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## **Supporting Information**

Co<sub>3</sub>O<sub>4</sub>/C/Graphene Nanocomposites as Novel Anode Materials for High Capacity Lithium Ion Batteries

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**Figure S1.** FTIR spectras of GF (a),  $Co(NO_3)_2 \cdot 6H_2O$  (b),  $GF/Co(NO_3)_2 \cdot 6H_2O$  (c) and  $Co_3O_4/C/graphene$  nanocomposite (d).



**Figure S2.** (a, b) SEM observation of  $Co_3O_4/C$ /graphene nanocomposite: SEM images of the crosssection in which  $Co_3O_4/C$  nanoparticles deposited on the graphene surfaces.



**Figure S3.** (a, b) TEM images of  $Co_3O_4/C/graphene$  nanocomposite with the energy dispersive spectrum and crystal lattice of the corresponding selected-area in the inset respectively.



**Figure S4.** The Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O/GF mass ration was varied as 2:3, 2:1, 1:1, 3:2 and 1:2 to optimize the lithium storage performance. The samples were named as Sample 1 (2:3), Sample 2 (2:1), Sample 3 (1:1), Sample 4 (3:2) and Sample 5 (1:2), respectively. It is obvious that Sample 3 (1:1) exhibited the highest specific capacity. In contrast, the specific capacity of the samples Sample 1 (2:3) and Sample 4 (3:2) decayed significantly. For Sample 2 (2:1) and Sample 5 (1:2), the specific capacity maintained only ~750 and ~540 mA·g<sup>-1</sup> after 40 cycles, respectively. The specific capacity of pure GF electrode was only 42 mA·g<sup>-1</sup>, which is much lower than that of Co<sub>3</sub>O<sub>4</sub>. Therefore, only with the optimal weight ratio of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O to GF, the nanocomposite electrode material can exhibit the best performance.



**Figure S5.** The electrochemical performances of a  $Co_3O_4$ /graphene traditional electrode at a current density of 100 mA·g<sup>-1</sup>. With the increase of cycling numbers, it exhibits a relatively stable capacity of ~900 mAh·g<sup>-1</sup>, which could be attributed to the gradual activation of nanocomposite in the first several cycles. Since the 35th cycle, however, the specific capacity begins to drop rapidly. The nanocomposite electrode only presents a lower capacity of 760 mAh·g<sup>-1</sup> after 50 cycles.



**Figure S6.** CV curves of the first two cycles of  $Co_3O_4/C/graphene$  nanocomposite electrode at a scan rate of 0.2 mV/s in the voltage range of 0.01-3.0 V. The observed main oxidation peak at about 2.27 V could be due to the delithiation reaction of  $Co_3O_4$  and the decomposition of  $Li_2O$ . The two reduction peaks have one broad peak at 0.95 V and another shoulder at 1.22 V, which are ascribed to the formation of SEI films and the electrochemical reduction reaction of  $Co_3O_4$  with Li, respectively.



**Figure S7.** (a) Charge-discharge profiles of  $Co_3O_4/C/graphene nanocomposite for the 1<sup>st</sup> and 2<sup>nd</sup> cycle at the current density of 100 mA·g<sup>-1</sup>. (b) Galvanostatic charge-discharge curves of <math>Co_3O_4/C/graphene$  nanocomposite cycled at the 1<sup>st</sup> between 3.0 and 0.01 V (vs. Li<sup>+</sup>/Li) at a current density of 50, 100, 200, 300, 500, 800, 1000 and 50 mA·g<sup>-1</sup>. In the initial processes of charging and discharging, there is a well-defined voltage plateaus at around 1.3 V before a smooth and long slope (Li<sup>+</sup> insertion into graphene layers), corresponding to the reduction of  $Co_3O_4$  to Co metal. The similar charge and discharge capacity (1104 and 1148 mAh·g<sup>-1</sup>, respectively) exhibited in the second cycle indicates that the amount of intercalated lithium ions matches with that of the deintercalated ones.



**Figure S8.** Nyquist plots of  $Co_3O_4/C/graphene nanocomposite before and after the second galvanostatic charge-discharge cycles, which measures at the open-circuit potential with an amplitude of 5 mV over the frequency range of 100 kHz and 1 Hz, with an Ac amplitude of 5 mV. The diameter of the arc and values of the line part for the fresh electrode has not changed much compared with those of the cycled one. The semicircle measured at the high region represents surface resistance of the film that mainly due to the migration of lithium ions passing through SEI films. While the line part displayed at low frequency region represents the diffusion impedance in the electrode.$ 

