Contract No:

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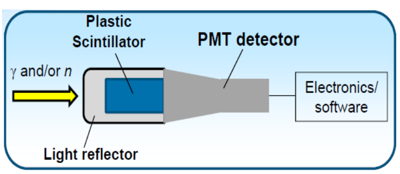
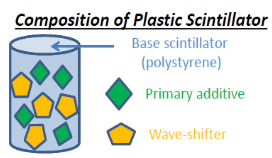
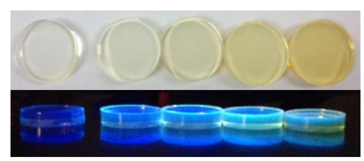
Nano-carbon Dyes for Use in Plastic Scintillators

The protection of civilians, soldiers, and facilities against radiological or nuclear threats represent a true challenge due to the increase of world trade and population movements. This requires the need for developing devices that can readily detect the presence of Special Nuclear Materials (SNM) on the battlefield, shipping ports, and international borders. This need has led to the development of plastic scintillators (PS) because they are robust, stable, reliable, and scalable relative to single inorganic crystals and ^{3}He-filled radiation detectors. A PS contains dyes which are fluorescent molecules that interact with incident radiation and emit visible light that can then be detected. However, improvements in the dyes are necessary for PS to displace state of the art single crystal inorganic and organic scintillators. The goal of this project is to evaluate the photophysical properties of a series of nano-carbon dyes and assessed their ability to be used as dyes in plastic scintillators. This R&D activity supports the SRNL and DOE mission to develop game-changing innovation and tools to advance the national security agenda of the US in the area of field deployable radiation detection.







Awards and Recognition

No awards and/or recognitions were received due to participation in this FY15 LDRD project.

Intellectual Property Review

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publically published in its current form.

SRNL Legal Signature

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Signature **Date**

LDRD-2015-00052
LDRD Report

Nano-carbon Dyes for Use in Plastic Scintillators

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Subcontractor: Clemson University (Tim DeVol, Valery Bliznyuk)

Thrust Area: Non-Proliferation & Nuclear Deterent

Project Type: Standard

Project Start Date: October 1, 2014
Project End Date: September 30, 2015

Scintillation based detectors are desirable for many radiation detection applications (portal and border monitoring, safeguards verification, contamination detection and monitoring). The development of next generation scintillators will require improved detection sensitivity for weak gamma ray sources, and fast and thermal neutron quantification. Radiation detection of gamma and neutron sources can be accomplished with organic scintillators, however, the single crystals are difficult to grow for large area detectors and subject to cracking. Alternatives to single crystal organic scintillators are plastic scintillators (PS) which offer the ability to be shaped and scaled up to produce large sized detectors. PS is also more robust than the typical organic scintillator and are ideally suited for deployment in harsh real-world environments. PS contain a mixture of dyes to down-convert incident radiation into visible light that can be detected by a PMT. This project will evaluate the potential use of nano-carbon dyes in plastic scnitillators.

FY2015 Objectives

- Identify and characterize the photophysical properties of a series of nano-carbon dyes (carbon quantum dots and polycyclic aromatic hydrocarbons)
- Develop a methodology/formulation for the homogeneous incorporation of the nano-carbon dyes in a plastic matrix
- Use the scintillation response to an X-ray source as a screening tool for the down-selection of samples that be further analyzed
- Expose selected samples to a neutron (^{252}Cf) and measure the scintillation response

Introduction

It has been recently demonstrated by a group at LLNL that it is possible to discriminate between high energy neutrons and gamma radiation by means of pulse shape discrimination (PSD) utilizing a PS composed of polyvinyl toluene plastic doped with 2,5-diphenyloxazole (PPO) as a dye.[1] They were able to achieve a PSD of gamma and neutrons that has a figure of merit (FOM) comparable to that of common liquid scintillators. Building upon the PS work of the LLNL group, the addition of a second dye material (known as a wave-shifter) was necessary. This additional dye component is necessary to minimize self-absorption, increase attenuation length, and aid in light collection in complex geometries resulting in an improved PSD capability. In general, all of the state-of the-art PS examined for gamma and neutron PSD contain 3 common components (Figure 1): the base scintillator/plastic (i.e. polyvinyl toluene or polystyrene), primary additive dye (i.e. PPO), and a wave-shifter dye(i.e. 1,4-di-(2-(5-phenyloxazolil))-benzene, POPOP).[2,3] The purpose of the base plastic is to interact with the incident radiation, which is the dominant component of the PS, and serves as an energy donor to the primary

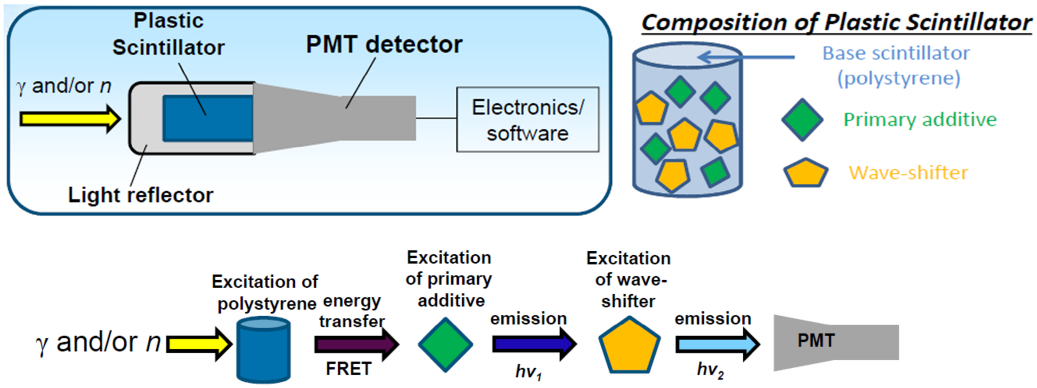

Figure 1. *(top) diagram of radiation detector and the formulation of the scintillating plastic. (bottom) Energy down-conversion process in a plastic scintillator.*

additive through a Forster resonance energy transfer (FRET) mechanism. FRET is a non-radiative energy transfer process involving a resonant dipole-dipole interaction between two electronically similar species. This strong coupling (between the base plastic and primary additive) sharply increases the sampling speed and the light yield of the PS. The primary additive (now in the excited state) emits a photon as it returns to the ground state. Typically, this emitted photon has energy in the UV portion of the spectrum and not optimal for detection by the PMT detector. The purpose of the wave-shifter is to absorb the UV photon emitted by the primary additive and emit another photon further toward the red portion (longer wavelength) of the visible spectrum where the PMT has higher spectral sensitivity (Figure 1, bottom).

The discrimination between fast and thermal neutrons requires the incorporation of neutron targets (i.e. ^{6}Li and ^{10}B) into the PS. Some research groups have successfully achieved Li and B loading of up to 5 wt % in a polystyrene based PS containing 2,5-diphenyloxazole (PPO) as the primary additive and 9,10-diphenylanthracene (DPA) as the wave-shifter. [4,5] Upon the addition of 5 wt % B to the composite, the same composite is now capable of distinguishing simultaneously between fast and thermal neutrons as well as gamma radiation.

Approach

SRNL synthesized nano-carbon dyes (polycyclic aromatic hydrocarbons and carbon quantum dots) and optimized their photophysical properties for scintillation applications. This will include a thorough photophysical characterization of candidate nano-carbon dyes by a variety of spectroscopic techniques (absorption, emission and excitation spectra). Clemson University and SRNL will develop a methodology to incorporate the nano-carbon dyes into a base scintillating plastic such as polystyrene or polyvinyl toluene. Clemson University will be responsible for evaluating the scintillating ability of the PS samples by first using an X-ray source as a screening tool. The promising samples from the screening tests will be excited by a ^{252}Cf source. The ability of the PS to simultaneously discriminate between gamma and neutron (fast and thermal) will be measured by researchers at Clemson University. The primary focus is to develop neutron (fast and thermal) and gamma-ray discriminating multi-functional composites that can be mass produced at low cost and have the potential to be integrated into portable or large area detectors.

Results/Discussion

Two candidate nano-carbon dyes were identified and examined as potential dyes for PS: carbon quantum dots (CQD) and polycyclic aromatic hydrocarbons (PAH). The absorption, emission, and excitation spectra for the candidate nano-carbon dyes were obtained. It was found that the emission maximum of the CQDs is tunable based ion the concentration of the dye in solution with blue emission

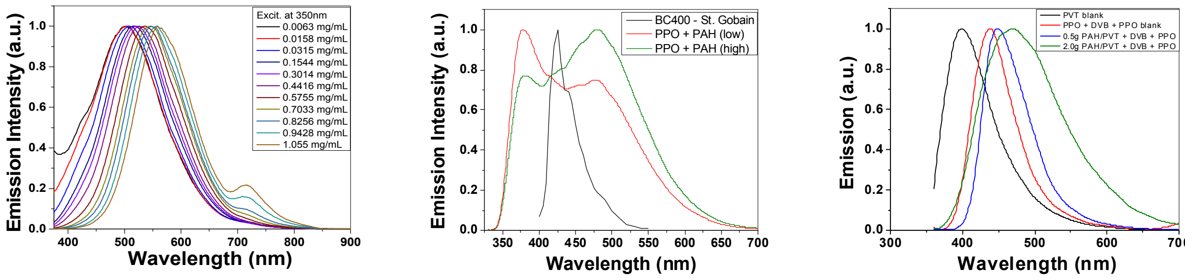

Figure 2. *(left) Fluorescence of CQDS with increasing concentration. (middle) Comparison of PAH/PPO solution fluorescence with commercially available plastic scintillator, (right) Fluorescence comparison of PAH and PPO in PVT.*

observed for low dye concentrations and red emission observed for high dye concentrations. The PAH dyes showed an emission maximum at ~500 nm in a variety of solvent and concentrations. The quantum yield for the CQDs is 12% while the PAHs have quantum yields of 55% in solution. A methodology was developed to infuse polystyrene and polyvinyl toluene (PVT) using a divinyl benzene (DVB) cross-linker with various concentrations of the nano-carbon dyes by in-situ polymerization. A series of sample were prepared with the CQDs and PAHs serving as the primary or wave-shifting dye. Additional samples were prepared with added carborane ($C_2B_{12}H_{12}$) to improve the neutron detection efficiency.

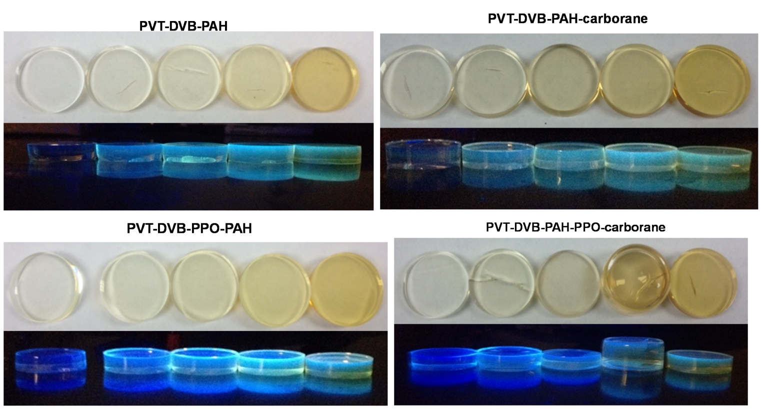

Figure 3. *PVT containing PAH samples as the primary and wave-shifting dye in normal room lighting and UV excitation. Carborane and PPO containing samples are shown as well.*

Excitation with an X-ray source was used as a screening tool to determine which candidate nano-carbon dye containing samples should be further studied. This determined that the CQD dyes were not ideal candidates due to their low light output while the PAH containing samples showed good light output and should be further evaluated. Selected samples were also excited by a ^{252}Cf source and shown in Figure 4. Sample #42 is a blank polyvinyl toluene sample without any added dye. Sample #43 is a commercial plastic scintillator. Samples #46 and #50 are PS samples containing the PAH

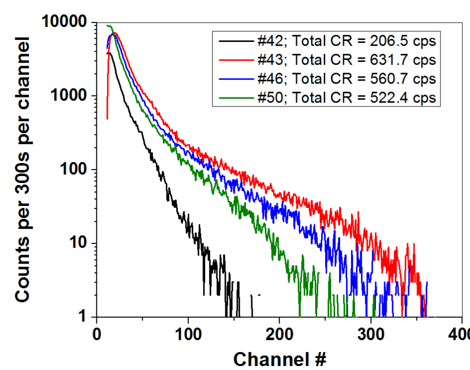

Figure 4. *Response of selected PS samples to ^{252}Cf excitation.*

dyes. This indicates that we are able to successfully prepare PAH containing PS that behave similar to commercially available PS. The use of PAH in this application is worthy of further study because they are relatively abundant and present in crude oil and coal deposits. This could potentially lead to lower cost plastic scintillators because the fluorescent dye is its most expensive component.[2] Also, the PAH dye could potentially be more stable than commonly used dyes (i.e PPO) over longer periods owning to its similarity to graphene and lack of heteroatoms (i.e. N, O).

FY2015 Accomplishments

- Measured the photophysical properties (absorption, excitation, and emission) of CQDs and PAHs in solution and in base plastics (polystyrene and polyvinyl toluene)
- Quantum yields of greater than 50% were achieved for PAH samples
- Developed a formulation and methodology for infusing the base plastic with the PAHs and CQDs while maintaining good optical transparency
- Utilized an X-ray source as a screening tool on 60+ samples to identify which formulation will be suitable for scintillation applications
- Exposed samples to a ^{252}Cf source and measured the light output for the most promising samples identified by the X-ray screening technique

Future Directions

- Compare the scintillation ability of the PAH containing PS with known PS formulations reported in the literature
- Determine the Figure of Merit (FOM) values for pulse-shaped discrimination (PSD) of the nano-carbon dye and boron infused PS to discriminate between thermal and fast neutrons simultaneously
- Examine the use of the nano-carbon dyes in other energy conversion device such as PV solar cells for improved light harvesting and increased

FY 2015 Publications/Presentations

1. “Science and Technology of Hydrogen in Energy Storage and Conversion Devices” Clemson University, Department of Chemistry Seminar Series (November, 2014)
2. “Synthesis and photophysical characterization of fullerene derived polycyclic aromatic hydrocarbons (PAH)” manuscript in preparation.

References

[1] Nuclear Instruments and Methods in Physics Research A 668 (2012) 88–93
[2] Nuclear Instrument sand Methods in Physics Research A 750 (2014) 1–11
[3] Nuclear Instruments and Methods in Physics Research A 761 (2014) 92–98
[4] Nuclear Instruments and Methods in Physics Research A 751 (2014) 62-69
[5] Nuclear Instruments and Methods in Physics Research A 729 (2013) 747–754

Acronyms

CPS- Counts per second
CQDs – carbon quantum dots
PAHs – polycyclic aromatic hydrocarbons

PMT – photomultiplier tube
PPO – 2,5-diphenyloxazole
PS – plastic scintillator

Total Number of Post-Doctoral Researchers/Students

Three postdoctoral researchers (Patrick Ward, SRNL; Josef Velten, SRNL; and Valery Bliznyuk, Clemson University), and one summer intern (Hope Hartman, University of South Carolina) were involved with this project. Two graduate student research assistants at Clemson University (J. Elizabeth Glenn, Kirk Freeman) assisted with the collection of the x-ray and neutron irradiation measurements.