SELECTIVE SYNTHESIS OF SMALL GOLD CLUSTERS WITH ODD OR EVEN SIZES

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Gold clusters are highly interesting for their unique physical and chemical properties, having attractive applications as highly selective nanocatalysts, active sites in chemical sensors, etc... Their properties vary strongly atom-by-atom, and even- or odd-numbered clusters have qualitatively different features due to the change in the number of valence electrons. However, for practical applications it is necessary to develop new production techniques beyond the standard mass-selection techniques which provide too low yields. In a recent work, we have reported the synthesis in solution (with a procedure based in the two-phase method) of small gold clusters (Au_N, with $2 \leq N \leq 18$) in large quantities, selecting only the odd-numbered ones [1] (see Fig. 1a). We now report an easy procedure of selecting the parity of the clusters produced, by a change in the type of capping agent during the solution synthesis, which results in preferential formation of even-numbered clusters (see Fig. 1b). In parallel to the experiments, we have also performed DFT simulations of the stability, charge state and mutual interaction of small gold clusters. The simulations show that the qualitatively different cluster-counterion interaction leads to different cluster charge states during growth, which linked to the intrinsic differences between odd- and even-numbered clusters results in selective production of a given cluster parity (see Fig. 1c). Also, we find different growth mechanisms, atom-by-atom in the cationic case, and by coalescence in the neutral case (see Fig. 1d). The simplicity of the synthesis procedure and the ability to easily control a key cluster feature as the open-shell character (which has a direct relationship to the cluster reactivity), opens new possibilities for the mass production of these clusters and their extensive use in novel industrial applications.
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References:

[1] M. J. Rodríguez-Vázquez, C. Vázquez-Vázquez, J. Rivas and M. A. López-Quintela, *Eur. Phys. J. D*, 52 (2009) 23.

Figure 1: a) M*ass spectra (positive ions) of gold clusters synthesized by the two-phase method at increasing amounts of reducing agent. b) The same spectra using a different type of capping agent. c) Growth energies for neutral, cationic and bromine-capped gold clusters. Growth energies for capture of Au+ cations are also shown (solid squares). d) Interaction energy (with respect to separate fragments) as a function of mutual cluster distance for the coalescence process of* Au_5, Au_5^+ *and* $BrAu_5$ *clusters.*