

Supporting Information

ZnSe Microsphere/Multiwalled Carbon Nanotube Composites as High-Rate and Long-Life Anodes for Sodium-Ion Batteries

Chunjuan Tang,^{1, 2} Xiujuan Wei,¹ Xinyin Cai,¹ Qinyou An,¹ Ping Hu,¹ Jinzhi Sheng,¹ Jiexin Zhu,¹ Shulei Chou,³ Liming Wu,^{*1} Liqiang Mai^{*1}

¹*State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Luoshi Road 122, Wuhan, 430070, P. R. China*

²*Department of Mathematics and Physics, Luoyang Institute of Science and Technology, Luoyang, 471023, P. R. China*

³*Institute for Superconducting and Electronic Materials, Australian Institute for Innovative Materials, University of Wollongong, Innovation Campus Squires Way, North Wollongong, NSW 2522, Australia*

*E-mail: liming_wu@whut.edu.cn;

mlq518@whut.edu.cn

Material Preparation

All the reagents used in the experiment were of analytical grade and used without further purification.

Zn(NO₃)₂·7H₂O, NaOH, and SeO₂ are used as raw materials. Firstly, 2 mmol Zn(NO₃)₂·7H₂O is dispersed into 60 mL deionized water under stirring. Then 3.2 g NaOH is added into the above solution. After stirring for 15 min, 2 mmol SeO₂ is added into the mixture. 5 mL N₂H₄·H₂O is then added dropwise into the above mixture under continuous stirring. Finally, the obtained solution is transferred into a

100 mL Teflon-lined stainless-steel autoclave and heated at 150 °C for 12 h. After naturally cooling to room temperature, the product is collected by centrifugation, washed with distilled water and ethanol for several times, and then dried at 70 °C for 12 h under vacuum.

ZnSe/MWCNT composites are synthesized by grinding the as-prepared ZnSe with commercial MWCNTs (a weight ratio of 8:1) in an agate mortar. For comparison, the ZnSe/AB composites are obtained using the same procedure, but the carbon matrix is replaced as AB.

Material Characterization

X-ray diffraction (XRD) patterns were recorded using a D8 Advance X-ray diffractometer with a non-monochromated Cu K α X-ray source. For *in-situ* XRD measurements, the electrochemical cell module with a beryllium window was used, which the electrode was obtained by ground active materials, acetylene black, and poly(tetrafluoroethylene)(PTFE) at a weight ratio of 70: 20: 10. Raman spectra were obtained using a Renishaw IN VIA micro-Raman spectroscopy system. Brunauer-Emmett-Teller (BET) surface areas were measured using a Tristar II 3020 instrument. X-ray photoelectron spectroscopy (XPS) analysis was done on a VG Multilab 2000. Field emission scanning electron microscopic (FESEM) images and energy dispersive spectra (EDS) were collected using a JEOL-7100F microscope. Transmission electron microscopy (TEM) images and high-resolution TEM (HRTEM) images were recorded by using a JEM-2100F microscope.

Electrochemical Measurements

The working electrode was obtained by dispersing as-prepared ZnSe/MWCNTs or ZnSe/AB in carboxyl methyl cellulose (CMC) at a weight ratio of 9:1. 2016 coin cells were assembled in a glove box filled with pure argon gas. Sodium chips were used as the counter electrode. The electrolyte was 1 M sodium trifluoromethanesulfonate (NaCF_3SO_3) dissolved in diethyleneglycol dimethylether (DIGLYME). Galvanostatic charge/discharge measurements were performed at a potential range of 0.2 - 3.0 V vs. Na^+/Na using a multichannel battery testing system (LAND CT2001A). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were tested by electrochemical workstations (CHI600D and Autolab Potentiostat Galvanostat 302N). All of the measurements were carried out at room temperature.

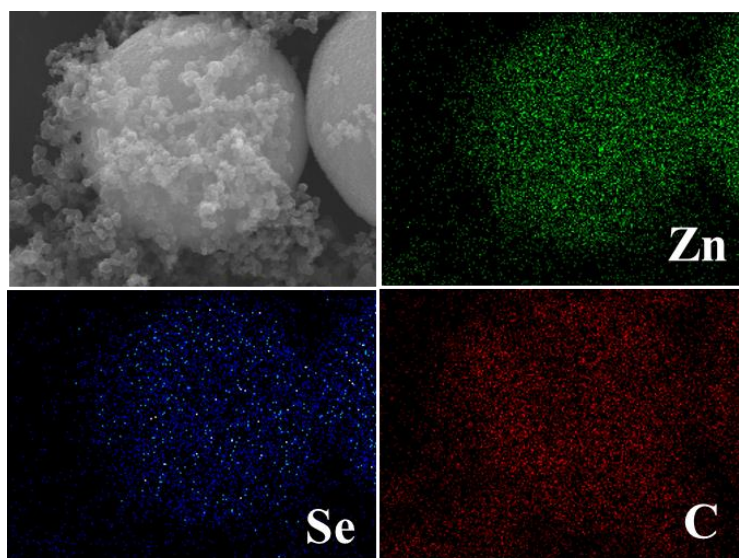


Figure S1. EDS mapping images of ZnSe/AB.

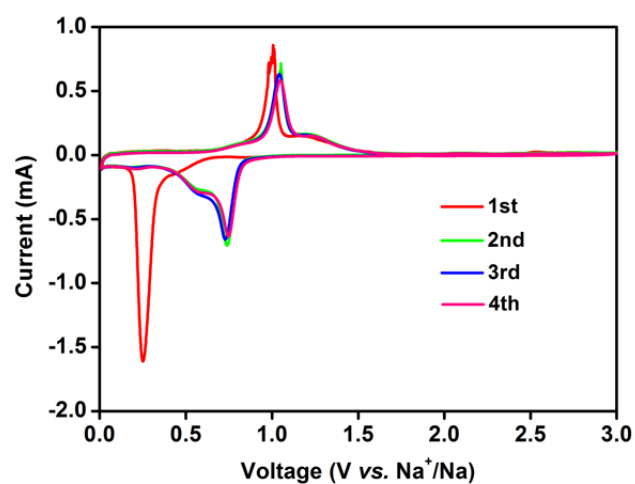


Figure S2. CV plots of ZnSe/MWCNTs at a scan rate of 0.1 mV s^{-1} .

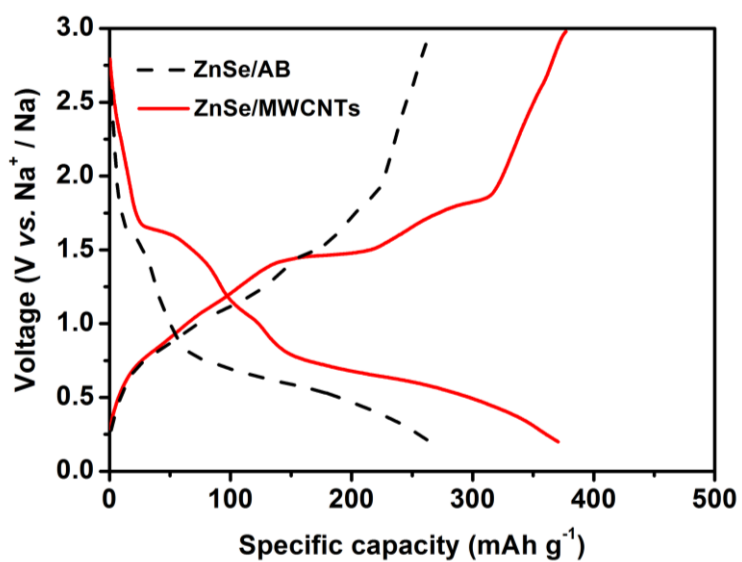


Figure S3. The charge-discharge curves of as-prepared ZnSe/MWCNTs and ZnSe/AB electrodes after 80 cycles at 0.2 A g^{-1} .

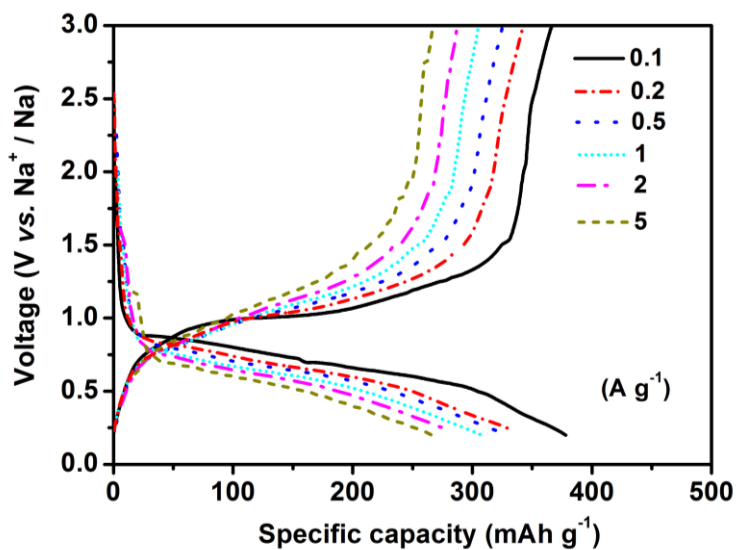


Figure S4. The charge–discharge profiles of ZnSe/MWCNTs at different rates.

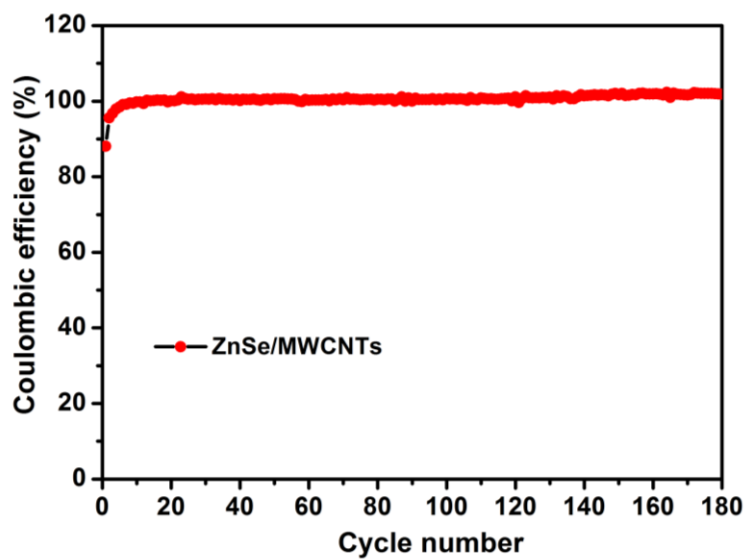


Figure S5. Coulombic efficiency of ZnSe/MWCNTs at a high current density of 0.5 A

g^{-1} .

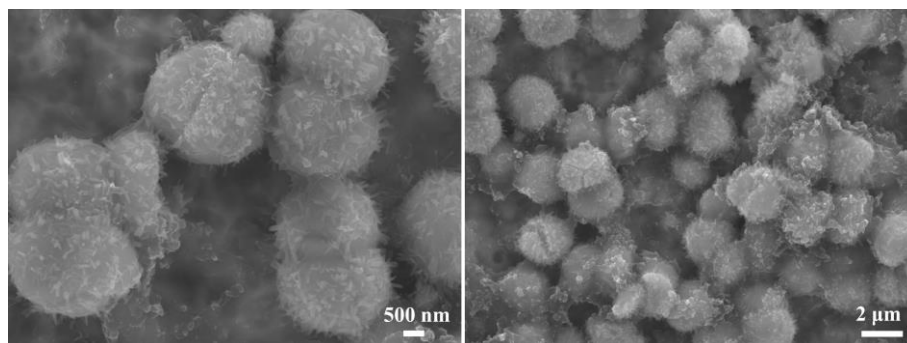


Figure S6. SEM images of as-prepared ZnSe/AB after 100 cycles.

Table S1 The fitted resistance values of EIS results

| | R_s | R_{SEI} | R_{ct} |
|-------------|-------|-----------|----------|
| ZnSe/MWCNTs | 6.329 | 9.668 | 11.3 |
| ZnSe/AB | 12.14 | 9.732 | 11.8 |