# Colloidal Polymerization of Polymer Coated Ferromagnetic Nanoparticles into Cobalt Oxide Nanowires

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## Supporting Information

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### (1) TEM analysis of the calcined $Co_3O_4$ nanowires

TEM observation was conducted to interrogate the effect of calcination on the interior morphology and porosity of $Co_3O_4$ nanowires.  PS-cobalt oxide nanowires dispersion were drop cast onto a carbon coated Ni grids and calcined in air at 400 °C, as Cu grids were observed to embrittle after the high temperature thermal treatment.  Figure S-1 confirmed that both the 1-D morphology and interior porous inclusions of $Co_3O_4$ nanowires were preserved after the calcination process.
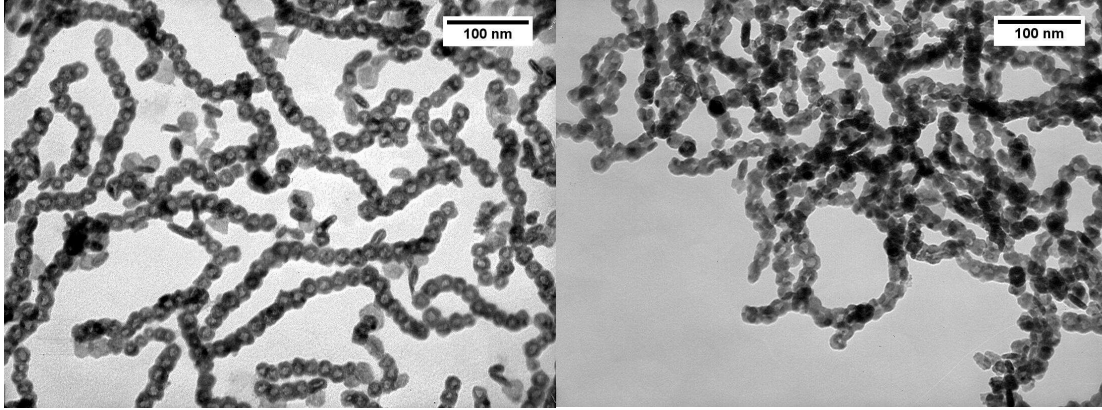
Figure S1: TEM of PS-Co$_3$O$_4$ nanowires on carbon coated Ni grid before (a) and after calcinations (b) with average particle and void dimension of 22 nm and 9 nm, respectively.

## (2) Spectroscopic determination of band edge energy levels of Co$_3$O$_4$ nanowires
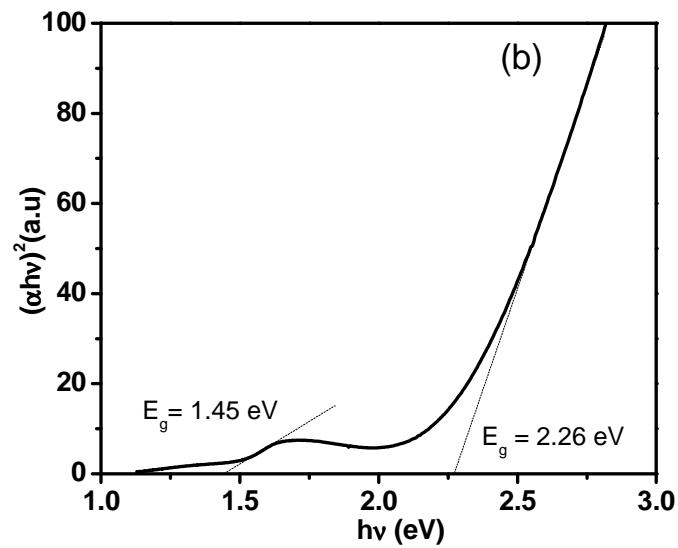


Figure S-2: Optical band gap energy Co$_3$O$_4$ nanowires obtained by extrapolation to $\alpha = 0$.

Co$_3$O$_4$ is a p-type semiconductor, in which the optical band gap (E$_g$) can be obtained from the absorption spectra. The band gap energies can be calculated using the equation 1:

$$(\alpha h v)^n = B(h v - E_g) \ldots\ldots\ldots\ldots\ldots \text{Eq 1}$$

where, $\alpha$ is the absorption coefficient, $hv$ is the photon energy, $B$ is a constant characteristic to the material, and $n$ equals either 1/2 for an indirect transition, or 2 for a direct transition. The absorption coefficient ($\alpha$) was obtained using the optical transmission data at different wavelengths based on equation (2).

$$I = I_0 \exp(-\alpha t) \dots\dots\dots\dots \text{ Eq 2}$$

The band gap was determined by plotting $(\alpha hv)^2$ versus photon energy (Tauc plot) as shown in Fig. S-2. The band gap energy was estimated by extrapolating the Tauc Plot to $\alpha = 0$ with intercepts at 1.45 and 2.26 eV, respectively. The best fit of $(\alpha hv)^2$ versus photon energy was found to be n = 2, suggesting that the obtained $Co_3O_4$ nanowires are semiconducting with a direct band gap transition.[1, 2]


### (3) Cyclic voltammetry of PS-coated cobalt oxide nanowires.

The electrochemical activity of hollow cobalt oxide nanowires (D ~ 30 nm) prepared via solution oxidation were investigated using cyclic voltammetry (CV). For spin-coated films of PS-CoO and PS-$Co_3O_4$ on ITO, film thicknesses were found to range from 50-60 nm as determined from AFM. PS-CoO and PS-$Co_3O_4$ nanowires on ITO electrodes were cycled between 0.8V to -0.9V, using 0.1-M NaOH as the electrolyte. In CV experiments taken at pH = 7 using 1M $LiClO_4$ as the electrolyte, only capacitive behavior of thin films were observed. In basic conditions (pH $\geq$ 10), voltammograms with peaks arising from Faradaic processes both in cathodic and anodic scans were afforded. These results were consistent with extensive reports from cobalt oxide films prepared via electrodeposition methods where reversible redox reactions were observed in basic aqueous media to the formation of various cobalt oxide and hydroxide phases.[3-5] CV measurements for both PS-CoO (after 3 hr. oxidation) and PS-$Co_3O_4$ (after 1-wk oxidation) nanowire films, anodic peaks were observed at 0.55 V and 0.8 V, while broad peak transitions in cathodic scans were also observed at 0.5 V and 0.7 V (Fig. S-3). At negative potentials scan beyond -1.0 V was not conducted due to the delamination of ITO. Exact assignment of these peaks with the various allotropic phases of cobalt oxides and cobalt hydroxides was complicated due to the presence of mixed phases in the initial PS-CoO and PS-$Co_3O_4$ samples as indicated in powder XRD of these materials (see Fig. 6). Nevertheless, the observation of redox activity in these samples was surprising due to the

presence of the polystyrene coating on nanowires, which was anticipated to exclude electrolyte accessibility to the metal oxide phase. These thin films on ITO were also stable to repeated cycling in alkaline media (Fig. 13).
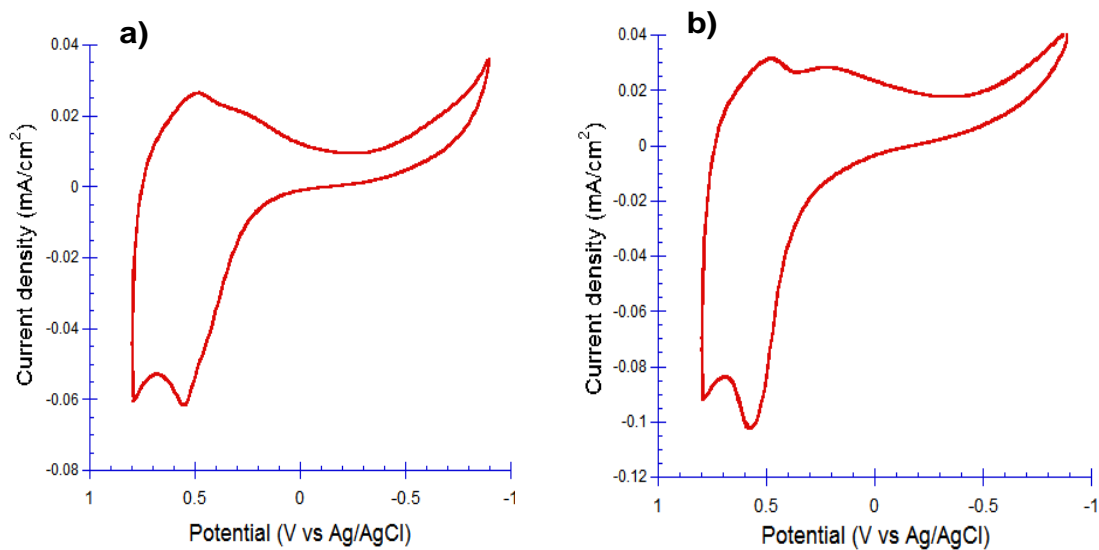


**Figure S-3:** Cyclic voltammogram of polystyrene coated nanowires after (b) PS-CoO and (c) PS-Co$_3$O$_4$ thin films after 78 cycles in 0.1 M NaOH electrolyte solution. All films were spin coated onto ITO from toluene dispersions (c = 25 mg/mL) and then dried in the vacuum oven at 70 °C prior to electrochemical experiments.

References

1.      Wang, G.; Shen, X.; Horvat, J.; Wang, B.; Liu, H.; Wexler, D.; Yao, J. Hydrothermal synthesis and optical, magnetic, and supercapacitance properties of nanoporous cobalt oxide nanorods. *J. Phys Chem. C* **2009,** *113*, (11), 4357-4361.
2.      Barreca, D.; Massign, C.; Daolio, S.; Fabrizio, M.; Piccirillo, C.; Armelao, L.; Tondello, E. Composition and microstructure of cobalt oxide thin films obtained from a novel cobalt(II) precursor by chemical vapor deposition. *Chem. Mater.* **2001,** *13*, 588-593.
3.      Lichusina, S.; Chodosovskaja, A.; Selskis, A.; Leinartas, K.; Miecinskas, P.; Juzeliunas, E. Pseudocapacitive behavior of cobalt oxide films on nano-fibre and magnetron-sputtered substrates. *Chemija* **2008,** *19*, (3-4), 7-15.
4.      Casella, I. G. Electrodeposition of cobalt oxide films from carbonate solutions containing Co(II)-tartrate complexes. *J. Electroanal. Chem.* **2002,** *520*, (1-2), 119-125.
5.      Barbero, C.; Planes, G. A.; Miras, M. C. Redox coupled ion exchange in cobalt oxide films. *Electrochem. Commun.* **2001,** *3*, (3), 113-116.