Characterization of Core-Shell Nanoparticles Using Field-Flow Fractionation and Single-Particle ICP-MS

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ABSTRACT

A methodology has been developed to measure mass, size and density of the core and the shell of Silver-shelled Gold nanoparticles for the first time. The FFF-based methodology allows for the measurement of the mass of the nanoparticle using Centrifugal Field-Flow Fractionation and the volume by Asymmetrical Flow Field-Flow Fractionation. The nanoparticle density can then be calculated from the obtained mass and volume data. Mass of the core was measured either by Single-Particle ICP-MS or by the FFF analysis of the uncoated core nanoparticle. The nanoparticle diameter was measured as 56 nm with the core diameter and shell thickness of 30 nm and 13 nm respectively. The nanoparticle mass was measured as 8.76×10^{-19} kg with a shell/core mass ratio of 3.5. The densities of the core, shell and core-shell nanoparticle were measured as 12800 kg/m^3, 8900 kg/m^3, and 9500 kg/m^3 respectively.

Keywords: Field-Flow Fractionantion, Single-Particle ICPMS, Core-Shell nanoparticles, Nanoparticle density, Nanoparticle size

1 INTRODUCTION

A characterization methodology is developed to measure the mass, volume, and the density of a core-shell nanoparticle sample. Centrifugal and Asymmetrical Flow Field-Flow Fractionation techniques were used to measure nanoparticle's mass and volume. The shell thickness and core size were measured by analyzing the non-coated core nanoparticles or directly by analyzing the core-shell nanoparticle sample with Single-Particle ICPMS (sp-ICPMS) and TEM.

Field-Flow Fractionation is an elution-based technique for separation and characterization of nanoparticles, particles, polymers, proteins, emulsions, cells and viruses [1]. The separation takes place in an open flat channel, where sample species are interacting with an external physical field whose direction is perpendicular to the direction of channel flow. An equilibrium will be reached when the field-induced and diffusion-induced migrations of sample species are balanced. Smaller sized sample species located closer to the channel center will be swept out faster than the larger ones.

In Centrifugal Field-Flow Fractionation, (CFFF) separation is a result of the interaction between a centrifugal field and sample species. The separation in CFFF is based on particle buoyant mass. In Asymmetrical Flow Field-Flow Fractionation (AsFlFFF), the separation filed is cross flow and separation is based on sample diffusion coefficient or hydrodynamic size.

2 THEORY

2.1 FFF

The mathematical derivations of the retention time are described in detail elsewhere [1-2]. The retention time, t_r in CFFF is related to particle buoyant mass, m' using the equation below:

$$t_r = \frac{t^0 m' G w}{6kT} \tag{1}$$

Where G is acceleration, w is channel thickness, t^0 is void time, k is Boltzmann constant, and T is temperature in Kelvin.

The retention time in AsFlFFF is related to the hydrodynamic diameter, d_h using the equation below:

$$d_h = \frac{2kT}{\pi\eta w^2 \ln\left(1+\alpha\frac{\overset{\circ}{V}_c}{\overset{\circ}{V}}\right)} t_r \tag{2}$$

Where η is carrier viscosity, $\overset{o}{V}_c$ is cross flow rate, $\overset{o}{V}$ is channel flow rate, and α is geometrical factor.

2.2 Mass and density measurements

The buoyant mass, m' of a nanoparticle can be calculated from:

$$m' = m_P - V_P \rho_c \qquad (3)$$

Where m_P is nanoparticle mass, V_P is nanoparticle volume and ρ_c is carrier density. The nanoparticle density, ρ_P can then be calculated from:

$$\rho_p = \frac{m_P}{V_P} \qquad (4)$$

3 EXPERIMENTAL

3.1 Materials

The Silver-shelled Gold core and the Gold core samples used in this study was purchased from NanoComposix, San Diego California. Three polystyrene latex standards (50 nm, 100 nm and 150 nm) were purchased from Thermo Scientific. The Silver-shelled Gold core sample and latex standards were was diluted 50 and 200 times respectively using the carrier solution for the FFF analysis. A 0.05% FL-70 solution was used as the carrier solution in the FFF experiments. The FL-70 was purchased from Fisher Scientific.

3.2 Instrumentation

A CF2000 (CFFF) and a AF2000 (ASFlFFF) mid temperature systems, Postnova Analytics, GmbH, Landsberg, Germany were used to analyze the nanobparticles. A NexION 300 ICPMS, Perkin Elmer was used to analyze the FFF fractions in sp-ICPMS mode. A FEI Tecnai T-12 TEM was used to image the nanoparticles with magnification of 26,000 and working voltage of 120 keV.

4 RESULTS AND DISCUSSION

Figures 1 and 2 show the fractograms of the Silver-shelled Gold core and Gold core samples analyzed by CFFF at different field strengths. The retention time at the peak maximum of each run was used to calculate the buoyant mass. The average buoyant masses of the shelled core and core nanoparticles were measured as $7.8 \times 10^{-19} \pm 0.2\times10^{-19}$ kg and $1.8\times10^{-19} \pm 0.05\times10^{-19}$ kg respectively. The buoyant mass of the Silver shell was calculated as 6×10^{-19} kg using equation 1.

Figure 3 shows the results of AsFlFFF analysis of the Silver-shelled Gold core, Gold core and polystyrene latex standards. The hydrodynamic diameters of the core and shelled core nanoparticles were calculated as 41.9 ± 0.4 nm and 70.3 ± 0.5 nm respectively using equation 2. The FFF-measured values were confirmed by on-line DLS and size calibration using latex standards.

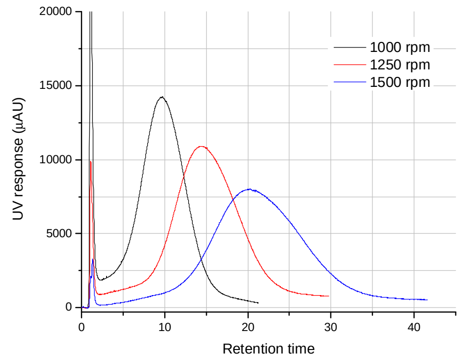

Figure 1: CFFF analysis of the Silver-shelled Gold core sample at different field strengths .

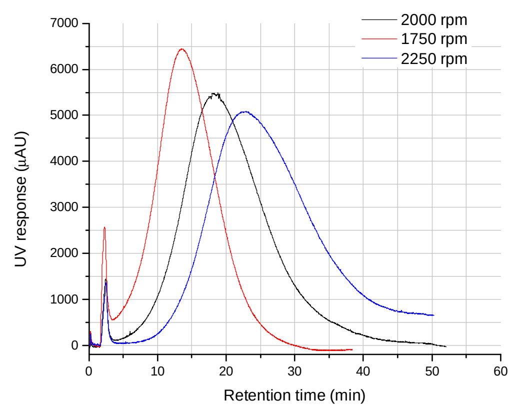

Figure 2 : CFFF analysis of the core Gold sample at different field strengths.

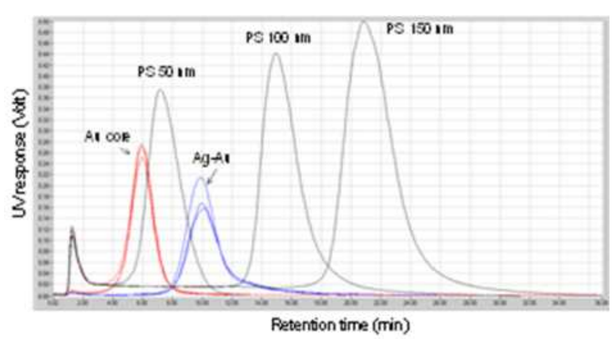

Figure 3: AsFlFFF analysis of the Silver-shelled Gold core , Gold core and three polystyrene latex bead standards

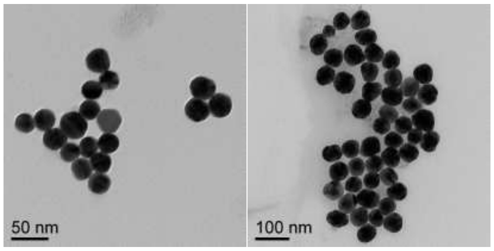

Figure 4 TEM images taken from Gold core (left) and Silver-shelled Gold core (right) samples.

Figure 4 shows representative TEM images of the Gold core and Silver-shelled Gold core bulk samples. About 150-200 nanoparticles were counted and average diameters of 30 nm and 56 nm were obtained for the Gold core and Silver-shelled Gold core respectively.

Several fractions were collected from the CFFF fractograms of the Silver-shelled Gold core and Gold core samples at 1000 rpm and 1750 rpm respectively and analyzed by sp-ICPMS to measure the core diameter of the Silver-shelled Gold core and Gold core samples. The measured values by sp-ICPMS were in a good agreement with those of TEM.

FFF-DLS appears to over-estimate the size of the nanoparticles by about 10 nm. It can be speculated that the nanoparticles are coated (5 nm thickness) with the surfactant molecules of the carrier FL-70 solution. The TEM and sp-ICPMS sizes are smaller because the coating film would not be detectable either by TEM or sp-ICPMS.

Silver-shelled Gold core and Gold core nanoparticles were assumed to be spheres and their volumes were calculated as 9.2×10^{-23} m^3 and 1.5×10^{-23} m^3 respectively, given the measured TEM diameters. The shell thickness and volume were calculated as 13 nm and 7.7×10^{-23} m^3 respectively using TEM measurements. Using equation 3, the masses of the Silver-shelled Gold core, Gold core nanoparticles and Silver shell were calculated as $8.8\times10^{-19} \pm 0.2\times10^{-19}$ kg, $2.0\times10^{-19} \pm 0.05\times10^{-19}$ kg and 6.2×10^{-19} kg respectively. The densities of the Silver-shelled Gold core, Gold core and shell were calculated as 9525 kg/m^3, 12792 kg/m^3 and 8865 kg/m^3 respectively using equation 4. The same methodology was used to verify the density of polystyrene latex nanoparticles.

The measured densities of core and shell are lower than the bulk densities for gold and silver (19300 and 10500 kg/m^3), suggesting that the hybrid nanoparticle has a porous core and shell structure.

5 CONCLUSION

A multi-technique methodology based on FFF, TEM and sp-ICPMS was developed to measure the mass, size and density of a shell-core (Silver-Gold) nanoparticle. The masses of the Gold core and shell-core nanoparticles were measured using CFFF and the shell mass was obtained from the difference. The overall size of the nanoparticle was obtained by direct measurement using TEM imaging. The size and mass of the core and mass of the shell were verified using sp-ICPMS. Combination of the information obtained from the CFFF, TEM and sp-ICPMS, allowed for the calculation of the nanoparticle density. The methodology was verified using standard latex samples. The measured densities of core and shell were lower than that of the bulk, suggesting porosities within the hybrid nanoparticle.

REFERENCES

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