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Thiol-modified gold nanoparticles deposited on silica support using dip coating

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ABSTRACT

In our work, we have prepared thin layers of gold nanoparticles deposited via dip coating technique on silica glass substrate. The prepared thin layers were modified by two different ligands, namely 1,4-dithiothreitol (sample Au-DTT NPs) and L-glutathione (sample Au-GSH NPs). The spectral, structural and magnetic properties of the prepared samples were investigated. The modification of Au nanoparticles with thiol ligands leads to change of their plasmon resonance fields, as indicated by UV–vis spectra. The magnetic measurements showed that the magnetization of the samples is composed from two magnetic contributions: diamagnetic contribution and low field ferromagnetic contribution. Our experimental results show that the charge transfer between Au and S atoms gives rise to the ferromagnetic behaviour of prepared thin layers.

1. Introduction

Transition metal nanoparticles are intensively studied systems due to their novel electronic, optical and magnetic properties. These nanostructured systems play an important role in many different fields of science such as chemical catalysis, nanoelectronics, biology and recently in biomedical applications, for instance, in the labelling of cells with nanoparticles [1]. Particularly, the magnetic properties of clusters of elements of the eleventh group of the periodic table (especially gold), which are non-magnetic as bulk materials, have attracted much of attention [2–4]. Size reduction of bulk gold down to the nanometer-scale gives rise to novel electronic, optical, and catalytic properties due to size and surface effects [5,6]. Gold has been the target of many investigations either as thin films with or without an organic layer on the top [7,8], or as nanometric particles with or without capping molecules [9,10]. The high affinity of sulphur for the gold allows modifying the nanoparticles with various thiolate functionalities and thus tailoring the surface properties of the nanoparticles. For example self-assembled monolayers of alkanethiols and dialkanethiols on gold are key elements for building many systems and devices with applications in the field of nanotechnology [11]. An example of novel properties resulting from such size reduction is the ferromagnetism in thiol-passivated gold films and gold nanoparticles in opposite to diamagnetism of the bulk gold. Since the first discovery of ferromagnetism at Au—S interfaces, the occurrence of ferromagnetism even at room temperature has been reported in a number of papers [10,12–14]. However, despite of all the efforts in this field, the permanent magnetism shown by these systems is not yet fully understood [4,15,16].

In the present paper we have studied the effect of the organic capping layer created by 1,4-dithiothreitol and L-glutathione (see Scheme 1) on magnetic properties of gold nanoparticles deposited on glass substrate. According to our best knowledge, the magnetic properties of gold nanoparticles modified by these thiols were not studied up till now. Recently the effect of these thiols on biological activity of Au nanoparticles has been studied. Martínez et al. [17] studied inactivation of purified phenylalanine hydroxylase by dithiothreitol. Stobiecka et al. [18] studied the interactions of a biomolecule glutathione with citrate-capped gold nanoparticles (Au NPs). The work of Antosova et al. [19] described anti-amyloidogenic activity of glutathione-covered gold nanoparticles. Moreover, glutathione-mediated drug release from Tiopronin-conjugated gold nanoparticles for acute liver injury therapy studied by Bao et al. [20]. In the present study Au nanoparticle thin layers, modified by 1,4-dithiothreitol (DTT) and L-glutathione

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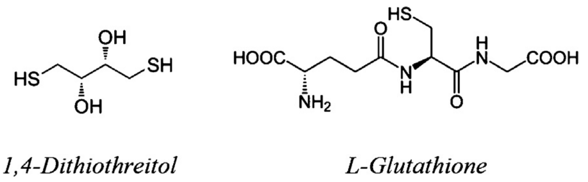

Scheme 1.

(GSH) are investigated by UV–vis spectroscopy, AFM, TEM and XPS measurements and by SQUID magnetometry.

2. Experimental part

2.1. Materials

All chemicals were purchased from Sigma–Aldrich and used as received without further purification. The use of clean glassware is critically important for the successful synthesis of gold nanoparticles, therefore all used glassware followed a rigorous cleaning procedure, which involved: the cleaning of the glass slides by sonication in soap for 15 min, flooding and sonication of slides with distilled water for at least 10 min, followed by sonication in acetone for another 10 min.

2.2. Preparation of gold colloid

Gold colloids were prepared by adding 2 mL of the 5 mM solution of $AuCl_3$ to 100 mL of deionized water followed by heating to boiling. Then 3 mL of 25 mM trisodium citrate solution was added [9]. After an hour the gold colloid with a bright red colour was obtained.

2.3. Deposition of gold nanoparticles

To improve the adhesion of gold nanoparticles on glass, the substrates were functionalized with aminopropyl-trimethoxysilane (APTS). The glass slides were immersed in a mixture of 3 mL APTS in 10 mL of 95% methanol for 24 h and then they were rinsed with distilled water and dried. This silanization process was found necessary to obtain a consistently high deposition.

Gold nanoparticles were deposited on the glass support using dip coating technique using WPTL5-0.01 programmable dip coater. Glass substrates were dipped into the colloidal solution at rate of 5 mm/min. The process was repeated 3 times. The prepared samples were dried at laboratory temperature.

2.4. Preparation of thiol modified thin layers

The prepared thin layers of gold nanoparticles were immersed into 10^{-2} M solution of 1,4-dithiothreitol for 2 h to form Au—S bonds and subsequently washed by water and air dried. The same procedure has been followed by a modification by L-glutathione. After the modification the colour of the samples changed from red colour of the non-modified Au sample to purple-grey colour for Au-GSH modified NPs layers and to blue-green for Au-DTT for modified NPs layers.

3. Characterization

UV–vis characterization of the colloidal gold nanoparticles was performed using a SPECORD 250-222P155 UV-Vis instrument in the scan range 780–300 nm. The thickness of the Au layers was investigated by FR-Vis/NIR tool from Theta-Metrisis company.

To characterize and analyze the morphology of prepared Au nanoparticles deposited on the silica support the atomic force microscope (AFM) from Veeco Nanoscope company was employed. AFM images were obtained in the standard tapping mode using typical 1866SPM tip.

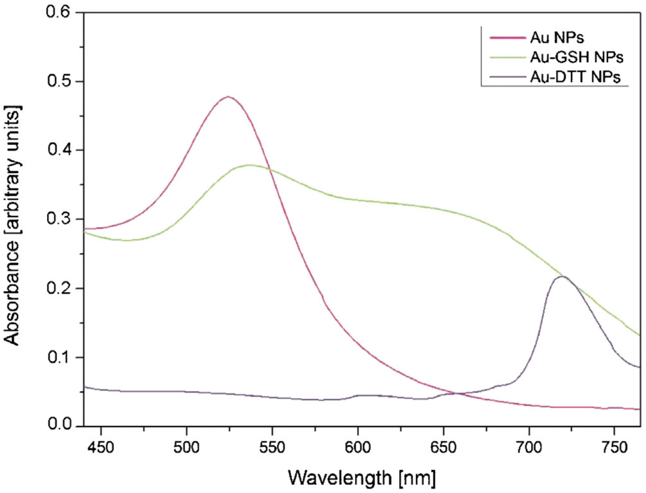

Fig. 1. UV–vis spectra of Au NPs sample and the samples modified with 1,4-dithiothreitol (Au-DTT NPs) and L-glutathione (Au-GSH NPs).(For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article)

GISAXS experiments were performed at the B1 beamline (DESY-HASYLAB, Hamburg) using wavelength of $\lambda = 0.8856$ Å and a sample-to-detector distance of 3150 mm. The scattering signal was recorded with a 2D PILATUS 1M detector. The GISAXS measurements were performed at the angle of incidence of 0.05° and treated with the Fit2D software.

The HRTEM micrographs were taken with a JEOL 2100F microscope. Copper grid coated with a holey carbon support film was used to prepare samples for the TEM observation. The bright-field TEM image was obtained at 200 kV. The particle size was measured as average particle size from multiple TEM images.

The surfaces of samples were analyzed by X-ray photoelectron spectroscopy (XPS). XPS measurements were performed using XPS instrument (SPECS) equipped with PHOIBOS 100 SCD and non-monochromatic X-ray source. The survey surface spectrum was measured at 40 eV transition energy and core spectra at 50 eV at room temperature. All spectra were acquired at a basic pressure of 2×10^{-8} mbar with Mg Kα excitation at 10 kV (150 W). The data were analyzed by SpecsLab2 CasaXPS software (Casa Software Ltd.). A Shirley type baseline was used for all peak-fits. The spectrometer was calibrated against silver (Ag 3d).

Magnetic measurements were performed on a commercial superconducting quantum interference device-based magnetometer (SQUID) from Quantum Design MPMS 5XL over a wide range of temperatures 2–300 K and applied dc fields up to 5 T. Complete magnetization curves M versus H were measured by a standard procedure from the field −5 to +5 T. Measured samples were catted to the square encapsulated to the plastic sample holder. The diamagnetic contribution corresponding to the sample holder was previously measured and subtracted from the total magnetization. Also, since the glass support can significantly influence the measured magnetization data, the pristine silica glass support with the same square shape and weight as the studied Au NPs samples was measured and extracted from the total magnetization data.

4. Results and discussion

4.1. UV–vis characterization

A representative UV–vis spectrum of the gold nanoparticles layer is shown in Fig. 1 (curve Au NPs). The sample of Au