Electronic Supplementary Information

Porous hollow carbon spheres decorated with molybdenum diselenide nanosheets as anode for highly reversible lithium and sodium storage

Xing Yang, Zhian Zhang*, Yun Fu, Qiang Li

School of Metallurgy and Environment, Central South University, Changsha, Hunan 410083, China

Experimental section

1.1 Preparation of porous hollow carbon spheres (PHCS)

The porous hollow carbon spheres were prepared using a one-step method under Stőber reaction conditions as previously reported[1,2]. Briefly, in a typical synthesis process, 1.6 mL of ammonia aqueous solution (28 wt%) was added to a mixture of 5.5 mL deionized water and 37.8 mL ethanol with stirring for 30 minute at room temperature. Subsequently, tetrathoxysilane (TEOS) (1.5 mL), resorcinol (0.21 g) and formaldehyde solution (0.31 mL, 37 wt%) were added to the above solution at intervals of 10 minutes. After that, the mixture was vigorously stirred for 24 h at 30 ^{o}C and transfer to a 60 mL Teflon-lined autoclave under static conditions (100 ^{o}C) for another 24 h. Solid SiO_2@resorcinol-formaldehyde products were filtered and washed with absolute ethanol and distilled water three times, after oven-drying, the solid samples were carbonized by heating at 750 ^{o}C for 2 h under argon gas flow in a tube furnace. Finally, the SiO_2 template was removed by treating the material in dilute HF solution overnight, then the final PHCSs were obtained after dried in vacuum at 80 ºC for 24 h.

1.2 Preparation of $MoSe_2$@porous hollow carbon spheres

0.1 g of porous hollow carbon spheres were first ultrasonically dispersed in a mixture of 20 ml distilled water and 30 ml ethanol to form a suspension, into which 0.4188 g Na_2MoO_4 was added next. In a separate flask, 0.3158 g selenium powder was dissolved in 10 ml of hydrazine hydrate solution in air atmosphere. Instantly, the color of the mixture solution changed from colorless to red and remains uncharged under atmospheric conditions at least for 36 h. Then the hydrazine hydrate-Se solution was slowly injected into 50 ml of Na_2MoO_4 mixture solution at room temperature with rigorously stirring. The mixture turned dark red and the ratio of selenium and molybdenum is 2:1. Then the mixture was transferred into a Teflon-lined autoclave with 100 ml capacity, followed by hydrothermal treatment at 200 ºC for 10 h in an oven. After cooled to room temperature, the black product was collected by centrifugation at 10000 rpm for 8 min, then washed with distilled water and ethanol several times, and recollected by centrifugation. Then black powders were obtained after dried in vacuum at 80 ºC for 24 h. Finally, the as-synthesized sample was annealed at 600 ^{o}C to improve to crystallinity of $MoSe_2$. For comparison, $MoSe_2$ nanosheets were prepared through the same method in the absence of porous hollow carbon sphere.

1.3 Material characterization

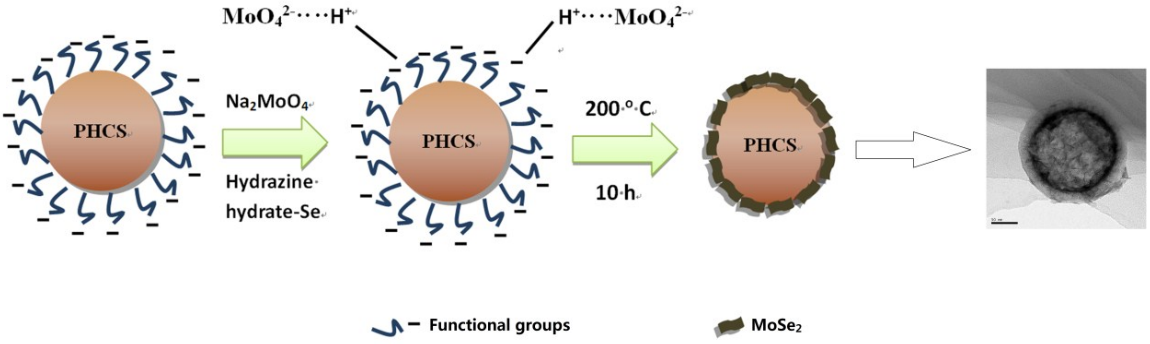
Field emission scanning electron microscopy (SEM, Nova NanoSEM 230) and transmission electron microscopy (TEM, Tecnai G2 20ST) were applied to investigate the morphologies, particle sizes, and elemental compositions of the materials. The elements on the surface of the samples were identified by energy-dispersive X-ray spectroscopy (EDX). Powder X-ray diffraction (XRD, Rigaku3014) using Cu Kα radiation was employed to identify the crystalline phase of the materials. Thermogravimetric analysis (TGA, SDTQ600) was conducted in determining the $MoSe_2$ content in the $MoSe_2$@PHCS composites. N_2 adsorption/desorption measurements were performed by using a Quantachrome instrument (Quabrasorb SI-3MP) at 77 K.

1.4 Cell assembly and Electrochemical characterizations

The electrode was prepared by mixing 80 wt% active material ($MoSe_2$@PHCS or $MoSe_2$ nanosheets), 10 wt% acetylene black, and 10 wt% sodium alginate (SA) binder in deionized water solvent. The slurry was spread onto copper foil, and dried at 60 ^{o}C overnight, then the cathodes were cut into pellets with a diameter of 1.0 cm and dried for 12 h in a vacuum oven at 60 ^{o}C. The typical mass loading of the active material was 0.9-1.1 mg cm^2. All capacities in this study were calculated based on $MoSe_2$ mass. The electrochemical performance was performed using a CR2025 coin-type cell. CR2025-type coin cells were assembled in an argon-fillled glove box (Universal 2440/750) in which oxygen and water contents were less than 1 ppm. The electrolyte used for lithium battery was 1 M $LiPF_6$ (Aldrich) in ethylene carbonate/dimethyl carbonate/diethyl carbonate (1:1:1 in volume) and used for sodium was a solution of 1 M $NaClO_4$ (Aldrich) in a 1:1

volume mixture of ethylene carbonate/dimethyl carbonate (EC/DMC) with 5 wt% fluoroethylene carbonate. A lithium metal or a sodium metal was used as the counter electrode and the reference electrode and a Celgard 2400 was used as a separator. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were conducted using a PARSTAT 2273 electrochemical measurement system. CV tests were performed at a scan rate of 0.2 mV s^{-1} in the voltage range of 0.01 to 3.0 V. Galvanostatic charge-discharge tests were performed in the potential range of 0.01 to 3.0 V at 25 ^{o}C by using a LAND CT2001A battery-testing instrument.

1. J. Liu, S. Z. Qiao, H. Liu, J. Chen, A. Orpe, D. Zhao and G. Q. Lu, *Angewandte Chemie*, 2011, **50**, 5947-5951.
2. A. B. Fuertes, P. Valle-Vigon and M. Sevilla, *Chemical communications*, 2012, **48**, 6124-6126.



Scheme 1 Schematic illustration for the synthesis of $MoSe_2$@PHCS.

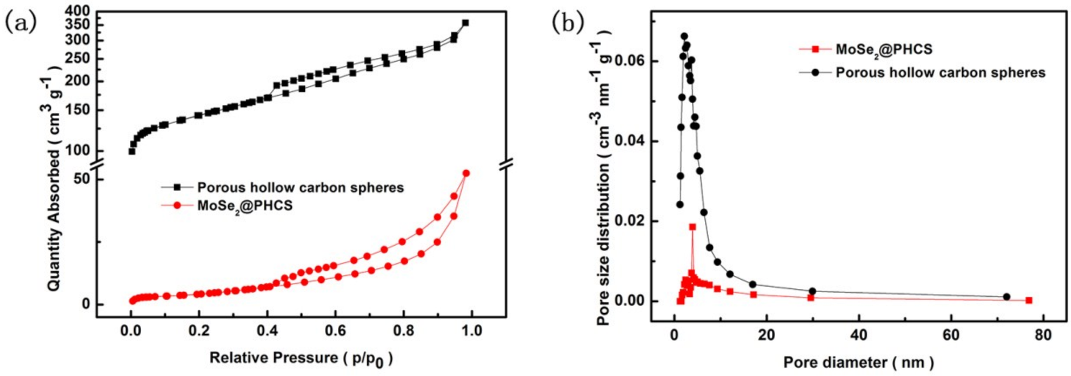


Fig. S1 Nitrogen adsorption-desorption isotherms and pore size distribution curves of porous hollow carbon spheres and $MoSe_2$@PHCS.

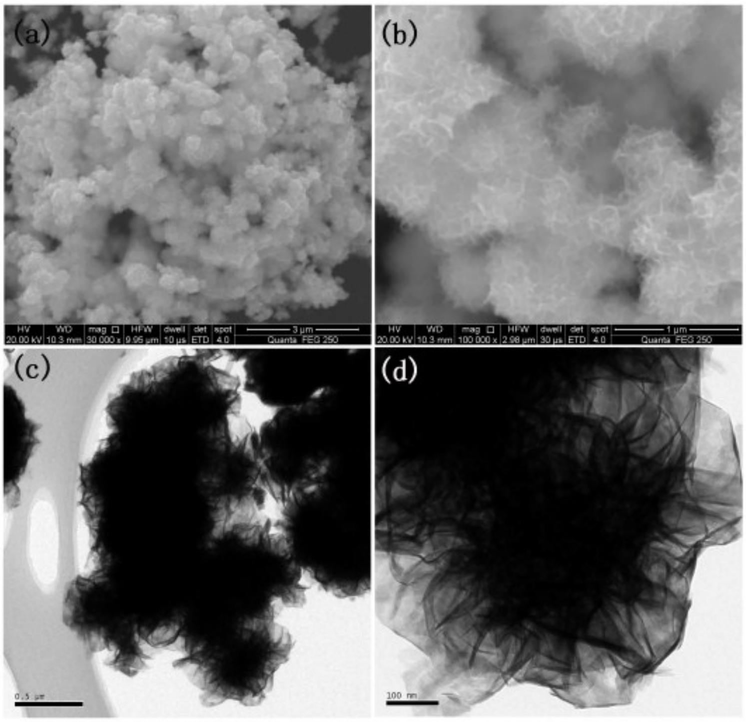
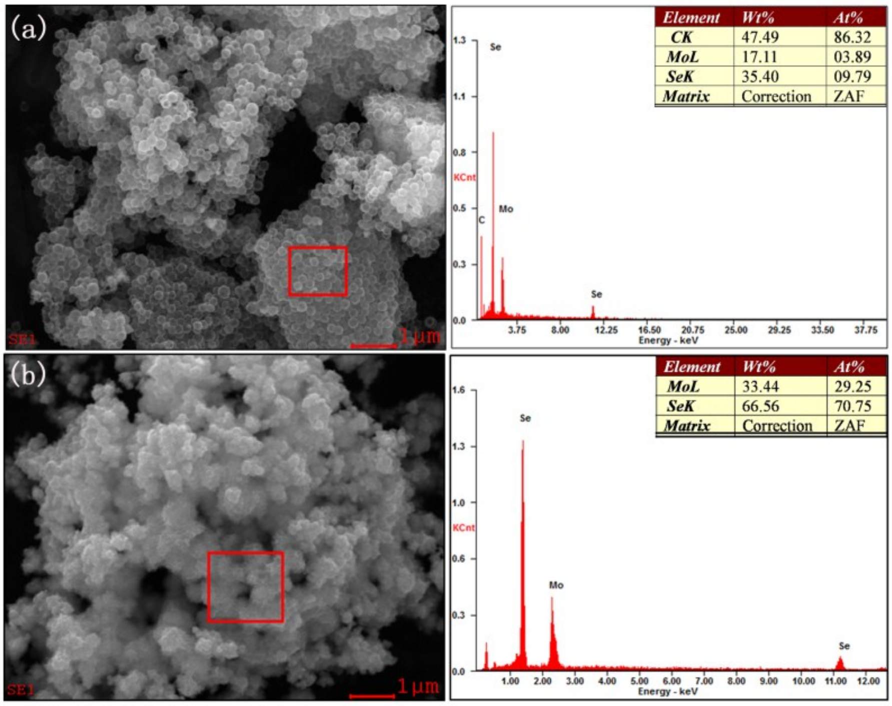


Fig. S2 SEM images (a, b) and TEM images (c, d) of $MoSe_2$ nanosheets.



Element	*Wt%*	*At%*
CK	47.49	86.32
MoL	17.11	03.89
SeK	35.40	09.79
Matrix	Correction	ZAF

Element	*Wt%*	*At%*
MoL	33.44	29.25
SeK	66.56	70.75
Matrix	Correction	ZAF

Fig. S3 SEM-energy dispersive X-ray (EDX) spectrum of the $MoSe_2$@PHCS (a) and $MoSe_2$ nanosheets (b).

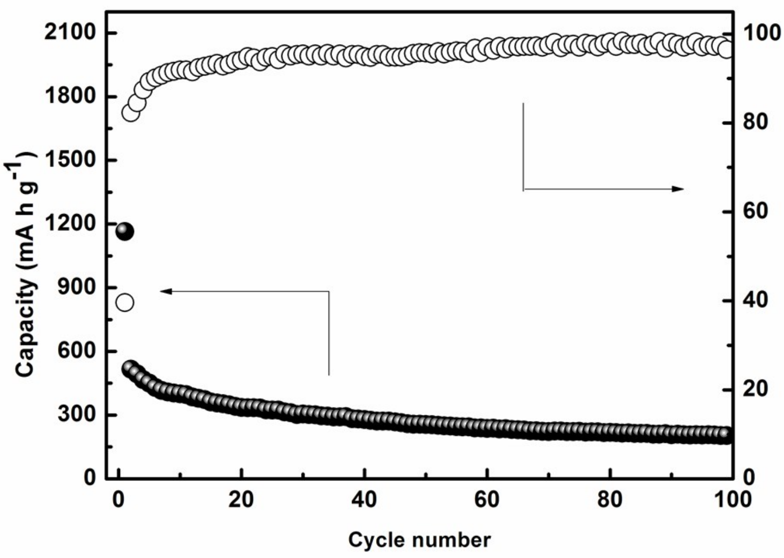


Fig. S4 Cycling performance and coulombic efficiency of porous composite hollow carbon spheres at current density of 1A g^{-1} within a voltage range of 0.01-3.0 V for lithium battery.

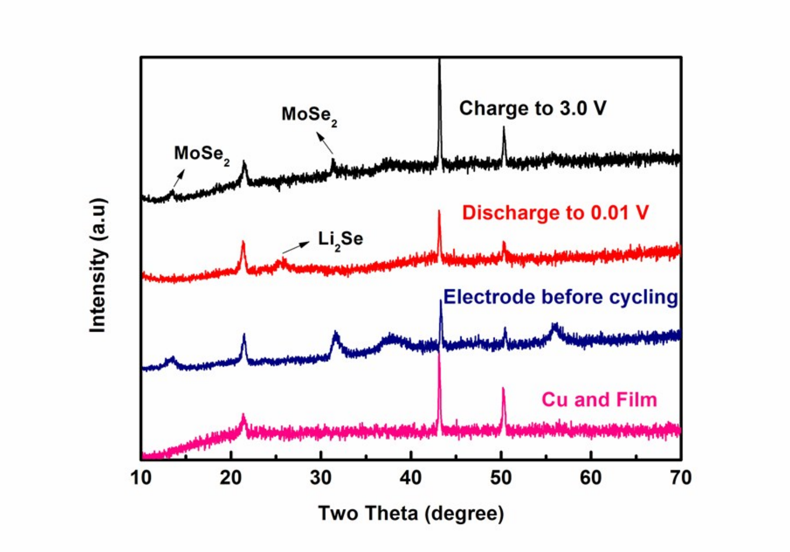


Fig. S5 The XRD measurements of MoSe$_2$@PHCS electrode before and after 100 cycles.

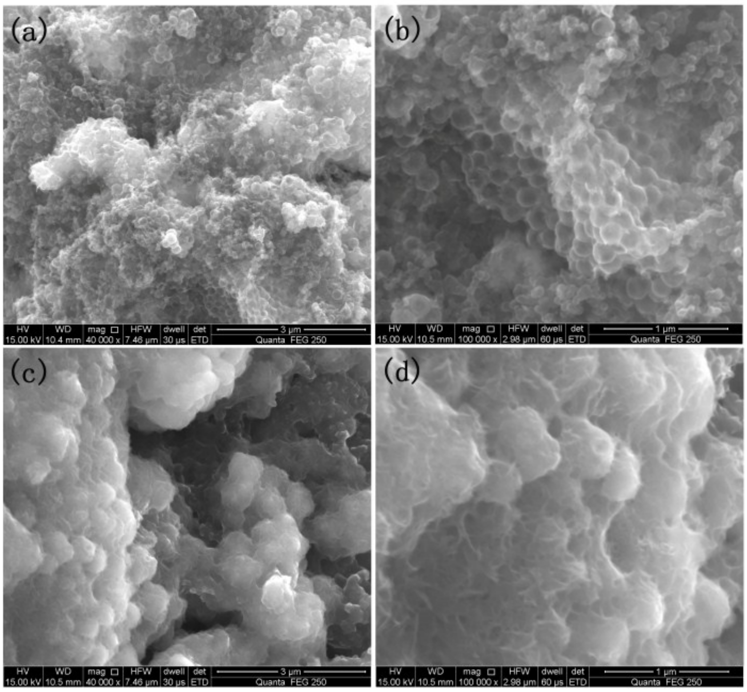


Fig. S6 SEM image of $MoSe_2$@ PHCS before cycling (a, b) and after cycling (c, d) with current density of 1 A g^{-1} for 100 cycles.

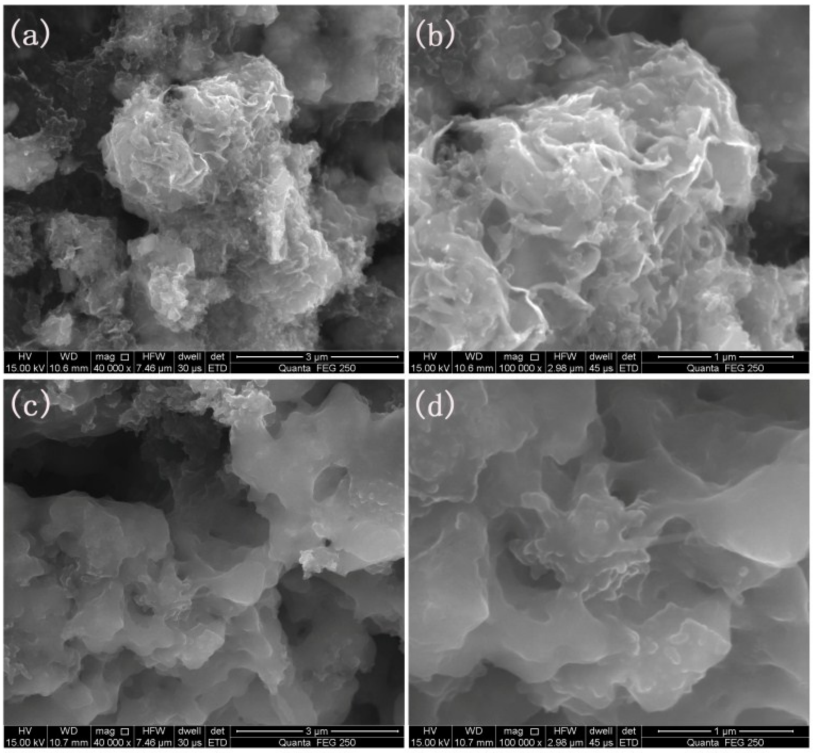


Fig. S7 SEM images of $MoSe_2$ nanosheets electrode before cycling (a, b) and after cycling (c, d) with current density of 1 A g^{-1} for 100 cycles.

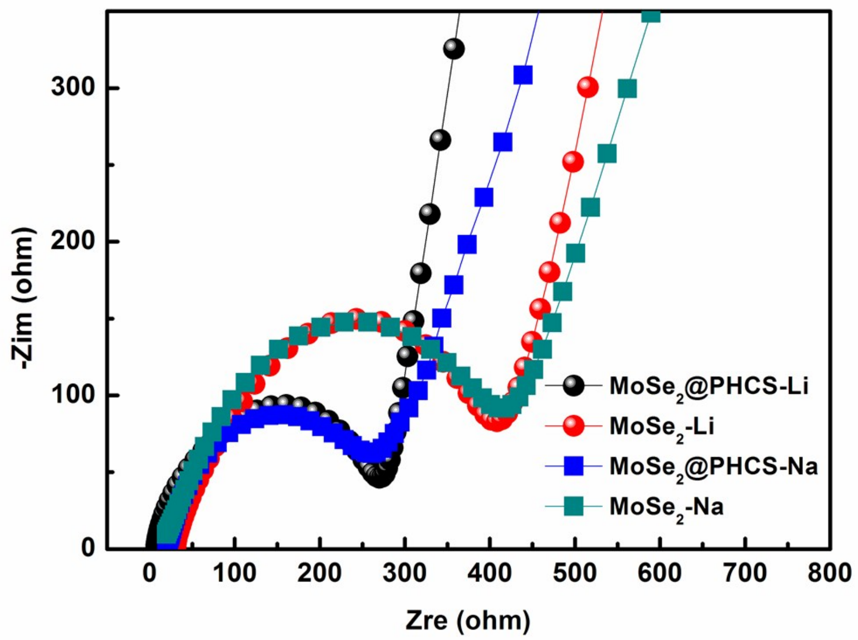


Fig. S8 Impedance plots of MoSe$_2$@ PHCS composite electrode and MoSe$_2$ nanosheets electrode for both lithium and sodium battery before cycling.