

Adsorption of Gold Nanoparticle Multilayers

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Abstract — Gold nanoparticles are the subject of prosperous research, with vast applications in the interdisciplinary areas. When preparing the surface nanocomposites the first stage is the adsorption process and this procedure has to be investigated in detail.

This study describes gold nanoparticle assay formation using LBL (layer-by-layer) method and estimating spectrophotometry and atomic force microscopy measurements.

This multilayer assay of gold nanoparticles study should provide insights for future modifications of bio analytical sensors.

Key words — adsorption, electrolytes, gold nanoparticles, multilayers, surface plasmon resonance.

I. INTRODUCTION

Demand for sensitive, reliable, efficient analytical systems suitable for fast analyte detection, environmental monitoring and diagnosis of diseases are increasing annually. It is the driving force in the engineering of sensors.

Application of gold nanoparticles (Au-NPs) in the design of analytical systems is of considerable interest [1-6].

Citrate-capped Au-NPs modified by poly-L-lysine (PLL) were applied in gene delivery systems [3]. Stobiecka and co-workers noticed several important aspects of PLL-coated NPs: low toxicity and bactericidal and virucidal injections applications. Since direct binding of PLL to AuNP is not strong at neutral pH, Stobiecka's group has focused on PLL interactions with carboxylated self-assembled monolayers (SAM) on Au-NPs, such as the citrate-capped Au-NPs. The double-shell nanoparticles Au-NPs@Cit/PLL do not contain any toxic thiols. Therefore the advantage of the proposed approach is that in contrast to thiol-functionalized Au-NPs, no toxicity related to the thiol release is expected during gene delivery [3]. Byung-Wook group [4] reported a few important notations: if the concentration and the duration of Au-NPs deposition have increased, the surface became rougher, and the electron transfer resistance decreased; when SAM was formed on Au-NPs, the electron transfer resistance increased. Ling Li group [2] showed that gold nanoparticles could be grown on horizontally aligned single walled carbon nanotubes and such system exhibit excellent response, ultrahigh sensitivity, great selectivity and reusability. Yasumoto group [1] fabricated immunoassay based on a mixture of AuNPs with heavy metals – cadmium, hexavalent chromium and lead. They examined the microfluidic heavy metal immunoassay system based on absorbance measurements using gold nanoparticle-labelled antibodies.

Recent advances in the synthesis of gold nanoparticles offered new opportunities to form multilayers. Layer-by-Layer (LBL) self-assembly technique [7,8] is very attractive because of opportunity to control film thickness on the nanometre scale, monitoring the surface shape and roughness, which is very important during application. Fabrication of multilayers by consecutive adsorption of polyanions and polycations [7] is a method in which synergy between distinct materials might be achieved in a straightforward, low-cost manner [8]. Moreover, the electroactivity through polyelectrolyte multilayers [9-11] can be distributed over a number of layers containing electrochemically active units such as ions, redox groups, electrocatalytic centres, etc. Farhat group [9] investigated transport of redox-active probe ions through multilayers, made from highly charged polyelectrolytes, and concluded that there are no sites for the exchange of small ions within the bulk of multilayers because of the intrinsic charge balance between polyelectrolyte ion pairs. By exposing a substrate to polyelectrolyte solution, a film of controlled thickness may be obtained.

Sensing properties of gold nanoparticles by evaluation of the surface plasmon resonance (SPR) related effects have been already well investigated in many researches [15-18]. Surface plasmon resonance phenomena at the metal-dielectric interface empowered biochemical sensing applications. Surface plasmon resonance sensors can be classified according to the way in which light interacts with the surface plasmons. These interaction ways could be: angular, intensity, wavelength, and phase or polarization modulation [13]. Some metals including gold exhibit SPR as a result of interaction between electromagnetic radiation and loosely bound electrons to the metal surface [15]. Kadam et al. showed that the SPR phenomenon by embedded gold NPs can exclusively be used to enhance the optical modulation in an electrochromic host matrix [15]. Some researchers also investigated the effect on SPR signal of different shape

and size gold nanoparticles and found the SPR signal varied due to different plasmon absorbance bands of NPs [16].

The aim of this work was the development of platform based on Layer-by-Layer deposited AuNPs.

II. EXPERIMENTAL

1. Materials

All chemicals were of analytical grade and were used without further purification. All solutions were prepared in deionized water purified with a Millipore S.A. water purification system (Molsheim, France).

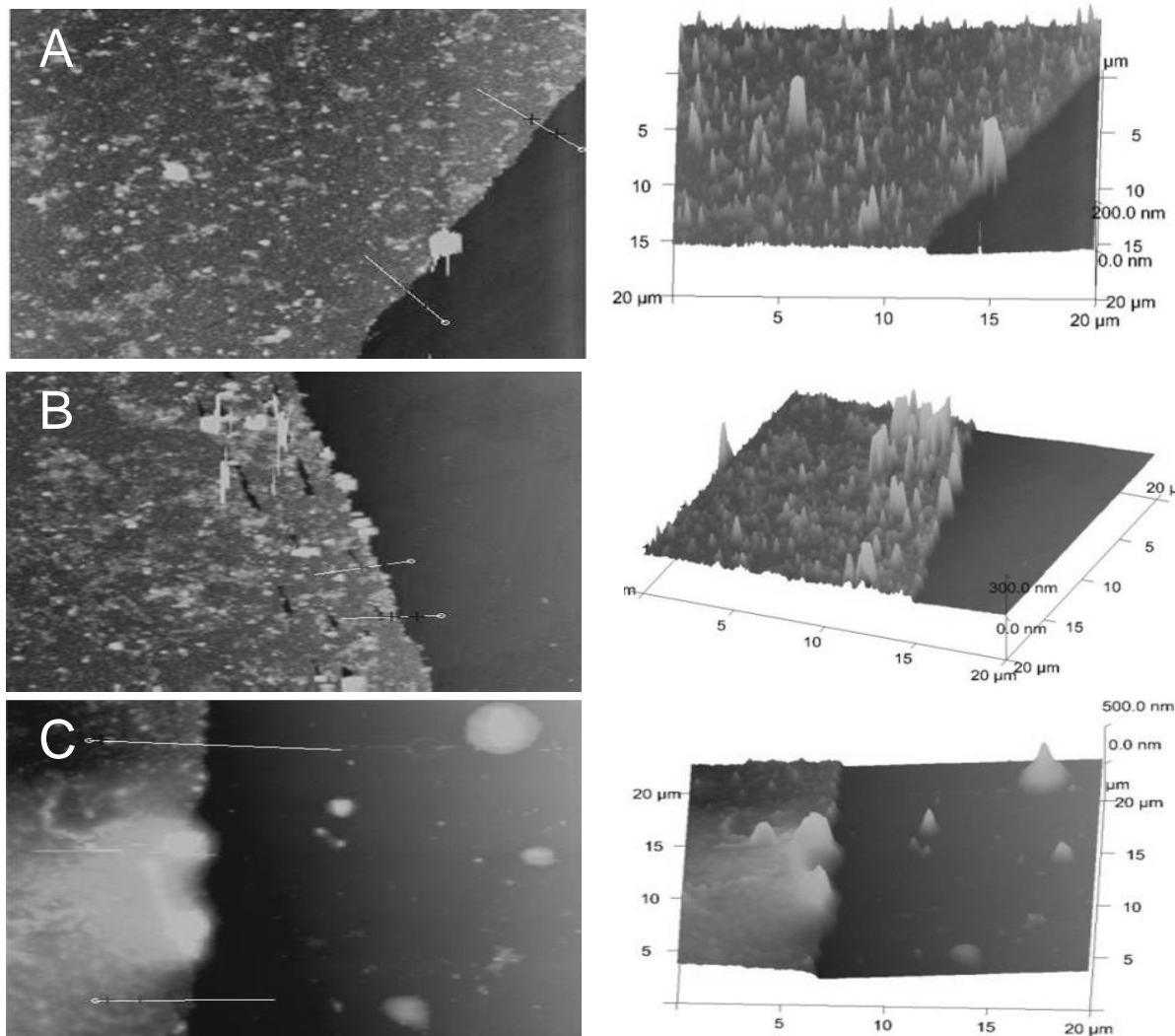


Fig. 1. AFM images of gold nanoparticle layered structures. A – 6 layers of gold nanoparticles aggregates; B – 9 layers of gold nanoparticles aggregates; C – 12 layers of gold nanoparticles aggregates.

Gold nanoparticles were prepared according to previously described procedure [14]. ‘Solution-A’ consisted of 80 ml of distilled water mixed with 1 ml of 1% of hydrogentetrachloroaurate (III) trihydrate received from Alfa Aesar GmbH (Karlsruhe, Germany). ‘Solution-B’ consisted of 4 ml 1 % of tri-sodium citrate received from UAB Avsista (Vilnius, Lithuania) mixed with 16 ml of distilled water and tannic acid received from Carl Roth GmbH&Co (Karlsruhe, Germany). Using a 1 ml or more of tannic acid to maintain a constant pH value was applied the same 0.025mol/l volume of potassium carbonate solution because an amount of tannic acid has an influence on the size and stability [19-21] of gold nanoparticles. Both solutions were covered with foil, then

solutions were heated to 60°C and when they reached the desired temperature, the solution A was poured into the solution B, while stirring constantly with a magnetic stirrer. When acquired a red colour, the solution temperature was increased to 95 °C, when constantly stirring, and after 15 minutes the solution was evenly cooled at room temperature ($20 \pm 2^\circ\text{C}$). Gold nanoparticles of 13 nm diameter were formed.

Poly-L-lysine (PLL) is a small natural homopolymer of the essential amino acid L-Lysine. Poly-L-Lysine 0.01% was purchased from Sigma Aldrich Company, UK. The optimal concentration of PLL used attachment of Au-NPs was 0.002%.

Au-NPs layers were prepared on glass chip using poly-L-lysine, which was used to attach gold nanoparticles on glass surface. The chemical growth of Au-NPs layers was performed.

2. Methods

Spectrophotometry

Scanning double-beam spectrometer (Lambda 25 UV/VIS spectrometer, from PerkinElmer Inc., USA) for the UV/VIS range, controlled by PC was used. Measurements were made in spectral range between 300 nm to 900 nm.

Atomic Force Microscopy

Atomic Force Microscope, Catalyst from Veeco Instruments Inc., (Santa Barbara, USA) was used to evaluate size, shape, and height of prepared samples. Contact mode, was chosen for all measurements. RTESP (Phosphorus doped Si) and NP (non-conductive Silicon Nitride) tips were used.

III. RESULTS

The Atomic Force Microscope images presented in figure 1 illustrates formation of Au-NPs-based layers. The visible increase in diameter and the surface roughness is observed in the course of nanoparticle deposition. Thickness of formed layers was measured by AFM.

In order to evaluate thickness of the layered structures a gentle scratch with metallic needle was made, it is seen in AFM pictures as dark area (Fig. 1.). A few white lines represented in AFM images shows areas, which were evaluated in order to calculate thickness of Au NPs-based layered structures, which was approximately 40 nm for 6 layers, 75 nm for 9 layers and 95 nm for 12 layers.

Zhang and Gu [22] found that enhanced electromagnetic field at the surface of the nanoparticles focus at the junction of aggregates. The surface chemistry affection to physical properties of the gold aggregates brings the importance of interaction. Gold nanoparticles interacts differently due to aggregation or agglomeration processes which, according to Zhang and Gu, depends on light, temperature, embedding environment, and the chemical nature of the surface. Heat, as another important factor, can be generated due to light absorption and effect further agglomeration of the gold nanoparticles [22]. The additional cause for agglomeration attributes to a thermal detachment of surface ions due to reversible changes of the illumination or direct heating [22].

Spectrophotometric evaluation of Au-NPs-based layered structures showed that Au-NPs-related peak of absorption band depends on the number of deposited Au-NPs layers.

IV. CONCLUSIONS

It could be concluded that Au-NPs aggregation processes changes optical and morphological nanoparticle geometry therefore surface plasmon absorption occurs as an integrated transverse and longitudinal dipole polarization.

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