

Materials

The MoS_2 , WS_2 , MoO_3 , TiO_2 , ZrB_2 , TiB_2 , (99%) were purchased from Aladdin Co., Ltd, China. MnS and V_2O_3 were purchased from Xiya Co., Ltd, China. The Fe_3O_4 were synthesized by microwave-assisted solvothermal method. A typical synthesis method is as following. 2 mmol FeCl_3 (95% CP, Sinopharm, China) and 0.9 g polyacrylic acid (PAA 99%, Aladdin) were dissolved in 20 mL ethylene glycol (99% Kemio, China) and stirred continuously. After 2 h, 3 mL $\text{NH}_3\cdot\text{H}_2\text{O}$ (25~28%, Sinopharm) was added into the mixture solution and stirred for 0.5 h. The obtained homogenous precursors were sealed in a teflon lined autoclave microwave autoclave (100 mL capacity, Preekem, Co., Ltd, China) and annealed at 230 °C for 2 h. Then it was cooled to room temperature.

Characterizations

Structure and composition analysis of the cathode materials were characterized by X-ray diffraction (XRD) using Rigaku 2500, with $\text{Cu-K}\alpha$ radiation ($\lambda = 0.154056$ nm). The diffraction patterns were recorded over the 2 theta angle of 10–80° at 40 kV, 100 mA, at step mode with a step size 0.02°. The morphology and elemental distribution were characterized by a field emission scanning electron microscope (FESEM, Zeiss Supra 55, Carl Zeiss Co, Ltd, Germany) with an energy dispersive spectrometer attachment (Oxford X-Max 20).

The zinc ion storage and reversible ability of cathode materials were characterized by cyclic voltammetry (CV) with a Bio-logic VMP3 potentiostat (Bio-Logic Science Instruments SAS, France) using CR2032 type coin cells. The cathode electrodes in the CR 2032 type coin cells were prepared by mixing the cathode materials, acetylene carbon black, Polyvinylidene Fluoride (PVDF, Canrd, China) with a ratio 7:2:1 in N-Methyl pyrrolidone (NMP, Sinopharm) to form a slurry. The homogenous slurry was pasted onto a 10 μm thick stainless-steel foil and dried in a vacuum oven at 80 °C for 12 h. The CR 2032 type coin cells were assembled with the prepared electrodes as cathode, Zn metal foil as anode, the air-laid paper as the separator, 2 M (mol L^{-1}) ZnSO_4 aqueous solution as electrolyte. The galvanostatical cycling were measured by the Land battery test instrument and the test voltage range were defined from the range of oxidation peak and reduction peak of different cathode materials.

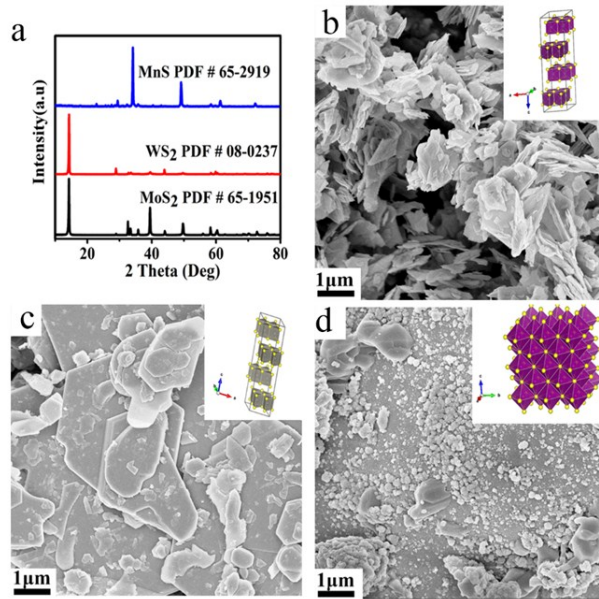


Fig. 1 (a) X-ray diffraction patterns of MoS₂, WS₂ and MnS. (b) MoS₂, (c) WS₂ and (d) MnS. Morphologies of (b) MoS₂, (c) WS₂ and (d) MnS. The insert window shows the crystal structure illustrations

The XRD patterns of MoS₂, WS₂ and MnS are shown in Fig. 1a. The diffraction peaks of MoS₂ and WS₂ can be indexed to the hexagonal phase with the space group of P6₃ / mmc (JCPDF no.69-1951 and 08-0237). The morphologies of MoS₂ and WS₂ (Fig. 1b and c) show that they are composed of small particles with layered structure. The diffraction peaks of MnS is indexed to the face-centered cubic phase with the space group of Fm-3m (JCPDF no.65-2919). The crystal structure illustration of MnS is a classic NaCl structure as shown in Fig. 1d. The morphology of MnS particles were not uniform with micron dimension

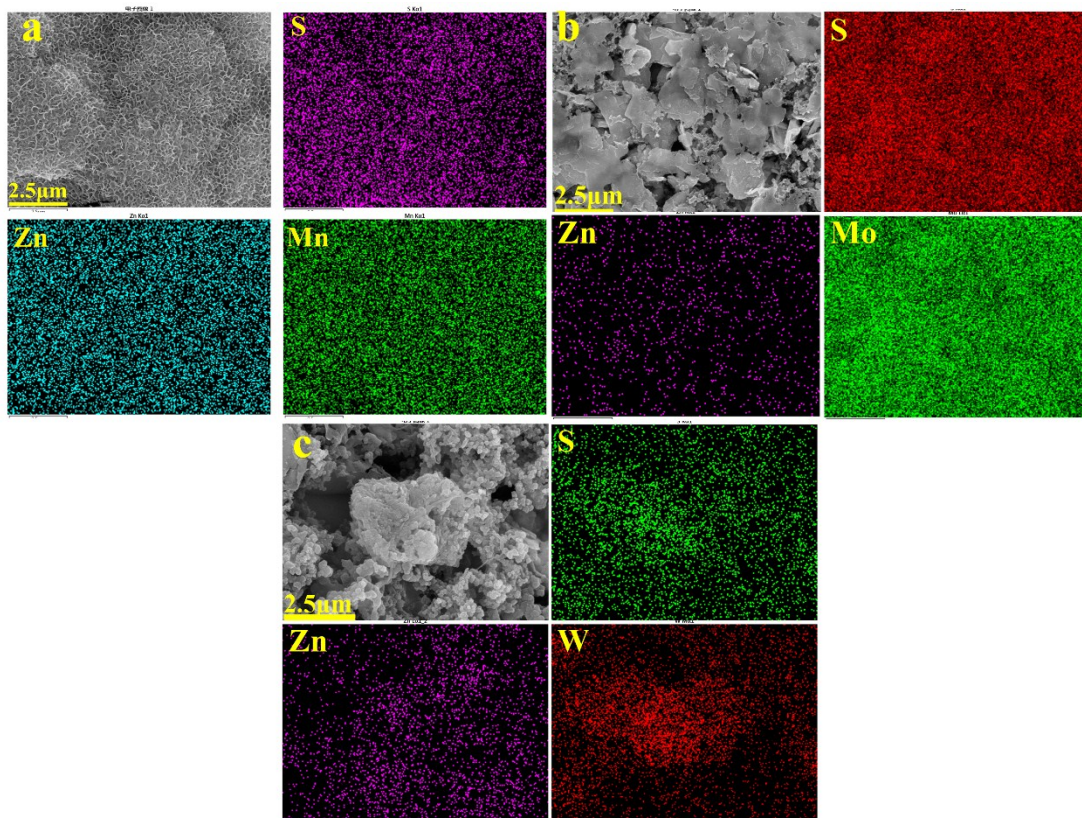


Fig. 2 EDS images of fully discharge state of (a) MnS, (b) MoS₂, (c) WS₂

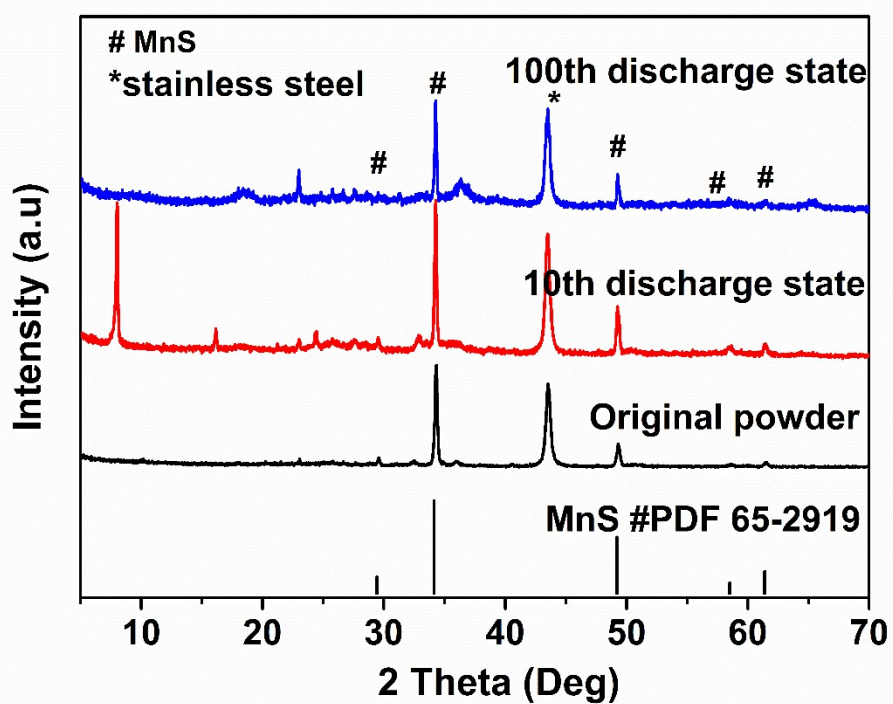


Fig. 3 ex situ XRD of MnS in the zinc ion battery.

The ex situ XRD was carried from the 10 cycles to the 100 at the discharge state. The 2 theta peaks in of 8°, 16° and 24° 10th of cycles discharge state may be an material formed in the electrochemical activation process and after the initial few electrochemical activation cycles the peaks disappeared.

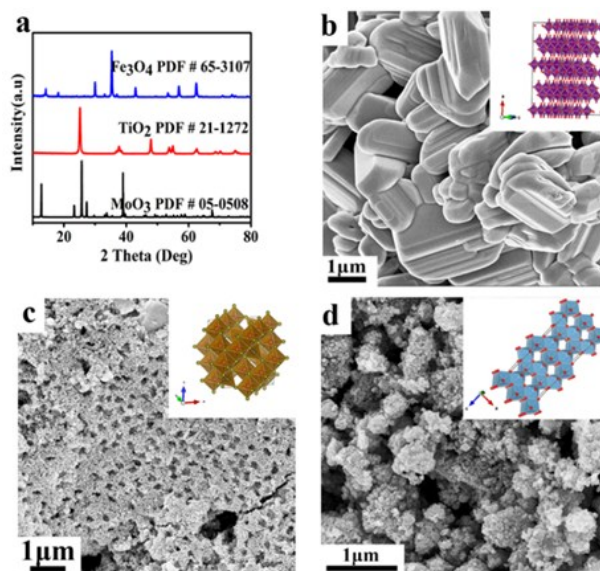


Fig. 4 (a) XRD patterns of MoO₃, TiO₂ and Fe₃O₄. Crystal structure illustrations of (b) MoO₃, (c) TiO₂ and (d) Fe₃O₄. SEM image of (b) MoO₃, (c) Fe₃O₄ and (d) TiO₂. The insert window of SEM image was the crystal structure illustrations.

The crystal phase and morphology of MoO₃, TiO₂, Fe₃O₄ were identified by XRD, SEM. All the diffraction peaks of MoO₃ (Fig. 4a) can be indexed to the orthorhombic phase with the space group of Pbnm (JCPDF no.05-0508). All the diffraction peaks are sharp and 0k0 lines are stronger than hkl lines, which indicates that the MoO₃ has a preponderant growth orientation at 0k0 planes. The interlayer spacing between Mo-O octahedron layers stack along the b-axis direction. It is in accordance with the morphology of MoO₃ (Fig. 4b), which shows the small particles with a layered structure.

The crystal phase, morphology and electrochemical performance of Fe₃O₄ were identified by XRD, SEM and CV. The XRD peaks of Fe₃O₄ (Fig. 4a) can be indexed to a cubic phase with the space group of Fd-3m (JCPDF no. 65-3107).

The crystal phase, morphology and electrochemistry of TiO₂ were identified by XRD, SEM and CV. All the diffraction peaks of TiO₂ (Fig. 4a) can be assigned to the tetragonal phase with the space group of I41/amd (JCPDF no. 22-1272). The TiO₂ has an anatase structure (Fig. 4d). We can see that the TiO₂ is composed of the small nanocrystal particles with a nano-size below 25 nm.

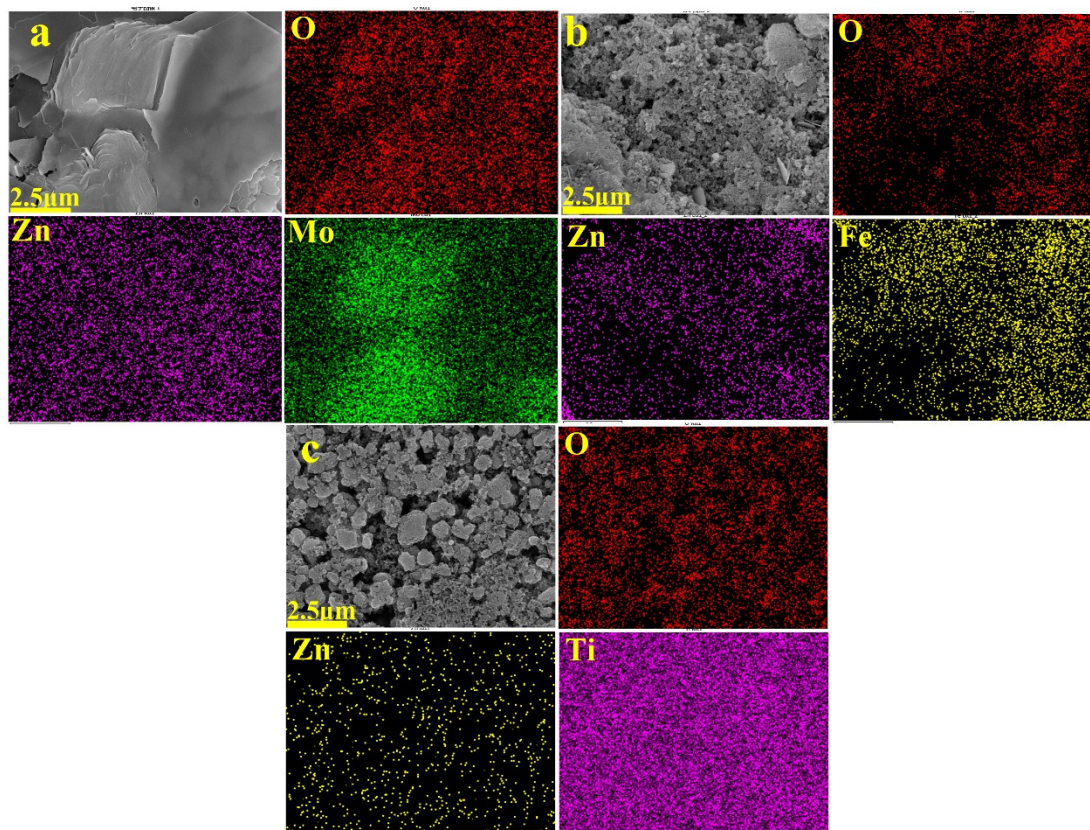


Fig. 5 EDS images of fully discharge state of (a) MoO₃, (b) Fe₃O₄, (c) TiO₂

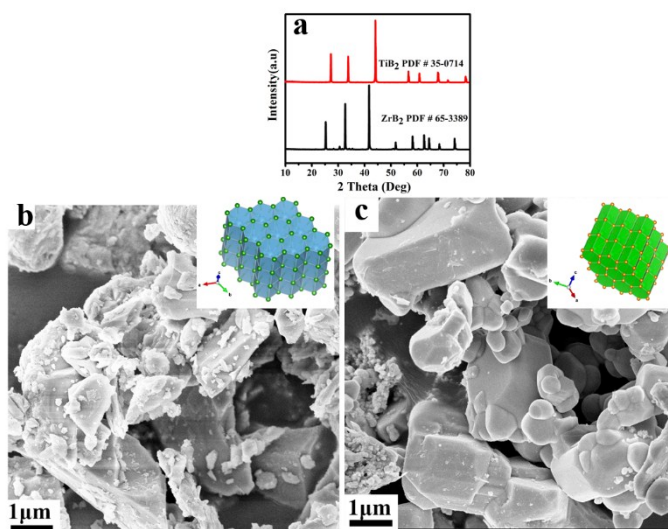


Fig. 6 (a) XRD patterns of ZrB₂ and TiB₂. CV images of (b) TiB₂ and (c) ZrB₂. SEM images of (d) TiB₂ and (e) ZrB₂, the insert window is the crystal structure illustration.

From Fig. 6 we can see the diffraction peaks of ZrB₂ and TiB₂ can be indexed to hexagonal phase with space group of P6/mmm (JCPDF no. 65-3389 and 35-0741, respectively). The SEM images of ZrB₂ and TiB₂ (Fig. 6d and e) show that they are composed of the micron-level particles.

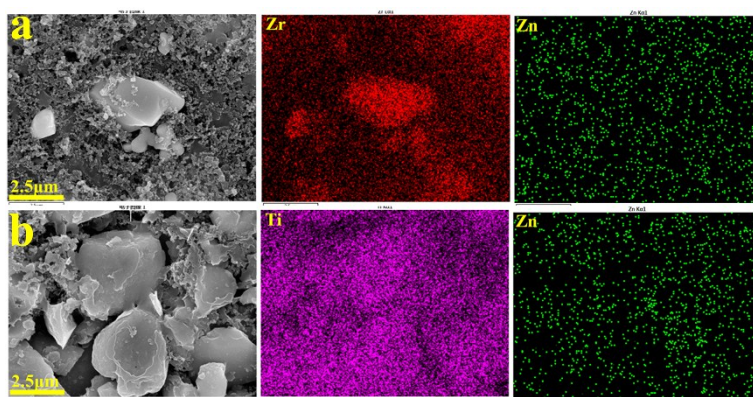


Fig. 7 EDS images of fully discharge state of (a) ZrB₂, (b) TiB₂

1. K. Bindumadhavan, S. K. Srivastava and S. Mahanty, *Chem. Commun.*, 2013, **49**, 1823.