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Formation of uranium based nanoparticles via gamma-irradiation

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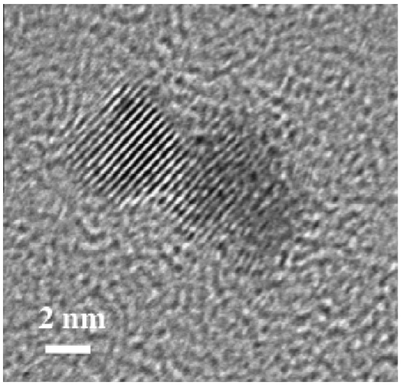
HIGHLIGHTS

- d-U nanoparticles were grown in solution by gamma irradiation.
- The reaction solution does not exceed 25 °C (room temperature).
- Only after multiday exposure to air is there evidence of oxidation of the d-U nanoparticles.
- Evidence of d-U alloy nanoparticle formation confirmed by TEM/energy-dispersive X-ray (EDS) analysis.

GRAPHICAL ABSTRACT



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ABSTRACT

The ability to fabricate nuclear fuels at low temperatures allows for the production of complex Uranium metal and alloys with minimum volatility of alloy components in the process. Gamma irradiation is a valuable method for the synthesis of a wide range of metal-based nanoparticles. We report on the synthesis via room temperature radiolysis and characterization of uranium (depleted, d-U) metal and uranium–lathanide (d-U*Ln*, *Ln* = lanthanide surrogates) alloy nanoparticles from aqueous acidic salt solutions. The lanthanide surrogates chosen include La and Eu due to their similarity in ionic size and charge in solution. Detailed characterization results including UV–vis, TEM/HR-TEM, and single particle EDX (elemental analyses) are presented for the room temperature formed nanoparticle products.

1. Introduction

Metals and metal oxides nanoparticles (NP) have high and often tunable surface energies per unit volume, a property that allows them to be flexibly manipulated and consolidated under mild (low temperature) thermal and chemical conditions. This is of potential value when contrasted to the high temperature processing of actinide mixtures to mixed metal oxide fuels. It can be very difficult to produce phase-pure mixed metal and oxide bulk phases as the components have great variation in their thermal properties. Furthermore, traditional high temperature sintering may result in volatilization of alloy components (eg., Am, mp ≈ 994 °C), rendering the bulk product inconsistent in composition and requiring extensive sequestration of the volatile component during processing.

Therefore, the search for a low temperature NP synthesis route for applications in nuclear fuels production is underway. However, many standard approaches to nanoparticle synthesis, such as room temperature chemical reduction by borohydride in the presence of surfactants, are ineffective when applied to acidic actinide solutions with very low reduction potentials, and can introduce byproducts that are difficult to remove.

Radiolysis is a room temperature procedure for the synthesis of nanoparticles. Recently, it has been used in the synthesis and study of metallic [1], and particularly alloyed [1–5], nanoparticles (NPs).

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This method provides a strong reducing environment that allows for the formation of nanoparticle products that are uniform in size, shape and composition. Recently, there has been significant investigation of aqueous uranium chemistry, including our recent studies on the formation of UO_2 nanoparticles by radiolysis [6], the formation of uranyl nanoclusters [7], and the effect of alpha [8] and gamma (γ) irradiation on U oxidation states [9–11]. However, little has been reported on NP synthesis from actinide precursors via γ-irradiation [12]. We expect that the use of radiolysis for actinide NP formation will allow for precise control of product composition. Furthermore, the uniform size and shape of NPs formed should allow for a lowering in temperature for NP consolidation and sintering [13]. This is of particular interest for the fabrication of advanced alloy nuclear fuels with complex compositions. Furthermore, it addresses a manufacturing pathway to reprocess dissolved used uranium salts into usable advanced nuclear fuels thereby ensuring an adequate supply of fuel is created or maintained [14]. Furthermore, room temperature radiolysis synthesis of uranium metal and alloy nanoparticles can be used as an inexpensive method to make research quantities of fuel surrogates for advanced materials studies and use in fuel cycle advanced reactor concepts.

In the formation of NPs under radiolysis, γ-irradiation creates hydrated electrons, H atoms and hydroxyl radicals in the aqueous reaction solution (see Eq. (1)):

$$H_2O \Rightarrow e^-_{aq}, H_2, OH^\cdot, H^\cdot, H_3O^+ \tag{1}$$

Hydrated electrons reduce metal (M) ions in solution to produce metal NPs (see Eq. (2)):

$$M^{n+} + ne^-_{aq} \Rightarrow M^0 \tag{2}$$

The reported nanoparticles formed via radiolysis [1–4] are comprised of metals whose standard redox potentials are no more than a few hundred millivolts more negative than water and show stability when alloyed in NPs with more noble metals. Contrary to this, actinides have standard reduction potentials about 2 V more negative than water [15], presenting a challenge to the formation of stable metallic particles in water. However, under certain conditions, some intermediate oxidation states of actinides are rendered insoluble or are able to form colloids in an aqueous environment. The use of γ-irradiation as a method to form a highly reducing aqueous environment can be a convenient pathway to the formation of the actinide colloids. Research by both our group [6] and Roth et al. [12] has shown that the use of radiolysis has led to the successful reduction of uranyl (UO_2^{2+}) ions to UO_2 NPs. Furthermore, we were successful in sintering the nanoparticles at temperatures in the range of 500–600 °C, which is between 700 and 1000 °C lower than reported bulk UO_2 sintering temperatures.

Fig. 1. Glass reactor made for radiolysis experiments. The reaction solution is deaerated by bubbling Ar into the vessel through a heavy gauge needle in the top stopper, while air and excess Ar are allowed to escape through a needle in a secondary stopper. Both needles are removed prior to radiolysis.

Herein, we report on the synthesis via room temperature radiolysis and characterization of uranium metal and uranium–lathanide alloy nanoparticles. We present studies on U and U*Ln* (*Ln* = La and Eu) nanoparticles in acidic aqueous solutions; La, Eu were chosen due to their similarity in ionic size and charge in solution. Characterization of the nanoparticles is achieved with the use of UV–vis, high resolution transmission electron microscopy (HRTEM), and elemental analyses. The specific reaction (see Eq. (3)) guiding this formation via radiolysis expected in this case is:

$$U^{4+} + 4e^-_{aq} \Rightarrow U(s) \tag{3}$$

2. Experimental section

2.1. Sample preparation

Only depleted uranium containing reactants were used for all experiments; *Ln* in the mixed compositions represents La or Eu. For a pure uranium sample preparation: a 12.5 ml aqueous solution containing 4×10^{-3} M UCl_4 (International Bio-Analytical Industries), in aqueous solutions of deionized water with methanol, 0.1 M sodium citrate and 0.1 M PVA (polyvinyl alcohol). Solution compositions of U and 50/50 U/*Ln* (*Ln* = Eu, La), respectively, were targeted in the experimental setup. For the alloy sample preparations: a 12.5 mL aqueous solution is made containing 2–4×10^{-3} M UCl_4, 0–2×10^{-4} M $EuCl_3 \cdot 6H_2O$, 0–2×10^{-4} M $LaCl_3 \cdot 7H_2O$, 1×10^{-2} M sodium citrate, 0.5 M methanol, and 1×10^{-2} M (0.66 g/L) poly(vinyl alcohol) (PVA, *Mw*) 88,000). All reactions are then deaerated by bubbling Ar for 12 min and then irradiated in a ^{60}Co-γ source (Sandia National Laboratories Gamma Irradiation Facility (GIF)) at a dose rate of 350 rad/s for a total of 24 min. Reagents are from Aldrich unless otherwise specified. The samples were prepared in specially made glassware: 100 mL vessels with quartz cuvette sidearms having a 0.5 cm optical pathlength (see Fig. 1). The solutions were irradiated in these vessels. To ensure completeness of reactant salt reduction, two additional 6 min irradiation runs (350 rad/s) were performed. This corresponds to approximately five times the dose required for total reduction of U^{4+} and La^{3+} ions.

2.2. Characterization

Ultraviolet–visible (UV–vis) spectroscopy and transmission electron microscopy (TEM) techniques were used to analyze the solutions and the NP products. Before and after each irradiation, plus after 7 days of aging post final irradiation, the samples were analyzed with ultraviolet–visible (UV–vis) spectroscopy using a Varian Cary 300 Scan UV–visible Spectrophotometer. pH was measured using an Accumet Model 20 pH meter. Due to the reaction vessel design, UV–vis spectroscopy was carried out without the need to open the vessel and expose the reaction to oxygen.

General TEM characterization was carried out on carbon TEM grids with a Tecnai G(2) F30 S-Twin 300 kV TEM (FEI Company) at the Center for Integrated Nanotechnologies at Sandia National Laboratories. The unit performs Selected Area Diffraction (SAD) and is equipped with energy-dispersive X-ray (EDX) analysis for detection of characteristic X-rays for elemental analysis and with an electron energy-loss spectrometer (EELS) for characterizing composition. This instrument is equipped with *Z-contrast* capability (to differentiate between elements) with a resolution of