

Electronic Supplementary Information for

Facile synthesis of a mesoporous Co₃O₄ network for Li-storage via thermal decomposition of an amorphous metal-complex

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Experimental section

Synthesis

Porous ZnCo₂O₄: 0.833 g Co(NO₃)₂·6H₂O, 0.426 g Zn(NO₃)₂·6H₂O and 1.750 g glycine (C₂H₅NO₂) were dissolved in 10 mL deionized water in a crucible to form a solution, which was then transferred to a preheated furnace maintained at 400 °C for ca. 16 min to finish the decomposition reaction, which resulted in a black foam. The as-combusted sample was then heated at 480 °C for 2 h in air at a heating rate of 5 °C min⁻¹ to achieve finally the porous ZnCo₂O₄.

Porous NiO: 1.250 Ni(NO₃)₂·6H₂O and 1.750 g glycine (C₂H₅NO₂) were dissolved in 10 mL deionized water in a crucible to form a solution, which was then transferred to a preheated furnace maintained at 400 °C for ca. 16 min to finish the decomposition reaction, leading to a black foam. The as-combusted sample was then heated at 550 °C for 1 h in air at a heating rate of 5 °C min⁻¹ to achieve finally the porous NiO.

Characterization

X-ray diffraction (XRD) measurements were conducted on a XRD-6000 diffractometer (SHIMADZU) with Cu K α radiation, operated at 40 kV, 40 mA (λ = 0.15406 nm). The powder morphology was observed using a field emission scanning electron microscopy (FE-SEM, with EDS capabilities, Hitachi S-4800, Tokyo, Japan) and a FEI-F20 transmission electron microscopy (TEM, FEI, USA) working at 200 kV. A STA-449F3 instrument (NETZSCH-Gerätebau GmbH, Germany) was used to carry out the thermogravimetric (TG) analysis of the as-combusted samples in air atmosphere at a heating rate of 5 °C min⁻¹ from room temperature to 800

°C. The Brunauer-Emmett-Teller (BET) approach using adsorption data was utilized to determine the specific surface area. The sample was degassed at 150 °C for 14 h to remove physisorbed gases prior to the measurement.

Lithium storage test

The working electrodes were prepared by a slurry coating procedure. The slurry consisted of 80 wt. % Co_3O_4 powders, 10 wt. % acetylene black, and 10 wt. % polyvinylidene fluoride (PVDF) dispersed in N-methyl pyrrolidinone (NMP), and was coated on a copper foil, which acted as a current collector. The active material (Co_3O_4) was 0.4–0.6 mg/cm^2 on each electrode and the coating thickness was ca. 3.5 μm . Electrodes with a much higher mass loading of 1.5–2.5 mg/cm^2 were also characterized. The film was dried at 120 °C for 12 h in vacuum. The cells were assembled in an argon-filled glove box using Li foil as a counter electrode and polypropylene (PP) film (Celgard 2300) as a separator. The electrolyte was 1 M LiPF_6 in a 50:50 (w/w) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The charge–discharge tests were conducted on a LAND 2001A system at a current density of 100 mA g^{-1} and 1000 mA g^{-1} between 0.005 V and 3.0 V. The cyclic voltammetry was performed on a CHI660D electrochemical workstation.

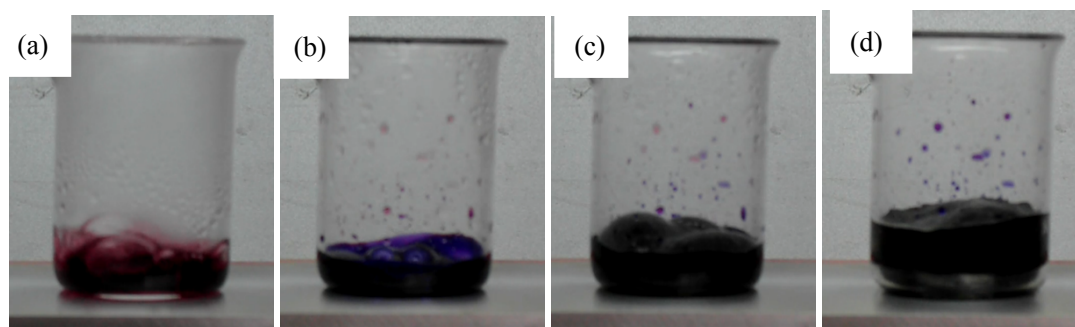


Fig. S1 The decomposition process of the precursor solution: (a) boiling of the pink solution (0 min), (b) changing to blue and bubbling (6.0 min), (c) bubbling, decomposition and release of gases (7.0 min), and (d) the formation of the black product (13.5 min).

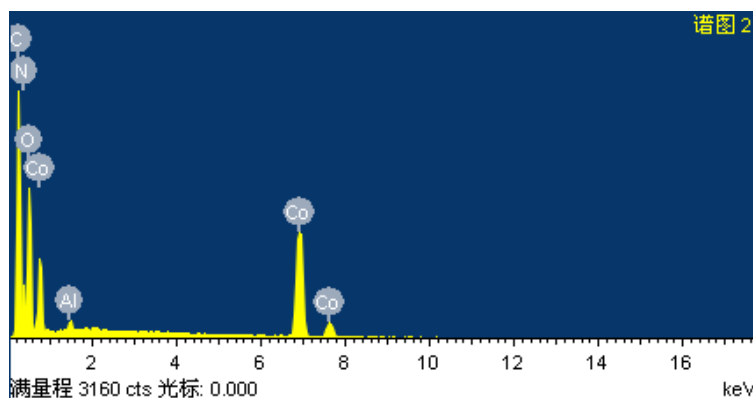


Fig. S2 EDS spectrum of the as-synthesized cobalt-based complex. The Al element in EDS spectrum is from the SEM holder.

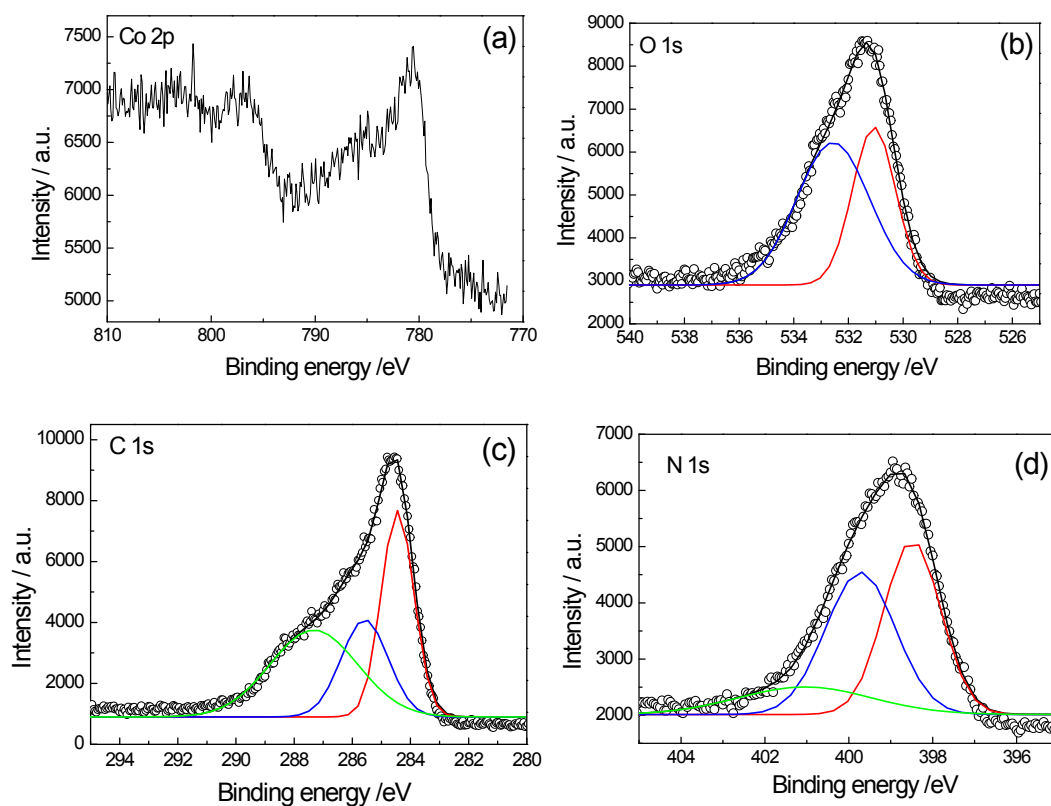


Fig. S3 High-resolution XPS spectra of as-synthesized cobalt-based complex: (a) Co 2p, (b) O 1s, (c) C 1s, and (d) N 1s.

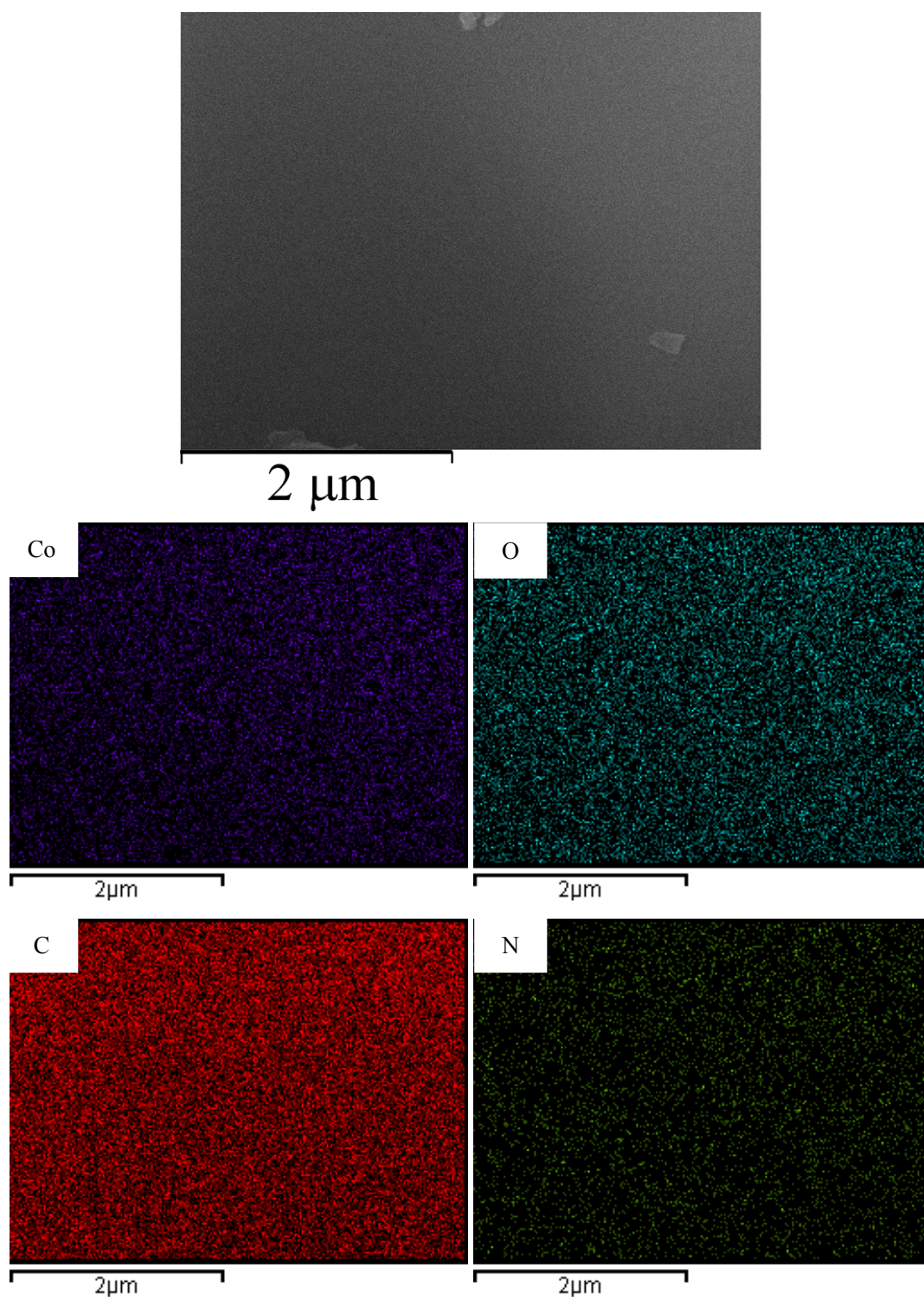


Fig. S4 The as-synthesized cobalt-based complex and the corresponding elemental mappings of Co, O, C, and N.

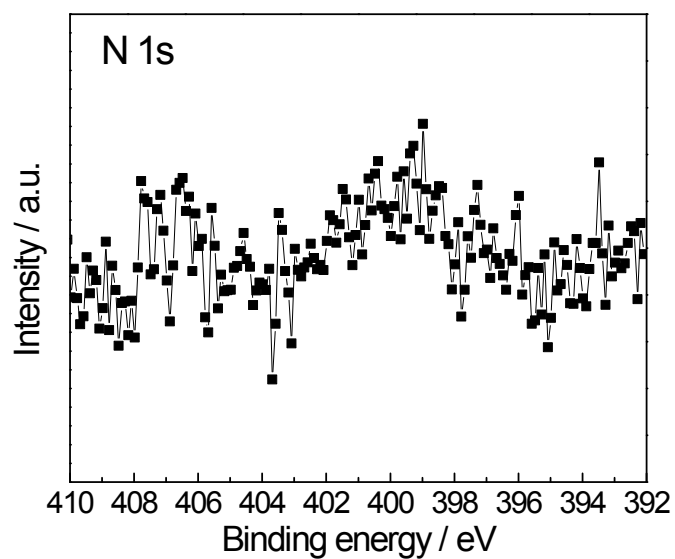


Fig. S5 N 1s high-resolution XPS spectrum of the porous Co_3O_4 .

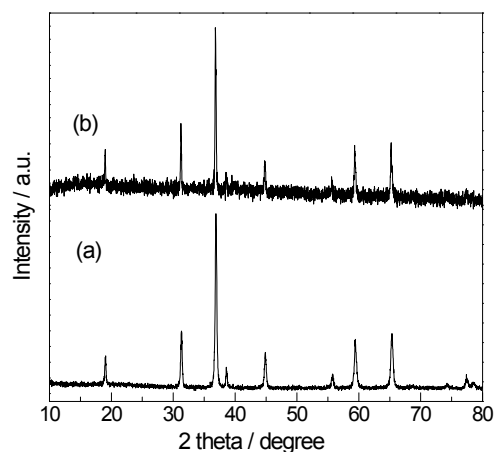


Fig. S6 XRD patterns of the as-synthesized cobalt-based complex after calcination at different temperatures for 1 h: (a) 450 °C and (b) 550 °C.

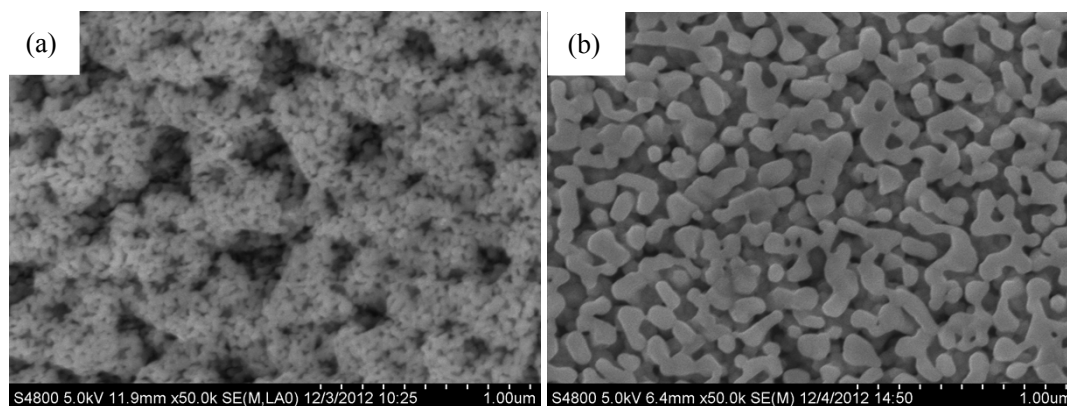


Fig. S7 SEM images of the as-synthesized cobalt-based complex after calcination at different temperatures for 1 h: (a) 450 °C and (b) 550 °C.

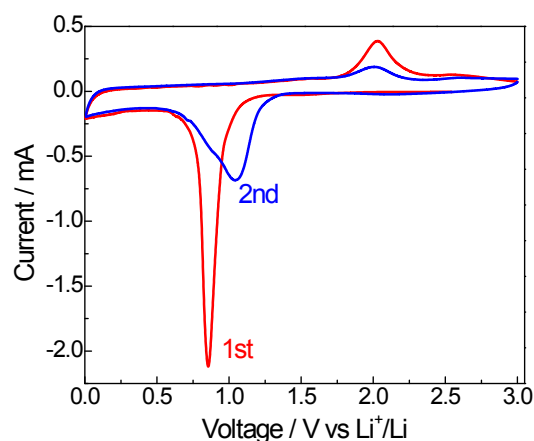


Fig. S8 The cyclic voltammetry (CV) curves of the porous Co_3O_4 scanned at a rate of 0.1 mV s^{-1} .

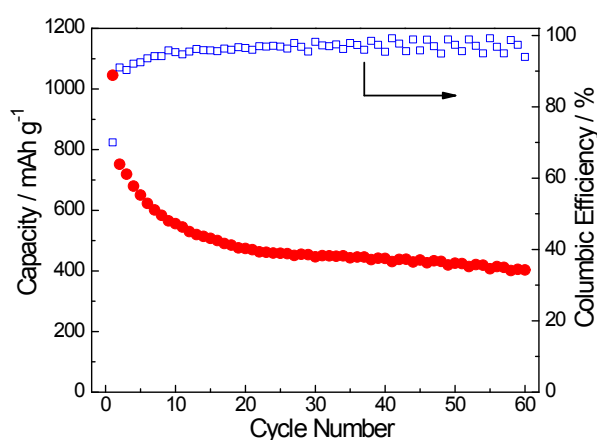


Fig. S9 Cycling performance of commercial Co_3O_4 nanoparticles (30 nm in size, Aladdin Reagent Co. Ltd., China) at a current density of 100 mA g^{-1} . The mass loading of the active material (Co_3O_4) was ca. 0.5 mg cm^{-2} .

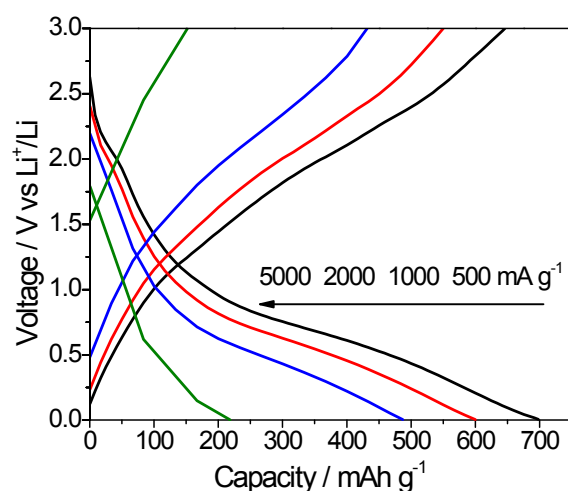


Fig. S10 The discharge-charge profiles of the porous Co_3O_4 at different current density. The rate performance is measured after the cycling test at 1000 mA g^{-1} for 390 cycles to stabilize the capacity because discharge capacity of the present porous Co_3O_4 firstly decreases and then gradually increases during the cycling (Fig. 6b and 6c).

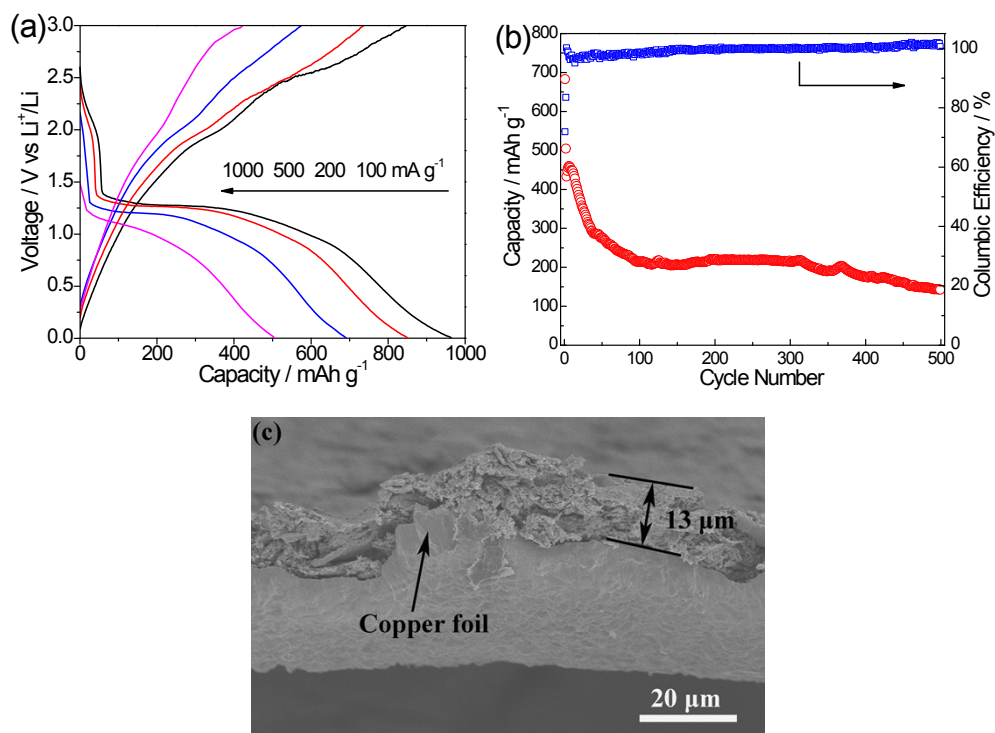


Fig. S11 (a) The discharge-charge profiles of the porous Co_3O_4 at different current density. (b) Cycling performance of the porous Co_3O_4 network at a current density of 1000 mA g^{-1} . (c) Cross sectional SEM image of an electrode, showing the thickness of the coating is ca. 13 μm . The active material (porous Co_3O_4) was 1.5–2.5 mg cm^{-2} on each electrode.

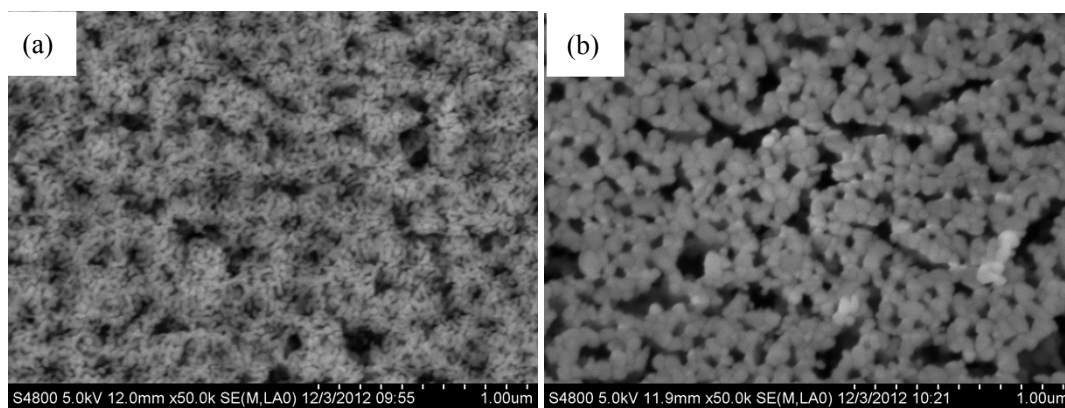


Fig. S12 SEM images of porous ZnCo_2O_4 (a) and porous NiO (b).

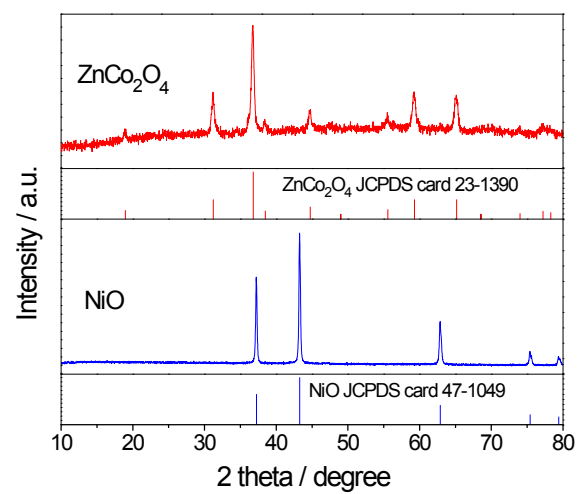


Fig. S13 XRD patterns of porous ZnCo_2O_4 and porous NiO .