SYNTHESIS OF SILICA-COATED Au WITH Ag, Co, Cu, AND Ir BIMETALLIC RADIOISOTOPE NANOPARTICLE RADIOTRACERS

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Received January 04, 2012

Accepted for Publication February 21, 2012

Silica-coated Au with Ag, Co, Cu, and Ir bimetallic radioisotope nanoparticles were synthesized by neutron irradiation, after coating SiO₂ onto the bimetallic particles by the sol-gel Stöber process. Bimetallic nanoparticles were synthesized by irradiating aqueous bimetallic ions at room temperature. Their shell and core diameters were recorded by TEM to be 100 – 112 nm and 20 – 50 nm, respectively. The bimetallic radioisotope nanoparticles' gamma spectra showed that they each contained two gamma-emitting nuclides. The nanoparticles could be used as radiotracers in petrochemical and refinery processes that involve temperatures that would decompose conventional organic radioactive labels.

KEYWORDS : Bimetallic Radioisotope Nanoparticles; Au-Ag@SiO₂, Au-Co@SiO₂, Au-Cu-SiO₂, Au-Ir@SiO₂

1. INTRODUCTION

Radioisotopes are useful tracers because their chemical properties are the same as those of stable isotopes and they show higher detection sensitivity than other tracers. Their usefulness has been demonstrated in fluorescence experiments in diverse areas including life science, medicine, and engineering. SiO₂-coated radioisotope Au core-shell nanoparticles (Au@SiO₂ NPs) were first synthesized by sol-gel reactions of aqueous Au NPs induced by γ irradiation without reduction agents [1]. Their SiO₂ shells were physically stable in high-energy gamma environments. Radioisotope Au@SiO₂ NPs with Au-198 exhibited a half life, $T_{1/2}$, of 15 days and emitted energy, E , of 0.412 – 1.088 MeV, making them unsuitable for use as radiotracers for long periods in high-temperature petrochemical and refinery processes. Bimetallic NPs have exhibited better electronic, optical, catalytic, and magnetic properties than the corresponding monometallic NPs and can improve sensors' stability and selectivity [2-5]. Ni-based NPs have potentially useful catalytic and magnetic properties. Completely miscible Cu-Ni NPs can selectively inhibit hydrogenolysis [6]; Pt-Ni intermetallic NPs have demonstrated enhanced electrocatalytic activity towards oxygen reduction compared with Pt alone [7]; and Sn-Ni alloys have shown

unique catalytic selectivity in the dehydrogenation of cyclohexane [8]. PVP-protected bilayered Pd-Ni NPs have exhibited enhanced magnetic susceptibility at low temperatures due to quantum size effects [9]. However, radioisotope NPs containing two gamma emitters for use as radiotracers, have yet to be reported.

Silica NPs have useful properties such as inertness and suitability for encapsulation and surface modification [10]. They are generally 20 to 300 nm in size and can be prepared at room temperature by the Stöber method, using sol-gel. Quantum dots (QDs) and magnetite (Fe₃O₄) NPs have been encapsulated in silica NPs for use as high-brightness and magnetically guided biomarkers for living cancers [11]. To prevent nanoparticles' aggregation at high temperatures, SiO₂ NPs can be encapsulated onto radioisotope NPs by sol-gel reactions at room temperature [1].

This work reports the synthesis of radioactive silica-coated bimetallic NPs (Au-Ag@SiO₂, Au-Co@SiO₂, Au-Cu@SiO₂, and Au-Ir@SiO₂) by neutron irradiation after coating SiO₂ onto the bimetallic NPs by the Stöber method. The resulting particles could act as durable tracers for high-temperature use. The bimetallic core nanoparticles were synthesized at room temperature by the radiation-induced reduction of aqueous metal ions without a reducing agent. The core-shell Au-Ag@SiO₂, Au-Co@SiO₂, Au-

Cu@SiO₂ and Au-Ir@SiO₂ NPs were fabricated by sol-gel reactions at room temperature. They were characterized by TEM and EDS. The NPs were calcined, irradiated with neutrons in a nuclear reactor, and then characterized by neutron activation gamma spectroscopy.

2. MATERIALS AND METHODS

2.1 Materials

HAuCl₄·nH₂O, AgNO₃, CoCl₂·6H₂O, CuCl₂·2H₂O, IrCl₄·nH₂O, tetraethoxysilane (TEOS, 98%), 2-propanol, and poly(vinyl pyrrolidone) (PVP, molecular weight 40,000) were of analytical reagent grade and from Sigma-Aldrich Korea. Each was used without further purification. Water was purified in a Milli-Q plus water purification system (Millipore Co. Ltd. USA) to a final resistance of 18.2 MΩcm⁻¹ and degassed prior to each measurement. Other chemicals were of reagent grade.

2.2 Synthesis of PVP-stabilized Bimetallic NPs

Hydrogen tetrachloroaurate (III) (HAuCl₄ = 5.0 × 10⁻⁴ M) and cobalt nitrate (CoCl₂ = 5.0 × 10⁻⁴ M) were dissolved in water (376 mL) with 2-propanol (24.0 mL) and PVP (1.0 g) to form a primary solution, through which nitrogen was bubbled for 30 min to remove oxygen. It was irradiated with γ-rays from a Co-60 source under atmospheric pressure and ambient temperature. A total irradiation dose of 30 kGy was administered at 1.0 × 10⁴ Gy/h. Au-Co bimetallic nanoparticles of various sizes resulted. The Au-Cu and Au-Ir bimetallic NPs were similarly prepared. The Au-Ag bimetallic NPs were synthesized using 5.0 × 10⁻⁴ M HAuCl₄ and 2.0 × 10⁻³ M AgNO₃, because the remaining Ag⁺ ions were used as precursors for the synthesis of Au-Ag bimetallic NPs after precipitation of AgCl in the primary solution.

Core-shell Au-Co@SiO₂ NPs were prepared by sol-gel reactions of TEOS in the presence of the Au-Co bimetallic NPs: 4.0 mL Au-Co bimetallic NPs were mixed with 20 mL 2-propanol and 0.5 mL NH₄OH in a round flask, under stirring for 2 hrs at room temperature. Solid state Au-Co@SiO₂ bimetallic NPs were obtained by centrifuging, and then calcined to remove organic compounds under an N₂ flow. The other bimetallic NPs were similarly treated.

2.3 Neutron Irradiation

13 mg Au-Co@SiO₂ bimetallic NPs were irradiated with neutrons in the nuclear research reactor of the Korea Atomic Energy Research Institute, HANARO (flux: 2.863 × 10¹³/cm²·sec). This produced activated Au-198 radioisotopes within the NPs. Radioactivity was determined by several parameters – the relationship between them is given in Eq. (1) [12].

$$Activity = \frac{W}{M} \cdot N_A \cdot f \cdot \Phi_{thermal} \cdot \sigma_0 (1 - e^{-\lambda t_i}) \quad (1)$$

where W is the sample's weight, M its molar weight, N_A is Avogadro's number, $\Phi_{thermal}$ is the thermal neutron flux, σ_0 is the cross-section, λ is the decay constant, and t_i is the irradiation duration.

2.4 Characterization of the Bimetallic NPs

Particles' sizes and morphologies were analyzed by HR-TEM (JEOL, JEM-2010F, Japan). An energy dispersive X-ray spectrometer (EDXS) attached to the HR-TEM was used to analyze their chemical compositions. The NPs' chemical purities were assessed through gamma spectroscopy measured with an HPGe detector (EG&G Ortec, 25% relative efficiency, FWHM 1.85 keV at 1332 keV of ⁶⁰Co) coupled to a 16K-multichannel analyzer.

3. RESULTS AND DISCUSSION

3.1 Synthesis and Characterization of the Bimetallic NPs

Novel polymer-protected metallic NPs can be synthesized by one-step radiation-induced reductions of aqueous metallic ions in the presence of 2-propanol. Two active species, such as free radicals and solvated electrons (e_{aq}^-), can be achieved during γ-irradiation [13-15]:

The oxidized metallic ions can then be reduced by strongly reducing the e_{aq}^- and $H\cdot$ radicals (Eqs. (3) and (4)):

Au-Ag bimetallic NPs were synthesized by the one-step radiolytic reduction of aqueous Au³⁺ and Ag⁺. The Au-Co, Au-Cu, and Au-Ir NPs were synthesized as above. Hydroxyl radicals (OH·) could also reduce the metal ions to zero-valence metal atoms. 2-propanol was added to the reaction mixture to protect the oxidizing agent (OH·). OH· radicals reacted with 2-propanol as per equation (5). The metal ions were then reduced to zero-valence metal atoms by the 2-propanol radicals as follows:

PVP-protected Au colloids have been prepared by the radiation-induced reduction of aqueous Au³⁺ ions with 2-propanol in the presence of a PVP colloidal stabilizer [1,16]. TEM showed Au NPs of below *ca.* 50 nm with a broad

size distribution. ELS showed the Au NPs to exhibit two size distribution regions, due to primary Au NPs, and secondary aggregations of the primary particles. Au-Ag alloy NPs were synthesized using highly concentrated AgNO_3 (2.0×10^{-3} M, compared with HAuCl_4 at 5.0×10^{-4} M) as a source of aqueous Ag^+ ions, that also precipitated as AgCl from reaction with Cl^- ions from the gold salt (HAuCl_4). TEM showed spherical particles of *ca.* 40 nm (Fig. 1). Peaks from Au (M) and Ag (L) are observable in the EDS data at 2.123 KeV and 2.984 KeV, respectively (Fig. 1). The EDS data indicate atomic ratios of Au and Ag of 96.1% and 3.90%, respectively. The low presence of Ag was likely due to AgCl precipitation.

The TEM image of the Au-Co bimetallic NPs (Inset, Fig. 2) shows variously sized bimetallic NPs of below *ca.* 10 nm due to aggregation from the primary bimetallic NPs. The particles' EDS data show peaks from Au (M) and Co (K) at 2.123 KeV and 7.840 KeV, respectively (Fig. 2). Atomic ratios of Au and Co were determined to be 82.2% and 17.8%, respectively, from the EDS data. This was attributed to the standard reduction potential of the Au^{3+}/Au couple ($E^0 = +1.50$ V) being significantly greater than that of the Co^{2+}/Co couple ($E^0 = -0.280$ V), which resulted in Au^0 being more easily synthesized than Co^0 in the aqueous solution during γ -irradiation.

TEM showed very finely distributed Au-Cu bimetallic NPs of *ca.* 10 nm obtained by the radiation-induced reduction of the two metal ions (Inset, Fig. 3). The particles' EDS data show peaks from Au (M) and Cu (K) at 2.123 KeV and 8.041 KeV, respectively (Fig. 3), and atomic ratios of Au and Cu of 59.2% and 40.8%, respectively. This composition ratio was attributed to the smaller difference of the standard reduction potentials of the Au^{3+}/Au and Cu^{2+}/Cu ($E^0 = +0.34$ V) couples, which allowed Au^0 and Cu^0 to be synthesized with similar atomic ratios by the reduction of their metal ions, using hydrated electrons prepared during γ -irradiation.

TEM showed that the Au-Ir NPs were spheres of *ca.* 12 nm diameter (Inset, Fig. 4). The particles' EDS data

show peaks attributable to Au (M) and Ir (M) at 2.123 KeV and 1.977 KeV, respectively (Fig. 4) and indicate atomic ratios of Au and Ir of 72.8% and 27.2%, respectively, which resulted from the standard reduction potential of the Au^{3+}/Au couple being slightly higher than that of the Ir^{4+}/Ir couple ($E^0 = +0.835$ V).

Fig. 2. TEM and EDS Data of Au-Co Bimetallic NPs.

Fig. 3. TEM and EDS Data of Au-Cu Bimetallic NPs.

Fig. 1. TEM and EDS Data of Au-Ag Bimetallic NPs.

Fig. 4. TEM and EDS Data of Au-Ir Bimetallic NPs.

Scheme 1. Synthesis Procedure of the Radioisotope Au-M@SiO₂ (M=Ag, Co, Cu and Ir) NPs. Fig. 5. TEM and EDS Data of Au-Ag@SiO₂ Core-shell NPs. Fig. 6. TEM and EDS Data of Au-Co@SiO₂ Core-shell NPs.

Aggregation of the metallic NPs was prevented by coating them with silica via sol-gel reactions of TEOS in 2-propanol and ammonia in the presence of the particles (Scheme 1).

The Au-Ag@SiO₂ NPs were shown by TEM to be coated particles of *ca.* 105 nm overall diameter and 35 – 50 nm core diameter (Inset, Fig. 5). The particles' EDS data indicate atom compositions of 38.3% O, 30.6% Si, 2.7% Ag, and 28.5% Au (Fig. 5), demonstrating the successful synthesis of Au-Ag@SiO₂ NPs for use as radioisotope tracers. ELS has shown that SiO₂ coating increases particles' outer diameters. Shell thickness has been shown to be controllable through the use of TEOS in the NPs' reactions [1]. An aggregation-dominated model of formation is proposed for pure silica colloids. In this model, nucleation and aggregation proceed simultaneously in the reaction solution; with nucleation occurring immediately after the addition of the TEOS monomer, the aggregation of nuclei does not occur due to their instability. Competition between nucleation and aggregation is dependent upon the experimental conditions, e.g. the concentrations of ammonia, water, and TEOS.

TEM showed the Au-Co@SiO₂ core-shell NPs to be of *ca.* 100 nm outer diameter and 3 – 15 nm inner diameter (Inset, Fig. 6). EDS showed that the coated NPs comprised 38.3% O, 27.2% Si, 6.2% Co, and 27.2% Au, indicating the successful synthesis of Au-Co@SiO₂ core-shell NPs

Fig. 7. TEM and EDS Data of Au-Cu@SiO₂ Core-shell NPs.

for use as radioisotope tracers (Fig. 6).

TEM images of Au-Cu@SiO₂ (Inset, Fig. 7) and Au-Ir@SiO₂ (Fig. 8) core-shell NPs prepared by sol-gel reaction, show the particles to have shell thickness of *ca.* 30 nm and 3–7 nm, respectively, and core diameters of 23–25 nm and 2 nm, respectively. EDS showed the Au-Cu@SiO₂ core-shell NPs to comprise 49.0% O, 28.1% Si, 4.5% Cu, and 18.4% Au, indicating the successful synthesis of particles for use as radioisotope tracers.

Fig. 8. TEM Image of Au-Ir@SiO₂ Core-shell NPs (a) and (b). Fig. 9. Gamma Spectrum of the Radioisotope Au-Ag@SiO₂ NPs. Fig. 11. Gamma Spectrum of Radioisotope Au-Cu@SiO₂ NPs. Fig. 10. Gamma spectrum of Radioisotope Au-Co@SiO₂ NPs. Fig. 12. Gamma Spectrum of Radioisotope Au-Ir@SiO₂ NPs.

3.2 Neutron Activation Gamma Spectrum of the Silica-coated Bimetallic Radioisotope NPs

To allow the particles to be used as radioisotope tracers, they were irradiated with neutrons in a nuclear reactor.

The Au-Ag@SiO₂ core-shell NPs' activity was estimated by Eq. 1 to be 2.12×10^8 dps (disintegration per second). Their recorded spectrum (Fig. 9) shows peaks attributable only to Au-198 (412, 676, and 1088 KeV) and Ag-108 (434 and 633 KeV), indicating their successful preparation as radiotracers. These radioisotope NPs could be used as tracers in high-temperature petrochemical and refinery pro-

cesses because of their physical and chemical stability [1].

The gamma spectrum of the radioisotope Au-Co@SiO₂ NPs (Fig. 10) shows characteristic gamma peaks of Au-198 (411, 675, and 1087 KeV) and Co-60 (1173 and 1332 KeV). The Au-Cu@SiO₂ NPs' gamma spectrum (Fig. 11) shows characteristic peaks of Cu-66 (833 and 1345 KeV). The Au-Ir@SiO₂ NPs showed characteristic gamma peaks of Ir-192 and Ir-194. The neutron-irradiated samples' gamma spectra suggest that each would be suitable for use as radiotracers in high-temperature petrochemical and refinery processes because of their physical and chemical stability.

4. CONCLUSION

Au-Ag, Au-Co, Au-Cu, and Au-Ir NPs were prepared by radiation-induced reduction and encapsulated onto silica gel by Stöber's method. These particles were calcined and irradiated by neutrons to form radioisotope bimetallic NPs suitable for use as industrial radiotracers. The irradiated particles showed gamma peaks characteristic of the radioisotopes of their component metals. These gamma-emitting bimetallic NPs could be used as tracers in petrochemical and refinery processes at extremely high temperatures that would decompose conventional organic radioactive labeling compounds.

ACKNOWLEDGMENTS

This work was supported by a National Research Foundation of Korea grant funded by the Korean Government (2011-0006407), and partially supported in the frame of the Radiation Technology Development Program (2011-0002265) by the Korean Ministry of Education, Science and Technology and the R&D project of KAERI.

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