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Electronic Supplementary Information

Hierarchical MoS_2 microboxes constructed by nanosheets with enhanced electrochemical properties for lithium storage and water splitting

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Experimental Details

Materials Synthesis. The $MnCO_3$ microcubes were synthesized according to a literature method (*Adv. Mater.* 2008, 20, 452). Typically, 10 mmol of $MnSO_4 \cdot H_2O$, 70 mL of ethanol, and 100 mmol of $(NH_4)_2SO_4$ were dissolved in 700 mL of de-ionized water to form solution A. 100 mmol of NH_4HCO_3 was dissolved in 700 mL of de-ionized water to form solution B. Solution B was added into solution A under vigorous stirring. Then, the mixed solution was heated and maintained at 50 ℃ for 9 h. The white $MnCO_3$ precipitate was collected by filtration, washed thoroughly with de-ionized water, and dried at 60 ℃.

To grow hierarchical MoS_2 shell on the $MnCO_3$ microcube templates, 0.4 g of $MnCO_3$ microcubes was dispersed into 40 mL of de-ionized water by ultrasonication for 60 min. 0.6 g of sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$) was then added to the above solution. After ultrasonication for 10 min, 2.5 g of L-cysteine was added. After ultrasonication for another 10 min, the reaction solution was then transferred to a 60 mL Teflon-lined stainless steel autoclave and kept in an electric oven at 220 ^oC for 24 h. The autoclave was then left to cool down to room temperature in the oven. The black precipitate of MnS@MoS_2 core-shell microcubes was collected by centrifugation, washed thoroughly with ethanol, and dried at 60 ^oC for 12 h.

To obtain hierarchical MoS_2 microboxes, 50 mg of MnS@MoS_2 core-shell microcubes was dispersed in 40 mL of 1.0 M HCl for 24 h at room temperature under stirring to remove MnS cores. The black product of hierarchical MoS_2 microboxes was rinsed with deionized water until the solution became neutral, and finally dried at 60 ^oC. Afterwards, the as-prepared hierarchical MoS_2 microboxes were further annealed at 800 ^oC in the atmosphere of 5% H_2 balanced by N_2 for 2 h with a heating rate of 1 $^oC\ min^{-1}$ to obtain the highly crystalline hierarchical MoS_2 microboxes. The preparation process of MoS_2 microparticles is similar to that for hierarchical MoS_2 microboxes,

except for the addition of $MnCO_3$ microcube templates.

Materials Characterization. X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advanced X-Ray Diffractometer with Ni filtered Cu Kα radiation (λ=1.5406 Å) at a voltage of 40 kV and a current of 40 mA. Field-emission scanning electron microscope (FESEM) images were acquired on a JEOL JSM-6700F microscope operated at 5 kV. Transmission electron microscope (TEM) images were taken on JEOL JEM-2010 and JEOL JEM-2100F microscopes. Nitrogen sorption measurement was performed on Autosorb 6B at liquid N_2 temperature.

Electrochemical Measurements. Lithium-ion batteries: the electrochemical tests were carried out in two-electrode Swagelok cells. The working electrode consists of 70 wt% of active material, 20 wt% of conductive carbon black (Super-P-Li), and 10 wt% of polymer binder (polyvinylidene fluoride, PVDF). The electrolyte is 1M $LiPF_6$ in a mixture of ethylene carbonate and diethyl carbonate (1:1 by weight). The typical mass loading of active materials is about 1 mg cm^{-2}. Lithium disc was used as both the counter electrode and reference electrode. Cell assembly was carried out in an Ar-filled glovebox with moisture and oxygen concentrations below 1.0 ppm. The charge-discharge tests were performed on a NEWARE battery tester. Cyclic voltammograms (CV) were obtained on a CHI 660D electrochemical workstation.

Hydrogen evolution reaction: all electrochemical measurements were conducted on an Autolab PGSTAT302 potentiostat (Eco Chemie, Netherlands) in a three-electrode cell at room temperature. A Pt foil (4.0 cm^2) and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The working electrode was prepared on a glassy carbon (GC) disk as the substrate. Typically, a mixture containing 2.0 mg of catalyst, 2.5 mL of ethanol and 0.5 mL of Nafion solution (0.05 wt%, Gashub) was ultrasonicated for 15 min to obtain a well-dispersed ink. Then 40 μL of the catalyst ink (containing 26.6 μg of catalyst) was loaded onto a glassy carbon electrode of 5

mm in diameter (loading density ~0.136 mg cm^{-2}). The presented current density refers to the geometric surface area of the glassy carbon electrode. Linear sweep voltammetry with a scan rate of 5 mV s^{-1} was conducted in 0.5 M H_2SO_4. The working electrode was mounted on a rotating disc electrode with a rotating speed of 1000 rpm during the test. In all experiments, the electrolyte solutions were purged with N_2 for 15 min prior to the measurement in order to remove oxygen. During the measurements, the headspace of the electrochemical cell was continuously purged with N_2. All the potentials reported in our manuscript were referenced to a reversible hydrogen electrode (RHE) by adding a value of (0.241+0.059 pH) V.

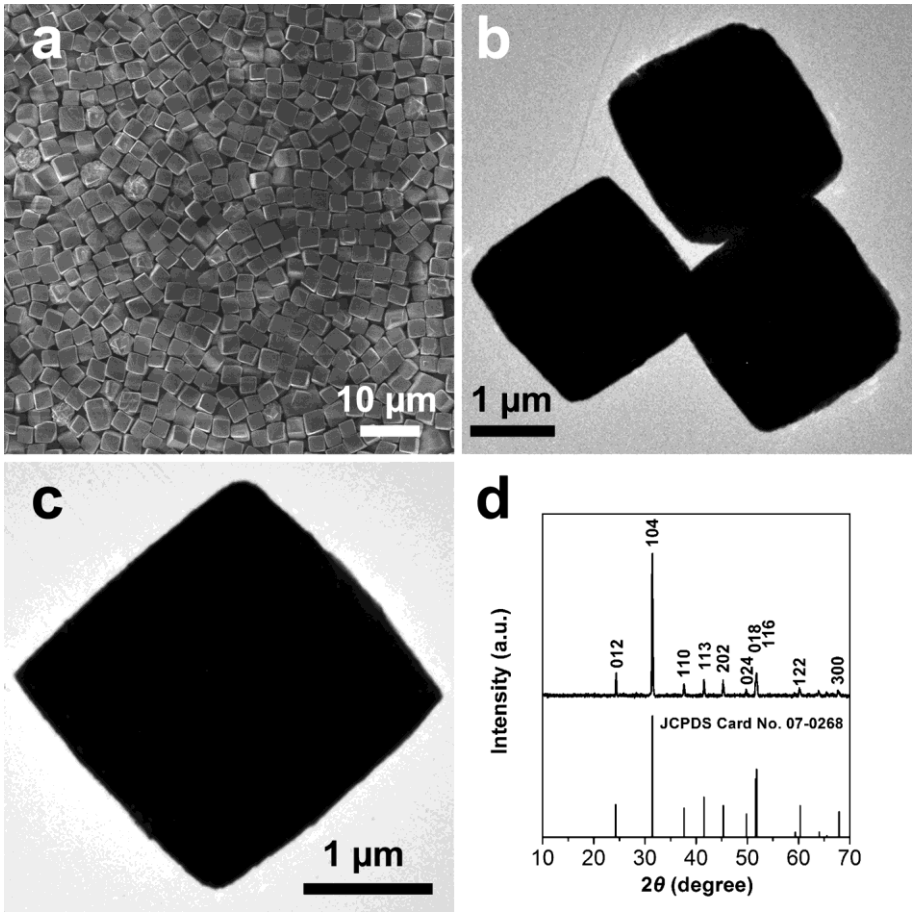

Fig. S1 FESEM (a), TEM (b, c) images and XRD pattern (d) of $MnCO_3$ microcubes.

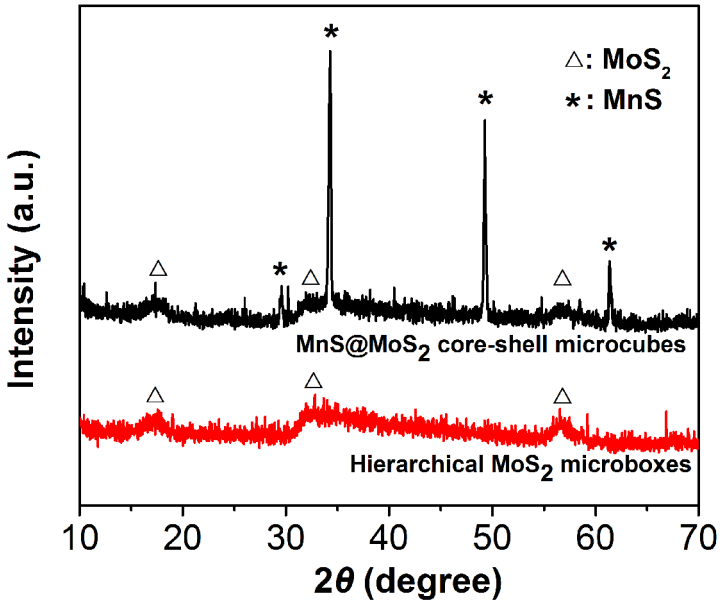

Fig. S2 XRD patterns of as-prepared hierarchical MoS_2 microboxes and MnS@MoS_2 core-shell microcubes.

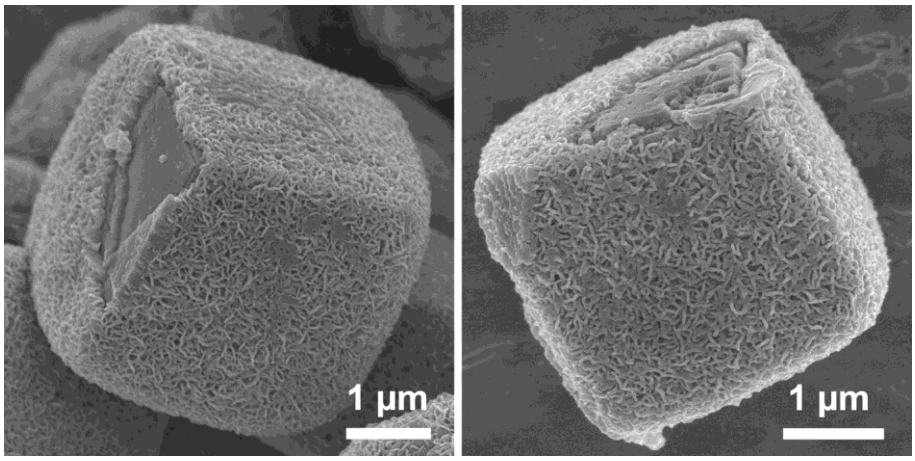

Fig. S3 FESEM images of cracked MnS@MoS_2 core-shell microcubes with hierarchical shell structures.

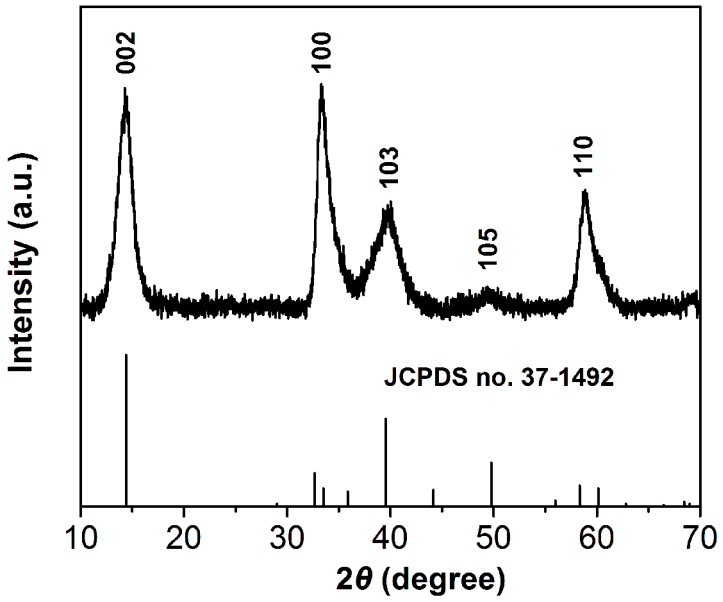

Fig. S4 XRD pattern of annealed hierarchical MoS_2 microboxes.

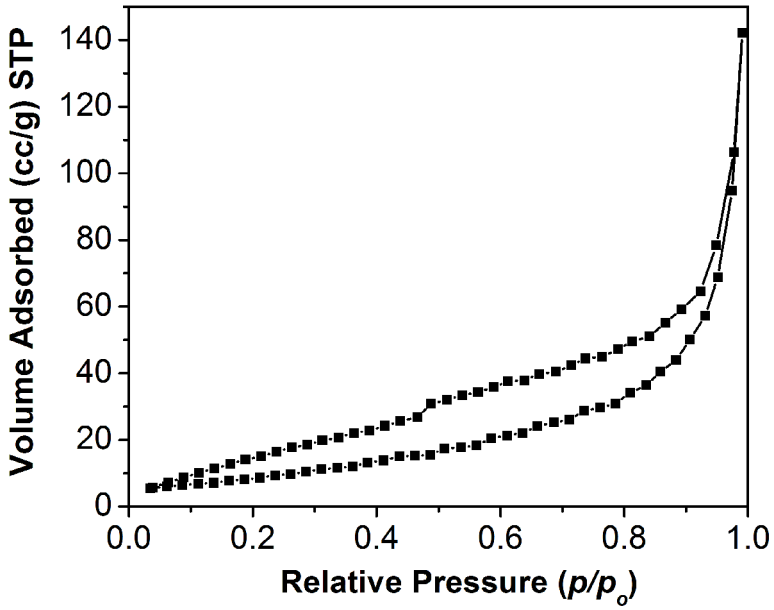

Fig. S5 N_2 adsorption-desorption isotherm of as-prepared hierarchical MoS_2 microboxes.

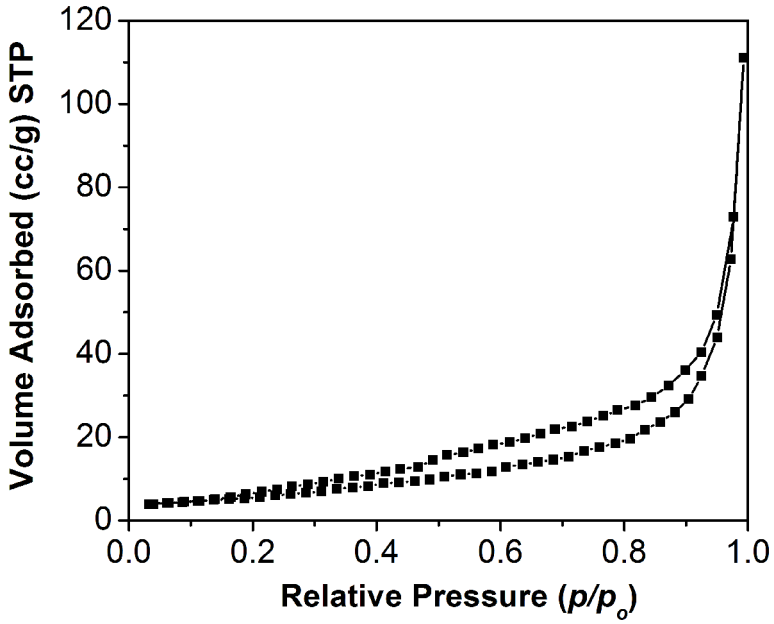

Fig. S6 N_2 adsorption-desorption isotherm of annealed hierarchical MoS_2 microboxes.

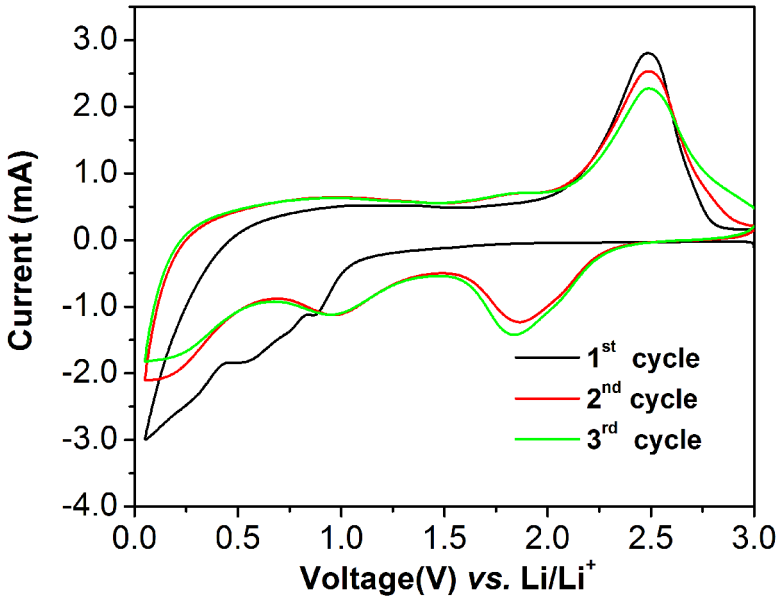

Fig. S7 CV profiles of annealed hierarchical MoS_2 microboxes showing the 1st, 2nd and 3rd cycles between 0.05 and 3.0 V at a scan rate of 0.5 mV s^{-1}.

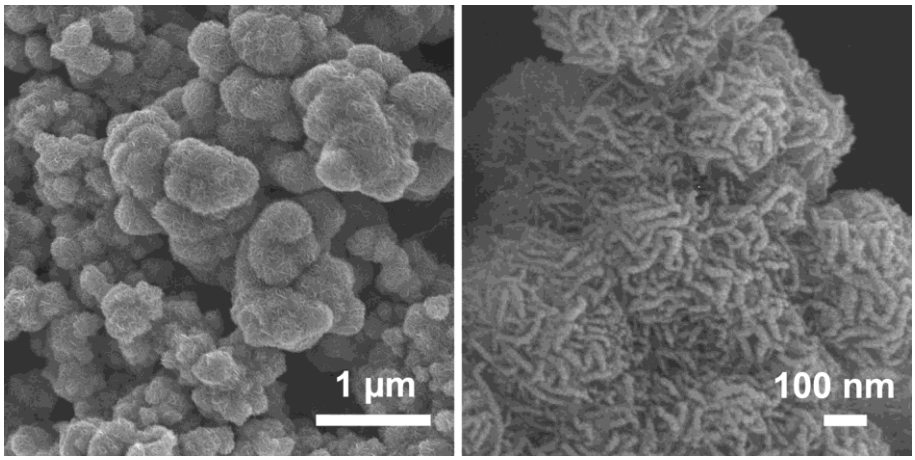

Fig. S8 FESEM images of the MoS_2 microparticles obtained without adding $MnCO_3$ microcubes templates.

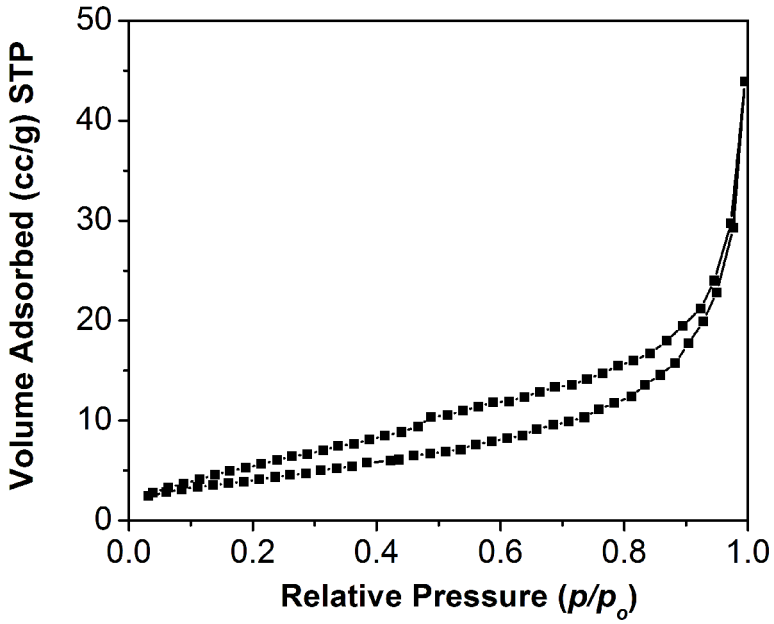

Fig. S9 N_2 adsorption-desorption isotherm of as-prepared MoS_2 microparticles.

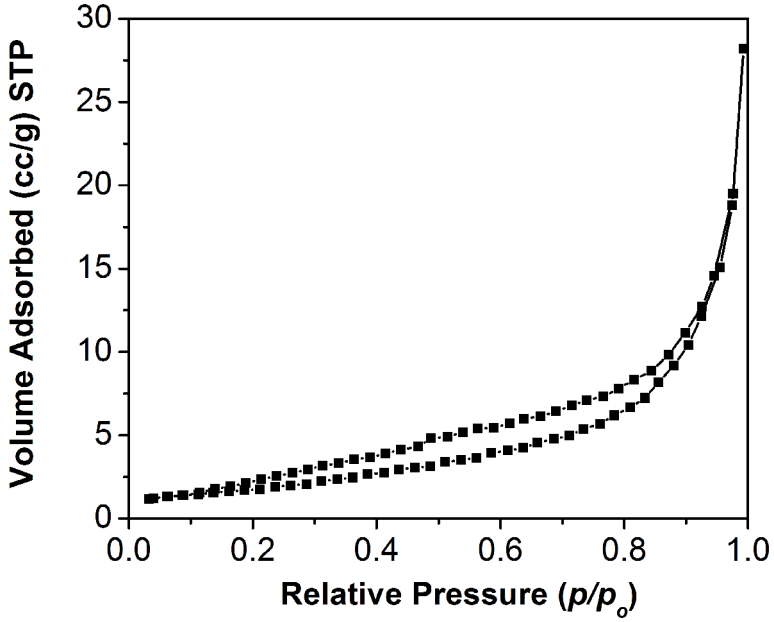

Fig. S10 N_2 adsorption-desorption isotherm of annealed MoS_2 microparticles.

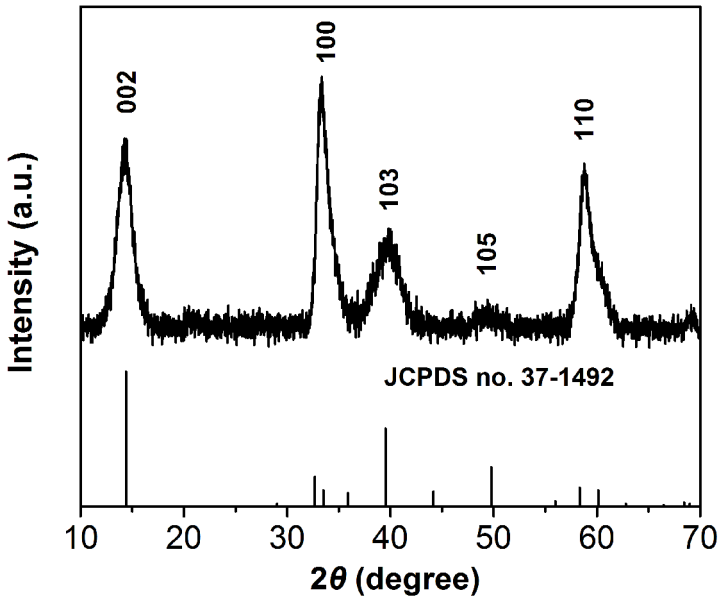

Fig. S11 XRD pattern of annealed MoS_2 microparticles.

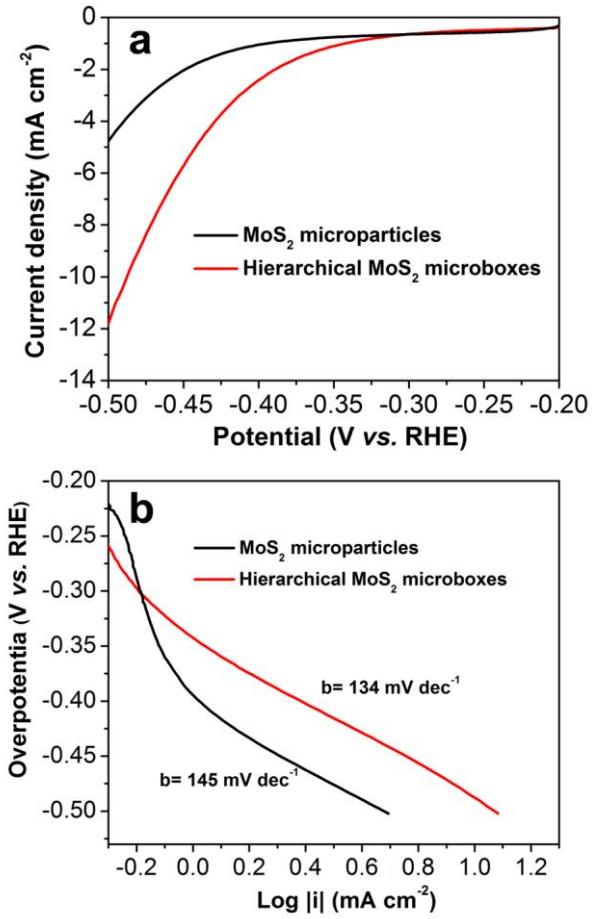

Fig. S12 (a) Polarization curves and (b) Tafel plots for the as-prepared hierarchical MoS_2 microboxes and MoS_2 microparticles.

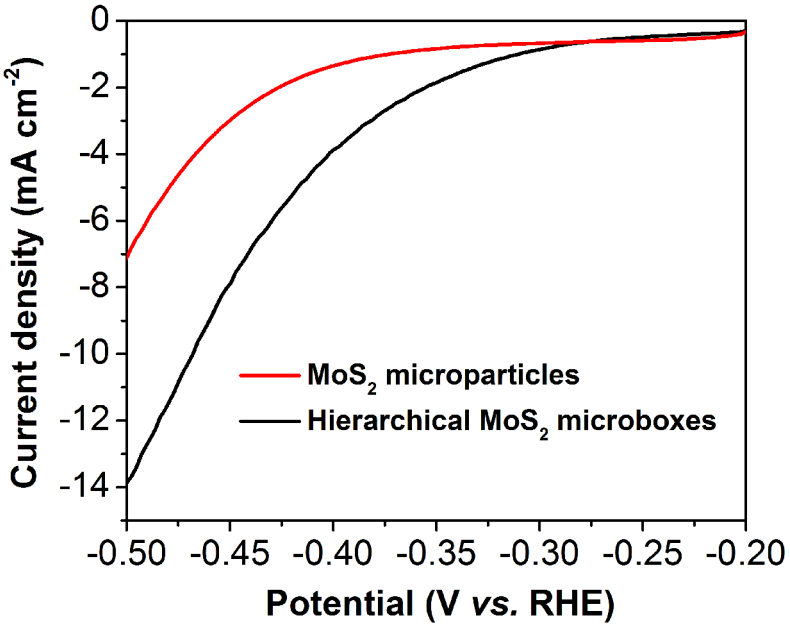

Fig. S13 Polarization curves (the 500th cycle) of the as-prepared hierarchical MoS_2 microboxes and MoS_2 microparticles.

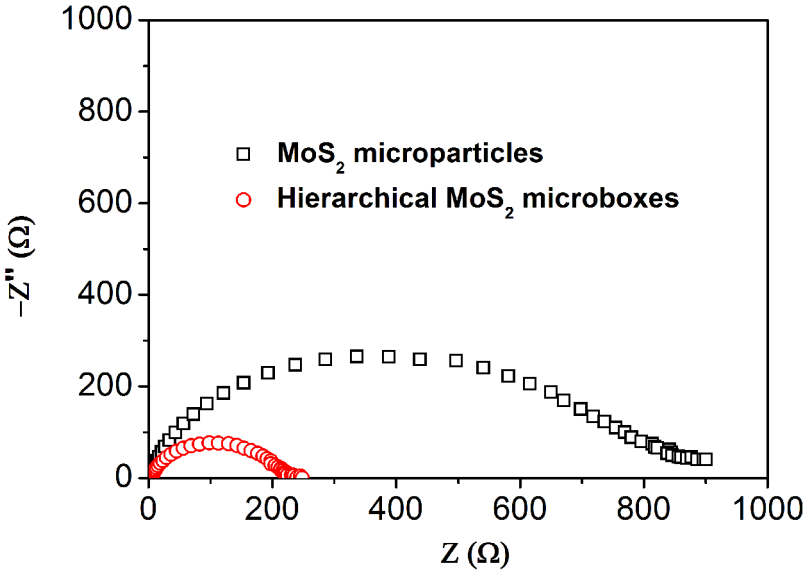

Fig. S14 Nyquist plots of the electrodes composed of as-prepared hierarchical MoS_2 microboxes and MoS_2 microparticles.

Table 1 Summary of discharge capacity of various MoS_2-based anodes.

MoS_2-based anodes	discharge capacity (mA h g^{-1})	voltage range (V)	Current density (mA g^{-1})	Reference
Hierarchical MoS_2 microboxes	900 (after 50 cycles)	0.05-3.0	100	Present study
MoS_2 nanoplates	917 (after 10 cycles)	0.0-3.0	10600	[1]
Hierarchical MoS_x/CNT nanocomposites	1000 (after 45 cycles)	0.01-3.0	50	[2]
Hierarchical MoS_2/Polyaniline Nanowires	952.6 (after 50 cycles)	0.01-3.0	100	[3]
MoS_2/N-doped graphene nanosheets	1021.2 (after 50 cycles)	0.01-3.0	100	[4]
MoS_2-Coated 3D graphene networks	877 (after 50 cycles)	0.01-3.0	100	[5]
Layered MoS_2/Graphene Composites	1187 (after 100 cycles)	0.01-3.0	100	[6]
MoS_2/graphene nanosheet composites	1290 (after 50 cycles)	0.01-3.0	100	[7]
MoS_2 nanospheres	706 (after 30 cycles)	0.01-3.0	100	[8]
Exfoliated MoS_2/PEO nanocomposite	~1000 (after 50 cycles)	0.01-3.0	50	[9]
Hierarchical MoS_2 microspheres	672 (after 50 cycles)	0.01-3.0	100	[10]

References

1. H. Hwang, H. Kim and J. Cho, *Nano Lett.*, 2011, **11**, 4826-4830.
2. Y. M. Shi, Y. Wang, J. I. Wong, A. Y. S. Tan, C. L. Hsu, L. J. Li, Y. C. Lu and H. Y. Yang, *Sci Rep*, 2013, **3**, 2169.
3. L. C. Yang, S. N. Wang, J. J. Mao, J. W. Deng, Q. S. Gao, Y. Tang and O. G. Schmidt, *Adv. Mater.*, 2013, **25**, 1180-1184.
4. K. Chang, D. Geng, X. Li, J. Yang, Y. Tang, M. Cai, R. Li and X. Sun, *Adv. Energy Mater.*, 2013, **3**, 839-844.
5. X. H. Cao, Y. M. Shi, W. H. Shi, X. H. Rui, Q. Y. Yan, J. Kong and H. Zhang, *Small*, 2013, **9**, 3433-3438.
6. K. Chang and W. X. Chen, *ACS Nano*, 2011, **5**, 4720-4728.
7. K. Chang and W. X. Chen, *Chem. Commun.*, 2011, **47**, 4252-4254.
8. S. K. Park, S. H. Yu, S. Woo, J. Ha, J. Shin, Y. E. Sung and Y. Piao, *Crystengcomm*, 2012, **14**, 8323-8325.
9. J. Xiao, D. W. Choi, L. Cosimbescu, P. Koech, J. Liu and J. P. Lemmon, *Chem. Mater.*, 2010, **22**, 4522-4524.
10. S. J. Ding, D. Y. Zhang, J. S. Chen and X. W. Lou, *Nanoscale*, 2012, **4**, 95-98.