Preliminary investigation of a luminescent colloidal quantum dots-based liquid scintillator

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Abstract. Nanoparticles are appealing materials because of their versatility in addition to the uniqueness of their properties enabling one to use them in different applications. Radiation detection with colloidal quantum dots (cQDs) is one of the domains where the nanoscience entered lately. The luminescent nanocrystals that are cQDs are of particular interest in scintillation dosimetry, where they could play the role of the fluorophore in a liquid scintillator. The study presented in this paper investigates the response of a cQD-based liquid scintillator to X-ray radiation in order to characterize the dose and cQDs concentration dependence of the radioluminescence (RL) signal. For a beam energy of 180 kVp, the latter was found to be linear as a function of dose, with a majority of the signal (~80%) coming from the cQDs and not the solvent, in this case hexane. Even with an ultra low concentration (μM), cQDs emit sufficient light to be detected. The RL intensity followed also a linear trend as a function of cQDs concentration, independently of the exposure time.

1. Introduction

The interest for nanotechnology has been constantly growing over the last decades because of the opportunities offered by nanoscale physics. This young science has first reached the medical sciences when nanoparticles (NPs) were used for drug delivery and optical imaging. It gained popularity in medical physics too where, nowadays, gold NPs are used as dose enhancers during radiotherapy treatments. Different declinations of NPs are available and allow one to choose the right type for the intended application. One of those types is particularly interesting for applications in scintillation dosimetry: colloidal quantum dots (cQDs), luminescent nanocrystals (NCs) of semiconductors. cQDs benefit from the quantum confinement of their charge carriers to have discrete energy levels. Their properties are then proper to the NC size and shape due to a modulation of the bulk medium properties of the same composition. One example of these properties is that they are brighter light emitters than their bulk counterpart. They also have a size-dependent broad absorption and narrow emission spectra [1]. The latter is of interest when considering the match of the scintillation wavelength to the photodetector sensitivity range. Finally, the surface chemistry of the NCs, and their small size, allows

for the dispersion of cQDs in many physical supports (matrices), including water, in an ultra low concentration, of the order of the ppb.

Consequently, the motivation of using a cQD-based liquid scintillator for 3D dosimetry is to get a liquid scintillator with easy control on the scintillation peak wavelength, on the type of solvent and to get a scintillator with low energy dependence. Even if the scintillating cQDs are composed of high-Z elements, the really low concentration of NCs in the liquid could allow one to get rid of this dependence. Lecavalier *et al* [2] have already investigated preliminarily the response of cQDs to cobalt irradiation and obtained promising results concerning the use of cQDs dispersed in hexane and in water for liquid scintillation applications. The study presented in this paper describes further investigation of the response to ionizing irradiation of a cQD-based liquid scintillator. The objective of this particular work is to characterize the scintillation of cQDs dispersed in hexane as a function of dose and concentration.

2. Materials and methods

2.1. cQDs synthesis and composition

The NCs are synthesized in a three-neck flask: the cores are first grown with precursors heated at 250°C to get CdSe, than the shells are synthesized using the successive ion layer adsorption and reaction (SILAR) method [2]. Multiple shells surround the cQDs' core in order to passivate the dangling bonds responsible for the reactivity of the cQDs with their environment. They are successively composed of CdS, $Cd_{0.5}Zn_{0.5}S$ and ZnS as depicted in figure 1. The cQD diameter and elementary composition dictates the peak emission wavelength. Figure 2 presents different colors available for CdSe cQDs. The cQDs were dispersed in hexane and four dilutions were prepared at 1/5, 1/10, 1/20 and 1/30 of the initial concentration, which was 22.5 micro molar (μM). These dilutions fractions correspond respectively to 588, 294, 147 et 98 parts per billion (ppb).
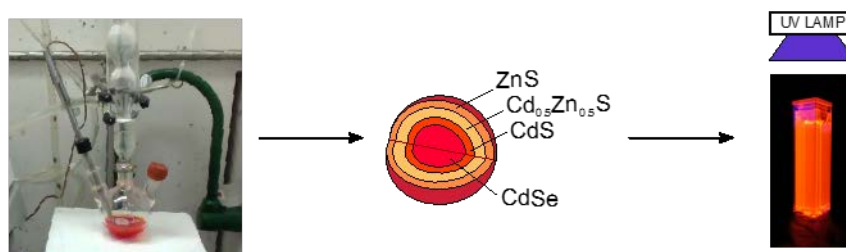

Figure 1. At the end of the synthesis, the cQDs are dispersed in hexane and already have a bright color. When exposed to a UV lamp, the an intense visible photoluminescence is seen. The scheme in the middle of the figure depicts the different layers of the cQDs totalizing a radius of 3 to 4 nm.

Figure 2. CdSe cQDs peak emission wavelengths available sweep widely the visible spectrum as a function of the NCs size (picture from our laboratory LabOMC, Laboratoire d'Optique de la Matière Condensée,).

2.2. Irradiation conditions

The cQDs liquid preparations were irradiated with an orthovoltage device Xstrahl 200 at 180 kVp with a dose rate of 369 MU/min. The field had a diameter of 5 cm and a SSD to D_{max} of 20 cm. The cQDs were also irradiated at 6 MV (Varian Clinac iX) with a 10 x 10 cm² field. The 6 MV measurements were also achieved with a commercial liquid scintillator (Ultima Gold, Perkin Elmer) to get a basis of comparison of the cQDs' intensity.

2.3. Detection set-up

A CCD camera was used to image the vial/cuvette with the cQDs in hexane placed 1 cm away from the field applicator. The set-up was covered with black blankets to cut the residual ambient light contamination. A vial containing only hexane was also irradiated in the same conditions to account for the Cherenkov light production in the solvent.

3. Results and Discussion

3.1. Dose and energy dependence

The radioluminescence (RL) signal collected at 180 kVp was found to be linear with exposure time, hence with dose deposited in the cQDs. Figure 3 presents this linear dependence of the RL intensity over a dose range up to 2.5 Gy. It also shows that the majority (~80%) of the RL intensity is due to cQD scintillation with the remaining 20% from Cherenkov (or fluorescence) from hexane. This implies that the energy transfer between the solvent and the cQDs is good, which is promising since the solvent could be eventually changed to optimize this energy transfer. There is no need for a third component acting in the energy transfer because the cQDs have a broad absorption spectrum, which can be tuned by their size. Even if the NCs have a concentration in the μM range, the signal is sufficient for scintillation measurement. This ultra low concentration lets us believe that cQDs will not perturb the beam for dose measurement purposes.
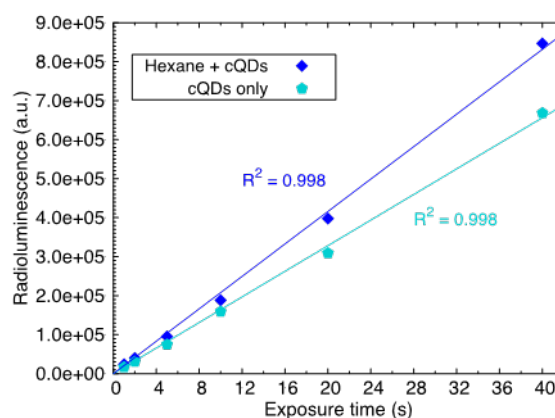

Figure 3. Radioluminescence intensity of the cQD-based liquid scintillator follows a linear trend on a dose range up to 2.5 Gy, with the majority of the signal resulting from the cQDs scintillation. The "cQDs only" curve represents the total signal of cQDs in hexane from which was subtracted the signal from hexane only irradiated in the same conditions.

The collected signal at 6 MV for the cQDs in hexane represents about 3% of the total signal of the Ultima Gold scintillator. At first, this proportion may seem low, but one has to keep in mind that the concentration of fluorophore in the Ultima Gold is far more important than that of the cQDs in hexane. When comparing the proportion of Cherenkov produced in hexane only to the total scintillation signal of cQDs in hexane, we get that the scintillation signal is 120% that of the Cherenkov's. Since the cQDs emission wavelength is at 615 nm, we looked up only at the red channel of the CCD to see the change in that proportion: the percentage reaches up to 500%.

3.2. RL intensity as a function of cQDs concentration

Each dilution was irradiated in the same conditions to characterize the dependence of the RL intensity as a function of the cQD concentration. At the same time, we also collected the RL signal as a function of dose, which gave similar results to figure 3 for all concentrations. As for the concentration

dependence, we found a linear trend of the signal as shown in figure 4, which is valid for the 4 exposure times tested.
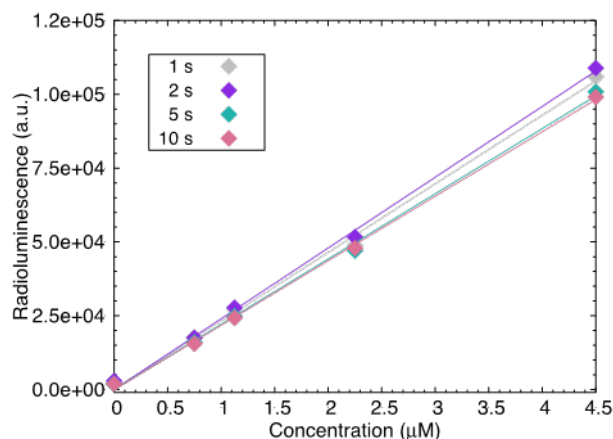

Figure 4. Changing the cQDs concentration of the liquid scintillator affect linearly the radioluminescence intensity. No saturation is seen in this concentration range, the reabsorption of the scintillation light is not significant enough to lower the overall emission quantum yield.

No saturation point, where the RL intensity starts to decrease, was reached so far as it could be observed in photoluminescence [3]. Beyond differences in sample concentration, the excitation sources, ionizing vs. visible, do not have the same energy fluence and energy values (eV vs keV). This could affect the energy transfer mechanism that stays optimal for ionizing radiation. Overall, the linearity observed offers a great way of normalizing the scintillation signal and a possibility to optimize the efficiency by increasing the concentration while remaining in the ppb range.

4. Conclusion
The first preliminary results presented here for cQD-based liquid scintillators are promising. The scintillator fulfills an important requirement for dosimeters to be suitable for applications, that is the linearity of its signal as a function of the dose. Also, it was shown that the concentration of the liquid samples can be taken as a normalization tool and could be chosen to be higher to get a better light production. Further investigation will look into the energy transfer dependence as a function of the solvent, in particular in toluene, alkyl benzene and water, the last two making it easier to manipulate as 3D dosimeters.

5. Acknowledgements

6. References
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