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

Pei Yuin Keng,† Bo Yun Kim,† In-Bo Shim,† Rabindra Sahoo,† Peter E. Veneman,† Neal R. Armstrong,† Heemin Yoo,† Jeanne E. Pemberton,† Mathew M. Bull,† Jared J. Griebel,† Erin L. Ratcliff,† Kenneth G. Nebesny,† and Jeffrey Pyun†‡

†Department of Chemistry, University of Arizona, Tucson, Arizona 85721, and ‡Department of Nano and Electronic Physics, Kookmin University, Seoul, Korea 136-702

The preparation of nanostructured conductive metal oxides is an important technological challenge toward the creation of improved materials for energy storage and (photo)electrochemical catalysis for water splitting. 1–4 Semiconducting metal oxides, such as, TiO2, RuO2, Fe2O3, and Co3O4 have been widely explored as electrode materials in a number of energy related applications in photovoltaics, (photo)electrolytic water splitting, batteries, and supercapacitors. 5–8 Cobalt oxides, such as, cobalt cobaltite (Co3O4) have been widely investigated as electrode materials for lithium batteries, catalysts for water reduction, and carbon monoxide oxidation, electrochromic materials, and gas sensors. 9–16

The preparation of nanostructured Co3O4 has been explored as a route to enhance the electrochemical and catalytic properties of these materials via both an increase in the electroactive surface of the electrode films and improved charge transport from nanoscale ordering. 11,12,14 Co3O4 thin films have been prepared by numerous routes, including electrodeposition and sputtering techniques. 17–25 Colloidal forms of Co3O4 have been synthesized using solvothermal/hydrothermal techniques to synthesize well-defined nanocrystals and hollow nanospheres. 26–40 Nanostructured mesoporous materials have also been prepared using sol–gel precipitation in the presence of either hard, or soft templates. 41–45 One-dimensional (1-D) Co3O4 nanomaterials have also recently been prepared using a variety of different approaches, namely, sol–gel precipitation, 13,15 oxidation of metallic cobalt (Co) foils, 46 hydrothermal processes, 47,48 polylol reduction, 49 and electrospinning. 50–52 Despite these numerous advances, the preparation of high aspect ratio 1-D Co3O4 nanowires, without the use of structure-directing templates, remains an important synthetic challenge in gram-scale quantities.

The use of nanoparticle precursors as chemical reagents has recently gained significant attention as a novel approach to prepare hierarchically complex materials. Recent examples of using nanoparticles as “colloidal molecules” have been reported for the preparation of novel colloidal crystals, 53 well-defined clusters, 54 supramolecular amphiphiles, 55 and mesoscopic polymer chains. 56,57 The assembly of nanoparticles into one-dimensional (1-D) nanomaterials has been achieved using a number of approaches, notably, selective ligand chemistry on Au, or iron oxide NPs 58–61 and chemical linking of dipolar colloids. 62–78 An elegant demonstration of using nanoparticles as reagents in chemical reactions has...
been the preparation of hollow semiconductor colloids via the nanoscale Kirkendall effect. Alivisatos et al. reported the preparation of discrete hollow cobalt oxide, or cobalt sulfide NPs by the oxidation/sulfidation of dispersed superparamagnetic CoNP precursors.79,80 Hollow cobalt selenide (CoSe2) nanowires have also been prepared by the combination of dipolar NP assembly81 and the nanoscale Kirkendall effect using ferromagnetic CoNPs passivated with small molecule surfactants.77 Using these design principles we have developed a facile synthetic methodology to use ferromagnetic nanoparticles as dipolar precursors to prepare cobalt oxide nanowires.

Herein, we report the synthesis and characterization of hollow cobalt oxide nanowires via the “colloidal polymerization” of ferromagnetic polystyrene coated cobalt nanoparticles (PS-CoNPs). The colloidal polymerization process is described as a combination of dipolar nanoparticle assembly and a chemical reaction converting colloidal precursors into a fused 1-D material. In this report, cobalt oxide nanowires were formed by the magnetic preorganization of metallic PS-CoNPs into 1-D mesostructures and subsequent oxidation of the assembled colloids. This process is reminiscent of the step-growth polymerization of A-B small molecule monomers to form macromolecules, as dipolar metallic PS-CoNPs were employed as “colloidal monomers” to form interconnected 1-D mesostructures and is a mesoscale variation of supramolecular polymerization.82-85 This particular approach enabled the preparation of very fine cobalt oxide nanowires that were passivated with a polymeric steric layer that imparted colloidal stability when dispersed in organic media. Furthermore, calcination of the polymer-coated cobalt oxide nanowires was achieved along with spectroscopic, electrical, and electrochemical characterization of these nanomaterials, which confirmed for the first time the viability of this synthetic methodology (i.e., colloidal polymerization via dipolar assembly and the Kirkendall effect) to form electroactive materials.

RESULTS AND DISCUSSION

Colloidal Polymerization of Ferromagnetic Metallic Cobalt Nanoparticles into 1-D Cobalt Oxide Nanostructures. The synthesis of PS-coated cobalt oxide nanowires was conducted by bubbling O2 into 1,2-dichlorobenzene (DCB) dispersions of ferromagnetic PS-CoNPs at 175 °C for varying reaction times in the absence of an external magnetic field (i.e., zero field conditions) (Scheme 1). Well-defined ferromagnetic PS-CoNPs were prepared using amine end-functional polystyrene surfactants in the thermolysis of dicobaltotacarbonyl (Co2(CO)8), as reported previously. Amine-terminated PS surfactants were synthesized using controlled polymerization,86-88 namely, atom transfer radical polymerization (ATRP)89 which enabled precise control of polymer molar mass, composition, and functional group placement. TEM images of ferromagnetic PS-CoNPs (Figure 1a,b) confirmed the preparation of uniformly sized colloids (D = 20 ± 2.4 nm) that self-assembled into 1-D mesostructures from interparticle dipolar associations when deposited onto a supporting substrate in zero field. We previously reported that our synthetic methods for PS-CoNPs enabled the preparation of well-defined colloidal building blocks in appreciable quantities (~800 mg per reaction) and were easily redispersible in various organic solvents (e.g., toluene, tetrahydrofuran, methylene chloride) due to the polymer coating passivating the magnetic colloid. These synthetic conditions for this report were further optimized to enable nearly doubling of the yield of ferromagnetic PS-CoNPs (yield = 1.53 g) that were also readily stored as powders and re-dispersed into organic solvents.

In the conversion of PS-CoNPs into PS-coated cobalt oxide nanowires, the oxidation reaction was carried out by bubbling oxygen into the PS-CoNP ferrofluid at elevated temperature (T = 175 ºC). The use of ferromagnetic PS-CoNPs was essential to the formation of cobalt oxide nanowires under zero field conditions, as superparamagnetic CoNPs were unable to polymerize due to the absence of a permanent dipole above cryogenic temperatures.71 A striking feature of 1-D mesostructures formed via this colloidal polymerization was the presence of hollow inclusions in every nanoparticle repeating unit within cobalt oxide nanowires. These hollow inclusions were formed in the oxidation reaction due to a nonuniform diffusion and reaction of O2 with Co atoms throughout the metallic NP. Under these conditions, oxidation of the NP was confined to the outer shell, resulting in depletion of Co atoms from the colloidal core to satisfy the valency of O atoms in the growing cobalt oxide phase. This phenomenon has been described by the nanoscale Kirkendall effect and resulted in
both the formation of hollow cores and a dimensional expansion of the cobalt oxide NP shell. PS-coated nanowires were formed because of the coalescence of expanding cobalt oxide NP shells formed in the oxidation reaction of preorganized PS-CoNP colloidal monomers. By varying the oxidation time of metallic PS-CoNPs in DCB, nonaggregated nanowires of either cobaltous oxide (PS-CoO), or cobalt cobaltite (PS-Co$_3$O$_4$) could be achieved as determined using X-ray diffraction (XRD) after a reaction time of 3 h or 1 week, respectively. The yields of these PS-coated cobalt oxide nanowires were also conducted on gram scales (yield = 1.04 g) that were enabled by improvements in the synthesis of ferromagnetic PS-CoNPs.

**Figure 1.** TEM images of the polystyrene-coated cobalt nanoparticles with particle size, $D = 20 \pm 2.4$ nm after oxidation for (a,b) 0 h; (c,d) 3 h, with particle diameter $= 29 \pm 2.7$ nm, and (e,f) 1 week, with particle diameter $= 32 \pm 3.5$ nm. All TEM samples were drop-casted from 0.5 mg/mL toluene dispersion onto a carbon-coated copper grid at zero field.

**TEM and FE-SEM Imaging of PS-CoNPs and PS-Cobalt Oxide Nanowires.** The formation of interconnected hollow nanowires was confirmed using transmission electron microscopy (TEM) of samples drop cast onto supporting surfaces (Figure 1a,b). The dipolar PS-CoNP precursors were imaged as discrete colloids ($D = 20$ nm $\pm 2.4$ nm) assembled into NP-chains spanning micrometers in length. TEM showed that the native polymer-coated cobalt nanoparticles appeared as a dark solid sphere due to the high electron density of the cobalt core (Figure 1 a,b). After the oxidation reaction, a hollow inclusion in every cobalt oxide nanoparticle could be observed along the structurally intact 1-D nanostructure. The kinetics of the colloidal polymerization were followed by the removal of aliquots over varying reaction times.
time for TEM imaging. After a reaction time of 3 h (Figure 1c,d), three distinct regions of nanoparticle could be observed in TEM: (1) a lower electron density of the cobalt oxide shell, (2) a dark inner sphere of the cobalt core and (3) interior voids corresponding to the coalescence of vacancies at the interface. After 24 h, PS-coated cobalt oxide nanowires were observed to be completely hollow due to the conversion of metallic CoNPs into CoO phases, as indicated by XRD (see later discussion). As the oxidation time of PS-CoNPs in the DCB ferrofluid was extended over a period of 1 week, a similar morphology was observed. These hollow nanoparticles were also connected into a 1-D morphology (Figure 1e,f) that spanned from several hundred nanometers to micrometers in length, as imaged via SEM (Figure 2).

High resolution TEM (HR-TEM) provided further evidence of 1-D connectivity of these cobalt oxide NPs into nanowires. HR-TEM imaging (Figure 2) confirmed that cobalt oxide NP shells were fused together to form 1-D chains after reaction times of 3 h (Figure 1), along with a dimensional expansion of nanowires from the conversion of PS-CoNPs into PS-CoO nanowires \((D_{\text{eff}} = 29 \, \text{nm})\). In contrast, PS-CoNPs precursors \((D_{\text{eff}} = 20 \, \text{nm})\) were imaged as discrete solid colloids that were separated by the outer PS shells (Figure 2a). An additional dimensional expansion of the cobalt oxide nanowire diameters \((D_{\text{eff}} = 32 \, \text{nm})\) were observed from HR-TEM over extended oxidation times of 1 week and were attributed to the gradual conversion of PS-CoO nanowires into CoO phases (Figure 2b).

PS-CoNPs and PS-cobalt oxide nanowires were deposited onto ITO substrates via spin coating and imaged using field emission scanning electron microscopy (FE-SEM) to ascertain if discrete 1-D mesostructures were formed from the colloidal polymerization process. Thicker films of PS-cobalt oxide nanowires were cast onto ITO substrates and FE-SEM revealed the presence of nonaggregated 1-D chains that packed into a mesoporous film (Figure 3a). Discrete, nonagglomerated nanowires were also cast and imaged on ITO from dilute dispersions and were found to possess a distribution of chain lengths spanning hundreds of nanometers to several micrometers (Figure 3b), which was attributed to the step-growth-like nature of the colloidal polymerization of PS-CoNPs. FE-SEM qualitatively imaged morphology differences between the native PS-CoNPs and the PS-cobalt oxide nanostructures. SEM images of the PS-CoNPs (Figure 3c) showed 1-D chains of individual colloids that were associated via magneto-static interactions, but separated by the polymer encapsulating shell. In contrast, PS-cobalt oxide nanowires were imaged via FE-SEM as beaded, but continuous 1-D mesostructures ranging from hundreds of nanometers to micrometers in length. (Figure 3d).

Solid-State Characterization of PS-Coated Cobalt Oxide and Calcined CoO Nanowires. To further improve the crystallinity of the cobalt oxide phase within the nanowire and to remove the PS organic shell, the solution-deposited films on ITO were calcined at 400 °C in air for 16 h. Thermogravimetric analysis (TGA) of PS-coated nanowires confirmed that organics were fully degraded under these calcination conditions. FE-SEM of PS-CoO films on ITO imaged the presence of 40 nm wide nanowires spanning micrometers in length. High resolution FE-SEM imaging visualized PS-coated nanowires possessing a relatively smooth surface morphology due to the glassy-like nature of the polymer shell (Figure 4a, b). FE-SEM after calcination revealed that the 1-D morphology of CoO films were maintained, but the surface topography was considerably more roughened as evidenced by facets and small domains along oxidized nanowires (Figure 4c,d). We have also confirmed via TEM that both the 1-D morphology and the porous inclusions of CoO nanowires were preserved after the calcination process (see Supporting Information, Figure S-1).
Figure 3. FE-SEM images of thick films (a) and isolated nanowires (b) of PS-Co$_3$O$_4$ materials spin coated onto ITO; (c) high magnification FE-SEM of discrete chains of PS-CoNPs; (d) high magnification FE-SEM of PS-Co$_3$O$_4$ single nanowires.

Figure 4. FE-SEM images of PS-Co$_3$O$_4$ nanowires cast on ITO at both high (a) and low (b) magnification and after calcinations in air at 400 °C at high (c) and low (d) magnification.
Powder X-ray diffraction was used to characterize the solid-state structure of PS-CoNP, PS-coated nanowires and calcined cobalt oxide materials. The XRD results confirmed the initial PS-CoNP precursors exhibited a metallic fcc-cobalt phase of low crystallinity (Figure 5a). Subsequent oxidation of PS-CoNPs in DCB at 175 °C over a 3 h period converted these precursors to a mixture of rock salt-CoO and residual fcc-cobalt (Figure 5b). Prolonged oxidations of PS-CoNPs over a period of 1 week predominantly yielded an amorphous phase of Co3O4 (Figure 5c). Further calcination of PS-CoO NPs in air at 400 °C burned out the organic PS outer shells and yielded polycrystalline spinel Co3O4 material, in which all diffraction peaks were indexed to bulk spinel Co3O4 (Figure 5d).

The magnetic properties of PS-coated and calcined cobalt oxide nanocomposites were measured using vibrating sample magnetometry (VSM) at room temperature and at 60 K (Figure 6). The general trend from the magnetometry indicated that both the saturation magnetization ($M_s$) and coercivity ($H_c$) significantly decreased after the colloidal polymerization process which was in agreement with the formation of antiferromagnetic CoO and Co3O4. The native PS-CoNPs (Figure 6a,1), exhibited weakly ferromagnetic behavior at room temperature ($M_s = 41.2$ emu/g; $H_c = 713$ Oe). The magnetometry at room temperature revealed that PS-CoO materials (Figure 6a,2) were weakly ferromagnetic after a 3 h oxidation in DCB and exhibited a significant decrease in the saturation magnetization ($M_s = 4.6$ emu/g; $H_c = 78$ Oe).
emu/g) and coercivity ($H_c = 362$ Oe) at room temperature. This ferromagnetic behavior was attributed to the presence of residual metallic cobalt, which was further supported by the XRD data in Figure 5. Similar magnetization behavior was also observed in wurtzite CoO, in which the presence of metallic Co impurities resulted in a hysteresis curve. The magnetization ($M = 2.07$ emu/g at 10000 Oe) and coercivity ($H_c = 260$ Oe) of PS-Co$_3$O$_4$ were further decreased by prolonged 1 week oxidation times. The magnetometry of PS-Co$_3$O$_4$ materials exhibited a linear relationship of magnetization ($M$) vs applied field ($H$) behavior due to the presence of rock-salt CoO and spinel Co$_3$O$_4$ phases as indicated by the linearity of magnetometry above and below 5000 and $-5000$ Oe (Figure 6b). The magnetometry of the PS-coated Co$_3$O$_4$ nanocomposite (Figure 6b) also exhibited weakly ferromagnetic behavior as evidenced by a small hysteresis which was attributed to trace Co metal. Calcined Co$_3$O$_4$ nanowires (Figure 6c) exhibited a linear magnetization curve with a reduced $M$ value. The linear curve was consistent with the paramagnetic behavior of Co$_3$O$_4$ nanoparticles at room temperature as reported elsewhere.

Spectroscopic Characterization of Co$_3$O$_4$ Nanowires. Characterization of polymer-coated and calcined cobalt oxide nanowires was conducted using Raman spectroscopy to confirm the formation of the spinel Co$_3$O$_4$ phase (Figure 7). Raman spectroscopic characterization was complicated by the strong absorption of Co$_3$O$_4$ films in the visible wavelength regime, as evidenced by the black appearance of this material. Although Raman spectroscopic characterization of Co$_3$O$_4$ materials has primarily been conducted using microprobe Raman techniques, we were able to acquire quality Raman spectra of Co$_3$O$_4$ nanowire films using standard approaches by processing of thin films on reflective Ag substrates. PS-coated cobalt oxide nanowires were spin-coated onto clean Ag substrates and measured both before and after calcination reactions in air at 400 °C. The preparation of PS-Co$_3$O$_4$ nanowires after a solution oxidation time of 1-wk was confirmed in the Raman spectra by the presence of peaks at 483, 528, and 692 cm$^{-1}$, which correspond to $E_g$, $F_{2g}$, and $A_{1g}$ vibrational modes, respectively, for Co$_3$O$_4$. After calcination of PS-coated nanowires, sharper and more intense peaks at 483, 528, and 692 cm$^{-1}$ were observed. In addition, the $A_{1g}$ peak shifted from 690 to 692 cm$^{-1}$, which has been correlated with an enhancement in electrical conductivity of Co$_3$O$_4$ thin films. After calcination, an additional broad peak at 600 cm$^{-1}$ was observed and assigned to a second $F_{2g}$ mode that was expected based on previous Raman assignments of Co$_3$O$_4$ thin films. However, the relative intensity of this peak at 600 cm$^{-1}$ was intuitively too high to arise solely from the formation of more crystalline Co$_3$O$_4$ nanowire thin films and was identified to be trace graphitic carbon (other broad carbon peaks around 1600 and 1350 cm$^{-1}$ also observed) that was formed from pyrolysis of the organic PS coating.

X-ray photoelectron spectroscopy (XPS) was also used to confirm the formation of Co$_3$O$_4$ nanowires after calcination in air at 400 °C. Al K$\alpha$ XPS was conducted of thin films deposited onto ITO substrates and measured in the regions of Co$2p$ and O$1s$ binding energy regions. XPS in the Co$2p$ region of binding energies exhibited two major peaks at 796.1 and 780.6 eV that corresponded to 2$p_{3/2}$ and 2$p_{1/2}$ spin−orbit components, respectively, with the Co$3p_{3/2}$ peak at 796.1 eV being more intense (Figure 8). Weaker satellite peaks at 819.6 and 803.6 eV were also observed and assigned to Co$2d$ orbitals.
Surface of calcined Co$_3$O$_4$ materials as observed by the nanowire and the high degree of corrugation on the surface revealed two broad absorption bands centered around 450 and 750 nm, which were consistent with other literature reports on the optical properties for spinel type Co$_3$O$_4$ thin films. The optical band gap energies were determined using the Tauc plot method and were in reasonable agreement with previous spectroscopic studies of cobalt oxide thin films indicative of two optical transitions at 1.45 and 2.26 eV. The optical transition from Co$_3$O$_4$ nanowires at 2.26 eV was attributed to a band gap transition from the valence band of the metal oxide, which was proposed to comprise a mixture of both Co$^{2+}$ and Co$^{3+}$ 3d and O 2p states. The lower energy transition at 1.45 eV was assigned to transitions from midgap states into the conduction band due to the presence of defect sites within these hollow Co$_3$O$_4$ nanowires. As previously discussed, Co$_3$O$_4$ nanowires prepared via colloidal polymerization resulted in the formation of hollow inclusions in nanoparticle repeating units that were fused along the 1-D mesostructure. As a result, these nanomaterials were anticipated to contain defect sites in the metal oxide phase, as a likely consequence of a greater number of surface Co ion sites accompanied by ion vacancies in the partially coordinated Co$^{2+}$ ions within the spinel Co$_3$O$_4$ lattice. These assumptions were based on the presence of both hollow interior inclusions along the nanowire and the high degree of corrugation on the surface of calcined Co$_3$O$_4$ materials as observed via TEM and FE-SEM, respectively. These band gap and midgap states assignments were also supported by modeling and valence band photoemission studies of nonstoichiometric Co$_3$O$_4$ films, in which the valence band was assigned to a mixture of both Co$^{2+}$ and Co$^{3+}$ 3d and O 2p states. Extensive reports on the optical spectroscopy of Co$_3$O$_4$ materials have assigned these optical transitions to two direct band gaps from solely O 2p states in the valence band into Co$^{2+}$ 3d conduction band states at 2.26 eV and into Co$^{3+}$ conduction band 3d states at 1.45 eV. However, given the strong likelihood of defect sites being present in Co$_3$O$_4$ nanowires prepared via colloidal polymerization, it is anticipated that optical transitions observed were not from two direct band gaps but arose from discrete band gap and midgap transitions.

Because of the novel nanoscale structure of the cobalt oxide nanowires prepared via colloidal polymerization, UPS of calcined Co$_3$O$_4$ nanowire on Au substrates was conducted to determine the highest energy of the valence band (VB) in the metal oxide semiconductor. In the UPS experiment, the kinetic energy of the photoexcited electrons emitted from Co$_3$O$_4$ films were measured assuming electrical equilibration between the Au substrate, in which a common Fermi level ($E_F = 0$) was established (Figure 10). Because electrical contact and equilibrium between the Au substrate and the film was required, UPS measurements of PS-coated nanowires were not conducted. While more detailed UPS studies have been conducted with full spectroscopic assignments of photoemitted electrons from Co$_3$O$_4$ thin films, our interest for this investigation was focused on the determination of highest energy levels of the Co$_3$O$_4$ VB. The UPS spectrum of Co$_3$O$_4$ on a Au substrate shown in Figure 10a has been normalized to the Fermi level of Au, in which $E_F = 0$. The edge of the highest energy population of the VB for Co$_3$O$_4$ was observed as a sharp increase at $-0.5$ eV relative to the mutual Fermi level of Au and the spectrometer ($E_F = 0$) in the UPS spectrum, while the lowest energy electrons were found at the $-16.4$ eV. The absolute difference in energies between the lowest and highest kinetic energy edges of the UPS spectrum was defined as the spectral width (SW), which afforded a SW = 15.9 eV. The threshold ionization potential (IP) of the Co$_3$O$_4$ nanowire material was obtained as the difference of the incident photon energy (for He(I) source $= 21.2$ eV) and the spectral width (15.9 eV) of the UPS spectrum (Figure 10a), which afforded an IP = 5.3 eV.

From the UPS IP data, the energy of the Co$_3$O$_4$ VB with respect to vacuum was set to 5.3 eV, which in conjunction with the optical band gaps determined from the optical absorption spectroscopy (Figure 9), afforded a proposed band edge energy diagram for calcined Co$_3$O$_4$ nanowires as shown in Figure 10c. Because of the polycrystalline nature of the Co$_3$O$_4$ nanowires prepared via colloidal polymerization, an assignment of the exact valence band and conduction band was difficult, because earlier calculations and modeling of band edge energies was primarily based on crystalline Co$_3$O$_4$. Based on the optical absorption spectroscopy studies of Co$_3$O$_4$ epitaxy film by Langell and the optical band gap measurements (Figure 9), the highest energy level of valence band was assigned to a mixture of Co$^{2+}$ ions 3d and O 2p orbitals with a band gap energy of 2.26 eV and a midgap transition of 1.45 eV. It is important to note that the values of the Co$_3$O$_4$ VB (5.3 eV) and conduction bands (3.04 eV) are determined from UPS in vacuum and may deviate from values determined photoelectrochemically via Mott—Schottky measurements since solvent effects were not accounted for using the described methodology.

The current density ($J$)–voltage ($V$) characteristics of calcined Co$_3$O$_4$ nanowires were determined via conductive probe atomic force microscopy (C-AFM). Nanowires...
were spin-coated onto Pt-coated Si substrates and then analyzed with a Pt tip for C-AFM J-V measurements in 20 μm² areas, with a bias of +1.0 to −1.0 V in air at room temperature. The wormlike morphology of the Co₃O₄ nanowires (Figure 11a) was first resolved by tapping mode AFM using a silicon nitride cantilever. In height contrast imaging, bright features were assigned to the Co₃O₄ nanowires, while dark regions corresponded to voids formed from the interdigitation of 1-D components, which was consistent with the FE-SEM of the calcined film (Figure 3a). The topography of the film was also imaged in tapping mode using a Pt cantilever for C-AFM prior to electrical probing as shown in Figure 11b; however, resolution of nanowire features was compromised because of the use of nonoptimal Pt tips for visualization of individual nanoscale wires. Nevertheless, these Pt tips were effective in current contrast C-AFM, which imaged very delicate nanoscale features, confirming that nanowires were uniformly conductive, as visualized as bright regions corresponding to Co₃O₄ semiconducting nanowires (Figure 11c). Darker features in current-mapped C-AFM images also corresponded to porosity generated from the void spaces in the nanowire thin film. The J-V characteristics of these Co₃O₄ NP films revealed a linear relationship (Figure 11e) from −0.12 to +0.12 V, indicative of Ohmic contact between the Pt tip and Co₃O₄ nanowires, while space-charge limiting current was observed above these potentials. The symmetrical J-V plot further showed that these Co₃O₄ nanowires were in Ohmic contact with both the Pt tip junction as well as the Pt substrate on the bottom contact. This current–voltage behavior was consistent with the predicted behavior of Co₃O₄, which is a p-type semiconductor with electrical conductivity arising from hole carriers. Quantitative determination of carrier mobilities via C-AFM was complicated by the 1-D nanoscale morphology of Co₃O₄ nanowires due to the additional geometrical terms in the space charge-limited current equation that is only valid for solid films. Quantitative measurements of electrical conductivity are currently in progress via microwave techniques.

Cyclic Voltammetry (CV) of Calcined Co₃O₄ Nanowire Films on ITO. Cyclic voltammetry was used to characterize calcined Co₃O₄ nanowire films on ITO. To afford polycrystalline Co₃O₄ materials, PS-Co₃O₄ films on ITO were first calcined in air at T = 400 °C prior to electrochemical measurements and cleaned by exposure to UV—ozone to remove residual organics from the metal oxide surfaces. FE-SEM of calcined films confirmed that the 1-D morphology of nanowires remained intact, as discussed previously (see Figure 9).
Cyclic voltammetry was performed on the films in 0.1 M NaOH electrolyte solution while cycling from 0.7 to 0.9 V at 20 mV/s with respect to a Ag/AgCl (3 M KCl) reference electrode (Figure 12). Multiple peaks within the voltammogram were consistent with the formation of a number of cobalt oxide phases at different oxidation states, specifically, anodic peaks at 0, 0.2, and 0.6 V and corresponding cathodic peaks at 0.5, 0.2, and −0.5 V. Assignments of these peaks were in agreement with previously reported phases of cobalt in water in the Pourbaix diagram and other recent reports which can be associated with the following reactions:10,21,22,102

Anodic Scan (toward Positive Potentials).

peak I (0.3 V), Co3O4 formation:

\[
3\text{Co(OH)}_2 + 2\text{OH}^- \rightleftharpoons \text{Co}_3\text{O}_4 + 4\text{H}_2\text{O} + e^- \quad (1)
\]

peak II (0.5 V), CoOOH formation:

\[
\text{Co}_3\text{O}_4 + \text{OH}^- + \text{H}_2\text{O} \rightleftharpoons 3\text{CoOOH} + e^- \quad (2)
\]

peak III, Co2O4 formation:

\[
\text{CoOOH} + \text{OH}^- \rightleftharpoons \text{Co}_2\text{O}_4 + \text{H}_2\text{O} + e^- \quad (3)
\]

peak IV, oxygen evolution reaction (OER):

\[
4\text{OH}^- \rightleftharpoons \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \quad (4)
\]

Cathodic Scan (toward Negative Potentials).

peak V, CoOOH formation:

\[
\text{Co}_2\text{O}_4 + \text{H}_2\text{O} + e^- \rightleftharpoons \text{CoOOH} + \text{OH}^- \quad (5)
\]

peak VI, Co3O4 formation:

\[
3\text{CoOOH} + e^- \rightleftharpoons \text{Co}_3\text{O}_4 + \text{OH}^- + \text{H}_2\text{O} \quad (6)
\]

peak VII, Co(OH)2 formation:

\[
\text{Co}_3\text{O}_4 + \text{H}_2\text{O} + 2e^- \rightleftharpoons 3\text{Co(OH)}_2 + 2\text{OH}^- \quad (7)
\]

As previously determined by powder XRD (Figure 6d), the initial state of the calcined cobalt oxide nanowires was found to be polycrystalline Co3O4 phase, which consisted of both the Co3+ and Co2+ oxidation...
states and can be seen in the cyclic voltammogram (peak I). In the anodic scan, from potential 0 to 0.2 V, the CoO$_2$ phase was oxidized to the cobalt oxyhydroxide (CoOOH) phase with a Co$^{4+}$ oxidation state and an uptake of hydroxide ions and water from the electrolyte media (peak II-eq 2). Further anodic scanning to 0.6 V resulted in oxidation of the CoOOH to cobalt peroxide (CoO$_2$) with a Co$^{6+}$ oxidation state and condensation reactions to release water (peak III, eq 3). A large anodic peak in the voltammogram at 0.7 V was observed and attributed to electrocatalytic oxygen evolution (OER) by the Co$_3$O$_4$ phase oxidized to the cobalt oxyhydroxide (CoOOH) phase with a Co$^{3+}$ oxidation state and condensation reactions to release water (peak VII, eq 6). As shown in Figure 10, these nanostructured cobalt oxides prepared via colloidal polymerization (i.e., magnetic assembly and nanoscale Kirkendall reaction) undergo electrochemical charge transfer reactions Co(II)$\leftrightarrow$Co(III)$\leftrightarrow$Co(IV) in basic electrolyte, making these nanowires potential candidates for pseudocapacitive electrodes in hybrid electrochemical capacitors.\(^2\)

CONCLUSION

Colloidal polymerization of ferromagnetic PS-CoNPs into 1-D cobalt oxide nanowires is reported. We demonstrate that the combination of dipolar assembly and oxidation of dipolar nanoparticles is a facile and robust method to prepare well-defined polymer-coated cobalt oxide nanowires in gram scale quantities. We also demonstrate for the first time that these nanostructured cobalt oxide materials are electrically and electrochemically active and of interest for potential applications in energy storage. Future work will examine the effect of the nanoporosity of these cobalt oxide wires as electrochemical supercapacitors and investigate Li ion insertion for Li batteries.

EXPERIMENTAL SECTION

**Materials and Characterization.** Anhydrous 1,2-dichlorobenzene (DCB), toluene, lithium perchlorate (LiClO$_4$, 95%), and NaOH (99.9%) were purchased from Aldrich and used as received without further purification. Dichlorobutylcarbonyl (Co$_2$(CO)$_8$) was purchased from Strem Chemicals and used as received. Compressed oxygen gas was purchased from Matheson Trigas. Thermolysis reactions were performed using an Omega temperature controller CSC23 with a K-type utility thermocouple and a Glass-Col fabric heating mantle. Calcination of the polymer-coated cobalt oxide nanowires was performed in a Barnstead/Thermolyne small benchtop muffled furnace at 400 °C in air. Indium-doped tin oxides-coated glass (ITO) was obtained from Colorado Concept Coatings, LLC. Electrochemical measurements were performed with a CH-instrument 600c potentiostat/galvanostat and a Glas-Col fabric heating mantle. Calcination of the polymer-coated cobalt oxide nanowires was performed in a Barnstead/Thermolyne small benchtop muffled furnace at 400 °C in air. Indium-doped tin oxides-coated glass (ITO) was obtained from Colorado Concept Coatings, LLC. Electrochemical measurements were performed with a CH-instrument 600c potentiostat/galvanostat and a Glas-Col fabric heating mantle. Calcination of the polymer-coated cobalt oxide nanowires was performed in a Barnstead/Thermolyne small benchtop muffled furnace at 400 °C in air. Indium-doped tin oxides-coated glass (ITO) was obtained from Colorado Concept Coatings, LLC. Electrochemical measurements were performed with a CH-instrument 600c potentiostat/galvanostat and a Glas-Col fabric heating mantle. Calcination of the polymer-coated cobalt oxide nanowires was performed in a Barnstead/Thermolyne small benchtop muffled furnace at 400 °C in air. Indium-doped tin oxides-coated glass (ITO) was obtained from Colorado Concept Coatings, LLC. Electrochemical measurements were performed with a CH-instrument 600c potentiostat/galvanostat and a Glas-Col fabric heating mantle. Calcination of the polymer-coated cobalt oxide nanowires was performed in a Barnstead/Thermolyne small benchtop muffled furnace at 400 °C in air.
Preparation of Amine End-Functional Polystyrene Surfactants (PS-NH₂). PS-NH₂ was synthesized according to our previous report.  

**Preparation of PS-CoNPs (1), Using Amine End-Functional Polystyrene Surfactants, PS-NH₂.** PS-NH₂ (0.400 g; 7.27 × 10⁻² mmol) was dissolved in DCM (10 mL) and transferred into a three-neck round-bottom flask containing DCB (30 mL) and heated to 175 °C. Separately, Co₂(CO)₈ (1.00 g; 2.92 × 10⁻² mol) was dissolved in DCB (8 mL) at room temperature in air, and was rapidly injected into the hot polymer solution via syringe. Upon injection, the reaction temperature dropped to 160 °C and the reaction mixture was maintained at 160 °C for 60 min followed by cooling to room temperature under argon. PS-CoNPs were isolated by precipitation into hexanes (500 mL), yielding a black powder (yield = 0.784 g) that was soluble in a wide range of organic solvents (e.g., methylene chloride, THF, toluene). The sample for TEM analysis was prepared by dispersing the isolated powder (1 mg) in toluene (2 mL) via sonication for 15 min followed by drop casting onto a carbon-coated Cu grid. The particle size of the PS-CoNPs was determined to be 20 ± 2.4 nm via TEM. Magnetic properties of PS-CoNPs were measured using VSM at room temperature:

- Mₘ = 41.2 emu/g, Hₘ = 713 Oe; and at 60 K, Mₘ = 43.7 emu/g, Hₘ = 1440 Oe. TGA analysis showed 41% of organics by mass.

**Preparation of PS-CoO Nanostructures (2).** A three-neck round-bottom flask equipped with a reflux condenser and a stir bar was charged with 16 mL of the as-prepared ferrofluid of PS-CoNPs. The ferrofluid was heated to 175 °C and stirred at 300 rpm, while bubbling with oxygen for 3 h of oxidation. The mixture was then allowed to cool to room temperature. The ferrofluid was isolated by precipitation into hexanes (500 mL), followed by centrifugation at 5000 rpm for 15 min to yield a black powder (yield = 0.302 g) that was soluble in a wide range of organic solvents (e.g., methylene chloride, THF, toluene). The sample for TEM analysis was prepared by dispersing the isolated powder (1 mg) in toluene (2 mL) via sonication for 15 min followed by drop casting onto a carbon-coated Cu grid. The particle size of the PS-CoNPs was determined to be 20 ± 2.4 nm via TEM. Magnetic properties of PS-CoNPs were measured using VSM at room temperature:

- Mₘ = 14.2 emu/g, Hₘ = 713 Oe; and at 60 K, Mₘ = 43.7 emu/g, Hₘ = 1440 Oe. TGA analysis showed 41% of organics by mass.

**Gram Scale Preparation of PS-Co₃O₄ Nanostructures.** Isolated powders of PS-CoNPs (1.36 g) was redispersed in DCB (50 mL) via sonication for 15 min. The black solution was charged into a three-neck round-bottom flask equipped with a reflux condenser and a stir bar. The ferrofluid was heated to 175 °C and stirred at 300 rpm, while bubbling with oxygen for a specific period of time. After 1 week of oxidation, the reaction was cooled to room temperature. The ferrofluid was isolated by precipitation into hexanes (500 mL), followed by centrifugation at 5000 rpm for 15 min to yield a black powder (yield = 1.04 g) that was soluble in a wide range of organic solvents (e.g., methylene chloride, THF, toluene). TEM sample was prepared as previously described. The diameter of the PS-cobalt oxide nanowire 3 was determined to be 32 ± 3.5 nm via TEM. Magnetic properties of PS-cobalt oxide 3 were measured using VSM at room temperature:

- Mₘ = 0.2 emu/g at 10000 Oe; and at 60 K, Mₘ = 0.38 emu/g at 10000 Oe. TGA analysis showed 11% of organics by mass.

**Calcined Cobalt Cobaltite, Co₃O₄ Nanostructures (4).** The as-synthesized PS-cobalt oxide nanowire powders 3 were calcined at 400 °C in the furnace for 16 h in air to yield polycrystalline Co₃O₄ nanowires 4 as determined from XRD. The magnetic properties of the calcined powders were measured using VSM at room temperature:

- Mₘ = 0.09 emu/g at 10000 Oe; and at 60 K, Mₘ = 0.25 emu/g at 10000 Oe.

**Preparation of Cobalt Oxide Films on ITO.** ITO slides were cut and then cleaned with 10% aqueous Triton X-100 solution followed by rinsing and sonication in nanopure (18 MΩ cm) water for 10 min. The ITO was then sonicated in absolute ethanol for 10 min. Once removed from ethanol, the slides were dried under a stream of N₂ and immediately etched with H₂ (50% aqueous solution). The acid-etched slide was immediately spin coated (1000 rpm) with the nanoparticle dispersion in toluene (c = 25 mg/mL) to obtain thin films of the polymer-coated colloids on ITO. Film thickness ranged from 50–60 nm as determined from AFM. The films were then dried under vacuum heating at 70 °C for several hours. For the calcined cobalt oxide film on ITO, a dispersion of polystyrene-coated cobalt oxide was deposited as described previously. Then, the film was heated at 400 °C in air for 16 h.

**UV—Visible Absorption Spectroscopy.** A dispersion of polystyrene-coated cobalt oxide nanowires was deposited onto ITO and calcined at 400 °C in air as described previously. The UV—vis absorption spectra of the Co₃O₄ film on ITO were recorded using the Agilent UV—visible spectrometer (no. 8453A) and the spectra obtained were analyzed by Chemistation software.

**Cyclic Voltammetry Measurements.** A potential versus current profile for the polymer-coated cobalt nanoparticles and cobalt oxide thin films on ITO were obtained at a sweep rate of 20 mV/s at room temperature in the potential range of 0.8 and −0.9 V versus Ag/AgCl (saturated KCl) in 0.1 M NaOH (aq). The electrolyte solution was purged with argon for 30 min and then transferred into the electrochemical cell via syringe prior to cyclic voltammetry experiments.

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**Supporting Information Available:** Experimental procedures and additional TEM, band gap calculations, and cyclic voltammetry. This material is available free of charge via the Internet at http://pubs.acs.org.