Supporting information

Facile synthesis of monodisperse porous Co_3O_4 microspheres with superior ethanol sensing properties

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Materials and Methods

Preparation of materials. In a typical synthetic condition, 0.002 mol of cobalt acetate hydrate ($Co(CH_3COO)_2.4H_2O$) was dissolved in 20 ml of distilled water and 20 ml of ethylene glycol (EG). A clean pink solution was obtained. 2 ml $NH_3.H_2O$ (29 wt.%) was then added dropwise into the above solution with stirring. The color of the solution changed to blue with dropping. The pH value of the blue suspension was about 9-10. This solution mixture was stirred for 30 min before being transferred into a 50 ml Teflon-lined autoclave. The autoclave was sealed, kept at 180 ^oC for 12 h in an electric oven, and then cooled to room temperature naturally. A pink precipitate was obtained by vacuum filtration, washed with distilled water and absolute ethanol three times, respectively, and then dried at 100 ^oC for 4h. A black Co_3O_4 powder was obtained by calcining at 500 ^oC for 4 h in air.

Characterization of materials. X-ray powder diffraction (XRD) patterns were step-scan recorded on a Philips x-ray diffractometer equipped with Cu K_α radiation in steps of 0.02° with a step time of 2 s over the 2θ range of 10° to 80° for each sample. Scanning electron microscopy (SEM) was performed on a Quanta 650 scanning electron microscope. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) were carried out on a JEOL 2010F transmission electron microscope. BET surface area and pore volume were tested with a Quantachrome Instruments NOVA4000 after the samples were vacuum dried at 300 °C over 5 h.

Gas-sensing measurement. The fabrication process of the existing Co_3O_4-based sensors is given in previous literature.[S1] Briefly, the products were dispersed in ethanol, and a drop of the suspension solution was dripped on a ceramic tube between Pt electrodes to form a thin film. A resistance heater in the ceramic tube was used to control the temperature. The sensitivity of the product in this study is defined as the resistance ratio of R_{gas} to R_a, where R_{gas} and R_a are the electrical resistance for the sensor in alcohol and in air, respectively.

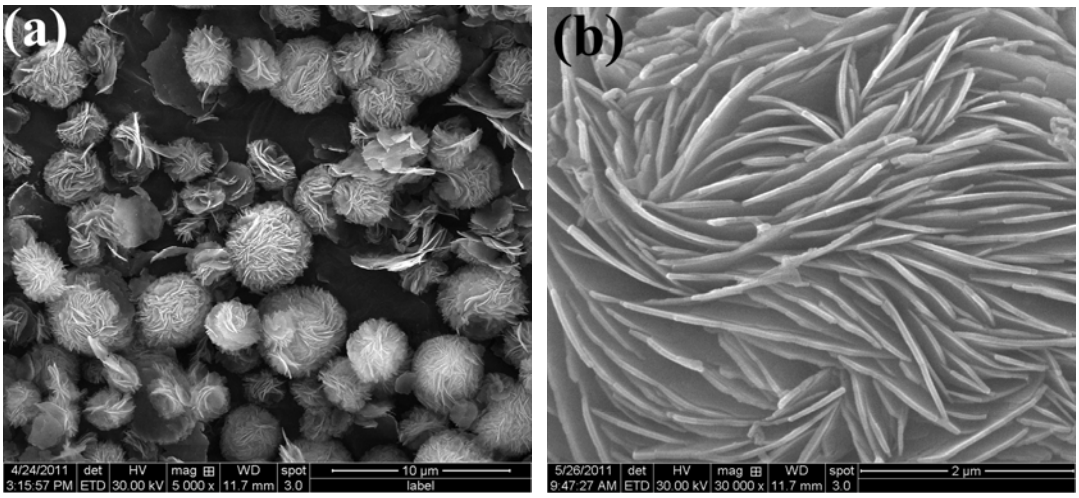

Figure S1. Representative SEM images of the *β*-$Co(OH)_2$ microspheres: (a) overall morphology of the products; (b) high-magnification SEM image of nanoplates in a microsphere.

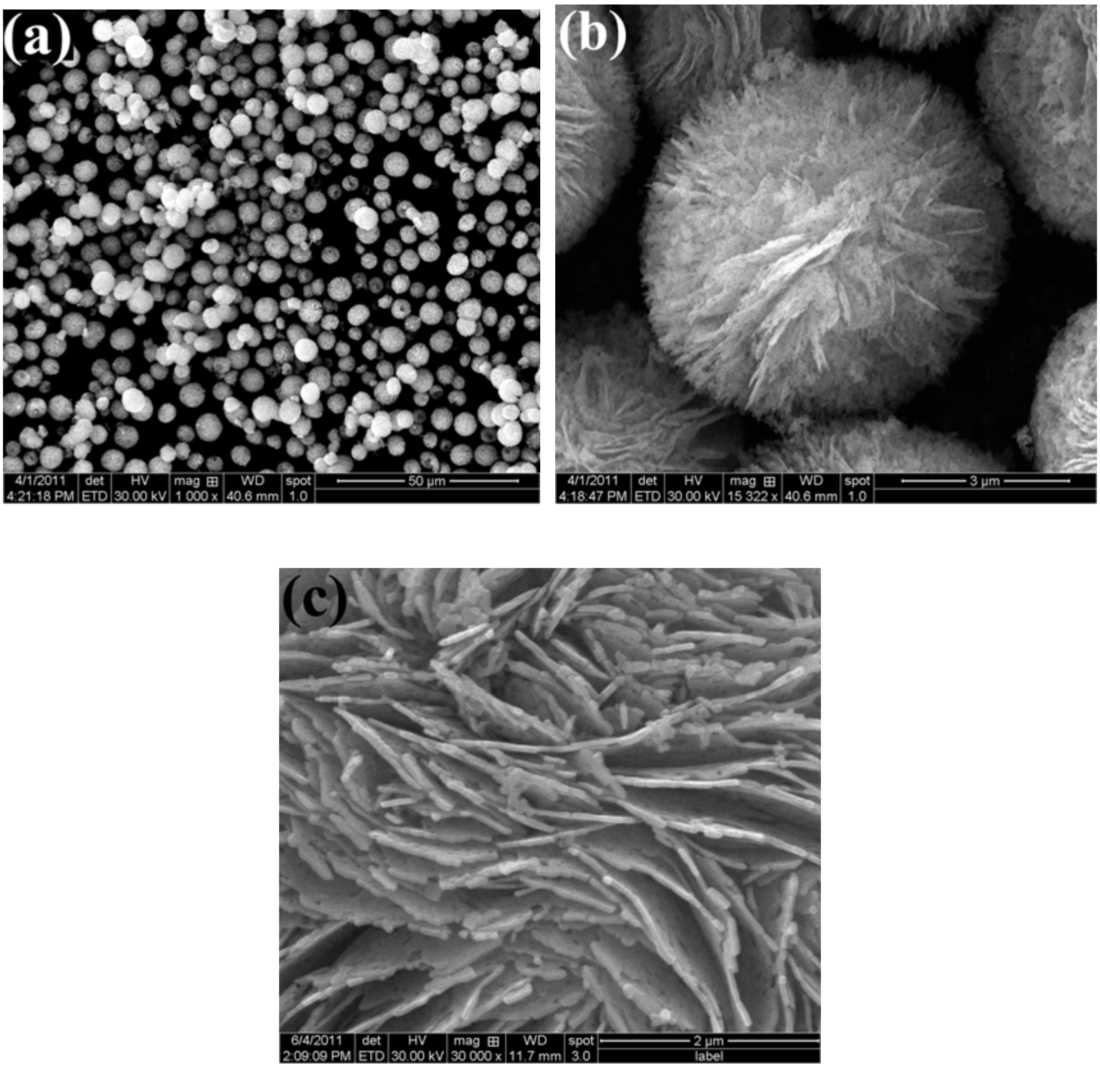

Figure S2. Representative SEM images of the Co_3O_4 microspheres: (a) overall morphology of the products; (b) high-magnification SEM image of an individual microspheres; (c) high-magnification SEM image of nanoplates in a microsphere.

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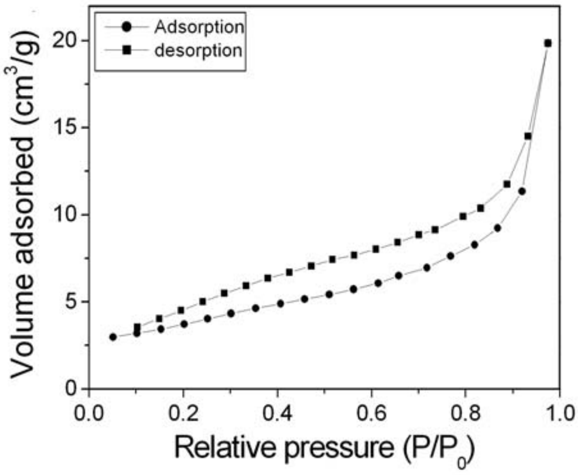

Figure S3. Nitrogen adsorption and desorption isotherms of the flowerlike Co_3O_4 microspheres.

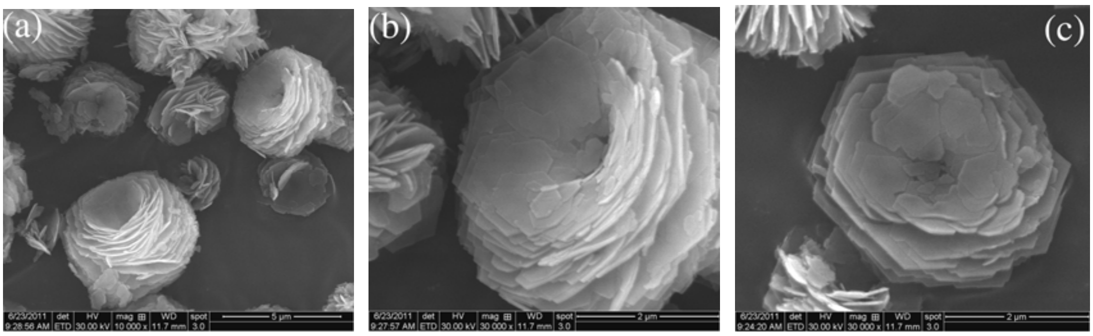

Figure S4. SEM images of the product obtained after hydrothermal reaction for 8 h, showing evidence of an assembly process of the microspheres via nanoplates.

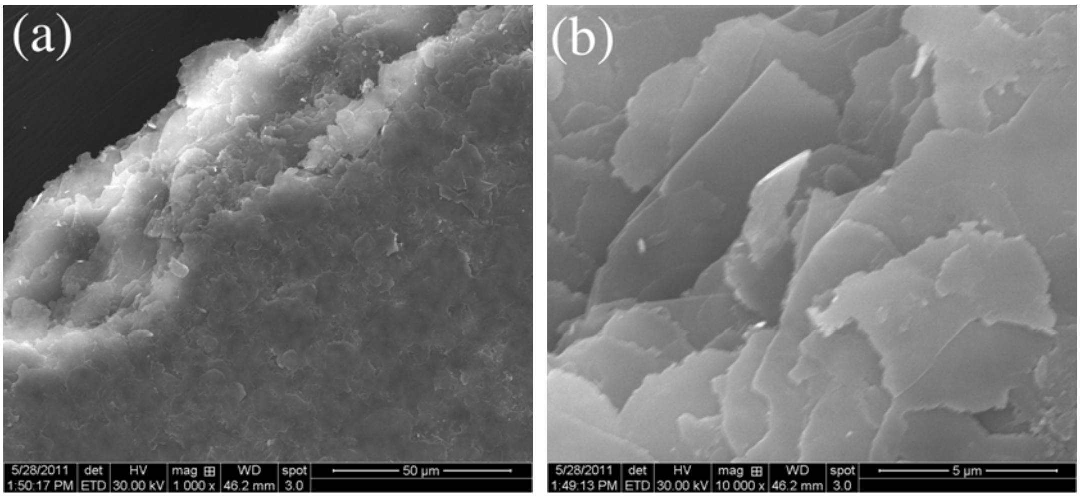

Figure S5. SEM images of the product obtained in the absence of $NH_3.H_2O$.

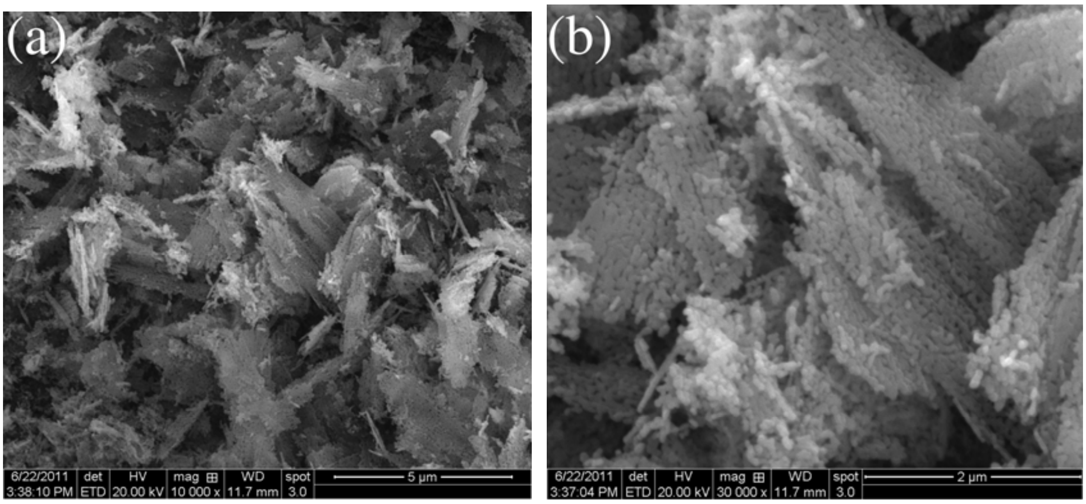

Figure S6. SEM images of the product consisting of nanocrystalline Co_3O_4 obtained with twice the amount of $NH_3.H_2O$ and calcining at 400 ^oC for 4 h.

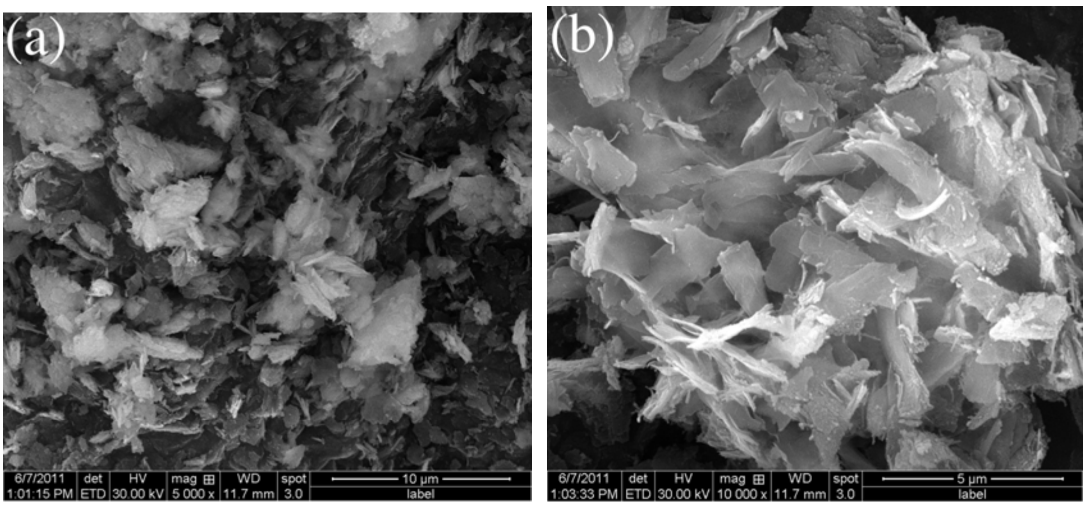

Figure S7. SEM images of the product obtained with ethanol in place of replace EG.

From Figure S5, S6, and S7, the results indicate that the appropriate amount of $NH_3.H_2O$ and the presence of ethylene glycol are critical factors for the formation of porous β-$Co(OH)_2$ microspheres.

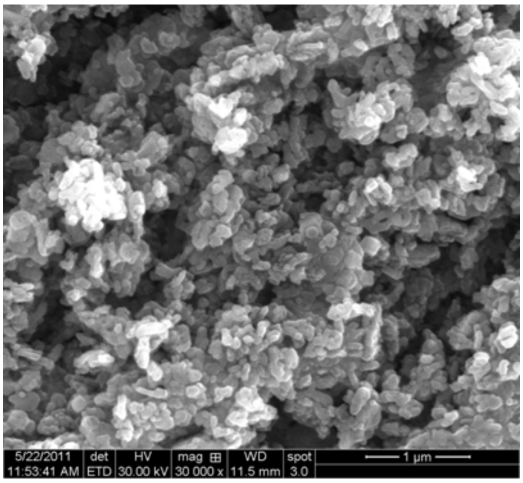

Figure S8. SEM image of the commercial Co_3O_4 powder (JOHNSON MATTHEY Inc.).

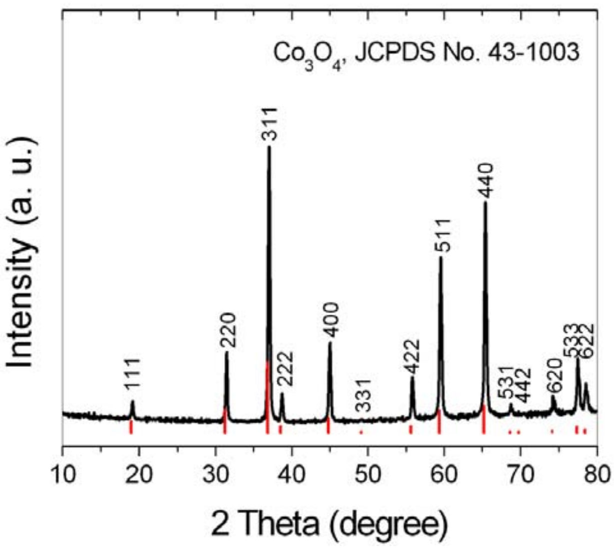

Figure S9. XRD patterns of the commercial Co_3O_4 powder.

Reference:

[S1] H. Men, P. Gao, B. Zhou, Y. Chen, C. Zhu, G. Xiao, L. Wang, M. Zhang, *Chem. Commun.* 2010, **46**, 7581-7583. Y.J. Chen, C.L. Zhu, G. Xiao, *Sens. Actuators, B* 2008, **129**, 639-642; Y.J. Chen, C.L. Zhu, G. Xiao, *Nanotechnology* 2006, **17**, 4537-4541.