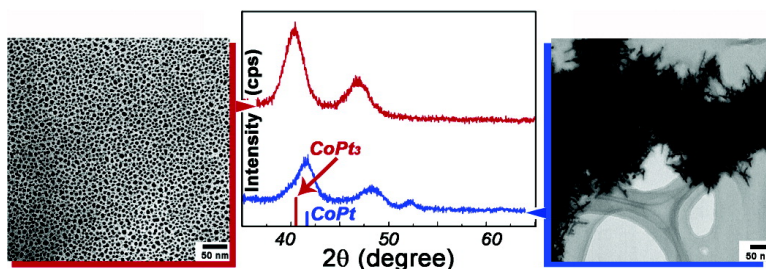


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Synthesis of CoPt Nanorods in Ionic Liquids

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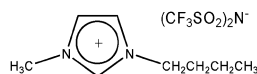
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Although various synthetic methods have been developed for the morphological controls of nanoparticles, rods, and wires of semiconductors, metals, and metal oxides, only limited success has been made in making alloy or intermetallic nanoparticles, such as FePt, CoPt, and AuCu.¹ Not all the compositions or broad particle sizes have been achieved at the nanometer scale. The formation of one-dimensional nanorods and nanowires has rarely been reported.¹ For technologically important Co–Pt and Fe–Pt systems, shape, crystal phase, and composition are essential for the outstanding catalytic, magnetic, and other properties.^{2,3} For example, the ordered CoPt₃ and FePt₃ have been predicted to have higher electrocatalytic activities than pure Pt in hydrogen oxidation reactions.³ The face-centered tetragonal FePt nanoparticles are the most designable material among the Fe–Pt system for magnetic data storage media applications.² The reaction temperatures, however, are usually high in order to obtain crystal phase- and composition-specific alloy nanomaterials,^{1h,4,5} except for a biotemplate synthetic method.⁶ These temperatures are typically above the boiling points of most of the conventional solvents. Postsynthesis high-temperature treatments often affect the particle size, size distribution, and structural property of the nanoparticles.

Ionic liquids (ILs),^{7,8} known for their nonvolatile, nonflammable, and thermally stable properties, have recently been used in making nanoparticles.^{9–15} The thermal stability and nonvolatility of ILs, however, have not been utilized as a high-temperature environment for the synthesis of nanomaterials, especially crystal phase- and composition-specific alloy nanomaterials. In this work, we demonstrate that nanorods, hyperbranched nanorods, and nanoparticles with different CoPt compositions can be synthesized in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide, [BMIM][Tf₂N].

[BMIM][Tf₂N] was chosen as the solvent because of its thermal stability.^{8,16} This IL was synthesized using a method reported previously (Supporting Information).⁸ Cetyltrimethylammonium bromide (CTAB) was used as the capping reagent because it has good solubility in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [EMIM][Tf₂N],¹⁷ which has a chemical structure similar to that for [BMIM][Tf₂N].

Scheme 1. Molecular Structure of [BMIM][Tf₂N]



Cobalt platinum nanorods were made in freshly dried [BMIM][Tf₂N] at 350 °C. Platinum acetylacetonate (Pt(acac)₂) and cobalt acetylacetonate (Co(acac)₃) were used as Pt and Co precursors, respectively. The Pt(acac)₂:Co(acac)₃:CTAB molar ratio was 0.5:1.5:10 (See Supporting Information). Figure 1 shows the representative transmission electron microscope (TEM) images of

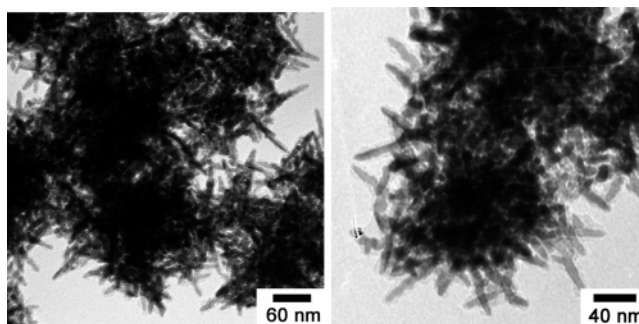


Figure 1. TEM images at low (left) and high (right) magnifications of the CoPt nanorods obtained at the Pt(acac)₂:Co(acac)₃:CTAB molar ratio of 0.5:1.5:10.

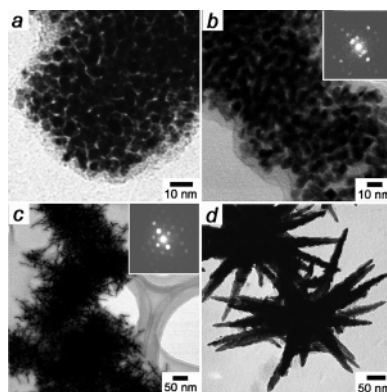


Figure 2. TEM images of the nanomaterials obtained at the different reactant molar ratios of Pt(acac)₂:Co(acac)₃:CTAB: (a) 10:3.3:10, (b) 3.3:3.3:10, (c) 3.3:10:10, and (d) 0.37:1:10. Insets show micro-EDs from an individual nanoparticle (panel b) and the tip of a nanorod (panel c).

bundles of CoPt nanorods. These nanorods had an average diameter of ~8 nm. Energy-dispersive X-ray (EDX) analysis indicated the average Co/Pt atomic ratio of these nanorods was Co₆₁Pt₃₉, Figure S1.

We examined the reaction at different Pt(acac)₂:Co(acac)₃:CTAB molar ratios to understand the formation mechanism and control the compositions and crystal phases. In all the tests, [BMIM][Tf₂N] used was kept at 4 mL and CTAB was at 0.375 mmol. Nanoparticles with an average diameter of ~5 nm formed when the Pt(acac)₂:Co(acac)₃ molar ratio was ≥ ~1, Figure 2a and b. Most of these particles formed aggregates similar to some other nanoparticles formed in ionic liquids.¹³ EDX analysis of nanoparticles shown in Figure 2a indicated the composition was Co₂₂Pt₇₈, which was close to the atomic ratio of CoPt₃ alloy. The Co/Pt atomic ratio of the particles shown in Figure 2b was Co₃₅Pt₆₅, which was very close to those for individual nanoparticles obtained using an ultrahigh vacuum scanning transmission electron microscope (UHV-STEM), Co₃₇Pt₆₃, Table S2 and Figure S2. Micro-electron diffraction (ED) analysis indicated that these nano-

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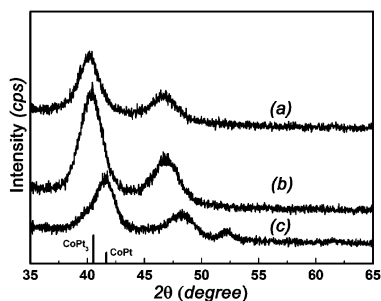


Figure 3. PXRD patterns of the Co–Pt nanomaterials obtained at the different reactant mole ratios of Pt(acac)₂:Co(acac)₃:CTAB: (a) 10:3.3:10, (b) 3.3:3.3:10, and (c) 3.3:10:10, respectively.

particles were highly crystalline, inset of Figure 2b. When the Pt(acac)₂:Co(acac)₃ molar ratio was below one, bundles of nanorods were the major product, Figure 2c. The average composition of the bundles of Co–Pt nanorods shown in Figure 2c was Co₆₈Pt₃₂, Table S3. This value was close but smaller than the number of Co₇₅Pt₂₅ (or Co₃Pt) obtained on selected individual rods. The micro-electron diffraction on the selected single rod revealed the single-crystalline nature of the individual rods, inset of Figure 2c. The estimated yield of the reactions based on Co elemental analysis was about 60%. The solvent properties¹⁸ of [BMIM][Tf₂N] IL appeared to play an important role in the formation of CoPt nanorods. Polydispersed nanoparticles, instead of nanorods, were obtained when we replaced [BMIM][Tf₂N] with trioctylamine as solvent and reacted at ~340 °C, Figure S4. Hyperbranched nanorods were obtained at relatively low concentrations of Pt(acac)₂ and Co(acac)₃, Figure 2d.

The anisotropic interaction between the capping agents and the different facets of Co–Pt crystals should also be essential for the formation of nanorods and hyperbranched nanorods. To examine the effect of surfactants on the growth mechanism, we replaced CTAB with *N,N*-dimethylhexadecylamine (DMHA), which had similar alkane chain length and an amine function group. Furthermore, DMHA could form from CTAB at high temperatures.¹⁹ Similar morphological control over Co–Pt systems was achieved using DMHA as surfactant, Figure S5. This result suggested that the amine should be the crucial functional group in the control of the anisotropic growth of Co–Pt nanorods.

Our EDX data indicated that different Co–Pt alloy nanoparticles and nanorods could be made. This result was confirmed by the powder X-ray diffraction (PXRD) study, Figure 3. The main diffraction peaks from nanoparticles made at Pt(acac)₂:Co(acac)₃ molar ratio of ~3 matched those for CoPt₃ alloy (space group: *Pm3m*). The peak position of (111) diffraction between 40° and 43° 2θ shifted toward high angle with the decrease of Pt(acac)₂:Co(acac)₃ molar ratio, suggesting the Co–Pt nanoparticles and nanorods form over a wide range of Co–Pt atomic ratios. The (111) diffraction of Co–Pt alloy for the nanorods shown in Figure 2c was at 41.6° 2θ, which belongs to CoPt alloy, Figure 3c.²⁰ It is noted that Weller et al. have studied the formation of Co–Pt nanoparticles in conventional organic solvents below 300 °C.^{1j} In those cases, only CoPt₃ nanoparticles could form over a wide range of Pt/Co precursor ratios. The combined high-temperature environment and the unique property of IL¹⁸ could attribute to the observed

formation of CoPt alloy nanoparticles and nanorods with different compositions and crystal phases. The decrease in melting point of nanoparticles²¹ could be relevant for the formation of stable CoPt alloys.

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Supporting Information Available: Synthetic procedures for [BMIM][Tf₂N], CoPt nanoparticles, nanorods, and hyperbranched nanorods. TEM, EDX, and UHV-STEM analysis of nanoparticles, Figures S1–5 and Tables S1–3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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