Supplementary information for

Synergistic Sodiation of Cobalt Oxide Nanoparticles and Conductive Carbon Nanotubes (CNTs) for Sodium-ion Battery

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1. METHODS

Nanocomposite preparation. Co_3O_4/CNT nanocomposites were synthesized by a simple and convenient hydrothermal method according to our group prior publication.[1, 2] In a typical experimental procedure, 200 mg cobalt (III) acetate tetrahydrated and 15 mg carbon nanotube were dissolved in 20 mL mixed solution of dimethylformamide (DMF) and water with volume ratio 8:2 by magnetic stirring for 30 min. Then the solution was transferred to a Teflon-lined autoclave of 25 mL capacity. The stainless steel autoclave was sealed and maintained at 120 ^oC for 2 h. After the autoclave was subsequently cooled to ambient temperature, newly produced precipitates were collected by filtration after being washed with ethanol and deionized water repeatedly, and dried in an oven at 60 ^oC.

***In situ* TEM experiments.** A nanobattery system was built inside TEM by using the nanofactory STM-TEM holder, which could provide a positive/negative bias between two electrodes in the circuit. Co_3O_4/CNT were adhered to one end of Au rod by using the conductive epoxy, acted as the working electrode. Sodium scratched directly by W rod was used as the counter electrode. Two electrodes of the nanobattery could contact each other by controlling precisely the pizo-motor with movement resolution by ~1nm inside TEM. The bias range of this holder is from -10 V to +10 V, which is enough for driven sodium ions moving from sodium source to react with active material in the nanobattery open cell. During the sodiation process, a negative bias -2.5 V was applied and a positive +3-4 V was applied to the circuit on desodiation. The electron dosage is carefully monitored in the experiments to minimize its effects on the current observations. In a controlled experiment, a similar reaction mechanism has been observed when the electron dose rate is $5*10^5$ e^-/ nm^2.

2. Supplementary Figures

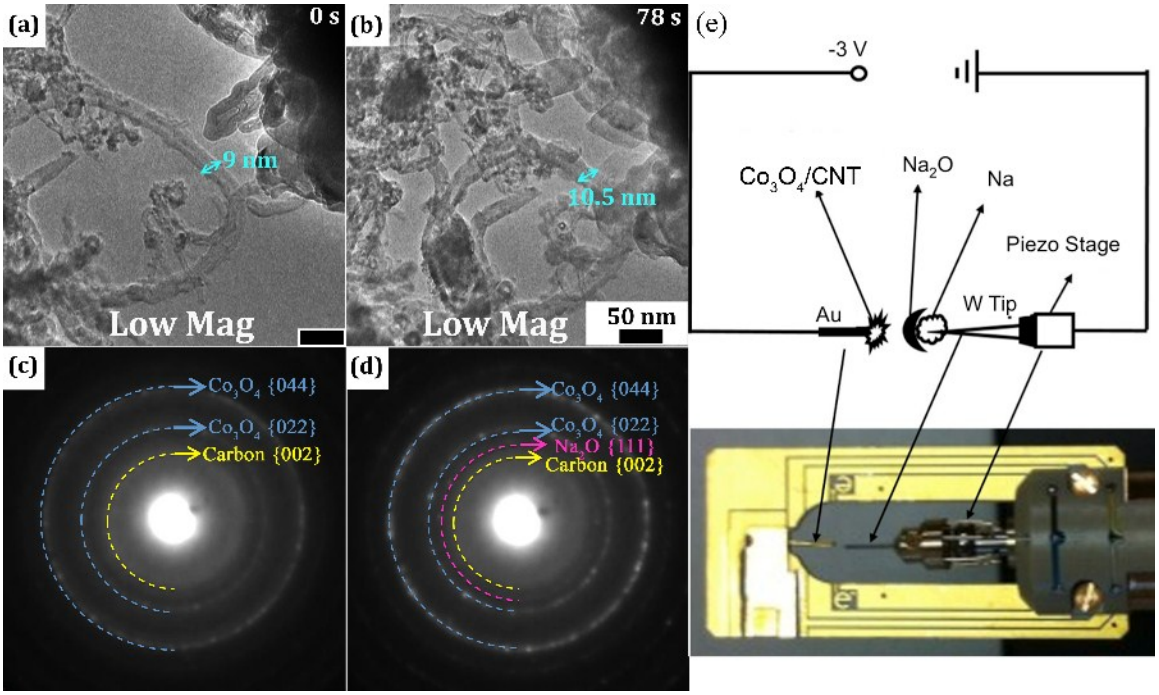

Figure S1. The first stage of sodiation process with Na_2O layer coating on both surfaces of Co_3O_4 nanoparticles and CNT. (a-b) The morphology before and after Na_2O layer coverage, accompanying the diameter of CNT increased from 9 nm to 10.5 nm. (c-d) The electron diffraction patterns of the Co_3O_4/CNT composite before and after Na_2O coating. (e) (e) Schematic diagram of the nanobattery built inside the TEM along with the tip of the Nanofactory in-situ TEM holder.

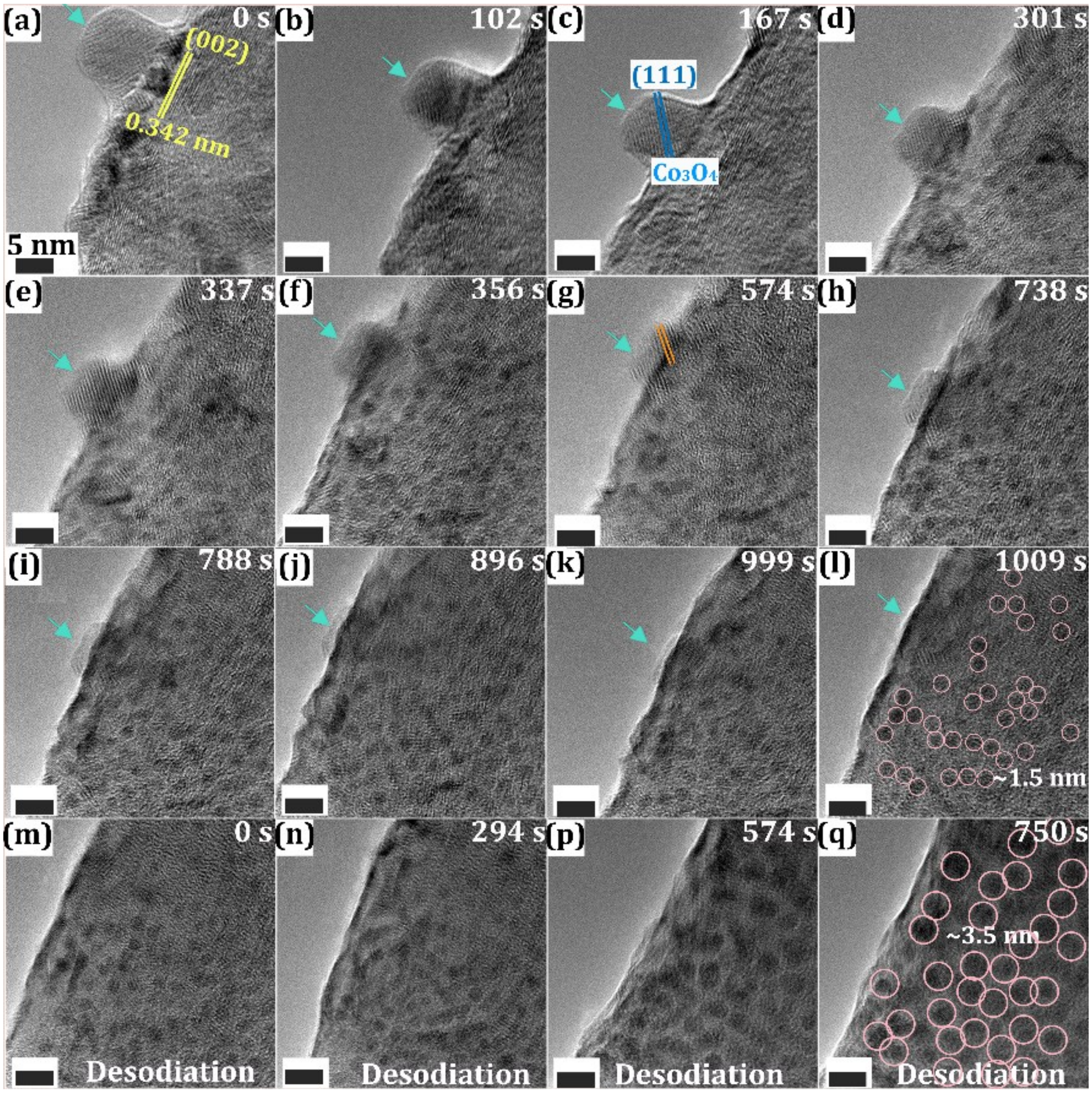

Figure S2. The propagation of the electrochemical conversion reaction of one single Co_3O_4 NP. (a) A HRTEM image of one Co_3O_4 NP and carbon nanotube, the d-spacing of 0.342 nm corresponded to the {002} lattice plane of carbon nanotube. (b-l) The evolutions of the Co_3O_4 nanoparticle in size and morphology along with the reaction with Na-ions in the first sodiation. (m-q) The morphology and structure evolution in the first desodiation.

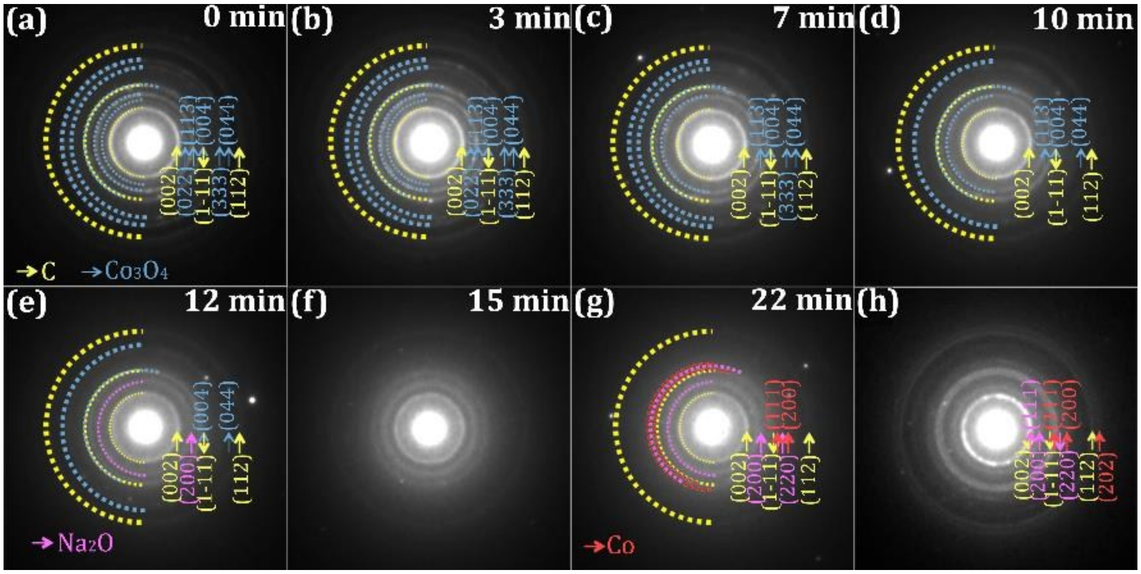

Figure S3. Microstructure evolution of Co_3O_4/CNT in the first sodiation process. (a) The diffraction pattern of pristine Co_3O_4/CNT nanocomposite. (b-e) Several diffraction rings of spinel Co_3O_4 (blue semicircle) gradually disappeared along with sodiation. (f-g) Na_2O diffraction rings and a diffused ring corresponding to Co gradually appeared in the late stage of sodiation. (h) The diffraction pattern was taken form the region with more materials and giving a stronger diffraction signal.

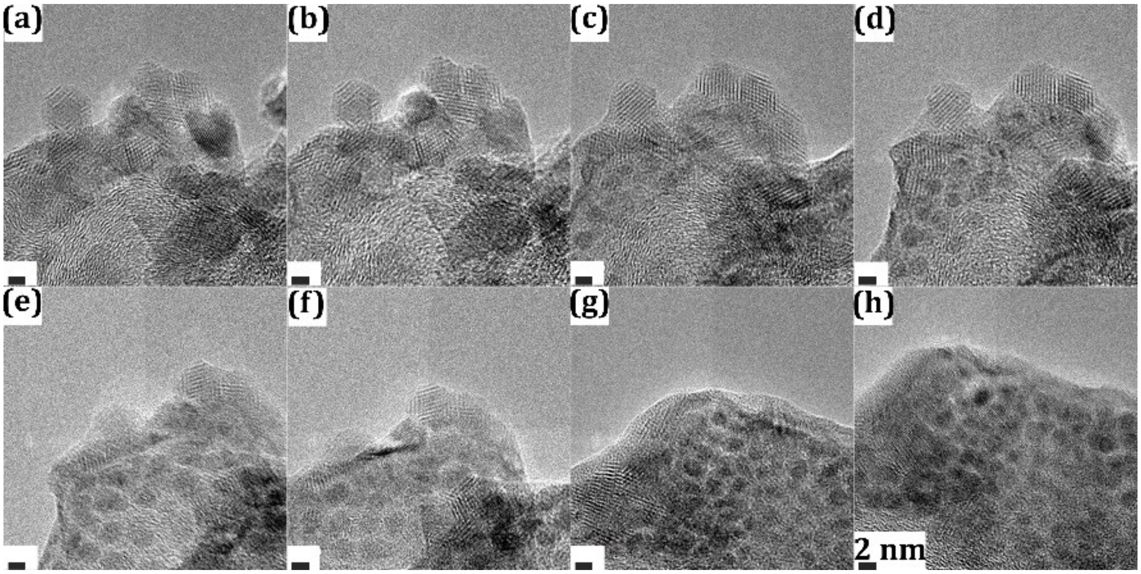

Figure S4. (a-h) The corresponding morphology evolution during the first sodiation process.

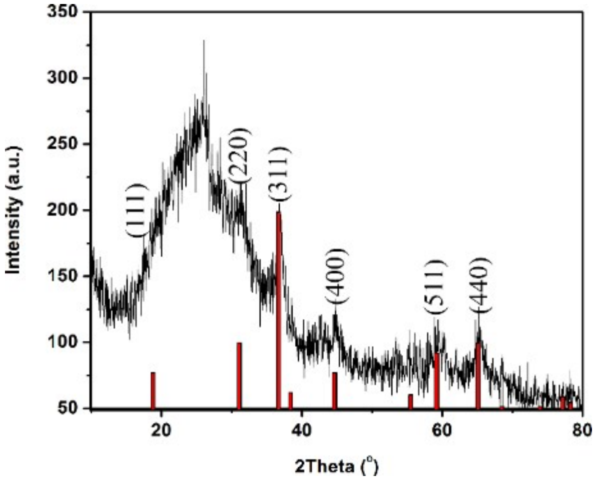

Figure S5. **X-ray powder diffraction pattern of the Co_3O_4/CNT composites**. All the diffraction peaks labelled can be indexed by the Co_3O_4 spinel phase, implying the high purity of the composite.

3. Supplementary Movies

Movie 1 Atomic resolution observation of electrochemical sodiation of single Co_3O_4 nanocube grown on carbon nanotube under bias of -2.5V.

Movie 2 Atomic resolution observation of electrochemical desodiation of Co_3O_4 nanocubes on carbon nanotube under bias of +4V.

Movie 3 Atomic resolution observation of electrochemical sodiation of Co_3O_4 nanocube clusters grown on carbon nanotube under bias of -2.5V.

Reference

1. J. Xu, J. Wu, L. Luo, X. Chen, H. Qin, V. Dravid, S. Mi and C. Jia, *J. Power Sources*, 2015, **274**, 816-822.
2. J. Cheng, L. Liu, J. Zhang, F. Liu and X. Zhang, *Journal of Electroanalytical Chemistry*, 2014, **722**, 23-31.