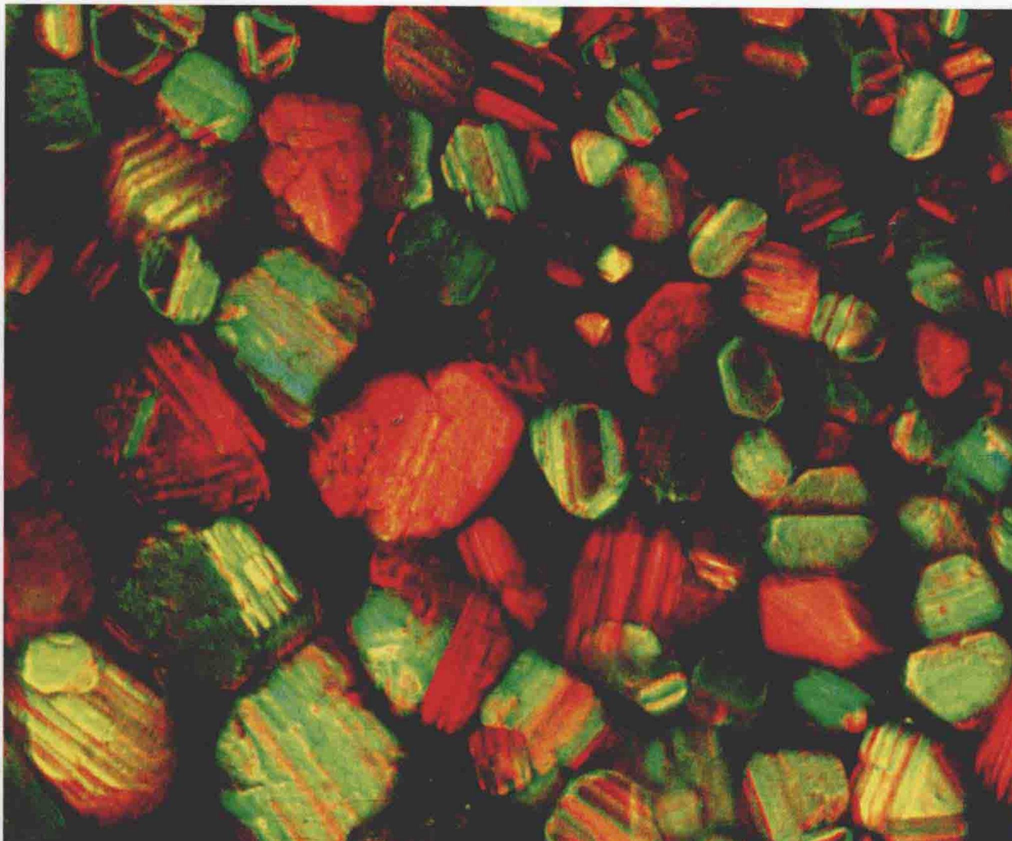
RSC Smart Materials

Edited by Yadong Yin

Responsive Photonic Nanostructures

Smart Nanoscale Optical Materials



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Preface

Among many types of smart materials, responsive photonic bandgap materials, or more commonly known as responsive photonic crystals, which can change their color in response to external stimuli, have attracted much attention due to their important uses in areas such as color displays, biological and chemical sensors, inks and paints, and many active components in optical devices. The unique colors originating from the interaction of light with periodically arranged structures of dielectric materials are often called structural colors, which are iridescent and metallic, cannot be mimicked by chemical dyes or pigments, and they are free from photobleaching unlike traditional pigments or dyes. Many interesting applications have been proposed for responsive photonic crystal structures. For example, they may be used as optical switches for full automation of optical circuits when significant improvements towards the quality of colloidal crystals and their response time are realized. Military vehicles covered with such materials may be able to dynamically change their colors and patterns to match their surroundings. Such materials might also be embedded in banknotes or other security documents for anti-counterfeiting purposes. The hidden information cannot be revealed until an external stimulus such as a pressure or temperature change is applied. The photonic effect can also be used as a mechanism to develop chemical and biological sensors for detecting target analytes by outputting optical signals. These types of crystals may also find great use as active color units in the fabrication of flexible display media, including both active video displays and rewritable paper that can be reused many times.

Compared to photonic crystals prepared by microfabrication methods, self-assembled photonic crystals, in particular colloidal crystals, can be produced at much lower costs and with higher efficiencies owing to the parallel nature of the self-assembly processes. It is also more convenient to modify the

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building blocks before or after the formation of crystal structures to enable responsiveness to a given stimulus. As a result, the majority of research on responsive photonic nanostructures has been focused on constructing the photonic crystal structures and incorporating stimulus-responsive materials into the self-assembled photonic crystal structures. In principle, the stimulus can be any means that can effectively induce changes in the refractive indices of the building blocks or the surrounding matrix, and changes in the lattice constants and/or spatial symmetry of the crystalline arrays. While various responsive mechanisms have been developed, such as mechanical stretching, solvent swelling, and temperature-dependent phase change, the research activities in the field have been focused on broadening the tunability of the photonic properties, enhancing the response rate to the external stimuli, improving the reversibility, and integrating into existing photonic devices.

This book highlights several recent areas of progress in the self-assembled responsive photonic nanostructures based on a number of different tuning mechanisms. Among all photonic crystal structures, one-dimensional Bragg reflectors that consist of alternative multilayers of two materials with different dielectric constants are regarded as the simplest type of photonic nanostructures. Calvo and Míguez first discuss recent progresses in the development of such materials for potential applications in sensing owning to their ability to respond to changes in the surrounding environment with a modification of their optical properties, generally caused by a variation of either their refractive index, the thickness of the constituent layers, or both. Self-assembled opals of close-packed colloidal crystals from monodisperse colloidal particles have predominantly served as the starting frameworks for constructing responsive photonic nanostructures. Stimulus-responsive materials can be incorporated into the periodic structures either as the initial building blocks or as the surrounding matrix so that the photonic properties can be tuned. Such colloidal crystals may also be used as the templates to fabricate inverse opals. Various versions of tunable opals and inverse opals have been developed that can respond to a wide range of external stimuli such as mechanical stretching, humidity, light, and temperature change, as reviewed separately by Fudouzi, Gu and Stein and coworkers. Since the opal structures themselves are relatively weak due to the fragile contact points between spheres within the structure, many structurally deformable photonic structures have been made from close-packed or nonclose-packed colloidal crystal arrays encapsulated within a hydrogel or polymer matrix that fills the void space surrounding the colloidal crystal, as discussed by Kanai and Takeoka. Through the infiltration of a defect layer of liquid crystals into photonic structures, the optical properties can be reversely manipulated by the external electric fields to realize the electrochromatic effect. The relevant research has been summarized by Ozaki and coworkers. Yin and coworkers also highlight recently developed magnetically responsive photonic nanostructures with widely, rapidly and reversely tunable structural colors across the entire visible and near-IR range, which utilize the magnetic field as the convenient stimulus to tune the optical properties by affecting the lattice constant, the orientation, and the structures of the colloidal assemblies. We hope this book will serve as a useful reference to researchers interested in smart nanoscale optical materials, in particular, responsive photonic nanostructures.

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CHAPTER 1

Responsive Bragg Reflectors

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1.1 Introduction

Multilayers have been a common subject of study of materials and optical scientists for many decades. The possibility to attain color from the stacking of films of transparent materials and, furthermore, the fine control over light transmission and reflection they offer, have attracted the attention of both scientists and technologists. Indeed, the industrial development of these materials has led to the realization of a myriad of passive optical elements that are commonly found in all kind of spectrophotometers or optical characterization setups. From the manufacturing perspective, most efforts have been put in the preparation of thin films as stable as possible against changes in the surrounding environment. This has been mainly motivated by their use as filters of a range of selected optical frequencies, which would not be constant if their structure varies in the presence of moisture or as a consequence of temperature variations. This feature implied that the constituent layers could not present accessible porosity in which condensation of vapor could take place. Also, unless pore sizes are in the nanoscale range, the presence of voids could easily lead to diffuse scattering that will deteriorate its optical quality.

There is currently a boost in the development of film deposition techniques that permit a strict control to be achieved over porosity at the mesoscale, thus preventing diffuse optical scattering phenomena. While porosity in general

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endows the film with the potential of hosting guest compounds in the interstitial space, such as potential functional groups or analytes transported from gas or liquid phase, fine tuning of the pore-size distribution yields command over the kinetics of vapor sorption in the layers or molecular-size-selective detection. Actually, many of the porous materials that can be prepared as thin films have already been incorporated in a multilayer structure with the aim of taking advantage of the interplay between the responsive properties that porosity provides. The same aim has been reached by employing a different approach based on the multilayer integration of polymeric films whose thickness and refractive-index change as a function of the species present in their surroundings. In this chapter we will review the main properties that make all these layers interesting building blocks to build responsive optical materials as well as the main synthetic procedures and representative applications that are being explored in this emerging field.

1.2 Fundamentals: Optical Properties of Multilayers

The *optical thickness* of a film is defined as the product of its geometrical thickness times its refractive index. This parameter determines the range of wavelengths for which optical interference effects are observed when a white light beam impinges on the slab surface. Both transmitted and reflected light will present spectral intensity fluctuations whose frequency will depend on the value of the optical thickness relative to the incident wavelength. For a dielectric film, reflectance maxima are expected when half an integer number of wavelengths, respectively, "fit" in the optical thickness of the film. The intensity of these maxima depends on the dielectric constant contrast between the film and the surrounding media, which typically are the air above the film and the substrate supporting it. Optical interferometry of dense thin films is commonly put into practice to prepare antireflection coatings to reduce light insertion losses in sunglasses or devices such as solar cells. For the case of porous films, the possibility was soon realized of making use of the sensitivity of the pattern of lobes observed in transmittance and reflectance spectra to the refractive index of the film for detection and recognition of specific targeted compounds, provided adequate functionalization of the pore walls was achieved. In fact, the first optically responsive films were developed by anchoring antigens to the inner walls of porous silicon films and exposing them to the corresponding antibodies, which gave rise to an increase of the average refractive index of the film that resulted in a redshift of the monitored optical features. The group of Sailor largely contributed in the 1990s and afterwards to the development of porous silicon structures for sensing of different sorts of species based on this approach. An example of this responsive behavior of a porous silicon film is shown in Figure 1.1. Today, there exist many different types of materials that could be shaped as porous films and thus employed as the basis for a responsive interferometric sensing device.

In the last decade, the possibility to stack porous films of different composition and structure preserving the accessibility of the network of