

Plasmonic nanoparticles ordered in self-assembled materials

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ABSTRACT

New “bottom-up” fabrication techniques are now effectively explored for the production of nanostructured functional materials, and specifically for nanophotonic devices and metamaterials (1). Expected benefits from bottom-up approaches include assembling true three-dimensional metamaterials and synthesizing 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 diblock copolymer 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.

Keywords: block copolymer, gold nanoparticles, nanocomposite, plasmonic coupling, ellipsometry

1. EXPERIMENTAL

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. Ordered nanocomposites are obtained by incorporating gold nanoparticles in the layered domains of ordered block copolymer lamellar phases. In a first 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) PS-PAA copolymer (2). In a second system, polystyrene-coated gold nanoparticles are incorporated in the poly(styrene) layers of

the ordered lamellar phase of a poly(styrene)-block-poly(methyl methacrylate) PS-PMMA copolymer. In a third system, gold nanoparticles are synthesized *in situ* via the thermal reduction of gold salts incorporated within the poly(methyl methacrylate) layers of the ordered lamellar phase of a PS-PMMA copolymer. The volume fraction of gold is varied in both bulk samples and thin films on silicon wafer.

2. RESULTS AND DISCUSSION

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2.1 Structural study of the nanocomposites

Small-angle scattering and reflectivity of X-rays, as well as atomic force and electron microscopies are used to get a detailed structural description of the nanostructured composites and validate the control of the density and of the 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 presence and organization of gold nanoparticles within the structure. For example, as shown in Figure 1, both pure PS-PMMA block copolymer and nanocomposite made of polystyrene-capped 5nm-diameter gold particles and PS-PMMA block copolymer present structure factor peaks revealing a lamellar organization. The shift Δq_0 of the first lamellar peak corresponds to a real-space lamellar period increase from $D_0=32.0\text{nm}$ without particles to $D_0=34.6\text{nm}$ in their presence. This shift, if simply attributed to the volume occupied by the particles embedded in the PS blocks, provides a way to estimate their quantity: with this hypothesis, we find that the nanoparticles present 13% of the volume of the composite domains containing PS and nanoparticles, which amounts to 7,5% of the total sample volume. Both the small-angle scattering results and TEM observations (cf. Figure 2) show the high degree of order of these bulk nanocomposites.

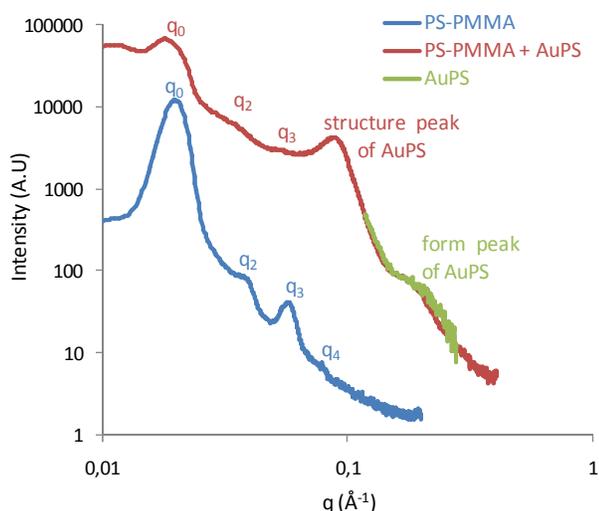


Figure 1. Small-angle X-ray scattering as a function of scattering vector for pure lamellar PS-PMMA copolymer (blue curve), neat PS-capped 5nm-diameter gold particles (green curve) and nanocomposite (red curve).

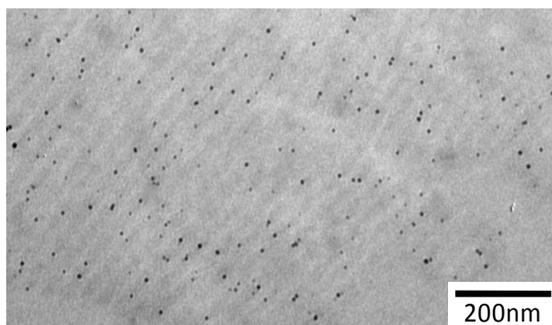


Figure 2. Transmission electron micrograph of an ultramicrotomed cut of a sample of ordered lamellar composite composed of AuPS and PS-PMMA. The gold nanoparticles appear as small black dots and are ordered in the dark bands, which correspond to the PS block.

2.2 Optical study of the nanocomposites

The optical properties of the nanocomposites are studied using spectrophotometry and spectroscopic ellipsometry. The experimental refractive index results are extracted from the spectroscopic ellipsometry data. An example of the *in situ* synthesized nanocomposites is shown on the Figure 3 (red lines), together with the experimental data of the pure block copolymer PS-PMMA (orange lines).

The experimental data of the nanocomposite are compared with a modified Maxwell-Garnett model (green lines) taking into account the finite size of the gold nanoparticles and a distribution of anisotropy of polarisabilities of the particles, which accounts for some degree of plasmonic coupling between them. These comparisons allow assessing the presence of plasmonic coupling between nanoresonators and relating them to their structural organization.

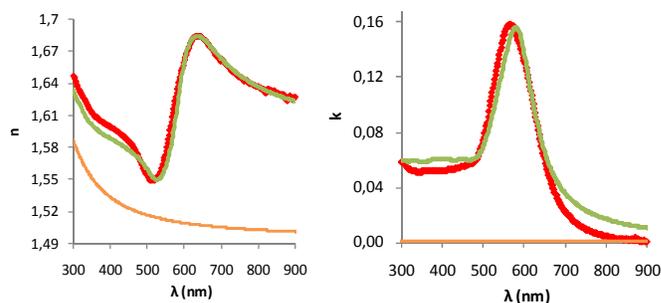


Figure 3. Optical index n (left) and absorption coefficient k (right) of a composite thin film of thickness of 290 nm of PS-PMMA and gold nanoparticles of gold volume fraction 2.8% (red lines), compared with a effective medium model (green lines) and the experimental data for the pure PS-PMMA copolymer (orange lines)

The volume fraction of gold nanoparticles in thin films is also varied from 1% to 10%. The plasmon peak position increases with the density of gold, due to the plasmonic coupling between the gold nanoparticles.

CONCLUSIONS

Spherical plasmonic gold nanoparticles are introduced in lamellar block copolymer matrices via different methods in both bulk and thin films. The structural properties are studied by small-angle scattering and reflectivity of X-rays, atomic force and electron microscopies. Optical properties are extracted from spectroscopic ellipsometry measurements. This methodology allows assessing and studying the plasmonic couplings between the nanoparticles in self-assembled systems. It can be further applied to other nanocomposites, for example with plasmonic nanorods or more elaborated nanoparticles.

ACKNOWLEDGEMENT

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