Engineering of colloidal magneto-photonic crystals by infiltration with superparamagnetic magnetite nanoparticles

PJ. Demeyer, M. Bloemen, T. Verbiest, and K. Clays

K.U.Leuven, Dept. of Chemistry, Celestijnenlaan 200D bus 2425, 3001 Heverlee, Belgium

The quality of magnetic-field sensors and optical isolators is largely determined by the efficiency of the active materials. This efficiency could be dramatically increased by integrating Faraday materials with photonic crystals. For this purpose, monodisperse polystyrene nanospheres were self-assembled into a photonic crystal and magnetic functionality was introduced by infiltrating this structure with superparamagnetic nanoparticles. Reflection measurements revealed clear relationships between the filling fraction and the position and strength of the photonic band gap. As such, an engineering approach is provided to carefully design the position and strength of the photonic band gap in magneto-photonic crystals.

Introduction

Modern demands for high speed technology for telecommunication and data processing have created the need for advanced materials and nanostructures allowing manipulation of electromagnetic radiation in the optical spectral range. Subsequent research has shown that photonic crystals provide excellent candidates to accommodate these needs. Photonic crystals are a relatively new class of materials in which the refractive index is periodic in 1,2 or 3 dimensions, with the scale of periodicity being on the same length scale as the wavelength of light one wishes to influence. In analogy with semiconductors, this periodicity gives rise to a photonic band gap, i.e. a range of wavelengths for which there are no modes available in the direction of the periodicity. As a result, light with a wavelength coinciding with the photonic band gap cannot propagate in the direction of the periodicity and is selectively reflected. This principle has been successfully implemented in e.g. photonic crystal fibers. Another interesting property of photonic crystals is the anomalous dispersion that occurs close to the photonic band gap (i.e. the band edge). This causes the group velocity of light to decrease considerably, allowing stronger interactions between the travelling light and the material of which the photonic crystal consists.[1]

When nonlinear optical materials are integrated into the photonic crystal structure, this effect can give rise to a large enhancement of both reciprocal and non-reciprocal optical phenomena. In the case of magneto-photonic crystals, magnetic material is introduced into the photonic crystal, enhancing their intrinsic magneto-optical properties (e.g. Faraday rotation). As such, they have strong potential for applications in highly efficient optical isolators and very sensitive magnetic field sensors.

Preceding research has shown that the Faraday response is indeed strongly increased near the band edge in 1D and 2D photonic crystals.[2,3] In colloidal 3D photonic crystal a smaller effect on the Faraday spectrum has been described but there is still significant room for improvement.[4,5] Currently, the main issue is to introduce sufficient magnetic material in the 3D photonic crystal in a uniform and reproducible way, without absorbing too much light (the Faraday effect is measured in transmission). An additional

trade-off exists between the amount of magnetic material in the 3D photonic crystal and the strength of the photonic band gap. As more magnetic material is introduced in the voids of the colloidal photonic crystal, the refractive index contrast is lowered, giving rise to a weaker and red-shifted band gap.[1] In this paper, a method is described to carefully control and fine-tune the amount of introduced magnetic material and hence the absorbance of the material and the position and strength of the photonic band gap.

Experimental

Polystyrene nanoparticles (Interfacial Dynamics Corporation, Portland) with diameters of 170 nm (Coefficient of Variation (CV) = 2,3%) and of 220 nm (CV = 5,3%) were dissolved separately in MilliQ water (7 ml) at a concentration of 0,3 wt%. The polystyrene nanoparticles suspension were poured in a glass vial and put in an oven at 55°C together with glass slides (18x18 mm, 170±5 μm thick) for convective self-assembly. After self-assembly, a short sintering step (5 min at 103°C) was performed to improve the mechanical properties of the photonic crystals. The reflectance of the photonic crystals was measured using a Lambda 900 UV/VIS/NIR spectrometer (PerkinElmer), a forked optical fiber and a home-made sample holder. The superparamagnetic magnetite nanoparticles were synthesized by thermal decomposition and subsequently silanised with methoxy(polyethyleneoxy)-propyltrimethoxysilane. Infiltration of the photonic crystals was achieved by repeated dipping of the photonic crystals in a suspension of superparamagnetic nanoparticles in ethanol (5mg/ml) using a home-made mechanical dipping system at a dipping speed of 10 cm per minute. After each dipping step, the reflection spectrum was recorded. Scanning Electron Microscopy (SEM) images were made using a XL30 FEG ESEM (Philips), Transmission Electron Microscopy (TEM) images were recorded with an EM900 (Zeiss).

Results and discussion

Photonic crystals were prepared by convective self-assembly of 170 nm or 220 nm polystyrene nanoparticles. After self-assembly, random hexagonal close-packed (Rhcp) crystal structures were obtained (Fig. 1a), with the (111) plane parallel to the glass surface. The monocrystalline domains (roughly 100 μm x 100 μm) were separated by large cracks in the crystal structure, as is typical in colloidal photonic crystals. Monodisperse superparamagnetic magnetite nanoparticles with a diameter of 9.3±1.6 nm (Fig. 1b) were silanised to prevent nanoparticle aggregation. In this way, the uniformity of infiltration is improved and loss of superparamagnetism is avoided.

After infiltration with magnetic nanoparticles, the photonic band gaps of both photonic crystals were weakened and red-shifted in a controllable way (Fig. 2a,2b). This can be explained by a decrease in the refractive index contrast when adding higher refractive index material to the lower refractive index medium (air) and is in accordance with the modeling work described in [6]. The peak intensity decreases and can be fitted with an asymptotic curve (Fig. 3a). This decrease continues until the refractive index of the voids (air and magnetic nanoparticles) is equal to that of the polystyrene nanoparticles. When the filling factor is increased even further, the refractive index of the voids becomes higher than that of the polystyrene spheres, leading to an increased refractive index contrast and an increasing peak intensity.[6] Note that this inversion point was not reached during the described experiments.

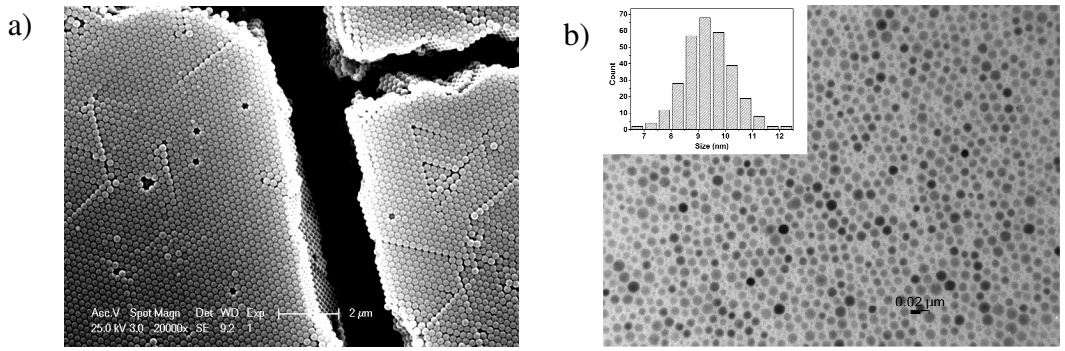

Figure 1: a) SEM image of a photonic crystal consisting of 220 nm polystyrene nanoparticles. b) TEM image of superparamagnetic magnetite nanoparticles and their size distribution (inset)

The volume fraction of magnetic material in the photonic crystal was calculated from the red-shift of the photonic band gap. First, the Bragg law for a fcc close-packed structure was used to calculate the effective refractive index, n_{eff} [7],

$$\lambda_{\max} = 2\sqrt{\frac{2}{3}} D.n_{eff} \ , \tag{1}$$

where λ_{max} is the spectral position of the band gap peak in reflection and D is the diameter of the polystyrene nanoparticles. Consecutively, the well-known Maxwell-Garnet equation for effective media was employed to determine the volume fraction of magnetic material, [8]

$$\frac{n_{eff}^2 - 1}{n_{eff}^2 + 2} = f_{PS} \frac{n_{PS}^2 - 1}{n_{PS}^2 + 2} + f_{air} \frac{n_{air}^2 - 1}{n_{air}^2 + 2} + f_{MNP} \frac{n_{MNP}^2 - 1}{n_{MNP}^2 + 2} \ , \tag{2}$$

where $f_{PS/air/MNP}$ are the filling fractions of respectively polystyrene, air and magnetic nanoparticles and $n_{PS/air/MNP}$ are the refractive indices of respectively polystyrene, air and magnetic nanoparticles. As the volume fractions of voids (26%) and spheres (74%) in a fcc crystal are known, also the volume fraction of the voids filled with magnetic material (i.e. the filling fraction) could be obtained (Fig. 3b).

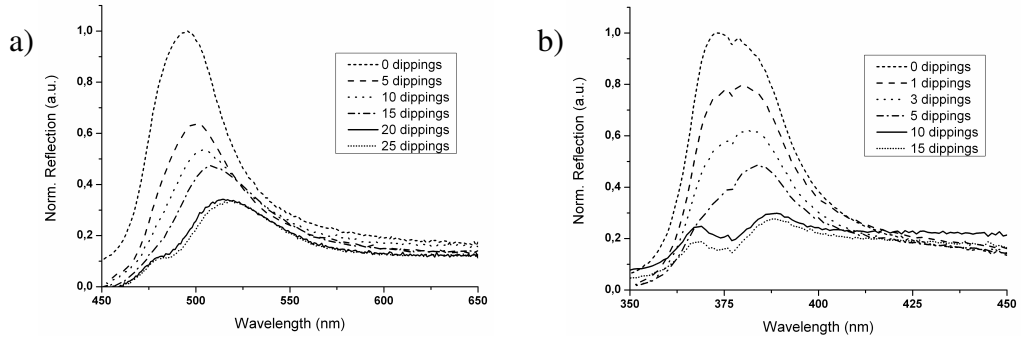

Figure 2: Normalized reflection spectra of the photonic crystals before and after repeated dipping. a) 220 nm polystyrene nanoparticles, b) 170 nm polystyrene nanoparticles

A stronger decrease in the peak intensity and a faster increase in the filling fraction were observed in the photonic crystal consisting of 170 nm polystyrene nanoparticles than in the one consisting of 220 nm polystyrene nanoparticles. As the voids are smaller in the photonic crystal with smaller spheres, the same amount of material will initially fill a higher volume percentage of the voids and therefore will also decrease the refractive index contrast faster. However, the pores are also smaller, leading to faster pore block-

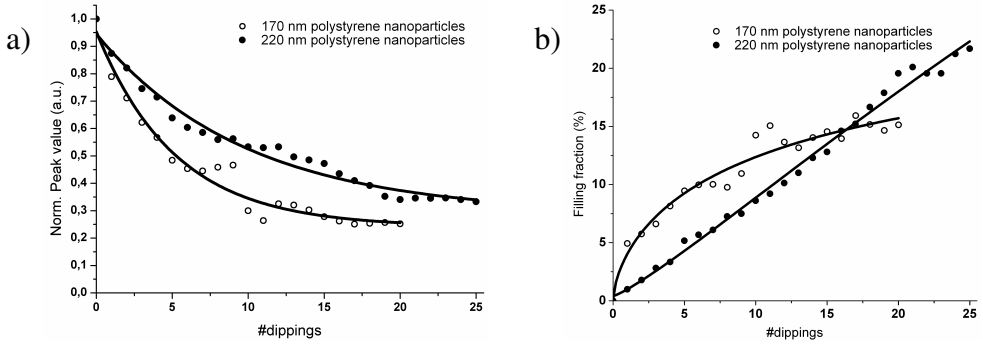

Figure 3: a) Normalized reflection peak values (asymptotic fits). b) Filling fractions calculated from the red-shift of the reflection peak maxima (logistic fits).

ing when using the same size of magnetic nanoparticles. This is clearly visible in Figure 3b as the 170 nm polystyrene nanoparticles already give rise to saturation while the curve of the 220 nm polystyrene nanoparticles is still in the linear regime. From these data it can be concluded that the use of smaller magnetic nanoparticles and larger polystyrene nanoparticles should give rise to higher filling fractions.

Conclusion

A method was described to carefully control and fine-tune the amount of magnetic material and hence the absorbance of magneto-photonic crystals and the position and strength of photonic band gaps. When using smaller polystyrene nanoparticles, lower filling fractions were achieved due to the earlier onset of pore blocking. Tailoring the properties of magneto-photonic crystals will allow application-specific designs and a better description of Faraday effects in 3D magneto-photonic crystals.

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