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PAPER

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.

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$_{1.5}$)O$_4$ cathode to accelerate the Mg^{2+} 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 Mg^{2+} ions.[10] Because of the same face-centered cubic Se$^{2−}$ 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 V$_2$O$_5$@polyaniline (PANI), by insertion of aniline into the V$_2$O$_5$ 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 microchannels, 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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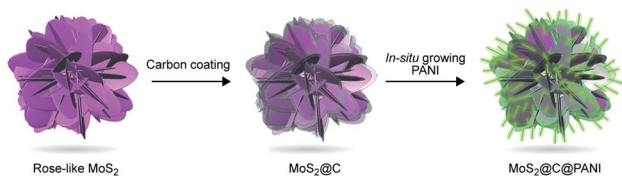‡ These authors contributed equally to this work.

Fig. 1 Illustration of the preparation of ternary MoS$_2$@C@PANI.

MoO_2 nanoparticles was reported, which had a good rate capability, high capacity and long cycling lifespan for lithium and sodium storage.[15] From these findings, we can see that the biomimetic structure has great potential for developing high-performance Mg batteries. However, the design and performance enhancement mechanism of biomimetic structures still remain as challenges.

Here, inspired by the special structure of rose, we developed a novel ternary nanocomposite with a rose-with-thorn structure. The carbon-coated rose-like molybdenum disulfide (MoS_2) is then coated with thorn-shaped PANI, forming a MoS_2@C@PANI nanocomposite, as illustrated in Fig. 1. The preparation process is presented in the ESI.† The conductive PANI nanoneedles *in situ* grown on the surface can improve the conductivity; the inner MoS_2 is wrapped by a carbon layer, which is beneficial for the polymer coating. The results show that the cathode has a high Mg-storage performance and a good stability at low temperatures.

Results and discussion

Fig. 2a and b show the scanning electron microscopy (SEM) images of flower-shaped MoS_2 with a size of about 400–500 nm. The transmission electron microscopy (TEM) image in Fig. 2c shows the flower structure, and the petals are layered. The coated carbon layer makes the surface of MoS_2 rough, as shown in Fig. 2d and e. The TEM image in Fig. 2f shows the coating of the carbon layer. The carbon layer enables nanoneedle-like PANI to be efficiently coated. The SEM image of MoS_2@C@PANI is shown in Fig. 2g and h and the TEM image is shown in Fig. 2i. High-resolution TEM (HRTEM) images are displayed in Fig. 2j and k. The thickness of the PANI layer is about 40–50 nm; however the crystalline lattice of the inner MoS_2 is not clear because of the PANI coating. The SEM and elemental mapping images displayed in Fig. 3 verify the uniform distribution of Mo, S, N and C.

Fig. 4a shows the X-ray diffraction (XRD) patterns. The diffraction peaks are assigned to MoS_2 (JCPDS card no. #75-1539). The disappearance of the peak at about 15° was caused by the carbon coating, and the broad peak at 17.5° is ascribed to carbon. In addition, the peak at about 58° is not clear for the composite; instead, a new peak appears, which is indexed to the crystal plane (008) of MoS_2. The energy dispersive X-ray spectroscopy (EDS) spectrum (Fig. 4b) confirms the elements, which are consistent with the mapping images.[16] Thermogravimetric analysis (TGA) curves are shown in Fig. 4c. The weight loss of the MoS_2@C@PANI composite between 300 and 380 °C is
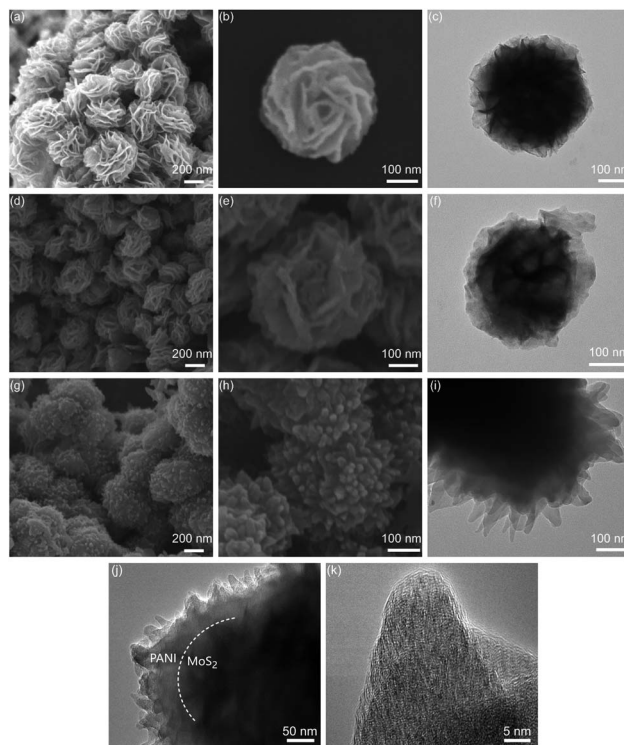

Fig. 2 SEM images of (a and b) flower-shaped MoS_2, (d and e) MoS_2@C, and (g and h) MoS_2@C@PANI. TEM images of the (c) bare MoS_2, (f) MoS_2@C composite and (i) MoS_2@C@PANI. (j and k) HRTEM images of MoS_2@C@PANI. The dashed line in j indicates the boundary between MoS_2 and PANI.

attributed to the weight loss after oxidation of MoS_2. The loss from 380 to 450 °C is ascribed to C and PANI, which is about 33% calculated from 55 − 22%. So, from the TGA curve of the composite, the percentage of MoS_2 is calculated to be 1 − 33 − 10% (moisture) ≈ 57%.

Fig. 5a shows the Fourier transform infrared spectroscopy (FTIR) spectra. The peak at 1569 cm^{-1} is from C–C.[17] The 1116 and 799 cm^{-1} peaks are indexed to C–H bending.[18] The Raman spectra in Fig. 5b show prominent Raman-active peaks. The peaks of sulfide are observed at 403 and 376 cm^{-1}. The peaks at
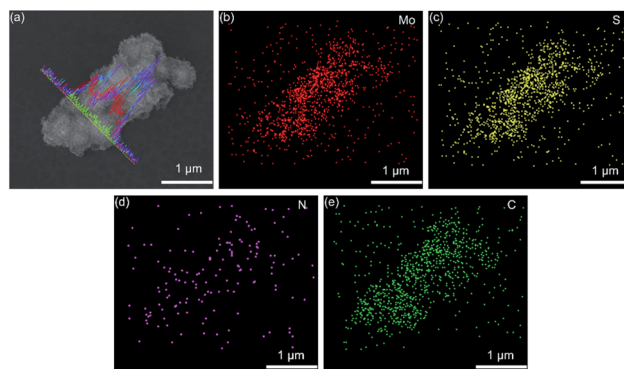

Fig. 3 (a) SEM and (b–e) elemental mapping images of MoS_2@C@PANI. Line-scan profiles are inserted in (a).

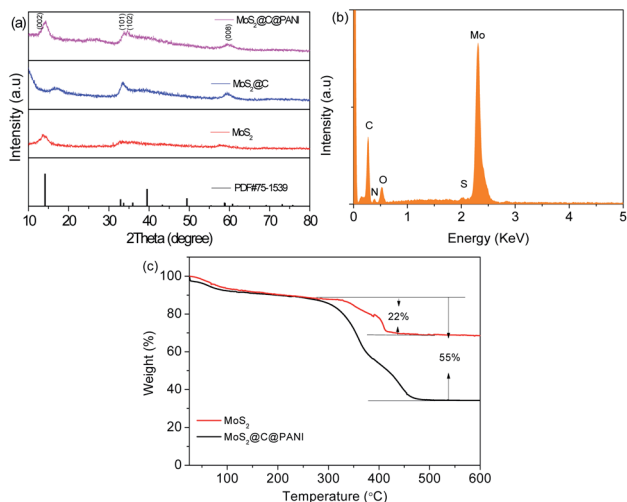**Fig. 4** (a) XRD patterns of MoS_2, $MoS_2@C$, and $MoS_2@C@PANI$. (b) EDS spectrum of $MoS_2@C@PANI$. (c) TGA curve of bare MoS_2 and $MoS_2@C@PANI$.
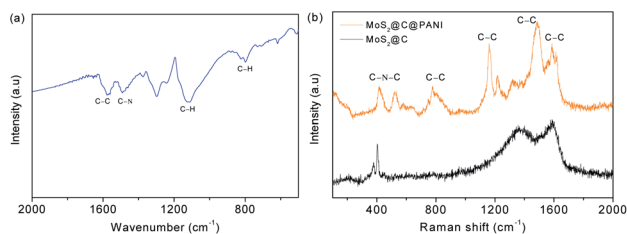

Fig. 5 (a) FTIR spectrum of $MoS_2@C@PANI$. (b) Raman spectra of bare MoS_2 and the $MoS_2@C@PANI$ composite.

1365 and 1587 cm^{-1} are assigned to the D-band and G-band of carbon, respectively. In $MoS_2@C@PANI$, 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 $MoS_2@C@PANI$ 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 MoS_2, 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 $MoS_2@C@PANI$ is also competitive, as shown in Table S1 (ESI†). Fig. 7c shows the CV profile of the $MoS_2@C@PANI$
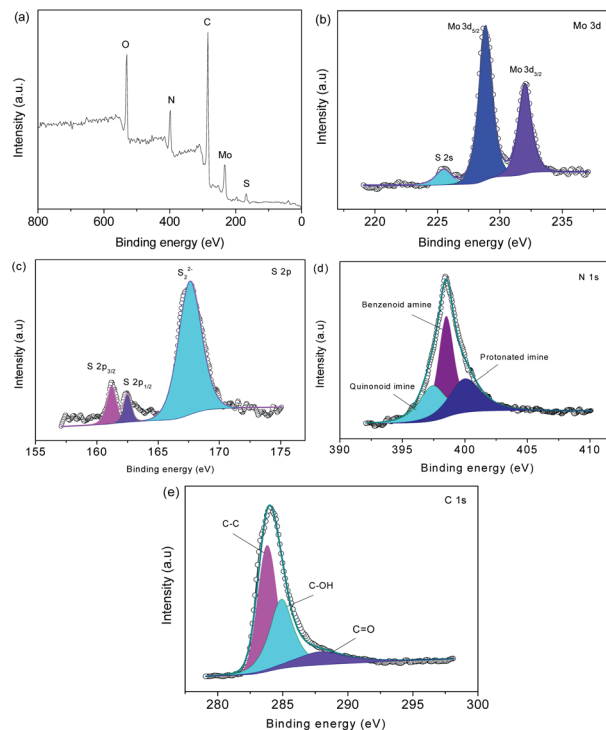
Fig. 6 (a) XPS survey spectrum, and (b) Mo 3d, (c) S 2p, (d) N 1s, and (e) C 2p spectra of $MoS_2@C@PANI$.

cathode. The anodic peaks around 0.6 to 1.2 and 1.9 V are ascribed to Mg^{2+} deintercalation, and the cathodic peaks at about 0.5, 1.25 and 1.75 V indicate the corresponding intercalation of Mg^{2+}.[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
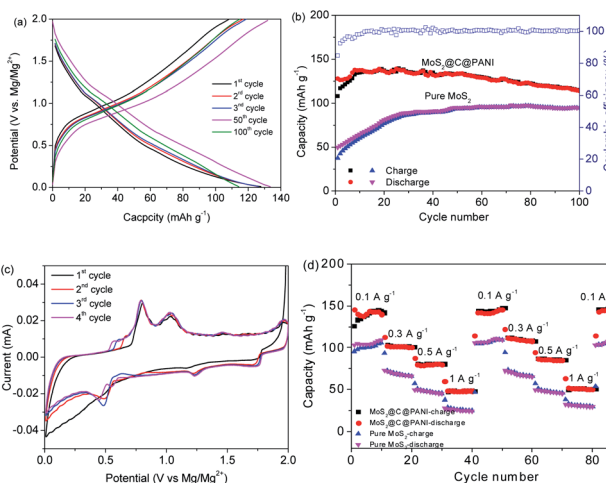

Fig. 7 (a) Charge–discharge curves of $MoS_2@C@PANI$ at 0.1 A g^{-1}. (b) Capacities and coulombic efficiency. (c) CV curves cycled at 0.1 mA s^{-1}. (d) Rate-performance.
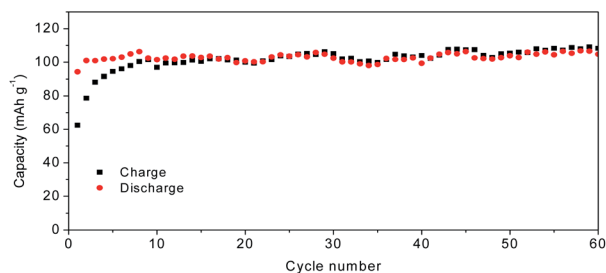
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