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Radiolytic Synthesis of Bimetallic Nanoparticles with High Aspect Ratio

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ABSTRACT

We present a technique to synthesize high aspect ratio metallic nanostructures based on the radiolysis method. In our experiments, we use gamma rays to irradiate aqueous solutions containing Ag and Pt ions and a water-soluble polymer. The aspect ratio of the nanoparticles is controlled by varying the radiation dose rate, the type of polymer, and the type of counter ions. Transmission electron microscopy shows that wire-like structures composed of grains with a face centered cubic (fcc) structure can be formed with a length of up to 3.5μm and typical diameters between 5 and 12nm. X-Ray absorption spectroscopy shows that Ag and Pt do not form an alloy, but remain segregated.

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 [3-12]. The mechanism of nanowire formation is not clear in its details; however, most synthesis techniques [3-12] share common features. In general, a noble metal is reduced at a slow rate in the presence of pre-formed metal clusters, which act as nucleation seeds, and a capping polymer. Reduction often takes place in a micellar environment [3-8]. We show here that nanoparticles with high aspect ratios can also be produced with the radiolysis method [3,11-14]. A large number of experiments were carried out to determine the parameters affecting nanowire formation. Parameters included total gamma ray dose, type of counter ions added to the solution, total and relative metal concentration, and polymer type and concentration.

EXPERIMENTAL DETAILS

Sample preparation

Metal salts used to prepare aqueous solutions were $AgNO_3$, Ag_2SO_4, H_2PtCl_6, and K_2PtCl_4. Solutions had a typical total metal ion concentration between 0.5 and $2x10^{-3}$ mol/l. Samples were prepared with Ag/Pt mole ratios varying from 100% to 0% Ag in steps of 10%. To scavenge $H^{\bullet}$ and $OH^{\bullet}$ radicals generated during irradiation, 0.2 mol/l of 2-propanol was added to the solutions. Poly(vinyl alcohol) (PVA) of varying molecular weight and degree of hydrolysis was used as a capping polymer. The characteristics of the capping polymers are reported in Table I. Polymer concentrations were varied between 2 and 12 g/l, corresponding to a concentration of monomer units between 0.09 and 0.5 mol/l. Due to their photosensitivity, the samples were stored in the dark after mixing. Before and after irradiation, the solutions were free of precipitates.