Supporting Information

for

Controlled Synthesis of Self-Assembled Metal Oxide Hollow Spheres Via Tuning Redox Potentials: Versatile Nanostructured Cobalt Oxides**

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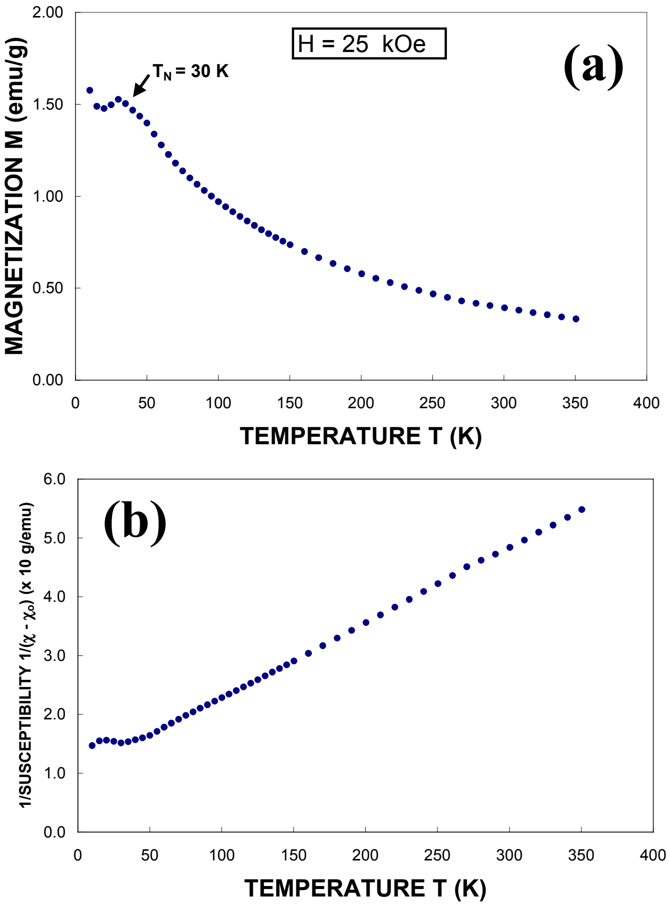
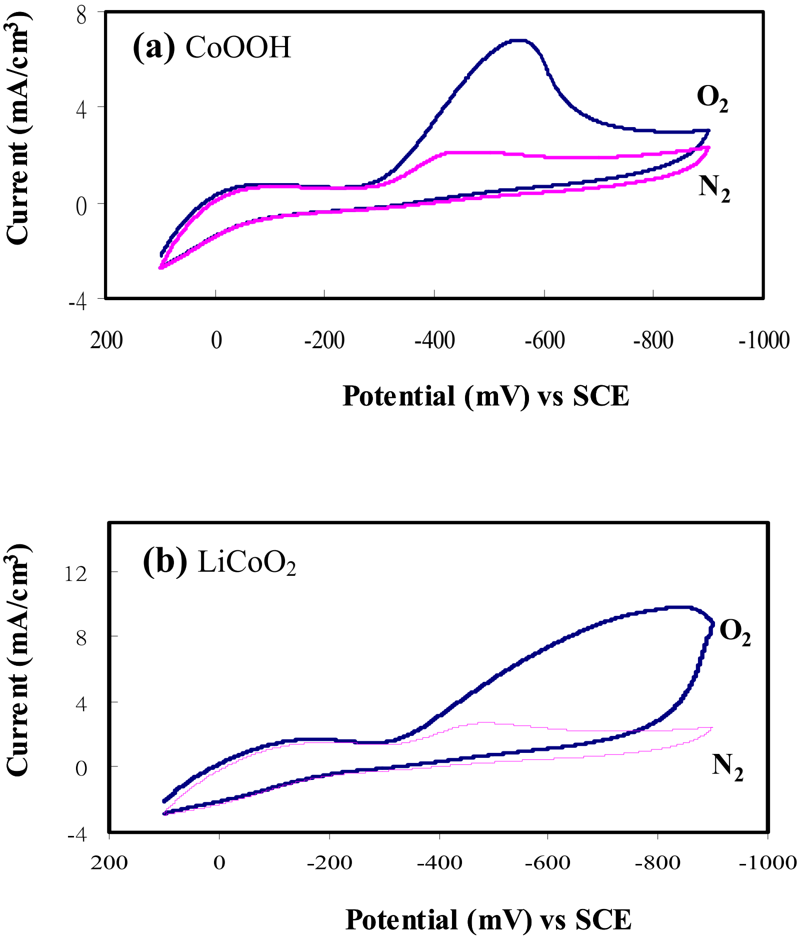
I. *Magnetic study of nanostructured* Co_3O_4 *micorspheres*

Figure S-1: The magnetic measurements of Co_3O_4; (a) Magnetization M (emu/g) versus temperature (K) in a magnetic field H = 25 kOe. An antiferromagnetic ordering is evident with a Néel temperature $T_N \approx 30$ K. (b) A fit of the magnetic susceptibility χ from 100 to 350 K to the Curie-Weiss law, $1/\chi$ (g/emu) versus T (K), yields an effective magnetic moment $\mu_{eff} = 3.90 \pm 0.05\ \mu_B$ per formula unit and Curie-Weiss temperature $\theta = -77 \pm 5$ K. (The magnetization-versus-field curves at various temperatures were completely linear and passed through the origin therefore enabling the calculation of a magnetic susceptibility and also indicating no significant ferromagnetic contamination.)



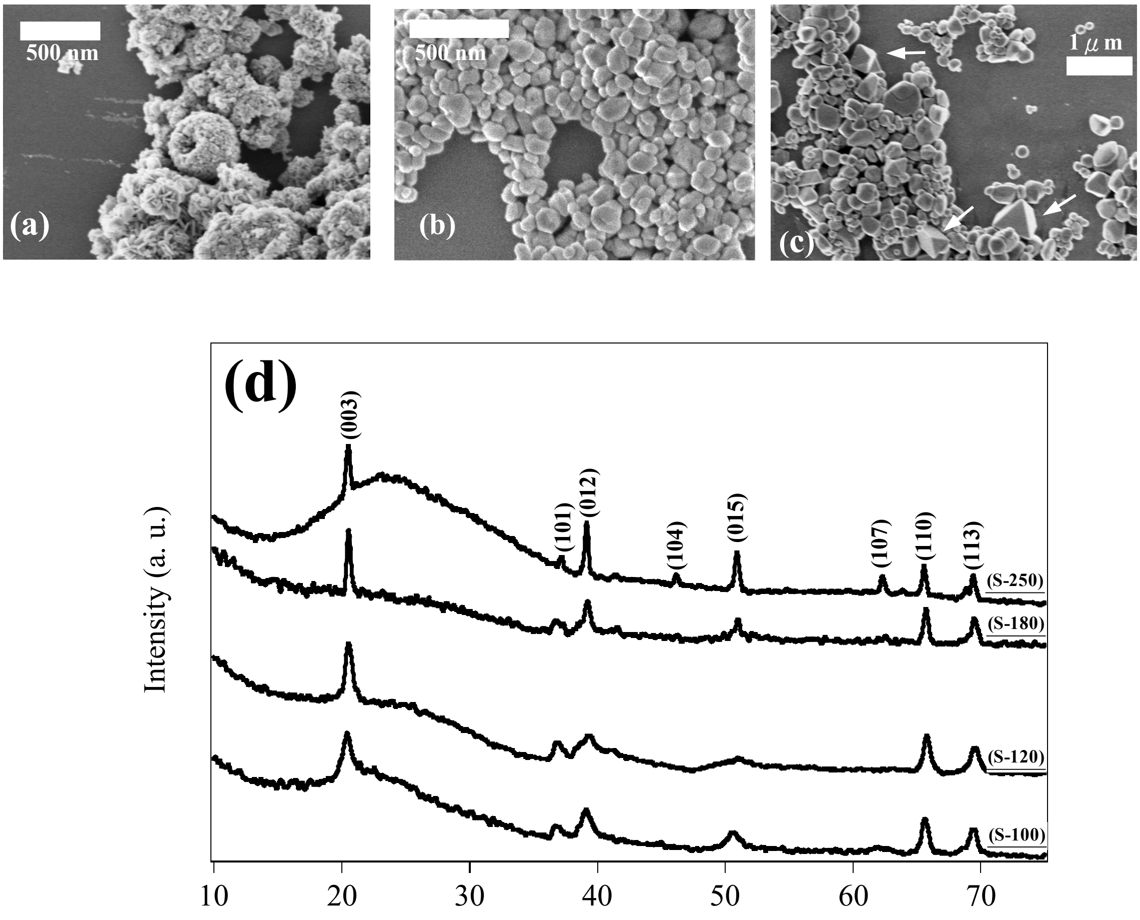
II. *Cyclic voltammetry study*

Figure S-2. The cyclic voltammetry of the electrodes composed of CoOOH (**S-100**), shown in (a), and nanostructured $LiCoO_2$ microspheres, shown in (b), were obtained in O_2 and N_2 atmosphere. Both of the electrodes are electrochemically inactive in a N_2 atmosphere under the experimental conditions of this study. Peak currents of reducing O_2 of CoOOH and $LiCoO_2$ are 6.3 and 8.5 mA at –555 and –835 mV, respectively. The peak current at –555 mV could be contributed to the occurrence of $2e^-$ reduction of O_2; the other peak at –835 mV could be due to $4e^-$ reduction.[1,2]



III. *Temperature effect of self-assembly of CoOOH*

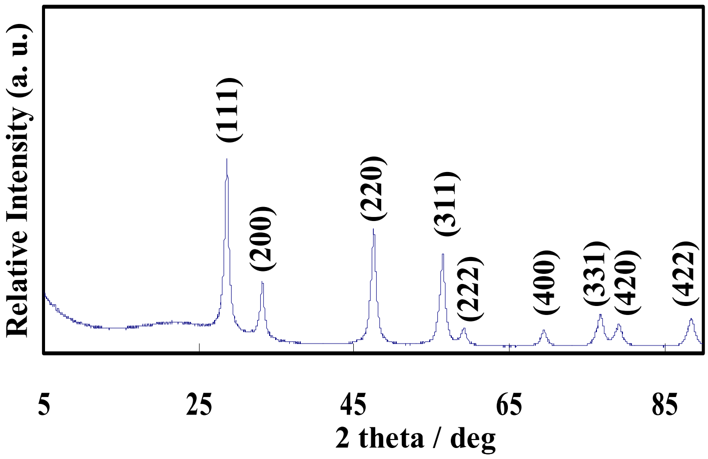
Figure S-3. The SEM images of CoOOH synthesized under (a) 120°C (**S-120**), (b) 180°C (**S-180**), and (c) 120°C (**S-250**), the white arrows in (c) point out the sharp-edge particles (eg. Octahedral-like particles); (d) the corresponding XRD patterns of these samples.



The SEM images show that the self-assembly of the spherical structure was observed with a diameter of several hundred nanometers for the tertiary structure at 120°C. The surface features exhibited similar physical stacking of the nanosized particles as compared to **S-100**, however, the size distribution of **S-120** microspheres was not as uniform as **S-100** in Figure 1. The reaction temperature was then increased to 180°C, and particle size was increased to several hundred nanometers without the presence of self-assembled microspheres. At 250°C, the particle sizes occurred in the micrometer to sub-micrometer range with some sharp-edged, octahedral shaped particles. The XRD patterns of these samples are shown in Figure S-3d. Sharper peaks and the appearance of weak reflections in **S-250** indicate that better crystallinity can be obtained by increasing reaction temperatures. For the low temperature sample (**S-100**), the nano-scale flakes produce broader diffraction peaks than the peaks of high temperature samples, which corresponds with the SEM observations of CoOOH nanoflakes in Figure 1.

IV. *XRD of CeO_2 hollow spheres*

Figure S-4. The XRD pattern of the as-synthesized CeO_2 hollow spheres. All peaks correspond to CeO_2 (JCPDS-34-394).



V. *Redox reactions of CoOOH*

$Co^{3+} + e^- \rightarrow Co^{2+}$ $E_0 = 1.808$ V

$S_2O_8^{-2} + 2\ e^- \rightarrow 2SO_4^{2-}$ $E_0 = 2.01$ V

$2\ CoSO_4 + (NH_4)_2S_2O_8 + 4\ H_2O \rightarrow 2\ CoOOH + (NH_4)_2SO_4 + 3\ H_2SO_4$ $E_0 = 0.202$ V

Reference

[1] C.-C. Chang, T.-C. Wen, *Electrochim. Acta* **2006**, *52*, 623.

[2] M. H. Shao, R. R. Adzic, *J. Phys. Chem. B* **2005**, *109*, 16563.