Plasmonic particles organized in nanostructured polymer matrices

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New "bottom-up" fabrication techniques are now effectively explored for the production of nanostructured functional materials, and specifically for nanophotonic devices and metamaterials. Expected benefits from bottom-up approaches include assembling true three-dimensional metamaterials and synthetizing resonators with sizes appropriate for the optical range. Nanochemistry and self-assembly appear as interesting nanofabrication tools. Among the promising self-assembled systems are the diblock copolymers made of two molecular chains of distinct chemical nature linked together, which present solid state spontaneous structures with long-range order and tunable characteristic sizes between 10 and 50 nm. In particular, alternating lamellar and hexagonally-ordered cylindrical structures are described in many systems. These are, however, organic materials exhibiting moderate susceptibilities and low optical constant contrast. Therefore, in their native state, they should be considered essentially as 'optically neutral' templates, used to spatially organize 'active' entities. Our work focuses on nanoparticles presenting plasmonic resonances as these 'active' entities. Recent developments in the wet chemistry synthesis of plasmonic nanoparticles have allowed for significant improvements in terms of control of composition, surface chemistry, properties and size. In our study, gold nanoparticles are incorporated in polymer matrices with different nanostructures. We wish to correlate the nature, density and spatial organization of the nanoparticles with the optical properties of the nanocomposite materials.

Two different experimental systems are studied. In the first system, 15-nm diameter gold spheres are dispersed randomly in poly(vinyl alcohol) thin films deposited on silicon wafers or glass plates. Volume fraction of gold is varied from 1 to 30% and film thickness from a few nanometers to 300 nm. The structure of the films is studied by atomic force microscopy (Fig. 1) and X-ray reflectivity. In the second system, 10-nm diameter gold nanoparticles are incorporated in the 18-nm thick poly(acrylic acid) layers of the ordered lamellar phase of a poly(styrene)-block-poly(acrylic acid) copolymer. Volume fraction of gold is varied in both thin films on silicon wafer and bulk samples. Small-angle scattering and reflectivity of X-rays, atomic force and electron microscopies (Fig. 2) are used to get a detailled structural description of the nanostructured composites and validate the control of the density and organization of the nanoparticles. The optical properties of the nanocomposites are studied using spectrophotometry and spectroscopic ellipsometry.

The refractive index results, in the visible and infra-red spectral regions, are confronted to effective medium models. As shown in Fig. 3, the classical Maxwell-Garnett model shows an important discrepancy with the measured results, and we will show how the situation can be improved taking into account the appropriate dispersion function for the nanoparticles, as well as substrate effects.

Similar systems using rod-shape gold nanoparticles, developments towards unsual optical properties at high gold fraction, and search for experimental evidence of anisotropic optical properties will also be described in this presentation. The conclusions will allow discussing the use of self-assembly for fabrication of new nanostructured optical materials.

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Figures

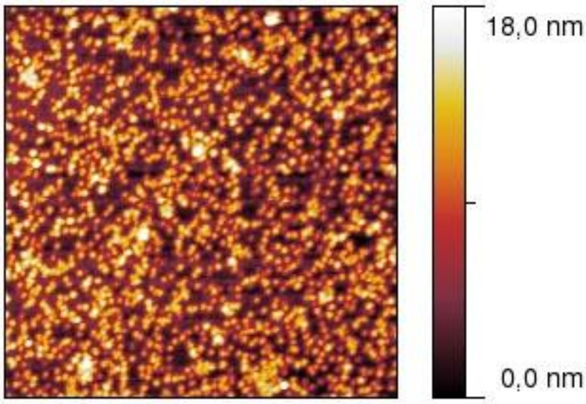

Fig. 1: 2 x 2 µm atomic force microscopy topography (upper-view) image obtained on a thin composite film of gold nanoparticles randomly dispersed in poly(vinyl alcohol).

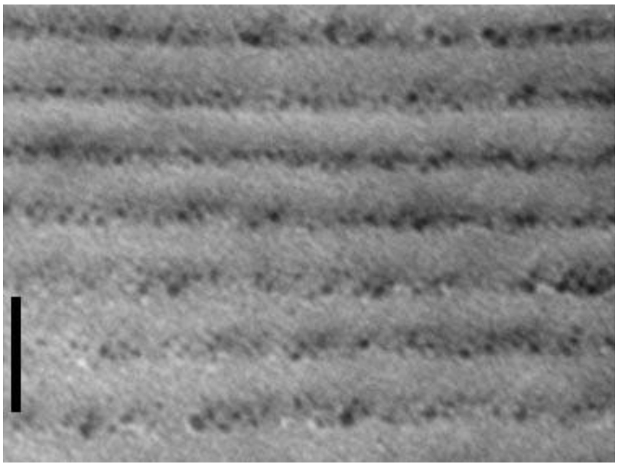

Fig. 2: Transmission electron micrograph (side view) of an ordered lamellar composite film of gold nanoparticles and poly(styrene)-b-poly(acrylic acid) copolymer. Bar = 50 nm.

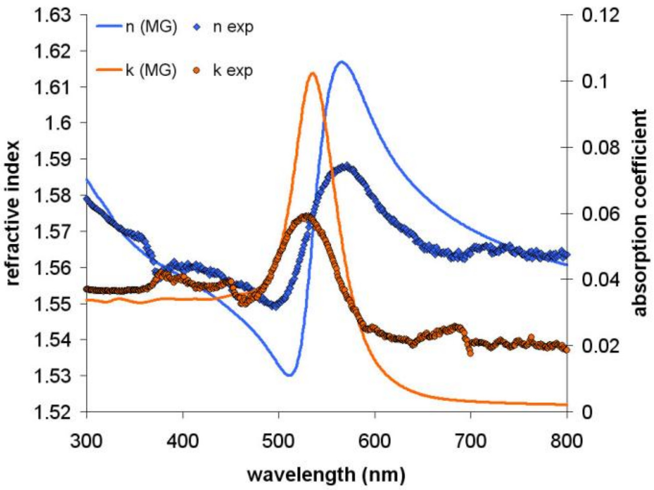

Fig. 3: Optical index n and absoption coefficient k, determined by analysis of spectroscopic ellipsometry data, of a 77nm-thick composite film of gold nanoparticles randomly dispersed in poly(vinyl alcohol), as a function of the wavelength. The discrepancy with a simple Maxwell-Garnett model (full lines) is apparent and motivates the inclusion of other effect such as electron confinement and substrate effects.