$CsPbBr_3$ quantum dot-PMMA composite coatings for spectroscopic performance improvement in GAGG:Ce scintillation detectors

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1. Introduction

Scintillation detectors are essential tools for gamma-ray spectroscopy in nuclear security, environmental monitoring, medical imaging, and industrial applications. However, their energy resolution remains one to two orders of magnitude inferior to high-purity germanium detectors. Key limiting factors include intrinsic scintillator properties, light collection efficiency losses from total internal reflection, spectral mismatch with photodetectors, and photodetector noise characteristics [1].

Perovskite quantum dots (QDs) have emerged as promising candidates for radiation detection enhancement through radioluminescence, wavelength shifting, and hybrid meta-scintillator structures [2, 3]. However, most prior studies have focused on radioluminescence intensity or X-ray imaging resolution, with limited systematic evaluation of gamma-ray spectroscopic performance metrics such as energy resolution and peak-to-valley ratio (PVR).

This study investigates $CsPbBr_3$ QD-PMMA composite coatings on GAGG:Ce scintillators, systematically evaluating gamma-ray spectroscopic performance with ^{137}Cs and ^{60}Co sources across QD concentrations of 1-4 wt.%, with PMMA-only controls to isolate QD contributions.

2. Methods and Results

A cylindrical GAGG:Ce scintillator (25 mm × 4 mm) was coupled to a PMT (H10828, Hamamatsu) via an optical pad, with a PTFE reflector on the opposite surface. Signals were processed through a preamplifier (CR-113, Cremat) and digitizer (DT5725, CAEN) with 600 s live time at -1000 V. $CsPbBr_3$ QDs (510±5 nm emission) were incorporated into PMMA at 1-4 wt.%. A multi-step coating process (primer + QD-PMMA drop-casting with 50-80 ℃ sequential drying) was applied. PMMA-only coatings served as controls. Standard ^{137}Cs(0.231 μCi) and ^{60}Co (0.636 μCi) disk sources were used. Energy calibration and Gaussian fitting were performed using MC^{2}Analyzer, with MATLAB deconvolution for unresolved peaks.

3. Experimental Results

QD-PMMA-coated scintillators exhibited sharper photopeaks and higher centroid positions. For ^{60}Co, the 1332.492 keV peak became resolvable after coating, whereas it was not observable in the bare spectrum. PMMA-only control degraded performance, confirming QD-specific enhancement.

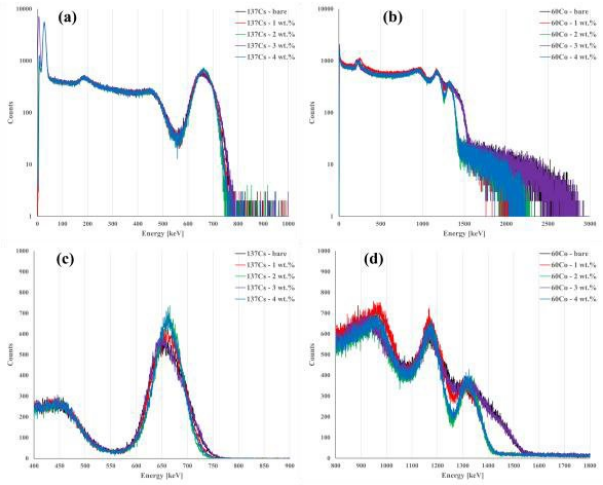

Fig. 1. Energy-calibrated spectra of bare and QD-PMMA-coated GAGG:Ce scintillators measured with ^{137}Cs and ^{60}Co sources. (a,b) Full spectra in log scale; (c,d) magnified photopeak regions in linear scale.

Table I. Key spectroscopic performance results.

Sample	ER (%) 661.657 keV	ER (%) 1173.228 keV	PVR (^{137}Cs)	PVR (^{60}Co)
bare	11.92±0.03	7.15±0.06	11.579	1.337
1 wt.%	10.67±0.02	7.12±0.14	14.694	1.893
2 wt.%	9.77±0.02	6.79±0.05	17.224	2.461
3 wt.%	11.90±0.08	7.31±0.15	12.015	1.417
4 wt.%	10.22±0.05	6.48±0.15	17.098	2.284

Energy resolution of the ^{137}Cs photopeak improved by ~18% at 2 wt.% (11.92% → 9.77%). PVR for ^{137}Cs increased by ~49% (11.58 → 17.22) and for ^{60}Co by ~84% (1.34 → 2.46) at 2 wt.%. Performance peaked at 2 wt.%, degraded 3 wt.%, and partially recovered at 4 wt.%.

4. Discussion

4.1 Evaluation of conventional QD-based mechanisms

Three photophysical mechanisms were systematically evaluated. FRET requires 1-10 nm donor-acceptor separation, but with ~30 μm coating thickness and bulk-distributed Ce^{3+} centers, only a negligible surface-proximate fraction could participate (efficiency scales as $1/r^6$) [4]. Direct scintillation from the QD layer is limited by its extremely low gamma-ray interaction probability: at 2 wt.% loading, the ~30 μm composite coating yields ~0.026% at 661.657 keV, contributing only 0.14% of GAGG:Ce bulk scintillation—far too small for the observed 18% improvement. Wavelength shifting is constrained because only 4.3% of GAGG:Ce emission falls within the QD absorption range; combined with 80% PLQY and a 9% reduction in PMT QE at re-emitted wavelengths, the net effect is a ~1.2% signal reduction rather than enhancement. None of these conventional mechanisms can account for the observed improvements.

4.2 Passive optical effects

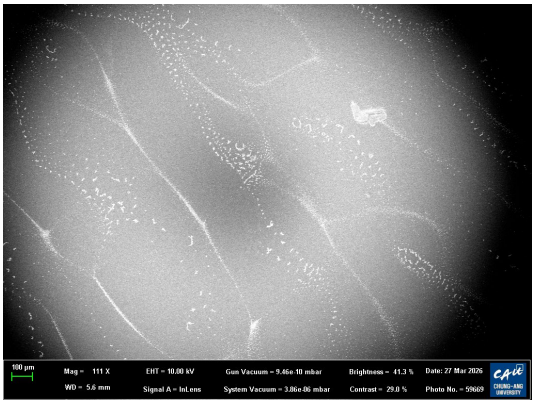

Fig. 2. SEM image of the 2 wt.% QD-PMMA coating s urface.

The evidence suggests that passive optical effects may be the primary contributors to the observed enhancement. During solvent evaporation, mechanical stresses in the QD–PMMA film may induce crack formation. Capillary-driven flow during the drying process can transport QD nanoparticles toward crack boundaries, potentially resulting in preferential accumulation of QD aggregates along these structures. SEM examination of the 2 wt.% coating surface revealed linear surface features forming an interconnected network with bright particulate features concentrated along these structures, which is consistent with this interpretation. Such a surface structure would introduce multiple refractive index discontinuities: the crack gaps themselves and the high-refractive-index QD aggregates ($CsPbBr_3$ $n \approx 2.3$) relative to the PMMA matrix ($n \approx 1.49$). In this scenario, QD aggregates may function not as photoluminescent emitters but as high-refractive-index scattering centers. Similar approaches using high-refractive-index nanoparticles in polymer matrices have achieved substantial light extraction enhancement in OLED devices through passive optical scattering, with nanoparticle agglomeration contributing to Mie scattering [5, 6]. The proposed mechanism is also supported by studies demonstrating that cracks in $CsPbBr_3$ films on scintillating wafers can guide scintillator emission with enhanced intensity [7, 8].

The observed concentration dependence is consistent with a structural origin. At intermediate loading (2 wt.%), crack formation combined with sufficient QD accumulation along crack boundaries may produce a favorable light-extracting surface structure, whereas at higher concentrations, excessive QD aggregation could alter the crack morphology or introduce additional scattering losses. If wavelength conversion were the dominant mechanism, performance would be expected to increase monotonically with QD concentration rather than exhibiting a pronounced optimum.

5. Conclusions

$CsPbBr_3$ QD-PMMA composite coatings significantly enhance GAGG:Ce gamma-ray spectroscopy performance: ~18% improvements in energy resolution at 661.657 keV, and PVR increases of 49% and 84% for ^{137}Cs and ^{60}Co, respectively. PMMA-only controls confirm QD-specific origins. Mechanistic analysis indicates passive optical effects dominate rather than conventional photophysical processes. Future work should focus on structural characterization via microscopy, systematic coating optimization, extension to other scintillators, and long-term stability testing.

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