Chemical Physics 373 (2010) 295–299

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

Morphological and electrical characteristics of amino acid–AuNP nanostructured two-dimensional ensembles

Anamaria Orza [a], Liliana Olenic [b,*], Stela Pruneanu [b], Florina Pogacean [b], Alexandru S. Biris [c,**]

[a] Babes-Bolyai University, Faculty of Chemistry and Chemical Engineering, Cluj-Napoca, Romania
[b] National Institute for Research and Development of Isotopic and Molecular Technologies, Donath Street No. 65-103, RO-400293 Cluj-Napoca, Romania
[c] University Arkansas at Little Rock, Arkansas Nanotechnology Center, Applied Science Department, 2801 S. University Ave., Little Rock, AR 72204, USA

ARTICLE INFO

Article history:
Received 6 April 2010
In final form 1 June 2010
Available online 8 June 2010

Keywords:
Gold nanoparticles layer
L-Lysine
L-Cysteine
Self-assembly

ABSTRACT

The interaction between amino acids (L-cysteine, L-lysine) and gold nanoparticle layers deposited on ITO glasses was investigated. The citrate capped gold nanoparticles (AuNP) were first deposited as a thin layer onto silanized ITO and subsequently linked with an amino acid, due to strong affinity of thiol and amine groups to gold. The gold nanoparticles had an elliptical shape, with size varying between 7 and 14 nm, as indicated by TEM analysis. After deposition on ITO substrate, the nanoparticles self-assembled into large aggregates with poor contact between, as revealed by AFM. After linking L-cysteine or L-lysine to the surface of nanoparticles layer, a change in morphology occured. A better contact between the gold aggregates boundary developed, which improved the conducting properties of the nanostructured layer. The electrical resistance of the AuNPs layer, obtained from *I–V* measurements, was very high (2.8×10^{13} Ω) and slightly decreased after linking the NPs with amino acids.

1. Introduction

The synthesis of one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) nanostructures using metallic nanoparticles and biomolecules is a subject of intensive research, due to their possible applications in microelectronics, optoelectronics, biosensor devices and medicine [1–3]. Several groups functionalized gold nanoparticles with surfactants [4] or organic molecules [5–8] in order to create the desired ensembles.

Zhong et al. [9] reported the interactions between colloidal gold and two main types of organic molecules: alkanethiols and amino acids. They have shown that in some amino acids the reactivity of the α-amine is pH dependent. At low pH, the linking with AuNP takes place via α-amine. At intermediate and high pH, this is suppressed due to electrostatic repulsion between the Au surface and the negatively charged α-carboxylate group. By exploiting the nanoparticles surface charge, extended nanostructures and functional materials were prepared [10–14]. In addition, metallic nanoparticles have been used to establish self-assembled nanostructures on various substrates. Their properties significantly rely on the size of gold nanoparticles and the pitch between them. Park et al. [15] immobilized AuNP on the gap surface between two microelectrodes (20 μm apart), through hybridization among target DNA, capture DNA and probe DNA. They reported that the current through the monolayer was below the detection limit. Zhang and Oyama [16] described an improved approach for the direct attachment and growth of mono-dispersed gold nanoparticles on ITO surfaces. They demonstrated that the as-prepared gold nanoparticle arrays exhibited catalytic activity toward the electrooxidation of nitric oxide, which could provide electroanalytical application for nitric oxide sensing. Our purpose was to obtain nanostructures comprising molecular and nanoparticles components, by self-assembling AuNP on silanized ITO substrate. The interaction of AuNP layer with amino acid (L-cysteine or L-lysine) changes not only the layer morphology but also its electrical characteristics. The results show that the self-assembly is a convenient tool for the construction of composite nanostructures on ITO surfaces. The morphological, optical and electrical characteristics of nanostructured ensembles were investigated by AFM, UV–Vis spectroscopy and *I–V* measurements. To our best knowledge, such studies have not been previously reported and can hold a great promise for advancements in a number of applications ranging from nanoelectronics, spectroscopic detection platforms, bio-functionalized surfaces for medical applications, and surfaces with high cellular proliferation and antimicrobial abilities.

2. Materials and methods

Amino acids (L-lysine and L-cysteine) were purchased from Fluka and used as received. Hydrogen tetrachloroaurate(III) trihydrate was obtained from Merck and 3-aminopropyltrimethoxysilan (APTMS) was obtained from Alfa Aesar, a Johnson Matthey Company. The

* Corresponding author.
** Corresponding author.
E-mail addresses: liliana.olenic@itim-cj.ro (L. Olenic), asbiris@ualr.edu (A.S. Biris).

0301-0104/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.chemphys.2010.06.001

amino acids solutions (aqueous) were prepared at the same concentration (1 mM) and the pH was adjusted at 2, by using few drops of hydrochloric acid. ITO glasses were used as substrates for assembling AuNP and amino acid–AuNP layers. They were thoroughly cleaned in solution containing NaOH then rinsed with ethanol and finally dried at a temperature of 130 °C, for few hours. The silanization process was carried out by immersing ITO glasses in a solution of 10% vol. APTMS in freshly distilled methanol, for 2 h. After silanization, the samples were rinsed with methanol and then with de-ionized water.

Colloidal gold solution (particles size between 7 and 14 nm) was prepared according to Turkevich et al. [17] method. After preparation, a clean ITO glass was immersed in the AuNP solution for 2 h (for comparison, another ITO glass was immersed in a diluted colloidal gold solution, 1:2). Subsequently, the AuNP/ITO and AuNP(1:2)/ITO were rinsed with de-ionized water and dried at room temperature. A change in color was observed, due to linking between gold nanoparticles and silane monolayer. The modified ITO glasses were following immersed in freshly prepared amino acid solution (pH 2) for 18 h. The electrical resistance of AuNP and amino acid–AuNP layers on silanized ITO substrate was obtained from *I–V* curves. Two electrical contacts (silver) 5 mm apart, were formed on layer surface. The voltage was varied between 1 and 3 V and the current recorded with a Keithley Electrometer. In order to diminish the electrical noise, the entire setup was introduced inside a Faraday cage.

2.1. UV–Vis spectroscopy

The optical properties of colloidal gold solution, AuNP/ITO and amino acid–AuNP/ITO were monitored using an UV–Vis spectrophotometer (JASCO V-570).

2.2. AFM

AFM imaging was performed in the air (AFM 5500, Agilent Technologies) using NanoProbe tips. All of the AFM images are height images taken in tapping mode, unless otherwise indicated.

2.3. TEM analysis

Transmission Electron Microscopy (TEM) images were collected on a field emission JEM-2100F TEM (JEOL Inc.) equipped with a CCD camera. The acceleration voltage was 100 kV for the AuNPs analysis. The nanostructures were homogeneously dispersed in 2-propanol under ultra-sonication for 30 min. Next, a few drops of the suspension were deposited on the TEM grid, dried, and evacuated before analysis.

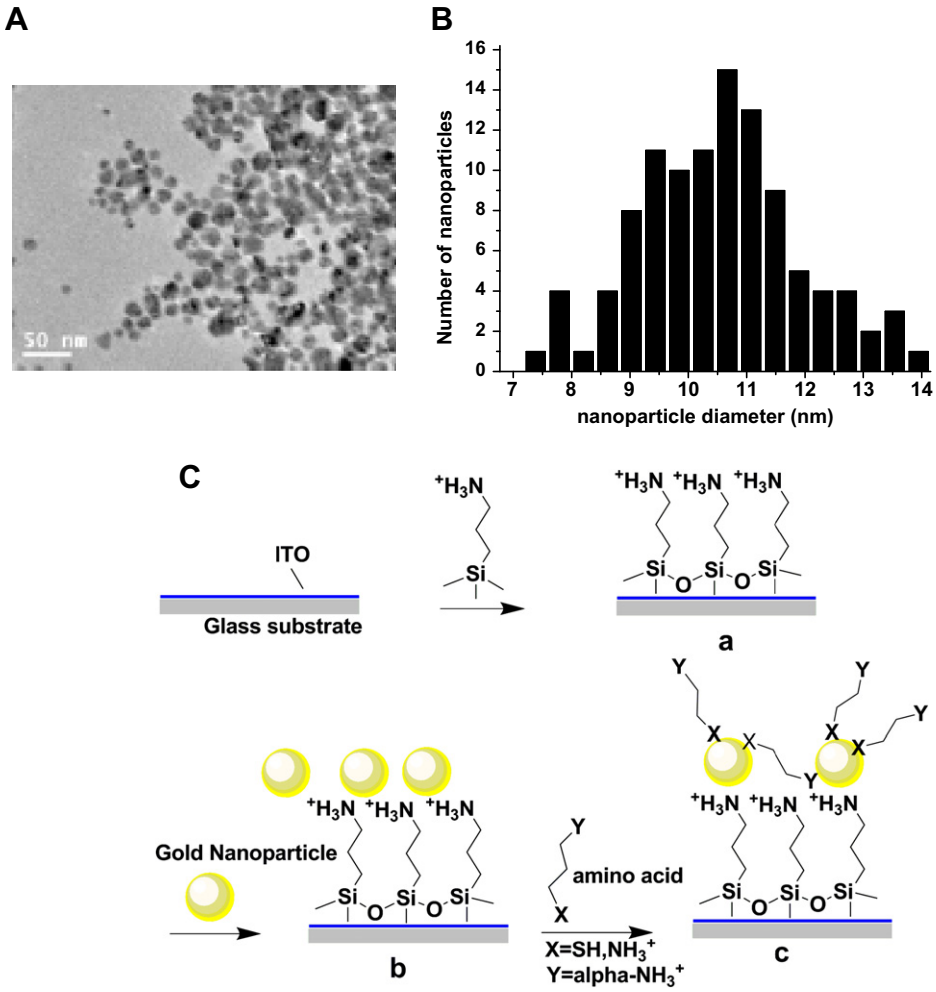

Fig. 1. TEM image of gold nanoparticles, showing their size (A); a representative histogram of nanoparticles size distribution (over 100 NPs were analyzed) (B). Chemistry of the attachment of amino acid to self-assembled AuNP layer: (a) surface silanization with APTMS; (b) addition of gold nanoparticles; (c) linking amino acid (L-lysine or L-cysteine) to AuNP layer.