SYNTHESIS AND CHARACTERIZATION OF MULTIPODAND CALIX[4]ARENE-PROTECTED GOLD NANOPARTICLES

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Monolayer-protected Au clusters^[1] (MPCs) have aroused significant scientific interest because these structures are known to be useful in many fields such as optoelectronics, catalysis and molecular sensing.^[2] Small MPCs (core < 2 nm) are particularly enticing owing to their quantum size effects.^[3] Indeed, it is known that as the core size decreases under the nanometer limit, the particles attain discrete electronic states and thus can show semiconductor-like electronic properties. The preparation of these compounds through direct methods has been, however, restricted to nanoparticles in which the gold passivation has been obtained with specific ligands such as tripeptides (glutathione), mercaptosuccinic acid and thiphenylphosphine derivatives.

Despite the large amount of data present in the literature on the synthesis of MPCs prepared with several thiol-based ligands, using the two phase method developed by Brust,^[4] the role played by the ligand "sulphur denticity" on the gold clusters size has not been yet systematically studied.

In this context we have recently explored the possibility to use multidentate calix[n]arene derivative **1** (see Figure 1), characterized by the presence of two convergent undecanthiol chains onto its lower rim, for the preparation of Au MPCs. The particular multidentate structure of the calixarene derivatives allows the preparation of rather monodispersed and size controlled clusters as shown by TEM measurements (see Figure 2). In particular, when the calixarene is used in excess with respect the aurate salt $AuCl_4^-$, clusters with very smaller core were obtained. These new MPCs were compared with gold nanoparticles stabilized by monodentated ligand **2** and dodecanthiol. The MPCs synthesized were also characterized with XPS to analyze the oxidation state of gold in the inorganic core. These results open new possibilities for the synthesis of MPCs with controlled and reduced size to be employed in the emerging field of the nanotechnology.

References:

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Figures:

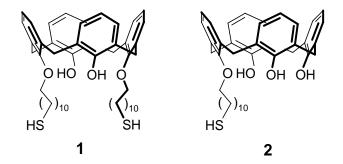


Figure 1. Polyalkylthiols lower rim functionalized calixarene derivatives for the preparation of Au MPCs.

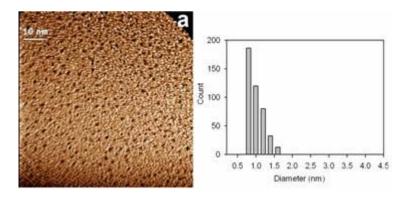


Figure 2. TEM image and core size distribution diagram of MPCs coated with calix[4]arene 1.