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Silver nanoparticle films for metal enhanced luminescence: Toward development of plasmonic radiation detectors for medical applications

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ABSTRACT

Research on new materials and devices for medical applications is of utmost importance. Here, we report on the growth of self-assembled Layer-by-Layer (LbL) silver nanoparticles (AgNP) films that were utilized to enhance the optically stimulated luminescence (OSL) emission, and increase the sensitivity of the radiation detectors. Multilayered chitosan/AgNP films were deposited over glass and aluminum substrates, with a top deposition of crystals with radiation-induced luminescence. Samples were irradiated with X-rays and the OSL intensities were recorded. The OSL intensity increases upon increasing the number of AgNP layers, so the detection sensitivity can be tuned accordingly. There is a remarkable OSL enhancement for films deposited over glass substrates, which is attributed to a plasmonic coupling of the X-ray induced luminescent centers and the plasmons at the nanoparticle film surface. However, AgNP films deposited on aluminum substrates led to insignificant OSL enhancement. Detection sensitivity can be tuned by controlling the number of deposited AgNP layers on the glass substrates, or by controlling the distance between the nanoparticle film and the aluminum substrates. These results indicate the potential application of silver nanoparticles films for development of more sensitive and miniaturized radiation detectors for medical applications.

1. Introduction

Research on new materials and devices for medical and biomedical applications has increased dramatically in recent years [1–6]. Great attention has been given to metal nanomaterials, due in large part to their unique optical properties [7–10]. Nanostructured gold and silver nanoparticle (AgNP) films have distinctive properties useful for technological applications in physics, chemistry, biology, and medicine. The plasmon resonance band presented by these films results from the interaction between the electric field of light and the conduction electrons at the nanoparticles surfaces [11]. Under such resonance conditions, a local electromagnetic field enhancement can be achieved [12], which is used to enhance physical phenomena like Raman scattering [13], and luminescent process like fluorescence, phosphorescence, and cathodoluminescence, among others [14–16]. Because the plasmon resonance band is highly sensitive to the medium's refractive index, noble metal nanoparticle films are also employed for the development of plasmonic sensors and biosensors [10,17,18].

The films are often produced by thermal evaporation but a large number of preparation methods have been developed such as chemical synthesis, lithography, laser ablation, etc. [19–21]. Here, we propose the use of the layer-by-layer (LbL) technique to grow AgNP films with plasmonic properties, by alternating nanoparticles and polyelectrolyte layers. Because our group is focused on the development of new advanced materials for radiation detection and dosimetry in medical applications such as radiation therapy and diagnosis, these AgNP films were employed as substrate to enhance optically stimulated luminescence intensity (OSL), thereby increasing the sensitivity of these radiation detectors and/or decreasing the lower limit detection of radiation dose.

OSL is a light emission process similar in principle to the well known thermoluminescence (TL), and involves light stimulation of an insulator/semi-conductor material previously exposed to

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ionizing radiation [22,23]. Electrons trapped in the band gap as a result of the ionizing radiation can be excited by light (usually blue); leading to an emission in the ultraviolet region [22,23]. The intensity of the overall photon emission is collected as a function of time, in the readout window ranging from $270 < \lambda < 370$ nm. The uniqueness of OSL is that radiation more energetic than the energy of the excitation can be detected, in contrast to other, non-dosimetric luminescence processes, such as photoluminescence [22]. The OSL signal consists of an exponential decay originated from the recombination of electron–hole pairs produced by the ionizing radiation. The OSL intensity (initial intensity and/or integral of the exponential decay curve) is proportional to the ionizing radiation dose previously absorbed by the material. Therefore, OSL is largely used for radiation detection and dosimetry in personnel radiation protection, and radiation assessment in medical procedures such as radiation therapy of cancer and exams involving ionizing radiation [22,23].

The growing need for cancer treatments that employ radiosurgery, intensity modulated radiation therapy (IMRT), and brachytherapy, which utilizes narrow photon beams and/or high dose gradients, requires the use of radiation detectors and dosimeters with high spatial resolution [24,25]. Thus, the utilization of miniaturized radiation detectors is required. Because the luminescence output of these radiation detectors depends on the mass and/or area of the material sensitive to radiation, a reduction in the size of the detector also diminishes its sensitivity [26]. Therefore, the use of plasmonic AgNP films could lead to enhanced OSL emission and consequently increase the sensitivity to radiation and enable the miniaturization of the detector.

This report outlines the synthesis and structure of the AgNP films deposited on two different substrates, describing the influence of the substrate, the effect of the number of AgNP layers, as well as the influence of the distance between the AgNPs and the substrate on the enhanced OSL emission of luminescent crystals. NaCl crystals were chosen because, among all alkaline halides, its F center absorption band, which is associated with the OSL emission, matches better with the plasmon resonance band of AgNP [27]. The observations are discussed in terms of enhancement of the OSL from NaCl crystals by surface plasmons in the nanoparticle films. Finally, the prospects for utilizing the enhanced emission for development of new OSL radiation detectors are discussed.

2. Materials and methods

2.1. Growth of the LbL multilayered films

The chemicals employed in the experiments were of analytical reagent grade and were used as received. Silver nitrate (99.8%) was provided by Cennabras, Sodium borohydride was purchased from Sigma. All the aqueous solutions were prepared with purified Milli-Q^{TM} water. AgNPs were produced by chemical reduction of silver nitrate [28]. To this end, a 2 mmol L^{-1} $AgNO_3$ aqueous solution was added to a freshly prepared 4 mmol L^{-1} $NaBH_4$ aqueous solution. The color of the system became immediately bright yellow, indicating the formation of a colloidal dispersion. To ensure the total reduction of the silver ions, the system was stirred vigorously for 12 h. UV–vis spectroscopy confirmed the formation of AgNPs as evidenced from the plasmonic absorption peak at 390 nm. The average size of the nanoparticles present in the freshly prepared colloidal dispersion was 30 nm with a -36 ± 2 mV zeta potential, as estimated by dynamic light scattering (DLS).

Thereafter, 0.1 wt.% chitosan was dissolved in acetic acid solution (pH = 4). The solution was filtered using a Millipore® membrane (0.45 μm pore size). Then, self-assembled films were produced by alternately depositing chitosan (positively charged) and AgNP (negatively charged) layers, over either glass or aluminum substrates (0.5 × 0.5 cm), by means of the LbL technique [29]. The glass substrates were previously cleaned using piranha solution and washed exhaustively with Mili-Q^{TM} water and acetone. Aluminum substrates were polished with sandpaper (1500 and 2000, 3 M, Brazil), pretreated in a KH_2PO_4/NaOH buffer solution (pH 7.5) that contained a nonionic surfactant, Span 20 (4.0×10^{-5} mol L^{-1}), for 5 min at 65 °C under ultrasound, and exhaustively washed with Milli-Q^{TM} water. The first and the last layers consisted of the positively charged polyelectrolyte (chitosan). The substrates remained for 20 min in each solution/dispersion. All layers were rinsed with Mili-Q^{TM} water for 5 min between each deposition step, in order to remove nonspecifically adsorbed chitosan/silver nanoparticles, and dried with N_2(g). This procedure was repeated several times to grow films with 3, 5 and 10 chitosan/AgNP bilayers. The films containing 3, 5, and 10 chitosan/AgNP bilayers were labeled as 3_AgNP, 5_AgNP, and 10_AgNP, respectively. At the end of the deposition of the chitosan/AgNP layers, both substrates became brownish yellow, indicating the growth of the films (Fig. 1E and F).

Poly(acrylic acid) (PAA) (0.2 wt.%) was dissolved at 60 °C in water. The Chitosan/PAA polymeric films were formed by alternating layers of chitosan and PAA on the aluminum substrates also by the LbL technique. Again, the substrates were immersed during 20 min in each solution, then rinsed with Mili-Q^{TM} water for 5 min and dried with N_2(g). This procedure was repeated several times to grow films with 1, 2, 4, and 6 chitosan/PAA bilayers.

Thereafter, 10 μL of a 0.02 mol L^{-1} NaCl solution (20 vol.% water and 80 vol.% acetone) was dropped over the deposited films and dried at 40 °C, to form the NaCl crystals responsible for the X-ray induced luminescence (OSL). The structure of these multilayered films is depicted in Fig. 1.

2.2. Characterization

UV–vis spectroscopy (transmission) was performed in a HP Vectra XM 5 Series 4. spectrophotometer. The presence of chitosan on the film surface was confirmed by attenuated total reflectance infrared spectroscopy (ATR-FTIR) (Shimadzu-IR prestige). Atomic force microscopy (AFM) was performed on a Shimadzu SPM 9600 microscope. Samples were irradiated in air using an X-ray tube (Magnun – Moxtek, USA) operating at 48 kVp and 0.2 mA. OSL was acquired using an OSL reader developed by the laboratory of Dosimetry and Nuclear Instrumentation of Universidade Federal de Pernambuco. Samples were excited with a blue LED with maximum emission at 470 nm; the detection system consisted of a photomultiplier and a Hoya U340 optical filter with transmittance in the 270–370 nm region. OSL signals were recorded in triplicate (three different samples). The error bars represent the experimental standard deviation for the three samples.

3. Results and discussion

Fig. 2A shows the UV–vis absorption spectrum (transmission) of the silver nanoparticle films grown over glass substrate. The plasmon resonance band characteristic of spherical AgNP can be detected at 420 nm for the film with 3 chitosan/AgNP bilayer. Upon increasing the number of deposited chitosan/AgNP bilayers there is an evident intensification of the plasmon resonance band, thereby evidencing the film growth. The addition of more chitosan/AgNP bilayers also causes a redshift of the plasmon band and an increase of the full width at half maximum (FWHM). The wavelength of the most intense peak was found at 437, 462, and 466 nm with a FWHM