Electrochemical Size Analysis of Gold Nanoclusters (Au-NCs) Isolated by Solvent Fractionation

Dilmi Waidyaratne[1], Francis P. Zamborini[1]

[1]*Department of Chemistry, University of Louisville, Louisville, Kentucky 40292, United States*

Abstract

Gold nanoclusters are particles smaller than about 2.5 nm with 500 or fewer atoms. This class of particles often shows size-dependent discrete electronic structure and molecule-like properties, making their properties tunable and potentially useful for many applications. Au-NCs comprise of a precise number of metal atoms (n) and stabilizing ligands (m) indicated as Au_nL_m. In recent years NCs have been synthesized in solutions using strongly bound capping agents, such as thiols for Au NCs with high purity. Examples of such clusters of molecular purity are $Au_{25}(SR)_{18}$, $Au_{38}(SR)_{24}$, $Au_{102}(SR)_{44}$, and $Au_{144}(SR)_{60}$. While it is possible to produce monodisperse atomically-precise NCs using thiol stabilizers, the very strong metal-thiolate interaction limits applications, especially in catalysis, and greatly hinders electrochemical size analysis by anodic stripping voltammetry (ASV). Phosphine and phosphonium-based stabilizers also produce Au-NCs, but the weaker interaction allows size analysis by ASV. We synthesized tetrakis(hydroxymethyl)phosphonium chloride (THPC)-stabilized Au NCs of 1.6 nm diameter but found that most of the time the product is a combination of 1.6 nm Au-NCs and 4 nm Au NPs. Solvent fractionation allows isolation of different-sized NPs from a disperse solution. Use of 1-propanol and ethanol mixed with water-soluble 1.6/4 nm THPC Au-NCs allowed selective precipitation of the 4 nm Au NCs, resulting in a more pure and uniform solution of 1.6 nm THPC Au-NCs. Fractionation, and attachment to indium tin oxide-functionalized glass electrodes allows the development of the optimum fractionation conditions by performing size analysis by ASV, which allows size determination based on the Au oxidation potential. This is much faster and cheaper than transmission electron microscopy or mass spectrometry. Our simple method of separation allows purification of THPC $Au_{1.6\ nm}$-NCs and concentration onto electrode surfaces for potential catalysis and sensing applications in the future.

Biography

Dilmi Waidyaratne is a 4th year graduate student in the chemistry department at the University of Louisville. She is currently working on electrochemical size-dependent studies of gold- nanoclusters and employing electrophoretic deposition to create highly porous gold-alginate films for potential catalytic activity.