Do Thiols Merely Passivate Gold Nanoclusters?

Recently, Häkkinen, Barnett, and Landman (HBL) [1] investigated the properties of a thiol-passivated gold cluster, using density functional theory (DFT). They considered a truncated-octahedral face-centered-cubic (TO-fcc) structure for the Au_{38} cluster, coated with a monolayer of 24 methylthiol (SCH_3) molecules. After a structural relaxation, they found: (i) that the octahedral symmetry persisted in the relaxed structure; (ii) small inward and outward relaxations of the different gold atoms; (iii) a charge transfer of $2e$ at the well-defined gold-thiol interface.

Here, we point out that the thiol monolayer has a much stronger effect than that reported by HBL [1]. We have used DFT, scalar-relativistic norm-conserving pseudopotentials, and a double-ζ basis set of numerical atomic orbitals [2]. Other details are similar to those used in our studies of bare gold clusters [3,4]. We have performed conjugate-gradient relaxations starting from different cluster-monolayer configurations. These include the one proposed by HBL and the same configuration with random atomic displacements to break the symmetry. Unless the octahedral symmetry is assumed, we invariably find a dramatic distortion (relaxed coordinates are available upon request). The final, stable structure is ≈ 4 eV lower in energy than that of the TO-fcc geometry. This energy difference has been reproduced using an independent, standard plane-wave (PW) pseudopotential code [5] and the same pseudopotential parameters and PW cutoff as HBL. In the relaxed structure, the inner cuboctahedron deforms into a disordered cluster core (a central atom surrounded by 15 atoms) made of distorted pentagonal bipyramid subunits. The ill-defined gold-thiol interface is formed by the remaining 22 gold atoms sitting at irregular
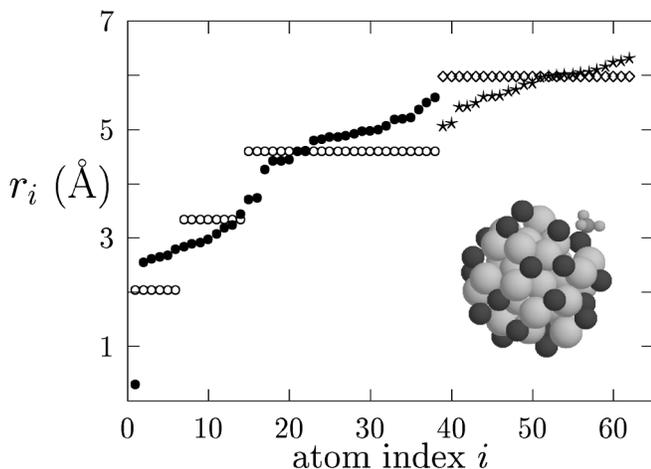
positions, and by the sulfur atoms of the thiol heads incorporated into the cluster surface. Figure 1 shows the clearly separated gold and sulfur atomic shells of the TO-fcc structure proposed by HBL and their distortion and overlap in our disordered configuration. Different patterns of charge transfer occur in this disordered, alloyed cluster surface, in contrast with the uniform charge transfer at the well-defined interface found by HBL [1].

Although the physicochemical details of the gold-thiol interaction in nanoparticle-size systems remain to be investigated, the existence of stable disordered gold nanoclusters is not unexpected. Evidence from several theoretical studies [3,4,6–8] (consistent with experiments, see Refs. [7,8]) shows that the lowest-energy structures of bare Au_{38}, Au_{55}, and Au_{75} nanoclusters are disordered.

In conclusion, we find that a methylthiol monolayer produces a dramatically distorted Au_{38} nanocluster with a disordered Au-S alloy interface. This is in sharp contrast to the claim of HBL [1], that its effect reduces to a radial relaxation of the TO-fcc geometry. We assign this discrepancy to an insufficient sampling of configuration space by HBL.

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FIG. 1. Distances of the gold ($i = 1-38$) and sulfur ($i = 39-62$) atoms from the cluster center of mass for the $Au_{38}(SCH_3)_{24}$ nanocluster in the disordered (closed circles and stars) and TO-fcc (open circles and diamonds) structures. The inset shows the relaxed disordered structure. Sulfur atoms are depicted as darker spheres and only one CH_3 group is shown.

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