Tunable Colors in Opals and Inverse Opal Photonic Crystals

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Colloidal photonic crystals and materials derived from colloidal crystals can exhibit distinct structural colors that result from incomplete photonic band gaps. Through rational materials design, the colors of such photonic crystals can be tuned reversibly by external physical and chemical stimuli. Such stimuli include solvent and dye infiltration, applied electric or magnetic fields, mechanical deformation, light irradiation, temperature changes, changes in pH, and specific molecular interactions. Reversible color changes result from alterations in lattice spacings, filling fractions, and refractive index of system components. This review article highlights the different systems and mechanisms for achieving tunable color based on opaline materials with close-packed or non-close-packed structural elements and inverse opal photonic crystals. Inorganic and polymeric systems, such as hydrogels, metallopolymers, and elastomers are discussed.

1. Introduction

Colors have been important throughout human history. They provide critical functions in both recognition and communication, linking interactions between the animate and inanimate worlds. Several mechanisms for generating color in materials are known, including preferential absorption, emission, birefringence, photochromism and other mechanisms.[1] Particularly interesting are chromotropic effects which refer to reversible color transformations in a material due to external chemical or physical influences.[2] A variety of external stimuli have been demonstrated to produce such color changes. For example, nematic or chiral liquid crystals can change color with temperature or upon application of an electric field; other thermochromic materials change color when they undergo phase transitions or change molecular configuration as a function of temperature; chemical indicators, such as phenolphthalein, change color with pH, etc. On the basis of this behavior, chromotropic materials have found applications in displays, sensors, information storage, decoration, camouflage, and art.

One important class of chromotropic materials is based on photonic crystals. Color-producing photonic crystals are periodically structured materials with a periodicity, whose length scale is proportional to visible wavelengths.[3–6] Diffraction effects result in the appearance of a photonic band gap (PBG) that forbids propagation of certain wavelengths of light. In a material with a complete PBG, light with a specific wavelength cannot propagate in any direction. Due to the limited options of materials with high refractive index that do not absorb visible light, it is challenging to obtain materials with a complete PBG in the visible range;[7] instead incomplete PBGs or pseudo PBGs are usually produced. A pseudo PBG in the visible range results in materials whose colors vary with the viewing angle. This phenomenon, called opalescence, iridescence or structural color, is exhibited throughout nature in butterflies,[8] other insects,[9] marine creatures,[10] and even in flora.[11]

Since the concept of photonic crystals was proposed, several methods of fabricating such materials have been explored.[12] Among these, self-assembly methods that produce three-dimensionally (3D) ordered arrays of monodisperse spheres—so-called colloidal crystals or synthetic opals—as well as inverse replicates of opals (3D ordered macroporous or 3DOM materials), have been studied intensively.[13–15] One of the advantages of colloidal photonic crystals is their versatility for changing the characteristic reflection peaks in their optical spectra (the "stop bands"). The optical reflection peaks are analogous to diffraction peaks in X-ray powder patterns but fall into the submicrometer range instead of the angstrom range (**Figure 1**). In these materials, the stop band positions depend largely on three factors: 1) the refractive index contrast between two periodic media (solid spheres or air spheres and the surrounding phase), 2) the lattice constant (the spacing between spheres), and 3) the filling factor (volume of the spheres compared to the volume of the surrounding phase) (**Figure 2**). The concept of tunable color in photonic crystals is based on changing the stop band characteristics reversibly through variation of any of these parameters by applying external stimuli.

In this report, we review the diverse routes that have been employed in order to generate reversible color changes based on two structure types: close-packed arrays and non-close-packed arrays in structures related to opals and inverse opals. Through appropriate functionalization or structural modification, each of these structure types can be designed to respond to diverse stimuli. Papers that use the term "tunable materials" but merely

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