## Supporting Information for

Uniqueness of Co<sub>3</sub>O<sub>4</sub>/Nitrogen-Doped Carbon Nano-spheres Derived from Metal-Organic-Framework: Insight of Superior Lithium Storage Capabilities Beyond Theoretical and Electrochemical Features in High Voltage Battery

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Figure S1 | Morphology and structural variation. SEM images of (a)  $Zn_3[Co(CN)_6]_2 \cdot nH_2O$  precursor, (b) Co/N-C intermediate, (c)  $Co_3O_4$ /N-C and (d) derivate of  $Co_3O_4$  nano-spheres with low magnification.



**Figure S2** | **Characterizations of composite materials.** (a) XPS survey spectrum of  $Co_3O_4/N$ -C. High resolution XPS spectra of (b) O 1s and (c) C 1s of the  $Co_3O_4/N$ -C hybrid nanospheres. (d) Raman spectra of  $Co_3O_4$  and  $Co_3O_4/N$ -C hybrid nanospheres. The O 1s XPS spectrum comprise three peaks at 532.9 eV (C-OH), 531.6 eV (O-C), 530.2 eV (O=C-OH) and 529.1 eV (Co-O), demonstrating the existence of elemental oxygen. In C 1s spectrum, the prominent peak located at 284.4 eV was assigned to C-C, while the peaks centered at the higher binding energies of 285.1, 286.2 and 288.5 eV were attributed to C-N, C-O, and O-C=O. A small peak at above 291.8 eV can be assigned to p–p\* shake-up satellites of sp<sup>2</sup> graphite-like carbon, which is consistence with the results observed in HRTEM. All information confirm that the composite has the chemical compositions of  $Co_3O_4/N$ -C.



**Figure S3** | **Electrochemical performances.** Typical voltage *vs.* capacity profiles of  $Co_3O_4/N-C$  in the (a) cycle and (b) rate capability test.



Figure S4 | Lithium diffusion constant. Comparative lithium diffusion coefficients of  $Co_3O_4/N-C$ ,  $Co_3O_4$  NPs and other kind of transitional metal oxides reported before.



Figure S5 | Electrochemical impedance spectroscopy. Nyquist plots of (a)  $Co_3O_4/N$ -C and (b) pure  $Co_3O_4$  electrodes.



**Figure S6** | **Electrochemical analysis.** (a) Cyclic voltammetry of pure  $Co_3O_4$  with the capacitive contribution at a scan rate of 0.5 mV s<sup>-1</sup> and (b) Normalized contribution ratio of capacitive capacities of  $Co_3O_4$  and  $Co_3O_4$ /N-C at different scan rates.