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- Supplementary information -

Synthesis of Hierarchical Lamellar Co₃O₄-CoMoO₄ Heterostructures for Lithium-Ion Batteries

Chunfeng He,^a Bin Han,^b Shuang Han,^a Qingchi Xu,^{*a} Zhihao Liang,^a Jia Yin Xu,^d Meidan Ye,^a Xiangyang Liu^{a,c} and Jun Xu ^{*a}

^aDepartment of Physics, Research Institution for Biomimetics and Soft Matter, Fujian Key Provincial Laboratory for Soft Functional Materials Research, Xiamen University,422 Siming Nan Road, Xiamen 361005, P. R. China. E-mail: xuqingchi@xmu.edu.cn; xujun@xmu.edu.cn
^bDepartment of Biomaterials, College of Materials, Xiamen University,422 Siming Nan Road, Xiamen 361005, P. R. China.
^cDepartment of Physics, National University of Singapore, 2 Science Drive 3, Singapore, 117542, Singapore
^dDepartment of Pharmacy, The First Affiliated Hospital of Xiamen University, 55 Zhen Hai Road, Xiamen 361005, P. R. China.

1. Experimental

Materials

Molybdenyl acetoacetonate ($MoO_2(acac)_2$), Cobalt (III) acetylacetonate ($Co(acac)_3$), glycerol, ammonia solution ($NH_3 \cdot H_2O$) and isopropanol were analytical grade and purchased from Xilong Scientific Co., Ltd. Double distilled water was used in all the experiments.

Synthesis of Co₃O₄-CoMoO₄ HLHs

50 mg of molybdenyl acetoacetonate (MoO₂(acac)₂) and 120 mg cobalt (III) acetylacetonate (Co(acac)₃) were dispersed in a mixture solvent containing 8 mL of glycerol, 10 mL of H₂O and 30 mL of isopropanol. Then 300 μ L of ammonia solution (NH₃·H₂O) was added quickly into the solution and mixed vigorously to obtain a dark green transparent solution. The mixture was sonicated for 24 h until the pH reached 9-10, and then transferred to a Teflon-lined autoclave (100 mL). The autoclave was heated at 190 °C for 3 h to obtain precursors of HLHs. After cooling down to room temperature, the precursor products were centrifuged, washed with ethanol/H₂O (V/V=3:1) and dried in vacuum oven at 60 °C overnight. To get the final Co₃O₄-CoMoO₄ HLHs, the as-synthesized precursor of HLHs was annealed under Air atmosphere at 450 °C for 2 h with a temperature ramp of 5 °C min⁻¹.

Characterization

The X-ray diffraction patterns were examined by a Bruker-axs X-ray diffraction (XRD), and transmission electron microscopy (TEM) characterization was collected from JEM 1400 & 2100, with operation voltage 120 kV and 200kV. Scanning electron microscopy (SEM) was conducted with SU70, Hitachi & SIGMA 500, Zeiss. The Brunauer-Emmett-Teller (BET) surface areas of the samples were estimated using N_2 sorption isotherms on a Micromeritics 3Flex Surface Characterization Analyzer. The compositions of the products were analyzed by energy-dispersive X-ray spectrometry (EDX) combined with FESEM and X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250).

Electrochemical measurements

Typically, 70 wt% Co₃O₄-CoMoO₄, 20 wt% acetylene black, 10 wt% sodium carboxymethylcellulose were mixed into homogeneous slurry. Then the black slurry was coated on copper foil collectors and dried at 120 °C under vacuum overnight to obtain anode electrodes. All of the electrochemical properties were tested with electrodes assembled in 2032-coin cells under Ar atmosphere in a glove box. Metal lithium foil as the counter electrode, cellgard 2400 as the separator and 1 M LiPF₆ dissolved in ethylmethyl carbonate, ethylene carbonate, and diethyl carbonate (1:1:1 v/v/v) as the electrolyte. The active mass loading on the electrode was about 1 mg cm⁻². The cell assembly was carried out in an Ar-filled glovebox with moisture and oxygen concentrations below 1 ppm. The charge/discharge characteristics were determined through cycling in the potential range of 0.01-3V at diverse current densities. Cyclic voltammetry (CV) measurements were performed on an electrochemical workstation (CHI 660) between 3.0 and 0.01 vs. $(Li/Li^+)/V$ at a sweep rate of 0.1 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) tests were performed from 100 kHz to 0.01 Hz with an ac amplitude of 10 mV.



Fig. S1 SEM images of Co_3O_4 -CoMoO₄ HLHs. Inset: the layer number distribution of HLHs.



Fig. S2 N_2 adsorption/desorption isotherms (77 K) and pore size distributions (inset) of LSNs.



Fig. S3 N_2 adsorption/desorption isotherms (77 K) and pore size distributions (inset) of SLNs.



Fig. S4 TEM images of products obtained at different solvothermal times of (a) 30 min, (b) 45 min, (c) 3 h, (d) 24 h and (e) 72 h. (f) SEM image of products obtained with solvothermal time of 72 h.



Fig. S5 Schematic illustration of the main chemical steps during solvothermal reaction.



Fig. S6 XRD pattern of the HLHs precursors that obtained at solvothermal time of 30 min.



Fig. S7 Elemental mapping of LSNs obtained at solvothermal time of 30 min.



Fig. S8 XPS full spectrum of LSNs obtained at solvothermal time of 30 min.



Fig. S9 XRD patterns of the as-prepared LSNs and HLHs after being annealed in air.



Fig. S10 (a) Low and (b) high magnification SEM images of the as-prepared sample, which was obtained by the following treatment: After 30 minutes of solvothermal reaction, the reaction was quenched and Mo precursors were supplemented into the supernatant. Subsequently, the solvothermal reaction was continued for 3 h.



Fig. S11 TEM image of products obtained with different molar ratio of Co/Mo precursor: (a) Co:Mo = 1:0, (b) Co:Mo = 2:1, (c) Co:Mo = 1:1, (d) Co:Mo = 1:3, (e) Co:Mo = 1:6, (f) Co:Mo = 0:1, (g) XRD patterns of the products obtained with different molar ratio of Co/Mo precursor.



Fig. S12 SEM image of products obtained with different concentration of glycerol: (a) 0 % v/v, (b) 9 % v/v, (c) 17 % v/v and (d) 29 % v/v.



Fig. S13 SEM image of products obtained with different volume ratio of IPA/H₂O: (a) pure IPA, (b) IPA/H₂O=3/1, (c) IPA/H₂O=1/3, (d) pure H₂O. SEM images of products obtained with solvent of (e) ethanol, (f) methanol.



Fig. S14 SEM image of products obtained with different concentration of $NH_3 \cdot H_2O$ (a) 0 μ L/mL, (b) 6 μ L/mL and (c) 20 μ L/mL; (d) the size distribution of nanoparticles in (c).



Fig. S15 (a) Low and (b) high magnification SEM images of the sample obtained by the following treatment: The solvothermal reaction was quenched after 30 min. The supernatant solution was isolated by centrifugation, and further treated by the solvothermal reaction for 3 h.



Fig. S16 Solvothermal treatment of (a) LSNs, (b) MoS_2 and (c) graphene oxide with fresh prepared Co precursor solution.



Fig. S17 CV curves of (a) $CoMoO_4$ and (b) Co_3O_4 in the voltage range of 0.01-3.0 V vs. Li/Li^+ at a scan rate of 0.1 mV s⁻¹.



Fig. S18 (a) TEM image and (b, c) HRTEM images of the cycled Co_3O_4 -CoMoO₄ HLHs.



Fig. S19 XRD pattern of the cycled Co_3O_4 -CoMoO₄ HLHs



Fig. S20 (a) Mo 3d and (b) Co 2p XPS spectrum of the cycled Co₃O₄-CoMoO₄ HLHs



Fig. S21 (a) Nyquist plots for the fresh cell of Co_3O_4 and $CoMoO_4$, (b) The corresponding relationship between real resistance and frequencies, the slope of the fitting line can be adopted to calculate the ion diffusion coefficient.

The Li-ion diffusion coefficients (D) of HLHs are determined by electrochemical impedance spectroscopy (EIS) analysis, and further evaluated according to the following formula:^{1, 2}

$$Z' = \sigma \omega^{-0.5}$$

$$D = (R^2 T^2)/2A^2 n^4 F^4 C^2 \sigma^2$$

where Z', R, T, A, n, F, C, and ω stand for the real part of Nyquist impedance, gas constant, absolute temperature, electrode area, electron number, Faraday constant, molar concentration of ions, and angular frequencies. The σ can be calculated from the low-frequencies plots of EIS (Fig. S21b). As deduce from EIS spectra, σ of the CoMoO₄/Co₃O₄ HLHs is 1.75, which is significantly smaller than that of CoMoO₄ (300.66) and Co₃O₄ (36.41). Therefore, if it assumes that other parameters are same, the D of CoMoO₄/Co₃O₄ HLHs is much higher than that of CoMoO₄.



Fig. S22 SEM image of the HLHs after 100 cycles.

Hydrothermal time	30 min	45 min	1 h	3h
Moles of Co that have reacted (10 ⁻⁶ mol)	8.88	59.78	67.40	134.4
Moles of Mo that have reacted (10 ⁻⁶ mol)	6.97	43.19	56.78	75.82
Moles of unreacted Co (10 ⁻⁶ mol)	224.58	173.68	166.06	99.06
Moles of unreacted Mo (10 ⁻⁶ mol)	69.93	33.71	20.12	1.08
Co:Mo (atomic ratio)	1.27	1.38	1.187	1.77

Table S1 Testing result of ICP.

Electrode material	Initial discharge capacity (mA h g ⁻¹)	Current density (mA h g ⁻¹)	Capacity retention cycle	Capacity retention (%)	Publication Date	Ref.
multi-layer circular nanoflake Co3O4-CoMoO4	1198.15	100	100	97.6	2019	This work
CoMoO4 nanorods	1496	100	100	41.98	2015	1
three-dimensional CoMoO4 nanowire arrays	790	1200	1000	96.71	2015	2
Porous CoMoO4 nanorods	834	400	300	72.3	2017	3
CoMoO4/Co3O4 hollow porous octahedrons	1175.1	200	100	96.1	2018	4
CoMoO ₄ Submicrometer Particles	990	100	50	100	2012	5
CoMoO4@G	994	100	40	97.3	2015	6
CoMoO4 microspheres	1019	500	150	100	2014	7
CoMoO₄@Graphene Nanofibers	735	100	200	80	2016	8
mesoporous CoMoO ₄	1128.05	100	150	87.76	2016	9
Hollow Co–Mo Mixed Oxide Nanostructures	918	200	100	100	2016	10
MoO ₃ @CoMoO ₄	887.36	200	140	85.3	2019	11
CoMoO ₄ Nanoparticles	920	740	600	91.3	2014	12

 Table S2 Comparison of electrochemical performances of multi-layer circular nanoflake Co₃O₄-CoMoO₄

 with previously reported CoMoO₄ composite electrodes for LIB.

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