## Supplementary Information for:

# Porous $Co_3O_4$ nanoneedle arrays growing directly on copper foils and their ultrafast charging/discharging as lithium-ion battery anodes

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### SI-1. Experimental materials

All chemicals were of analytical grade and used as purchased without further purification. Copper foils, $Co(NO_3)_2 \cdot 6H_2O$ and 1.2 g of $CO(NH_2)_2$ were all supplied by Sinopharm Chemical Reagent Co. Ltd.

### SI-2. Material synthesis

1.164 g of $Co(NO_3)_2 \cdot 6H_2O$ and 1.2 g of $CO(NH_2)_2$ were dissolved in 40 ml of water under stirring. After stirring for 15 min, the homogeneous solution was transferred into a Teflon-lined stainless steel autoclave. Then, a piece of cleaned copper foils with the size of 20×50 mm were immersed into the reaction solution closing to the inner wall of the autoclave. The autoclave was sealed and maintained at 95 °C for 8 h. After cooling down to room temperature spontaneously, the copper foil coated with NN arrays was picked out, rinsed with distilled water and ethanol, and dried at 60°C under vacuum for 2 h. Finally, the copper foil coated with NN arrays was annealed at 400 °C in argon ambience for 3 h.

### SI-3. XRD analysis

The crystal phase of $Co_3O_4$ NN arrays was identified by X-ray power diffraction (XRD; D/max

2550V, Cu Kα Radiation, λ=1.5416 Å).

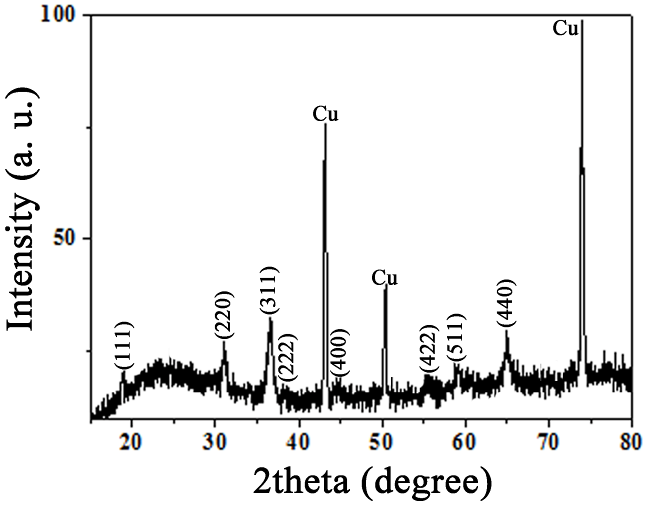

**Figure S1** XRD patterns of porous $Co_3O_4$ NN arrays on copper foils.

Fig. S1 is XRD pattern of $Co_3O_4$ NN arrays growing directly on copper foils, showing their crystal phase. The diffraction peaks at 19.0°, 31.3°, 36.9°, 38.5°, 44.8°, 55.7°, 59.4° and 65.2° can be indexed to (111), (220), (311), (222), (440), (422), (511) and (440) planes of $Co_3O_4$ crystal given by the standard data file (JCPDS file No. 42-1467, space group: Fd-3m (227); lattice constants: a = 8.083 A°). Such sharp diffraction peaks indicate the well crystallization of $Co_3O_4$ NN arrays. The other three strong diffraction peaks at 43.1°, 50.4° and 73.9° can be indexed to the copper foil substrate (JCPDS file No. 04-0836, space group: Fd-3m (225); lattice constants: a = 3.6150 A°) and no sharp peaks can be indexed to other impurities. These results indicate that $Co_3O_4$ NN arrays with high crystalline purity have been obtained.

## SI-4. Battery fabrication and electrochemical measurements

Before fabrication of LIBs, a thermal treatment of the copper foils coated with NN arrays was performed at 100 °C under vacuum for 12h to eliminate the condensed water and surface hydroxide groups. Pieces with the diameters of 15 mm were cut off and directly used as the electrodes without any ancillary materials. The 2016 coin-type cells were assembled in an argon-filled glove box, and pure Li foils were used as the counter electrodes. The electrolyte was made of 1 M $LiPF_6$ in the mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with the volume ratio 1:1. The cells were galvanostatically charged and discharged between 0.001 and 3.00 V versus $Li^+/Li$ at room temperature on a program-controlled test system.

### SI-5. TEM images of $Co_3O_4$ NNs.

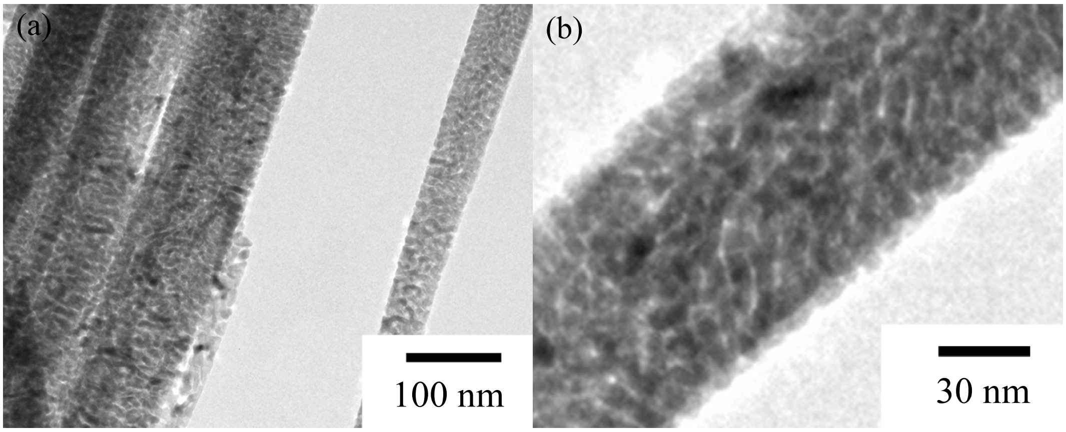

**Figure S2** TEM images of $Co_3O_4$ NNs in different magnification.

Fig. S2 are TEM images of $Co_3O_4$ NNs, showing that the average diameter of the pores is ~3 nm.