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To cite this article: G. Saatsakis *et al* 2017 *J. Phys.: Conf. Ser.* **931** 012030

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Preliminary Study of ZnS:Mn^{2+} Quantum Dots Response Under UV and X-Ray Irradiation

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Abstract. Quantum Dots are semiconductor nanocrystals, with their optical properties controlled by their size, shape and material composition. The aim of the present study is to examine the scintillation properties of Manganese Doped Zinc Sulfide (ZnS:Mn^{2+}) Quantum Dot (QDs) nanocrystals under UV and X-ray irradiation. ZnS:Mn^{2+} Quantum Dots, with typical diameter of ZnS dots of 13-20nm (also called scintillation QDs, stQDs), were developed and acquired by Mesolight Inc. The initial stQD sample was a solution of 75mg of ZnS:Mn^{2+} dissolved in 100 μL of Toluene, having a concentration of 75% w/v. Emission characteristics under UV and X-Ray excitation were examined. Two ultraviolet sources were incorporated (315 nm and 365 nm) as well as a medical X-ray tube with tube voltage from 50 to 130 kVp. Parameters such as Energy Quantum Efficiency under UV excitation and Luminescence Efficiency-LE (light energy flux over exposure rate) under X-ray excitation were examined. Luminescence Efficiency (LE) of ZnS:Mn^{2+} was higher than that exhibited by previously examined QDs, (ZnCdSeS:ZnS and ZnCuInS:ZnS). The ability of ZnS:Mn^{2+} to transform UV photons energy into optical photons energy, tends to increase while the incident UV wavelength decreases. Energy Quantum Efficiency of the sample exhibited a 6% increase when exposed to 315nm UV light compared to 365 nm. The emission spectrum of the stQDs, exhibited a narrow peak (~585nm) in the yellow range.

Keywords: Quantum Dots; Luminescence Efficiency; ZnS:Mn^{2+} ; polymer film

1. Introduction

X-ray medical imaging detectors incorporate a scintillator layer combined with various types of optical sensors [1-10]. Phosphors or scintillators, emit light upon ionizing radiation excitation (X, gamma etc.), which is captured by optical sensors. A development in scintillators could be materials with reduced grain size [7, 11-12]. Quantum dots (QDs) are materials that exhibit such properties [13-19]. QDs are semiconductor nano-crystals with particle size 1-20nm. Due to their unique optical and electrical properties, have already been used as optoelectronic sensors [17-20]. In comparison with traditional scintillators, QDs exhibit better resolution, lower decay time and absence of afterglow, leading to faster response. Furthermore QDs such as CdTe, CdHgTe, PbSe and PbTe, have high detection efficiency since they are prepared by high atomic number and density materials. Their band gap energy (E_g) 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) [11,12,21,22]. However, the reduced scattering and the high diffusion of



the emitted light, due to the reduced grain size, could downgrade image resolution. On the other hand this behavior may increase the emitted photons which reach the imaging device. The aim of the present study was to evaluate the response of Manganese Doped Zinc Sulfide ($ZnS:Mn^{2+}$) quantum dot nanoparticles in UV and X-ray energy range.

2. Materials and Methods

2.1. Quantum Dots preparation

The $ZnS:Mn^{2+}$ quantum dot samples dissolved in toluene were purchased from Mesolight Inc. $ZnS:Mn^{2+}$ has particle size of 13-20nm, excitation wavelength (λ_{ex}) below 370 nm, emitting wavelength 585 nm, full width at half maximum <20 nm and a quantum yield $\geq 30\%$ [24]. $ZnS:Mn^{2+}$ quantum dots were selected since they emit light in the yellow region of the optical spectrum, being compatible with the most common digital optical sensors which are utilized in biomedical instrumentation, such as CMOS, SiPMs. 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 tube voltage ranging from 50 to 130 kVp. An additional 20 mm filtration was introduced in the beam to simulate beam quality alteration by a human body [8]. Furthermore QDs were exposed to UV light sources of 315 nm (Vilber Lourmat, VL-215M) and 365 nm (Prizmatix). The experimental setup was carefully designed, in order to keep identical exposure conditions for both wavelengths. This enables direct comparison of the measurements.

2.2. Emission spectrum

The emitted light was measured by a grating optical spectrometer (Ocean Optics Inc., HR2000). The mean light photon energy $\overline{E_\lambda}$ was determined from the emitted light spectrum of the $ZnS:Mn^{2+}$ quantum dot samples.

2.3. Absolute Efficiency (AE)

The efficiency of a scintillator to emit light, after X-ray exposure, can be experimentally determined under clinical conditions by its Absolute Efficiency (AE), defined in terms of emitted light energy flux Ψ_λ per unit of incident exposure rate, i.e.:

$$\eta_A = \Psi_\lambda / X \quad (1)$$

Where X is the exposure rate measured with a Piranha P100B (RTI) dosimeter. Absolute Efficiency (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 [6].

2.4 Energy Quantum Efficiency

The intrinsic Energy Quantum Efficiency of a scintillator is the ratio of photon energy emitted from the luminescent sites to the total energy trapped at those sites. Absent from any non-radiative relaxation processes, this ratio is, $\eta = E_\lambda / \beta E_g$, where E_λ is the energy of emitted photons.

3. Results and Discussion

Figure 1 show the absorbance and emission spectrum respectively, of $ZnS:Mn^{2+}$ quantum dot samples in the 300-700 nm wavelength region. The $ZnS:Mn^{2+}$ quantum dot samples spectrum shows maximum at 585 nm, lying in the yellow region of the optical spectrum. Having a maximum at 585 nm, the mean light photon energy ($\overline{E_\lambda} = hc / \lambda$) results to 2.14 eV.

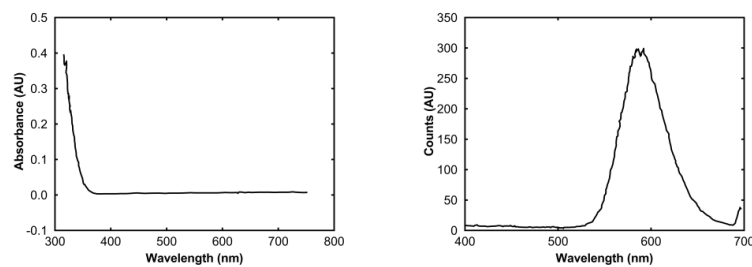


Figure 1. Left) Absorbance spectrum and right) emission spectrum of the ZnS:Mn^{2+} quantum dot.

Figure 2a presents the energy distribution emitted by the UV 315 nm source as well as the resulted energy distribution emitted by the ZnS:Mn^{2+} quantum dot, while in the same figure the Energy Quantum Efficiency is also shown as an insert. Replacing the UV source with the 365 nm, produce the results shown in figure 2b. From the above it is clearly shown that exciting the ZnS:Mn^{2+} with the UV 315 nm produces more scintillating photons compared with the 365 nm excitation, which is quite expected given the absorbance spectrum of the ZnS:Mn^{2+} . Also it is shown that greater amount of UV energy is transformed into visible photons when excited with UV 315 nm resulting in increased Energy Quantum Efficiency.

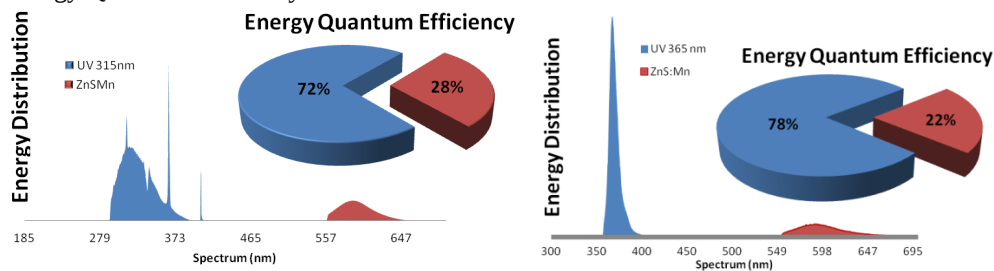


Figure 2. a) Distribution of the emitted photon energy of the UV 315 nm and the resulted ZnS:Mn^{2+} emission photon energy. Insert) Energy Quantum Efficiency of ZnS:Mn^{2+} excited by UV 315 nm. b) Distribution of the emitted photon energy of the UV 365 nm and the resulted ZnS:Mn^{2+} emission photon energy. Insert) Energy Quantum Efficiency of ZnS:Mn^{2+} excited by UV 365 nm.

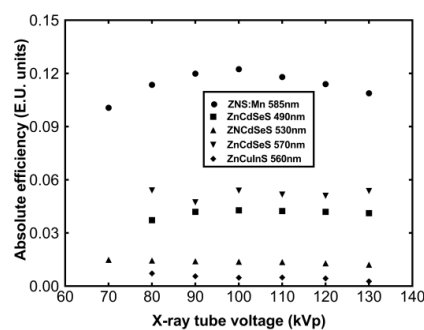


Figure 3. Absolute efficiency (AE) of quantum dots samples irradiated with X-rays.

Figure 3 shows the variation of the Absolute Efficiency (AE) of the ZnS:Mn^{2+} quantum dots with X-ray tube voltage, in comparison with two other QDs, in the range from 50 to 130 kVp. Absolute Efficiency values of the ZnS:Mn^{2+} quantum dots were increased with increasing voltage and saturated at 90-100 kVp. The Absolute efficiency values of the ZnS:Mn^{2+} sample were quite higher than that exhibited by ZnCdSeS and ZnCuInS making the ZnS:Mn^{2+} a good candidate for X-ray sensors.

4. Conclusions

Energy Distribution as well as Energy Quantum Efficiency of ZnS:Mn^{2+} was measured, when exposed to UV315 and 365 nm light. The distribution of the emitted light was symmetrical with a maximum at 585nm. AE of ZnS:Mn^{2+} was higher than that exhibited by ZnCdSeS and ZnCuLnS , making the material promising for X-ray detection applications like security devices or radiation protection and eligible for further investigation regarding imaging. The investigated QD, shown great performance in terms of Energy Quantum Efficiency, when exposed to UV light. Higher efficiency was demonstrated when exposed to UV315 nm compared to the UV365 nm. 28% of the UV energy trapped in the QD was directly transformed into visible light energy.

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