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In situ Formation of Plasmonic Gold Nanoparticles in Ordered Block Copolymer Films

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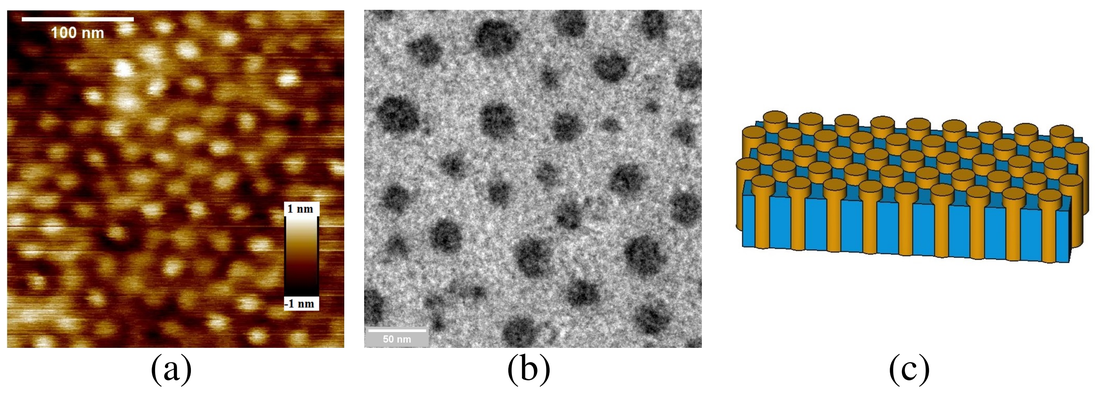
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Context

Metamaterials are of current interest for their unique optical properties. Although they are traditionally obtained by lithography, bottom-up ways of fabrication are now investigated for a precise nanometric control of the structure, through self-assembly and nanochemistry. To this end, organized films containing gold nanoparticles are widely studied for they combine the controlled structure of a film to the plasmonic properties of these nanoparticles.
We report here the *in situ* formation of gold nanoparticles (AuNPs) in a polystyrene-*block*-poly(vinylpyridine) (PS-b-PVP) copolymer solution, then cast as AuNP containing ordered films.
By use of an appropriate solvent, casting a block colymer solution can form films of oriented cylinders (perpendicular or parallel to the substrate). The addition of gold salt $_Au(III)chloride(AuCl_3)$- followed by ultra-sound treatment before casting the film gives birth to spherical AuNPs (2-3 nm in size) located, after deposition, inside the cylinders. For parallel cylinders, AuNPs are found to re-direct them to a quasi-perpendicular orientation, while no major perturbation is found for the perpendicular cylinders. Larger spherical AuNPs (3-4 nm) exhibiting a plasmon resonance are also obtained by successive additions of gold salt to the AuNPs and locate equally inside the cylinders after casting the film.
This method of *in situ* insertion of AuNPs in patterned films provides nanocomposite materials with plasmonic properties and opens new ways for the preparation of metamaterials.

AuNPs in perpendicular cylinders

- Solution of PS_{25}-b-$P4VP_7$ in non-selective mixed solvent tol/THF (80:20) spin-coated onto a silicon substrate ➞ cylinders oriented normal to the substrate

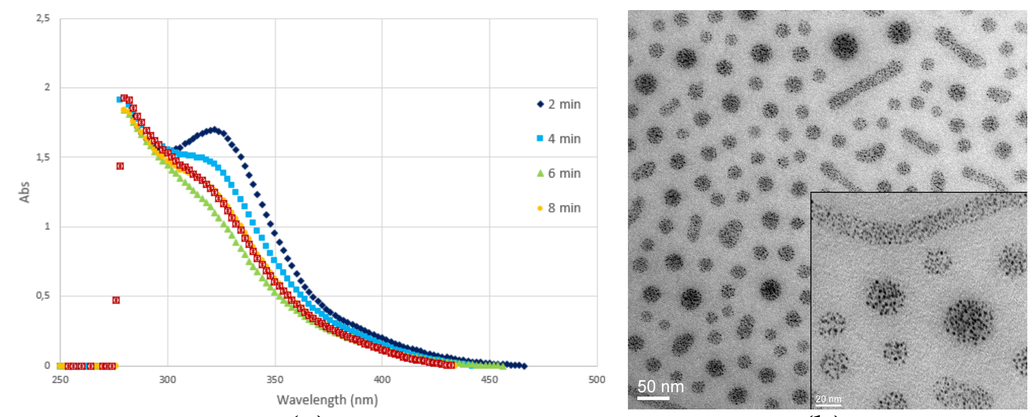


(a) (b) (c)

Figure 1: *a/ AFM height picture and b/ TEM picture of PS-b-P4VP cylinders oriented normal to the silicon substrate after spin-coating. The cylinders have a 2D-hexagonal organization and their average diameter is 40 nm; c/ 3D-illustration of the cylinders of PVP (orange) in the PS matrix (blue) with an orientation normal to the substrate and a hexagonal organization.*

➠ **Perpendicular order without gold addition**

- Gold salt ($AuCl_3$) addition to the solution, previous to casting, followed by sonication, then spin-coating ➞ reduction of the gold salt into AuNPs



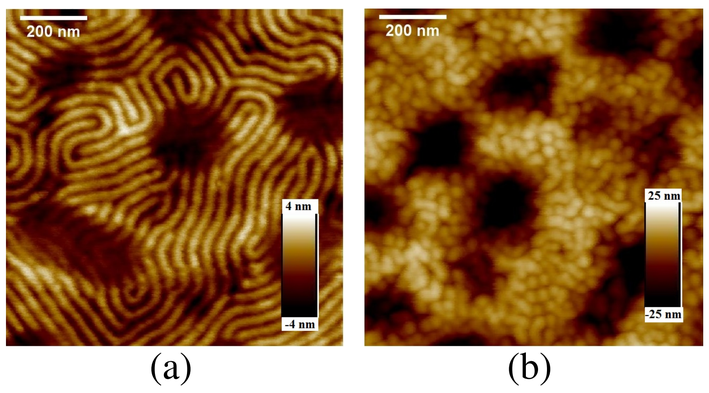
(a) (b)

Figure 2: *a/ UV-visible spectra showing the decrease of the gold salt peak over the sonication; b/ TEM picture of AuNPs formed by sonication and confined in PS-b-P4VP cylinders oriented normal to the substrate. The AuNP size is around 2 nm (see inset). The amount of gold per pyridine is 5 equivalents.*

➠ **Formation of AuNPs (diameter 2-3 nm) located inside the cylinders**

Re-orientation of parallel cylinders

- Solution of PS_{34}-b-$P2VP_{18}$ in chloroform ($CHCl_3$), spin-coated onto a silicon substrate + annealing in $CHCl_3$ vapors ➞ cylinders parallel to the substrate
- $AuCl_3$ addition before spin-coating and annealing in $CHCl_3$ vapors ➞ reduction of the gold salt into AuNPs + re-orientation of the cylinders



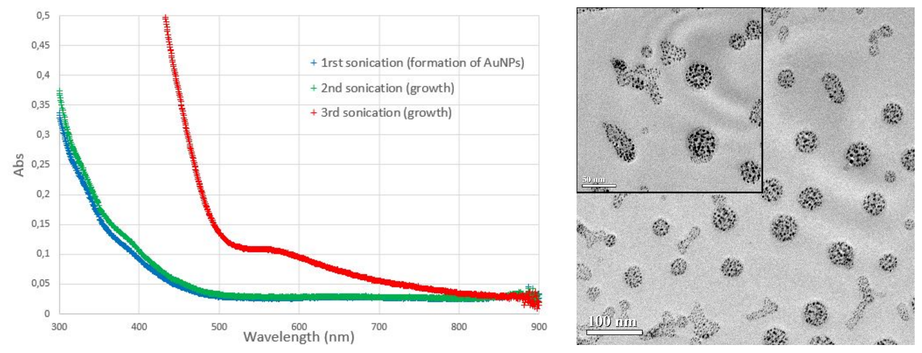
(a) (b)

Figure 3: *AFM height pictures of deposited and annealed PS-b-P2VP film a/ without and b/ with AuNPs formed by sonication. The presence of the AuNPs inside the cylinders triggers their re-orientation almost normal to the substrate.*

➠ **Loss of the cylinder orientation while adding the AuNPs. Not seen with perpendicular cylinders**

Formation of plasmonic AuNPs

- Further addition of $AuCl_3$ and sonication over a AuNPs/PS-b-P4VP solution in successive steps ➞ growth of the AuNPs



(a) (b)

Figure 4: *a/ UV-visible spectra: after the formation of AuNPs (blue) and the first addition/sonication (green), no plasmon is noticed. The plasmon peak (around 560 nm) appears after the second addition/sonication ; b/ TEM picture of the film for a AuNPs/PS-b-P4VP solution after formation and growth of the AuNPs. The AuNps are larger (3-4 nm, see inset), which explains their plasmon resonance and still located inside the cylinders. The amount of gold by pyridine is 10 equivalents and each growth step adds 2 more equivalents (for a total of 2 steps).*

➠ **Formation of larger AuNPs (diameter 3-4 nm) located inside the cylinders and exhibiting a plasmon resonance**

Conclusions and Perspectives

- Formation of AuNPs in copolymer solution by utra-sound treatment and insertion in ordered and oriented cylinders in copolymer films
- Re-orientation of the parallel cylinder to quasi-perpendicular ones by addition of the AuNPs
- Formation of plasmonic, spherical AuNPs (3-4 nm) by a succession of gold salt additions
- Simple methodology for the fabrication of nanocomposite materials exhibiting plasmonic properties
- Quantification of the optical properties for these materials

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