

Metallo dielectric Photonic Crystals Based on Diblock Copolymers

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Propagation of light inside a material is intimately linked with the response of the material to optical stimulus. The interaction between the optical field and the material is represented by the index of refraction. Photonic crystals are structures in which the refractive index is a periodic function of space. In a periodic refractive index structure, forbidden frequency bands can occur for electromagnetic waves. Photonic band gap materials facilitate the coherent localization of light which has resulted in novel quantum optical phenomena as well as important technological applications such as zero threshold microlasers, single-mode LED's and all-optical transistors[1-3]. The realization of photonic crystals for optical or near infrared frequencies is still a major technological challenge requiring new approaches for refractive index engineering. Whereas most of the current work is performed by lithographic methods, self-assembling structures hold the promise of relatively inexpensive, large-sized photonic band gap materials in the visible and near IR. Fink et al. [4] intro-

duced the idea of using self-assembled diblock copolymer structures as photonic materials. Unfortunately, because of the low dielectric contrast in virtually all block copolymers, the photonic gaps are small and non-overlapping.

In this contribution we show that periodic, metallo dielectric structures can be obtained by self-assembly of diblock copolymers and surface tailored gold nanocrystals. Selective sequestering of the nanocrystals within one domain increases the dielectric contrast between adjacent domains. By choosing small particle sizes and grafting poly(styrene) to the surface of the nanocrystals, it is possible to homogeneously sequester the nanocrystals within the target domain. The resulting photonic structures show high reflectivity in the visible regime, indicating that absorption losses can be diminished in periodically ordered microstructures. The outline of this approach is schematically shown in Figure 1.

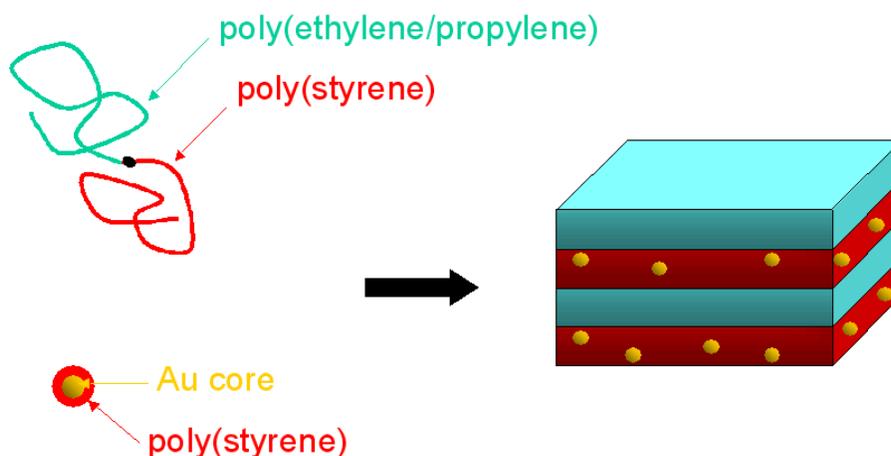


Figure 1: Schematic of the block copolymer template approach. Surface tailoring of nanocrystals allows preferential sequestering during self-assembly process.

As a model system to study the feasibility of our concept, we investigated a poly(styrene-*b*-ethylene/propylene) (PS-*b*-PE/P) diblock copolymer with a molecular weight of the respective blocks of 400 kg/mol and an index of polydispersity PDI=1.04. Transmission Electron Microscopy (TEM) revealed that the solution cast polymer self-assembles into a lamellar morphology with a lamellar spacing of about 200 nm. Since the wavelength for maximum reflectance at normal incidence is given by $\lambda = 2[L(\epsilon_{PS}d_{PS} + \epsilon_{PE/P}d_{PE/P})]^{1/2}$, where ϵ is the dielectric constant, $L=d_{PS}+d_{PE/P}$ the periodic spacing and d the layer thickness of the respective domain, a lamellar thickness of 200 nm is large enough to exhibit photonic characteristics in the visible regime[5]. Surface modified gold nanocrystals were synthesized by phase transfer reduction of $[AuCl_4]$ in the presence of thiol ligands. The mechanism of this reaction has been described elsewhere[6]. In order to preferentially sequester these clusters within the higher refractive poly(styrene) domain, we used thiol-terminated oligo(styrene) as a ligand. Applying a molar ratio gold to thiol of 1:10000 we obtained nanocrystals of about 2.5 nm in diameter having a narrow size distribution. The number-averaged size $d=2.5\pm 0.7$ nm was estimated by counting cluster sizes from TEM micrographs counting at least 150 nanocrystals for statistics. Starting out from the materials described above, the metallodielectric nanocomposites could be prepared by controlled solvent evaporation out of a solution of block copolymer and gold nanocrystals. After drying, shiny blue films could be obtained, which, without further annealing, exhibited highly reflecting grains of about 2 mm².

The morphology of the metallodielectric nanocomposite structures was determined by ultra-small angle X-ray scattering (USAXS) using beamline X10A and SAXS using beamline X27C at the NSLS, in addition to TEM. In the X-ray scattering experiments peaks occur at q/q_1 ratios corresponding to 1, 3.1 and 5.2, where q_1 is the modulus of the wavevector at the i^{th} maximum, indicating an almost symmetric lamellar geometry with a period of $d\sim 220$ nm. Figure 2 shows the combined USAXS and SAXS data obtained from the metal cluster containing sample.

The even order peaks are absent as expected for a symmetric layer structure with $\phi_{PS}=\phi_{PE/P}$. In order to determine the distribution of the gold nanocrystals within the block copolymer microstructure, TEM was performed on *unstained* samples taking advantage of the phase contrast between the PS and PE/P domain and the high electron density of the gold nanocrystals. A TEM micrograph for a sample corresponding to a gold weight fraction of 10% ($\phi\sim 0.02$) is shown as inset in Figure 2. The micrograph reveals that the gold colloids preferentially sequester within the target PS domain

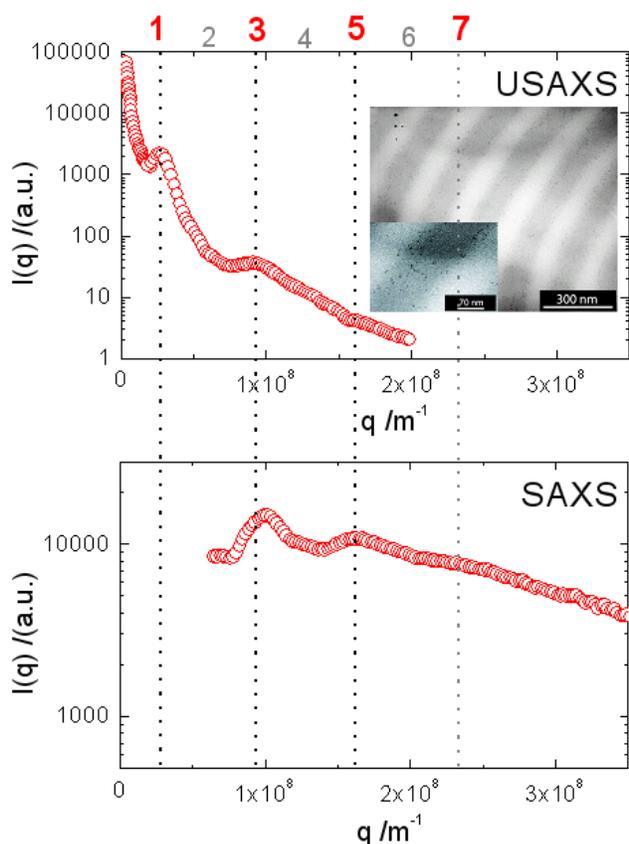


Figure 2: USAXS (X10A) and SAXS (X27C) data obtained from block copolymer/gold nanocrystal film. The direction of the incident beam is parallel to the lamellae orientation. The numbers on the top indicate the reflection order and reveal the absence of even order reflections. Shown in the inset is an underfocused bright field TEM micrograph of a section of the unstained block copolymer/nanocrystal film after sectioning a fracture surface. The gray areas correspond to PS layers and the bright regions to PE/P layers. The gold nanocrystals visualized by amplitude (mass thickness) contrast appear as dark spots within the PS domains.

and are almost homogeneously distributed within these domains. For determining the intrinsic photonic structure of our materials we performed subdomain reflectance measurements using a modified ZEISS Axiophot microscope equipped with a spectrophotometer. The reflectance at normal incidence of the gold nanocrystal containing sample as well as for a reference PS-*b*-PE/P sample is shown in Figure 3a.

In order to compare our experimental results with theoretical predictions, we performed calculations of the expected reflectivity using the transfer matrix method. Application of the transfer matrix method requires the assumption of an effective dielectric function for the metal cluster containing domains. Since in our case the composite topology is discrete, Maxwell Garnett's formula provides a useful approximation of the effective dielectric function[6]. The calculated re-

flectance curves shown as solid lines in Figure 3a account within the range of experimental error for the experimentally observed optical properties and confirm the validity of our model.

Our study shows, that by preferential sequestering of tailored metal nanocrystals into a self-assembled lamellar diblock copolymer, metallodielectric photonic structures can be obtained that exhibit high rejection level for light in the visible range. The utility of the block copolymer template approach lies in the spatial control of the morphology that is determined by the block composition and the molecular weight, so that an extension of our approach to 2D and 3D systems is feasible. For a crystal filling fraction of about 0.2, the formation of a robust reflection band is expected as shown in Figure 3b demonstrating the potential of the template approach for photonic crystal engineering. Since the optical properties of metal nanoclusters are size dependent, the cluster size is an additional parameter that might be used to tailor the optical properties of the nanocomposites. The thereby obtained metallodielectric structures may find applications that not only capitalize on the optical properties of the nanocrystals but also from the periodic morphology of the template material.

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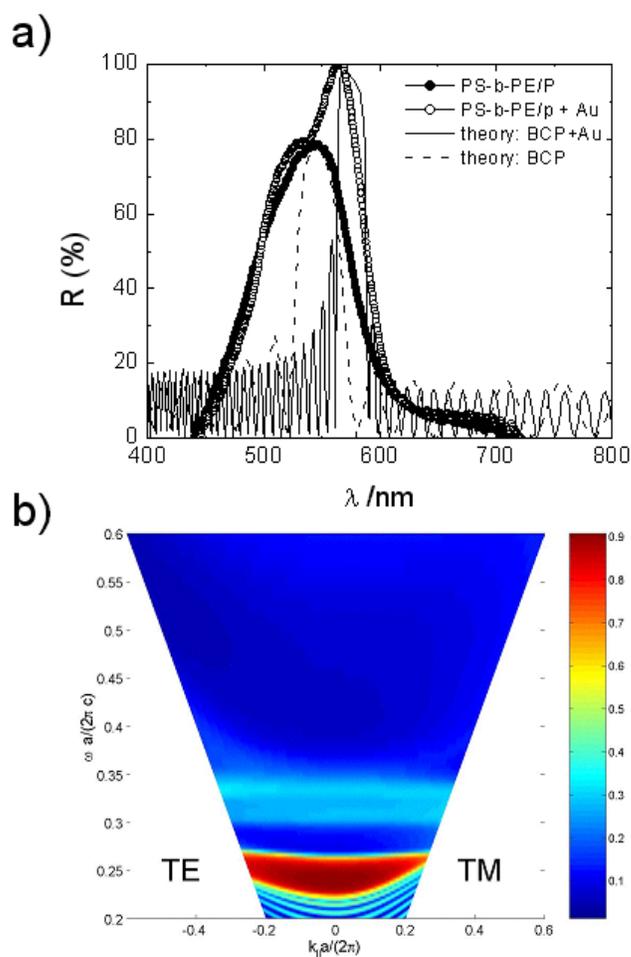


Figure 3a: Plot of the measured reflectivity for normal incidence of the pure block copolymer (■) and the block copolymer/nanocrystal (○) sample along with the calculated reflectivity for the nanocomposites (solid line) and the pure block copolymer sample (dotted line). Details on the calculation can be found in [5].

Figure 3b: Simulated frequency dependence of reflectivity for gold crystal filling fraction ($f=0.2$) for TM and TE polarization calculated for the system described in Figure 3a.