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ADP014289

TITLE: Radiolytic Synthesis of Bimetallic Nanoparticles with High Aspect Ratio

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TITLE: Materials Research Society Symposium Proceedings Volume 740
Held in Boston, Massachusetts on December 2-6, 2002. Nanomaterials for
Structural Applications

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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 3.5 μm and typical diameters between 5 and 12 nm. 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

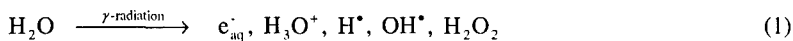
Sample preparation

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 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 $\text{H}^\bullet$ and $\text{OH}^\bullet$ 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.

Table I. Types of poly(vinyl alcohol) polymers employed in the experiments. Molecular weights indicated with * are estimated from a viscosity-molecular weight conversion table available from Celanese Chemicals

Poly(vinyl alcohol) (brand name)	Hydrolysis (%)	Molecular Weight (amu)	Supplier
Celvol 540	87-89	146 000 – 186 000 *	Celanese
-	87-89	88 000 - 97 000	Alfa Aesar
Celvol 205 and 502	87-89	13 000 - 52 000 *	Celanese
Celvol 165 and HA-70	99.3+	146 000 - 186,000+ *	Celanese
-	98-99	88 000 - 97 000	Alfa Aesar

Radiolysis of aqueous solutions is an efficient method for the reduction of metal ions and formation of homo- and hetero- nuclear clusters of transition metals [3,11-13]. In the radiolysis method, aqueous solutions are exposed to γ -rays, as shown in equation 1, to create solvated electrons, e_{aq}^- [14]. The solvated electrons reduce the metal ions, as shown in equations 2 – 3. The metal atoms coalesce to form clusters as shown in equation 4.



Samples were irradiated with gamma radiation from the fission products of the University of Missouri-Rolla’s pool nuclear reactor. In the experiments described here, the dose rate decreased exponentially from a value of about 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.

Characterization

TEM measurements were carried out with a Philips EM430T microscope operated at 300 keV. Selected area electron diffraction (SAED) was employed for structural characterization. The chemical composition of the nanoparticles was determined with energy dispersive X-ray chemical analysis (EDS). SAED and EDS had a spatial resolution of 150 nm. X-ray Absorption Fine Structure (XAFS) was performed at the MR-CAT undulator beamline at Advanced Photon Source, Argonne National Laboratory. A double crystal Si(111) monochromator was utilized for energy selectivity and a Rh harmonic rejection mirror was used to eliminate the higher harmonics of the desired energy range (Pt L₃-edge). XAFS measurements were performed in fluorescence mode using a 13-element Ge detector. The incident photon intensity was measured by an ion chamber filled with 80% He, 20% N₂ gas mixture.

DISCUSSION

A bright-field TEM micrograph showing typical nanoparticles produced is shown in Figure 1. These particles were produced by irradiating a solution with a total metal concentration of 2x10⁻³ mol/l, and a mole ratio of 70%Ag, 30%Pt with 0.5 kGy. Nearly spherical particles, with diameters in the 20-30 nm range, were observed. EDS showed that these particles were composed of pure Ag, and SAED

yielded diffraction rings characteristic of a fcc structure. The fact that Ag was reduced first can be explained based on electrochemical arguments. Reduction of $\text{Pt}^{\text{IV}}\text{Cl}_6^{2-}$ to Pt metal occurs in two steps. The first step, $\text{Pt}^{\text{IV}}\text{Cl}_6^{2-}/\text{Pt}^{\text{II}}\text{Cl}_4^{2-}$, has a reduction potential of 0.68V and the second step, $\text{Pt}^{\text{II}}\text{Cl}_4^{2-}/\text{Pt}^0$, has a reduction potential of 0.74V. The reduction potential of Ag^+ to Ag metal in acidic solution is $E^0 = +0.79$ V, and is more positive than both Pt reduction steps. Thus, Ag^+ is the more noble species in our solutions. When ionizing radiation at low dose rates is employed to reduce metal ions in aqueous solutions, clusters of the more noble metal (Ag in our case) form first because charge is transferred from the less noble to the more noble species [12,13].

Figure 1b shows typical nanoparticles obtained after exposure to a total dose of 3.5 kGy for solutions with the same total metal ion concentration as those shown in Figure 1a. Nanowires are evident, and they are typically made up of thin filaments, with diameters of 2-5 nm, that join large particles, with typical diameters of 20-30 nm. Nanoparticle chemical composition was determined with EDS. The spatial resolution of our instrument (about 150 nm) prevented a precise determination of individual cluster composition. We did establish, however, that regions surrounding the large particles have a typical composition of 80-90 at% Ag. Regions containing only filaments have a typical composition close to 50 at% Ag. The EDS results suggest that the larger particles are made from the Ag particles that form in the early stages of reduction, and that Pt-rich filaments nucleate out of these Ag particles. Figure 1c shows a SAED obtained from a filament region. Diffraction spots are distributed on rings, and indicate that the filaments are polycrystalline. The rings are consistent with fcc structures, and indicate that the filaments are made up of fcc grains. The low particle density of the filaments and their small diameter resulted in a small number of broad diffraction spots, and prevented an accurate determination of lattice parameters with SAED. The upper left quadrant of Figure 1c, shows the rings expected for the (111) and (200) reflections of bulk Ag and Pt. Some diffraction spots are broader than the distance between the Ag and Pt rings. It is not possible to determine if the spots originate from reflections of isolated Pt and Ag particles, or, for example, from a Ag-Pt alloy with a lattice parameter intermediate between those of Ag and Pt. SAED taken from regions surrounding the larger particles yielded results comparable to those obtained for the filaments.

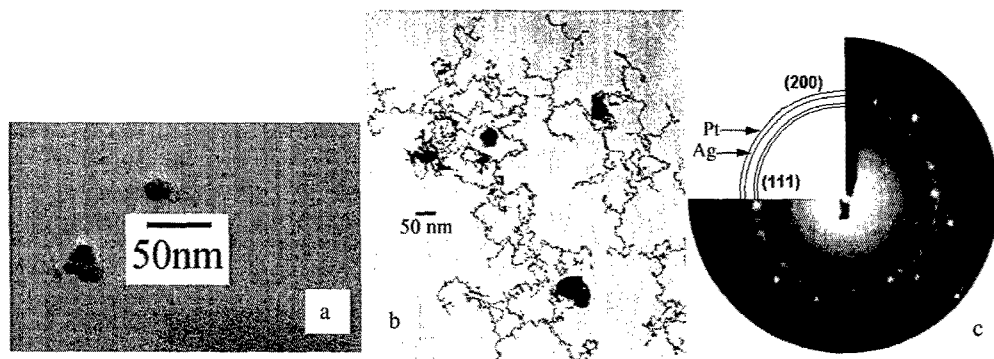


Figure 1. (a) Bright field TEM micrograph of nanoparticles obtained after exposure to a total dose of 0.5 kGy. Spherical particles are 20-40nm in diameter (b) Bright field TEM micrographs of nanoparticles obtained after exposure to a dose of 3.5 kGy. Larger spherical particles are 20-35nm while the smaller clusters are on the order of 1 or 2nm (c) Typical SAED of a filament region. All samples were made with 70at% Ag and 30at% Pt nominal concentration, 8mg/ml PVA (MW 88,600-97,000, 87-89% hydrolysis), and a total metal ion concentration of 2×10^{-3} .

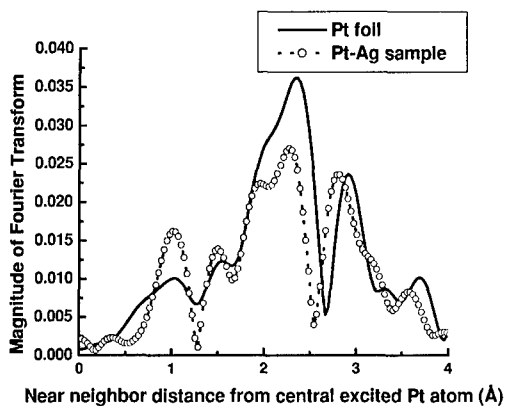


Figure 2. Fourier transform of Pt foil data (solid) and of a 60/40 at% Ag/Pt sample (dot) over the k -range 3 - 11.8 $\text{\AA}^{-1}$.

To determine whether or not the grains making up the filaments were Ag-Pt homogeneous alloys, XAFS of a 60/40 at% Ag/Pt sample was measured. The period of observed oscillations is a function of the bond-lengths of the neighbors of the absorbing atom, and the amplitude depends on the coordination number. The oscillations were extracted from the spectrum by a background subtraction and then Fourier-transforming the oscillations into real space. A Pt foil was first measured in transmission mode XAFS and as compared to the same type of measurements of the Ag/Pt sample. The first shell did not show any conspicuous trace of Ag; only Pt atoms coordinate the central Pt. This apparent reduction in bond length can be explained by the effect of disorder in XAFS [15-17], which suggests that the Pt atoms in this sample are in a disordered state compared to the Pt foil. Formation of a homogeneous Ag-Pt alloy would lead to an expansion of the lattice parameter of Pt, as expected from Vegard's law, and experimentally observed [16]. The absence of an expansion ruled out alloying. Rather, we observed a contraction in the Pt first shell bond length by 0.05 $\text{\AA}$, as seen in Figure 2. The coordination number is much lower compared to that of the bulk Pt, which is a reasonable characteristic of nanoparticle systems.

The high aspect ratio of the nanoparticles produced in our experiments is at odds with previous experiments, where radiolysis yielded nearly spherical Ag-Pt bimetallic clusters [12]. To better understand the nanowire formation mechanism, we varied numerous parameters, such as total and relative metal and polymer concentrations, counter ions, and type and molecular mass of the polymer. The effects of these parameters on the aspect ratio of the nanoparticles are summarized in Table II. For example, when K_2PtCl_4 was employed, spherical particles resulted. Similarly, nanowires did not form when AgNO_3 was employed instead of Ag_2SO_4 . Nanowires also did not form when the Ag^+ concentration was lower than 20% or higher than 80% of the total metal ion concentration. The degree of hydrolysis of the capping polymer PVA also played an important role. When PVA hydrolysis was on the order of 98-99%, spherical aggregates resulted. High aspect ratio nanoparticles were produced only with 87-89% hydrolyzed PVA with a molecular weight of at least 31,000.

Our results suggest that polymer-metal complexes (and possibly micelles) are being formed. Partially hydrolyzed PVA can be envisaged as a copolymer, where hydrophilic vinyl alcohol groups are broken up by less hydrophilic, un-hydrolyzed vinyl acetate groups. The un-hydrolyzed groups are likely to aggregate in aqueous solution, presumably around hydrophilic species such as metal clusters or metal ions, possibly like a swollen micelle. The sensitivity of the synthesis to the presence of SO_4^{2-} and PtCl_6^{2-} ions also indicates polymer-ion complex formation. For example, polymer gels of modified PVA show great sensitivity to the presence of ions such as sulfate [19]. These specific interactions probably enhance the interaction of the metal ions (and ultimately particles) with PVA.

Table II. List of metal compounds, type of capping polymers and Ag/Pt mole ratios leading to, or preventing, nanowire formation. All conditions in the second row must be met to produce nanowires, any condition met in the third row prevents nanowire formation. The aspect ratio of the nanoparticles did not depend on the total metal ion concentration (tested range: 1×10^{-4} to 2×10^{-3} mol/l), or the polymer concentration (tested range: 2 to 12 g/l). Solutions were exposed to a total dose of 3.5 kGy.

PVA molecular mass (amu), hydrolysis degree (%)	Ag/Pt mole ratio	Ag, Pt compounds	Wire formed
MW: 31000-170000 and Hydrolysis: 87-89%	80/20 to 20/80	H ₂ PtCl ₆ and Ag ₂ SO ₄	Yes
MW: 20000 or Hydrolysis: 98%	100/0 or 90/10, or 10/90 or 0/100	K ₂ PtCl ₄ or AgNO ₃	No

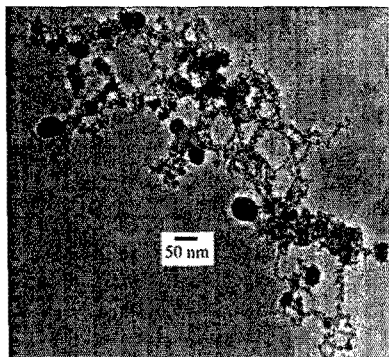


Figure 3. Bright field TEM micrographs of nanoparticles obtained after exposure to a dose of 3.5 kGy. The larger spherical particles are 30–45 nm while the filaments are on the order of 3 to 6 nm. Samples were made with 60 at% Ag and 40at% Pt nominal concentration, 5.7mg/ml PEO-block-PPO, and a total metal ion concentration of 2×10^{-3} .

The polymer-metal complexes might be micelles, since there is experimental evidence that copolymers made up of hydrophilic and hydrophobic blocks such as poly(ethylene oxide) – block – poly(methacrylic acid) [5], coordinated with metal ions of Ag, can give rise to micelles [20]. In Figure 3, we show preliminary results obtained by replacing PVA with a co-block polymer, poly(ethelene oxide) – block – poly(propylene oxide) (PEO-block-PPO). PEO is the hydrophilic part while PPO is the hydrophobic part of the polymer. Solutions containing a 2×10^{-3} total metal ion concentration of 60at% Ag and 40at%Pt were prepared with 57 g/l of PEO-block-PPO. The resulting nanoparticle structure alternated with large spherical particles and thin, filament-like aggregates. Regions where small clusters aggregated to give rise to large patches of high cluster density were also evident and were not detected when PVA was employed. The results suggest that alternating hydrophilic and hydrophobic groups in the capping polymer is a necessary condition for filament formation. The precise morphology of the nanoparticles, however, probably has a complex dependence on the compositions of the solutions.

CONCLUSION

We describe a technique to synthesize high aspect ratio bimetallic nanostructures. We employed radiolysis to reduce metal ions in aqueous solution and generate filament-like nanostructures that can be as long as several microns, with a diameter of a few nanometers. The filaments are polycrystalline, and are made up of grains with fcc structure. The grains have a Ag core-Pt shell structure, homogeneous alloying being ruled out by XAFS. Key parameters for nanowire formation are the mole ratio between

the two metals, the type of counter ions in solution, and the presence of hydrophobic groups in the capping polymer.

ACKNOWLEDGMENT

We thank William Bonzer for his assistance in irradiating our samples. We also thank Dr. S. Miller for his assistance with TEM measurements. A. T. Tokuhito, Director of the University of Missouri-Rolla Reactor (UMRR) Facility, thanks the Department of Energy for continued support of UMRR through the Reactor Instrumentation and Reactor Sharing Grant programs. The MRCAT beamline is supported by the US DOE under grant number DEFG0200ER45811.

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