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Fully Organic, X-ray Radioluminescent Crystalline Colloidal Arrays for Next-Generation Bioimaging

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Abstract: An organic, x-ray radioluminescent colloid is fabricated by copolymerizing an organic scintillating monomer within a polystyrene basis. The intensity of emitted light from the radioluminescent colloidal particles can be manipulated by photonic means.

1. Introduction

Colloidal particles for optical bioimaging have become an increasingly investigated area of research; however, their utility for optical bioimaging is limited due to the intense and inherent light scattering that occurs in the blue region of the visible spectrum. A promising strategy to mitigate this difficulty is to exploit scintillators to induce x-ray excited optical luminescence. Scintillating particles are attractive candidates for bioimaging due to their characteristic ability to convert ionizing energy, such as x-rays, into visible light. Additionally, x-rays offer the advantage of superior penetration depth compared to that of visible or ultraviolet light [1]. The use of scintillators for bioimaging is a growing research focus but is limited due to the potential toxicity of heavy metals, such as gadolinium [2,3], used in these bioimaging agents. Using a fully organic system and an organic scintillator, such as anthracene, the potentially harmful side effects associated with toxic heavy metals could be alleviated [4,5].

Photonic crystals describe a class of periodic dielectric materials which exhibit a photonic band-gap (i.e. rejection wavelength) corresponding to specific wavelengths of light where propagation through the crystal is forbidden [6]. In the past few decades, particular interest has focused on photonic crystals composed of crystalline colloidal arrays (CCAs) which exhibit iridescent structural colors similar to that of the precious opal [6-10]. These biomimetic colloids are composed of highly ordered, closed-packed electrically charged particles which are able to self-assemble into three-dimensional periodic arrays due to their repulsive Coulombic interactions [11,12]. While a CCA does not exhibit a complete photonic band-gap due to a low refractive index contrast [13-15], a CCA possesses a pseudo gap (i.e. stop band) in the visible regime that can be described by Bragg's equation. This rejection wavelength can be shifted across the full visible spectrum by a change in the interplanar spacing (d_{hkl}), a change in the refractive index (n_c), or a combination of the two parameters [16].

$$\lambda_0 = 2\, n_c\, d_{hkl} \sin\theta \qquad (1)$$

An anthracene methyl methacrylate monomer was copolymerized with styrene and propargyl acrylate monomers to generate a fully organic, x-ray radioluminescent poly(styrene-co-propargyl acrylate-co-anthracene methyl methacrylate) (PS-PA-PAMMA) CCA (87 nm) that exhibits the typical luminescence characteristics of anthracene. The rejection wavelength of this CCA can be shifted across the visible spectrum by the addition or removal of deionized water (cf. Figure 1(b)) which corresponds to a change in the d_{hkl} spacing. When the rejection wavelength of the CCA is outside of the radioluminescence (RL) spectra, typical anthracene emission behavior is detected. When the rejection wavelength is within the RL spectra of the CCA, a decrease in spontaneous emission at the rejection wavelength is clearly observed. In this system, the decrease in spontaneous emission corresponding to the rejection wavelength of the CCA can be shifted across the entire RL spectra of anthracene (cf. Figure 1(a)).

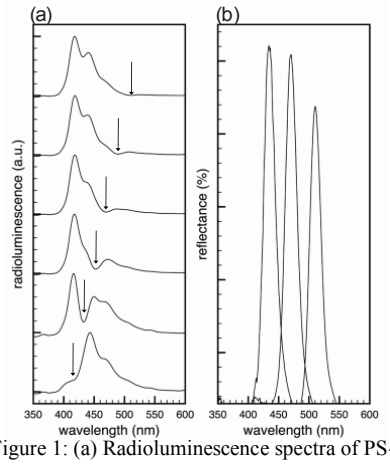

Figure 1: (a) Radioluminescence spectra of PS-PA-PAMMA particles with reflectance spectra denoted by an arrow and (b) Variation in the rejection wavelength of PS-PA-PAMMA particles by the addition of deionized water.

To further investigate the rejection wavelength effect on the spontaneous emission of the system, a small amount of an ionic impurity (NaCl) can be introduced to the CCA such that the crystal structure is destroyed. The RL spectra of the CCA with a rejection wavelength at 433 nm compared to that of the destroyed crystal is shown in Figure 2(a). The difference in

these two spectra is shown in Figure 2(b) where a 76 % decrease in the spontaneous emission of anthracene at 433 nm and a 20 % decrease in total emission is revealed.

2. Experimental

2.1 Materials

Monodisperse, x-ray radioluminescent nanoparticles were synthesized using a modified emulsion polymerization procedure described elsewhere [17,18] where a scintillating organic monomer (anthracene methyl methacrylate [19]) was covalently incorporated into the particle by copolymerization with the poly(styrene-co-propargyl acrylate) basis. The resulting poly(styrene-co-propargyl acrylate-co-anthracene methyl methacrylate) (PS-PA-PAMMA) nanoparticles were cleaned by dialysis in deionized water at 60 °C and shaken with excess mixed bed ion-exchange resin. The particle size and size distribution were measured using a Hitachi 7830 STEM and was determined to be 87 ± 10 nm.

2.2 Optical Characterization

Reflectance spectra of the colloid was collected using a bifurcated fiber optic bundle (Ocean Optics) attached to a fiber coupled spectrometer (Ocean Optics USB2000). The output arm of the fiber bundle was attached to the spectrometer and the input arm of the fiber bundle was attached to a white light source (Ocean Optics LS-1-CAL). The samples were irradiated with an Amptek Mini-X x-ray unit equipped with a tungsten target and operating at 25 kV and 158 μA. To collect the radioluminescence (RL) spectra, a MicroHR (Horiba Jobin-Yvon) monochromator and a cooled CCD detector (Synapse, Horiba Jobin-Yvon) was used. The signal was collected on a grating with 600 line mm^{-1} and a blaze of 500 nm and the exposure time for all samples was 30 seconds with a slit width was 1 mm. A SynerJY (Horiba Jobin-Yvon) software was used to analyze the spectra. The RL spectra was not corrected for the emission of the donor. The reflectance and RL spectra collections were performed at the [111] plane of the CCA.

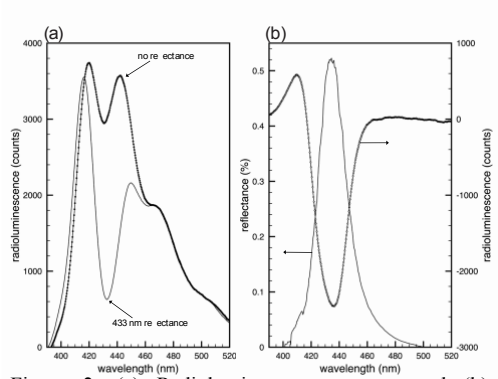

Figure 2: (a) Radioluminescence spectra and (b) Difference in radioluminescence spectra of PS-PA-PAMMA particles (1.55 x 10^{14} particles/mL) with a rejection wavelength at 433 nm and with no rejection wavelength. The rejection wavelength (reflectance spectra) is presented in the latter figure.

3. Acknowledgements

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4. References

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