Self-assembly as fabrication tool: Plasmonic particles organized in nanostructured polymer matrices

C. Tallet, J. Vieaud, O. Merchiers, A. Kumar, F. Nallet, A. Aradian and V. Ponsinet

Centre de Recherche Paul Pascal UPR 8641, Université Bordeaux 1 – CNRS
115, avenue Schweitzer, 33600 Pessac, France
Fax: + 33–556845600; email: ponsinet@crpp-bordeaux.cnrs.fr

Abstract

We study the organization and the optical properties of gold nanoparticles self-assembled in nanostructured polymer matrices. Both disordered and ordered nanocomposites are studied, and a detailed description of their structure is obtained using different scattering and microscopy techniques. Spectroscopic ellipsometry is used to determine the refractive indices, which are then confronted to effective medium models. This work aims at demonstrating the potential of self-assembly as fabrication tool for new optical materials.

1. Introduction

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 [1]. 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.

2. Nanocomposite structures

We study two different experimental systems. In the first system, 14-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 type of systems, spherical gold nanoparticles are selectively incorporated in the lamellar domains of block copolymers. In one system, water-dispersed gold nanoparticles are introduced within the poly(acrylic acid) layers of the ordered lamellar phase of a poly(styrene)-block-poly(acrylic acid) copolymer. In the other system, THF-dispersed and polystyrene-coated gold nanoparticles are incorporated in the poly(styrene) layers of the ordered lamellar phase of a poly(styrene)-block-poly(methyl methacrylate) copolymer.
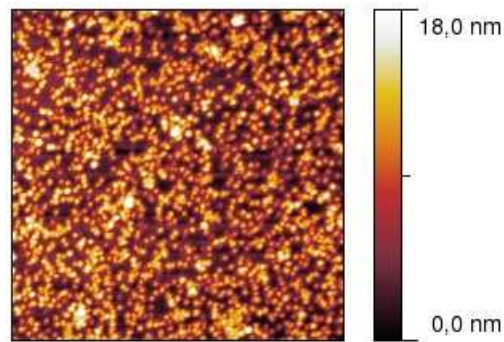
Fig. 1: 2 x 2 µm atomic force microscopy topography (upper-view) image obtained on a thin composite film of gold nanoparticles randomly dispersed in poly(vinyl alcohol).

Volume fraction of gold is varied in both thin films on silicon wafer and bulk samples. Atomic force and electron microscopies (Fig. 2), as well as small-angle scattering (Fig. 3) and reflectivity of X-rays, are used to get a detailed structural description of the nanostructured composites and validate the control of the density and of the lamellar organization of the nanoparticles. In particular, the differences in the small-angle scattering signals between the neat copolymer lamellar phase and the composite are analyzed as due to the nanoparticles, which leads to estimation of the gold volume fraction up to 30% within the chosen lamellar domains.
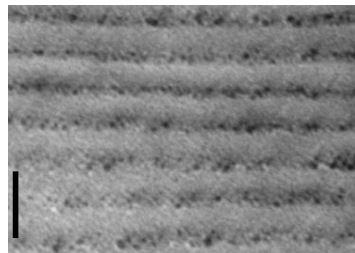

Fig. 2: Transmission electron micrograph (side view) of an ultramicrotomed sample of ordered lamellar composite composed of 10nm-diameter gold nanoparticles and poly(styrene)-b-poly(acrylic acid) copolymer. Bar = 50 nm.
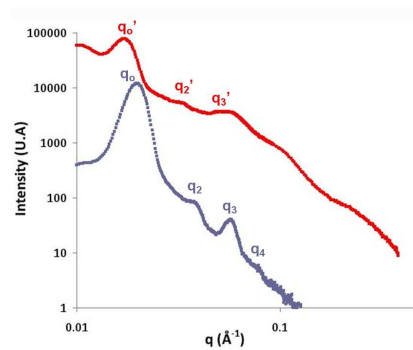

Fig. 3: Small-angle X-ray scattering intensity as a function of scattering wavevector for pure lamellar poly(styrene)-block-poly(methyl methacrylate) copolymer (lower curve) and composite of 6-nm diameter gold nanoparticles and poly(styrene)-block-poly(methyl methacrylate) copolymer (upper curve). The successive bumps are the lamellar structure factor peaks, labelled with their order. Lamellar periods are 32 nm and 36 nm respectively, with a shift attributed to the volume occupied by the gold nanoparticles within the structure.

3. Optical properties

The optical properties of the nanocomposites have been studied using spectrophotometry and ellipsometry. Spectroscopic ellipsometry measurements have been performed in the UV-visible range with different angles of incidence, in order to extract the complex refractive index of the films. The plots of

the refractive index n and the absorption k of the films as a function of the wavelength λ are shown in the Figure 4. The experimental data have been compared with effective medium models. We consider, in particular, the Maxwell-Garnett model, which simply relates the refractive index and the volume fraction f of inclusions of permittivity ε_{Au}, in a matrix of permittivity ε_m:

$$n + ik = \sqrt{\varepsilon_{eff}} \qquad (1)$$

$$\varepsilon_{eff} = \varepsilon_m + 3f\varepsilon_m \frac{\varepsilon_{Au} - \varepsilon_m}{\varepsilon_{Au} + 2\varepsilon_m - f(\varepsilon_{Au} - \varepsilon_m)} \qquad (2)$$

In the case of thin composite films of gold nanoparticles randomly dispersed in poly(vinyl alcohol), the global shape and the spectral position of the plasmon resonance are well reproduced, when taking into account the appropriate dispersion function for the nanoparticles (Fig. 4). The discrepancy in the resonance amplitude could be due to substrate effects and/or some particle aggregation.
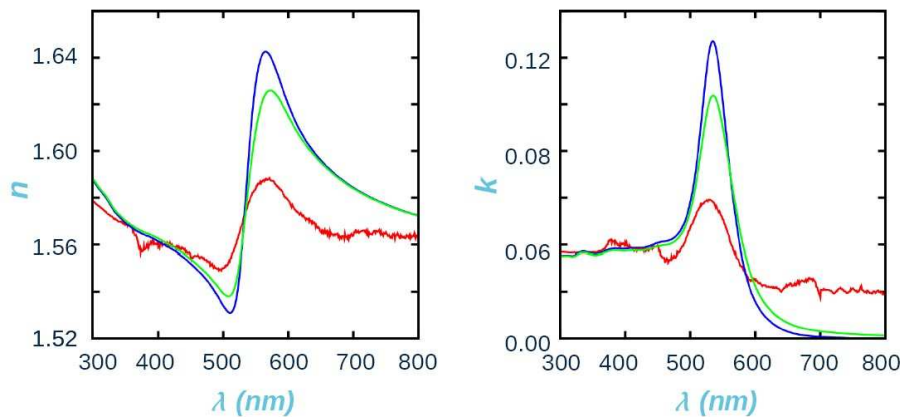

Fig. 4: Experimental n and k (red lines) of a composite film (e=49 nm) of gold nanoparticles (f=1.8%) and poly-vinylalcohol, extracted from the spectroscopic ellipsometry data. Comparison with Maxwell-Garnett models without (blue line) and with (green line) electron confinement effect.

In the case of ordered nanocomposite of gold nanoparticles and lamellar copolymers, the optical study aims at extracting the gold content, which can be confronted to the results of the structural study. On the other hand, our efforts have also been aimed at demonstrating the existence of anisotropic optical properties.

4. Conclusion

We study the relation between nanostructure and refractive indices for self-assembled nanocomposites of gold nanoparticles organized in polymer matrices. Both disordered and lamellar systems are studied with structural scattering and microscopy techniques and with spectroscopic ellipsometry. In these nanocomposites, self-assembly is shown to provide some control of the optical properties.

Acknowledgements

References

[1] V. Ponsinet, A. Aradian, P. Barois, S. Ravaine, Self-assembled and nanochemistry techniques for the fabrication of metamaterials in *Handbook Applications of Metamaterials,* F. Capolino Ed., CRC Press, Taylor and Francis, 2009, chap. 32.