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Gold Nanoparticles with Different Capping Systems: An Electronic and Structural XAS Analysis

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Gold nanoparticles (NPs) have been prepared with three different capping systems: a tetralkylammonium salt, an alkanethiol, and a thiol-derivatized neoglycoconjugate. Also gold NPs supported on a porous TiO₂ substrate have been investigated. X-ray absorption spectroscopy (XAS) has been used to determine the electronic behavior of the different capped/supported systems regarding the electron/hole density of d states. Surface and size effects, as well as the role of the microstructure, have been also studied through an exhaustive analysis of the EXAFS (extended X-ray absorption fine structure) data. Very small gold NPs functionalized with thiol-derivatized molecules show an increase in d-hole density at the gold site due to Au-S charge transfer. This effect is overcoming size effects (which lead to a slightly increase of the d-electron density) for high S:Au atomic ratios and core-shell microstructures where an atomically abrupt Au-S interface likely does not exist. It has been also shown that thiol functionalization of very small gold NPs is introducing a strong distortion as compared to fcc order. To the contrary, electron transfer from reduced support oxides to gold NPs can produce a higher increase in d-electron density at the gold site, as compared to naked gold clusters.

Room temperature permanent magnetism in thiol-capped Pd-rich nanoparticles

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Abstract

We report on the permanent magnetism exhibited by 1 nm sized thiol-capped palladium nanoparticles, up to temperatures above 300 K. The hysteresis loop does not change appreciably between 5 and 300 K. The local magnetic anisotropy constant was found to be stronger than 2 meV per Pd atom. The localized character of electrons and holes of the 4d residual band, revealed through the structureless plasmon resonance curve, suggests that the origin of the permanent magnetism is associated with localized magnetic moments.

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Magnetic and microstructural analysis of palladium nanoparticles with different capping systems

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Palladium nanoparticles capped with different protective systems in a size range between 1.2 and 2.4 nm have been obtained by varying the preparation chemical method. Magnetization curves for all the samples show hysteresis loops, evidencing a ferromagnetic or a permanent magnetism in the nanoparticles. The microstructure of the nanoparticles has been analyzed by x-ray absorption and transmission electron microscopy. The nature of the magnetic behavior found for all these Pd nanoparticles (NPs) is different depending on their sizes and structural features and is explained on the basis of two different suggested mechanisms. The particles protected by means of a surfactant (tetralkylammonium salts) present a ferromagnetic order related to the factors increasing the density of states just below the Fermi level. Whereas, when the nanoparticles are stabilized by covalent bonds with protective species (thiol derivatized alkane chains or surface oxidized Pd NPs), the increase of the 4d density of holes, localized by the bonded atoms (S or O), is giving rise to the observed ferromagneticlike behavior.

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