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Supporting Information

Preferential Growth of Co_3O_4 Anode Material with Improved Cyclic Stability for Lithium-Ion Batteries

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Experimental methods

Preparation of preferentially grown Co_3O_4 embedded in a carbonaceous matrix: The agarose gel was initially prepared by dissolving powdered agarose (1 g) in deionized (DI) water (99 mL) with vigorous stirring at room temperature. The solution was heated to boiling using a microwave oven. The above aqueous solution was then cast on stainless steel (SS) substrates (2 x 3 cm) by a dip-coating method, followed by gelation and drying at room temperature for 4 hours. 0.05 M of $Co(NO_3)_2$ and 0.075 M of $NaNO_3$ were added to the DI water. The electrodeposition was performed potentiostatically at – 1.0 V (vs Ag/AgCl) for various times (100, 200, 300, 400 s) at room temperature. The agarose coated SS was employed as a working electrode. A Pt plate and Ag/AgCl were used as the counter electrode and reference electrode, respectively. After electrodeposition, the as synthesized films were rinsed with DI water and dried at room temperature for 24 h. The resulting films were calcined at 350 ℃ for 2 h under a nitrogen atmosphere. For comparison, a pure Co_3O_4 film without an agarose template was electrodeposited following the similar procedure without an agarose template for 300 s.

Characterization: The surface morphology and composition of the electrodeposited films were obtained by scanning electron microscope (SEM, Carl Zeiss, SUPRA 55VP), focused-ion beam microscope (FIB, Carl Zeiss, AURIGA), and energy dispersive spectrometer (EDS, Bruker, Xflash5030 detector). X-ray diffraction (XRD, Rigaku, D/max-2200) was used to examine the composite structure. Chemical bonding information was studied with fourier transform infrared spectroscope (FT-IR, Thermo Scientific, Nicolet 6700).

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Electrochemical measurement: Electrochemical experiments were performed using a conventional coin cell (CR2032) assembled in an argon-filled glove box. A lithium foil and microporous polypropylenes were used as the counter electrode and separator, respectively. The electrolyte solution was a solution of 1 M $LiPF_6$ in a mixture of ethyl carbonate and diethyl carbonate with the volume ratio of EC/DEC = 1:1. The electrode capacity was measured by the galvanostatic charge and discharge method with a constant current density of 890 mA/g in the voltage range of 0.01-3.0 V on a battery tester (WonA tech, WBCS3000). The electrochemical impedance spectroscope (EIS) of the electrode was performed on an electrochemical workstation (WonA tech, ZIVE SP2). The frequency of EIS ranged from 0.01 Hz to 200 kHz at the open circuit potential.

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Supplementary Figures

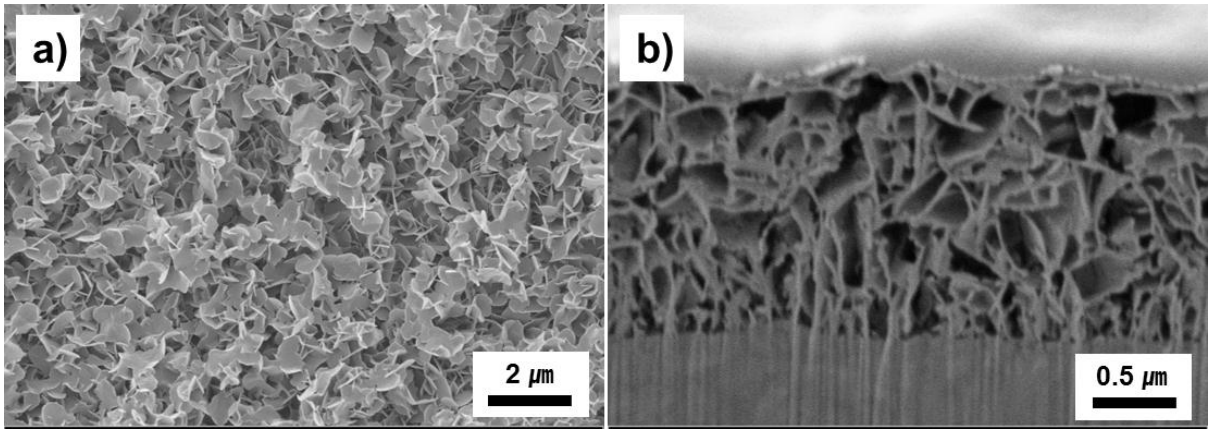

Fig. S1. SEM images of electrodeposited thin films; (a and b) top and side views of Co_3O_4 electrodeposited for 300s (Co_3O_4_300s).

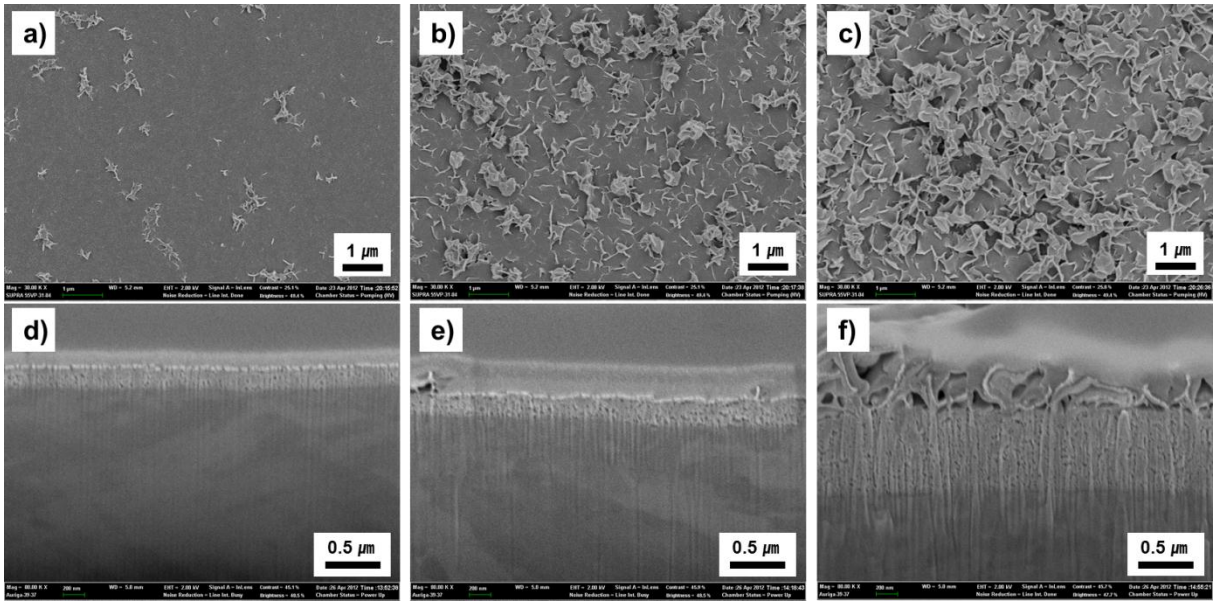

Fig. S2. SEM images of top and side views of as-synthesized Co_3O_4/C as a function of electrodeposition time; (a and d) 100 s, (b and e) 200 s, and (c and f) 400 s.

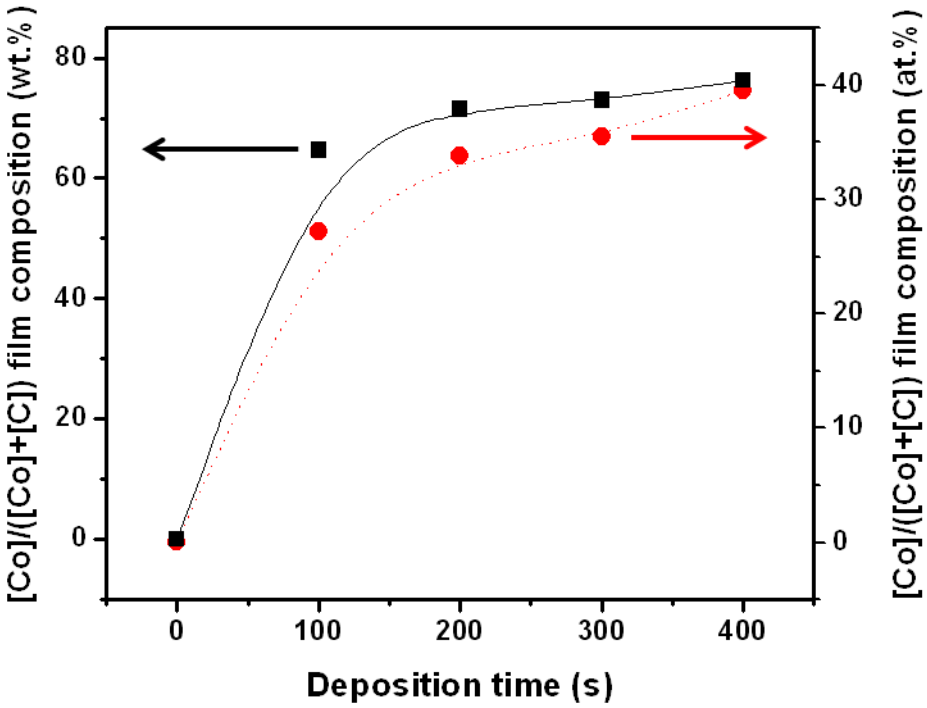

Fig. S3. Variations in Co content in the Co_3O_4/C composite as a function of electrodeposition time. Each value represents the average of three different deposits. The deviation of the film composition was less than 5 %.

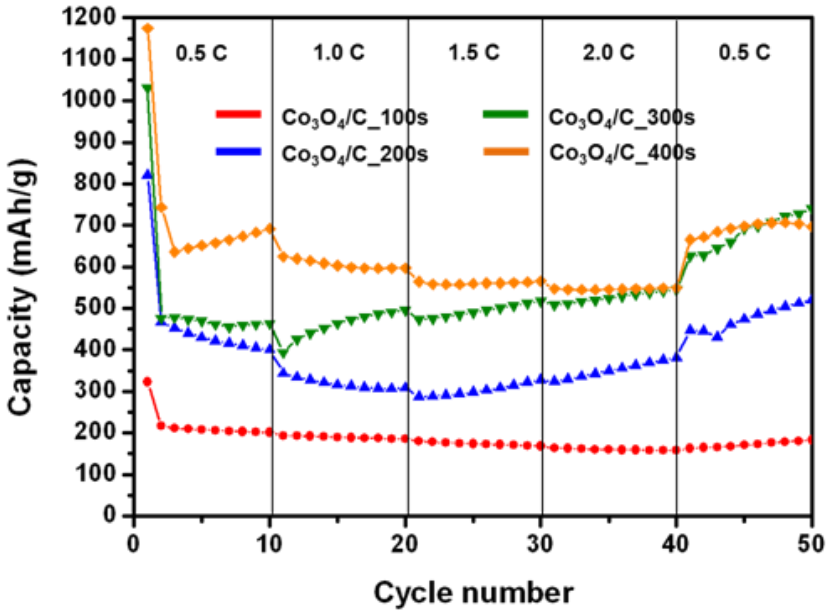

Fig. S4. Rate capability of as-synthesized Co_3O_4/C films at various current densities between 445 and 1780 mA/g.

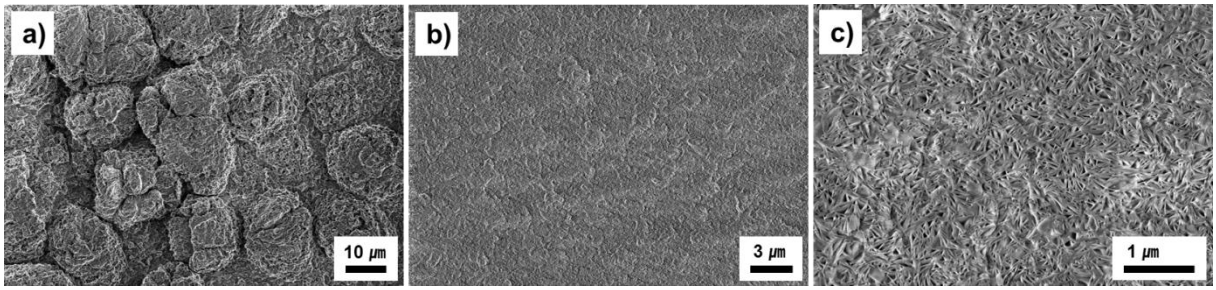

Fig. S5. SEM images of electrodes after 100 cycles; (a) Co_3O_4_300s and (b and c) Co_3O_4/C_300s.

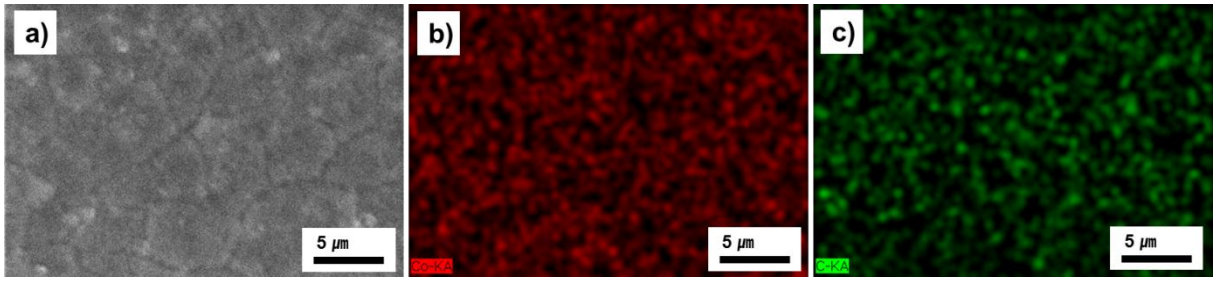

Fig. S6. EDS atomic analysis results of Co_3O_4/C_300s composite film after 100 cycles; (a) SEM image of thin films, (b) cobalt, and (c) carbon.