Consequences of molecular functionalization on the work-function and the optical properties of gold nanoparticles

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Gold nanoparticles are well-known for their particular optical properties due to the plasmon absorption in the visible. These plasmonic properties are closely related to the electronic properties of the particles: not only the electron density inside the particle but its entire electronic environment. In order to examine the electronic properties of a particle in a system, the work-function could be studied. The work-function is defined as the energy needed to extract an electron from the Fermi level to the vacuum. When this property is scaled down from bulk to nano-objects, many electrostatic effects can play a role: nanometer size, substrate effect or molecular environment. Zhang et al. have evidenced with Kelvin Probe Force Microscope (KPFM) measurements the size dependence of the change in work-function for spherical gold nanoparticles (AuNPs) grafted on silicon and they have explained it by charge transfers from the substrate. Starting from this point we show now how the work-function of spherical AuNPs can be tuned by a molecular functionalization and what is the effect of the particle size.

First, in order to minimize charge transfer from the surface, AuNPs are grafted on a gold substrate by a self-assembled monolayer (SAM) of di-thiol. Although the formation of SAMs on gold is well-known some experimental conditions remain controversial. We have evidenced that in liquid phase deposition, kinetics is critical. Rather quickly, free thiols endgroups tend to form disulfide (S-S) bonds which cannot attach AuNPs. Therefore we found how to obtain an efficient AuNPs grafting on gold.

Then we have measured work-function modifications of the functionalized gold nanoparticles with KPFM (see the figure below). The AuNPs functionalization is achieved with molecules having a thiol (HS-) head group molecules and two possible tails, -COOH or -NH2. Our KPFM measurements results show an evolution of work-function as a function of the AuNPs diameter and two different behaviors for the two tails. Density Functional Theory (DFT) calculations were carried out in order to calculate the work-function of these systems and support our KPFM measurements.

Figure 1.: KPFM measurements of gold nanoparticles grafted on gold and functionalized with 16-mercaptohexadecanoic acid: a) topography and b) relative work-function.

References

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