Colloidal Photonic Crystal Pigments with Low Angle Dependence

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ARTICLE

ABSTRACT Poly(methyl methacrylate) (PMMA)-based colloidal photonic crystals have an incomplete photonic band gap (PBG) and typically appear iridescent in the visible range. As powders, synthetic PMMA opals are white, but when infiltrated with carbon black nanoparticles, they exhibit a well-defined color that shows little dependence on the viewing angle. The quantity of black pigment determines the lightness of the color by controlling scattering. The combined effects of internal order within each particle and random orientation among the particles in the powder are responsible for this behavior. These pigments were employed as paints, using a mixture of polyvinyl acetate as a binder and deionized water as the solvent, and were applied to wood and paper surfaces for color analysis.

KEYWORDS: colloidal photonic crystals • synthetic opals • powder pigments • structural color

INTRODUCTION

Iridescence, i.e., angle-dependent, structural color, is one of the defining features of opals and inverse opal photonic crystals in the visible range. These materials have periodic structures in three dimensions, with a periodicity whose length scale is proportional to the wavelength of visible light. The color in opals and inverse opals is due to stop bands or incomplete photonic band gaps (PBGs) that result from multiple scattering and diffraction of light by the ordered structures (1−5). Structural color is particularly vivid in three-dimensionally ordered macroporous (3DOM) oxides with a relatively high refractive index (e.g., 3DOM ZrO_2 and 3DOM TiO_2), which rely on incomplete PBGs for the color effect (6−8). The color of these materials can be tailored by infiltration with solvents of different refractive indices, opening opportunities for new kinds of pigments. Similarly, photonic supraparticles composed of colloidal sphere arrays can exhibit striking opalescent colors (9−11). Several patents mention the use of opals as pigments infiltrated with different materials (12−14). For sufficiently large ordered domains of colloidal photonic crystals, multiple colors (i.e., iridescence) can typically be observed, depending on the viewing angle with respect to given photonic crystal planes. However, there are clues pointing at the possibility of obtaining more definite colors (without iridescence) from these kinds of structures. For example, Takeoka and coworkers developed a hydrogel membrane with 2−4 wt % of a polymer, which displayed a constant color over a viewing angle of 40° (15). Furthermore, the angle dependence of the color of silica sphere arrays could be largely eliminated by adding a second population of smaller spheres, thereby forming amorphous colloidal arrays (16).

Poly(methyl methacrylate) (PMMA) latex spheres have been widely used to fabricate synthetic opals and extended colorful opalescent films (17). However, as powders, such polymeric opals are white, sometimes with some brilliant colorful sparks. On the opposite scale is carbon black, a colloidal form of graphitic carbon and an important black pigment (18). The literature provides evidence that carbon nanoparticles can be used for enhancement of structural color. Pursiainen et al. reported that sub-50-nm carbon nanoparticles, which were uniformly incorporated in the interstices of highly ordered polymeric colloidal crystal films, enhanced the color of these elastomeric films (19). Wang and coworkers observed an enhancement of interference colors after applying a thin carbon layer onto an anodic aluminum oxide film with nanochannels (20). The appearance of pearlescent pigments can also be enhanced by carbon nanoparticles (21).

By mixing white and black powders, one might not necessarily expect to obtain color, but as this study shows, the dark background provided by carbon nanoparticles in contact with opaline domains produces distinctively colored pigments. In this report, the effects of carbon nanoparticles on structural colors of PMMA opals and the dependence of coloration on sphere size, carbon content, viewing angle, and paint vehicles are analyzed. On the basis of structural and spectral analysis of these samples, a qualitative model is proposed to explain the color enhancement and the low degree of angular dependence of the colors of these composite materials.

EXPERIMENTAL SECTION

Methyl methacrylate (99%, Aldrich) and 2,2′-azobis(2-methylpropionamidine) dihydrochloride (97%, Aldrich) were used for the preparation of PMMA spheres of different sizes (340 ± 10 nm, 322 ± 10 nm, 310 ± 10 nm, 270 ± 10 nm, 240 ± 10

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