

### Supporting information

## Sandwich shelled $\text{TiO}_2@\text{Co}_3\text{O}_4@\text{Co}_3\text{O}_4/\text{C}$ hollow spheres as anode materials for lithium ion batteries

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## 1. Experimental section

### 1.1. Materials

$\text{Ni}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ (AR),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (AR),  $\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ (AR), N-methyl-2-pyrrolidone (NMP), tetrabutyl titanate (TBOT, >99.0%) and polyvinylpyrrolidone(PVP, K29-32) were got by Aladdin Industrial Corporation. PVDF (polyvinylidene fluoride), copper foil (10 mm thickness), metallic Li (0.6mm thickness, 99.9%), a separator (Celgard 2325) and Super-P-Li (carbon black) were got by Lizhiyuan Battery Materials Company. Ammonium hydroxide (AR), sodium borohydride (AR), glucose (AR) were acquired from Sinopharm Chemical Reagent Corporation. The above chemicals are not further purified.

### 1.2. Material Synthesis

#### 1.2.1. Synthesis of $\text{TiO}_2 @ \text{Co}_3\text{O}_4 @ \text{Co}_3\text{O}_4 / \text{C}$

**$\text{Co}_3\text{O}_4 / \text{C}$ .** In a typical process, cobalt nitrate (0.5871 g) and glucose (0.2973 g) was added in DI water (20.0 mL), and stirring for 30 minutes. Next, the aerogel formed by the mixed solution was decomposed in a spray pyrolysis device at 380 °C, and the obtained sample was dried at 60 °C for 12 hours. Finally, the dried powder was calcinated in 350 °C for two hours in  $\text{N}_2$  atmosphere to obtain black products.

**$\text{Co}_3\text{O}_4 @ \text{Co}_3\text{O}_4 / \text{C}$ .** First, dissolve 0.2911 g  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 0.05 g  $\text{Co}_3\text{O}_4 / \text{C}$  companion in 10.0 mL deionized water and stir the solution evenly. Second, 0.10 g of PVP was dissolved in mixed solution. Then, 50 mL of deionized water was added to it. After sonication for 15 min, a homogenous mixed solution was obtained. Add the prepared 0.05 g/mL  $\text{NaBH}_4$  solution (2 mL) slowly and stir for 6 h. When this reaction was over, the collected samples were washed and dried. Finally, in a nitrogen atmosphere, the dried powder was calcinated in 400 °C for two hours to obtain  $\text{Co}_3\text{O}_4 @ \text{Co}_3\text{O}_4 / \text{C}$  nanosheets.

**$\text{TiO}_2 @ \text{Co}_3\text{O}_4 @ \text{Co}_3\text{O}_4 / \text{C}$ .** Typically, 0.075 g of  $\text{Co}_3\text{O}_4 @ \text{Co}_3\text{O}_4 / \text{C}$  nanosheets and 0.3 mL of 28 wt% ammonia water were added in 40 mL of deionized water. After 15 minutes of ultrasound, 0.75 mL of TBOT was dripped. The above solution was kept at 45 °C for 24 h in an oil bath while avoiding ethanol evaporation by condensing and refluxing. Subsequently, the product was obtained by washed and then dried. Finally, it was heated at 500 °C for two hours in  $\text{N}_2$  atmosphere, and then  $\text{TiO}_2 @ \text{Co}_3\text{O}_4 @ \text{Co}_3\text{O}_4 / \text{C}$  (CCoTi-O) was obtained.

#### 1.2.2. Synthesis of $\text{TiO}_2 @ \text{Fe}_2\text{O}_3 @ \text{Co}_3\text{O}_4 / \text{C}$ and $\text{TiO}_2 @ \text{NiO} @ \text{Co}_3\text{O}_4 / \text{C}$

First, we changed the second step of 0.1mol of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  to 0.1mol of  $\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$  and 0.1mol of  $\text{Ni}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ , and repeat the above operation. Finally, we will obtain  $\text{TiO}_2 @ \text{Fe}_2\text{O}_3 @ \text{Co}_3\text{O}_4 / \text{C}$  and  $\text{TiO}_2 @ \text{NiO} @ \text{Co}_3\text{O}_4 / \text{C}$ .

#### 1.2.3. Synthesis of $\text{TiO}_2 @ \text{Co}_3\text{O}_4 / \text{C}$

0.075g of  $\text{Co}_3\text{O}_4/\text{C}$  nanosheets and 0.3 ml of 28 wt% ammonia water were added in 40 mL of deionized water. After 15 minutes of ultrasound, 0.75 mL of TBOT was dripped. The above solution was kept at 45 °C for 24 h in an oil bath while avoiding ethanol evaporation by condensing and refluxing. Subsequently, the product was obtained by washed and then dried. Finally, it was heated at 500 °C for two hours in  $\text{N}_2$  atmosphere, and then  $\text{TiO}_2@\text{Co}_3\text{O}_4/\text{C}$  was obtained.

### **1.3. Characterization**

The crystalline phase of products was tested by XRD with Cu  $\text{K}\alpha$  radiation (Bruker AXS, D8 Advance). Element valence states on the surface of composite materials was analyzed with X-ray photoelectron spectroscopy with Al  $\text{K}\alpha$  X-ray radiation (XPS) (Thermo Fisher, ESCALAB 250XI). By high resolution transmission electron microscopy (HRTEM, FEI Tecnai G220), transmission electron microscopy (TEM, Hitachi HT-7700) and scanning electron microscopy (FESEM, Hitachi S-8100), we can observe the structure, size and morphology of the samples. We can analyze CCoTi-O's pore size distribution and specific surface area by automated gas sorption analyzer (Micromeritics, ASAP2010N). The thermogravi-metric analysis (TGA) was performed on thermogravimetric analyzer (TA, Q500) under air. We measured the composition of each metal element by ICP-OES (ICPOES730).

### **1.4. Electrochemical measurements**

The mixed slurry is made of the product obtained from the experiment, Super-P-Li, and PVDF in a weight ratio of 7:2:1. And it was coated onto clean Cu foil, and dried for 24 hours. The working electrode is assembled into a 2032 coin cells in a glove box, and the mass loading of working electrode's active material is 1.1-1.4  $\text{mg cm}^{-2}$ . 1 M  $\text{LiPF}_6$  added in the mixed ethylene carbonate/dimethyl carbonate (EC/DEC) (volume=1:1) was used as the electrolyte solution. Battery performance is tested on a battery test system (Neware, CT-4008) at 25°C. The cyclic voltammetry (CV) was tested on an electrochemical workstation (Chenhua, CHI660C) at a scan rate of 0.2  $\text{mV s}^{-1}$ . In addition, the electrochemical impedance spectroscopy (EIS) plots were tested at 10 mV of amplitude and in a frequency range from 0.1 MHz to 0.01 Hz.

## 2. Additional Figures

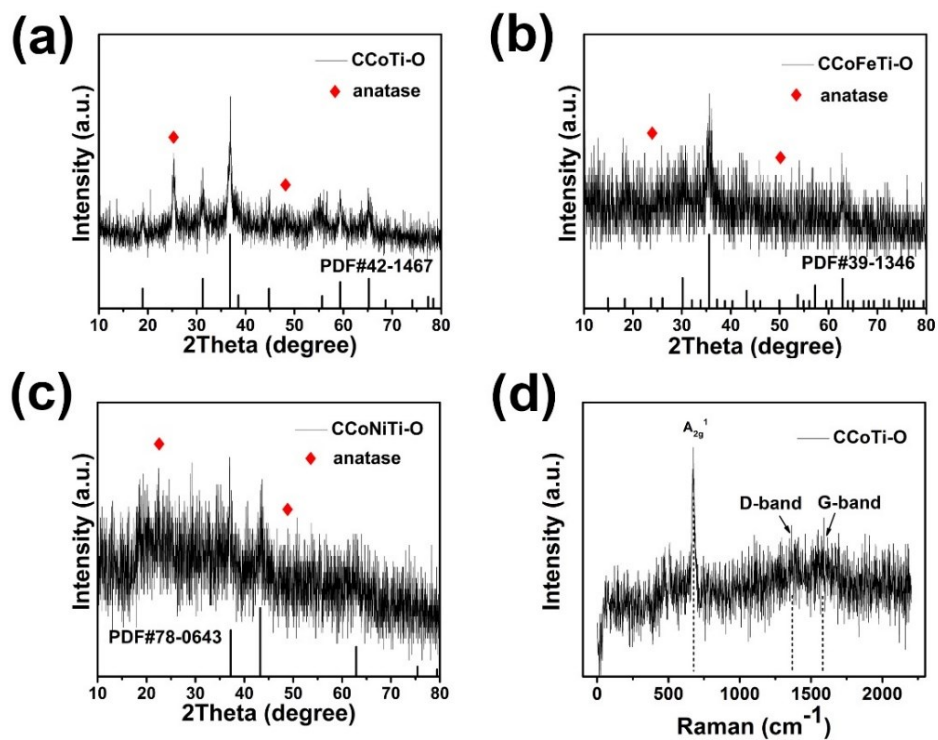


Figure S1. XRD patterns of (a) CCoTi-O, (b) CCoFeTi-O, (c) CCoNiTi-O and Raman spectrum of (d) CCoTi-O.

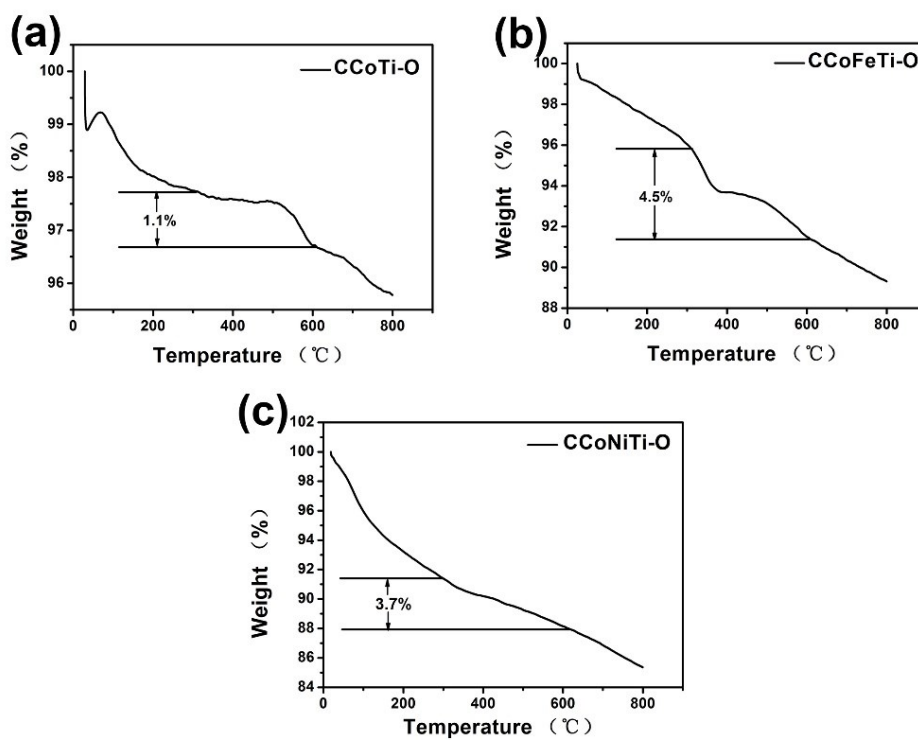
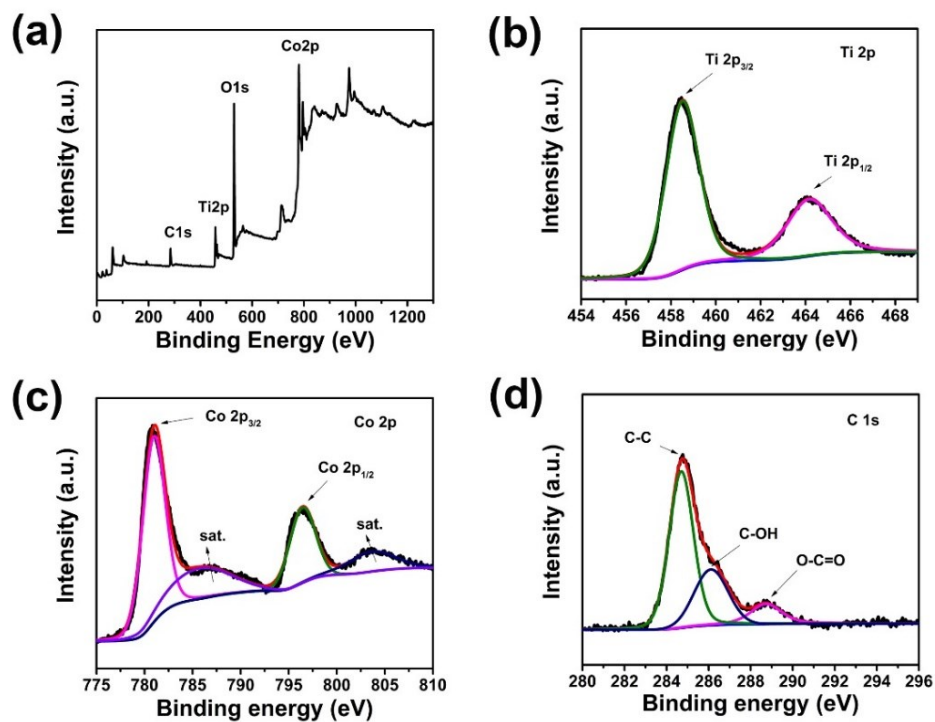
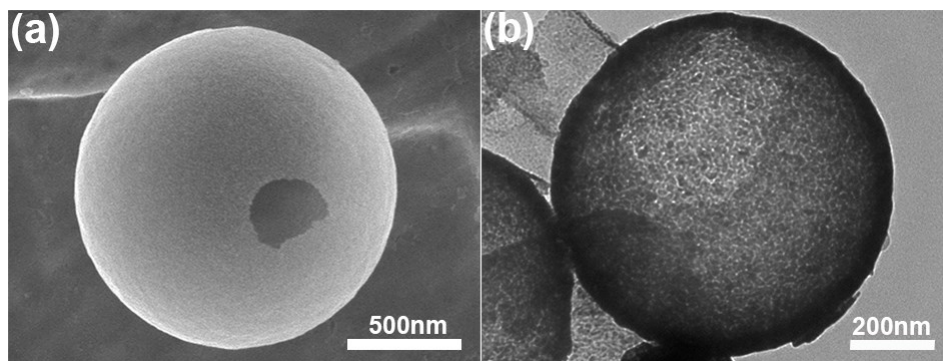


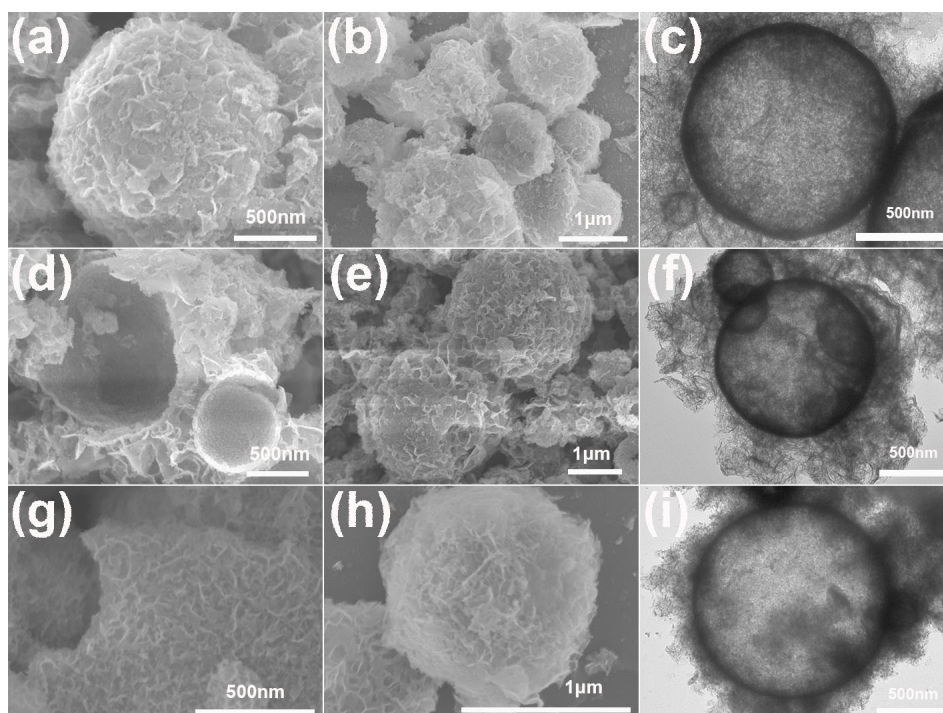
Figure S2. TGA microanalysis of three samples.



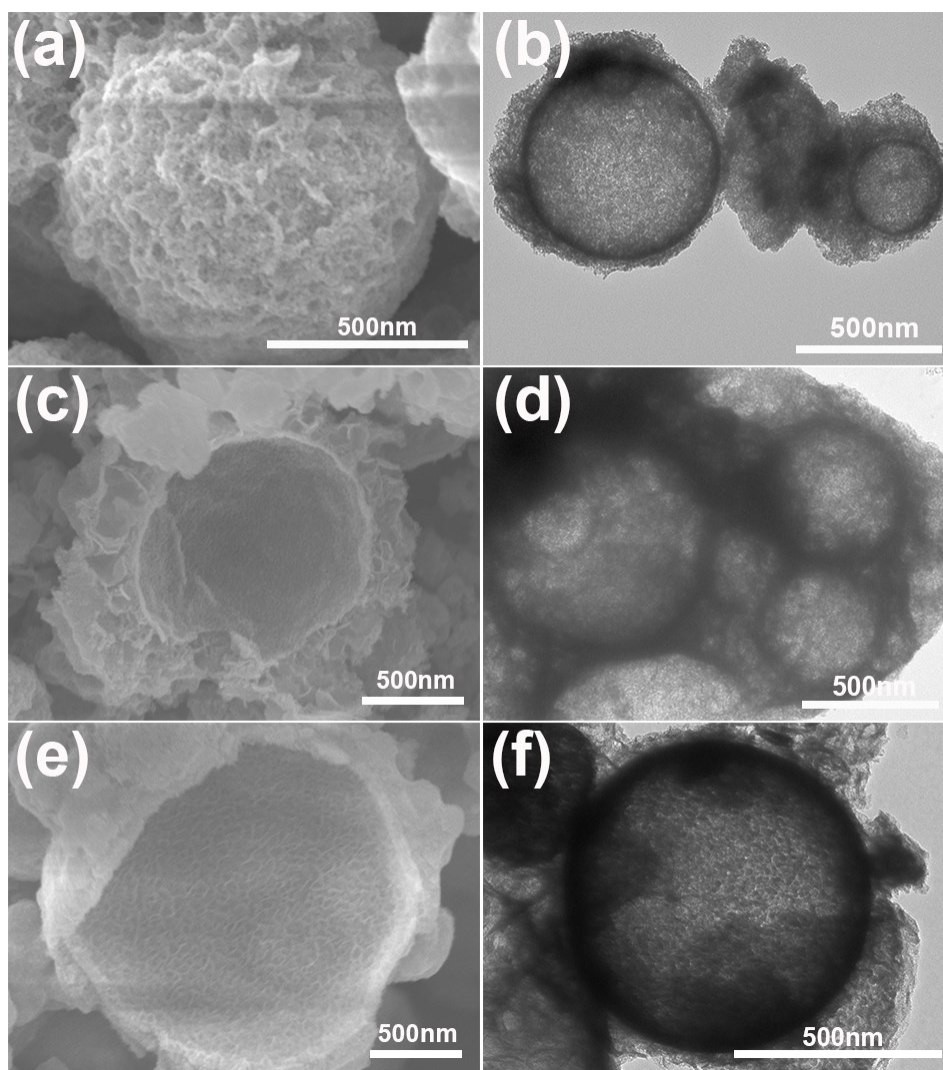
**Figure S3.** XPS spectra of the sample CCoTi-O, (a) Survey spectrum, high-magnification XPS spectrum of (b) Ti2p, (c) Co2p and (d) C1s.



**Figure S4.** SEM and TEM images of  $\text{Co}_3\text{O}_4/\text{C}$ .



**Figure S5.** SEM/TEM images correspond to (a, b, c)  $\text{Co}_3\text{O}_4@\text{Co}_3\text{O}_4/\text{C}$ , (d, e, f)  $\text{Fe}_2\text{O}_3@\text{Co}_3\text{O}_4/\text{C}$  and (g, h, i)  $\text{NiO}@\text{Co}_3\text{O}_4/\text{C}$ .



**Figure S6.** SEM and TEM images of CCoTi-O (a, b), CCoFeTi-O (c, d), and CCoNiTi-O (e, f).

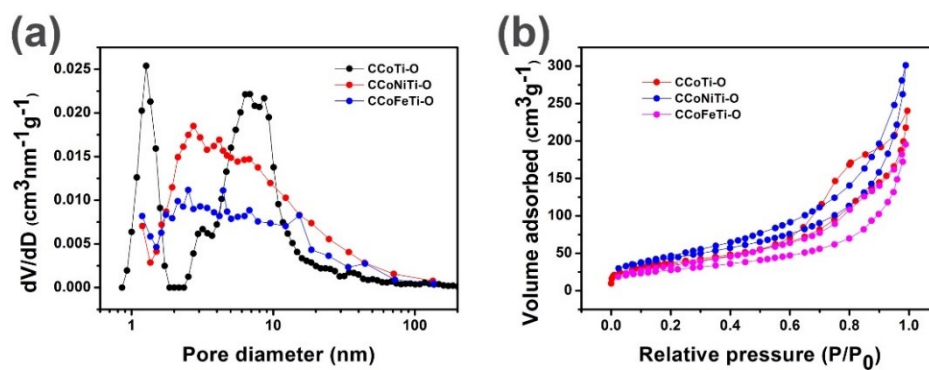


Figure S7. Pore size distribution curves (a) and N<sub>2</sub> adsorption-desorption isotherm (b) of CCoTi-O, CCoNiTi-O and CCoFeTi-O.

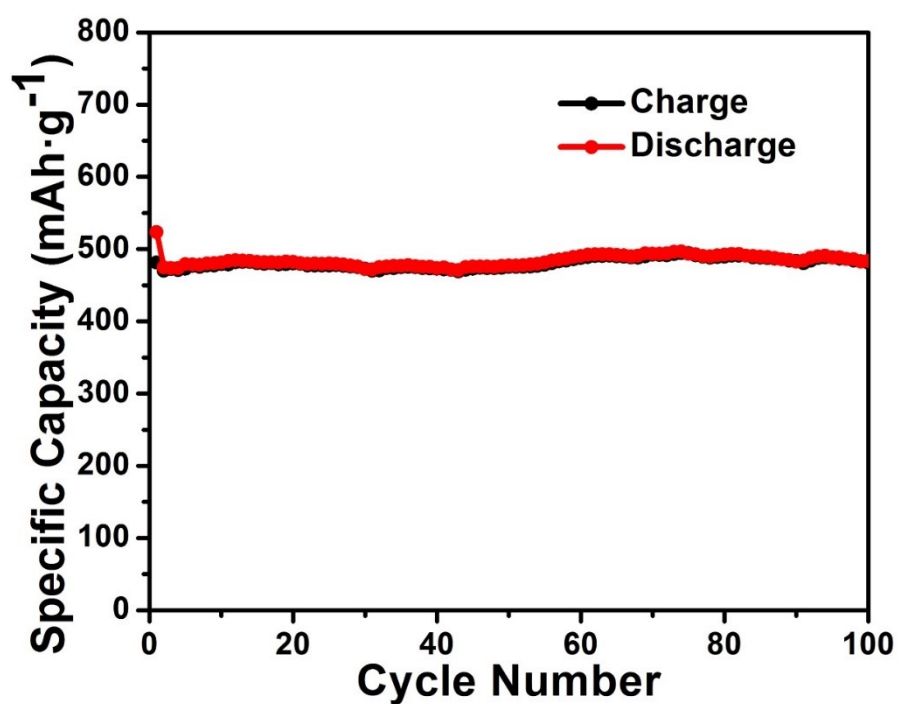


Figure S8. Cyclic performance of TiO<sub>2</sub>@Co<sub>3</sub>O<sub>4</sub>/C at the current density of 0.2 A g<sup>-1</sup>.



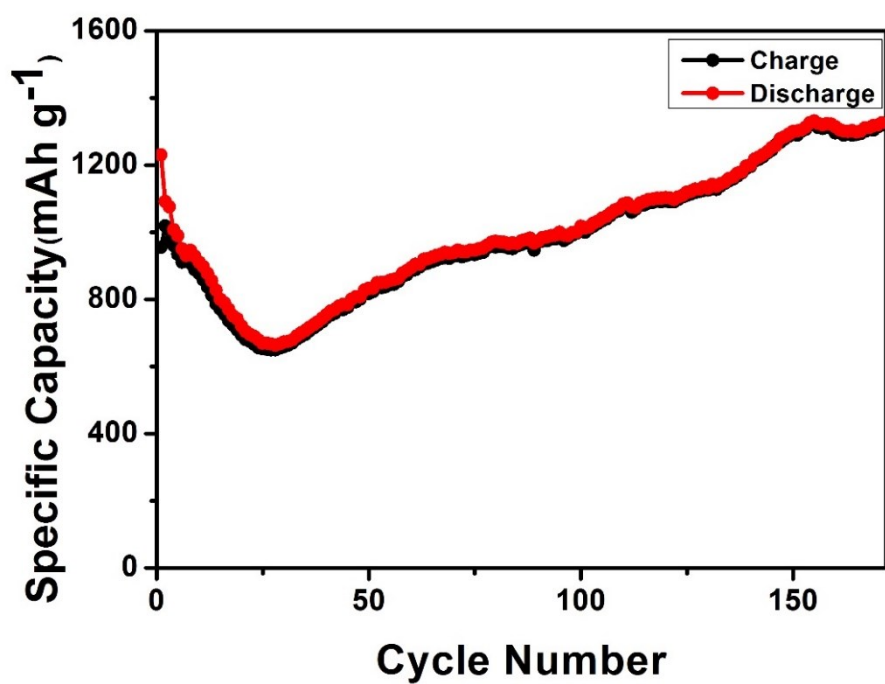


Figure S9. Cyclic performance of  $\text{Co}_3\text{O}_4@\text{Co}_3\text{O}_4/\text{C}$  at the current density of  $0.2 \text{ A g}^{-1}$ .

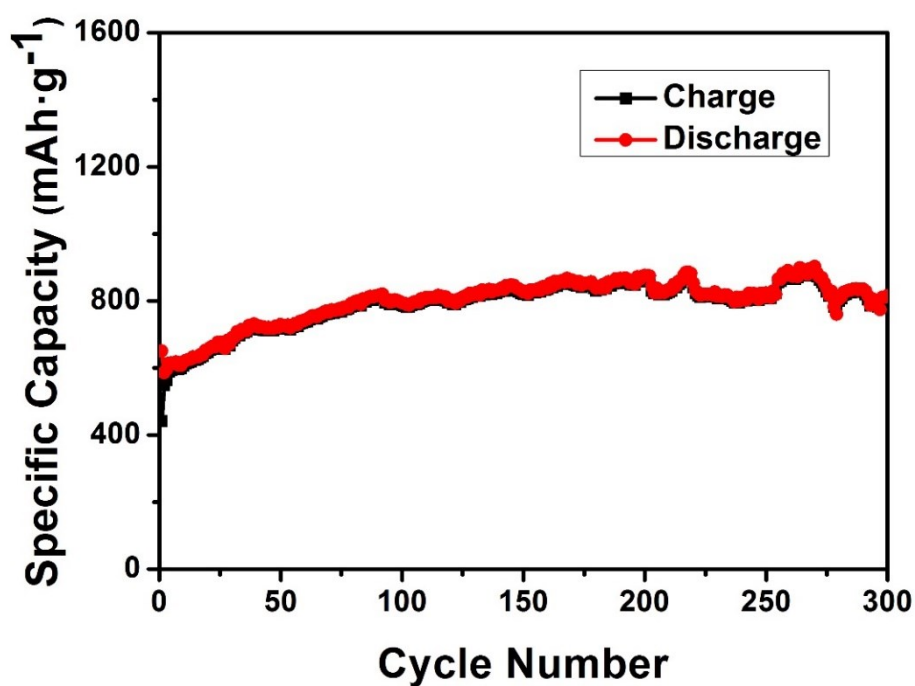
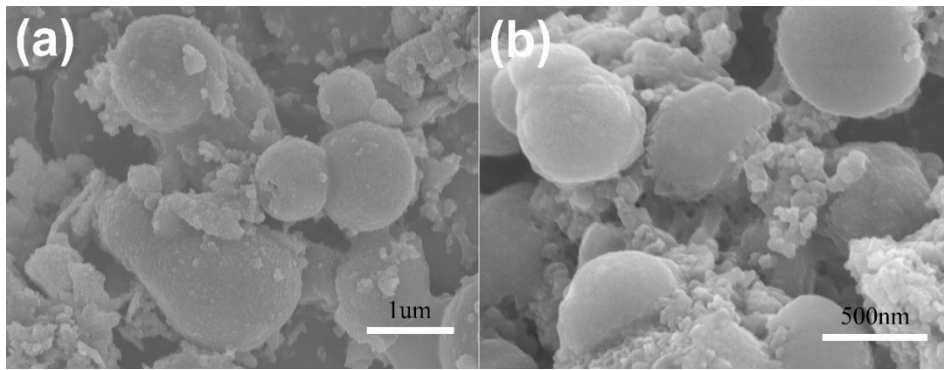


Figure S10. Cyclic performance of  $\text{TiO}_2@\text{Co}_3\text{O}_4@\text{Co}_3\text{O}_4/\text{C}$  at the current density of  $1 \text{ A g}^{-1}$ .



**Figure S11.** SEM images of the sample  $\text{TiO}_2@\text{Co}_3\text{O}_4@\text{Co}_3\text{O}_4/\text{C}$  after 100 cycles at  $0.2 \text{ Ag}^{-1}$  current density.

### 3. Additional Tables

**Table S1.** Comparison of some Co<sub>3</sub>O<sub>4</sub>/TiO<sub>2</sub> composites as anode material for the LIBs.

| Material  | Cycle Performance  | Initial Coulombic Efficiency | Capacity Retention | Rate Performance   | Ref.      |
|---|--|------------------------------|--------------------|--|-----------|
| Co <sub>3</sub> O <sub>4</sub> /TiO <sub>2</sub>  | 642 mAh g <sup>-1</sup><br>(0.5A g <sup>-1</sup> , 200th)    | 96.9%                        | 40%                | 642 mAh g <sup>-1</sup><br>(0.5 A g <sup>-1</sup> , 200th) | 1         |
| Co <sub>3</sub> O <sub>4</sub> -TiO <sub>2</sub>  | 1000 mAh g <sup>-1</sup><br>(0.2 A g <sup>-1</sup> , 100th)  | 77.9%                        | ~                  | 700 mAh g <sup>-1</sup><br>(1 A g <sup>-1</sup> , 10th)    | 2         |
| Co <sub>3</sub> O <sub>4</sub> @TiO <sub>2</sub> @C                                     | 380 mAh g <sup>-1</sup><br>(0.2 A g <sup>-1</sup> , 100th)   | 41.9%                        | 56.3%              | 219 mAh g <sup>-1</sup><br>(0.8A g <sup>-1</sup> , 10th)   | 3         |
| Co <sub>3</sub> O <sub>4</sub> @TiO <sub>2</sub>  | 787.5 mAh g <sup>-1</sup><br>(0.1 A g <sup>-1</sup> , 200th) | 72%                          | 84.8%              | 503 mAh g <sup>-1</sup><br>(2 A g <sup>-1</sup> , 10th)    | 4         |
| Co <sub>3</sub> O <sub>4</sub> @TiO <sub>2</sub>  | 813 mAh g <sup>-1</sup><br>(0.5 A g <sup>-1</sup> , 180th)   | 52%                          | 85%                | 1001.3 mAh g <sup>-1</sup><br>(2 A g <sup>-1</sup> , 10th) | 5         |
| Co <sub>3</sub> O <sub>4</sub> @TiO <sub>2</sub>  | 632 mAh g <sup>-1</sup><br>(0.2C, 100th)                     | ~                            | ~                  | 525 mAh g <sup>-1</sup><br>(0.5C, 100th)                   | 6         |
| TiO <sub>2</sub> /Co <sub>3</sub> O <sub>4</sub>  | 295 mAh g <sup>-1</sup><br>(0.1A g <sup>-1</sup> , 500th)    | 49.9%                        | ~                  | 180 mAh g <sup>-1</sup><br>(0.3 A g <sup>-1</sup> , 500th) | 7         |
| TiO <sub>2</sub> @Co <sub>3</sub> O <sub>4</sub> @<br>Co <sub>3</sub> O <sub>4</sub> /C | 1081.78 mAh g <sup>-1</sup> (0.2 A g <sup>-1</sup> , 100th)  | 95.5%                        | 101%               | 772 mAh g <sup>-1</sup><br>(1 A g <sup>-1</sup> , 300th)   | This work |

### References

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