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Synthesis and Size Control of Cobalt Phosphate Rosettes Using Surfactant-Templated Synthesis

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Novel cobalt phosphate rosettes have been synthesized. Control over the particle size and rosette geometry is afforded through the use of cationic quaternary ammonium salt surfactants. Small variations in the surfactant concentration allow for control over the rosette diameter.

One of the first applications of cobalt phosphate was as an ingredient in semiconductive glasses such as $CoO{-}P_2O_5$.[1] Since then, crystalline cobalt phosphates have found applications as ion-selective microelectrodes, catalysts, battery electrodes, and glass materials.[1−4] In addition, cobalt phosphate tipped microelectrodes have been used to analyze for phosphate ions in microbial flocs.[2] Cobalt phosphate has also been used as a solid-state catalyst in the oxidation of water, a reaction commonly seen in solar energy conversion.[3] Recent cobalt phosphate research is focused on its applicability as a cathode in rechargeable lithium ion batteries to provide increased energy storage and voltage output.[4]

Several groups have focused on altering the formation of the cobalt phosphate crystal lattice to afford products with alternate geometries in order to increase the surface area and porosity. Using a surfactant template allows cobalt phosphate to form around micelles and provides a product with multiple possible geometries. Cobalt phosphate with three-dimensional cubic geometry has been synthesized using amine-containing surfactants.[5] Xing et al. employed the use of a cationic surfactant to synthesize cobalt(II) phosphate with cylindrical geometry.[6] In addition to cubic and cylindrical product geometries, the use of surfactants to interfere with uniform crystal lattice formation is well-known for creating products with tubular, lamellar, or spherical geometries.[7]

The goal of this study was to synthesize unique geometries of cobalt phosphate and to control the particle size using a surfactant template. The cationic quaternary ammonium salt octadecyltrimethylammonium chloride (OTAC) was chosen as the surfactant because of its high solubility and nonhazardous nature. Altering the surfactant-to-water ratio within a reaction will allow micelles to form differing geometries.

The synthesis method consisted of preparing 100 mL of 0.11 M OTAC, pH(23 °C) = 6.71; solubility of the surfactant was attained by heating to 47.3 °C for 30 min. The solution was allowed to cool to room temperature, poured into a Teflon reaction vessel, and allowed to stir to promote micelle formation. A total of 1.35 mL of phosphoric acid was added with stirring for 5 min, bringing the pH to 1.44. A total of 4.05 mL of ammonium hydroxide was added with stirring for an additional 10 min to increase the pH of the reaction to 9.50. A total of 2.60 g of anhydrous cobalt(II) chloride was slowly added to the reaction vessel with stirring at room temperature for 15 min, and the Teflon reaction vessel was then placed in a 60 °C oven for 24 h. The precipitate was collected via vacuum filtration using a 0.45 μm filter, washed with deionized water, and dried under ambient conditions to afford a purple solid.

The product was analyzed with scanning electron microscopy (SEM), energy-dispersive spectrometry (EDS), and X-ray diffraction (XRD). A JEOL 840 scanning electron microscope equipped with a Robinson 6.0 backscatter detector was used to obtain the SEM images. The beam conditions were 20 keV acceleration and 1 nA beam current. The samples were mounted on an aluminum plate using double-sided tape and were carbon-coated under vacuum. Images were acquired using GATAN software, version 3.2, 1996. An Oxford ISIS 300 series energy-dispersive spectrometer was used to determine the chemical composition. EDS spectra were stored electronically using Oxford ISIS 300 software, version 3.2. The EDS spectra taken in this study were counted for 100 s with 30% dead time. XRD was performed using material ground in an agate mortar and pestle to < 500 mesh. A Scintag Inc. model 3520 PAD-V X-ray diffractometer was used, operated at 45 kV and 40 mA using a XGEN-4000 generator. Tungsten-filtered Cu Kα radiation of 1.54 Å was used with a Peltier-cooled Scintag

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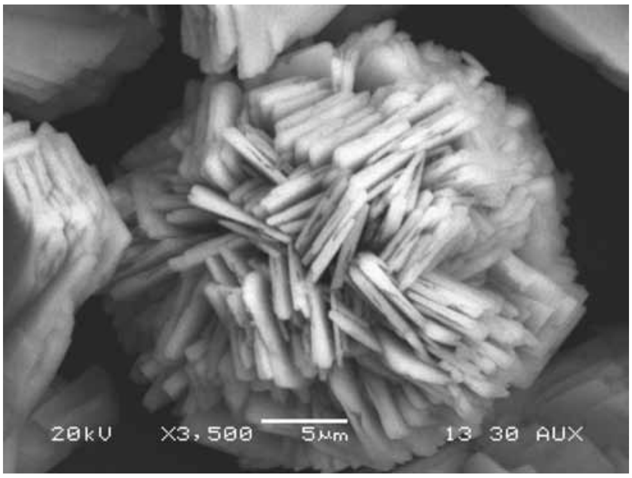

Figure 1. SEM image of a cobalt(II) phosphate rosette at 3500× magnification and 20 kV.

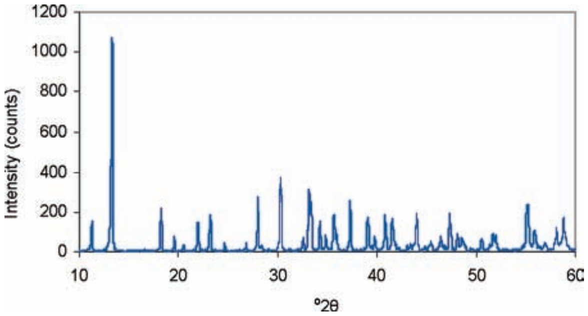

Figure 2. XRD scan of cobalt phosphate rosettes from $2\theta = 10$ to 60°.

Inc. Si (Li) solid-state detector. The sample was analyzed in the $2\theta = 10-60°$ range, with a step size of 0.02° and a 1 s count time at each step.

Analysis of the product by SEM revealed spherical particles composed of small lamellar plates (Figure 1). This geometric formation is commonly referred to as a rosette. No other investigations have been identified within the literature that depict the formation of a rosette geometry for cobalt phosphate compounds. Electron-dispersion spectroscopy confirmed that the product was composed of Co/P/O with a ratio of 2:1:5. Figure 2 presents the XRD pattern from $2\theta = 10$ to 60°. The pattern displays a highly crystalline product; however, no reference PDF patterns were identified by JADE coupled with the ICDD PDF-4^+ database. Complete crystallographic analysis is the subject of future work and will be detailed in a forthcoming paper.

In addition to the original synthetic method, three variations were conducted with decreasing surfactant concentrations. Lower surfactant concentrations (0.09−0.05 M) afforded the same rosette geometry as that seen in the original synthesis but with decreased rosette diameter. SEM images of the products afforded in these reactions are given in Figure 3a−d at 1700× magnification, from highest to lowest surfactant concentration.

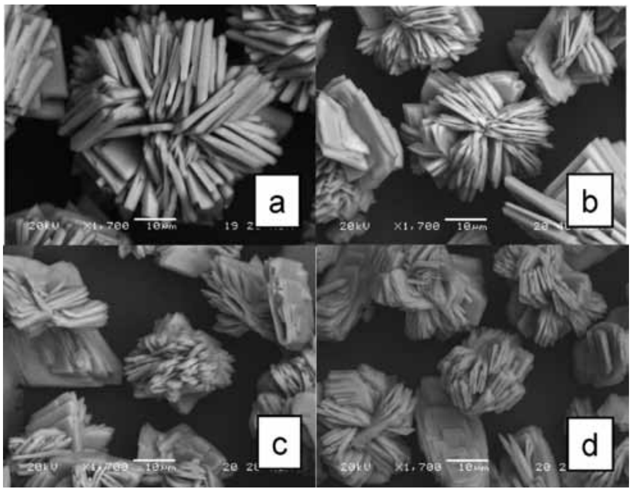

Figure 3. SEM images of rosette cobalt phosphate at 1700× magnification with surfactant concentrations of (a) 0.11 M, (b) 0.09 M, (c) 0.07 M, and (d) 0.05 M.

Table 1. Rosette Diameter as a Function of the Surfactant Concentration

surfactant concn (M)	rosette diameter (μm)	surfactant concn (M)	rosette diameter (μm)
0.11	51.61 ± 6.78	0.07	24.03 ± 3.44
0.09	31.17 ± 2.97	0.05	21.21 ± 3.93

The rosette diameter was successfully controlled by altering the surfactant concentration within the reaction. A decrease in the surfactant concentration decreased the diameter of the rosettes. Table 1 gives the relationship between the rosette diameter and the surfactant concentration. A sample size of 20 rosettes was measured for each surfactant concentration.

This communication details the controlled synthesis of the cobalt phosphate rosette geometry and particle size through the use of cationic quaternary ammonium salt surfactants. The altering of the concentration of the surfactant allows for multiple product geometries, and critical surfactant concentrations of 0.11−0.05 M afford cobalt phosphate in a rosette geometry. Additional cobalt phosphate geometries may be possible using other cationic quaternary ammonium salts and will be studied in due course.

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