



Ultrathin ReS₂ nanosheets growing on ordered microporous carbon for high capacity lithium ion batteries

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ABSTRACT

To improve the Li storage capability of rhenium disulfide (ReS₂) as anode materials for lithium ion batteries (LIBs), the ReS₂@CMK-3 composites were designed and prepared by using CMK-3 as a nano-reactor. The ReS₂@CMK-3 composites possessed a special nanosheets-on-channel architecture that the ultrathin ReS₂ nanosheets grown on the channel of CMK-3. Owing to the large surface area, ordered mesoporous structure and excellent electronic conductivity, the ReS₂@CMK-3 composites exhibited larger discharge capacity, superior cycling performance and higher rate performance compared with pristine ReS₂ when they were applied as anode materials for LIBs. As a result, the ReS₂@CMK-3 composites delivered a reversible capacity of 620 mAh g⁻¹ after 200 cycles at 0.5 A g⁻¹, indicating their potential as promising anode materials for LIBs.

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1. Introduction

Lithium ion batteries (LIBs), as a renewable power source, have occupied vast majority of portable electronics market in the last two decades due to its low self-discharge, no memory effect and long cycle life *etc.* [1–4] Rhenium disulfide (ReS₂), as a typical member of two-dimensional transition metal dichalcogenides (TMDs), has been widely studied in photodetectors, digital inverters, electrocatalysts and field-effect transistors due to its unique crystal structure [5–8]. In the recent two years, researchers discover that the two-dimensional ReS₂ has a potential application in LIBs for the followed factors. Firstly, ReS₂ can release a theoretical capacity of about 430 mAh g⁻¹ because per ReS₂ formula can accommodate 4 mol Li⁺ ions insertion [9]. Secondly, two-dimensional ReS₂ owns a weak interlayer coupling, indicating its potential in high-current-density LIBs [10]. Thirdly, the bulk two-dimensional ReS₂ possesses a larger interlayer distance of 0.614 nm compared to that of graphite (0.335 nm), suggesting that it may suffer from a relatively small volume expansion when it is

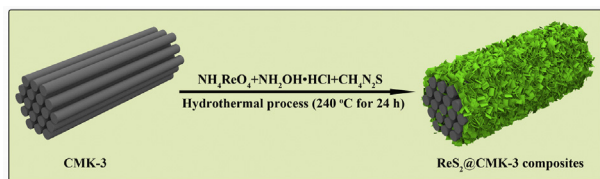
inserted with massive lithium ions [11,12]. However, the bulk ReS₂ encounters the problems of fast capacity fading and poor rate performance when it is used as anode material for LIBs. As reported, the commercial bulk ReS₂ only could release a low capacity of 13.3 mAh g⁻¹ at 86 mA g⁻¹ after 30 cycles, which was attributed to the poor conductivity of TMDs [13–15].

To obtain superior electrochemical performances, one of the most effective methods was fabricating hybrid materials by combining the TMDs with carbon materials. The enhanced electrochemical performances of hybrid materials were ascribed to the synergistic effect between the TMDs and carbon materials [16,17]. For example, Qi and co-workers found that ReS₂/rGO composites could keep a capacity of 745 mAh g⁻¹ at 86 mA g⁻¹ after 50 cycles [18]. CMK-3, as a famous member of carbon materials, has attracted much attention in term of ordered mesoporous channels, large pore volume and good conductivity [19,20]. Furthermore, CMK-3 is regarded as an outstanding nanoreactor to fabricate hybrid materials as improved anode materials for LIBs [21–24]. In addition, nanosheet structure is a good choice to enhance the electrochemical performance in term of the large surface area and shorter diffusion path for Li-ion transport [25,26]. Thus, compositing CMK-3 with ReS₂ nanosheets will be a good strategy to improve the Li storage performance of ReS₂. Considering that the specific surface

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Scheme 1. Illustration of the preparation of ReS₂@CMK-3 composites.

area of the composites will decrease when the nanochannels of CMK-3 are lumped with guest materials, thus, the nanosheets grown on the surface of CMK-3 will be more beneficial for enhancing the Li storage performance of ReS₂ [19].

Herein, the ReS₂@CMK-3 composites have been designed and synthesized by a facial hydrothermal reaction on a basis of CMK-3 (Scheme 1). The ReS₂@CMK-3 composites with nanosheets-on-channel architecture captured the merits of nanosheets, mesoporous structure and carbon materials. Thus, it would display a superior cycling performance and good rate performance.

2. Results and discussion

XRD patterns were characterized to investigate the crystal structure of the pristine ReS₂, CMK-3 and ReS₂@CMK-3 composites, as shown in Fig. 1. Fig. 1a displayed the small-angle XRD patterns of ReS₂@CMK-3 composites and CMK-3. One sharp diffraction peak with high intensity and two small diffraction peaks were observed in the pattern of CMK-3, which accorded with the (100), (110) and (200) lattice plane of CMK-3 (2-d hexagonal mesostructure with P6 m space group), respectively. But all the diffraction peaks disappeared in the pattern of ReS₂@CMK-3 composites, this phenomenon could be ascribed to the destruction of ordered structure of CMK-3 during the formation process of ReS₂ [27,28]. Fig. 1b showed the wide-angle XRD patterns of ReS₂@CMK-3 composites and pristine ReS₂. Same diffraction peaks were observed in the patterns of ReS₂ composites and pristine ReS₂@CMK-3, which were associated with the (100), (002), (201), (-112) and (2-42) lattice plane *s* of ReS₂ (JCPDS card No. 82–1379).

The structure of CMK-3, pristine ReS₂ and ReS₂@CMK-3 composites were further studied by Raman, as shown in Fig. 2. In the Raman spectrum of CMK-3, the two peaks at ~1340 and ~1598 cm⁻¹ matched with the D band (caused by disordered graphite) and G band (related to crystalline graphite) of carbon, respectively [29]. In the Raman spectrum of pristine ReS₂, the peak at ~150 cm⁻¹ represented the in-plane (E_g) vibrational modes of ReS₂ and another peak at 211 cm⁻¹ was accorded with the out-of-plane (A_g)

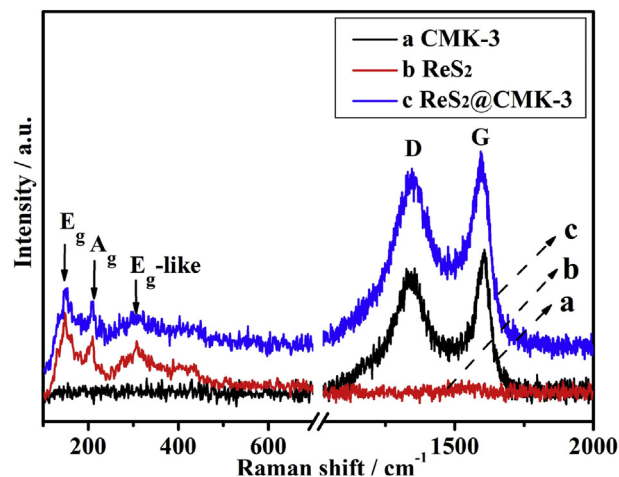


Fig. 2. Raman spectra of CMK-3, pristine ReS₂ and ReS₂@CMK-3 composites.

vibrational modes of ReS₂. It was worth mentioning that all aforementioned peaks in CMK-3 and ReS₂ appeared in the ReS₂@CMK-3 composites, indicating the existence of CMK-3 phase and ReS₂ phase in the ReS₂@CMK-3 composites. Furthermore, according to the TG curves (Fig. S1) and related calculation, the contents of ReS₂ and CMK-3 were 24.9% and 75.1%, respectively.

As illustrated in the SEM image of CMK-3 (Fig. 3a), the surface of CMK-3 was smooth. But many nanosheets were observed on the surface of CMK-3 after the hydrothermal process due to the formation of ReS₂ (Fig. 3b). In Fig. 3c, the straight lines in parallel revealed the ordered mesoporous structure of CMK-3, which was beneficial to the transportation of Li⁺ ions. In the TEM image of ReS₂@CMK-3 composites (Fig. 3d), the ReS₂ nanosheets distinctly stand on the channel of CMK-3. The HRTEM image of ReS₂@CMK-3 composites (Fig. 3e) exhibited a crystalline lattice with interplanar spacing of 0.61 nm, which matched with the (100) plane of ReS₂. And it could be found that the thickness of the ReS₂ nanosheets ranged from 2 to 5 nm, the ultrathin sheets could shorten the diffusion path of Li⁺ ions during lithiation/delithiation process. From the dark-field STEM image and the elemental mapping images (Fig. 3f), the C, S and Re elements uniformly distributed in the ReS₂@CMK-3. In addition, Fig. S2a and Fig. 2b displayed the SEM image of pristine ReS₂ with different dimensions. Fig. S2a indicated that the pristine ReS₂ had a sphere structure and aggregated together. After amplification, many nanosheets were observed on the surface of ReS₂ spheres (Fig. S2b). Furthermore, according to its TEM images (Fig. S2c and Fig. 2d), the ReS₂ spheres were solid and

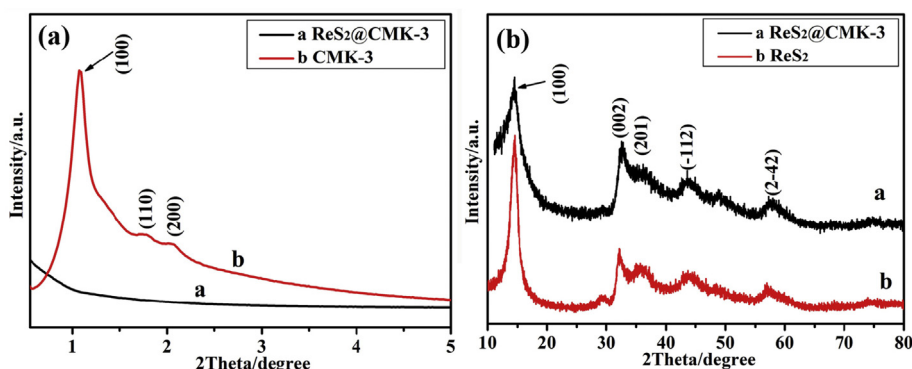


Fig. 1. (a) Small-angle XRD patterns of ReS₂@CMK-3 composites and CMK-3; (b) Wide-angle XRD patterns of pristine ReS₂@CMK-3 composites and ReS₂.

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