X-ray Radioluminescent Crystalline Colloidal Arrays Composed of Terpolymer Nanoparticles

Haley W. Jones, Yuriy Bandera, Stephen H. Foulger
Center for Optical Materials Science and Engineering Technologies (COMSET)
Department of Materials Science and Engineering
Clemson University, Clemson, SC 29634-0971, USA
foulger@clemson.edu

Abstract: X-ray active, terpolymer nanospheres are fabricated by copolymerizing styrene, propargyl acrylate, and anthracene methyl methacrylate. The strong Coulombic forces between particles induce spontaneous self-assembly into a crystalline colloidal array.

1. Introduction

Photonic crystals were first investigated in 1887 by Lord Rayleigh [1]; however, the term “photonic crystal” was not coined until 1987 by Yablonovitch [2] and John [3]. Photonic crystals exhibit a photonic bandgap (i.e., rejection wavelength), which corresponds to specific wavelengths where propagation through the crystal is forbidden [4]. Photonic crystals are typically fabricated by self-assembly using one of two methodologies, the first involving steric packing of particles [5,6] and the second using the repulsive Coulombic interactions between particles in a liquid medium [7-9]. In this work, the latter method was used to fabricate an x-ray radioluminescent crystalline colloidal array (CCA) composed of monodisperse, negatively charged terpolymer nanospheres. Due to the lattice spacing of the particles and the refractive index mismatch between the particles and matrix, CCAs possess a pseudo bandgap (i.e., stop band) on the order of visible light of which can be manipulated across the visible spectrum [10-12]. While CCAs have been exploited as precursors for various photoluminescent and optoelectronic advanced materials [13-15], difficulty remains when incorporating blue-absorbing fluorophores within the crystal due to scattering effects. This difficulty can be circumvented by incorporating scintillators in the CCA such that the CCA emits blue light upon x-ray irradiation. By incorporating an organic scintillator within the colloidal particles, the x-ray radioluminescence (XRL) of the CCA can be manipulated by photonic means.

Anthracene, which is the brightest organic scintillator [16], was used in this system such that the CCA emitted blue light upon x-ray irradiation. 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. When the CCA’s rejection wavelength (i.e., reflectance) was not overlapping the XRL, typical anthracene emission behavior was detected, including multiple emission peaks spanning 400 – 515 nm with a maximum at 420 nm. When the rejection wavelength was moved within the XRL, a decrease in spontaneous emission at the rejection wavelength was clearly observed. The decrease in spontaneous emission corresponding to the rejection wavelength was shifted across the entire XRL of the CCA and is shown in Figure 1(a), where an arrow denotes the rejection wavelength. The variation in reflectivity of the CCA is shown in Figure 1(b), which is blue-shifted by the addition of deionized (DI) water to the CCA.

To quantify this photonic effect on the CCA’s XRL, the XRL of the CCA with the rejection wavelength overlapping the emission at 432 nm was compared to the XRL of the CCA at the same particle density, but with a destroyed crystal structure (cf. Figure 2(a,b)). The crystal structure was destroyed by adding a small amount of an ionic impurity, which in this case was NaCl. By comparing the integral of the XRL curve at the rejection wavelength and over the total XRL curve, a 75 % and 21 % decrease in XRL was observed, respectively.

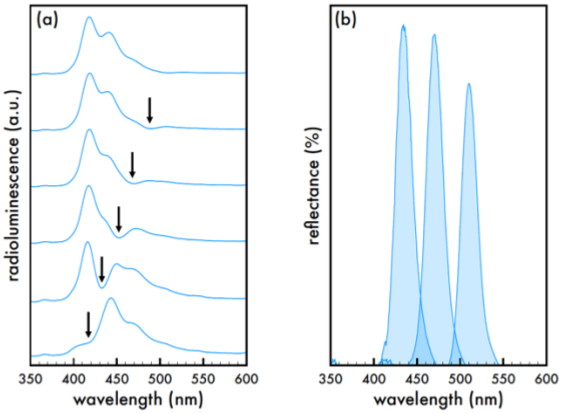

Figure 1: (a) XRL spectra of PS-PA-PAMMA CCA with reflectance spectra denoted by an arrow and (b) Variation in the reflectivity of PS-PA-PAMMA CCA.

In the future, the color of emitted light from the CCA can be adjusted to span the entire visible spectrum by copolymerizing organic fluorophores that form Förster resonance energy transfer (FRET) pairs with each other and the scintillator, such as naphthalimide and rhodamine B.

2. Experimental

2.1 Materials

A modified emulsion polymerization procedure was used to synthesize the radioluminescent CCA [17-19]. An organic scintillating monomer (anthracene methyl methacrylate [20]) was copolymerization in this reaction resulting in a poly(styrene-co-propargyl acrylate-co-anthracene methyl methacrylate) (PS-PA-PAMMA) CCA. The CCA was cleaned by gravity filtration, dialysis, and a mixed bed ion exchange resin. The diameter of the CCA particles was determined to be 87 ± 10 nm using a Hitachi 7830 STEM.

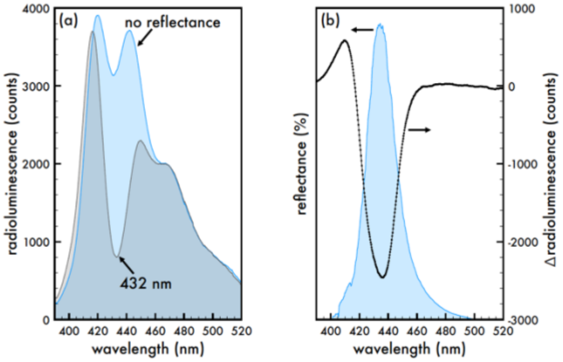

Figure 2: (a) XRL spectra and (b) Difference in XRL spectra of PS-PA-PAMMA CCA (1.55 x 10^{14} particles/mL) with a rejection wavelength at 433 nm and with no rejection wavelength. The rejection wavelength is presented in (b).

2.2 Optical Characterization

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

3. Acknowledgements

The authors thank the National Science Foundation (OIA-1632881) for financial support.

4. References

[1] Rayleigh. The propagation of waves through a medium endowed with a periodic structure. Philos. Mag. 1887, S.5, 24(147):145-159.
[2] Yablonovitch, E. Inhibited spontaneous emission in solid-state physics and electronics. Phys. Rev. Lett. 1987, 58(20):2059-2062.
[3] John, S. Strong localization of photons in certain disordered dielectric superlattices. Phys. Rev. Lett. 1987, 58(23):2486-2489.
[4] Okubo, T. Polymer colloidal crystals. Prog. Polym. Sci. 1993, 18, 481–517.
[5] Ackerson, B. J.; Paulin, S. E.; Johnson, B. Phys. Rev. E 1999, 59:6903.
[6] Cheng, Z.; Russel, W. B.; Chaikin, P. M. Nature 1999, 401:893.
[7] Hiltner, P. A.; Krieger, I. M. Diffraction of light by ordered suspensions. J. Phys. Chem. 1969, 73, 2386.
[8] Hiltner, P. A.; Papir, Y. S.; Krieger, I. M. Diffraction of light by nonaqueous ordered suspensions. Phys. Chem. 1971, 75, 1881–1886.
[9] Clark, N.; Hurd, A.; Ackerson, B. Single colloidal crystals. Nature 1979, 281, 57–60.
[10] Monovoukas, Y.; Gast, A. P. The experimental phase-diagram of charged colloidal suspensions. J. Colloid Interface Sci. 1989, 128, 533–548.
[11] Monovoukas, Y.; Gast, A. P. Microstructure identification during crystallization of charged colloidal suspensions. Phase Transitions 1990, 21, 183.
[12] Rundquist, P.; Photinos, P.; Jagannathan, S.; Asher, S. Dynamical bragg-diffraction from crystalline colloidal arrays. J. Chem. Phys. 1989, 91, 4932–4941.
[13] Lawrence, J. R.; Shim, G. H.; Jiang, P.; Han, M. G.; Ying, Y.; Foulger, S. H. Dynamic tuning of photoluminescent dyes in crystalline colloidal arrays. Adv. Mater. 2005, 17, 2344–2349.
[14] Lawrence, J. R.; Ying, Y.; Jiang, P.; Foulger, S. H. Dynamic tuning of organic lasers with colloidal crystals. Adv. Mater. 2006, 18, 300–303.
[15] Norton, J.; Han, M. G.; Jiang, P.; Creager, S.; Foulger, S. H. Electrochemical tuning the optical properties of crystalline colloidal arrays composed of poly(3, 4-ethylenedioxythiophene) coated silica particles. J. Mat. Chem. 2007, 17(12):1149-1153.
[16] Chandross, E. A.; Ferguson, J.; McRae, E. G. Absorption and emission spectra of anthracene dimers. J. Chem. Phys. 1996, 45(10):3546.
[17] Foulger, S. H.; Jiang, P.; Ying, Y. R.; Lattam, A.; Smith, D.; Ballato, Photonic bandgap composites. J. Adv. Mater. 2001, 13(24):1898.
[18] Woods, M. E.; Dodge, J. S.; Krieger, I. M.; Pierce, P. E. Monodisperse latices. I. Emulsion polymerization with mixtures of anionic and nonionic surfactants. J. Paint Technol. 1968, 40, 541.
[19] Papir, Y. S.; Woods, M. E.; Krieger, I. M. Monodisperse latices III: Cross-linked polystyrene latices. J. Paint Technol. 1970, 42, 571–578.
[20] Bilir, C.; Erdogan, T.; Odabas, S.; Unveren, E. Novel partially fluorinated graft block copolymer ionomer as potential proton exchange membrane material. Polymer 2016, 95, 91–101.