Bottom-up production of meta-atoms for optical magnetism in visible and NIR light

Philippe Barois, Virginie Ponsinet, Alexandre Baron, Philippe Richetti
Centre de Recherche Paul Pascal, CNRS - Université de Bordeaux, 115 Avenue Schweitzer, 33600 Pessac, France.
barois@crpp-bordeaux.cnrs.fr

Abstract. Many unusual optical properties of metamaterials arise from the magnetic response of engineered structures of sub-wavelength size (meta-atoms) exposed to light. The top-down approach whereby engineered nanostructure of well-defined morphology are engraved on a surface proved to be successful for the generation of strong optical magnetism. It faces however the limitations of high cost and small active area in visible light where nanometre resolution is needed. The bottom-up approach whereby the fabrication metamaterials of large volume or large area results from the combination of nanochemistry and self-assembly techniques may constitute a cost-effective alternative. This approach nevertheless requires the large-scale production of functional building-blocks (meta-atoms) bearing a strong magnetic optical response. We propose in this paper a few tracks that lead to the large scale synthesis of magnetic metamaterials operating in visible or near IR light.

1. Introduction: the race towards optical magnetism

Considerable research efforts have been devoted in recent years to control the magnetic permeability of optical materials from GHz to visible light frequencies [1]. It is a difficult challenge, not only because of the well-known absence of optical magnetism in natural dielectrics [2], but also because artificial optical magnetism, generated by induced currents in engineered composite materials, is a complex phenomenon that is not easily related to the familiar permeability parameter [3-5]. The first spectacular success was obtained in 2000 with the realization of the first negative index metamaterial (NIM) based on split-ring magnetic resonators operating in the GHz range. Later on, the observation of strong artificial magnetism at frequencies of visible or near-infrared light was reported in several types of planar plasmonic nanostructures made by top-down technologies and which are essentially two-dimensional and highly anisotropic [6-10]. In addition to the technological complexity linked to the nanometer world, plasmonic resonances suffer from strong optical losses which are likely to hinder future applications. The bottom-up approach is viewed as an alternative pathway that may offer an easier large scale production, including 3-dimensional materials. Furthermore, nanochemistry is able to produce high-refractive index Mie resonators that may usefully replace lossy plasmonic resonators. The aim of this paper is to propose a few tracks for the design and the fabrication of a new generation of optical resonators exhibiting a magnetic response to light.
2. Plasmonic resonators

One of the first theoretical models of optical magnetic resonators was proposed by Simovski and Tretyakov and is shown in figure 1a [11]. It consists of a corona of metallic nanoparticles surrounding a core dielectric nanoparticle. Light illumination excites a loop of plasmonic currents that act as a magnetic dipole. Such magnetic nanoclusters, sometimes referred to as “plasmonic raspberries”, were subsequently synthesized by several authors and their magnetic response was unambiguously demonstrated by optical experiments [12-15].

![Figure 1](image)

**Figure 1:** (a) Sketch of the Simovski-Tretyakov model of magnetic nanocluster. Plasmonic satellites are distributed around a dielectric core nanoparticle. (b-c) Examples of experimental realization with gold (b) and silver (c) satellites. (d) Scattering cross-sections of the magnetic nanocluster shown in (c). Red and blue colors show the contribution of the electric dipole (ED) and of the magnetic dipole (MD) plus electric quadrupole (EQ) respectively. Symbols are the experimental signal, solid lines are numerical simulations. Inset shows the separate contributions of the three scattering processes [15].

The Simovski-Tretyakov magnetic nanoclusters were subsequently assembled in a three-dimensional metamaterial in a micro-evaporator engineered on a microfluidic chip [16,17]. The effective magnetic permeability $\mu$ of the metamaterial was extracted from variable angle spectroscopic ellipsometry. Two important results were obtained for the first time namely (i) the real part of $\mu$ deviates significantly from the natural value $\mu = 1$ (in $\mu_0$ units) as $0.8 < \mu < 1.4$, hence breaking the well-known Landau-Lifshitz rule [2]. The strength of the magnetic response is more obvious if one notes that the effective magnetic susceptibility $\chi = \mu - 1$ is 3 to 5 orders of magnitude larger than the diamagnetic susceptibility of natural materials and (ii) a constant $\mu$ parameter describes the reflection from the metamaterial at all angles of incidence, hence showing that the measured permeability is not affected by spatial dispersion, a non-local phenomenon which usually precludes a valid description of optical magnetism by the sole permeability tensor [4,5]. These two results of fundamental importance follow from the hierarchical self-assembly process whereby the meta-atoms are engineered in a first step to provide the wanted magnetic response and assembled in a second step to produce a bulk sample. Far from being a disadvantage, the highly-symmetric liquid-like structural disorder of the metamaterial turns out to be highly favorable for the limitation of the spatial dispersion effects [15]. The bottom-up approach hence appears as a powerful method for the fabrication of magnetic metamaterials exhibiting a non-natural, but still effective magnetic permeability parameter.

The magnetic response of the plasmonic raspberries is however still too low to warrant useful applications. Indeed, the interesting domains $\mu$ near zero and negative $\mu$ are not reached yet. Although numerical simulations show that increasing the number and the size of the metallic satellites would increase the magnetic response of the plasmonic raspberries, the presence of Ohmic losses in metals undeniably constitutes a severe limitation for future applications in optical devices. All-dielectric meta-atoms exhibiting Mie resonances appear as a promising alternative [18].
3. All-dielectric Mie resonators

The absorption and scattering of light by a homogeneous spheres was worked out exactly by Gustav Mie in 1908 [19]. A remarkable feature is the presence of cavity-type resonances when the diameter of the sphere $D$ matches the wavelength $\lambda_0/n_{\text{sphere}}$ of light inside the sphere. At lowest dipolar order, two types of resonance are actually found namely an electric resonance for $D \approx 2\lambda_0/n_{\text{sphere}}$ and a magnetic one for $D \approx \lambda_0/n_{\text{sphere}}$. These two resonances are characterized by the radiation of a strong electric and magnetic dipole respectively, the latter being of crucial importance for the generation of optical magnetism. For a dielectric sphere and for wavelengths far from any absorption band of the dielectric material, optical losses are weak and the figure of merit of the resonances is very high. Mie resonators are thus expected to be far more efficient than plasmonic ones [18]. If effective optical parameters are wanted however, the homogeneity condition requires that the size $D$ of the resonators and the distance between them should be much shorter than the wavelength, which is inconsistent with the resonance conditions, unless the refractive index of the material satisfies $n_{\text{sphere}} >> 1$. For visible light, $D$ should not exceed a few tens of nanometers whereas a few hundreds may be acceptable for IR waves.

For material scientists, the challenge is therefore to synthesize nanoparticles with the following specifications:

(i) the dielectric material should have a refractive index with a large real part (ideally $n_{\text{sphere}} \sim 10$) and low imaginary coefficient $k$.

(ii) the size of the nanoparticles should be accurately controlled since the resonance condition depends critically on size.

(iii) the synthetic route should be able to produce large amounts of particles in environment-friendly processes.

These are very tough challenges which are not fully solved yet. Several types of dielectric materials are under investigation, among which crystalline silicon (c-Si), amorphous silicon (a-Si) and titanium dioxide (TiO$_2$) in its crystalline anatase form seem quite promising. Figure 2 below shows that the magnetic dipolar scattering efficiencies calculated from c-Si, a-Si and TiO$_2$ spheres of diameter $D = 150$ nm are much higher than the value obtained for plasmonic raspberries of the same size [21].

![Figure 2: Scattering efficiencies of the magnetic dipole computed for different nanospheres of diameter 150 nm, compared to the value measured on plasmonic raspberry of the same size (red line).](image)

For visible light applications, crystalline silicon (c-Si) appears as the most favorable material, although not ideal. Its refractive index is around 4 and the imaginary part is only a few $10^{-2}$ for wavelengths longer than 500 nm [21]. Figure 2 shows the evolution of the electric and magnetic scattering efficiencies of c-Si nanoparticles with diameter, as calculated from the Mie theory.
Figure 3: Electric (a) and magnetic (b) scattering efficiencies of crystalline silicon nanoparticles of various diameters (calculated from Mie theory in ethanol solvent of index 1.36).

The electric and magnetic resonances have indeed been observed and characterized in full agreement with the Mie theory on c-Si nanoparticles prepared by laser ablation [22-24]. These studies confirm that the crystallinity of silicon is critical. Although laser fabrication is able to prepare 2D arrays of c-Si particles of well controlled size [23], the implementation of a robust synthetic route able to produce macroscopic amounts (grams to kilograms) of c-Si nanoparticles at low cost would be welcome.

Despite ongoing efforts of nanochemists, c-Si nanoparticles of well-defined size in the range 50-200 nm are not yet available. However, large amounts of silicon nanoparticles are commercially available with a lower degree of crystalline purity and a broad distribution of sizes. Figure 3 shows the result of a light scattering study carried out on silicon nanoparticles purchased from American Elements [26]. The optical signal plotted in Fig. 3c is the ratio of the transverse to axial signals collected at 90° scattering angle along polarizations respectively perpendicular and parallel to the scattering. In the spectral region of the dipolar Mie resonances, it identifies with the ratio of the dipolar magnetic to dipolar electric scattering cross sections [14,27]. The measurement is fully consistent with a population of silicon nanoparticles with a log-normal distribution of size of average diameter 100 nm and a 40% crystallinity. Diffraction of electrons in TEM studies confirm the presence of crystalline and amorphous nanospheres in the commercial silicon powder. Despite a broad size distribution (+/- 20 nm in radius) and a low degree of crystallinity, the ratio of the magnetic to electric scattering reaches 0.6, whereas the maximum value for plasmonic raspberries does not exceed 0.28 [15].

Figure 4: (a) suspension of silicon nanoparticles purchased from American Elements in water. (b) TEM micrograph of the Si nanoparticles after 30 minutes exposure to NaOH at pH=12 to eliminate non-spherical oxide growth. A log-normal size distribution of average diameter 100 nm was extracted from TEM images. (c) Plot of the ratio of the magnetic (MD) to electric (ED) dipolar scattering cross sections. Experimental signal in black is well reproduced by a mixture of 40% crystalline and 60% amorphous particles (green line). Blue and red lines represent the signal computed with the same size distribution for 100% crystalline and 100% amorphous particles respectively.
These encouraging results show that silicon nanoparticles produced in large amounts and low cost by chemical companies can be a good starting point for optical applications. Narrower size distributions can in principle be obtained by powerful methods of physical chemistry like centrifugation in viscosity gradients [28], whereas thermal annealing may improve the crystalline fraction.

4. Conclusion:

The bottom-up route based on self-assembly of simple nano-sized building blocks has proved its efficiency in the production of metamaterials of large area and/or large volume. Structural disorder is not always detrimental for optical functionality, although it makes numerical simulations undeniably more difficult. The main challenge is the design and the large-scale availability of building units of well controlled morphology. Metallic oxide nanospheres such as TiO$_2$ are already commercially available with a good control of size and crystalline purity. Silicon nanospheres of well controlled size may become available in large amounts in a near future.

Acknowledgements:
This work was supported by the LabEx AMADEus (ANR-10-LABX-42) in the framework of IdEx Bordeaux (ANR-10-IDEX-03-02), France.

References
[1] Soukoulis, C. M., and Wegener, M. Past achievements and future challenges in the development of three-dimensional photonic metamaterials. *Nature Photon.*, 5, 523-530 (2011).
[2] Landau, L. D. & Lifshitz, E. M. Electrodynamics of Continuous Media, Pergamon Press, 1960).
[3] Agranovich, V. M., and Ginzburg V. L. *Crystal Optics with Spatial Dispersion, and Excitons*. Cardona, M., Fulde, P. and Queisser, H.-J. editors. Volume 42. (Springer-Verlag. Berlin, Heidelberg, 1984).
[4] Agranovich, V. M., and Gartstein, Y. N. Spatial dispersion and negative refraction of light. *Phys. Usp.*, 49, 1029-1044 (2006).
[5] Menzel, C., *et al.*, Validity of effective material parameters for optical fishnet metamaterials. *Phys. Rev. B*, 81, 035320 (2010).
[6] Grigorenko, A. N., *et al*. Nanofabricated media with negative permeability at visible frequencies. *Nature*, 438, 335-338 (2005).
[7] Linden, S. *et al.*, Magnetic Response of Metamaterials at 100 Terahertz. *Science*, 306, 1351-1353 (2004).
[8] Zhou, J., Zhang, L., Tuttle, G., Koscny, Th., and Soukoulis, C. M. Negative Index materials using simple short wire pairs, *Phys. Rev. B*, 73, 041101(R) (2006).
[9] Dolling, G., Wegener, M., Soukoulis, C. M & Linden S. Negative-index metamaterial at 780nm wavelength. *Optics Lett.*, 32, 53-55 (2007).
[10] Xu, T., Agrawal, A., Abashin, M., Chau, K. J., and Lezec, H. J. All-angle negative refraction and active flat lensing of ultraviolet light. *Nature*, 497, 470-474 (2013).
[11] Simovski C.R. and Tretyakov S.A., Phys. Rev. B 79, 045111 (2009).
[12] Mühlig S., Cunningham A., Scheeler S., Pacholski C., Bürgi T., Rockstuhl C., and Lederer F., ACS Nano 5, 6586 (2011).
[13] Sheikholeslami S.N., Alaeeian H., Koh A.L., and Dionne J.A., Nano Lett. 13, 4137 (2013).
[14] Ponsinet *et al.*, Phys. Rev. B 92, 220414(R) (2015).
[15] Gomez-Graña *et al.*, Mater. Horiz. 3, 596 (2016).
[16] Leng J., Lonetti B., Tabeling P., Joanicot M. and Ajdari A., Phys. Rev. Lett., 96, 084503 (2006).
[17] Angly J. et al., ACS Nano, 7, 6465 (2013).
[18] Jahani S., Jacob Z., Nat. Nanotechnol. 11, 23 (2016).
[19] Mie G., Ann. Phys. 25, 377 (1908).
[20] Bohren C.F., Huffman D.R., Absorption and Scattering of Light by Small Particles, Wiley-Interscience, New York, 1983.
[21] Values of the refractive indices are found in https://refractiveindex.info/
[22] Evlyukhin A.B. et al., Nano Lett., 12, 3749 (2012).
[23] Zywietz U., et al., Nat. Commun., 5, 3402 (2014).
[24] Dmitriev P.A. et al., Nanoscale, 8, 5043 (2016).
[25] L. Shi, J. Harris, R. Fenollosa, I. Rodriguez, X. Lu, B. A. Korgel, F. Meseguer, Nat. Commun. 2013, 4, 1904
[26] https://www.americanelements.com/
[27] Sharma N.L., Phys. Rev. Lett. 98, 217402 (2007).
[28] Qiu P. & Mao C., Adv. Mater., 23, 4880 (2011).