Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Construction of Hierarchical $MoSe_2$@C Hollow Nanospheres for Efficient Lithium/Sodium Ion Storage

Xueqian Zhang[a], Yali Xiong[a], Mengfei Dong[a], Zhiguo Hou[a] and Yitai Qian[b*]*

[a] School of Chemistry and Environment Engineering, Jiangsu University of Technology, Changzhou, Jiangsu 213001, China

[b] Department of Chemistry, University of Science and Technology of China, Hefei 230026, China

E-mail: hzg@jsut.edu.cn

Experimental Section

Synthesis of Mo-glycerate solid nanospheres (MoG): Mo-glycerate solid nanospheres were synthesized according to previous report[1]. In a typical synthesis, 120 mg $MoO_2(acac)_2$ and 100 mg glucose was dispersed in 10 mL H_2O, 30 mL isopropanol and 8 mL glycerol, then ultrasound for 10 min until dissolved. The formed solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave, heating at 190 ^oC for 3 h. After the reaction was completed and the autoclave was cooled to room temperature, the product was centrifuged and washed with water and ethanol for three times. The product was denoted as Mo-glycerate nanospheres (MoG). Finally, the as-prepared MoG was dispersed into 10 mL ethanol for next reaction (solution A).

Synthesis of $MoSe_2$@C hollow nanospheres ($MoSe_2$@C HNS): 100 mg Se powder was dispersed in 10 mL hydrazine hydrate solution under stirring at room temperature for 24 h (solution B). Solution B was added to solution A with 30 mL ethanol and 20 mL H_2O under stirring, 200 mg glucose was added in the mixed solution, stirring until

dissolved. The homogeneous solution was transferred into 100 mL Teflon-lined stainless-steel autoclave, heating at 200 ^{o}C for 12 h. The product was centrifuged and washed with water and ethanol for several times. After dried at 60 ^{o}C overnight in vacuum oven, the prepared $MoSe_2$ hollow nanospheres were annealed at 600 ^{o}C under Ar/H_2 atmosphere for 12 h with a heating rate of 3 ^{o}C min^{-1}.

Synthesis of bare $MoSe_2$: MoG precursors was ball-milling with 100 mg Se powder in ethanol. The mixture was heat-treated at 600 ^{o}C under Ar/H_2 atmosphere for 12 h with a heating rate of 3 ^{o}C min^{-1}.

Materials characterization: The phase and crystal characterization of samples were performed on X-ray powder diffraction (XRD, Philips) with Cu Ka radiation. Microstructure morphology is characterized by field-emitting scanning electron microscope (FESEM, JEOL-JSM-6700F). nanostructure morphology is characterized by transmission electron microscopy (TEM, Hitachi H7650 and HRTEM, JEOL 2010). Raman spectral was collected by Confocal Laser Micro-Raman spectrometer (JYLABRAM-HR). The elemental valence of samples was collected by X-ray photoelectron spectroscopy (XPS) on ESCALAB 250 spectrometer with Al Kα radiation.

Electrochemical measurements: The anode electrode was prepared by ball-milling the mixture of active material, super P and polyvinylidene fluoride (PVDF) with N-methyl pyrrolidinone (NMP) as solvent. The weight ratio of these component is 7:2:1. The well-mixed slurry was pasted to Cu foils and dried in a vacuum oven at 80 °C overnight. Each electrode was cut into circular plate with area of 1cm^2 and showed a

loading mass density of 1 mg cm^{-2}. All 2016 coin cells were assembled in a high-pure Ar-filled glove box with Li/Na foil as counter electrode. The electrolyte used in these LIBs is 1 M $LiPF_6$ dissolved in ethylene carbonate and dimethylcarbonate (EC/DMC, volume ratio 1:1, buy from Zhuhai Smoothway Electronic Material Company). The electrolyte used in these SIBs is 1 M $NaClO_4$ dissolved in ethylene carbonate and dimethylcarbonate (EC/DMC, volume ratio 1:1). Cyclic voltammetry curves and Nyquist plots were performed on Chenhua electrochemical workstation (CHI 660E, Shanghai). The $MoSe_2$@C HNS composite was etched in the mixture of HCl and H_2SO_4 to obtain carbon hollow nanosphere (CHNS). The electrochemical performance involving cycle stability and rate capability was recorded on LAND-CT2001A instruments.

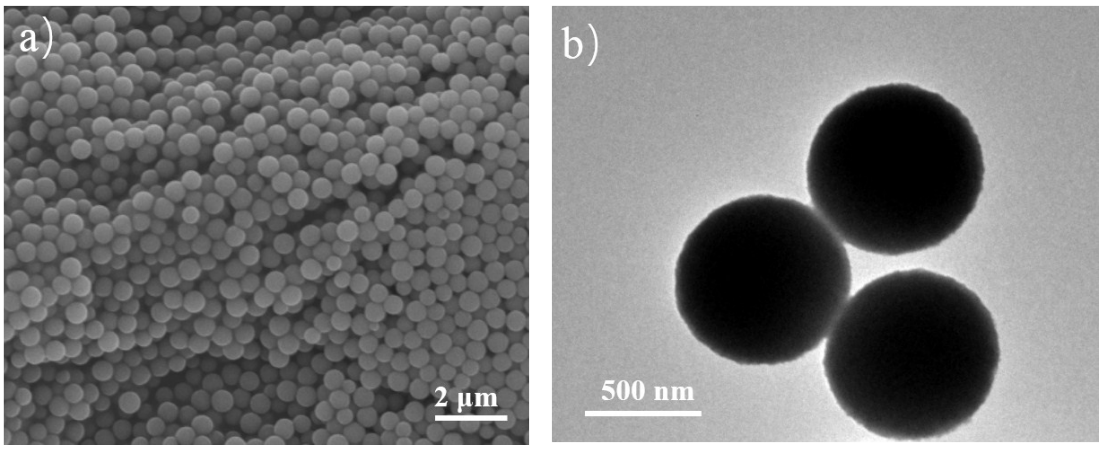

Figure S1. SEM and TEM images of MoG solid nanospheres precursors.

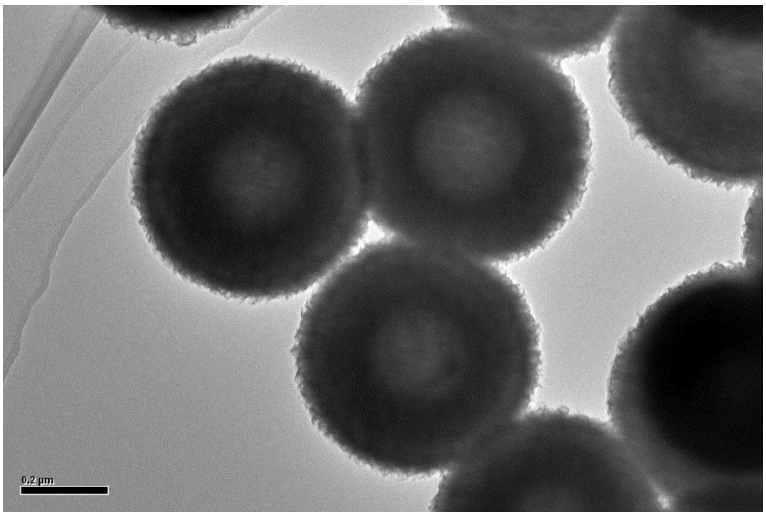

Figure S2. TEM images of $MoSe_2$@C HNS.

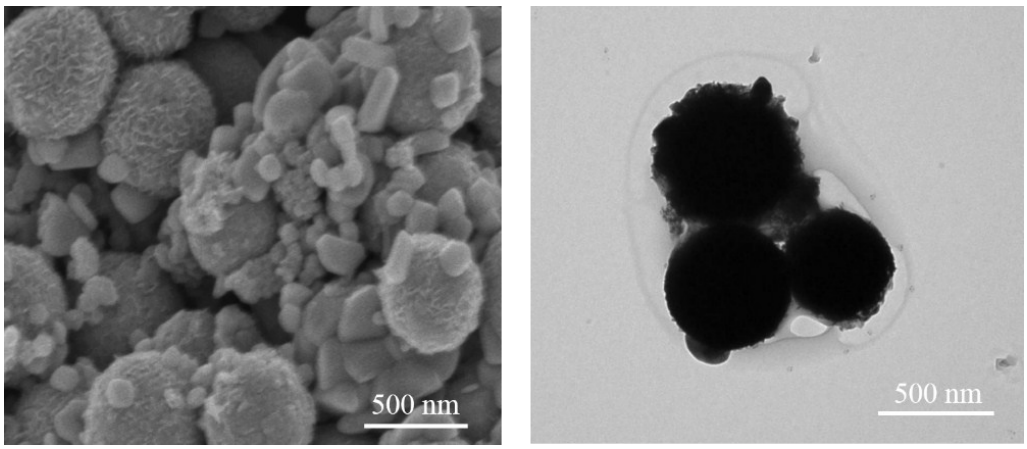

Figure S3. SEM and TEM images of bare $MoSe_2$.

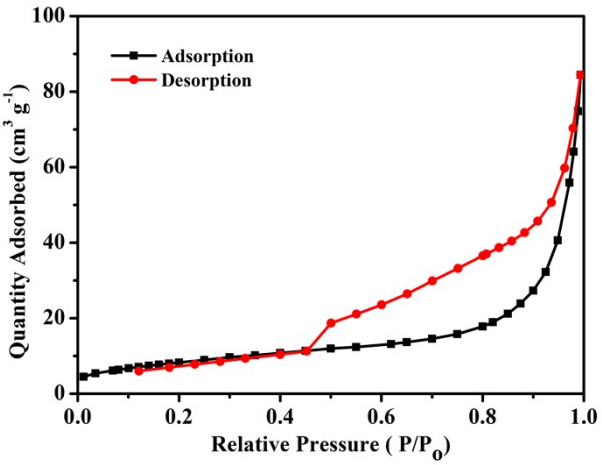

Figure S4. a) The nitrogen adsorption/desorption curve of the $MoSe_2$@C HNS composite.

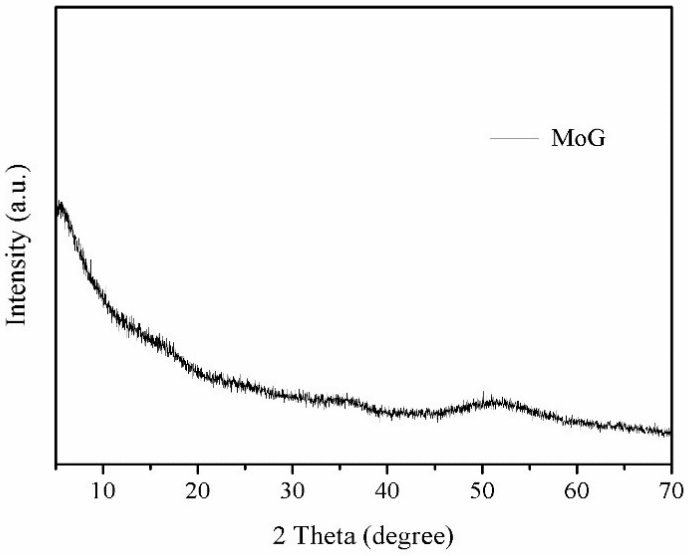

Figure S5. XRD pattern of MoG precursor.

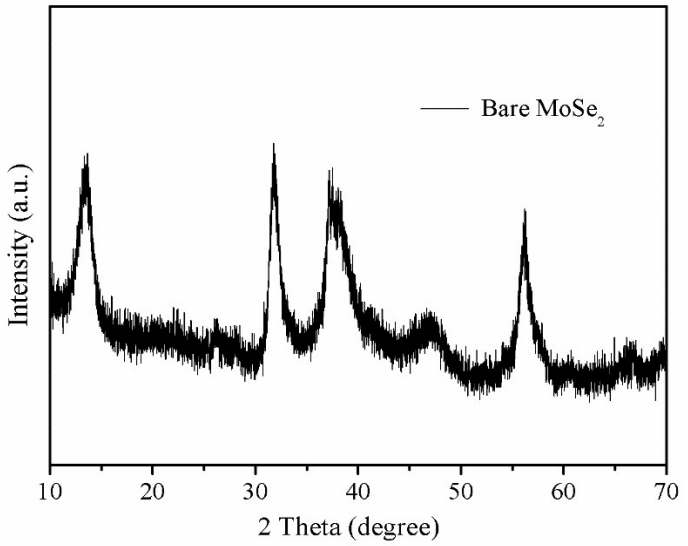

Figure S6. XRD pattern of bare $MoSe_2$.

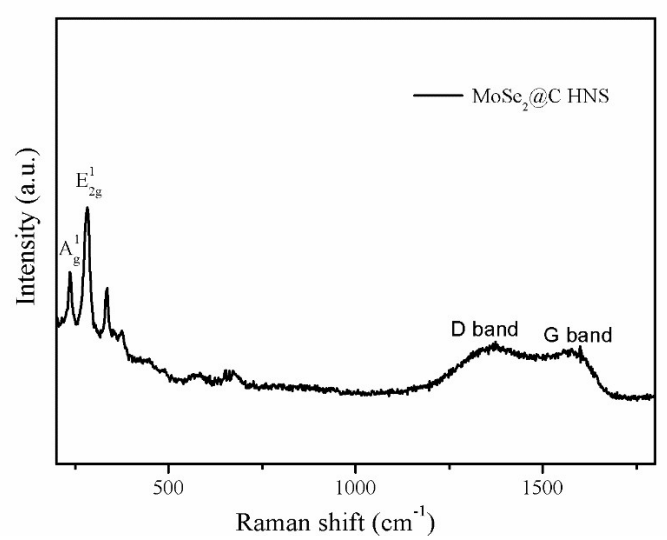

Figure S7. Raman scattering spectrum of $MoSe_2$@C HNS.

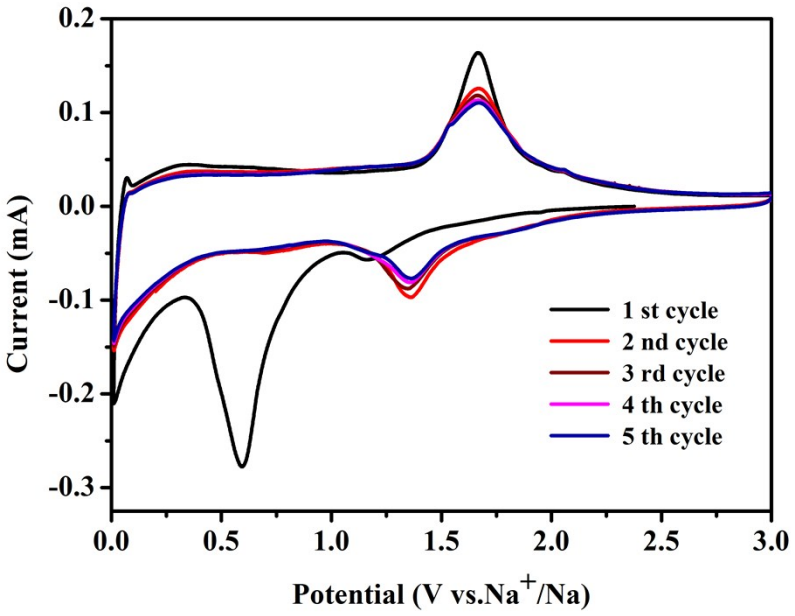

Figure S8. Cyclic voltammetry curves for first 5 cycles.

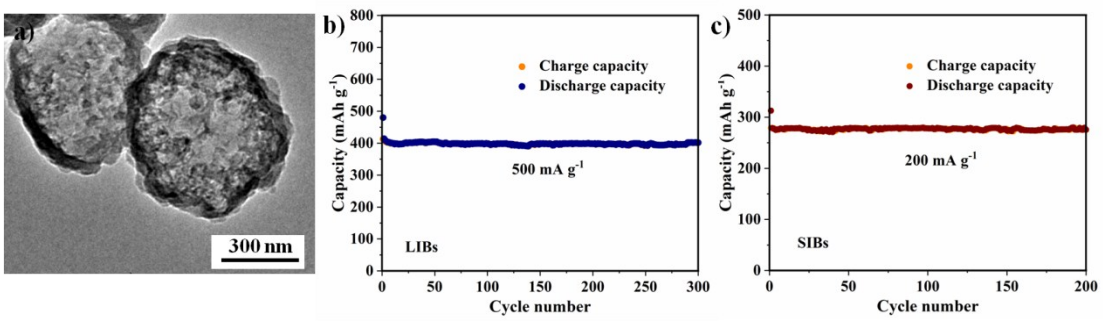

Figure S9. a) TEM image of CHNS, b) cycle performance of CHNS in LIBs at a current density of 500 mA g^{-1}, c) cycle performance of CHNS in SIBs at a current density of 200 mA g^{-1}.

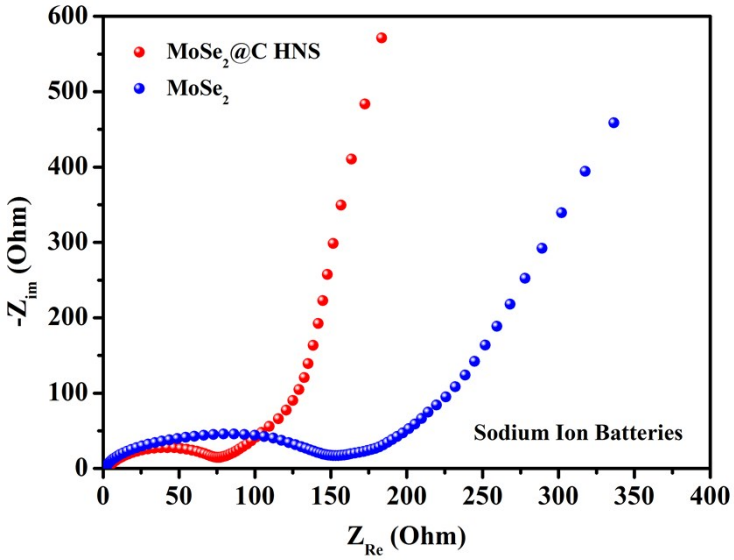

Figure S10. Electrochemical impedance spectroscopy of $MoSe_2$@C HNS and bare $MoSe_2$ for SIBs.

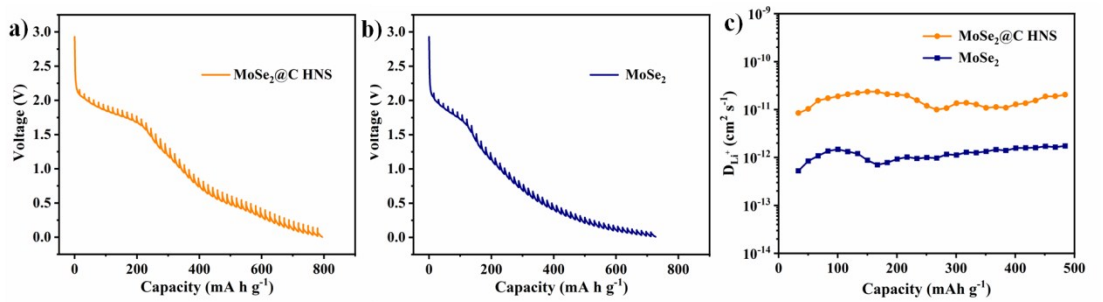

Figure S11. GITT curves of $MoSe_2$@C HNS (a) and bare $MoSe_2$ (b), D_{Li+} value calculated from GITT data (c).

Reference

1 Y. Wang, L. Yu and X. W. Lou, Synthesis of Highly Uniform Molybdenum–Glycerate Spheres and Their Conversion into Hierarchical MoS_2 Hollow Nanospheres for Lithium-Ion Batteries, *Angew. Chem. Int. Edit.*, 2016, **55**, 7423-7426.