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Synthesis and Colloidal Polymerization of Ferromagnetic Au−Co Nanoparticles into Au−Co_3O_4 Nanowires

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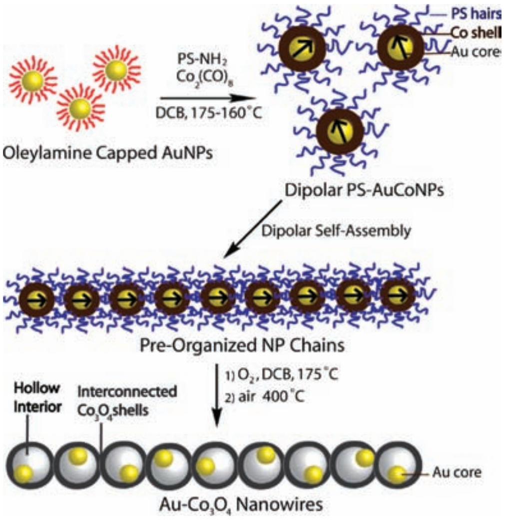
Cobalt oxide-based materials have generated considerable interest as electrodes and catalysts for energy storage and conversion. Nanostructuring of cobalt oxides has recently been investigated as a route for improving the electroactivity of these materials by controlling the nanoscale morphology and increasing the effective electroactive surface area.[1a−c] Despite these advances, cobalt oxide materials are inherently limited by poor electrical conductivity and low photoelectrochemical activity. A recent report by Woodhouse and Parkinson[1d] has demonstrated the ability to improve the photoelectrical properties of cobalt oxide materials via substitution with alternative cations (e.g., $CoAl_2O_4$). Alternatively, the electrochemical enhancement of cobalt oxide materials has been achieved for Li ion batteries via codeposition of gold nanoparticles (AuNPs) onto nanowires or encapsulation of AuNPs within metal oxide colloids.[1e,f]

Recent advances in nanoparticle chemistry have enabled the preparation of well-defined inorganic nanocrystals and complex heterostructures composed of disparate colloidal components.[2] Hollow NPs and core−shell colloids have recently been reported by the oxidation or chalcogenide/phosphide conversion of metallic nanoparticles via the *nanoscale Kirkendall effect*.[3a−e] Our group has recently prepared hollow cobalt oxide (Co_3O_4) nanowires via *colloidal polymerization* of ferromagnetic NPs, which we have defined as a combination of dipolar NP assembly and a chemical reaction (in this case, oxidation) to fuse colloidal precursors into one-dimensional materials.[3f] Earlier examples of this process for the formation of hollow semiconductor and metallic nanowires have been elegantly reported.[3g−i]

Herein, we report a novel methodology for preparing cobalt oxide nanowires with AuNP inclusions (Au−Co_3O_4 nanowires) via colloidal polymerization of ferromagnetic NP precursors composed of core−shell gold−cobalt NPs (AuCoNPs). In this system, the dipolar self-assembly of AuCoNPs was utilized to form Au−Co_3O_4 nanowires via oxidation of preorganized NP chains. We report for the first time the synthesis of dipolar core−shell NPs composed of a nondipolar core and a ferromagnetic shell. We further demonstrate that inclusion of AuNPs into Co_3O_4 nanowires enhances the electrochemical properties of the nanocomposite.

Ferromagnetic AuCoNPs were prepared using oleylamine-capped AuNPs (diameter $D = 13 \pm 3$ nm) as seeds[2c] in the thermolysis of $Co_2(CO)_8$ using amine-termined polystyrene (PS) surfactants (PS−NH_2; $M_n = 7000$ g/mol; $M_w/M_n = 1.07$) in 1,2-dichlorobenzene (DCB) at $T = 180$ °C (Scheme 1).[4a,b] Ferromagnetic PS−CoNPs ($D = 24 \pm 3$ nm; Figure 1a) were also synthesized using our previously reported method as reference materials for solid-state and morphological characterization. Transmission electron microscopy (TEM) confirmed the preparation of core−shell PS−AuCoNPs, as evidenced by an increase in particle size ($D = 22 \pm 4$ nm) relative to the AuNP seeds and by the formation of mesoscopic NP chains spanning hundreds of nanometers to micrometers in length. High-resolution TEM further confirmed the preparation of PS−AuCoNPs by the imaging

Scheme 1. Synthesis of Dipolar PS−AuCoNPs and Au−Co_3O_4 Nanowires



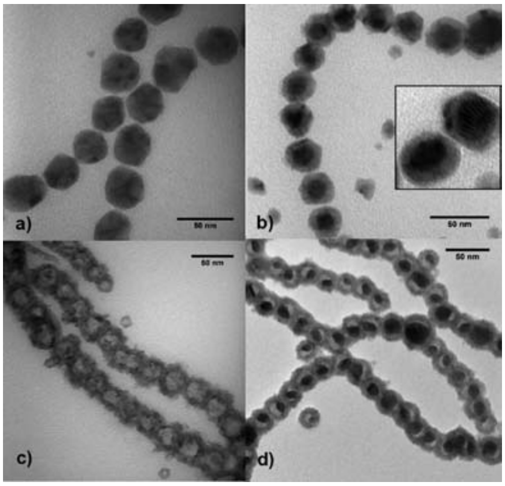


Figure 1. TEM images of ferromagnetic (a) PS-CoNPs ($D = 24 \pm 3$ nm), (b) core−shell PS−AuCoNPs ($D = 22 \pm 4$ nm, $D_{core} = 13 \pm 3$ nm), (c) PS−cobalt oxide nanowires ($D = 33 \pm 3$ nm), and (d) PS Au−Co_xO_y nanowires ($D = 31 \pm 4$ nm).

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10.1021/ja908481z

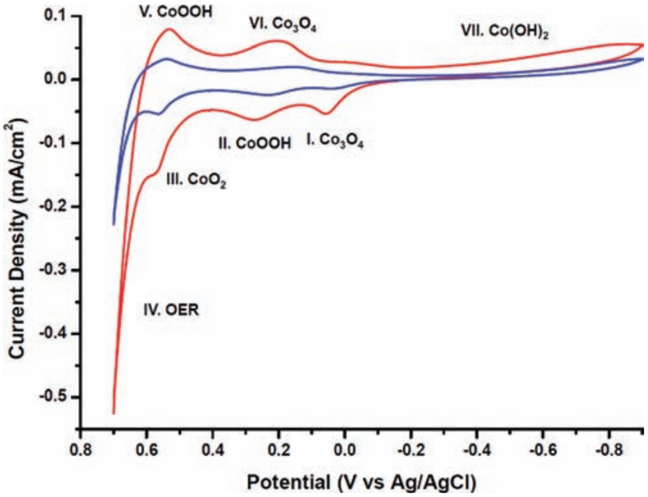

Figure 2. Overlay of cyclic voltammograms of calcined Au−Co_3O_4 (red) and Co_3O_4 (blue) films on ITO recorded using a scan rate of 20 mV/s in 0.1 M NaOH electrolyte solution.

of a discrete core−shell morphology composed of the darker high-atomic-number AuNP core (D_{core} = 13 ± 3 nm) and a lighter shell from the metallic cobalt (thickness = 4−5 nm (Figure 1b). Powder X-ray diffraction (XRD), optical spectroscopy, and vibrating sample magnetometry (VSM) also confirmed the preparation of the dipolar Au−Co NP material.[5]

Colloidal polymerization of PS−AuCoNPs was then conducted to afford PS-coated nanowires of amorphous cobalt oxide with AuNP inclusions (PS Au−Co_xO_y nanowires), as confirmed by XRD, X-ray photoelectron spectroscopy (XPS), and VSM.[5] TEM of PS Au−Co_xO_y nanowires imaged the presence of dark inner Au cores as well as interior voids corresponding to the dimensional expansion of the Co shells (D = 31 ± 4 nm) associated with the nanoscale Kirkdendall effect (Figure 1d). In contrast, a control experiment conducted with PS−CoNPs of comparable diameter afforded PS−cobalt oxide nanowires with completely hollow cores (Figure 1c). Calcination of PS Au−Co_xO_y films at 400 °C in air was conducted to remove the organic PS shell and form polycrystalline Au−Co_3O_4 nanowires without perturbing the morphology of the materials, as confirmed using TEM and XRD.

Electrochemical characterization and determination of the specific capacitance (C) of the calcined nanowire films was investigated by cyclic voltammetry (CV) (Figure 2 and Figures S11−S15 in the Supporting Information). Direct comparison of Au−Co_3O_4 and Co_3O_4 nanowire films with the same total nanoparticle coverage indicated at least a 2-fold enhancement of the background-corrected Faradaic electrochemical activity associated with redox transitions at the active sites (i.e., $CoO_2 > CoOOH > Co_3O_4$). The capacitive current was also enhanced, giving specific capacitances per NP of $C_{Au-Co_3O_4} = 1.21 \times 10^{-13}$ F and $C_{Co_3O_4} = 4.50 \times 10^{-14}$ F respectively.[5]

The difference in electrochemical activity induced by the AuNP cores was further explored for nanowires cast onto indium tin oxide (ITO) after O_2 plasma removal of all organics and thermal treatment of films at 23−400 °C. CV revealed significant sharpening of the voltammetric peaks in Figure 2 for both the Au−Co_3O_4 and Co_3O_4 nanowire films as a consequence of the increased crystallinity and electrochemical homogeneity of the electroactive sites in the oxide. A significant reduction in the capacitive current for the Co_3O_4-only nanowire films was observed, accompanied by a substantial dimensional contraction of calcined the Co_3O_4 nanowires relative to the Au−Co_3O_4 analogues, as imaged by TEM (Figure S20).[5] In contrast, the electrochemical capacitance of the Au−Co_3O_4 nanowire films was enhanced upon thermal annealing to 400 °C (Figures S18 and S19), suggesting that the AuNP inclusions suppressed densification of the cobalt oxide nanowire shell and increased the effective number of sites responsible for the capacitive response relative to Co_3O_4-only nanowires.[5]

Electrochemical impedance spectroscopy (EIS) of similarly calcined Au−Co_3O_4 and Co_3O_4 nanowire films on ITO was investigated from 1−100 kHz at 0.125 and 0.225 V (Figures S21−S23).[5] Plots of impedance and phase angle versus frequency and Nyquist plots for Au−Co_3O_4 nanowire films showed behavior consistent with three nested RC circuits accounting for interfacial, through-oxide, and through-pore RC terms. We observed a higher critical frequency and significant changes in phase angle at ∼200 kHz (at 0.125 and 0.225 V), consistent with the changes in voltammetric activity suggesting enhanced Faradaic and non-Faradaic activity for the Au−Co_3O_4 nanowires. It is intriguing to note that the inclusion of an inert nanoparticle core helps control the structure of the electroactive cobalt oxide and improve the electrochemical properties, which is predicted to enhance the activities in technologies utilizing these oxides, such as Li ion batteries and supercapacitors. Both applications of these Au−Co_3O_4 nanowires are currently being evaluated.

In conclusion, the synthesis and characterization of ferromagnetic core−shell AuCoNPs and Au−Co_3O_4 nanowires have been reported. We have demonstrated that dipolar core−shell materials can be prepared and polymerized to form heterostructured nanowires with enhanced electrochemical properties.

Acknowledgment. The ONR-YIP (N00014-07-1-0796), the NSF CAREER Program (DMR-0645618), the World Class University Program through the National Research Foundation of Korea, funded by the Ministry of Education, Science and Technology (R31-10013), and the Alfred P. Sloan Foundation are acknowledged for synthetic support of this work. The authors gratefully acknowledge the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy (Grant DE-FG03-02ER15753) for electrochemical and spectroscopic support.

Supporting Information Available: Experimental procedures and additional TEM, SEM, XPS, XRD, VSM, CV, UV, and EIS data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) See the Supporting Information for further details.

JA908481Z