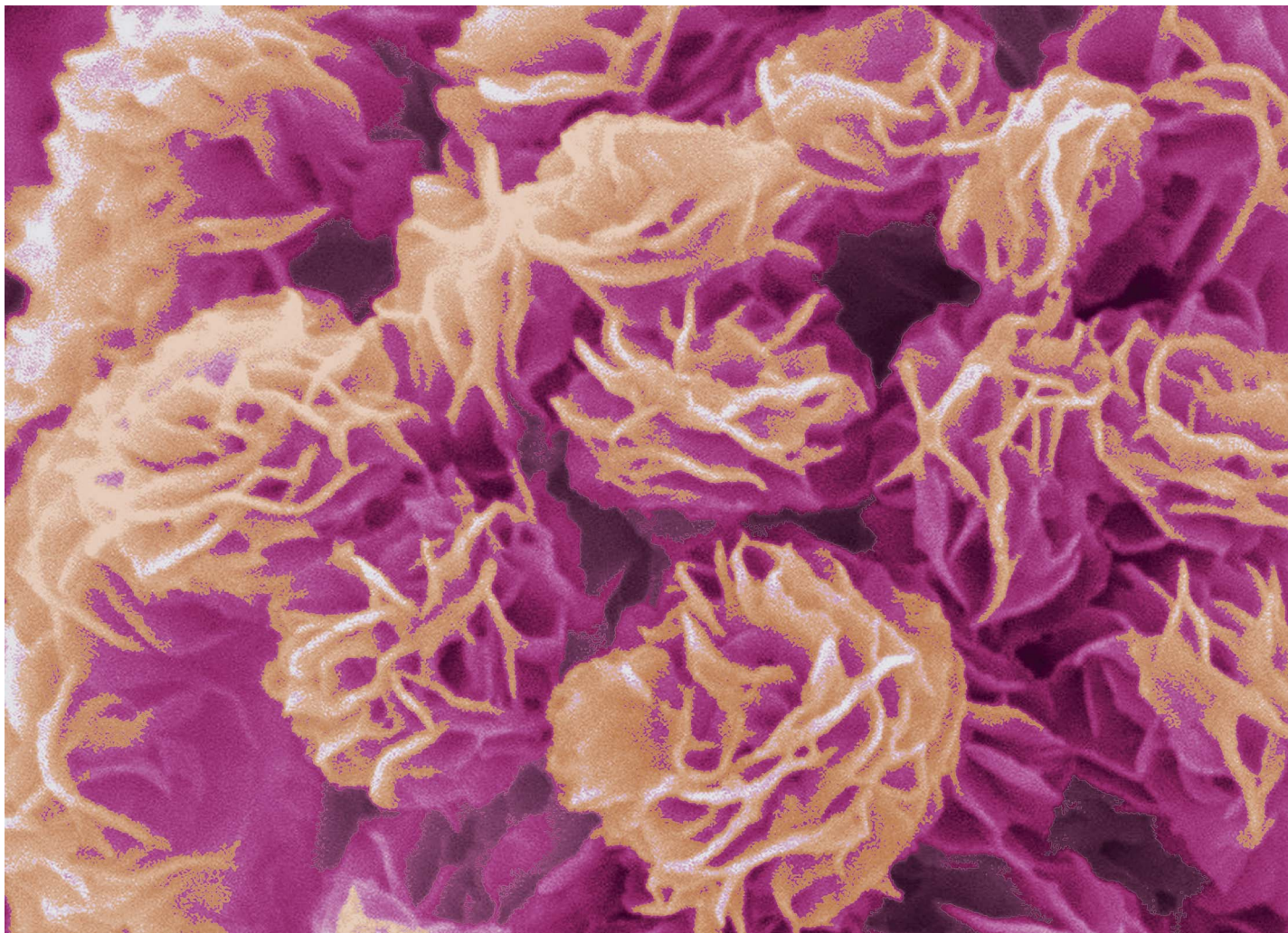


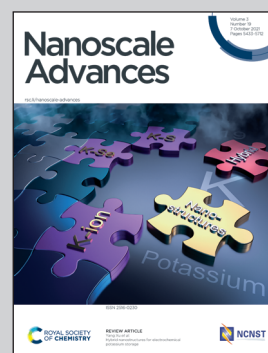


Showcasing research from Professor Jinyun Liu's laboratory, College of Chemistry and Materials Science, Anhui Normal University, Anhui, P.R. China.

A novel rose-with-thorn ternary MoS_2 @carbon@polyaniline nanocomposite as a rechargeable magnesium battery cathode displaying stable capacity and low-temperature performance

A novel rose-with-thorn ternary MoS_2 @carbon@polyaniline nanocomposite composed of carbon and polyaniline nanoneedles co-coated on MoS_2 is developed. The composite-based Mg battery displays a good capacity, and a recoverable rate-performance after repeated measurements. In addition, a stable capacity when cycling under a low temperature of $-5\text{ }^\circ\text{C}$ is also achieved, indicating a good potential for applications.

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A novel rose-with-thorn ternary MoS₂@carbon@polyaniline nanocomposite as a rechargeable magnesium battery cathode displaying stable capacity and low-temperature performance†

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Developing high-performance cathode materials for magnesium (Mg) batteries is of great significance. Here, a novel rose-with-thorn ternary MoS₂@C@polyaniline (PANI) nanocomposite composed of carbon and PANI nanoneedles co-coated on rose-like MoS₂ is developed. The conductive PANI needles on the surface of MoS₂ improve the conductivity, and the inner MoS₂ is wrapped by a carbon layer which is beneficial for the aniline coating. The MoS₂@C@PANI-based Mg battery cathode displays a good capacity of 114 mA h g⁻¹ after 100 cycles, and a recoverable rate-performance after repeated measurements. In addition, a stable capacity of 105 mA h g⁻¹ when cycled at a low temperature of -5 °C is also achieved, indicating good potential for applications.

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Introduction

Recently, magnesium (Mg) batteries have attracted much attention due to their outstanding advantages including no dendrite growth and stable performance.^{1–3} However, current Mg batteries still have some shortcomings, including slow ion transport, easy collapse of the structure, difficulty in deintercalation and insertion of Mg ions and the insufficient performance of Mg batteries in some special application conditions, such as different temperatures.^{4,5} In order to address these problems, a large number of studies have been conducted.^{6,7} In view of the low crystallinity of the cathode materials, even small changes in the preparation process will cause huge differences in the performance. Studies have been conducted to accelerate the extraction of Mg ions to promote the performance of batteries. For example, Zuo *et al.* used a spinel Mg(Mg_{0.5}V_{1.5})O₄ cathode to accelerate the Mg²⁺ ion extraction kinetics.⁸ The capacity was 102 mA h g⁻¹ over 100

cycles. Du *et al.* used a simple template-directed selenization reaction to construct thin-film-assembled hollow CuSe nanocubes at room temperature.⁹ Copper selenide Cu_{2-x}Se was synthesized by a solution method, and the copper ions in the sublattice based on Se could be reversibly replaced by Mg²⁺ ions.¹⁰ Because of the same face-centered cubic Se²⁻ sublattice, Cu_{2-x}Se and MgSe unit cell sizes are similar and the energy barrier is low, which improves the cycling stability. Based on the above research, it is found that multiple nanocomposites would improve the performance of the cathode, thereby improving the cycle capacity and stability.

In recent years, biomimetic technology has been introduced into the research of rechargeable batteries, which improves the capacity and cycle life. For example, Shen *et al.* developed a composite material with a cucumber-like structure,¹¹ which was characterized by flexibility and self-support. It buffered the volumetric change and improved the conductivity. Tao *et al.* used kapok fibers to synthesize fish-scale carbon nanosheets for lithium-sulfur batteries,¹² which have an excellent capacity retention rate of up to 95.4% after 90 cycles at 0.4 A g⁻¹. Zuo *et al.* synthesized a flower-like structure of V₂O₅@polyaniline (PANI), by insertion of aniline into the V₂O₅ interlayer,¹³ resulting in the composite having a larger gap between layers, thereby improving the battery performance. Inspired by the ultra-strong capillarity of wood's aligned hierarchical micro-channels, Miao *et al.* developed a nanofibrous organic cathode for sodium ion batteries, which displayed rapid ionic/electronic transport properties and ultrafast reaction kinetics.¹⁴ In addition, an agaric-like anode of porous carbon decorated with

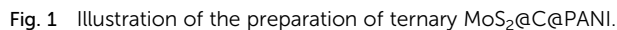
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‡ These authors contributed equally to this work.





Results and discussion

Fig. 3 (a) SEM and (b–e) elemental mapping images of MoS₂@C@PANI. Line-scan profiles are inserted in (a).

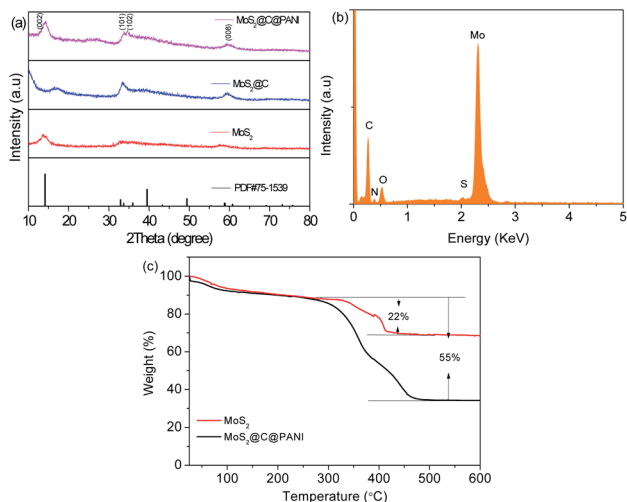


Fig. 4 (a) XRD patterns of MoS₂, MoS₂@C, and MoS₂@C@PANI. (b) EDS spectrum of MoS₂@C@PANI. (c) TGA curve of bare MoS₂ and MoS₂@C@PANI.

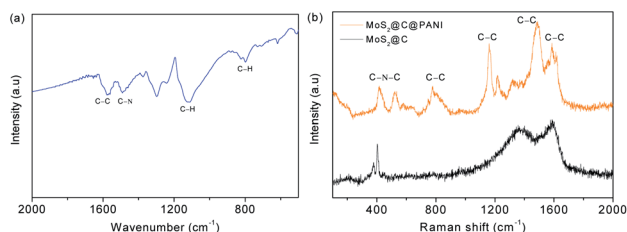


Fig. 5 (a) FTIR spectrum of MoS₂@C@PANI. (b) Raman spectra of bare MoS₂ and the MoS₂@C@PANI composite.

1365 and 1587 cm⁻¹ are assigned to the D-band and G-band of carbon, respectively. In MoS₂@C@PANI, the peaks at 1587, 1485, 1324, 1162 and 780 cm⁻¹ are from C-C.¹⁹ The peaks at 1384 and 1162 cm⁻¹ are ascribed to C-N and C-H, respectively, which verify PANI.²⁰ Fig. 6 shows the X-ray photoelectron spectroscopy (XPS) spectra. The survey spectrum in Fig. 6a verifies the composition. The Mo 3d spectrum is shown in Fig. 6b. There are two peaks at 228.8 and 231.7 eV which are attributed to Mo 3d_{3/2} and Mo 3d_{5/2}, respectively.²¹ A minor peak at 225.5 eV shows the presence of S 2s.²² In Fig. 6c, the peaks are indexed to S 2p_{3/2} and S 2p_{1/2}.²³ In Fig. 6d, the N 1s spectrum is deconvoluted into three peaks at 397.5, 398.5, and 400.5 eV.²⁴ The peaks at 284.0, 285.1, and 288.0 eV are assigned to C-C, C-OH, and C=O,²⁵ respectively, as shown in Fig. 6e.

Fig. 7a shows the charge–discharge curves of MoS₂@C@PANI cycled at 100 mA g⁻¹. As shown in Fig. 7b, when cycled at 100 mA g⁻¹, the capacity is 114 mA h g⁻¹ after 100 cycles. Moreover, the coulombic efficiency exceeds 99%. Compared to pure MoS₂, it shows a better cycling performance. It is noted that the PANI coating in the composite system also contributes to the capacity,²⁶ which improves the overall performance. When compared to some other cathodes, the developed MoS₂@C@PANI is also competitive, as shown in Table S1 (ESI[†]). Fig. 7c shows the CV profile of the MoS₂@C@PANI

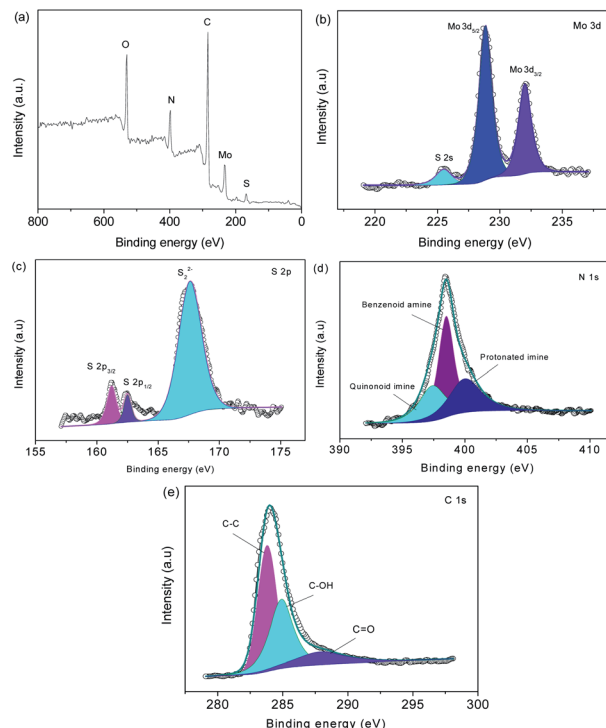


Fig. 6 (a) XPS survey spectrum, and (b) Mo 3d, (c) S 2p, (d) N 1s, and (e) C 2p spectra of MoS₂@C@PANI.

cathode. The anodic peaks around 0.6 to 1.2 and 1.9 V are ascribed to Mg²⁺ deintercalation, and the cathodic peaks at about 0.5, 1.25 and 1.75 V indicate the corresponding intercalation of Mg²⁺.²⁷ The rate-performance at 0.1, 0.3, 0.5, and 1 A g⁻¹ is displayed in Fig. 7d. It was repeatedly measured three times. The discharge capacity recovered to 143 mA h g⁻¹ once the rate returned to 0.1 A g⁻¹. The battery after the high current density impact can maintain the capacity without obvious decrease. Fig. 8 shows the capacity at a low temperature of

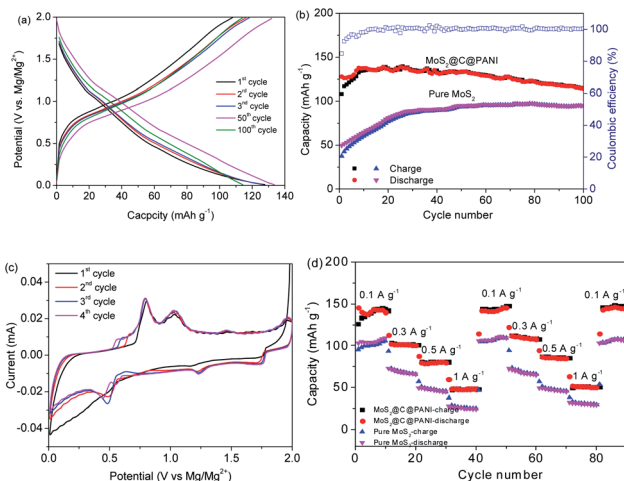


Fig. 7 (a) Charge–discharge curves of MoS₂@C@PANI at 0.1 A g⁻¹. (b) Capacities and coulombic efficiency. (c) CV curves cycled at 0.1 mA s⁻¹. (d) Rate-performance.



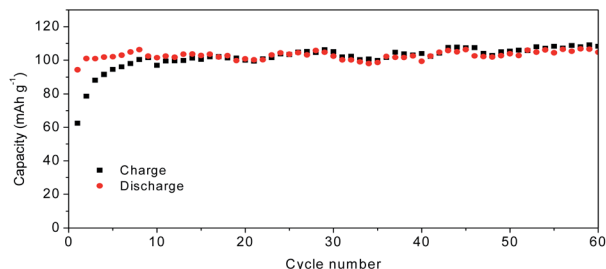


Fig. 8 Capacity of the MoS₂@C@PANI cathode cycled at 0.1 A g⁻¹ at -5 °C.

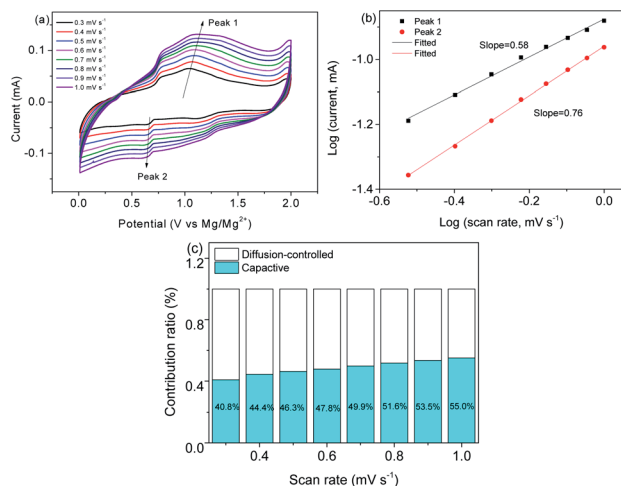


Fig. 9 (a) CV curves at different rates. (b) Log(v) to log(i) linear analysis. (c) Contribution ratios at different scan rates.

-5 °C. The initial Mg-storage capacity is relatively low, but it is stable. After cycling 60 times at 0.1 A g⁻¹, the capacity is 105 mA h g⁻¹. Furthermore, cycling at -10 °C (Fig. S1†, ESI†) shows a capacity of about 98 mA h g⁻¹, indicating potential for use under cold conditions. The decreased capacity is ascribed to the reduced activity of electrode materials and the reaction kinetics of ions and electrolyte.^{28–30}

Fig. 9a shows a series of CV curves which show that the peak position remains stable. Fig. 9b is obtained by fitting a qualitatively deduced charge storage equation $I(v) = av^b$,²⁶ where I stands for the maximum current.³¹ The b of peak 1 and peak 2 is 0.58 and 0.76, respectively, indicating that charging and discharging are mainly controlled by the capacitance. On the basis of $i = k_1v + k_2v^{1/2}$, where k_1v/i and $k_2v^{1/2}/i$ are the capacitive and

diffusion-controlled processes,³² respectively, the contribution ratios are calculated (Fig. 9c). When the scan rates increase, the capacitive process increases. Fig. 10a and b show the SEM images of post-cycled MoS₂@C@PANI. This indicates that the composite remains robust after cycling 100 times. Fig. 10c shows the TEM image after 100 cycles, which further confirms that the structure remains stable after the charge-discharge cycles. The stability would be useful for constructing some dual-ion batteries. For example, a series of Ni/Zn-CoS₂@C and ternary metal oxide-based Mg-Li ion batteries displayed good stability.^{33,34}

Conclusions

In summary, we present a novel rose-with-thorn ternary MoS₂@C@PANI nanocomposite by coating carbon and PANI nanoneedles on rose-like MoS₂. The conductive PANI would enhance the conductivity of the system; MoS₂ is coated and protected by the coating, which enhances the electrochemical properties. The MoS₂@C@PANI-based Mg battery cathode shows a stable capacity of 114 mA h g⁻¹ when cycled 100 times. Moreover, the cathode shows a recoverable rate-performance. At -5 °C, a capacity of 105 mA h g⁻¹ is maintained, which indicates potential for use under cold conditions. It is expected that the biomimetic design and good performance presented here could be used for developing many other energy-storage materials and systems.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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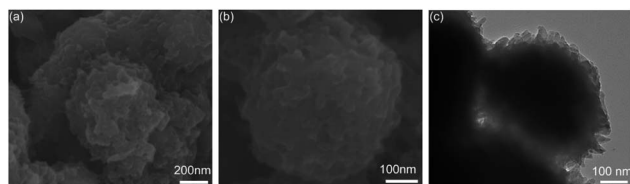


Fig. 10 (a and b) SEM and (c) TEM images of MoS₂@C@PANI after 100 cycles at 0.1 A g⁻¹.



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