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Effect of nanoscale size and medium on metal work function in oleylamine-capped gold nanocrystals

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ABSTRACT

The work function is an important material property with several applications in photonics and optoelectronics. We aimed to characterize the work function of clusters resulting from gold nanocrystals capped with oleylamine surfactant and drop-casted onto gold substrate. We used scanning Kelvin probe microscopy to investigate the work function, and complemented our study mainly with X-ray diffraction and X-ray photoelectron spectroscopy. The oleylamine works as an electron blocking layer through which the electrical conduction takes place by tunneling effect. The surface potential appears to depend on the size of the clusters, which can be ascribed to their difference in effective work function with the substrate. The charge state of gold clusters is discussed in comparison with theory, and their capacitance is calculated from a semi-analytical equation. The results suggest that at the nanoscale the work function is not an intrinsic property of a material but rather depends on the size and morphology of the clusters, including also effects of the surrounding materials.

1. Introduction

On the bulk material scale there exist concepts in physics and chemistry which are well established and traditionally associated with intrinsic properties of a given substance. However, since the early times of emerging nanotechnology back in the 90's [1], the scientific community had to progressively undergo a paradigm-shift and realize that nanoscale matter behaves differently. When the surface-to-volume ratio of particulate material increases with decreasing size of the nanoparticles, the surface effects become dominant and affect several material properties. This gives rise to useful applications of nanoparticles, for example in catalysis [2] and wetting [3] as well as in plasmonics [4] and electro-optical devices such as organic LEDs [5] and solar cells [6], due to the resulting modification of electronic bands of atoms. These effects, which can be correctly interpreted in the frame of quantum physics, could not be directly observed until approximately 30 years ago, due to the lack of appropriate techniques. In this respect, the introduction of scanning tunneling microscopy and especially atomic force microscopy has represented a big step towards modern nanoscience [7]. Scanning Kelvin probe microscopy (SKPM) [8,9] is a technique based on atomic force microscopy for the direct measurement of the local electrical potential emerging on the surface of sample at the nanometer scale. SKPM has been widely used to characterize biomolecular [10], organic [11] and semiconductor [12,13] materials. The measured quantity, namely the electrical surface potential, may arise on the sample due to electrostatic charging or to chemical potential differences between inhomogeneous chemical phases. In the physics of metals this is described by the concept of work function. Therefore, in the absence of electric charging due to previous contact with different materials, the measurement of surface potential can be converted into a mapping of local work function of the sample surface [14].

Several former works focused on the origin of the dependency of nanoparticles work function on the environment [12,15,16]. In gold nanoparticles the environment can affect the work function, which some researchers thought to be a consequence of electrostatic charging in the confined nano-particles volume, among other reasons [17]. In this work we addressed this issue by investigating oleylamine-capped gold nanocrystals (AuNCs) deposited onto a gold substrate by means of self-assembly. The oleylamine dielectric layer defined the Coulomb field at the interfaces among AuNCs and between them and the substrate. The work function of the stacked system, depending on the condition of AuNCs clustering, has been measured. The charge state of the gold clusters has also been extracted and compared with the theory.

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Throughout this manuscript the term cluster is used to refer to a group of primary particles, the AuNCs, which are packed together but not merged into one particle (i.e. non-aggregated). The effect of clustering appears to affect the observed phenomenon, due to the collective behavior of these primary nanoparticles. On the contrary, the term aggregate is used to indicate the increase in size of the AuNCs as a result of merging of pristine primary AuNCs into bigger ones.

2. Experimental

2.1. Gold nanocrystal synthesis

Oleylamine–capped AuNCs were synthesized using 35 mg of $AuCl_3$ dissolved in 10 mL of toluene together with 92 mg of dodecyldimethylammonium bromide. 40 μL of 9.4 M sodium borohydride aqueous solution was added drop-wise to this solution under vigorous stirring. The solution turned dark purple in a few minutes, and was still kept under vigorous stirring up to a total of 20 min. 1 mL of oleylamine was then injected and the solution was left stirring for additional 5 min. The resulting particulate was washed with ethanol and toluene, then re-dispersed in toluene, and finally the larger and unstable reaction products were precipitated out by centrifugation. Finally the supernatant was carefully collected, which constituted the AuNCs passivated with oleylamine.

2.2. Samples preparation

Several characterization techniques required the primary AuNCs and the resulting clusters to be in a dry state. For transmission electron microscopy (TEM) measurements the colloidal solution of oleylamine-capped AuNCs was dropped onto carbon coated 150 mesh copper grids CF-150-Cu50 (Electron Microscopy Sciences, USA) and let to dry in ambient air.

Different measurement techniques required the nanoparticles to be deposited onto compact supporting substrates. The substrates of choice for the SKPM measurements were $\sim 1\times 1\ \text{cm}^2$ pieces of 250 nm thick gold coated onto glass (Arrandee, Germany), which were used as received. For characterizations by means of X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM), we used as the substrates similarly sized pieces of a Si wafer, preliminarily washed with toluene and dried with Nitrogen. All the above samples were prepared by drop-casting 100 μL of the AuNCs solution, and letting the wet substrates to dry in a low-vacuum bell (with air extracted by a rotary pump Alcatel 2005SD, USA) for ~30 min. In some cases, before characterization the samples were annealed in vacuum ($\sim 10^{-3}$ mbar) at 280 °C for 30 min.

2.3. Characterization techniques

The colloidal solution resulting from the synthesis was diluted 1 to 20 in the same solvent (Toluene) and analyzed by means of a dynamic light scattering (DLS) system Zetasizer Nano ZS (Malvern Instruments, UK).

Spectra of absorbance and photoluminescence (PL) of the colloidal solution were acquired by means of an UV–vis spectrophotometer Cary 5000 (Agilent, USA) and a spectrofluorometer Fluoromax (Horiba Jobin Yvon, USA), respectively.

The particulate in the colloidal solution was also analyzed by means of TEM, using a JEOL JEM-1011 (Jeol, Tokyo, Japan) equipped with a thermionic electron source (tungsten filament) working at 100 kV.

High-resolution SEM imaging of gold clusters was carried out using a JEOL JSM 7500FA (Jeol, Tokyo, Japan). The SEM was equipped with a cold field emission gun source, operating at 15 kV acceleration voltage and using a backscattered electrons detector to obtain compositional contrast. The samples were preliminarily carbon-coated with a 10 nm thick film using an Emitech K950X high vacuum turbo system (Quorum Technologies Ltd, UK).

The surface chemistry of the AuNCs clusters was investigated by means of XPS, using a Specs Lab2 instrument (SPECS, Germany) equipped with a monochromatic X-ray source (set at 1253 eV) and with a Phoibos hemispherical energy analyzer has 3500. The applied voltage of the Mg K-alpha X-ray source was 10 kV and the applied current was 15 mA. The pressure in the analysis chamber was approximately 2×10^{-9} mbar. The large area lens mode was used for both wide and narrow scans. For the wide scan, the energy pass was 90 eV, the energy step was 0.5 eV, and the scan number was 2. For the narrow high-resolution scan, the energy pass was 30 eV, the energy step was 0.1 eV, and the scan number was 20. A flood gun was used to neutralize the surface charge, with an energy of 7 eV and a filament current of 2.6 A.

The crystalline phase of the clusters was investigated by XRD, using a SmartLab X-Ray diffractometer (Rigaku, Japan), equipped with a 9 kW Cu Kα ($\lambda = 1.542$ Å) rotating anode, operating at 40 kV and 150 mA. A Göbel mirror was used to convert the divergent X-ray beam into a parallel beam and to suppress the Cu Kβ radiation ($\lambda = 1.392$ Å). The diffraction patterns were collected at room temperature and over an angular range of 5° to 60°, with a step size of 0.05° and scan speed of 2°/min. An analysis of crystallite size and strain was carried out using the fundamental parameter method implemented in PDXL 2.1 software program from Rigaku.

The SKPM measurements were carried out with an MFP-3D AFM (Asylum Research, USA). We used Electrilevers AC240TM probes (Olympus, Japan). The cantilevers had typical spring constant and resonance frequency of -2 N/m and 70 kHz, respectively. The tips had nominal length and core diameter of 14 μm and 60 nm, respectively, and were coated with a 30 nm layer of Pt/Ir to provide electrical contact. The measurement was based on so-called two-pass mode: during the first pass, the cantilever was mechanically driven at its first resonance in air by means of a dither piezo pad, in order to track the surface topography. For each scan line, before moving on to the next line a second pass was carried out, called 'Nap' pass, making the tip fly over the sample surface at a constant elevation height, ΔH. During this second (Nap) pass the cantilever was driven at the same resonance frequency but by electrical means (applied AC voltage, V_{ac}). Simultaneously, the tip was also biased with a DC voltage V_{dc}. The sample was set to ground ($V=0$). The total electrical force acting on the tip was thus:

$$F(\omega) = \frac{\partial C}{\partial Z}\left(V_{sp} + V_{dc}\right)V_{ac}\sin(\omega t) \tag{1}$$

where V_{sp} was the contact potential difference appearing between the tip and the sample, called surface potential, and C was the capacitance between the same plates. The feedback acted on V_{dc} such as to cancel the electrical force F, in such a way that the required voltage to achieve this goal was $V_{dc} = -V_{sp}$.

3. Results

Fig. 1 shows the results describing direct characterization of the primary nanoparticles in the starting solution. In Fig. 1a a TEM image of the solution dried on a supporting grid is shown. The particles appear to be spherical and quite monodisperse in size, with typical diameter of ~5 nm. The DLS performed on the original