

Electronic Supplementary Information

Ultrathin and High-Ordered CoO Nanosheet Arrays for Lithium-Ion Batteries with High Cycle Stability and Rate Capability

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Experiment section

Synthesis of CoO Nanosheet Arrays (NSAs). All chemical reagents used in this study were analytical (AR) grade. Electrochemical deposition was carried out in a simple two-electrode electrolytic cell via galvanostatic electrodeposition, and the graphite electrode was used as a counter electrode (spectral grade). The details of the fabrication are described in the following procedures: 1) Co(OH)_2 was electrodeposited in solution of 0.1 M $\text{Co(NO}_3)_2$ with current density of 0.1 mA cm^{-2} at $70 \text{ }^\circ\text{C}$ for 20 min. The nickel foams (99.5%, 1.5 cm^2) were used as the substrates for electrodeposition, and they were prepared complying the following steps before each experiment: firstly dipped in HCl solution (about 6%) for 10 min, then rinsed with distilled water and ethanol in ultrasonic bath for 5 min, respectively; 2) CoO NSAs were obtained by calcining the Co(OH)_2 NSAs precursor at $200 \text{ }^\circ\text{C}$ in Ar flow for 3 h. The mass of CoO on nickel foam substrate is 1.20 mg, which is obtained by the high precision electronic balance (Sartorius AG, CPA225D, 0.01 mg).

Materials Characterization. The surface morphologies of the synthesized CoO NSAs were characterized by field emission scanning electron microscopy (SEM, Quanta 400) and transmission electron microscope (TEM, Tecnai™ G2 F30). The synthesized nanomaterials were also characterized by energy-dispersive X-ray spectroscopy (EDX, INCA 300) to determine the deposit compositions. Chemical-state analysis of deposits was carried out by X-ray photoelectron spectroscopy (XPS) using an ESCALAB 250 X-ray photoelectron spectrometer. All XPS spectra were corrected using the C 1s line at 284.8 eV. Curve fitting and background subtraction were accomplished.

Electrochemical Measurements. The electrochemical performance of the CoO NSAs were tested in a half cell (CR2025) which was assembled in an argon-filled glove box (Mikrouna, super 1220) where the oxygen and moisture contents were less than 1 ppm. Lithium metal was used as the counter electrode. The electrodes were separated by a glass fiber separator and liquid electrolyte mixtures containing 1 mol L^{-1} LiPF_6 and a solvent mixture of ethylene carbonate (EC) and diethyl carbonate (DMC) (1:1 by mass) (Beijing Institute of Chemical Reagents, China). The galvanostatical discharge and charge were performed with the voltage between 0.01 and 3.0 V vs. Li/Li^+ using a Battery Testing System (Neware Electronic Co., China). Cyclic voltammetry curves were measured at a scanning rate of 0.2 mV s^{-1} within the potential range of 0.01-3.0 V vs. Li/Li^+ using an electrochemistry working station (Zahner IM6ex).

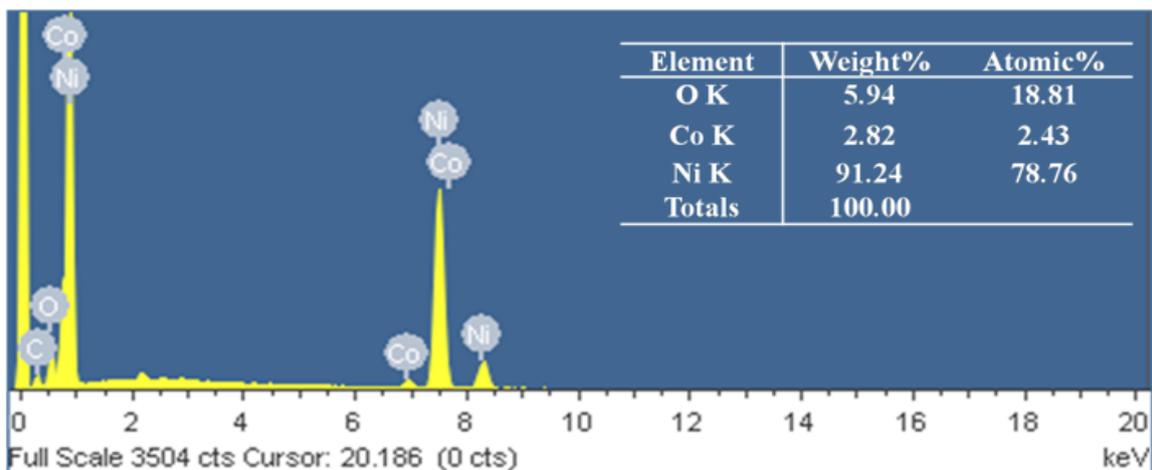


Fig. S1 EDX pattern of $\text{Co}(\text{OH})_2$ NSAs on nickel foam substrate (by SEM-EDX).

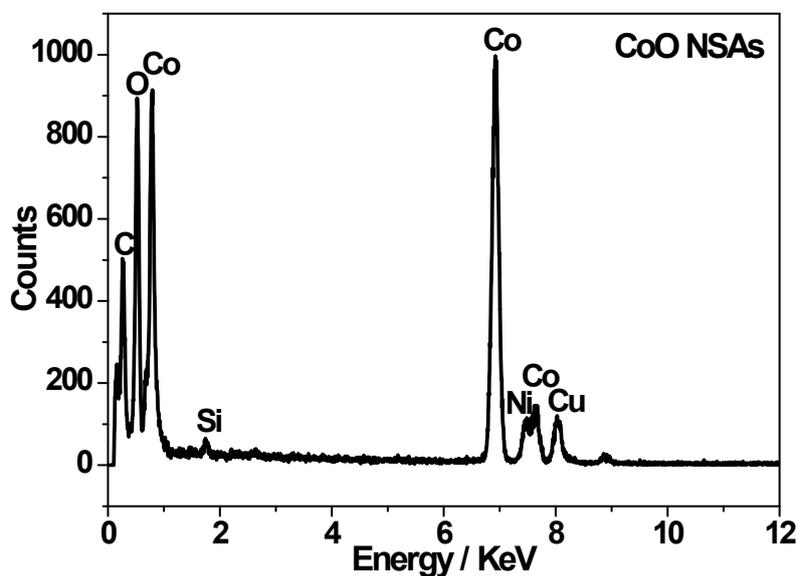


Fig. S2 EDX pattern of CoO NSAs (by TEM-EDX).

The chemical composition of the CoO NSAs was determined by energy-dispersive X-ray (EDX), and the Co/O atomic ratio is about 0.75 as shown in Fig. S2. The result suggest that there is a successful conversion of the precursor $\text{Co}(\text{OH})_2$ to CoO .

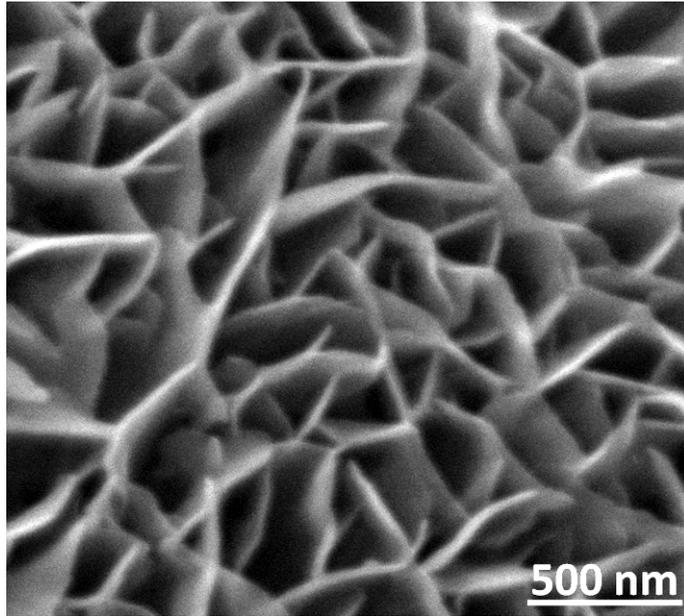


Fig. S3 SEM image of Co(OH)_2 NSAs.

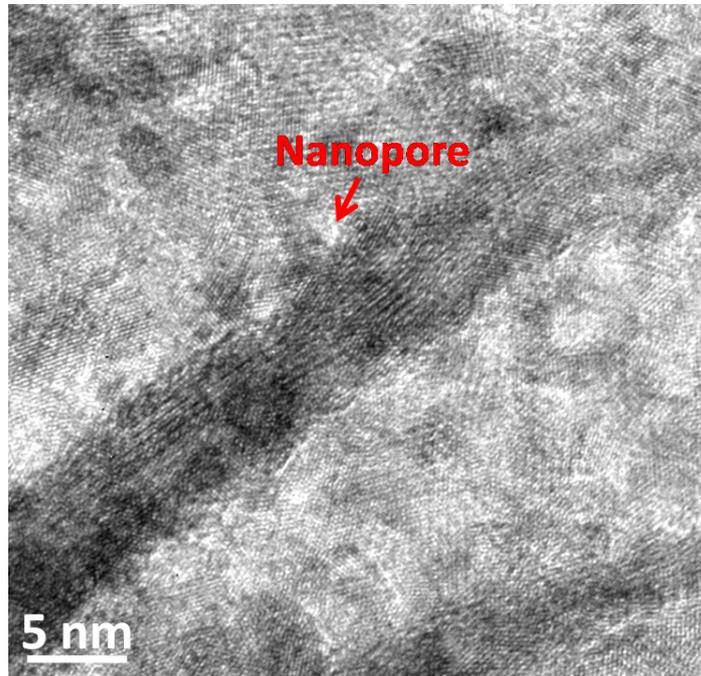


Fig. S4 HRTEM image of CoO NSAs.

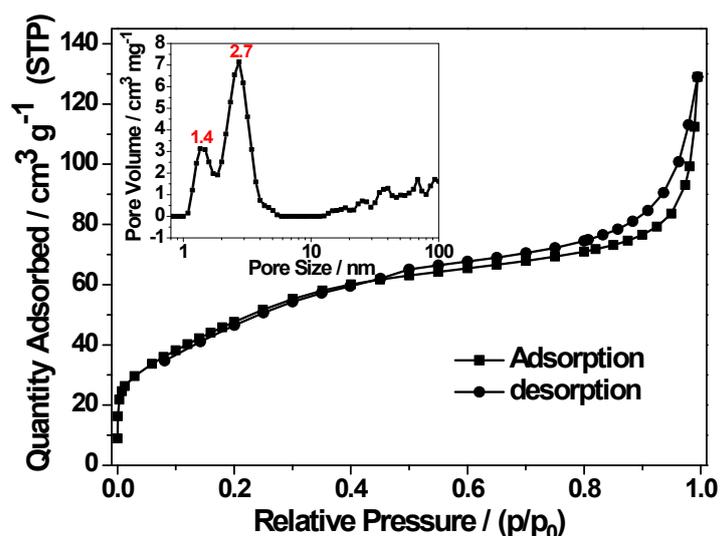


Fig. S5 N₂ adsorption/desorption isotherms and PSD (inset) of the CoO NSAs scratched down from the Ni foam.

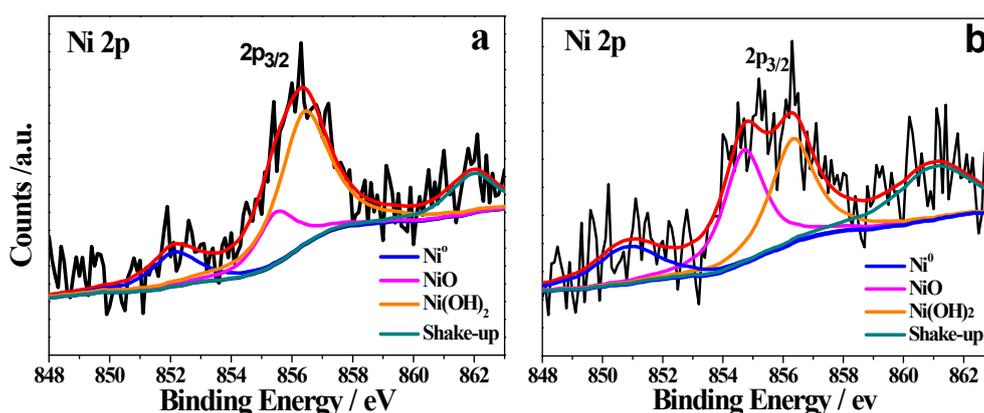


Fig. S6 XPS spectra of Ni 2p for (a) Co(OH)₂ NSAs and (b) CoO NSAs on the nickel foam substrates.

Fig. S6a and b show XPS spectra of Ni 2p for Co(OH)₂ NSAs and CoO NSAs on nickel foam substrates, respectively. The Ni 2p peaks (Fig. S6a) at binding energies of 856.4 and 854.7 eV are assigned to Ni(OH)₂ and NiO, respectively, which should be attributed to the partial oxidation of nickel foam substrate during the electrodeposition process in a high temperature precursor solution. Compared to the Ni 2p peaks in Fig. S6a, it can be seen that the peak intensity at binding energy of 856.4 eV in Fig. S6b significantly weakened while that at binding energy of 854.7 eV has an obvious enhancement. These results can be attributed to the conversion of the Ni(OH)₂ to NiO during the thermal treatment. In addition, a comparison of the integrated intensity of Ni 2p and Co 2p spectra shows that the NiO and Ni(OH)₂ compositions are almost negligible in the CoO NSAs electrode.

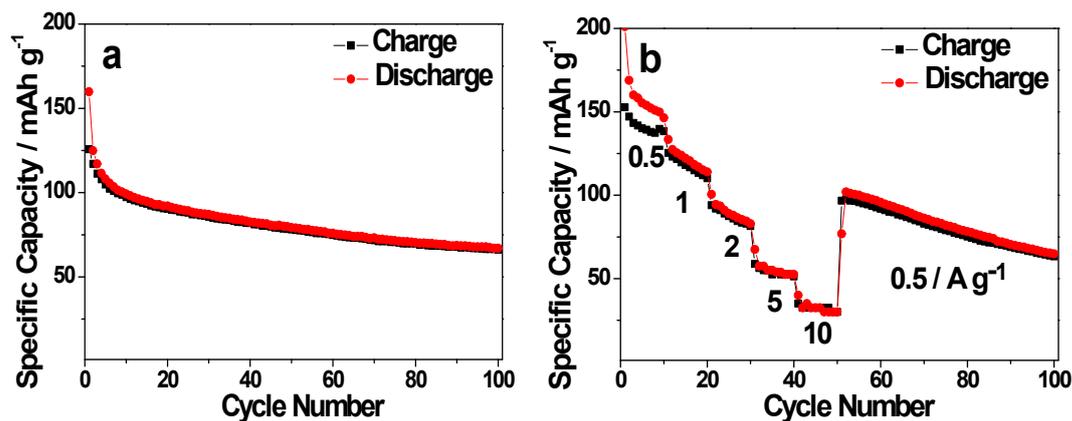


Fig. S7 (a) Cycling performance of the nickel foam electrode at a current density of 1 A g⁻¹ and (b) at various current densities of 0.5, 1, 2, 5, 10 A g⁻¹. All carried out in the voltage range 0.01-3.0 V vs. Li/Li⁺.

Considering NiO and Ni(OH)₂ can contribute to the capacity during charge and discharge cycles, herein, the nickel foam substrate was directly used as an anode for LIBs without electrodeposition of the CoO NSAs. Fig. S7a gives the cycling performance of the nickel foam electrode at a constant current density of 1 A g⁻¹. It is clearly seen that the first charge capacity of the nickel foam electrode is 125 mA h g⁻¹ and a rapid decline in the subsequent cycles. The same phenomenon is observed in Fig. S7b and the capacity is only 30 mA h g⁻¹ at the current density of 10 A g⁻¹, which indicates that the capacities of NiO and Ni(OH)₂ are negligible compared to the total capacity of CoO NSAs, especially at the high current density.