# Luminescence Efficiency of Zn-Cu-In-S / ZnS Quantum Dot films

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***Abstract*— The aim of this work was to prepare three composite ZnCuInS/ZnS (core/shell) quantum dot (QD) flexible films and to examine their luminescent properties under X-ray excitation for potential use in medical imaging modalities. Three PMMA/ QD ZnCuInS composite films, with emission at 530 nm prepared, with concentrations 2.5, 10.0 and 15.0 %w/v. Composite films prepared by homogenously diluting dry powder QD samples in toluene and subsequently mixing with a PMMA/MMA polymer solution. The Absolute Luminescence Efficiency (AE) of the produced films was assessed using medical X-ray excitation. It found that the AE of the films is decreasing in an almost linear way, with increasing X-ray tube voltage. Also, it found that for QDs concentration up to 10.0 %w/v, the AE is increasing rapidly while after that point the relative increase of AE is rather limited. The spectral compatibility of the ZnCuInS/ZnS screen, with various existing optical detectors, was investigated after emission spectra measurements. Highest compatibility (over 90%) found for most CMOS and CCD detectors used in modern imaging modalities.**

***Keywords*— *Quantum Dots; Luminescence Efficiency; ZnCuInS/ZnS; polymer film***

## I. INTRODUCTION

Quantum Dots are semiconductor nanocrystals, which have progressed during the last decade, with their optical properties controlled by their size, shape, and material composition [1], [2]. QDs resemble the particle size of the order of 1nm-20nm, which determines the width of the electronic bandgap [1]. Quantum dots (QDs) have attracted considerable scientific attention due to their distinct advantages of bright fluorescence, broad excitation spectrum, robust structure, and resistance to photobleaching [3]. The QDs have found applications as biological labels, light emitting devices, photovoltaic components and optoelectronic sensors [4]-[6]. Recent studies suggest that QDs can be employed as a good candidate for X-ray detection, in optical diffusion applications of high sensitivity (e.g. in nuclear medical imaging), nuclear physics to X-ray and gamma-ray astronomy [7], [8]-[11], as well as in modalities where high light spatial resolution is required (e.g. in X-ray projection medical imaging) [12-17].

On the other hand, increased awareness of the harmful effects of toxic heavy-metals compounds that could be used in QDs, has led authorities to provide relevant legislation like the European Union Directive 2011/65/EU "Restriction of the use of certain Hazardous Substances" (RoHS). The use of cadmium, a proven carcinogen with toxicity (LD50) of 100 – 300 mg/kg [18] is restricted ten-fold.

ZnCuInS/ZnS QDs are cadmium-free, hydrophobic core-shell structured nanocrystals with an inner core of Zinc Copper Indium Sulfide encapsulated by an outer core of Zinc Sulfide [19]. The ZnCuInS/ZnS quantum dots used in our experiment exhibit spectra emission at 530 nm. They are high luminosity inorganic particles soluble in various organic solvents such as toluene.

Herein, we present a simple and straightforward procedure for the fabrication of thin PMMA films doped with ZnCuInS/ZnS (core/shell) quantum dots. The fabricated composite thin films were of three different QDs

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concentrations. Furthermore, we investigated the Luminescence Efficiency of the fabricated thin films using diagnostic X-rays. Finally, the spectral matching of various optical detectors used in the medical field was estimated.

For the evaluation of ZnCuInS/ZnS, three polymer films doped with ZnCuInS/ZnS were fabricated. Fabricating issues, on different pure polymers doped with nanoparticles, such as aggregation, sample degassing and homogenization, have already been reported by others [20-24].

Our research aimed to evaluate cadmium free ZnCuInS/ZnS quantum dot under medical X-ray irradiation for possible use in medical imaging and detection applications.

## II. Materials and Methods

### A. Fabrication of PMMA/MMA and ZnCuInS/ZnS PMMA/MMA films

Polymethyl methacrylate (PMMA) and methyl methacrylate (MMA) were purchased from Sigma Aldrich and Alfa Aesar GmbH respectively, while the purity of the ingredients reaches 99%. Toluene was purchased from Fluka Chemica and held a purity of more than 99% as well. ZnCuInS/ZnS QDs purchased from PlasmaChem GmbH in powder form. According to the manufacturer's specifications, the QD samples were of 5 nm particle size with an emitting wavelength of 530nm ±15nm. Furthermore, ZnCuInS/ZnS does not contain any high toxicity compound like Cadmium, Lead, Mercury or Arsenide, thus making it quite attractive for utilization in the medical field.

PMMA/MMA low viscosity solution was prepared by mixing PMMA powder with liquid MMA as described in a previously published study [24] of our research group. It was confirmed that the optimum viscosity, in terms of further processing and handling, was established by mixing the two components in a ratio of 1:2.5.

Three samples of ZnCuInS/ZnS QDs in toluene prepared as follows: 25, 100 and 150 mg, were, dissolved in 1 mL toluene in order the final concentration of the nanoparticle colloidal solution to be 2.5, 10.0 and 15.0 %w/v respectively. An ultrasound bath, as well as, vortex stirring used in order to enhance the homogenization of the solutions. Consequently, 1.5 mL of the PMMA/MMA solution added in each test tube, under stirring in a vortex to attain complete homogeneity and afterward poured into molds. The molds placed under vacuum, in order to remove any air bubbles entrapped in the material and then left for further 24h in drying chamber under 50 ºC in order to eliminate residual solvent.

### B. X-ray irradiation of the PMMA/QDs films

QDs/PMMA films were exposed to X-rays on a BMI General Medical Merate tube with rotating Tungsten anode and inherent filtration equivalent to 2 mm Al, with energies ranging from 50 to 130 kVp. An additional 20 mm filtration was introduced in the beam to simulate beam quality alternation by a human body [25].

The experimental setup was carefully designed, in order to keep identical exposure conditions for all samples. The QD films were positioned on the input port of the integration sphere (Oriel 70451), whereas the calibrated photomultiplier was adapted on the integration sphere's output port. The photocathode of the photomultiplier was directly connected to a Keithley Model 6430 Sub-Femtoamp Remote SourceMeter (Keithley Instruments Inc., Ohio, USA) including a preamplifier (Keithley 6430 Remote Preamp), in order to avoid electronic noise amplification due photomultiplier's dynode high voltage.

### C. Absolute Luminescence Efficiency

Luminescent materials efficiency is often expressed in terms of absolute luminescence efficiency (AE) [26], [27], which may be defined as the ratio of the light energy flux (Ψ) emitted by an excited luminescent material over the incident radiation exposure rate (X), that is:

$$AE = \frac{\Psi_\lambda}{X} \tag{1}$$

AE is related to the radiation detection sensitivity of a luminescent material. High AE luminescent materials can be used in medical imaging and may significantly reduce patient radiation dose burden required for various medical imaging examinations.

### D. Spectral matching factor ($a_s$)

The spectral matching factor expresses the efficiency of a photodetector, to capture the light emitted from a scintillator $\alpha_s$ :

$$\alpha_s = \int \phi\lambda(\lambda) S_D(\lambda) d\lambda \,/\, \int \phi\lambda(\lambda) d\lambda \tag{2}$$

Where $\phi\lambda(\lambda)$ is the phosphor's emitted light spectrum and $S_{D(\lambda)}$ is the normalized spectral sensitivity distribution of the photodetector [28].

The emitted light, after excitation using a 365nm UV LED (Prizmatix multichannel LED light source), was measured by a grating optical spectrometer (Ocean Optics Inc., HR2000). The spectral sensitivities of the optical detectors obtained from manufacturers' data [29], [30].

Light absorption measurements on the QD samples conducted by a Perkin-Elmer UV-vis Lambda 15 Spectrophotometer (Perkin-Elmer Life And Analytical Sciences Inc., USA). To account for the potential degradation of the optical signal due to the quartz cuvette and possibly the toluene dissolver, a separate cuvette filled with toluene was placed beside the toluene diluted QD sample to allow for the automatic correction within the software which handled the operation of the Perkin-Elmer instrument.

## III. Results And Discussion

The spectrum of Fig.1 shows the normalized absorption spectrum of the ZnCuInS/ZnS QD sample obtained with the Perkin-Elmer UV-vis Lambda 15 Spectrophotometer in the range between 200 nm and 800 nm. From Fig. 1 a 70 nm wide absorption band, around 500 nm (blue-green region), can be observed. After 630 nm the absorption is less than 5%.

Fig. 2 represents the variation of absolute efficiency (AE) of ZnCuInS/ZnS QDs for X-ray tube voltages between 50 kV and 130 kV. In Fig. 2 also shown, as an inset, measured

spectra produced by the X-ray tube, used in the present study. The tube settings ranged from 60 to 130 kVp at 63 mAs.

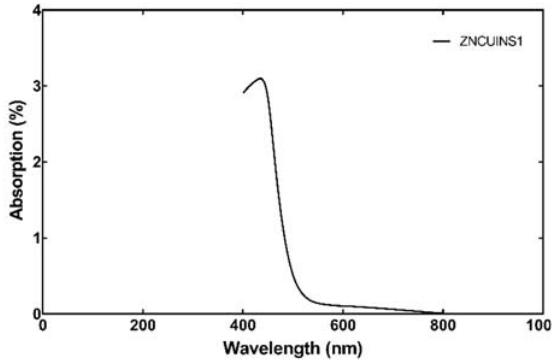


Fig. 1. Absorption of ZnCuInS/ZnS QDs.

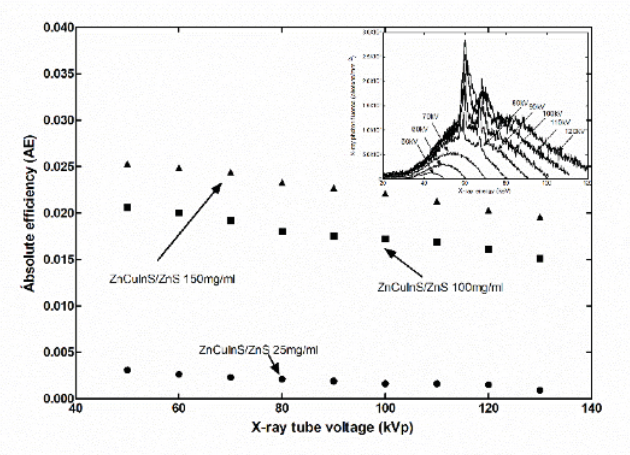


Fig. 2. Variation of absolute efficiency (AE) of ZnCuInS/ZnS QDs for X-ray tube voltages between 50 kV and 130 kV. AE units: μW s/mR m$^2$. "●" is for 2.5 %w/v, "■" is for 10.0 %w/v and "▲" is for 15.0 %w/v.

The absolute efficiency of ZnCuInS/ZnS QDs is decreasing in an almost linear way, with increasing X-ray tube voltage. This particular shape is determined by a) the quantum efficiency, which describes the X-ray absorption mechanisms within the QDs/PMMA films and depends on the coefficient and the film thickness, (b) the intrinsic X-ray to light conversion efficiency, and (c) the light transmission efficiency within the scintillating material, which depends on the light scattering and absorption coefficients as well as the QDs/PMMA films thickness [27], [28], [31].

The relative increase of AE is higher between the 2.5, 10.0 %w/v QDs than the 10.0 and 15.0 %w/v. The smaller relative decrease may be attributed to several light attenuation mechanisms, of which self-absorption is of high importance. The self-absorption of most quantum materials has been previously studied, and the explanation is well defined but not limited to the Stokes shift. When a system absorbs a photon, it gains energy and enters an excited state. One way for the system to relax is to emit a photon, thus losing its energy (another method would be the loss of energy as heat). When the emitted photon has less energy than the absorbed photon, this energy difference is the Stokes shift.

These overlapping bands inevitably lead to self-absorption effects through either non-radiative energy transfer mediated via electron-electron correlation process or actual emission and radiative energy transfer which involves emission and absorption of a photon due to spectral overlap. In the latter case, it can be defined as the reabsorption of luminescence by the phosphor within the excitation volume. It is apparent, that if self-absorption is minimized the QDs emission spectrum would be well separated from their absorption spectrum, i.e., the Stokes shift should be reasonably significant.

Another reason for the AE decrease related to the QDs concentration is that the optical photons in the higher QDs concentration were subjected to higher possibility of scattering. Notably, by increasing the concentration of scattering centers the absorption of the optical photons is also increasing. The scattering is attributed to the formation process of the quantum dot film, in which the QD aggregates with sizes that are comparable to the wavelength of visible light and from scattering centers since granular materials have an increased probability for the scattering effect by increasing the granules ingredient concentration as well as by increasing the energy of the irradiative photons [29].

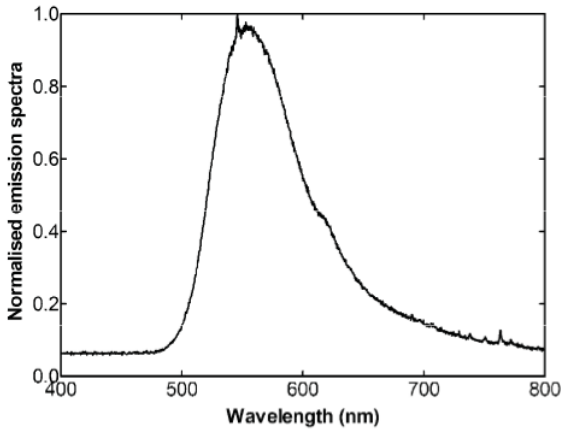


Fig. 3. Emission spectra of the ZnCuInS/ZnS QDs.

Figure 3 shows the emission spectra of the 530nm ZnCuInS/ZnS QDs. The peak of the emission found at 546.1 nm, close to the upper limit of the QD manufacturer's specification (530±15 nm).

The spectral compatibility of ZnCuInS/ZnS QDs with various optical detectors was also examined. Different types of photocathodes, with position sensitive and silicon photomultipliers (SiPMs) used in indirect nuclear medical imaging detectors as well as with complementary metal-oxide semiconductors (CMOS), used in digital radiography and mammography systems, were examined. ZnCuInS/ZnS QDs showed excellent compatibility with complementary metal-oxide semiconductors (CMOS), used in digital radiography and mammography systems, showing maximum value when coupled with a hybrid blue CMOS (0.97). Moreover, excellent compatibility found with photocathodes, incorporated in various types of photomultipliers, such as gallium arsenide photocathodes GaAs (0.97) as well as with charge-coupled devices (CCD) (0.92), and with non-passivated amorphous hydrogenated silicon photodiode (a-Si:H) (0.91), employed in photodiodes and thin film transistors in active matrix flat panel detectors.

## IV. Conclusions

The luminescence efficiencies of the prepared films were evaluated using X-rays for excitation. The results obtained show a decrease in the AE when increasing the X-ray tube voltage. This is quite expected given the X-rays absorption mechanisms that take place inside a scintillator, which directly affect the attenuation coefficient of the scintillator. The variation of absolute efficiency of ZnCuInS/ZnS QDs for three different concentrations 2.5, 10.0 and 15.0 %w/v also examined. It turns out that up to a concentration of 10.0 %w/v the AE is rapidly increasing while after that point the increase in QDs concentration has a slight impact. That is due to many loss mechanisms of which self-absorption and scattering are of great importance. High concentration of granular ingredient like QDs, dramatically increases the number of scattering centers thus decreasing the number of optical photons exiting the scintillator.

Furthermore, since the emission spectrum of ZnCuInS/ZnS showed excellent match with amorphous silicon photodiodes, this material could be incorporated in X-ray imaging devices such as charged-coupled devices (CCD) and complementary metal oxide semiconductors (CMOS), as well as with photocathodes and silicon photomultipliers.

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