ICAM2009
11th International Conference
on Advanced Materials
Rio de Janeiro Brazil
September 20 - 25

Gold nanoparticles obtained in PAH/PAA-based multilayers: Synthesis and Characterization

Nicolle Dal'Acqua[1], Rosiana Boniatti[1], Marcelo Giovanela[1], Sérgio R. Teixeira[3], Janaina S.Crespo[1], Liane Rossi[2], Giovanna Machado[1]

(1) Universidade de Caxias do Sul, Centro de Ciências Exatas e Tecnologia, Rua Francisco Getúlio Vargas, 1130 - CEP 95070-560 , Caxias do Sul - RS – Brasil. Email giovannamachado@uol.com.br.
(2) Institute of Chemistry, Universidade de São Paulo – USP, Av. Prof. Lineu Prestes 748, São Paulo 05508-000, SP, Brazil.
(3) Laboratory of Thin Films, IF-UFRGS, Av. Bento Gonçalves 9500, P.O. Box 15051, 91501-970, Porto Alegre, RS, Brazil.

Abstract – It is well known that carboxylic acid groups in the PAH/PAA-based multilayers can bind metal cations by ion exchange with the acid protons. This study presents a novel way to introduce nanoparticle in multilayers produced by the layer-by-layer assembling technique (LbL). The method consists of firstly synthesizing the gold nanoparticles that are, in sequence, diffused into LbL layers. The nanoparticles are then reduced using the citrate method and form small nanoparticles with diameter ranging from 8-12 nm. No aggregation was observed using this method, however, depending on the pH used in the formation step, several morphologies, ranging from a gold monolayer or totally separated gold nanoparticles can be obtained.

Keywords: *gold, PAH/PAA, multilayers,TEM, AFM*.

Nanotechnology has brought some new challenges, such as the development of the quality and synthesis processes of nanostructures based on inorganic and organic substances. Several methods of synthesis can be used to prepare metal nanoparticles. Among these methods, the layer-by-layer (LbL) processes are notable as a route to obtaining nanoparticles of specific size through the colloidal methodology [1, 2]. The polyelectrolyte multilayer (PEM) has been frequently used to produce nanoparticles. This process involves deposition of weak electrolytes from diluted aqueous solution, based on electrostatic interactions of opposite polymer charges, on specific substrates. A glass substrate was immersed in an aqueous solution of high molecular weight poly(diallyldimethylammonium chloride) PAH (Mw=70,000 g mol^{-1}) for 15 min and then withdrawn from the solution and rinsed in deionized water. The substrate was then immersed in a 25% aqueous solution of high molecular weight poly(acrylic acid) PAA (Mw=90,000 g mol^{-1}) for 15 min and then rinsed in deionized water. The films were prepared for combinatorial experiments: $(PAH_{3.5}/PAA_{3.5})_{10}$ and $(PAH_{7.5}/PAA_{3.5})_{10}$, where 3.5 and 7.5 are the pH of the PEM solution and 10 is the number of bilayers. These PEMs were immersed in a gold aqueous solution (5 mM, pH 6.0) [3] for 1 h and then removed and rinsed in deionized water for 1 min three times. Figure 1 shows the AFM images, where Figure 1a shows lower roughness and thickness in comparison to Figure 1b. For the $(PAH_{3.5}/PAA_{3.5})_{10}$ system the decrease in PAA layer thickness results from the decreasing segmental population of loops and tails that occurs as the PAA chains become more highly charged with increasing pH. The increase in the PAH layer thickness, results from the increasing surface charge density of a previously adsorbed PAA chain with increasing pH (the more oppositely charged PAH is needed to neutralize the higher surface charge of the more highly ionized PAA surface chains). The increase in the $(PAH_{7.5}/PAA_{3.5})_{10}$ layer thickness results from the PAH adsorbing fully charged polyelectrolytes and is deposited as very thin layers in opposition segmental population of loops and tails that occurs as a consequence of PAA chains becoming more charged with increasing pH. Figure 2a shows the cross-sectional TEM image of a $(PAH_{3.5}/PAA_{3.5})_{10}$ multilayer in which gold nanoparticles show a diffusion process, while in Figure 2b, showing the $(PAH_{7.5}/PAA_{3.5})_{10}$ system, a bilayer of gold nanoparticles is verified on the top surface. The explanation for this behavior is that when PAH has a pH of 3.5 the amine groups are totally fully charged, and the gold nanoparticles that are stabilized by a negative charge (sodium citrate) diffuse toward the amine groups that are not totally conjugated to the carboxylic acid. On the other hand, the PAH has a pH of 7.5, and the amine groups are partially charge and consequently conjugated with part of the carboxylic acid, with no diffusion of these particles. Because the negative charge of gold nanoparticles stabilizes the sodium citrate it will be blocked due to electrostatic repulsion of these nanoparticles, with the PAA having a pH of 3.5 resulting in a superficial bilayer of gold nanoparticules (see Figure 2b).

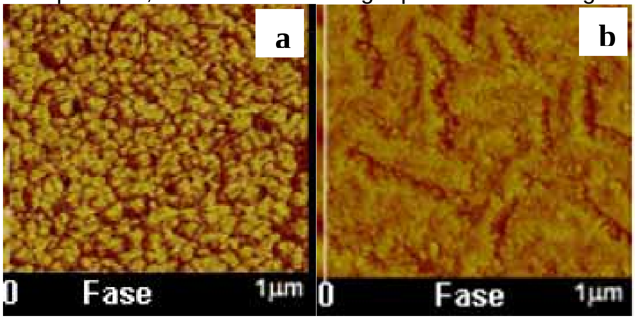

Figure 1. *AFM image:* ***(a)*** *$(PAH_{3,5}/ PAA_{3,5})_{10}$;* ***(b)*** *$(PAH_{3,5} / PAA_{3,5})_{10}$*

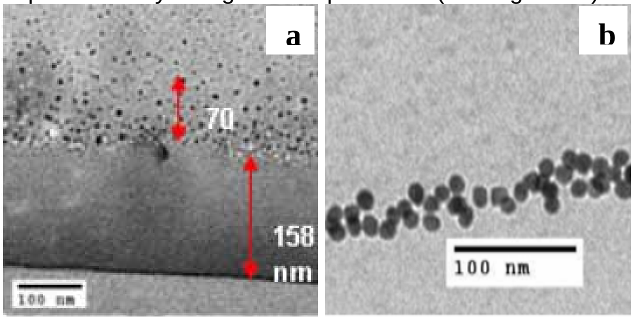

Figure 2. *TEM image:* ***(a)*** *$(PAH_{3,5}/ PAA_{3,5})_{10}$;* ***(b)*** *$(PAH_{3,5} / PAA_{3,5})_{10}$ both immersed in gold solution during 1 h*

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