Effect of the Concentration on the X-ray Luminescence Efficiency of a Cadmium Selenide/Zinc Sulfide (CdSe/ZnS) Quantum Dot Nanoparticle Solution

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Abstract. In the current study preliminary results on the luminescence efficiency (LE) of toluene dissolved Cadmium Selenide/Zinc Sulfide (CdSe/ZnS, Sigma-Aldrich, Lumidot 694622) quantum dot samples (QDs) after exposure to X-rays of variable radiation flux are shown. The distinctive influence of the weight over volume (w/v) concentration of the samples in LE was investigated. The light emission of the QDs was additionally measured after UV irradiation. The distribution of the emitted light was symmetrical with a maximum at 590 nm. The w/v concentration of the QDs varied between 7.1x10⁻⁵ mg/mL to 28.4x10⁻⁵ mg/mL. The samples were handled in a cubic 12.5x12.5x45mm³ quartz cuvette. Each sample was excited under X-ray irradiation, in the energy range from 50 to 130 kVp using a BMi General Medical Merate tube with rotating Tungsten anode and inherent filtration equivalent to 2 mm Al. The X-ray LE, induced by the 28.4x10⁻⁵ mg/mL QDs found higher, however, the distinction was vague in the highly concentrated samples. The maximum efficiency was obtained at the 90 kVp for QDs with 21.3x10⁻⁵ mg/mL w/v concentration. In the high energy range (120-130 kVp) all concentration levels exhibited comparable X-ray induced LE. The luminescence properties of the investigated QDs appear promising for X-ray detection applications.

Keywords: Quantum Dots; Luminescence Efficiency; CdSe/ZnS

1. Introduction
X-ray medical imaging detectors incorporate a scintillator layer combined with various types of optical sensors [1-14]. Phosphors or scintillators, emit light upon ionizing radiation excitation (X, gamma etc.), which is captured by optical sensors. A development in scintillators is materials with reduced grain size [7, 10, 15-17]. Nanophosphors materials with these properties are Quantum Dots (QDs). [18-24]. QDs are semiconductor nano-crystals with particle size 1-20nm. Due to their unique optical and electrical properties have already been applied in optoelectronic sensors [23-26]. In comparison with traditional scintillators, QDs exhibit better resolution, lower decay time and absence of afterglow, leading to faster response. Furthermore QDs have higher detection efficiency since they are prepared by high atomic number and density materials, such as CdTe, CdHgTe, PbSe and PbTe. Their band gap energy (Eg) can be adjusted in order to be optimally combined with the maximum spectral sensitivity of charged coupled devices (CCD) and complementary metal oxide
semiconductors (CMOS) [16,17,27,28]. However the reduced scattering, due to the reduced grain size, could downgrade image resolution due to high diffusion of emitted light. On the other hand this behavior may increase the emitted photons which reach the imaging device. The aim of the present study was to investigate the effect of the concentration of Cadmium Selenide/Zinc Sulfide (CdSe/ZnS) core-shell type quantum dot nanoparticles on the luminescence efficiency, in the radiography energy range.

2. Materials and Methods

2.1. Quantum Dots preparation
The CdSe/ZnS quantum dot samples were purchased from Sigma-Aldrich (Lumidot 694622) and were dissolved in toluene. CdSe/ZnS has particle size of 4 nm, extinction coefficient 1.6x10^5 L mol^-1 cm^-1, density of 0.865 g/ml at 25°C, excitation wavelength (λ_ex) 575 nm, emitting wavelength 590 nm, full width at half maximum <40 nm and a quantum yield ≥30% [29]. The attenuation of light, at a given wavelength is described by the extinction coefficient. The particular CdSe/ZnS QD has an intermediate extinction coefficient value, compared to other QDs of the same series [29]. This was selected since others with very small extinction coefficient (0.02x10^5 L mol^-1 cm^-1) emit light in the blue region of the optical spectrum, being incompatible with the most common digital optical sensors which are sensitive in the red part of the spectrum. The samples were handled in a cubic 12.5x12.5x45mm³ quartz cuvette. The distinctive influence of the weight over volume (w/v) concentration of the samples in LE was investigated. The w/v concentration of the QDs varied between 7.1x10^-5 mg/mL to 28.4x10^-5 mg/mL. QDs 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 [11].

2.2. Emission spectrum
The emitted light was measured by a grating optical spectrometer (Ocean Optics Inc., HR2000). The mean light photon energy \( \overline{\lambda} \) was determined from the emitted light spectrum of the CdSe/ZnS quantum dot samples.

2.3. Luminescence efficiency (LE)
The efficiency of a scintillator to emit light, after X-ray exposure, can be experimentally determined under clinical conditions by their luminescence efficiency (LE), defined in terms of emitted light energy flux \( \Psi_\lambda \) per unit of incident exposure rate, i.e.:

\[
\eta_A = \Psi_\lambda / \dot{X}
\]

Where \( \dot{X} \) is the exposure rate measured with a Piranha P100B (RTI) dosimeter. AE is expressed in efficiency units (E.U.) \( \mu W \times m^{-2} / (mR \times s^{-1}) \). The light flux measurements were performed using a light integration sphere (Oriel 70451), coupled to a photomultiplier (PMT) (EMI 9798B), connected to a Cary 401 vibrating reed electrometer [9].

3. Results and Discussion
Figure 1 shows the emitted optical spectrum of CdSe/ZnS quantum dot samples normalized to unity in the 400-700 nm wavelength region. The CdSe/ZnS quantum dot samples spectrum shows maximum at 590 nm, lying in the yellow region of the optical spectrum. Having a maximum at 590 nm, the mean light photon energy \( \overline{\lambda} = hc / \lambda \) results to 2.11 eV.

Figure 2 shows the variation of the luminescence efficiency of the CdSe/ZnS quantum dots with X-ray tube voltage, in the range from 50 to 130 kVp. Luminescence efficiency values of the quantum
dots were increased with increasing concentration and saturated in the concentration range of 300 to 400 mg/L. The maximum efficiency was obtained at 90 kVp for a QD concentration of 300 mg/L. In the high energy range (120-130 kVp) all concentration levels exhibited close luminescence efficiency values.

![Normalized emitted light spectrum of the CdSe/ZnS quantum dot samples](image1.png)

**Figure 1.** Normalized emitted light spectrum of the CdSe/ZnS quantum dot samples.

![Luminescence efficiency variation with increasing concentration of the CdSe/ZnS quantum dots](image2.png)

**Figure 2.** Luminescence efficiency variation with increasing concentration of the CdSe/ZnS quantum dots, in the range from 50 to 130 kVp.

### 4. Conclusions

In the present study preliminary results on the luminescence efficiency (LE) of toluene dissolved Cadmium Selenide/Zinc Sulfide (CdSe/ZnS, Sigma-Aldrich, Lumidot 694622) quantum dot samples (QDs), after exposure to X-rays are reported. The influence of the weight over volume (w/v) concentration of the samples in LE was investigated. The w/v concentration of the QDs varied between $7.1 \times 10^{-5}$ mg/mL to $28.4 \times 10^{-5}$ mg/mL. The distribution of the emitted light was symmetrical with a maximum at 590 nm. The X-ray LE, induced by the $28.4 \times 10^{-5}$ mg/mL QDs found higher. The
maximum efficiency was obtained at the 90 kVp for the QDs of the 21.3x10^{-5} mg/mL w/v concentration. In the high energy range (120-130 kVp) all concentration levels exhibited comparable X-ray induced LE. The luminescence properties of the investigated QDs appear promising for X-ray detection applications.

5. References
[1] Antonuk L E 2006 Phys. Med. Biol. 47 R31.
[2] Antonuk L El-Mohri Y and Wang Y 2000 Med. Phys. 27 289.
[3] Doi K 2006 Phys. Med. Biol. 51 R5.
[4] Rossa W, Cody D, Hazle J 2006 Med. Phys. 33(6) 1888.
[5] Gupta R, Grasruck M, Suess C, Bartling S, Schmidt B, Stierstorfer K, Popescu S, Brady T, Flohr T 2006 Eur. Radiol. 16 1191.
[6] Yaffe M, Mainprize J, Jong R 2008 Health Phys. 95(5) 599.
[7] van Eijk C 2002 Phys. Med. Biol. 45 R85.
[8] Michail C, David S, Liaparinos P, Valais I, Nikolopoulos D, Kalivas N, Toutountzis A, Sianoudis I, Cavouras D, Dimitropoulos N, Nomicos C, Kourkoutas K, Kandarakis I, Panayiotakis G 2007 Nucl. Instrum. Meth. Phys. Res. A 580, 558.
[9] Michail C, Valais I, Seferis I, Kalivas N, David S, Fountos G, Kandarakis I 2014 Radiat. Meas. 70 59.
[10] Blasse G and Grabmaier B 1994 Luminescent materials (Berlin:Springer).
[11] Michail C, Kalivas N, Valais I, David S, Seferis I, Toutountzis A, Karabotsos A, Liaparinos P, Fountos G and Kandarakis I 2013 J. Lumin. 144 45.
[12] Nagarkar V, Miller, S, Tipnis S, Lempicki A, Brecher C, Lingertat H 2004 Nucl. Instr. Meth. B. 213 250.
[13] Michail C, Fountos G, David S, Valais I, Toutountzis A, Kalivas N, Kandarakis I and Panayiotakis G 2009 Meas. Sci. Technol. 20 104008.
[14] Michail C, Kalivas N, Valais I, Fudos I, Fountos G, Dimitropoulos N, Koulouras G, Kandakis D, Samarakou M, Kandarakis I 2014 Biomed. Res. Int. 2014 634856.
[15] Kandarakis I and Cavouras D 2001 Nucl. Instrum. Meth. Phys. Res. A 460 412.
[16] Seferis I, Michail C, Valais I, Fountos G, Kalivas N, Stromatia F, Oikonomou G, Kandarakis I, Panayiotakis G 2013 Nucl. Instrum. Meth. Phys. Res. A 729 307.
[17] Seferis I, Michail C, Valais I, Zeler J, Liaparinos P, Fountos G, Kalivas N, David S, Stromatia F, Zych E, Kandarakis I, Panayiotakis G 2014 J. Lumin. 151 229.
[18] Zych E, Meijerink A and Doneg C 2003 J. Phys.: Condens. Matter 15 5145.
[19] Kim S, Park J, Kang S, Cha B, Cho S, Shin J, Son D, Nam S 2007 Nucl. Instrum. Meth. Phys. Res. A 576 70.
[20] Konstantatos G, Clifford J, Levina L and Sargent E 2007 Nat. Photonics 1, 531.
[21] Konstantatos G and Sargent E 2010 Nat. Nanotechnol. 5 391.
[22] Rauch T, Böberl M, Tedde S, Fürst J, Kovalenko M, Hesser G, Lemmer U, Heiss W and Hayden O 2009 Nat. Photonics 3 332.
[23] Eychmuller A 2000 J. Phys. Chem. B 104 6514.
[24] Ma Y, Qi L, Ma J, Cheng H, Shen W 2003 Langmuir 19 9079.
[25] Guo S, Konopny L, Popovitz-Biro R, Cohen H, Sirota M, Lifshitz E, Lahav M 2000 Adv. Mater. 12 302.
[26] Wang C, Chen A, Chen I 2006 Polym. Adv. Technol. 17 598.
[27] Michail C, Spyropoulou V, Fountos G, Kalivas N, Valais I, Kandarakis I, Panayiotakis G 2011 IEEE Trans. Nucl. Sci. 58(1) 314.
[28] Michail C, Valais I, Seferis I, Kalivas N, Fountos G and Kandarakis I 2015 Radiat. Meas. 74 39.
[29] Lumidot CdSe/ZnS 610, core-shell type quantum dots, specification sheet, 694614 Sigma-Aldrich, http://www.sigmaaldrich.com/catalog/product/aldrich/694614?lang=en&region=GR