alleviate the volume effect of MoS_2 in the charge/discharge process, which would improve the electrochemical performance to a great extent.

2.6. Electrochemical Properties

To investigate the electrochemical properties of the MoS₂-AC-RGO-0.1 composite and MoS₂-RGO composite, the cyclic voltammetry (CV) were conducted over the potential range from 0.01 to 3.0 V at a scan rate of 0.1 mVs⁻¹. As shown in Figure 9a, in the first cycle the two prominent peaks at 0.62 and 1.09 V, respectively, are observed for the cathodic process. The first reduction peak at 1.09 V can be ascribed to the lithium insertion into the interlayer of MoS₂ to form Li_xMoS₂ and the phase transition of Li_xMoS₂ from 2H to 1T.^[8,43,44] The second reduction peak at 0.62 V is indicative of the conversion reaction of Li_vMoS₂ to Li₂S and metallic Mo, accompanying the formation of solid electrolyte interphase (SEI) film due to the degradation of electrolyte from electrochemically driven.^[8,40-45] The whole reaction during this process can be considered as $MoS_2 + 4Li^+$ $+4e^{-} \rightarrow Mo + Li_2S^{[46,47]}$ In the subsequent cathodic sweeps, two remarkable reduction peaks and a weak peak are emerging at 1.87, 1.01 and 0.26 V, respectively, which can be associated with the following three reactions respectively: $2Li^+ + S + 2e^- \rightarrow Li_2S$, $MoS_2 + xLi^+ + xe^- \rightarrow Li_x MoS_2$, and $Li_xMoS_2 + (4-x)Li^+ + (4-x)e^- \rightarrow$



Figure 8. The nitrogen adsorption-desorption isotherms and BJH pore-size distribution curves of the MoS₂-AC-RGO-0.1 composite (a, c) and MoS₂-RGO composite (c, d).



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Figure 9. Cyclic voltammograms of the MoS₂-AC-RGO-0.1 composite (a) and MoS₂- RGO composite (b) electrodes at a scan rate of 0.1 mVs⁻¹.

 $Mo + Li_2S$.^[8,40,41] During the anodic sweeps, two peaks approximately located at 1.78 and 2.29 V can be observed. The inconspicuous peak at 1.78 V corresponds to the formation of MoO_2 by the partial oxidation of Mo, and the following prominent peak at 2.29 V may be due to the oxidation of Li_2S to form S.^[48,49] Figure 9b shows the cyclic voltammetry profiles of MoS_2 -RGO composite. In comparison with those of MoS_2 -AC-RGO-0.1, the CV profiles of MoS_2 -RGO show a little bit irregular rectangle shape (see the low voltage side). Anyway, they are in good accordance with their charge/discharge voltage profiles.

Figure 10a shows the initial charge/discharge voltage profiles of the MoS_2 -AC-RGO-X (X = 0.05, 0.1 and 0.2) composites and MoS_2 -RGO composite electrodes at a current density of 200 mAg⁻¹ in the voltage range of 0.005–3 V, which are consistent with the aforementioned CV study. For instance, for the MoS_2 -AC-RGO-0.1 composite electrode, two plateaus at approximately 1.1 and 0.7 V are observed, which correspond to the reduction peak at 1.09 and 0.62 V in the first CV curves, respectively. The sloping curve of the MoS_2 -AC-RGO-0.1 composite below 0.7 V could be attributed to the formation of the solid electrolyte interface (SEI) film and the reversible reaction

between Mo and Li_2S .^[7,50,51] As shown in Figure 10b, in the subsequent discharge curves, the plateaus showed in the first curve disappears but three new plateaus emerged respectively at around 2.0, 1.1 and 0.4 V, which is in agreement with the lithiation processes. In the charge curves the plateau located at about 2.2 V can be clearly identified, which might be attributed to the oxidation of Li_2S .^[7,45,52]

Figure 11 shows the cycle performance of these four composite electrodes at the current density of 200 mAg^{-1} . It can be found that MoS₂-AC-RGO-0.1 composite is superior to other three composite cathodes in both the discharge capacity and cycling stability. The initial discharge capacity of the MoS₂-AC-RGO-0.1 composite is estimated to be 1051 mAhg^{-1} and the corresponding charge capacity is 862 mAhg⁻¹ with columbic efficiency of 82%. Especially, both the MoS₂-AC-RGO-0.1 sample and the MoS₂-RGO sample reveal remarkable cycling stability with high reversible specific capacities of 910 and 743 mAhg⁻¹ after 70 cycles, respectively, with 86% and 99% capacity retention. After 120 cycles, the reversible capacity of MoS₂-RGO sample fade quickly and shows a low capacity of only 468 mAhg⁻¹ with a 62% capacity retention merely. The



Figure 10. The initial charge–discharge voltage profiles of the four different composite electrodes (a) and the 1st, 2nd, 3rd, and 70th cycle charge–discharge curves of the MoS_2 -AC-RGO-0.1 composite electrode (b) at a current density of 200 mAg⁻¹.



Figure 11. Cyclic performance of the MoS₂-AC-RGO–X (X = 0.05, 0.1 and 0.2) composites and MoS₂-RGO composite at a current density of 200 mA g^{-1} .

reversible capacities of MoS2-AC-RGO-0.05 and MoS2-AC-RGO-0.2 composite electrodes were declined rapidly also even after 50 cycles. In comparison with the MoS₂-RGO composite, the MoS₂-AC-RGO-0.1 composite electrode exhibit much higher reversible capacity and dramatically improved cyclic stability. After 120 cycles, MoS₂-AC-RGO-0.1 composite still remains the reversible specific capacity as high as 881 mAhg⁻¹ with a corresponding capacity retention of 84%. Interestingly, it can keep a stable reversible specific capacity as high as 780 mAhg⁻¹ at a current density of 500 mA g^{-1} for 70 cycles (see Figure S4). The high reversible capacity and excellent cyclic stability of the MoS₂-AC-RGO-0.1 sample may be due to the presence of amorphous carbon which acts as a medium for the interaction of MoS₂ and RGO, resulting in a more homogeneous hybrid with compact contact and much larger specific surface, which then can provide extensive contact area between the electrode material and electrolyte and then facilitate the lithium ion insertion/extraction process and alleviate the volume change during cycling.

In order to investigate the high-rate capability, a multiplecurrent galvanostatic testing as shown in Figure 12 has been



Figure 12. Rate capability of the MoS₂-AC-RGO–X (X = 0.05, 0.1 and 0.2) composites and MoS₂-RGO composite at different current densities.

conducted. The discharge capacities of the four composite electrodes decrease to different degrees as the rate increased from 100 to 2000 mAg⁻¹. It is clear that the capacity of the MoS_2 -AC-RGO-0.05 and MoS_2 -AC-RGO-0.2 composite electrodes fade rapidly and cannot recover to the initial levels after high rate cycling even at low discharge currents. After 10 cycles, the MoS_2 -AC-RGO-0.1 composite and the MoS_2 -RGO composite deliver reversible capacities of 910 and 585 mA h g⁻¹, respectively, at a current density of 100 mA g⁻¹.

When the current density increase, the decrease of capacity is not significantly, and the reversible capacities were of about 854 and 591 mAhg⁻¹, respectively, at 200 mAg⁻¹, 776 and 561 mAhg⁻¹ at 500 mAg⁻¹, 718 and 545 mAhg⁻¹ at 1000 mAg⁻¹, and 645 and 518 mAhg⁻¹ at 2000 mAg⁻¹ are delivered by these two composite electrodes. The reversible capacities of both the MoS₂-AC-RGO-0.1 sample and the MoS₂-RGO sample return to their original value as the current drops back to 100 mAg⁻¹, demonstrating the prominent reversibility of the composites.

To further illustrate the superior electrochemical performance of the MoS₂-AC-RGO-0.1 composite electrode, electrochemical impedance spectroscopy (EIS) is measured in the frequency range from 100 kHz to 0.01 Hz before and after the galvanostatic cycles. Figure 13 shows the Nyquist plots and the corresponding equivalent circuit. It can be clearly seen in Figure 13 that the two curves both contain two semicircles at high and medium frequencies, which could be assigned to the resistance $R_{\rm f}$ and CPE_1 of the SEI film and the charge transfer resistance R_{ct} and CPE₂ of the electrode/electrolyte interface. A slope line at low frequencies can also be observed, which represents the Warburg impedance (Z_w) .^[18,53] As one can see from panels (a) and (b) of Figure 13 that the diameter of the semicircles for both the two composites are increased after 120 cycles than those before cycle. This might be due to the structure change of the composite spheres during the charge/ discharge progress. However, the diameters of semicircles for MoS₂-AC-RGO-0.1 composite electrode before and after the cycle are dramatically smaller than those of MoS₂-RGO composite, demonstrating a lower charge transfer resistance of the former one. It is believed that graphene and amorphous carbon existing in the system were responsible for the lower charge transfer resistance of the composite material. The synergy effect of the AC and RGO could effectively lower the contact resistance and charge transfer resistance of the composite electrode and thus give rise to enhanced electron transfer speed especially during the high-rate lithium insertion/ extraction process, leading to superior rate performance of the MoS₂-AC-RGO-0.1 composite.

3. Conclusions

MoS₂-AC-RGO composite anode materials with superior electrochemical performance have been prepared by a solvothermal method with the assistance of ultrasonic spraying technique using thiourea as both sulfur precursor and the solvent for cellulose. An interesting intermediate named intercalation





Figure 13. Nyquist plots of a) the MoS₂-AC-RGO-0.1 composite and b) the MoS₂-RGO composite tested in a frequency range of 0.01 Hz to 100 kHz. c) Equivalent circuit model corresponding to the Nyquist plots of the studied system.

compound of cellulose-MoS₂ has been obtained after the hydrothermal step. The intercalations then were converted into MoS_2 -AC-RGO composite after a calcinations process. Control experiments reveal that the MoS_2 -AC-RGO-0.1 composite exhibits better electrochemical performance, and a high capacity of 910 mA h g⁻¹ could be retained at a current density of 200 mA g⁻¹. The cellulose/graphene network in the composites plays an essential role in the formation of MoS_2 structures. The addition of cellulose can not only contribute to the homogeneous integration of RGO sheets with the MoS_2 nanosheets but also enhance the conductivity of the composite and thus lead to the outstanding electrochemical performance of the composites. It is believed that the methodology presented herein and the rationally designed structures can also be generalized to other practical applications.

Experimental Section

Materials

Cellulose with a viscosity-average molecular weight of 8.5×10^4 was obtained from Hailong Chemical Fibre Co., Sodium molybdate dehydrate, thiourea, sodium hydroxide, acetic acid and ethanol (Sinopharm Chemical Reagent Co., Ltd) were of AR grade and used as received without further purification. Graphene oxide powder, kindly provided by the sixth element (Changzhou) Ltd, was sonicated for 3 h before the application.

Synthesis of MoS₂-AC-RGO Composite Microspheres

Flower-like MoS₂-AC-RGO composite microspheres were prepared by a spraying coagulation assisted hydrothermal method combined with calcinations. In a typical preparation, sodium hydroxide (1.756 g) and thiourea (2.455 g) was dissolved in distilled water (20 ml), and then an amount of cellulose was added to the obtained solution under stirring. The suspension was stirred for 1 h and then transferred to fridge at -10 °C for 12 h, resulting in a homogenous thiourea aqueous solution of cellulose after melting. In parallel, Na₂MoO₄·2H₂O (1.89 g) and GO (0.25 g) were dispersed in 5 wt% acetic acid aqueous solution (60 ml) and then irradiated with a high power sonicator for 2 h. Subsequently, the cellulose thiourea aqueous solution was dispersed into the resulted Na₂ MoO₄/GO mixture with an ultrasonic sprayer under vigorous stirring. After stirring for 2 h, the mixture was transferred into a 150 ml Teflon-lined autoclave and heated up to 200 °C, and then maintained at this temperature for 12 h. After the autoclave was naturally cooled to room temperature, the resultant black precipitate was collected by centrifugation and washed thrice with distilled water and ethanol. The black products composing of cellulose-MoS₂/RGO was named as CL-MoS₂/RGO and were dried at 60°C for 12 h in air. CL-MoS₂/RGO composites prepared with different amounts of cellulose (0.05, 0.1 and 0.2 g) were designated as CL-MoS₂/RGO-X (where X=0.05, 0.1, and 0.2 respectively). Control sample synthesized without cellulose was denoted as pristine MoS₂/RGO composite. The obtained CL-MoS₂-RGO-X composites and pristine MoS₂/RGO composite were annealed at 750 °C for 3 h under a high purity nitrogen atmosphere. Samples denoted as MoS₂-AC-RGO-X composites (AC: abbreviation of amorphous carbon; where X = 0.05, 0.1, and 0.2 respectively.) and MoS₂/RGO composite, respectively, were derived after the calcinations. A schematic illustration of the formation process of the MoS₂-AC-RGO composite microspheres is depicted in scheme 1.



Characterization

The crystallographic information and composition of the products were investigated using a Rigaku Ultima IV X-ray diffractometer (XRD, Cu–K α radiation λ =0.15418 nm). Raman spectra were collected using a Renishaw inVia Plus Micro-Raman spectroscopy system equipped with a 50 mW DPSS laser at 532 nm. The specific surface areas were estimated with the Brunauer-Emmett-Teller (BET) method with N₂ adsorption data in the relative pressure range of $P/P_0 = 0.05 - 0.35$. The pore size distributions were calculated using the Barrett-Joyner-Halenda (BJH) model applied to the desorption branch of the N₂ isotherms obtained with a Quantachrome Autosorb-IQ-MP/XR surface area and pore analyzer. The thermogravimetric analysis was performed with a Mettler Toledo TGA-2 thermal gravimetric analyzer under an oxygen atmosphere with a heating rate of 10°Cmin⁻¹. The morphologies and the structures of the samples were examined by a JEOL JSM-7800F scanning electron microscope (SEM) and a JEOL JEM-2100 transmission electron microscope (TEM).

Electrochemical Testing

The working electrodes were fabricated by mixed the active material (MoS₂-AC-RGO or MoS₂-RGO composite), acetylene black (super-P) and polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidinone (NMP) (Aldrich) with a weight ratio of 80:10:10 and then grinding them to a homogeneous slurry. The slurry was coated onto Cu foils and dried at 110°C in a vacuum oven for 10 h to remove the solvent completely. The electrode sheet was pressed and punched into 10 mm diameter electrodes and then weighed. The accurate mass loading of active materials were controlled in the range of 1.45-1.65 mg \cdot cm⁻². 2016 coin-type cells were then assembled in an argon-filled glove box using Celgard 2400 film as separator and 1 mol L⁻¹ LiPF₆ in a mixture solution of ethylene carbonate (EC)/dimethyl carbonate (DMC) /ethylene methyl carbonate (EMC) (1:1:1 v/v/v) as the electrolyte. Lithium metal foil was used as the counter electrode. The galvanostatic chargedischarge tests were carried out on a LAND Cell Test System (2001 A, Wuhan, China) with a voltage range of 0.01-3 V at different current densities. Cyclic voltammetry (CV) tests in two electrode coin-type cells were performed between 1.5 V and 3 V at 0.1 mV s⁻¹ on a CHI760D electrochemical working station. The electrochemical impedance spectroscopy (EIS) tests were measured on a CHI760D electrochemical working station in a frequency range of 0.01 Hz to 100 kHz.

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Conflict of Interest

The authors declare no conflict of interest.

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