Electronic Supplementary Information

Experimental

Preparation of solid Cu₂O nanocubes

All chemicals used in this work were analytical grade and used without further purification. The typical synthetic experiments were carried out as follows. 4.45g PVP (K30) was added into 100 mL of aqueous solution of $CuCl_2 \cdot 2H_2O(0.01M)$ with stirring, after 10 min, 10 ml of NaOH(2M) was added dropwise under 55°C. After 30min,10ml 0.6 M ascorbic acid was added to the above solution and an earthy yellow turbid liquid was formed. The reaction was finished within 2 h. The resulting red product was harvested by several rinse-precipitation cycles with deionized (DI) water for further characterization.

Preparation of hollow octahedra ZnCo₂O₄ nanocages

Cu₂O templates (15.0 mg), CoCl₂·6H₂O (2.0 mg), ZnCl₂ (1.7 mg) were added into ethanol-water solvent (10.0 ml, 1:1 v/v) in the presence of PVP K30 (1.6532 g) with stirring. After 20 min, 4 ml of aqueous Na₂S₂O₃ solution (2M) was added dropwise. The reaction continued for 3 min under ambient conditions until the color of the suspension changed from earthy yellow to yellow at temperature of 70 °C. Subsequently, the resulting product (ZnCo_x)O(OH) was harvested by several rinse-centrifugation cycles with deionized water and ethanol, and finally dried at room temperature for further characterization. Eventually, the product was harvested by several rinsecentrifugation cycles with DI water and ethanol, and finally dried at room temperature. Eventually, certain amount of (ZnCo_x)O(OH) nanoboxes was successively annealed in Ar flowing at 450 °C for 4 h with a slow ramp rate of 1 °C min⁻¹ to make the hollow octahedra ZnCo₂O₄ nanocages.

Characterization

XRD patterns are carried out using a Bruker D8 Advance X-ray diffractometer at 40 kV and 40 mA over 10° to 90° 20 range with a Cu K α radiation. Sample morphology is examined by a scanning electron microscope (AMRAY 1000B). TEM images and the high resolution images are recorded using a high resolution transmission electron microscope (HRTEM, JEM-2010). The lattice structure is identified by selected area electron diffraction (SAED) technique. Nitrogen adsorption-desorption measurements are conducted at 77 K on a Micromeritics Tristar apparatus. The specific surface area is determined following the Brunauer-Emmet-Teller analysis. The contents of Zn and Co are measured by an ICP-AES instrument (Varian 710) and AAS HITACHI Z-2000 (the precursor and final product dissolved in aqua regia).

Electrochemical Measurements

For electrochemical performance evaluation, half-cell studies were performed. The working electrodes is prepared as by doctor-blade casting on a copper foil, and the slurry consisted of the active materials (80 wt. %), carbon black (20 wt. %) and PVDF (10 wt. %). Then the coated electrodes are dried in vacuum at 80 °C for 48 h. The electrolyte is 1 M LiPF₆ solution in a mixture of ethylene carbonate, dimethyl carbonate, and diethylene carbonate (EC: DMC: DEC= 1: 1: 1, v/v/v), and polypropylene micro-porous film (Cell-gard 2400) is acted as the separator. The electrochemical performances are studied using CR2016 coin cells. The coin cells are assembled in an argon-filled glove-box. The galvanostatic charge-discharge tests are at room temperature between 0.01 V and 3.0 V versus Li/Li⁺ by a Land 2100A tester. The cyclic voltammetry (CV) is performed on CHI660A electrochemical workstation between 0.01 and 3.0 V with scan rate of 0.01 mVs⁻¹.



Fig. S1 TEM image of the obtained hollow TiO₂ nanocages.



Fig. S2 TEM image of the obtained hollow CeO_2 nanocages.



Fig. S3 TEM image of the obtained hollow NiO nanocages.



Fig S4. (a) The SEM image of $ZnCo_2O_4$ nanoparticles prepared with the same procedure except without adding Cu₂O; (b) Cycling performance of hollow prepared hollow octahedral $ZnCo_2O_4$ nanocages and the reference electrode at constant specific density of 200 mAg⁻¹