

PHOTONIC STRUCTURES VIA THE SELF- ASSEMBLY OF NANOSIZED BUILDING BLOCKS

Venerdì, 15 Novembre, 2024

10:00

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Abstract

Self-assembled materials exhibiting hierarchical morphologies are promising for fabricating photonic crystals (PhCs) as they offer a straightforward approach to manipulating light-matter interactions^[1], which is particularly relevant in several technological applications. We explore two distinct methods for producing photonic structures, namely (i) the confined self-assembly of block copolymers in emulsion droplets and (ii) the DNA-mediated self-assembly of colloidal patchy particles.

Our first objective revolves around block copolymer (BCP) microparticles showing tunable, structural coloration.^[2] These are achieved by directing BCPs to organize themselves into well-defined morphologies via a simple evaporation-induced self-assembly process in emulsion droplets. The choice of the BCP type and the processing conditions leads to either highly ordered (i.e., concentric or stacked lamellae) or quasi-random (i.e., presenting only a short-distance order) structures. These consist of alternated domains with refractive index mismatch, thus generating a light reflection that can be tuned within the entire visible range via the simple addition of “swelling agents”.^[3] We then combine these structurally colored microparticles with diverse inorganic nanomaterials, including plasmonic, magnetic, and oxide nanoparticles and light-emitting quantum dots. This is achieved by a one-step solvent evaporation-induced co-assembly approach.^[4] The spatial arrangement of the inorganic nanomaterials within the resulting nanostructured particles is manipulated by fine-tuning the enthalpic and/or the entropic interactions between the block copolymers and the ligands on the surface of the nanomaterials.

Our second objective focuses on controlling the self-assembly of DNA-functionalized colloidal patchy particles to manufacture photonic materials with a controlled degree of order/disorder.^[5] Our approach entails preparing patchy particles consisting of anisotropically-patterned particles. This is achieved through an experimental protocol that involves the colloidal fusion of solid polymer nanoparticles mixed with smaller droplets of polymerizable oil. We demonstrate that it is possible to achieve clusters with different coordination numbers (i.e., dimers, trimers, tetramers, pentamers, hexamers, etc.) by finely adjusting the size ratio of the polymer nanoparticles to the oil droplets.^[6] These superstructures can be further processed through the controlled deformation of the polymer nanoparticles by adding a plasticizer (i.e., selective solvent). The deformation results in the extrusion of the liquid core from the clusters, thus generating well-defined patches that can be functionalized with specific ligands, such as DNA strands. These are ultimately used to regulate the self-assembly of the resulting patchy particles to fabricate photonic structures with a defined degree of order/disorder.

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