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Hydrogel Films Encapsulating Fully Organic Scintillating Crystalline Colloidal Arrays with Tunable Emission

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Abstract: Radioluminescent copolymer nanoparticles that self-assembled into a crystalline colloidal array due to electrostatic repulsion were encapsulated within hydrogels. The rejection wavelength of the gels was tuned through drying and swelling the system. © 2021 The Author(s)

1. Introduction

Periodic dielectric structures that stop photonic propagation at particular light wavelengths are known as photonic crystals [1]. One method of forming the periodic structures of photonic crystals is utilizing long-range electrostatic interactions which cause self-assembly into a crystalline colloidal array (CCA) [1-3]. CCAs exhibit iridescence due to pseudo-bandgaps with rejection wavelengths inside the visible light spectrum [4]. These iridescent CCAs have unique optical properties that have been of recent interest [1, 4-7]. A CCA system with an incorporated scintillating agent exhibits the typical radioluminescence of the scintillator, given that the pseudo-bandgap does not overlap the emission. If the rejection wavelength shifts into the range of the emission of the scintillator, the signal is blocked [7,8]. Bragg's equation can be used to relate the interplanar spacing to the observed rejection wavelength of the CCAs.

$$\lambda_0 = 2n_c\, d_{hkl} \sin\theta \tag{1}$$

As the above equation shows, altering the interplanar spacing (d_{hkl}) or the refractive index (n_c) of the particles changes the rejection wavelength of the CCA, and therefore the hydrogel [9]. Different methods of adjusting the interplanar spacing may be employed. Before hydrogel encapsulation, diluting the CCA with deionized water would increase the interplanar spacing, effectively red shifting the rejection wavelength across the visible light spectrum. Once the hydrogel is synthesized, the system can be dried to blue shift the rejection wavelength as the lattice shrinks with evaporated water.

Poly(styrene-co-propargyl acrylate-co-anthracene methyl methacrylate) (PS-PA-PAMMA) nanoparticles were formed by covalently incorporating a scintillating anthracene monomer into a poly(styrene-co-propargyl acrylate) (PS-PA) basis by an emulsion copolymerization. The resulting PS-PA-PAMMA spheres self-assembled into a face-centered cubic (fcc) crystal structure, forming the CCA. Ionic impurities can quickly destroy the crystalline structure [5], so the system was encapsulated in a poly(ethylene glycol) methacrylate (PEGMA) based hydrogel network for stabilization. When excited with X-rays, the emission of the gels exhibited the typical radioluminescence characteristic of anthracene with a maximum peak at ca. 420 nm as long as the rejection wavelength of the CCA did not overlap with the anthracene emission. The reflectance peak of the hydrogels was able to be blue shifted by drying the film. Once the reflectance peak shifted into the region of anthracene emission at ca. 450 nm, the radioluminescence signal was decreased surrounding the peak wavelength (cf. Figure 1).

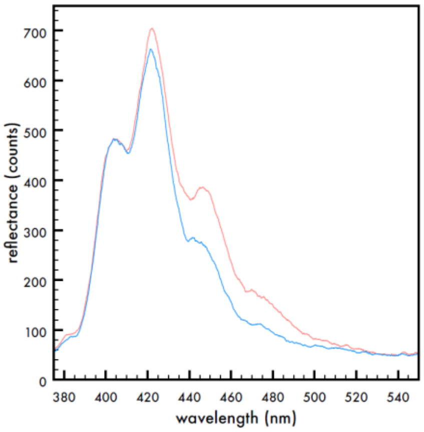

Figure 1. PEGMA based hydrogel encapsulated PS-PA-PAMMA CCA radioluminescence spectra with a rejection wavelength outside anthracene emission at ca. 540 nm (red) versus with rejection wavelength at ca. 450 nm (blue).

2. Experimental

2.1 Materials

The method for the emulsion copolymerization in which the fully organic, X-ray radioluminescent copolymer nanoparticles were produced has been detailed elsewhere [10,11]. In short, a poly(styrene-co-propargyl acrylate)

(PS-PA) basis with anthracene methyl methacrylate (AMMA) covalently incorporated as a scintillating monomer formed poly(styrene-co-propargyl acrylate-co-anthracene methyl methacrylate) (PS-PA-PAMMA) monodisperse nanoparticles. A heated dialysis bath with frequently changed deionized water at 60 °C was used to clean the copolymer nanoparticles for two weeks, then the particles were shaken for 24 hours with excess mixed bed ion exchange resin beads. Dynamic light scattering (Coulter N4 Plus) was used to determine the particle size and size distribution, which were found to be 117 ± 10 nm. The hydrogel encapsulating the CCA was synthesized by mixing the PS-PA-PAMMA CCA with a monomer, poly(ethylene glycol) methacrylate (PEGMA) (MW=360 g mol^{-1}), a crosslinking agent, poly(ethylene glycol) dimethacrylate (PEGDMA) (MW=550 g mol^{-1}), and a photoinitiator, 2,2-diethoxyacetophenone (DEAP). This mixture was injected into a glass cell formed by two glass slides spaced by two layers of Parafilm (total thickness of 250 μm) with 2 cm x 1 cm cutout. The PEGMA based network was photopolymerized in situ with the CCA by placing the filled glass cell under ultraviolet light for four minutes. The gel was then removed from the glass cell and stored in deionized water.

2.2 Optical Characterization

The reflectance spectra of the hydrogel films were collected using a fiber coupled spectrometer (Ocean Optics USB2000) connected to a bifurcated fiber optic bundle (Ocean Optics). A white light source (Ocean Optics LS-1-CAL) was attached to the input arm of the fiber bundle, and the output arm was attached to the spectrometer.

The hydrogel films were irradiated with an Amptek Mini-X X-ray unit equipped with a tungsten target operating at 25 kV and 158 μA. The radioluminescence spectra were collected with a MicroHR (Horiba Jobin-Yvon) monochromator and a cooled CCD detector (Synapse, Horiba Jobin-Yvon). The spectra were always collecting using a slit width of 1 mm and an exposure time of 60 seconds. A grating with 600 line mm^{-1} and a blaze of 500 nm was used to collect the signal. Horiba Jobin-Yvon SynerJY was the software used to analyze the spectra. The plane of the CCA on which the spectra were collected was the [111] plane. The radioluminescence spectra did not account for the emission of the donor.

3. Acknowledgements

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