A FIRST PRINCIPLES STUDY OF THIOL-CAPPED Au NANOPARTICLES

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I. Introduction

Nanoparticles (NPs) have become a subject of major research due to their new optical, electronic and/or magnetic properties which may be controlled by varying the NP size or shape. Functionalizing these NPs with adequate organic capping layers further provides chemical specificity to the clusters, thus becoming highly interesting for biological applications (e.g. drug delivery within the body). In particular, gold NPs have received great attention because bulk gold is inert and, most surprisingly, several experiments recently reported on the ferromagnetic nature of these Au Nps [1,2]. There exist, however, conflicting results regarding the conditions required for achieving such magnetic clusters; whereas the first experiments required sulfur based capping ligands (alkane-thiols), subsequent theoretical and experimental works point to the existence of a permanent magnetism in bare gold clusters [3]. In this work, we address precisely the role that an alkane-thiol capping layer plays on the structural, electronic and magnetic properties of Au NPs by means of *ab initio* Density Functional Theory (DFT) based calculations.

II. Theoretical

We have modeled Au clusters of different sizes ranging from just 1 up to 38 gold atoms. The largest cluster considered, Au_{38}, has an octahedral shape preserving the bulk fcc arrangement. We considered short alkane-thiols of just two C atoms ($S-C_2H_5$) and systematically varied the thiol coverage for each of the Au clusters. The highest coverage considered here were 24 thiols, which amounts to a 3:4 ratio between the number of gold surface atoms (32 in the bare cluster) and the number of thiols. Starting from different initial trial configurations comprising adsorption at bridge sites, "staple" motifs [4], and ...-S-Au-S-Au... chain like structures, we explored their stability via Molecular Dynamics (MD) runs.

All calculations have been performed with the DFT based SIESTA code [5] under the Local Density Approximation (LDA). The electronic and magnetic properties of the clusters were studied by inspection of the Mulliken charges, the atom projected Density of States (PDOS) together with any net magnetic moments after Local Spin Density (LSD) calculations.

III. Results

Atomic Structure

Our calculations confirmed the ability of the Au NPs to adsorb a large number of thiols. Figure 1 shows several relaxed structures for the Au_{38} cluster and for different thiol coverages. In general, the relaxed geometries contain mixtures of the three adsorption models considered, making it difficult to extract a unique and simple picture for the structure of thiol capped NPs. As the coverage is increased, the reconstruction of the gold NP becomes more prominent. Indeed, we have often found that the stability of the cluster may strongly depend on the level of restructuring that takes place for the Au core atoms.

Electronic Structure

Figure 2 shows the evolution of the DOS for the Au_{38} cluster and for different thiol coverages. We include the projections on the gold and sulfur atoms as well as on the organic ligands (C_3H_5). As the coverage increases, the peaks are smeared and bands are formed implying that electrons become delocalized. The evolution of the Mulliken charges reveals that in the absence of thiols, there is a charge transfer from the core region to the surface atoms, thus leaving the inner (outer) regions in the NP positively (negatively) charged. The addition of thiols, however, cancels this charge transfer so that the core region becomes progressively neutral while the surface atoms reverse their net charge (see figure 3).

Magnetic properties

We have not found any evidence for ferromagnetism in any of the large clusters studied; the spin polarization vanished in all cases. Even for clusters with an odd number of electrons, the exchange split was of just a few meV and hence, the spin polarization became negligible after using a finite temperature in the Fermi occupation function. Whereas the Au_{38} cluster showed a slight paramagnetic behavior [6], thiol adsorption tends to remove any peaks close to the Fermi level thus reducing the number of d-holes. From

these results, it is clear that thiol capping does not help the development of any spin polarization in the cluster.

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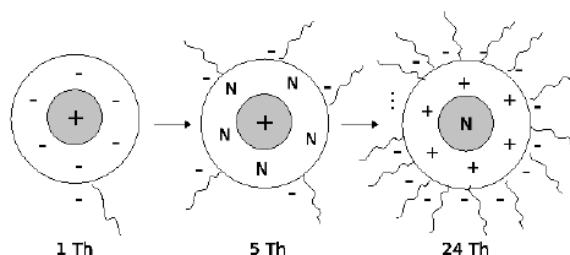[6] R. J. Magyar *et al* Phys. Rev. B **75** 144421 (2007)

Figures:
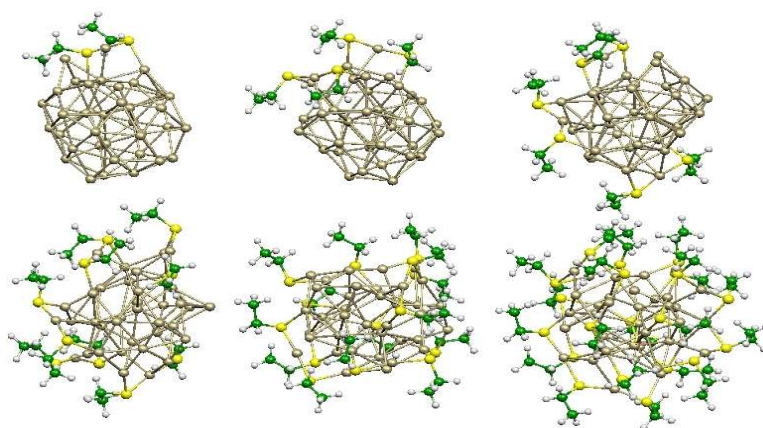
Fig. 1. Sketch of the relaxed Au_{38} clusters for different thiol coverages: 2, 4, 6, 10, 14 and 20.
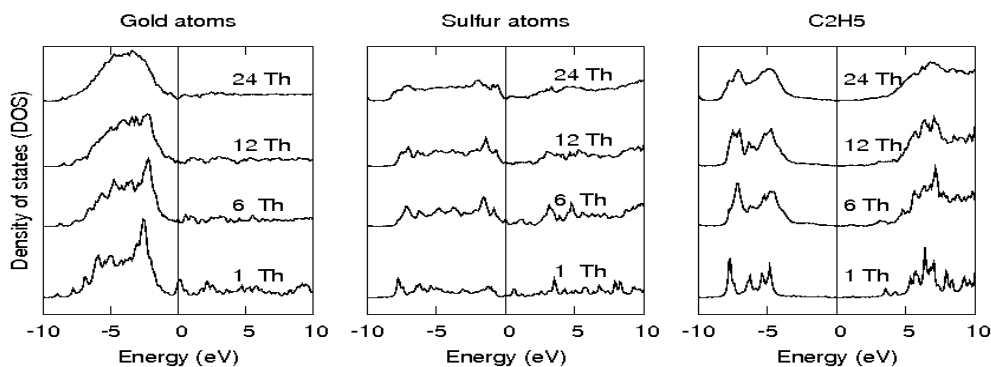
Fig. 2 PDOS corresponding to the Au_{38} cluster covered by 1, 6, 12 and 24 thiols. Left, middle and right panels correspond to the projections on the gold atoms, sulfur atoms and thiols, respectively.

Fig. 3 Sketch of the charge distribution for NPs with 1, 5 and 24 thiols. Each NPs is split into three regions: core, surface and alkane-thiols. At nth = 1 (left) core atoms are positively charge and the surface is negatively charged. For nth = 5 (middle), the surface becomes neutral while core atoms still hold some positive charge. Finally, for nth = 24 (right), all the charge transfer occurs from the surface to the thiols.