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Using reversed-phase liquid chromatography to monitor the sizes of Au/Pt core/shell nanoparticles

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ABSTRACT

This paper describes the use of reversed-phase liquid chromatography (RPLC) to rapidly characterize Au/Pt core/shell nanoparticles (NPs) produced through seed-assisted synthesis. We monitored the sizes of Au/Pt core/shell NPs by using a porous silica-based RPLC column (pore size: ca. 100 nm) and 30 mM sodium dodecyl sulfate in deionized water as the mobile phase; the plot of the retention time with respect to the logarithm of the size of the Au NPs was linear ($R^2 = 0.997$) for diameters falling in the range from 5.3 to 40.1 nm; from five consecutive runs, the relative standard deviations of these retention times were less than 0.4%. We used the optimal separation conditions of the RPLC system to study the effects that the rate of addition of the reducing agent and the volumes of the seed, shell precursor metal ion, and reducing agent solutions had on the sizes of the Au/Pt core/shell NPs. A good correlation existed between the sizes of the Au/Pt core/shell NPs determined through RPLC and those determined using transmission electron microscopy. RPLC appears to be a useful technique for monitoring the sizes of NPs and nanomaterials in general.

1. Introduction

Metal nanoparticles (NPs) are attracting a great deal of attention from practitioners in a wide variety of scientific fields [1–6]. Because the physical and chemical properties of NPs are directly related to their chemical compositions, sizes, and surface structural characteristics [7–10], the design, synthesis, and characterization of nanostructures have become very important aspects of the emerging field of nanomaterials, where macroscopic properties are directly influenced by subtle nanostructural changes. Among the many metals currently under investigation for their nanomaterial properties, platinum (Pt) is one of the mostly researched noble metals because it is widely used in the fabrication of biosensors, in fuel cell technology, and as an effective catalyst for many industrial reactions [11–16].

The particle size effect is related to the variation of a reaction rate, selectivity, and/or sensitivity with respect to the characteristic dimensions of metallic clusters at the electrified solid–liquid interface [17–20]. Therefore, the design and synthesis of Pt nanostructures having well controlled sizes or shapes is of critical importance for their successful application, especially in the field of catalysis [21–24].

In a previous study, we prepared core/shell Au/Pt NPs through "seed-assisted synthesis," a successive reduction process that is effective for the size-controlled synthesis of Pt metal NPs [25]. The seed-assisted synthesis of Au/Pt NPs involves reducing Pt ions on the surfaces of preformed Au seeds – using a mild reducing agent (e.g., ascorbic acid) [25] – by minimizing the degree of nucleation while maximizing particle growth to achieve a shell of uniform thickness. Because the size of the core (seed) is predetermined, the overall dimensions of the core/shell NPs are dependent upon the thickness of the shell material.

When a set number of preformed seeds is used as nucleation centers for the fabrication of core/shell NPs, the NP growth conditions can be controlled simply through varying the fabrication parameters—e.g., the ratio of seeds to the shell metal precursor ions [1] or the rate of addition of the reducing agent [26]. Because there are other important parameters that influence the final sizes and shapes of core/shell NPs, when developing a new medium for the core/shell NP synthesis, it would be ideal if the final NP products could be characterized rapidly in terms of their final sizes to provide feedback so that the synthetic conditions could be optimized.

Reversed-phase liquid chromatography (RPLC) has been employed recently to separate and characterize water-soluble NPs [27]. After using transmission electron microscopy (TEM) to calibrate NP standards, RPLC analysis can then be applied as a stand-alone technique to determine the sizes of synthetic NPs. The prevalence of automated LC systems suggests that, in some instances, such approaches might be superior to other techniques

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typically employed for the characterization of NPs, such as dynamic light scattering (DLS) [28,29] and TEM [30,31].

Core/shell NPs exhibit a variety of properties depending on the nature of their components and their thicknesses. For example, the high electrocatalytic activities of Pt NPs toward many molecules can be adjusted by changing the thickness of the Pt shell of Au/Pt core/shell NPs [32,33]; therefore, before investigating their applicability, it would be useful to determine the NPs' sizes to establish the relationship between the catalytic behavior and the NP size. Because LC is a rapid, economical technique for separating NPs, we suspected that it might allow us to efficiently determine the size phenomena of fabricated Au/Pt core/shell NPs. Therefore, in this study, we investigated the effects of several important parameters – the rate of addition of the reducing agent and the volumes of the added seeds, shell metal ion precursor, and reducing agent solutions in the reaction medium – on the RPLC separations and sizes of Au/Pt NPs fabricated through seed-assisted synthesis. Because TEM is an accurate reference method for observing the morphologies of NPs [30], we also compared the accuracies of using RPLC- and TEM-based methods to characterize the sizes of Au/Pt core/shell NPs.

2. Experimental

2.1. Apparatus

A Hitachi L-2000 liquid chromatography system (Tokyo, Japan) was used for RPLC separation of the NPs. The RPLC apparatus was equipped with a diode array detection (DAD) system. A Nucleosil C_{18} column (Macherey-Nagel, Duren, Germany; 250 mm × 4.6 mm; pore size: 100 nm; particle size: 7 μm) and a 0.2-μm pre-column filter were employed for analytical separation, using a mobile phase of 30 mM sodium dodecyl sulfate (SDS) in deionized water at a flow rate of 1.0 mL min^{-1}; the detection wavelength was 520 nm and the injection volume was 20 μL. To confirm the accuracy of the size characterization by RPLC, a JEOL JEM-2010 transmission electron microscope (Tokyo, Japan) was used to independently analyze the Au/Pt core/shell NPs. A KDS 100 syringe pump (KD Scientific, Holliston, MA, USA) was used during the synthesis of the NPs.

2.2. Chemical reagents

Hydrogen tetrachloroaurate ($HAuCl_4$) and hydrogen hexachloroplatinate (H_2PtCl_6) were purchased from Acros Organics (Geel, Belgium). Ascorbic acid and sodium citrate were obtained from Merck (Darmstadt, Germany). SDS was obtained from Tokyo Chemical Industry (Tokyo, Japan). Standard Au NPs having a mean diameter of 5.3 nm [standard deviation (SD): 0.5 nm] were obtained from Sigma (St. Louis, MO, USA). Au NPs having mean diameters of 40.1 nm (SD: 3.2 nm) were obtained from BB International (Cardiff, UK). All eluents were prepared afresh each day and filtered through a 0.45-μm nylon membrane filter (Alltech, Deerfield, IL, USA) prior to use. Deionized water (>18 MΩ cm^{-1}) was used throughout the experiments.

2.3. Preparation of Au NPs

The synthetic procedure for the formation of smaller-sized Au NPs through citrate-mediated reduction of $HAuCl_4$ has been described elsewhere [28]. The resulting Au NPs were spherical; after digitizing TEM images, 2D-grain analysis revealed particle diameters of 12.1 ± 0.9 nm.

For the preparation of larger-sized Au NPs, two 20-mL sample vials (labeled A and B, respectively) were charged with deionized water (10 mL); a volume of 12.1-nm Au NPs (serving as seeds: 0.3 mL in A; 0.1 mL in B) was added to each vial, followed by $HAuCl_4$ solution (3.0×10^{-3} M, 0.5 mL). While the solutions were stirring, ascorbic acid (1.0×10^{-2} M, 0.5 mL) was added slowly (0.5 mL min^{-1}) from a burette to each vial. The resulting solutions were then stirred for 30 min. These procedures were performed at room temperature (ca. 25 °C). The resulting Au NPs were spherical; after digitizing TEM images, 2D-grain analysis revealed particle diameters for samples A and B of 21.2 ± 3.6 and 29.4 ± 3.1 nm, respectively.

2.4. Seed-assisted synthesis of Au/Pt core/shell NPs: varying the rate of addition of the reducing agent

Three 20-mL sample vials (labeled C–E, respectively) were charged sequentially with deionized water (7.5 mL), 12.1-nm Au seeds (0.75 mL), and H_2PtCl_6 solution (1.0×10^{-3} M, 2.5 mL). Ascorbic acid (1.0×10^{-2} M, 0.5 mL) was added to each vial via a syringe pump (operated at rates of 5.0, 200, and 2000 mL h^{-1} for vials C–E, respectively), while stirring. Finally, SDS (8.0×10^{-2} M, 10 mL) was added to each vial and the resulting solutions stirred for 30 min. These procedures were performed at room temperature (ca. 25 °C).

2.5. Seed-assisted synthesis of Au/Pt core/shell NPs: in the presence of various seed volumes

Two 20-mL sample vials (labeled F and G, respectively) were charged sequentially with deionized water (7.5 mL), 12.1-nm Au seeds (1.0 and 0.4 mL for vials F and G, respectively), and H_2PtCl_6 solution (1.0×10^{-3} M, 2.5 mL). Ascorbic acid (1.0×10^{-2} M, 0.5 mL) was added to each vial via syringe pump (at a rate of 5.0 mL h^{-1}), while stirring. Finally, SDS (8.0×10^{-2} M, 10 mL) was added to each vial and the resulting solutions stirred for 30 min. These procedures were performed at room temperature (ca. 25 °C).

2.6. Seed-assisted synthesis of Au/Pt core/shell NPs: in the presence of various volumes of shell precursor metal ions

Two 20-mL sample vials (labeled H and I, respectively) were charged sequentially with deionized water (7.5 mL), 12.1-nm Au seeds (1.0 mL), and H_2PtCl_6 solution (1.0×10^{-3} M; 4.5 and 5.5 mL for vials H and I, respectively). Ascorbic acid (1.0×10^{-2} M, 0.5 mL) was added to each vial via a syringe pump (at a rate of 5.0 mL h^{-1}), while stirring. Finally, SDS (8.0×10^{-2} M, 10 mL) was added to each vial and the resulting solutions stirred for 30 min. These procedures were performed at room temperature (ca. 25 °C).

2.7. Seed-assisted synthesis of Au/Pt core/shell NPs: in the presence of various volumes of reducing agent

Three 20-mL sample vials (labeled J–L, respectively) were charged sequentially with deionized water (7.5 mL), 12.1-nm Au seeds (1.0 mL), and H_2PtCl_6 solution (1.0×10^{-3} M, 2.5 mL). Ascorbic acid (1.0×10^{-2} M; 0.5, 1.0, and 1.5 mL for J–L, respectively) was added to each vial via a syringe pump (at a rate of 5.0 mL h^{-1}), while stirring. Finally, SDS (8.0×10^{-2} M, 10 mL) was added to each vial and the resulting solutions stirred for 30 min. These procedures were performed at room temperature (ca. 25 °C).

3. Results and discussion

3.1. Evaluation of the formation of Au/Pt NPs by seed-assisted synthesis

Before employing RPLC to study the sizes and size distributions of the Au/Pt core/shell NPs, we first confirmed that it was possible