



# Quaternized chitosan mediated assembly of gold nanoparticles multilayers



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## ABSTRACT

Self-assembled multilayers of quaternized chitosan (QCHI) and gold nanoparticles (AuNPs) were built up on quartz and gold substrates. To evaluate the effect of the surface coverage of AuNPs on the structural, optical and electrochemical properties of multilayers prepared with different AuNPs adsorption time were compared. UV-Vis and AFM characterization indicated that AuNPs in each bilayer are spatially separated, and interparticle interactions are mainly produced between bilayers. The complex refractive index and thickness of the QCHI-AuNPs multilayers were properly determined using an anisotropic single layer model. The optical constants obtained were quite different from those of bulk gold, and their values depend on the coverage of AuNPs. The thickness per bilayer of the structures present a progressive increase as AuNP's coverage augments, reaching a value close to the nominal AuNPs diameter after 60 min of adsorption. These results indicate that the interpenetration of bilayers in the structure depends on the surface concentration of AuNPs. The charge transport through the QCHI-AuNPs film was studied using different redox probes. The effects of the adsorption time of AuNPs and the number of bilayers ( $n$ ) of the structure on the charge transfer rate constants,  $k_{ct}$ , were analyzed. The incorporation of AuNPs in the structure produces an increase of  $k_{ct}$ , as the adsorption time of AuNPs rise. In addition, the values of  $k_{ct}$  were independent of  $n$ , in the interval studied (up to  $n = 5$ ), suggesting that the electronic communication in the multilayered structure was mediated by the AuNPs.

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## 1. Introduction

Materials at the nanoscale have received significant attention in the last few decades because of their interesting and well-known properties associated with quantum confinement and surface energy effects [1]. Extensive research has been reported about synthesis [2], functionalization [3] and applications [4,5] of nanoparticles. Among the different types of metal nanoparticles, gold nanoparticles (AuNPs) have been extensively studied because their synthesis and functionalization is relatively simple and they exhibit excellent biocompatibility with biological components. These properties make AuNPs very attractive for their applications in sensors, electrocatalysis and medical diagnostic, among others [6]. In order to develop devices that exploit the properties of AuNPs, they should be anchored in a stable way on a surface,

which often represents a critical step. In this sense, the construction of layer-by-layer (LbL) assembled structures with polymers is quite attractive because of its simplicity, flexibility and effectiveness [7,8]. The LbL method is well established in forming highly dense and compact ultrathin films using various kinds of organic or polymeric materials, with precise control of layer composition and thickness [9]. Multilayer thin films of gold nanoparticles linked with cationic polyelectrolytes such as poly(allylamine hydrochloride) (PAH) [10,11], polyethylenimine (PEI) [12], chitosan [13], modified chitosan [14], among others [15,16] have been reported. The morphology of these polymeric-AuNPs self-assembled structures depends on the environmental conditions, including pH, ionic strength, temperature, and nature of the ions and co-solvent of the adsorption medium [17].

AuNPs included in these self-assembled arrays present strong interactions with the matrix and neighboring AuNPs in the same layer (intralayer) as well as between layers (interlayer) [18]. These interactions generate collective surface plasmon resonances (SPR) controlled by the packing density and the interparticle distances along with the changing dielectric constant of interparticle media [19]. For example, Tsukruk and co-workers [20] have reported the

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fabrication of LbL assembled films containing gold nanoparticles with control of the aggregation state by the design of multilayered films with various combinations of polymers interlayers [20]. Accordingly, assemblies of polymers/gold nanoparticles can be used to tune the optical properties providing a cheap and effective bottom-up approach for fabrication of plasmonic devices to develop sensors and biosensors systems [5].

In addition, electrode/polymer/nanoparticles assemblies present interesting electronic and catalytic properties. Understand the effect of the charge, size and density of nanoparticles, as well as the thickness of the structures on the efficiency of electron-transfer kinetics is required to exploit rationally the properties of these systems in sensing and electrocatalysis. Our main goal in this work is deepen on the relationship between the structural and electrochemical properties self assembled structures of gold nanoparticles. In a previous work [14] we evaluate the effect of quaternized chitosan (QCHI) and gold nanoparticles (AuNPs) multilayer as platform for the adsorption of glucose oxidase (GOD) and we determine the influence of the AuNPs in the enzymatic response of the biosensor. In relation with that work, in the present publication we extend our studies towards the structural and electrochemical characterization of QCHI/AuNPs self assembled multilayers to correlate its physicochemical properties with the electrochemical response reported in ref. 14, such as the improvement of conductivity, the increment of the oxidation of the hydrogen peroxide produced by GOD, the higher amperometric response and the better analytical performance of electrodes modified with self assembled layers of QCHI/AuNPs. For this purpose, in the present contribution we study the properties of self assembled multilayer films of quaternized chitosan (QCHI) and gold nanoparticles (AuNPs) to evaluate the influence of the surface coverage of nanoparticles,  $\Gamma_{\text{AuNPs}}$ , on the structural (thickness, distribution), and optical (refractive index, anisotropy) properties of the multilayers and correlate them with the electron-transfer kinetics at the modified electrode. QCHI/AuNPs multilayers were built up on quartz and gold substrates employing different AuNPs adsorption time. The systems were characterized using optical (UV-Vis, ellipsometry), microscopic (AFM, TEM, SEM) and electrochemical techniques (CV, EDR, EIS) and the evolution of the complex refractive index and thickness of each structure were evaluated as a function of  $\Gamma_{\text{AuNPs}}$ . The heterogeneous charge transfer rate constants of different redox probes were determined varying two parameters, the adsorption time of nanoparticles or the number of bilayers of chitosan/nanoparticles. The results presented in this contribution evidence that the adsorption of AuNPs improves the conductivity of the structure as well as its electrochemical reactivity. Both characteristics depend, in turn, on the structural properties of the chitosan/AuNPs arrays.

## 2. Experimental section

### 2.1. Reagents

Citrate-stabilized gold nanoparticles (AuNPs) with  $\lambda_{\text{max}} = 518 \text{ nm}$ ,  $(11.0 \pm 0.7) \text{ nm}$  average diameter and  $3.72 \times 10^{12}$  nanoparticles  $\text{mL}^{-1}$  were from Sigma. The average size of AuNPs was confirmed by transmission electron microscopy, see supporting information S1. The sodium salt 3-mercapto-1-propanesulfonate (MPS) was obtained from Aldrich. Quaternized chitosan (QCHI) was synthesized as described in reference [21] from chitosan of 190 kDa molecular weight (Pronova). The average molecular weight of QCHI was 52.75 kDa and the content of quaternized amine 40.0 mol %. Other chemicals were of reagent grade and were used without further purification. All solutions were prepared with ultra-pure water ( $18 \text{ M}\Omega \text{ cm}$ ) from a Millipore-MilliQ system.

### 2.2. Equipments

UV-Vis experiments were performed with a Shimadzu UV1601 Spectrophotometer and a quartz cuvette with a 0.1 cm path length. Atomic force microscopy (AFM) images were obtained with a Multiview 1000 Nanonics Microscope using a cantilevered optical fiber probe of 10 nm of diameter coated with Al. Images were collected in air using intermittent mode and processed with the WSXM software [22]. Scanning electron microscopy (SEM) images were obtained with a Field Emission Gun Scanning Electron Microscope (FE-SEM, Zeiss, SIGMA model). Ellipsometric experiments were performed with a Rudolf Research rotating analyzer automatic ellipsometer (vertical type, 2000FT model), equipped with a 75 W tungsten lamp as the light source and filters (632.8 and 546.1 nm). All measurements were performed at an incidence angle of  $70.00^\circ$ . A homemade gold electrode of 7 mm of diameter was used as substrate. The gold electrode was horizontally mounted in a Teflon holder and aligned before each experiment. The adsorption of QCHI and AuNPs was carried out without variations of the substrate position to keep the system alignment. The ellipsometric angles ( $\Psi$  and  $\Delta$ ) were collected in  $5.00 \times 10^{-2} \text{ mol dm}^{-3}$  phosphate buffer solution pH 7.40 after each adsorption step. The operator-triggered mode was employed for taking the measurements. Cyclic voltammetry (CV) was performed with a 173 EG&G PAR potentiostat/galvanostat (Princeton Applied Research, USA) coupled to a 175 EG&G PAR signal generator and a 7090A Hewlett Packard plotting recorder. Stationary potential/current curves were obtained at a gold rotating disk electrode (Radiometer Analytical, EDI101) using a rotation speed controller (Radiometer Analytical, CTV101). Electrochemical impedance spectroscopy (EIS) experiments were performed with a Solartron potentiostat/galvanostat (SI 1287) coupled to a frequency response analyzer Solartron FRA 1260. Measurements were performed at the open circuit potential with a 10 mV of amplitude signal in the frequency interval from 10 mHz to 0.1 MHz was applied. Gold disk electrodes (Au) of 2 mm diameter (CHI 101) were used as substrate during the electrochemical experiments. A platinum wire and an Ag/AgCl/3 mol  $\text{dm}^{-3}$  NaCl electrode (Model RE-5B, BAS) were used as counter and reference electrodes, respectively. The reported potentials are referred to this reference electrode. All experiments were performed at room temperature.

### 2.3. Surface Modification

#### 2.3.1. Gold modification

Gold electrodes were cleaned before each experiment by polishing for 6 min with  $0.05 \mu\text{m}$  alumina, followed by sonication in deionized water for 5 min, immersion in "Piranha" solution (1:3 V/V  $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ ) for 5 min, and rinsing with ultrapure water. The surfaces were stabilized by cycling at  $10 \text{ V s}^{-1}$  of scan rate in  $0.50 \text{ mol dm}^{-3}$  sulphuric acid solution between 0.200 V and 1.650 V until a reproducible voltammogram corresponding to a clean gold surface was obtained. To check the surface condition and to obtain the electro-active area, a voltammogram in  $0.50 \text{ mol dm}^{-3}$  sulphuric acid solution at  $0.100 \text{ V s}^{-1}$  was performed at the end of the cleaning procedure.

ArrandeeTM glass slides of 11 x 11 mm covered with a gold deposit were used as substrates for AFM and SEM experiments. To promote the development of Au (111) planes, the substrates were annealed in a butane flame during two minutes, cooled under constant  $\text{N}_2$  flux and placed immediately in the dipping solution.

The first step in the preparation of the multilayer was the adsorption of MPS by soaking the substrates for 30 min in  $2.00 \times 10^{-2} \text{ mol dm}^{-3}$  MPS solution prepared in  $1.6 \times 10^{-3} \text{ mol dm}^{-3}$  sulphuric acid solution, followed by a careful rinsing with deionized water. The adsorption of QCHI was performed for 20 min from a  $0.50 \text{ mg mL}^{-1}$  QCHI solution prepared in  $5.00 \times 10^{-2} \text{ mol}$

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