Radiolytic Synthesis of Bimetallic Ag–Pt Nanoparticles with a High Aspect Ratio

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Aqueous solutions of Ag–Pt ions and poly(vinyl alcohol) were irradiated with gamma rays at dose rates below 0.5 kGy/h to generate nanoparticles. The nanoparticles were characterized with several experimental techniques. Transmission electron microscopy showed that, surprisingly, the nanoparticles were not spherical but had a high aspect ratio. Wirelike structures were generated with lengths up to 3.5 μm and diameters between 3 and 20 nm. Selected-area diffraction showed that the wires were polycrystalline and that individual grains making up the wires had a face-centered cubic (fcc) structure. The optical absorption of samples, with a Ag/Pt mole ratio higher than 80%, exhibited a Ag surface plasmon absorption band centered around 400 nm. The plasmon band broadened with increasing Pt molar ratio and was replaced by a monotonically decaying background for a Pt molar ratio higher than about 30%. Alloying in the Ag–Pt nanoparticles was investigated with X-ray absorption spectroscopy. The Pt L_3 edge (11.564 keV) was excited to determine the local structure around the Pt atoms. A contraction in the first shell of 0.05 Å was observed, which ruled out the formation of a Ag–Pt homogeneous alloy and suggested the formation of core–shell particles. To understand the mechanism of formation of the nanoparticles, several experimental parameters such as the total radiation dose, type of polymer, metal and polymer concentrations, and type of counterions in solution were varied. The most relevant parameters inducing filament growth were the counterions added to the solution, the mole ratio between the two metals, and the capping polymer. For example, spherical particles resulted if $AgNO_3$ was used instead of Ag_2SO_4, if the Ag/Pt mole ratio was higher than 80% or lower than 20%, and if the degree of hydrolysis of the poly(vinyl alcohol) was higher than 98%.

1. Introduction

Metallic nanostructures with high aspect ratios are promising candidates for the development of sensors[1], nanoscopic electrical connections, and catalysts.[2] Several techniques have been developed to synthesize nanoparticles with predefined aspect ratios and crystalline habits. Limiting our discussion to wet chemistry and photolysis synthesis techniques, high aspect ratio nanoparticles are usually produced in a micellar environment,[3–6] sometimes with the aid of preformed seeds.[7–10] There are also reports of nanowires produced with a polyol technique in the presence of metal cluster seeds[11] and by the photoreduction of noble-metal ions in aqueous solution.[12] The above-mentioned synthesis techniques share common features. In general, a noble metal is reduced at a slow rate in the presence of preformed metal clusters, which act as nucleation seeds, and a capping polymer. The aspect ratio of the nanoparticles is, in general, controlled by varying ion and polymer concentrations, the type of polymer, and the velocity of reduction.

In this work, we show that nanoparticles with high aspect ratios can also be produced with the radiolysis method.[3,13–17] Our technique can produce bimetallic nanowires where at least one of the metals is a transition metal. These features are not common among wet chemistry techniques, which are often limited to syntheses of noble, monometallic nanowires. A large number of experiments were carried out to determine the parameters affecting nanowire formation. Parameters included the total gamma ray dose, type of counterions added to the solution, total and relative metal concentrations, and polymer type and concentration. The most relevant parameters were the counterions, the Ag/Pt mole ratio, and the capping polymer. Our experiments show that Ag clusters were formed in the initial stages of reduction and that Pt–Ag, or pure Pt, clusters nucleated or coalesced around the seeds. Nanowire synthesis was also extremely sensitive to the counterions of the solution and to the degree of hydrolysis of the PVA capping polymer. The important role played by the counterions and the polymer suggested that polymer–metal ion complexes and possibly micelles were formed.

2. Experimental Section

Sample Preparation. Aqueous solutions were prepared with $AgNO_3$, Ag_2SO_4, H_2PtCl_6, K_2PtCl_4, and 2-propanol, all purchased from Alfa Aesar. Solutions had a typical total metal ion concentration between 0.5 and 2×10^{-3} mol/L. Samples were prepared with Ag/Pt mole ratios varying from 100 to 0% Ag in steps of 10%. To scavenge $H^•$ and $OH^•$ radicals generated during irradiation, 0.2 mol/L of 2-propanol was added to the solutions. As a capping polymer, seven different types of PVA were tested. Their characteristics are reported in Table 1. Polymer concentra-

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