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EXAFS Studies of Bimetallic Ag-Pt and Ag-Pd Nanorods

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Abstract

Nanoparticles of Ag-Pt and Ag-Pd with high aspect ratios were synthesized using a radiolysis method. Gamma rays at dose rates below 0.5 kGy/h were used for irradiation. The nanoparticles were characterized by transmission electron microscopy (TEM), optical absorption spectroscopy and X-ray Absorption Fine Structure (XAFS) spectroscopy. Bright field micrographs show that Ag-Pt nanowires are composed of large particles with diameters ranging from 20–30 nm and joined by filaments of diameter between 2–5 nm. The Ag-Pd nanowires have diameters of 20–25 nm and lengths of 1.5 μm. For XAFS measurements, the Pt L_3 edge (11.564 keV), Ag K-edge (25.514 keV) and Pd K-edge (24.350 keV) were excited to determine the local structure around the respective atoms in the cluster. The Ag-Pt particles were found to possess a distinct core-shell structure with Pt in the core surrounded by Ag shell, with no indication of alloy formation. However, nanorods of Ag-Pd have formed an alloy for all the alloy compositions.

1. Introduction

Nanocrystalline materials are of great interest and are being widely studied because many physical and chemical properties of these materials are found to be dissimilar to those of conventional polycrystalline, coarse-grained materials. Such difference in properties arise because of the large fraction of atoms (5–50%) located at the surfaces and/or interfaces. Quantum size effects are observed in metal and semiconductor fine particles if their size is small enough so that the spacing between the discrete levels in the electronic energy spectrum becomes comparable with some of the characteristic energy parameters like kT, μH, $h\omega$, etc., thereby giving rise to changes in the thermodynamic, magnetic and optical properties respectively [1]. Nanocrystalline materials have been found to exhibit increased strength and hardness, enhanced diffusivity, improved ductility, reduced density, etc. compared to the bulk. Hence, these materials have found applications in microelectronic and optoelectonic devices, catalysis, sensing, drug delivery, etc. Metallic nanostructures with high aspect ratios are promising candidates for the development of sensors, catalysts and nanoscopic electrical connections.

Bimetallic nanoparticles are of greater interest than the monometallic ones, both technologically and scientifically [2]. The selective behavior of such bimetallic catalysts can be controlled by changing their composition ratios [3, 4]. Earlier studies have mostly been done on inorganic oxide-supported bimetallic nanoparticles [5]. Recently, novel techniques like microemulsion [6], decomposition of organometallic precursors [7], radiolysis [8], etc. have been developed for the synthesis of colloidal suspensions of these nanoparticle systems. Such systems are advantageous for study since the interference of substrate interaction is absent. A detailed review of bimetallic nanoparticles in dispersion has been published [9]. In this paper, we have used TEM and XAFS to investigate alloy formation in radiolytically synthesized Ag-Pt and Ag-Pd bimetallic nanoparticles in solution, possessing high aspect ratio. Such systems with high aspect ratio are particularly interesting because of their potential application as barcodes in sensors [3].

2. Experimental Section

2.1. *Synthesis*

Ag-Pt and Ag-Pd nanowires were synthesized by radiolysis [10, 11]. Radiolysis of aqueous solutions is an effective method to reduce metal ions and form homo- and heteronuclear clusters of transitions metals [10, 11]. In the radiolysis method, aqueous solutions are exposed to γ-rays (equation 1) to create solvated electrons, which in turn reduce the metal ions (equations (2) and (3)). The latter coalesce to form aggregates (equation (4)).

$$H_2O \rightarrow e^-_{aq}, H_3O+, H^*, OH^*, H_2O_2, \quad (1)$$

$$e^-_{aq} + M^{m+} \rightarrow M^{(m-1)+}, \quad (2)$$

$$e^-_{aq} + M^+ \rightarrow {M_0}^0, \quad (3)$$

$$n{M_0}^0 \rightarrow {M_2}^0 + (n-2)M0 \rightarrow \ldots\ldots\ldots {M^0}_n. \quad (4)$$

The samples were irradiated with γ radiation from the fission products of University of Missouri-Rolla's nuclear reactor pool. The reactor was operated at 180 kW for 1 hour and the samples were positioned 1 h after the reactor shutdown to prevent neutron bombardment and activation of samples. The dose rate was decreased exponentially from a value of 0.5 kGy/h in the first hour to about 0.05 kGy/h 48 hours after shutdown. Exposure to a total dose between 3 and 3.5 kGy typically required 36 to 48 hours. Total doses were measured with Thermoluminescent Dosimeters (TLD) placed in vials adjacent to the samples to be irradiated.

To obtain nanowires, parameters that were varied, were (a) total gamma ray dose and dose rate, (b) type of counterions added to the solution, (c) total and relative metal concentration, and, (d) polymer type and concentration. The most relevant parameters were the counter ions, the molar ratio between Ag and Pt or Pd, and the capping polymer. The data strongly suggests that polymer-metal ion complexes are formed, possibly in micellar form. Also, at least two conditions typical for nanowire formation, i.e. the presence of seeds and slow velocity of reduction, are met by the experiments. Samples were prepared with Ag-Pt and Ag-Pd

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