Ligand-free synthesis of gold nanoparticles incorporated within oriented cylindrical block copolymer films : towards optical metamaterials

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Abstract

We report a method to incorporate non-functionalized gold nanoparticles (AuNPs) in oriented cylindrical phases of poly(styrene)-b-poly(vinylpyridine) (PS-b-PVP) block copolymers, perpendicular to a substrate. The combination of AFM, TEM, GISAXS and spectroscopy allows complete characterization of the nanocomposites. AuNPs are produced by the ultra-sound reduction of a gold salt in the copolymer solution, prior to the deposition of the films by spin-coating. The AuNPs are found to be located within the PVP cylinders exclusively. The seeded-growth of these pre-formed AuNPs by a further ultra-sound treatment produced plasmonic AuNPs (up to d =10 nm). For perpendicular cylinders, the PVP domains are swollen without any change in their orientation. Ellipsometric optical properties of these plasmonic AuNPs embeded into oriented cylinders show a definite extinction in reflectivity at a precise energy and incidence angle.

1. Introduction

Hybrid nanocomposites including noble metal nanostructures have gained great interest due to their unique optical, properties.[1] They are essential elements of nanophotonics which explore the possibility of modulating light propagation with a very small amount of matter using nanoscale phenomena. The occurrence of plasmons at metal/dielectric interfaces is indeed one of the key phenomena used in nanophotonics towards the fabrication of nanostructured noble metal–dielectric materials and surfaces. In this context, increasing interest focuses on the incorporation of gold nanoparticles (AuNPs) into block copolymer (BCP) matrices, which allows the combination of the localized surface plasmon resonance[2] of the AuNPs with the ability of the BCP to self-assemble into well-organized 3D nanostructures,[3] such as lamellae, cylinders or spheres. Here, we report on the formation of PS-b-PVP films organized in cylindrical mesophases and containing AuNPs, a geometry akin to hyperbolic ones which are very promising for providing unusual wave propagation.[4] The incorporation of AuNPs in polymer was performed by a two step procedure: (1) the AuNPs were produced by sonication of the solution prior to (2) casting of films. This synthesis method avoids adding extra-species such as a ligand or a reducing agent in the solution. We also proved the efficiency of the seeded-growth method to obtain larger AuNPs exhibiting plasmon resonance. The processes of sonication and spin-coating of a gold-containing copolymer solution allow for an easy and controllable formation of self-organized plasmonic hybrid films. The full characterization of the perpendicular of PS-b-P4VP and PS-b-P2VP was achieved by Atomic Force Microscopy(AFM), Transmission Electron Microscopy (TEM) and Grazing-Incidence Small-Angle X-ray Scattering (GISAXS) experiments. First optical characterization of these films was achieved by variable angle spectroscopic ellipsometry. In particular, p-polarized visible radiation incident on the films containing the plasmonic nanoparticles presents an extinction accompanied by a phase jump at a specific wavelength and incidence angle. Furthermore, these wavelengths and angles were found to depend on the nanoparticle size.

2. Experimental

2.1. Materials

Two different diblock copolymers of poly(styrene)-block-poly-(4-vinylpyridine) (PS-b-P4VP) and one diblock copolymer of poly(styrene)-block-poly(2-vinylpyridine) (PS-b-P2VP) were purchased from Polymer Source, Inc., and used as received. Gold(III) chloride ($AuCl_3$, 99.99%) and sodium bromide (NaBr) were purchased from Sigma Aldrich and used as received.

2.2. Film preparation

The PS_{48}-b-$P4VP_{25}$ and PS_{27}-b-$P4VP_7$ copolymers were dissolved in a mixture of toluene/tetrahydrofurane (THF) in order to yield 1 wt% solutions. These solutions were spin-cast at 2000 rpm for 1 minute to yield ~100 nm-thick films. The residual solvent in the spin-cast films was removed by placing the films in vacuum for 2 h. For some samples, solvent annealing in vapors of a mixture chloroform/ethanol (10 : 1) was performed for 1 min at 60°C. The films were then quickly removed from the vapor chamber and dried with nitrogen and finally placed in vacuum for 2 h.

2.3. In situ formation of gold nanoparticles (AuNPs) by sonication

Copolymer solutions were prepared as described above and then mixed with a 0.1 M $AuCl_3$ solution in toluene in order to obtain various gold/pyridine molar ratios (from Au/Pyr = 0.1 to Au/Pyr = 5.5). The solution was protected from light and stirred overnight. AuNPs were synthetized by sonication in a bath (Elmasonic P30H, 37 kHz, 120W) for a given time (from 1 to 10 min) at room temperature. The films were then spin-cast as described above. Seeded growth kinetics were studied by adding more gold salt (Au/Pyr = 0.2, each addition) in the copolymer solution containing the previously formed AuNPs (initially with a ratio of Au/Pyr = 0.5). The mixture was sonicated again to grow metallic gold on the surface of the AuNPs. This process of gold addition/sonication was repeated four times, in order to get AuNPs bigger in size.

2.4. Characterization

Atomic Force Microscopy, Transmission Electron Microscopy and GISAXS were used as described in Ref. 5.

3. Results and Discussion

Addition of a gold salt ($AuCl_3$) in the PS_{27}-b-$P4VP_7$ copolymer solution and further sonication leads to the formation of AuNPs as demonstrated by UV/visible spectroscopy, evidencing the decrease of the Au(III) peak at 325 nm. TEM image (Fig. 1) of a dropcast film from the solution shows that the AuNPs formed by sonication were confined inside the P4VP domains, due to the affinity between gold and the pyridine group of P4VP. The average NP diameter determined by image analysis on the TEM micrographs was found to be 2–3 nm and could reach up to 10 nm after the seeded growth process was used. The conservation of the perpendicular orientation of cylinders when AuNPs are incorporated in the PS27-b-P4VP7 films was evidenced by AFM, TEM and GISAXS experiments, leading to an anisotropic structure with plasmonic features localized in perpendicular cylinders. Only a moderate increase of the cylinders diameter due to AuNPs incorporation was measured. At different growth steps of the gold nanoparticles by sonication, the films were studied using variable angle spectroscopic ellipsometry. The information contained in the ellipsometry data can be represented as the (Ψ, Δ) angle pair of the complex ratio of p and s polarized reflectivities $r = r_p/r_s = \tan(\Psi)\_\exp(i\Delta)$. The ellipsometric data of the films, show the existence of a cancellation of the ellipsometric intensity angle Ψ, while the ellipsometric phase angle Δ jumps abruptly of more than 180° at a given incidence angle and photon energy. In the example shown in Fig. 2, for the film with the AuNPS obtained by two growth cycles (AuNP diameter of 7 nm), this specific behavior occurs at an incident light energy of 2.55 eV and an incidence angle of Θ = 65°.

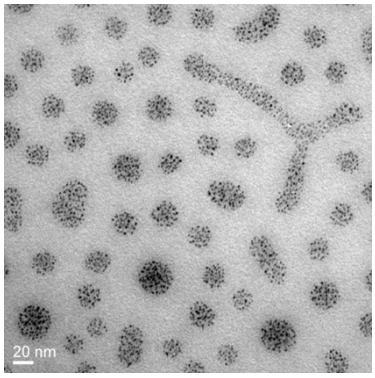

Fig. 1 : TEM picture proving AuNPs insertion in oriented polymer cylinders

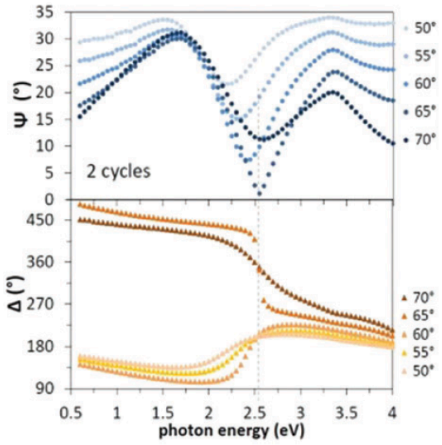

Fig. 2 : Annulation of Ψ and a jump in Δ are visible for an energy of 2.55 eV (λ = 486 nm) and an angle of incidence of Θ = 65°.

4. Conclusions

We produced anisotropic films of the block copolymer PS-b-PVP containing in situ synthetized plasmonic AuNPs of controlled sizes between 2 nm and 4 nm aligned along oriented cylinders. This method offer a very controlled way for easily inserting dense population of small sized AuNPs (2 nm) in an organic nanostructured film. Finally, we demonstrate promising optical properties of these hybrid films since they exhibit a sharp extinction accompanied by a phase jump at a specific wavelength and incidence angle.

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