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Optical Enhancing Properties in Layer-by-Layer Films of Dendrimer and Gold Nanoparticles

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Summary: Portable multilayer films containing gold nanoparticles embedded in a dendrimer matrix have been fabricated using the layer-by-layer (LbL) technique, characterized and tested for applications in surface-enhanced Raman scattering (SERS). Film formation was monitored by microgravimetry measurements using a quartz crystal microbalance (QCM) and UV-visible spectroscopy. The surface morphology was investigated with atomic force microscopy (AFM) measurements. SERS was recorded for 2-Naphtalenethiol(NFT) cast onto the LbL film and the results show that the optical enhancing ability is a function of the number of bilayers. The analytes show an increase of SERS effect that follows the surface roughness, being stabilized after a certain number of bilayers are deposited.

Keywords: composites; dendrimer; layer-by-layer; Raman spectroscopy; SERS

Introduction

Surface-enhanced spectroscopy benefits from optical enhancement assisted by surface plasmon excitations in metallic nanoparticles.[1–3] For ultrasensitive chemical analysis, the most successful enhancing substrates in surface-enhanced Raman scattering (SERS) are gold and silver nanostructures.[4,5] The latter have been fabricated using a variety of physical and chemical methods, such as evaporation of metal, electrochemical roughening of metal electrodes, and lithographic techniques.[6,7] In the fabrication of nanostructured materials the main challenge is the control of the size and shape of nanoparticles in order to achieve specific physical properties. In addition to size and shape control, for some practical applications it is advantageous to produce films that can be used as substrates or portable sensors for spectrochemical analysis.[8,9] In this context, we and others are exploiting the chemical methods using the layer-by-layer (LbL) technique. LbL films are produced by alternating the immersion of a substrate in cationic and anionic solutions, usually polyelectrolytes. These films can be viewed as dense, stratified hydrogels made of polyelectrolyte layers and with a certain degree of interpenetration. In this model, the cross-linking density, or mesh size, is controlled by the charge distribution along the chain. The formation of LbL films is not restricted to polyelectrolyte pairs; it has been applied to polymer/proteins, polymer/ceramics and polymer/metals.[10,11] A number of external parameters, which can be varied during the deposition process, are known to influence the resulting layer structure. These include the ionic strengh of the deposition solutions, the polyion concentration, the charge density of the polyion and the molecular weight. The exact control of these factors can generate surfaces with specific properties. Included in the materials that are particularly well suited for use in LBL films are dendrimers.[12] In contrast to conventional polymers, dendrimers have precisely controlled structures, molecular weights, and chemical functionalities. They have been employed as stabilizers in the synthesis of

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metallic nanoparticles of gold and silver, with reducing agents such as borohydrate and citrate. In some cases, dendrimers were applied directly as reducing agents for the production of metallic nanoparticles. Recently, the fabrication of dendrimer LbL films of various architectures containing silver nanoparticles, and their application toward SERS, were reported.[13] In the films, Ag nanoparticles were shown to be effectively immobilized and stabilized with increased control over their spacing and aggregation. Here, we report multilayer films containing gold nanoparticles and dendrimer, which are proved to be suitable for Raman analisys and SERS activity was monitored using 2-Naphtalenethiol (NFT).

Experimental Details

The gold nanoparticles were prepared by adding 2.5 mL of trisodium citrate 1% into 100 mL of potassium gold chloroaureate 0.01%. This solution was heated up to the boiling point, kept at this temperature for 10 minutes, then allowed to cool down to room temperature. Glass slides were cleaned employing the RCA method before the deposition. The substrates were immersed alternately in a 1.0 g/L aqueous water solution of DAB-Am64-Polypropyleneanimine tetrahexacontamine dendrimer generation 5 (DAB) (Aldrich) and in a solution of gold nanoparticles. In each case they were rinsed with Milli-Q water after each deposition. Adsorption studies were performed by measuring the frequency changes with deposition on the substrate using a quartz crystal microbalance (quartz crystal – Stanford Research Systems INC QCM200- fundamental frequency about 5 MHz). The mass deposited was calculated using the Sauerbrey equation.[14]

Topographical measurements were performed by Atomic Force Microscopy (AFM) in tapping mode with a silicon cantilever (NCH model, Nanosensor) operating at a resonant frequency of 243 kHz. Images were collected with high resolution (512 lines/sample) at a scan rate of 0.5 Hz. The data were collected under ambient conditions, and each scan was replicated to ensure reproducibility. In addition, images were collected on at least 3 different spots of the same sample. For SERS experiments, 10 μL of 10^{-4} M of 2-Naphtalenethiol, 2-NAT, (Aldrich) in ethanol, were cast onto the LbL films. Inelastic scattering was measured employing a micro-Raman InVia Renishaw system with excitation at 633 nm with energy density at the sample of ca 1.6 x 104 W/cm^2.

Results and Discussion

In order to optimize the conditions for LbL deposition, an adsorption study employing a quartz crystal microbalance (QCM) was carried out. Initially, the QCM electrode was immersed for 10 minutes in the DAB solution (1.0 g/L at pH 5), rinsed with Milli-Q water, and dried keeping the same conditions used in our previous work [8,9]. This electrode was swelled for 2 minutes in water and then immersed in a gold nanoparticle solution, as described in the experimental section. Figure 1 displays the data points measured for mass thickness of film formation versus time starting with the addition of colloidal solution to the cell. The amount adsorbed increases continuously without reaching an upper limit even after 5 hours of exposure. The adsorption process is attributed to the interaction between the negatively charged amino

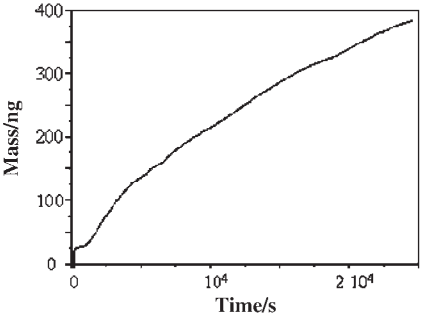

Figure 1.
Adsorption plot (mass thickness vs time) of gold nanoparticles on DAB for 1-layer film.

groups of DAB and citrate double layer of the gold nanoparticles. However, a fast process with saturation should be expected if adsorption was governed only by ionic interactions between adjacent layers.[15,16] The continuous mass increase in Figure 1 indicates that other interactions exist, including aggregation between nanoparticles in solution and the adsorbed nanoparticles. Further experiments are underway to take advantage of this peculiar adsorption process.

A broad plasmon absorption spectrum of gold nanoparticles in solution (dashed line, Figure 2) shows a maximum at 520 nm, characteristic of a distribution of spherical gold nanoparticles of about 20 nm radius in water. The Mie computation for spherical gold spheres of 20 nm radius immersed in water gives a plasmon absorption centred at 520 nm, as can also be seen in Figure 2. For LbL films produced with an immersion time of 1.5 hours in gold nanoparticle solution, the maximum in the UV-Vis spectra is first observed at 535 nm then shifts to 635 nm as the number of bilayers is increased from 1 to 7, as shown in Figure 2. Assuming that the refractive index in the LbL layers remains constant, the red-shifting of the plasmon absorption maximum (from 535 to 635 nm), and its broadening, indicate nanoparticle growth and aggregation in the solid multilayer film.

Figure 3 shows AFM images taken of LbL films with various numbers of bilayers. The root mean square (RMS) surface roughness of the films increases from 5.1 nm up to ~14 nm, as the number of bilayers increases from 1 to 5, after which it remains practically constant for 7 and 9-bilayer films. It should be noted that the glass substrate surface gives 1.78 nm of roughness. This trend is similar to that observed in our previous work with LbL nanoparticles films. However, higher roughness values were found in AFM measurements for LbL films fabricated on mica surfaces.[13]

The enhancement of optical properties could be used for characterization of the fabricated LbL films with embedded gold nanoparticles and, in particular, they provide suitable substrates for SERS applications. The reference Raman spectra of the LbL film fabricated with 5 DAB dendrimer/Au was consistent with the known Raman spectrum of the dendrimer, with an overall low absolute intensity. The spontaneous Raman spectrum of 2-Naphtalenethiol powder is shown in Figure 4. The SERS of 2-NAT has been previously reported and the observed vibrational fundamentals in

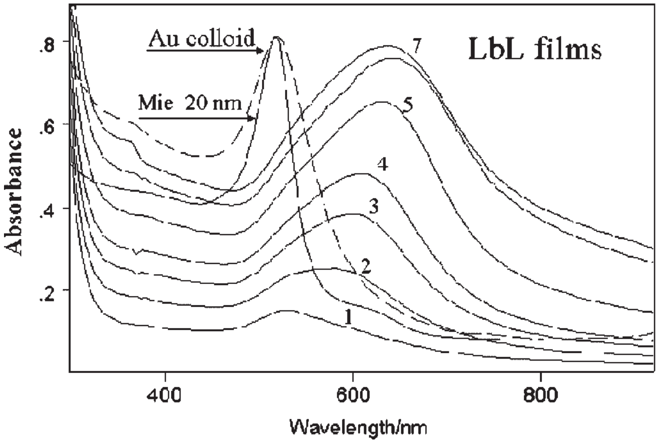

Figure 2.
Plasmon absorption spectrum of colloidal gold nanoparticles (dashed line), the result of Mie calculation for a 20 nm radius gold particle in water, and the plasmon absorption of LbL films with 1 to 7 bilayers of gold nanoparticles and DAB.

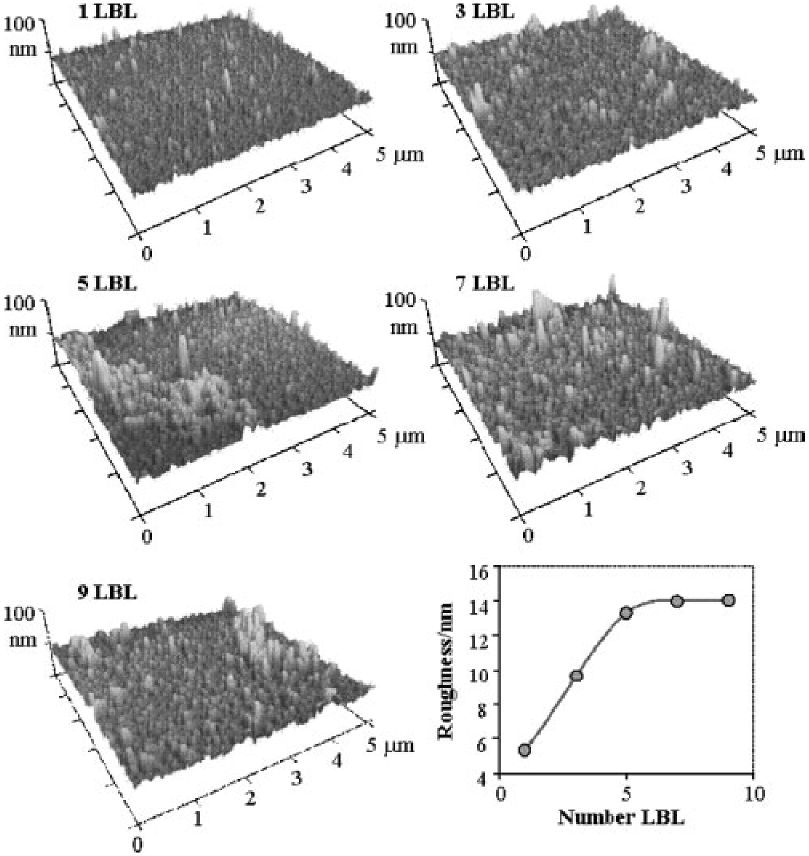

Figure 3.
AFM micrographs for LbL films of dendrimer/gold nanoparticles, with several numbers of bilayers, and the roughness (RMS) vs. number of deposited bilayers.

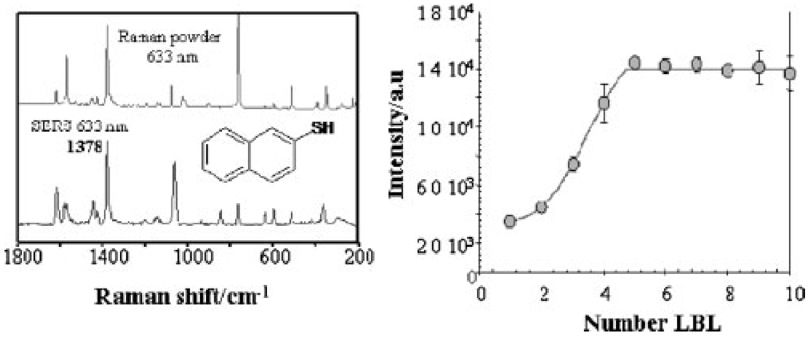

Figure 4.
Raman for a powder sample and SERS spectrum of 2-NAT deposited on 9-bilayer LbL film substrate. SERS intensity of 2-NAT vs. number of bilayers in the LbL film.

the spectrum have been assigned,[17] showing a slightly different vibrational intensity pattern when compared with the reference Raman spectrum of the powder, as can be seen in Figure 4. In addition, the SERS spectrum of 2-NAT lacks the strong Raman band due to S-H stretching mode (not shown in the Figure), clearly seen in the Raman spectrum of the powder. The latter is a characteristic of the chemical adsorption of thiols on gold.

2-NAT has been extensively characterized and successfully used as a probe molecule in previous references. In this work, we observed the same trend for the SERS signal obtained on DAB/Au nanoparticles films and this trend is shown in Figure 4. The measured SERS intensity represents an average SERS signal from 5 spectra. This average intensity when measured at the maximum of 1378 cm^{-1} band increases almost 70 fold when the multilayer film grows to contain 5 bilayers or more. From the fifth layer on, the average photon count stabilizes following an asymptotic behaviour seen in Figure 4, which follows the roughness behaviour shown in Figure 3. This illustrates the importance of substrate roughness in the SERS effect.

Conclusions

In this work, the layer-by-layer technique was successfully applied to the fabrication of unique substrates containing gold nanoparticles for optical enhancement. SERS and SERRS were demonstrated for the analyte (2-naphthalenethiol) cast onto the LbL film. The SERS effect followed the surface roughness, first increasing with the number of bilayers and then reaching a saturation value after a certain number of bilayers had been deposited. These LbL films containing gold nanoparticles with enhancing optical properties may offer the potential for developing selective SERS analytical substrates for ions and weak acids, by using architectures that enhance film adsorption of the probed analyte.

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