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Organic X-Ray Radioluminescent Crystalline Colloidal Arrays Encapsulated in Poly(Ethylene Glycol) Methacrylate Based Hydrogel Films

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Abstract: Due to Coulombic forces, X-ray active copolymer nanoparticles self-assembled into crystalline colloidal arrays which were stabilized through encapsulation in hydrogels. The system was able to emit blue light when pumped with an X-ray source.

1. Introduction

X-ray radiography contrast agents typically contain heavy metals within the imaging probe, which can be toxic [1,2]. The scintillating particles used in this work are organic, potentially less toxic, and a promising imaging probe that does not contain a heavy metal component [3]. The scintillator is covalently incorporated into a photonic crystal system through an emulsion copolymerization. Photonic crystals are dielectric materials with periodic structures which inhibit the propagation of photons at specific wavelengths of light, known as a photonic bandgap, or rejection wavelength [4]. Recently, particular interest has examined photonic crystals composed of crystalline colloidal arrays (CCAs) that exhibit iridescence [4-8]. The monodisperse nanoparticles of the CCA assume a minimum energy configuration, which is directly shaped by long-range electrostatic repulsive interactions [9,10]. The CCA exhibits a pseudo gap within the visible light spectrum which can be described Bragg's equation.

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

The rejection wavelength of the CCA (and therefore the hydrogel) can be tuned by altering the interplanar spacing (d_{hkl}) or the refractive index (n_c) of the particles [11]. The interplanar spacing can be altered through the dilution of the CCA with deionized water, effectively red shifting the rejection wavelength across the visible light spectrum.

A scintillating anthracene monomer was covalently incorporated into a poly(styrene-co-propargyl acrylate) (PS-PA) basis through an emulsion copolymerization to generate poly(styrene-co-propargyl acrylate-co-anthracene methyl methacrylate) (PS-PA-PAMMA) nanoparticles. The copolymer spheres self-assembled into a face-centered cubic (fcc) crystal structure. The crystalline structure is susceptible to ionic impurities [5], so the CCA was encapsulated in a poly(ethylene glycol) methacrylate (PEGMA) based hydrogel network for stabilization. The emission of the gels exhibits the typical radioluminescence characteristic of anthracene with a maximum peak at ca. 420 nm (cf. Figure 1).

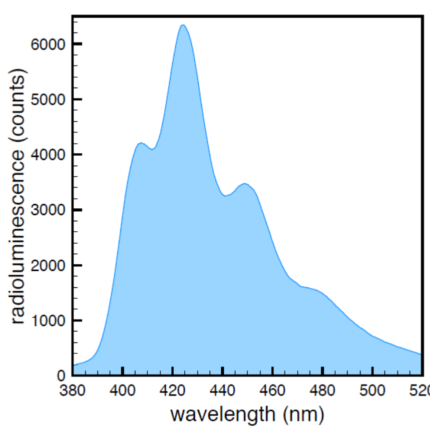

Figure 1: Radioluminescence spectra of PS-PA-PAMMA CCA encapsulated in PEGMA based hydrogel with a rejection wavelength beyond the range of the anthracene emission.

2. Experimental

2.1 Materials

Fully organic, X-ray radioluminescent copolymers were produced by an emulsion copolymerization as described elsewhere [12,13]. The monodisperse nanoparticles synthesized were poly(styrene-co-propargyl acrylate) (PS-PA) based with a covalently incorporated scintillating monomer, anthracene methyl methacrylate (AMMA), to form poly(styrene-co-propargyl acrylate-co-anthracene methyl methacrylate) (PS-PA-PAMMA). The copolymer nanoparticles were cleaned in a dialysis bath with deionized water changed frequently at 60 °C for two weeks, then shaken with mixed bed ion exchange resin beads in excess. The particle size and size distribution were measured with dynamic light scattering (Coulter N4Plus) and were found to be 155.1 ± 10.5 nm. To encapsulate the CCA in a hydrogel, a poly(ethylene glycol) methacrylate (PEGMA) based network was photopolymerized in situ with the CCA. The gel was formed by mixing the PS-PA-PAMMA CCA with PEGMA monomer (MW=360 g mol^{-1}), poly(ethylene glycol) dimethacrylate (PEGDMA) (MW=550 g mol^{-1}) as a crosslinking agent, and 2,2-diethoxyacetophenone (DEAP) photoinitiator. The mixture was placed into a 2 cm x 1 cm space between two glass slides separated by two adhered layers of Parafilm for a thickness of 250 µm. The glass cell was then placed under ultraviolet light to photopolymerize the hydrogel for four minutes.

2.2 Optical Characterization

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

3. Acknowledgements

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