

# Nanocrystal-based Scintillators for Radiation Detection

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Abstract. Several metal chalcogenides (e.g., ZnS, CdSe/ZnS) are known to be highly efficient scintillators. Concerns related to the use of these commercially available inorganic compounds (particle size:  $\mu\text{m}$ ) include their low solubilities in organic and polymeric matrices. Their preparation in inorganic matrices, such as sol-gels, results in non-transparent gels, thus lowering their efficiency as scintillating devices. By reducing their particle sizes from commonly used micrometer- into nanometer-size regimes, their optical properties and solubilities in **both** polar and nonpolar solvents can be controlled. The combination of sol-gel technique and the chemistry of inorganic nanocrystalline quantum dots will be demonstrated as a powerful method in preparing scintillating devices.

## INTRODUCTION

Uses of commercially available inorganic semiconductors (bulk particle size range:  $\mu\text{m}$ ) as scintillators have been limited by their low solubilities in organic and polymeric matrices. Likewise, their preparation in inorganic matrices, such as sol-gel, results in optically opaque gels with the lowering of photoluminescence (PL) quantum yields.

During the past two decades, there have been extensive investigations on semiconductor nanocrystals or quantum dots (QDs). These nanocrystals are often composed of atoms from groups II-VI or III-V elements in the periodic table. When the sizes of these QDs become comparable to or smaller than the bulk exciton Bohr radius, unique optical and electronic properties occur [1-4]. These effects arising from the spatial confinement of electronic excitations to the physical dimensions of the nanocrystals are referred to as quantum confinement effects. One such effect is the quantization of the bulk valence and conduction bands which results in discrete atomlike transitions that shift to higher energies as the size of the nanocrystal decreases. With the size-dependent optical properties of QDs (especially photoluminescence property), QDs with specific sizes can be made for specific detection wavelengths over the whole UV/Vis range.

In 1993, Bawendi and coworkers [5] were the first group to synthesize highly luminescent CdSe QDs by using high-temperature organometallic procedure. Later, the deposition of a surface-capping layer such as ZnS or CdS in the core/shell QD

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structure was also found to dramatically increase the quantum yields of CdSe nanocrystals up to 40 – 50 % at room temperature [6–8]. Other key advances in this area also include the synthesis of highly luminescent CdTe, CdSe, and CdS QDs in large quantities [9–10], better understanding of the QDs' surface chemistry and the preparation of water-soluble nanocrystals [11–13], enabling their applications in microelectronics, optoelectronics [1–4] such as light emitting devices [14–15], and in biological and medical applications such as multicolor fluorescent labels for ultrasensitive detection and imaging [11–13, 16–17].

We report here the application of highly luminescent II-VI semiconductor QDs (particle size range: *ca* 1 to 20 nm) as an entirely new class of neutron detectors. The QDs prepared were compatible to various inorganic and organic matrices. The quantum confinement effects enabled the QDs to be used with a wide variety of detectors. With the combination of advantages from nanochemistry and sol-gel chemistry, the QDs were embedded into sol-gel matrix and optically clear sol-gel scintillators were obtained.

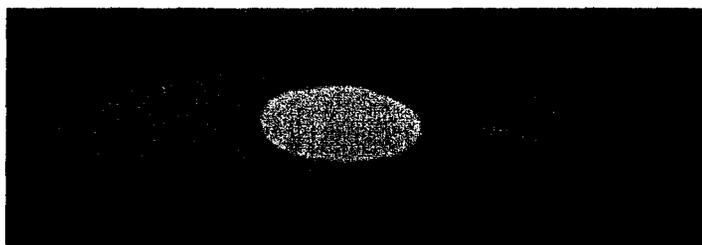
## Objectives of Nanoparticle Research

This research is expected to contribute to the development of new methodologies leading to significantly greater efficiencies of position-sensitive neutron detectors and will give rise to a new generation of scintillating materials. The specific objectives are: (1) to synthesize a new class of radiation scintillators using nanomaterials (ZnS, CdS, CdSe, ZnSe, and shelled nanoparticles); (2) to develop a scientific basis for a new methodology to greatly enhance fluorescent efficiencies induced by nuclear reactions through quantum confinement effect.

## RESULTS AND DISCUSSION

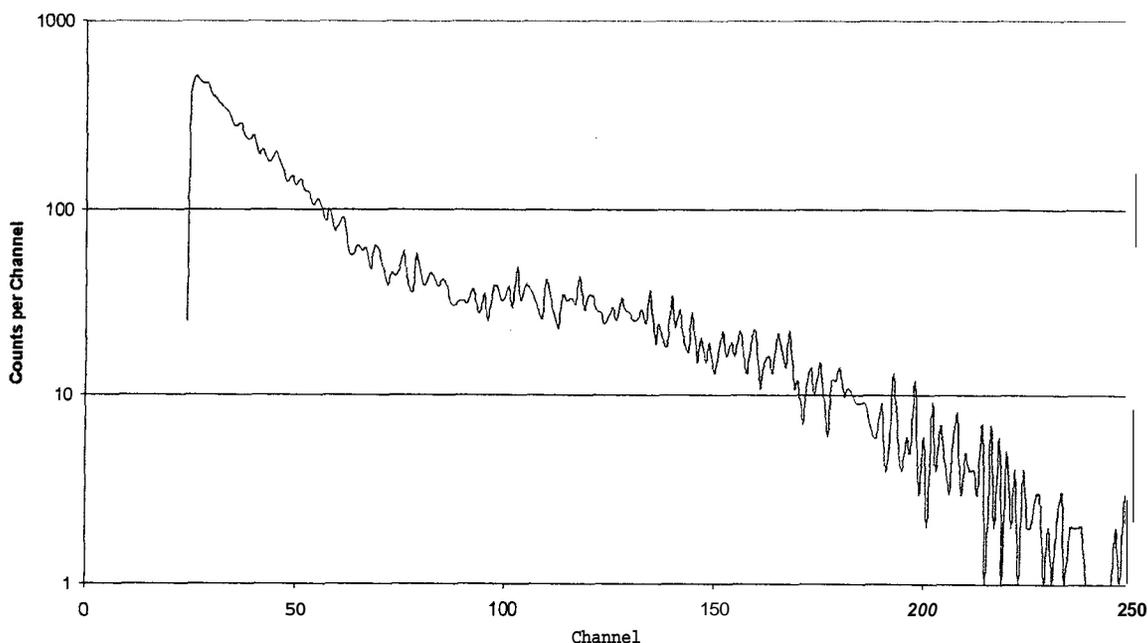
Two types of QDs were synthesized, namely core/shell (CdSe)ZnS and ZnS QDs. The syntheses involve the use of long chain phosphine oxide or phosphinic acid coordinating agents. In the presence of these surfactant molecules, reverse micelle structures are formed and the nucleation and particle growth of semiconductors occur only in the centers of reverse micelles, resulting in the control of particle sizes. At elevated reaction temperatures (150 – 360 °C), highly crystalline QDs are formed.

The core/shell (CdSe)ZnS QDs with various particle sizes were synthesized by a two-step method modified from the literatures [6, 9]. The first step involves the size-controlled synthesis of CdSe QD cores and the second step involves the passivation of CdSe core surface defect sites by the ZnS QD shell. Upon the surface passivation of CdSe core by the ZnS shell, the QDs' photoluminescence was enhanced by three orders of magnitude and the reported quantum yields were as high as 50% [6]. To obtain water soluble QDs, the surface ligand exchange with a hydrophilic ligand, dithiothreitol (DTT), was performed according to the procedure reported by Thompson and coworkers [13]. Hydrophilic QDs were then added during the preparation of lithiated (<sup>6</sup>LiOH) gels. The resulted nanocrystal-based scintillators in sol-gel matrices were transparent and highly luminescent (FIGURE 1).



**FIGURE 1.** Photoluminescence from (CdSe)ZnS QD sol-gel scintillators with various particle sizes of QDs.

A test scintillator sample was fabricated consisting of sol-gel doped with (CdSe)ZnS nanocrystals with a peak fluorescence emission wavelength around 590 nm. The sample was irradiated with alpha particles from a small Po-210 alpha source and the scintillation pulses were detected and recorded using a standard photomultiplier tube, amplifier, and multi-channel board setup. **FIGURE 2**, the resulting pulse height spectrum of the scintillation pulses, shows the distribution of the pulses across the different amplitude values. Comparison with the signal from background radiation showed that the Po-210 source produced pulses in the scintillator that were comparable in amplitude to those produced in existing inorganic scintillators.



**FIGURE 2.** Pulse height spectrum of (CdSe)ZnS QD scintillator.

ZnS QDs were synthesized at an elevated temperature, giving rise to highly crystalline and highly luminescent QDs with a peak fluorescence emission wavelength at **380 nm** (**FIGURE 3**, at the excitation wavelength of **337.1 nm** using dye LASER). The photoluminescence band from the ZnS QDs presented here is much narrower

(FWHM 18 nm) than those reported from the ZnS nanocrystals prepared either at room temperature or by other methods (FWHM of at least 80 nm) [18–20]. Sol-gel based neutron sensors containing  $^6\text{Li}$  and highly luminescent ZnS QDs with various dopants, including  $\text{Ag}^+$ ,  $\text{Mn}^{2+}$ , and  $\text{Ce}^{3+}$ , are currently under an investigation in our group.

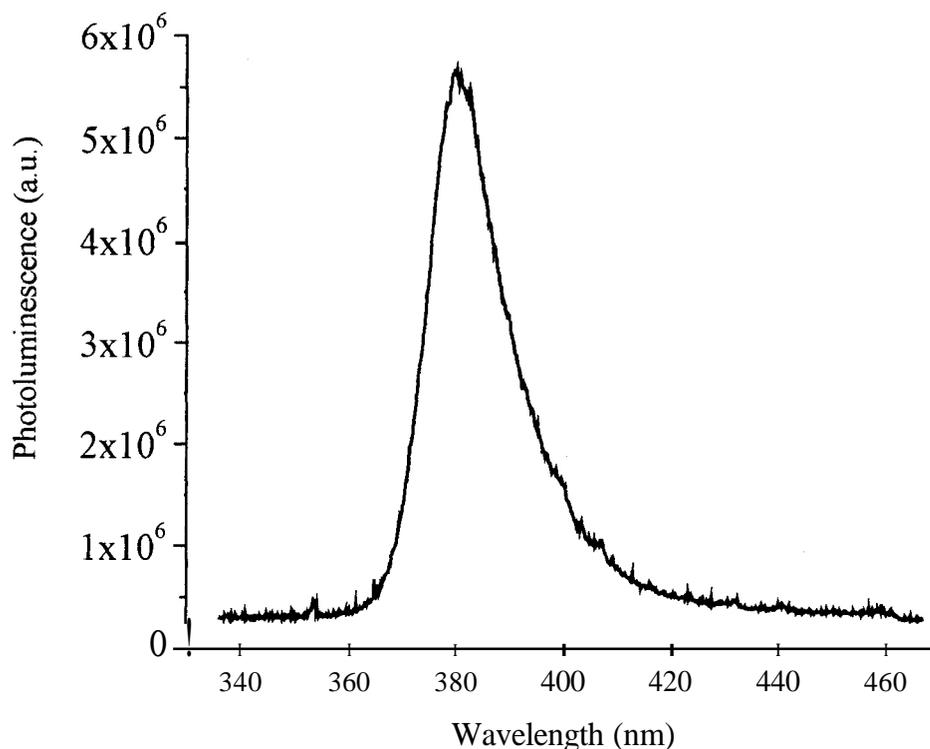


FIGURE 3. Photoluminescence spectrum of ZnS QD (excitation wavelength at 337.1 nm).

## ACKNOWLEDGMENTS

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