Chiral gold nanoparticles

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Introduction

Gold Monolayer Protected Nanoparticles (MPNs) are of considerable interest in various fields such as bio-sensing, catalysis, electronics and nanotechnology. We prepared and size separated small gold MPNs protected with chiral thiols, such as N-acetyl-L-cysteine, N-phenylacetylcysteine or N-isobutyryl-D-cysteine. The physical properties of these MPNs are largely determined by their metal core, whereas their chemical properties depend on the protection layer. These particles were characterized by Vibrational and Electronic Circular Dichroism (VCD and ECD). Density Functional theory (DFT) calculations of N-acetyl-L-cysteine adsorbed on gold clusters were used to simulate VCD spectra in order to determine the conformation of the adsorbed thiol. ECD spectra reveal optical activity in transitions located in the metal core, indicating that the latter is intrinsically chiral.

Preparation of gold MPNs

MPNs are prepared by the conventional chemical route based on nucleation of zerovalent metal atoms in the presence of thiol. Such a method inevitably produces a distribution in the core sizes due to statistical fluctuations in the nucleation process (see Transmission Electron Microscopy on right).

Comparison between calculated and experimental VCD

These MPNs exhibited vibrational circular dichroism activity in vibrations associate with the adsorbed NALC. DFT calculations of the most stable conformers of NALC adsorbed on gold clusters were used to simulate VCD spectra. These calculations revealed a strong dependence of the VCD spectra on the conformation of the adsorbed thiol, whereas the structure of the underlying gold cluster was less important.

The calculated VCD spectrum of the most stable conformer (green) compared well with the experimental spectrum (black). This structure is characterized by an interaction of the carboxylate group with the metal, which represents a second anchoring point besides the strong sulfur-gold bond. This structure is further favored at high coverage, as it uses only little surface space and allows dense packing. The latter property increases the MPNs stability.

SDS-PAGE electrophoresis

Isolation of MPNs with well-defined sizes was achieved by sodium dodecyl sulfate-polyacrylamide gel electrophoresis (SDS-PAGE). Such separations reveal a non-uniform size-distribution with a high abundance of certain particle sizes (magic numbers). A photograph of a typical gel separation is shown (on right).

Experimental ECD

Chirality is often associated with organic molecules, inorganic salts and biological materials. However, chirality can also be bestowed to metal surfaces. The latter can be intrinsically chiral or become chiral through adsorption of chiral molecules. MPNs can be viewed as the nanometer-size analogues of extended metal surfaces. Optical activity in circular dichroism of MPNs are associated with transitions located in the metal core indicating that the latter is chiral.

Conclusions and Perspectives

MPNs can be viewed as the nanometer-size analogues of self-assembled monolayers (SAMs). Our results indicate that VCD spectroscopy may greatly help elucidating the structure of chiral molecules adsorbed on metal particles and that ECD should help in the same way to understand surface chirality.

References:


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