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Research Seminar

When: November 13, 2023
Time: 3:00 p.m.
Location: CBLL-16

Electrochemistry of Nanoscale Gold: Size Analysis Following Solvent Purification and Charge Transport Through Dense Hybrid Hydorgel Films

Abstract:

Gold nanoclusters (Au NCs) are particles smaller than 2 nm in diameter with 500 or fewer atoms. They show size-dependent discrete electronic structure and molecule-like properties, making their properties tunable and potentially useful for many applications. Au-NCs comprise 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 with high purity using strongly bound capping agents, such as thiols (SR). Examples include $Au_{25}(SR)_{18}$, $Au_{36}(SR)_{23}$, $Au_{38}(SR)_{24}$, $Au_{102}(SR)_{44}$, 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 prevents 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 the product is a combination of 1.6 nm Au-NCs and ~4 nm Au NPs. Solvent fractionation allows isolation of the smaller fraction, leading to purified 1.6 nm Au NCs. Mixing methanol, ethanol, or propanol with water-soluble 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. It is important to find optimal conditions that allow a high coverage of pure 1.6 nm Au NCs attached to electrode surfaces for potential applications. The optimal volume of alcohol, separation time, and use of centrifugation or not depended on the type of alcohol. Typically, optimized conditions included a 3:7 or 4:6 Au NCs:alcohol ratio, separation time of 1 hour or more, and electrode soaking time of greater than 30 minutes. Solvent fractionation and attachment to indium tin oxide-functionalized glass (glass/ITO) electrodes allows for determining the size analysis by ASV based on the Au oxidation potential, which is much simpler, cheaper, and faster than transmission electron microscopy (TEM) or mass spectrometry for size analysis. Our simple method of purification of 1.6 nm diameter THPC Au NCs and attachment onto electrodes opens the door for numerous fundamental studies of these unique materials and potential applications in the future in catalysis and sensing.

_______The co-deposition of 15 nm diameter citrate (cit)-stabilized Au nanoparticles (NPs) and sodium alginate (Alg) onto an electrode surface by electrophoretic deposition (EPD) followed by exposure to Ca^{2+} leads to thick (mm level) hydrogel-Au NP hybrid films. The EPD occurs on glass/ITO electrodes by Au NP-catalyzed oxidation of hydroquinone (HQ), which leads to a pH drop at the electrode/electrolyte interface, triggering film formation via charge neutralization of the cit-Au NPs and Alg. UV-visible spectroscopy provides information about the thick Ca-Alg-AuNP hydrogel films by monitoring the localized surface plasmon resonance (LSPR) band for the Au NPs at ~530 nm. In contrast, cit-Au NPs deposited without Alg shows a broad absorption from 300 nm – 600 nm, indicating the formation of a more aggregated metallic Au film on the electrode surface. Porous Au films (or aerogels) form upon connecting the Au NPs within the hydrogel film by electrodeposition of Au and removal of Ca-Alg with chelating agents, such as EDTA. The Alg/Au ratio controls the porosity and conductivity of these films. The electrochemical properties of Ca-Alg-AuNP hydrogel films and Au aerogel films with various redox probes provides information about electroactive surface area, charge transfer, mass transport, and ion transport within these materials. The Ca-Alg-AuNP hydrogel films could be electroactive without the use of additional supporting electrolyte solution due to the presence of Ca-Alg hydrogel, which provides a medium for charge transfer and ion transport. These unique materials may find use in energy storage or electrochemical sensing devices.

References:

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