

## TiO<sub>2</sub>/Au NANOPARTICLES ASSEMBLED IN PAH/PAA MULTILAYERS

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Nanotechnology has brought some new challenges, such as the development of quality synthesis processes regarding nanostructures based on inorganic and organic substances. Much attention has been given to nanoparticle (NP) synthesis due to their properties and unusual applications. The polyelectrolyte multilayer (PEM) processes is highlighted as a route to obtain NPs with specific sizes through colloidal methodology <sup>[1, 2, 3, 4]</sup>. The process of PEM involves the deposition of weak electrolytes from dilute aqueous solution based on electrostatic interactions of opposite polymer charges on specific substrates (glass, silicon). This work has as goal the study of sequential process L-b-L from nanoparticles deposition stabilized with opposite charge. The PEM assembly were formed by immersing substrates in polycation (PAH+TiO<sub>2</sub> (1:1)) and polyanion (PAA+Au (1:1)) solutions. The films were prepared by mix of [(PAH)<sub>7.5</sub>+(TiO<sub>2</sub>)<sub>5.0</sub>]+[(PAA)<sub>3.5</sub>+(Au)<sub>6.0</sub>]<sub>10</sub>, where 3.5, 5.0, 6.0 and 7.5 correspond the solution pH and 10 is number of bilayer. The mean size of TiO<sub>2</sub> and Au nanoparticles correspond 20 and 12nm, respectively. A XP-2 Ambios profilometer was used to measure films of thicknesses around 200 nm. X-Ray Diffraction (XRD) measurements were performed in a Shimadzu XRD 6000 diffractometer. The diffraction data were collected at room temperature in Bragg–Brentano  $\theta$ -2 $\theta$  geometry with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) with a scan range between 20° and 70°. The UV-visible absorption spectra of the described samples were captured on a Cary 5000 spectrophotometer in the range 300-800 nm. For Transmission Electron Microscopy (TEM), the nanoparticles multilayer films were deposited on polystyrene (PS) cover slips were embedded in an epoxy resin at 50 °C, after for 48 h the embedded specimens were cut in ultra-thin cross-sections using a diamond knife at 45° at room temperature and immediately mounted onto 200 mesh copper grids. Finally, they were observed using a FEI MORGAGNI 268D TEM operating at an accelerating voltage of 100 kV. Figure 1a displays X-ray diffractograms for TiO<sub>2</sub>/Au nanoparticles assembled in PAH/PAA multilayers, it is possible to confirm the existence of two structural crystalline for TiO<sub>2</sub> anatase and Au (0). The most representative Bragg reflections for TiO<sub>2</sub> and Au(0) were found at 25.32° and 38.18°, corresponding to the (101) and (111) indexed planes, respectively. The XRD pattern of the TiO<sub>2</sub> phase showed a sharp crystalline peak suggesting the presence of larger TiO<sub>2</sub> particles. Thin film optical extinction spectra of these structured films show the corresponding TiO<sub>2</sub> and Au plasmon resonances (see figure 1(b)). The TiO<sub>2</sub> and Au resonant plasmon peaks in structure at 395 and 537 nm suggests an effective value due to the large concentration <sup>[5]</sup>, which affects the dielectric composition of the PAA and PAH. An observed shift to 560 and 660 nm of this maximum represents the interference of multiple reflections within this single thicker film. The total thicknesses were measured around 210 nm, for 10 L-b-L this results present good concordance with TEM results (see figure 2). The TEM image shows the presence of TiO<sub>2</sub>/Au with a good distribution of these nanoparticles as consequence of nanoparticles stabilizations. The nanoparticles were used as a way to formed multilayers, allowing the manipulation of growth and spatial distribution.

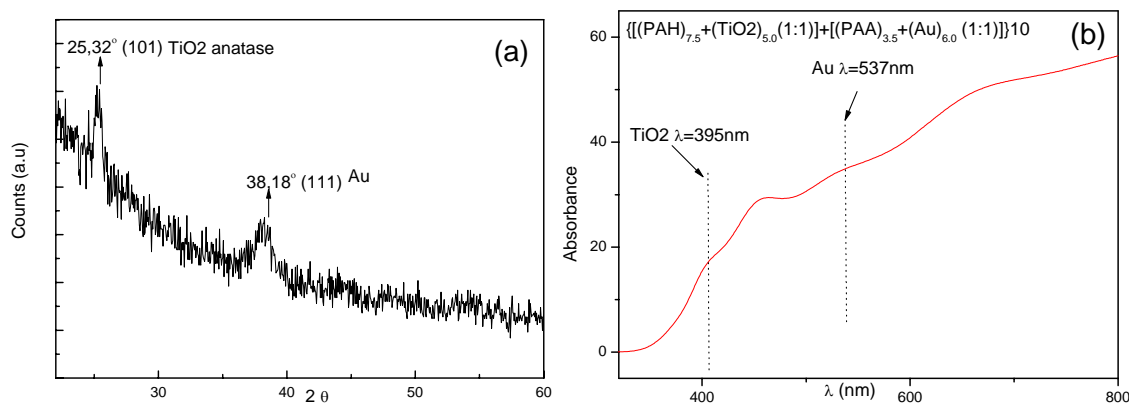


Figure 1 – TiO<sub>2</sub>/Au nanoparticles assembled in PAH/PAA multilayers analyzed by (a) XRD diffractograms, (b) UV-VIS:

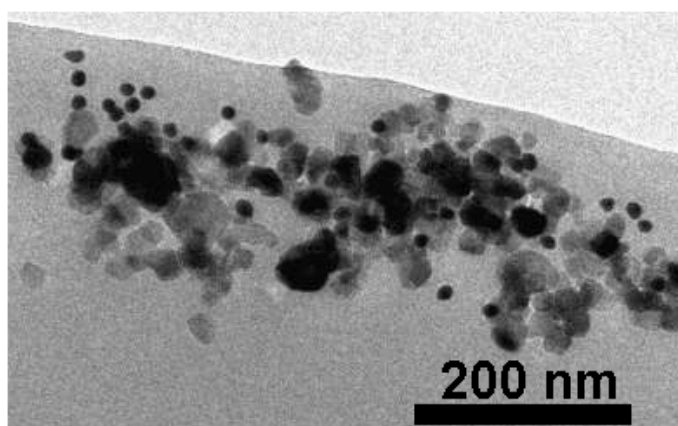


Figure 2 – TEM images for TiO<sub>2</sub>/Au nanoparticles assembled in PAH/PAA multilayers

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