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Photonic Glass: A Novel Random Material for Light**

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From medieval stained glass windows to future photonic chips, understanding light interaction with complex dielectric media has been the key to design and tailor the optical properties. From random to periodic media, the engineered internal microstructure of a dielectric is at the basis of many new optical properties which are unexpected in homogeneous dielectric media. Very promising examples are represented by "left-handed" materials which show negative values of permeability and permittivity,[1,2] and for which light propagation, Doppler effect, Cherenkov radiation, and even Snell's law are found to be strongly affected. Another important example is given by photonic crystals,[3,4] where the dielectric function (ε) varies periodically on the length scale of the light wavelength, and which exhibits anomalous refraction,[5] super-refraction (superprism effect),[6] small group velocity,[7] and, for certain structures, even the opening of a complete photonic bandgap (PBG).[8] In both cases, the nanometer and micrometer sized building blocks are arranged periodically to induce the required properties.

Usually, defects in photonic crystals are regarded as undesirable features that spoil optical quality and performances. However, they can also be viewed as an enriching factor since, when controlled, they can be used to build up cavities, waveguides etc. being the base of future circuits of light. This only happens when a strict control is exerted on defects amount, position, shape, and other morphological characteristics. The amount of defects in photonic crystals produced by self-assembly is partly out of control and the achievement of the highest quality possible is a common goal of the colloidal community, for which many routes have been tested.

Disordered microstructured dielectrics, which are based on an opposite assembly strategy, are a rich and novel photonic medium. Random packing of hard spheres has been focus of considerable attention[9] for the last decades as a model to pack objects efficiently. Nevertheless, the packing of spheres is, apparently, the exception rather than the rule showing the highest possible filling fraction.[10] A number of interesting new optical phenomena have also been studied in random media such as coherent backscattering enhancement,[11,12] Anderson localization of light,[13–16] random lasing[17–19] only to mention a few. Three-dimensional random systems have been mainly achieved by the use of very polydisperse distributions of different materials powders or clusters.[20] A random distribution of monodisperse building blocks forming a solid phase has not yet been achieved. Using spheres, which has been tried in colloidal suspensions,[21] offers a very interesting advantage as they are the simplest object for which light resonances. Moreover, the interaction between light and a dielectric sphere can be described completely by Mie theory, an exact solution of the Maxwell's equations. Some experiments have been already performed in a single[22] or a small group[23] of micro-spheres. A new range of interesting phenomena will be affected by monodispersity of spheres, giving rise to a resonant behaviour[24,25] of diffusion constant, transport mean free path and energy velocity or random lasing action in macroscopic arrangements of this kind of scatters.

In this work, we present a new material that we call "photonic glass". This new three dimensional system is composed by monodisperse polymer spheres arranged in a completely disordered (random) way. Due to the resonant behaviour of the spheres, discrete light states exist, and therefore every sphere acts as a meta-atom[26] for light. We describe two different approaches to grow completely random distributions of monodisperse polymeric spheres with diameters from 200 nm to 2300 nm. The first method is based on rheology and takes advantage from the two-body interaction between polymeric spheres in colloidal suspensions. Very thick (from a few hundred microns to millimetres) and uniform samples can be grown attenuating the sphere-sphere repulsive potential by dissolving a low concentration of electrolytes (ions) in the colloidal suspension. The second method is based on vertical deposition,[27] which is commonly used to grow colloidal photonic crystals providing extremely high quality structures. By combining a binary colloidal suspension composed by polymethyl methacrylate (PMMA) and polystyrene (PS) spheres and by selective etching of one of them, thin disordered films can be grown.

Contrary to intuition, the introduction of arbitrarily high amounts of disorder is an unsuspected equally difficult task as obtaining defects-free systems. Few methods were tested here to get a completely disordered arrangement of monodisperse spheres such as rapid sedimentation or modified vertical deposition, being completely unsuccessful. Only the two methods presented here after were found to be fruitful.

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