

RESEARCH ARTICLE

Passivation engineering via silica-encapsulated quantum dots for highly sensitive photodetection

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Abstract

Organometal halide perovskites are promising semiconducting materials for photodetectors because of their favorable optoelectrical properties. Although nanoscale perovskite materials such as quantum dots (QDs) show novel behavior, they have intrinsic stability issues. In this study, an effectively silane barrier-capped quantum dot (QD@APDEMS) is thinly applied onto a bulk perovskite photosensitive layer for use in photodetectors. QD@APDEMS is synthesized with a silane ligand with hydrophobic CH₃-terminal groups, resulting in excellent dispersibility and durability to enable effective coating. The introduction of the QD@APDEMS layer results in the formation of a low-defect perovskite film with enlarged grains. This is attributed to the grain boundary interconnection effect via interaction between the functional groups of QD@APDEMS and uncoordinated Pb²⁺ in grain boundaries. By passivating the grain boundaries, where various trap sites are distributed, hole charge-carrier injection and shunt leakage can be suppressed. Also, from the energy point of view, the deep highest occupied molecular orbital (HOMO) level of QD@APDEMS can work as a hole charge injection barrier. Improved charge dynamics (generation, transfer, and recombination properties) and reduced trap density of QD@APDEMS are demonstrated. When this perovskite film is used in a photodetector, the device performance (especially the detectivity) stands out among existing perovskites evaluated for energy sensing device applications.

KEYWORDS

grain boundary passivation, perovskite quantum dots, photodetectors, photosensitive layers, trap

Ji Yun Chun, Byung Gi Kim, and Jin Young Kim contributed equally to this study.

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1 | INTRODUCTION

Photodetectors, which convert an optical signal (light) into an electrical signal, are key energy sensing components in industrial applications such as image sensing,^{1–3} healthcare monitoring,^{4,5} and optical communication.^{6–8} To develop effective photodetectors, it is important to select proper semiconducting materials for the photo-sensitive layer. Organometal halide perovskites are one of the most promising semiconducting materials for these applications because of the following advantages: solution processability, tuneable band gap (1.5–2.5 eV), low exciton binding energy (<10 meV), high charge mobility, and long charge diffusion distance.^{9–13} Nano-sized perovskite materials such as quantum dots (QDs) have additional novel properties arising from the quantum confinement effect, and are actively being developed. Such materials have suitable optoelectrical properties for optoelectronic energy device applications, such as facile wavelength tunability, a high quantum yield (QY), narrow spectral emission (full-width at half maximum, FWHM < 25 nm), and a variety of colors that can be emitted.^{14–17} However, despite these advantages, perovskite QDs have major stability issues. To develop stable materials for diverse applications, the drawbacks including their low environmental stability (against moisture, heat, and oxygen) and ligand dissociation need to be overcome.^{18–22} In this regard, encapsulation has been proposed as an efficient method for protecting QDs from the external environment.^{23–25} Among possible encapsulation materials, carbon-based silica shells are chemically stable for protecting the perovskite from moisture. They also have high transparency in the visible region, and thus, do not affect the optical properties of the perovskite.¹⁸ Therefore, many researchers have investigated silica core-shell QDs for improving the stability of QD materials. Previously, $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X} = \text{Br}, \text{I}$) QD@APDEMS was successfully synthesized using the split-ligand mediated re-precipitation technique, which maintained a stable polar environment by the addition of oleic acid as a stabilizer.²⁶ When a carbon-based silane ligand is selected, QD aggregation may occur in the presence of silane ligands such as those from the widely used tetraethyl orthosilicate and tetramethyl orthosilicate.^{27,28} Therefore, 3-aminopropyl (diethoxy)methyl silane (APDEMS) with three hydrophobic terminal groups ($-\text{CH}_3$) was selected in another study, and thus QD@APDEMS with excellent durability and dispersibility was formed.²⁹

Herein, the QD@APDEMS layer was thinly coated onto a bulk perovskite photosensitive layer to passivate grain boundaries and improve the optoelectrical performance. The bulk perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ was selected due to its good reproducibility and absence of phase separation.^{30–32} Various types of QDs could be synthesized

by changing the amount of silane ligand or halide composition.²⁹ Among them, $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QD and QD@APDEMS were selected because of their suitable energy level and deeper highest occupied molecular orbital (HOMO) level than that of bulk perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$, which is effective in hole blocking for photodetector devices. The formation of the QD@APDEMS structure were confirmed by comparative analyses such as high-resolution transmission electron microscopy (HR-TEM), ultraviolet-visible (UV-vis) spectroscopy, and X-ray diffraction (XRD). In addition, the formation of the QD@APDEMS layer was confirmed by observing the oxygen peak by energy-dispersive spectroscopy (EDS) due to the presence of APDEMS. The surface properties and roughness were characterized by contact-angle measurements and atomic force microscopy (AFM). The formation of perovskite grains and defect state of the film with QD@APDEMS were observed by field emission-scanning electron microscopy (FE-SEM) and Urbach energy analysis. The effects of the grain boundary interconnection and hole injection barrier (deep HOMO level) were analyzed in depth through dark current density graphs and assessment of device performance, especially in terms of trap density and shunt leakage current. Using conductive atomic force microscopy (c-AFM), the film conductivity was measured under various voltage bias conditions. The charge dynamics in the perovskite films was evaluated using methods such as time-resolved photoluminescence (TRPL), photoluminescence (PL), and electrochemical impedance spectroscopy (EIS). The trap density was also measured by the space charge limited current (SCLC).

The findings of this study suggest that the silane barrier-capped QD@APDEMS (with a deep HOMO level) effectively passivates grain boundaries, thereby suppressing trap and enhancing charge-carrier properties, yielding superior photodetector performance.

2 | EXPERIMENTAL SECTION

Details regarding the Chemical and Reagents, Synthesis of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QD, Synthesis of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QD@APDEMS, Device Fabrication, and Characterizations and Additional Measurements are presented in the Supporting Information.

3 | RESULTS AND DISCUSSION

QDs and QD@APDEMS were synthesized based on the split-ligand mediated re-precipitation technique.²⁶ A precursor containing $\text{CH}_3\text{NH}_3\text{Br}$ and PbBr_2 was mixed with dimethylformamide (as a good solvent) and a ligand

was added. Octylamine was used for synthesizing $\text{CH}_3\text{NH}_3\text{PbBr}_3$ QD, and the APDEMS ligand was used for synthesizing QD@APDEMS, a silane barrier-structured QD (Figure 1A). Each ligand-mixed perovskite precursor was rapidly injected into toluene containing oleic acid under vigorous stirring at room temperature. Oleic acid acts as a stabilizer in the QD synthesis process by balancing the charge, and its effect has been previously reported.^{26,33} When the perovskite precursor is injected under stirring, there is a change in the color of the precursor from transparent to yellow-green due to the crystallization of the perovskite phase. For QD synthesis, the perovskite precursor was injected and obtained using an immediate purification process. However, for QD@APDEMS synthesis, the perovskite precursor was injected and additional stirring time was allowed for the hydrolysis and condensation reactions to

occur.²⁹ Subsequently, a purification process was performed to obtain barrier-structured QD with a hydrophobic terminal group ($-\text{CH}_3$). The average size of the synthesized QD was 6.48 nm, with a lattice constant of 2.95 Å, and the average size of the QD@APDEMS was 8.16 nm, with a lattice constant of 3.2 Å (Figure 1B,C). Optical analysis of the synthesized particles (Figure 1D) showed that the QD had a PL emission peak at 531.0 nm (FWHM of 19.79 nm), while QD@APDEMS showed a peak at 552.8 nm (FWHM of 22.36 nm). The PL emission peak of the QD was lower than that of QD@APDEMS, which can be attributed to the quantum confinement effect in relation to the particle size.^{34–37} The QYs of the synthesized QD and QD@APDEMS were 90.6% and 91.2%, respectively, which were calculated using the relative QY measurement method. The XRD patterns of both types of synthesized QD (Figure 1E) showed the

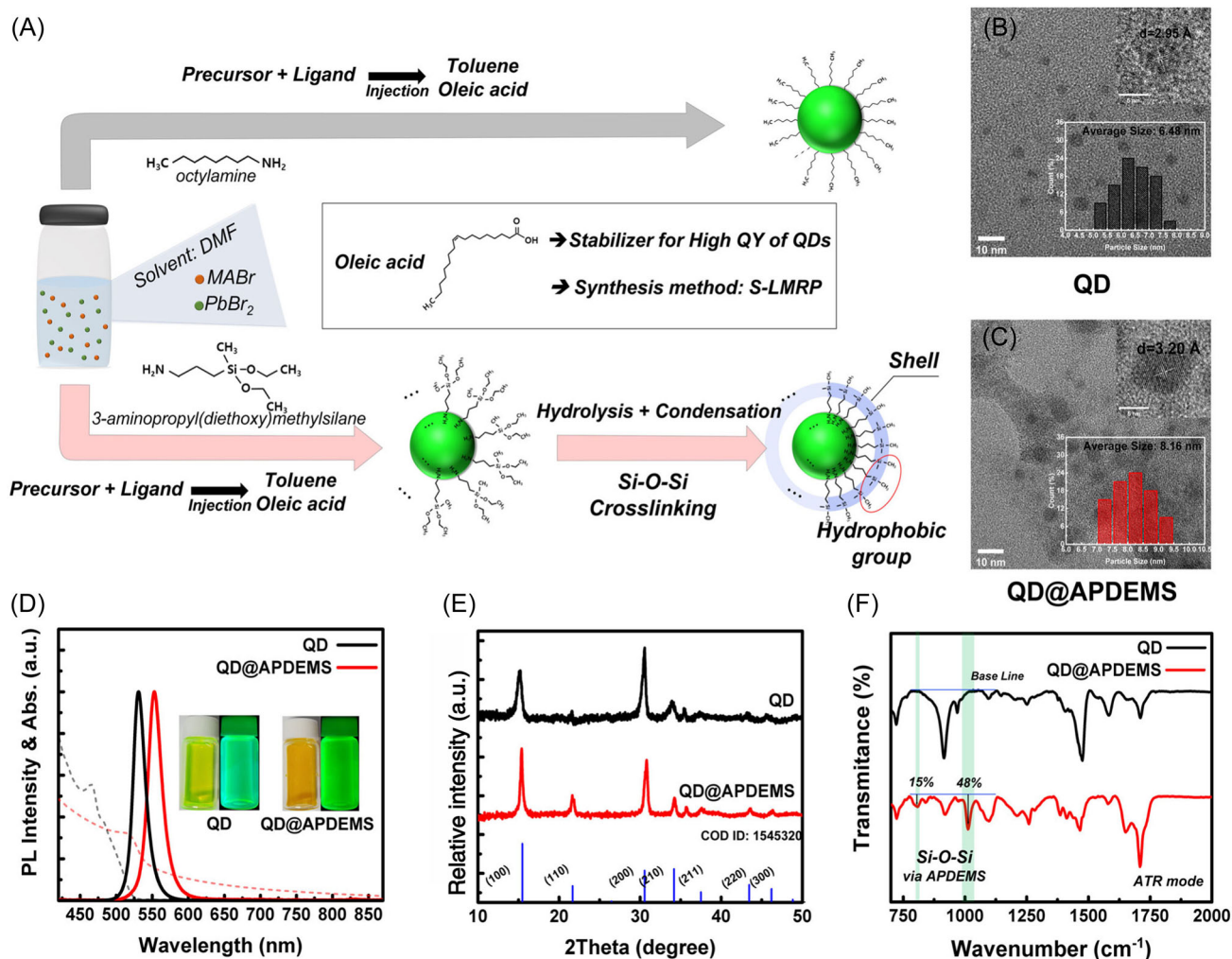


FIGURE 1 (A) Schematic illustrating the synthesis of QD and QD@APDEMS with octylamine and APDEMS ligands, respectively, using the split-ligand-mediated re-precipitation method. TEM and HR-TEM (inset) images of (B) QD and (C) QD@APDEMS. (D) Absorption spectra, PL spectra, and photographs (inset) of QD and QD@APDEMS. (E) XRD patterns of QD and QD@APDEMS. Reference lines in the bottom are for $\text{CH}_3\text{NH}_3\text{PbBr}_3$ (COD ID: 1545320). (F) FT-IR spectra of QD and QD@APDEMS.

characteristic peaks for $\text{CH}_3\text{NH}_3\text{PbBr}_3$ (COD ID: 1545320) with a well-defined three-dimensional cubic structure, confirming that the perovskite core was well formed. In addition, Fourier-transform infrared (FT-IR) spectroscopy analysis was performed to confirm the difference between the chemical bonding characteristics of the QD and QD@APDEMS. As shown in Figure 1F, the Si-O-Si bonding peak (green area) was observed only for QD@APDEMS. In the FT-IR spectra of QD@APDEMS, the Si-O-Si in the small and large wavenumber increased by 15% and 48%, respectively, compared with the baseline, indicating shell formation in the case of APDEMS.

We used the relative QY measurement method to confirm the efficiency of the synthesized QD and QD@APDEMS (Figure S1). To determine the relative QY, a rhodamine 101 ($\Phi = 0.96$) substance dissolved in ethanol was used as a reference. To measure the relative QY, additional information about the reference (rhodamine 101) and the sample (QD and QD@APDEMS) is required, and by substituting the result into Equation (1), the efficiency of the sample to be measured can be confirmed.

$$\begin{aligned}\Phi_S &= \Phi_X \cdot \frac{F_S \cdot \varepsilon_X \cdot C_X \cdot L_X \cdot n_S^2}{F_X \cdot \varepsilon_S \cdot C_S \cdot L_S \cdot n_X^2} = \Phi_X \cdot \frac{F_S \cdot A_X \cdot n_S^2}{F_X \cdot A_S \cdot n_X^2} \\ &= \Phi_X \cdot \frac{\text{Grad}_S \cdot n_S^2}{\text{Grad}_X \cdot n_X^2},\end{aligned}\quad (1)$$

where subscript X and S stand for rhodamine and the sample, respectively. F and A represent the area of the PL spectrum and the absorbance at the excitation wavelength, respectively. n is the refractive index for the solvent, and those of rhodamine 101 dissolved in ethanol and samples (QD and QD@APDEMS) dissolved in hexane are 1.37 and 1.375, respectively. As a result of substituting the information of rhodamine and samples into Equation (1), the QYs of QD and QD@APDEMS were 89.7% and 91.2%, respectively. After confirmation that the intended QD and QD@APDEMS were synthesized, they were applied to a perovskite film. Also, in terms of the energy level, QD@APDEMS had the deepest HOMO level (5.78 eV), followed by QD (5.57 eV) and bulk perovskite (5.43 eV) (Figure S2). Thus, QD and QD@APDEMS worked as effective hole carrier injection blocking layers due to the deeper HOMO level compared with bulk perovskite.³⁸ Furthermore, the thin layer of QD and QD@APDEMS with a wide band gap would function as a tunneling layer to improve charge-carrier transport and reduce recombination.³⁹

EDS analysis was performed to identify the elements in the $\text{CH}_3\text{NH}_3\text{PbI}_3$ film and after coating with the QD or QD@APDEMS (Figure S3A–C). Pb, Br, and I from the perovskite were identified. To confirm the effect of

applying QD@APDEMS in detail, we focused on O from APDEMS as the silica precursor.²⁹ Stronger O peaks were confirmed for the film with QD@APDEMS (Figure S3D–F), indicating that QD@APDEMS with the silica shell based on APDEMS was coated onto the $\text{CH}_3\text{NH}_3\text{PbI}_3$ film. This was also supported by the EDS elemental maps (Figure S4), where the green signal corresponding to O was noticeably more distributed for the film with QD@APDEMS than the film without the QD and with the QD.

UV-vis and PL spectroscopy was performed to characterize the optical properties of the thin films (Figure S5A,B). The absorbance was similar for all samples, indicating that QD@APDEMS did not affect the optical properties due to the transparency of the silica shell.¹⁸ The Urbach energy, which is the energetic disorder at the band edge, was calculated to confirm the defect state of the film (Figure S5C). The Urbach energy (E_u) was calculated using the following equation^{40,41}:

$$E_u = \frac{E - E_g}{\ln \left(\frac{\alpha(E)}{\alpha_g} \right)}, \quad (2)$$

where E , E_g , $\alpha(E)$, and α_g represent the photon energy, the band gap energy, the absorption coefficient, and the absorption coefficient at the band gap energy, respectively. The lower E_u indicates the low number of defects in the film, which is conducive to the charge transfer and extraction.⁴² Also, especially perovskite films with lower E_u have been reported to show large diffusion lengths and carrier lifetimes.^{41,43} As a result, E_u values were 0.52, 0.49, and 0.41 eV for the films without the QD, and with QD, and with QD@APDEMS, respectively. The lowest E_u for the film with QD@APDEMS confirmed the formation of a low-defect film.

Contact angle measurements in deionized water were conducted to check whether the QD and QD@APDEMS coatings changed the surface properties of the perovskite film. First, the contact angles were 29.52°, 53.22°, and 60.26° for the bare glass, the QD single film, and the QD@APDEMS single film, respectively (Figure S6A–C). Since QD@APDEMS has a more hydrophobic surface than the QD, the silane barrier is formed toward the QD rather than the outside. Moreover, the contact angles were 16.72°, 17.89°, and 22.84° for the perovskite film without QD, and those with QD and QD@APDEMS, respectively (Figure S6D–F). The contact angle of the perovskite film with QD@APDEMS was 26% higher than that of the perovskite film without QD. This is attributed to the hydrophobic characteristics of the silane precursor (APDEMS) with hydrophobic $-\text{CH}_3$ terminal groups used to synthesize QD@APDEMS.²⁹ These findings confirm

that the addition of QD@APDEMS increased the hydrophobicity of the perovskite film, which led to higher interfacial affinity with the upper hydrophobic PC₇₀BM layer. In addition, it was confirmed that the QD@APDEMS layers can be successfully applied to the device as a passivation layer.⁴⁴

The AFM images in Figure S7A–C show the surface morphology of the three sample types over a 5 $\mu\text{m} \times 5 \mu\text{m}$ area (whole profile analysis). The peak-to-valley (R_{pv}) and root-mean-square (R_{q}) values represent the surface roughness. The smallest R_{pv} and R_{q} of 74.38 and 9.84 nm were observed for the film with QD@APDEMS (Table S1). This indicates that the film with QD@APDEMS has the smoothest surface topography.⁴⁵ To observe the surface morphology in detail, line profiles were acquired along the diagonal of the areas in Figure S7A. The height distribution of the perovskite grains was obtained, which showed the Gaussian curve (statistical data) (Figure S7D–F). The film with QD@APDEMS showed the smallest standard deviation of 5.32 nm and the film without QD showed the largest standard deviation of 14.36 nm (Table S1). AFM analysis showed that the QD@APDEMS film provided a smooth surface with a uniform height distribution.

The thickness of the layers was observed from cross-sectional FE-SEM images (Figure S8). The layer thicknesses were found to be 230.4 nm, 243.7 nm, and

246.6 nm for the bulk perovskite without QD, with QD, and with QD@APDEMS, respectively. Thus, it is confirmed that the QD and QD@APDEMS layers were thinly stacked about 13–16 nm. The formation of perovskite grains was characterized by top-view of FE-SEM (Figure 2A–C), and the average grain size was calculated by Gaussian fitting of the diameter distribution data (Figure 2D–F). The largest average grain size was observed for the film with QD@APDEMS (279.42 nm), followed by that of the film without QD (201.35 nm), and with QD (187.53 nm). In the case of QD, smaller grains were formed compared with the film without QD. From an energy point of view, the bond dissociation energy is 142 kJ/mol for Pb–I and 201 kJ/mol for Pb–Br, which means that the Pb–Br bond is thermodynamically more stable.⁴⁶ Since the QD was not passivated with any shell, the bulk perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) would react with the Br element considering the thermodynamic stability. It has been reported that the grain size decreases when the Br/I content increases.⁴⁷ Thus, the perovskite grain size reduction was attributed to the reaction between QD and bulk perovskite. On the other hand, in the case of QD@APDEMS, the reaction with the bulk perovskite was inhibited due to the passivation of the silica shell. Also, the functional groups of the shell combined with the uncoordinated Pb^{2+} (dangling bond) of the grain boundaries, resulting in interconnection of the grain

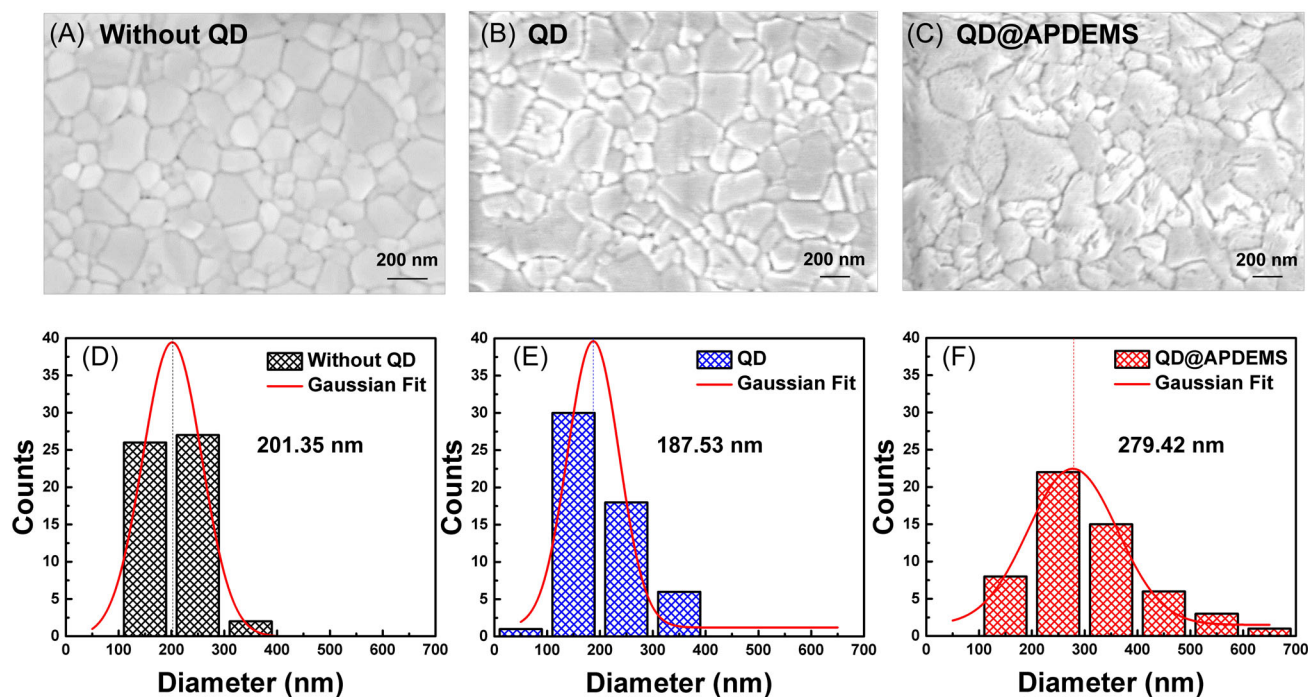


FIGURE 2 Top-view FE-SEM images of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films (A) without QD, (B) with QD, and (C) with QD@APDEMS. Grain size distribution of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films derived from FE-SEM images: (D) without QD, (E) with QD, and (F) with QD@APDEMS. The curves are Gaussian fits of the distributions.

boundaries.⁴⁸ Based on the chemical and structural properties (CH₃-end capping) of ligand APDEMS, the grain boundary was passivated and led to the larger grain size of the film with QD@APDEMS.⁴⁸ The increased grain size of the photosensitive layer was expected to enhance light absorption.⁴⁹ In addition, the larger grain size corresponded to fewer grain boundaries. Since the grain boundaries act as low-resistance ohmic shunting pathways in a polycrystalline perovskite, the larger grain size was also expected to inhibit the shunt route and reduce charge recombination.^{50,51}

The XRD patterns were analyzed to identify the CH₃NH₃PbI₃ structure and confirm the crystallinity of the perovskite grains. In Figure 3A, the peak at 13.91° corresponding to the (110) plane is marked in yellow and the peak at 28.20° corresponding to the (220) plane is marked in green.⁵² The peak intensity, FWHM, and crystallite size of each peak are summarized in Figure 3B–D, respectively. For the three parameters, the same tendency is observed for each condition with the (110) and (220) peaks. Therefore, the analysis of the (110) peak is presented. The data for each peak and sample are listed in Table 1. The film with QD@APDEMS had the highest peak intensity (5936 a.u.) and the narrowest FWHM (0.0806°), followed by the film without QD (5163 a.u., 0.0908°) and that with QD (4054 a.u., 0.0961°). The FWHM values of the peaks were derived from Gaussian fitting. The highest intensity and the narrowest FWHM of the perovskite main peak imply that

the film with QD@APDEMS had enhanced crystallinity. The crystallite size (L) was calculated using the following equation:

$$L = \frac{K\lambda}{FWHM \cdot \cos \theta}, \quad (3)$$

where K , λ , and θ are the shape factor, wavelength, and peak angle, respectively. L was the largest for the film with QD@APDEMS (1030.19 Å), followed by the film with the QD (914.48 Å) and the film without the QD (863.78 Å). These results showed the same tendency as the grain size derived from FE-SEM analysis (Figure 2). Thus, the largest perovskite grains with high crystallinity were formed by applying QD@APDEMS. These properties are favorable when using the perovskite film as a light absorber, as fewer grain boundaries result in a reduced number of surface traps, while higher crystallinity enhances charge transfer.^{49,53,54}

In Figure 4A, the grain boundary interconnecting effect of QD@APDEMS is shown. By protecting the CH₃NH₃PbBr₃ QD core, the functional group of the APDEMS interacted with the uncoordinated Pb²⁺ (dangling bond) of the grain boundaries, which resulted in grain boundary interconnection and larger grain sizes.⁴⁸ Also, in terms of the energy level, QD@APDEMS with the deepest HOMO level (−5.78 eV) worked as an effective hole carrier injection blocking layer (Figure S2). Accordingly, by extending it to device application,

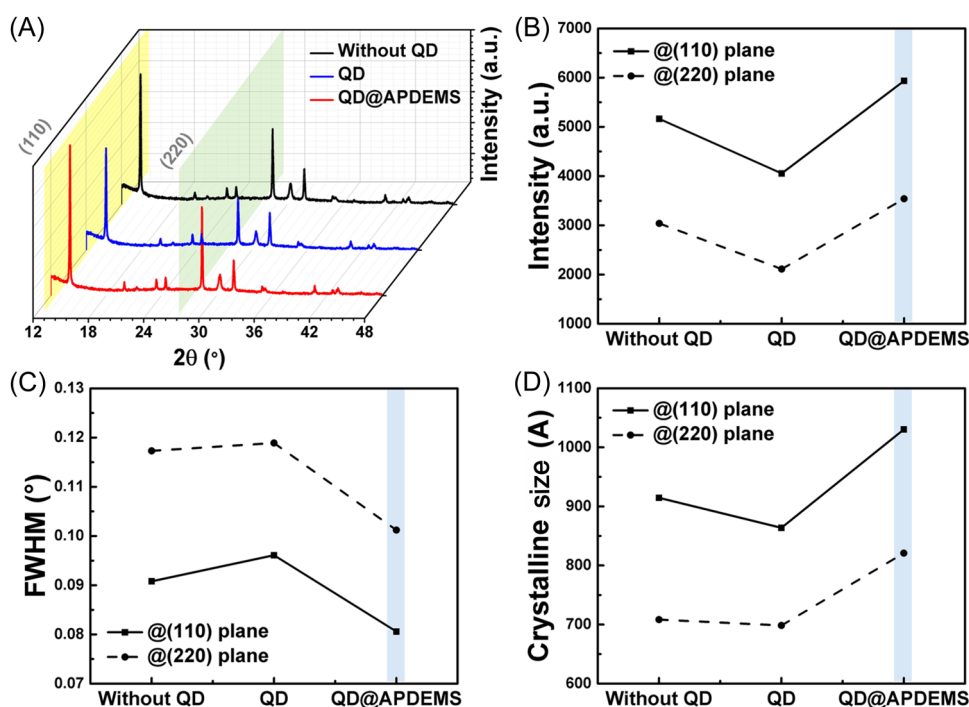
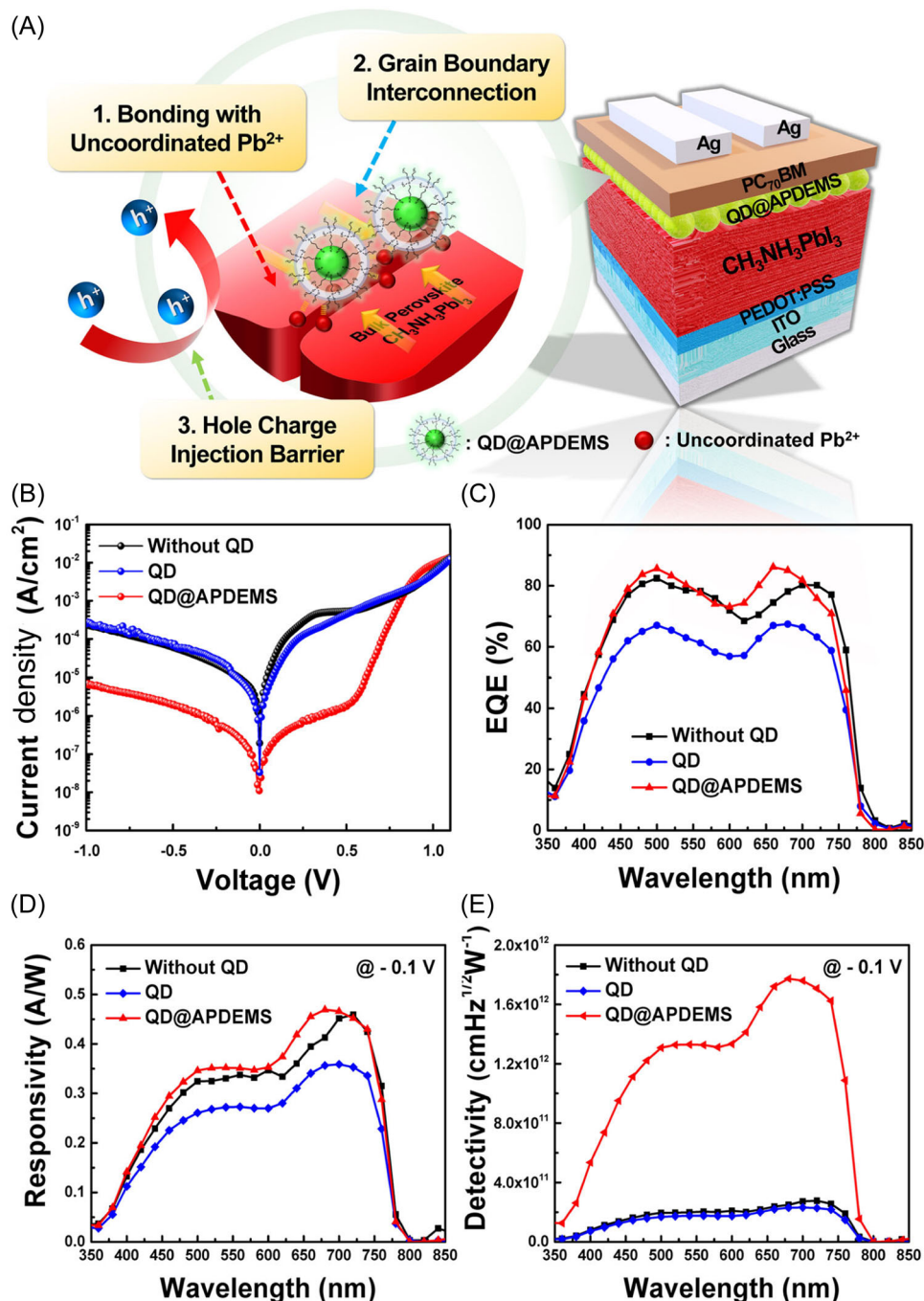


FIGURE 3 (A) XRD patterns, (B) peak intensity, (C) FWHM, and (D) crystalline size of the (110) and (220) planes of CH₃NH₃PbI₃ films.

TABLE 1 Peak intensity, FWHM, and crystallite size of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films derived from XRD patterns shown in Figure 3.

Condition	@ (110) plane			@ (220) plane		
	Intensity (a.u.)	FWHM (°)	Crystallite size (Å)	Intensity (a.u.)	FWHM (°)	Crystallite size (Å)
Without QD	5163	0.0908	914.48	3039	0.1173	708.36
QD	4054	0.0961	863.78	2112	0.1189	698.48
QD@APDEMS	5936	0.0806	1030.19	3540	0.1012	820.86

**FIGURE 4** Device performance characterization. (A) Scheme for the effect of QD@APDEMS on the bulk perovskite surface and the photodetector device structure. (B) Dark J - V curves, (C) EQE spectra, (D) responsivity (under -0.1 V bias), and (E) detectivity (under -0.1 V bias) of photodetector devices without QD, with QD, and with QD@APDEMS.

photodetector devices were fabricated using the structure shown in Figure 4A.

First, on measuring photocurrent under illumination (Figure S9), the highest power (2.93 mW) was found for the device with the QD@APDEMS-coated perovskite film as the active layer, based on the enhanced open-circuit voltage (V_{oc}) and the short-circuit current (I_{sc}) (Table S2). Therefore, the device with QD@APDEMS showed improved photovoltaic performance. The higher photocurrent is attributed to the high-quality film on applying QD@APDEMS (Figures 2 and 3).⁵⁵ The photo-energy sensing device performance was measured based on the photodetector circuit shown in Figure S10.⁵⁶

The dark current density is shown in Figure 4B and discussed in Figure S11, which divided into three regions. Region I relates to the leakage (shunt) current, region II to the recombination current, and region III to series resistance.^{57,58} For a clear comparison of the three domains, we additionally calculated the leakage (shunt) current. In the photodetector without the QD, the higher leakage current is observed in the region I, which is induced by the Shockley–Read–Hall (SRH) recombination related to high trap density in the grain boundaries.^{57–59} The high trap density of the pristine perovskite causes region II to appear at a higher voltage. However, the photodetector with QD@APDEMS reveals reduced dark current in both regions I and II. In detail, it showed low values of 7.49×10^{-6} A/cm² and 2.19×10^{-7} A/cm² for the device with QD and with QD@APDEMS, respectively, indicating higher charge recombination resistance.⁶⁰ This is the result of the deep HOMO level of CH₃NH₃PbBr₃ QD and QD@APDEMS (Figure S2), which is attributed to the effective prevention of hole injection. Furthermore, in the case of QD@APDEMS, the additional effect of grain boundary passivation led to more suppressed dark current and reduced charge recombination.³⁸

To analyze the trap-assisted injection current, the charge recombination and defect states in the photodetector devices were investigated. By obtaining the ideality factor (η), we can confirm the charge recombination occurring within the photodetector structure as shown in Figure S12A. When η is close to 1, it

indicates ideal recombination, whereas when η is close to 2, it represents the additional SRH recombination caused by high trap density.^{61,62} The value of η is 1.758 for the device without QD, 1.933 for the device with QD, and 1.289 for the device with QD@APDEMS. As a result, the device with QD@APDEMS suppressed the SRH recombination because the η value was close to 1 due to passivation of grain boundaries. Furthermore, the deep defect states of the perovskite photodetectors were obtained from the trap-assisted tunneling (TAT) current equation (inset of Figure S12B).^{61,63} The defect states were calculated to be 0.295 eV for the device without QD, 0.278 eV for the device with QD, and 0.133 eV for the device with QD@APDEMS. Thus, the device with QD@APDEMS showed shallow defect states compared with the other devices, which means that the surface trap density in the grain boundary of perovskite is reduced.

The external quantum efficiency (EQE) is a measure of the conversion rate from photons to electrons.^{56,64} Figure 4C shows higher EQE values in the visible region for the device with QD@APDEMS, indicating its improved ability to convert light into electrical current.

Responsivity (R) refers to the ability of a device to respond to optical signals and is expressed as^{65,66}

$$R = \frac{I_p - I_d}{PA}, \quad (4)$$

where I_p , I_d , P , and A are the photocurrent, the dark current, the incident light power, and the active area, respectively. The R values of the devices were compared at a wavelength of 700 nm (around the peak value for all devices; Figure 4D and Table 2). Under a -0.1 V bias, the R values were 0.469, 0.459, and 0.359 A/W for the devices with QD@APDEMS, without QD, and with QD, respectively. The device with QD@APDEMS showed a higher R than the other devices over the entire visible region (400–800 nm).

Detectivity (D^*) indicates the ability of a device to detect a weak signal and is expressed as^{66,67}

$$D^* = \frac{A^{1/2}R}{(2qI_d)^{1/2}}, \quad (5)$$

TABLE 2 Photodetector parameters: dark current density, responsivity, and detectivity of CH₃NH₃PbI₃-based devices without QD, with QD, and with QD@APDEMS under -0.1 V bias extracted from Figure 4.

Condition	Dark current density (A/cm ²)	Responsivity (A/W)	Detectivity (cm Hz ^{1/2} /W)
Without QD	8.57×10^{-6}	0.459	2.77×10^{11}
QD	7.49×10^{-6}	0.359	2.28×10^{11}
QD@APDEMS	2.19×10^{-7}	0.469	1.77×10^{12}

where q is the elementary charge. The D^* values were also compared for all devices at 700 nm (Figure 4E and Table 2). Under a -0.1 V bias, the D^* values were 1.77×10^{12} , 2.77×10^{11} , and 2.28×10^{11} cm Hz^{1/2}/W for the devices with QD@APDEMS, without QD, and with QD, respectively. This improved performance is attributed to the suppressed dark J , owing to the charge injection barrier effect of QD@APDEMS and the suppressed shunting pathway (fewer grain boundaries) (Figures S2 and 2).^{38,68}

Additionally, R and D^* were observed under a 0 V bias condition (Figure S12 and Table S3), and superior and durable performance of the device with QD@APDEMS was confirmed. In detail, the value of R was 0.426 A/W for the device without the QD, 0.375 A/W for the device with the QD, and 0.466 A/W for the device with QD@APDEMS. The value of D^* was 1.71×10^{12} cm Hz^{1/2}/W for the device without the QD, 3.63×10^{12} cm Hz^{1/2}/W for the device with the QD, and 7.85×10^{12} cm Hz^{1/2}/W for the device with QD@APDEMS. In addition,

enhanced durable device operation was confirmed in the device with QD@APDEMS in Table S3. This performance was confirmed to be outstanding compared with that of recently reported perovskite-based devices (Figure S14 and Table S4).^{8,65,69–73}

Using c-AFM, the current signal and charge properties of the films were examined under self-powered and reverse-voltage bias conditions (Figure 5).^{74,75} The I_{sc} and open-circuit current (I_{oc}) were measured at 0 and -1 V bias under illumination, respectively (Figure 5A–H). In addition, the dark drift current (I_{dd}) was measured with a -2 V bias in the dark (Figure 5I–L). The strongest I_{sc} signal was measured for the film with QD@APDEMS under illumination, followed by the film without the QD and the film with the QD. In addition, the same tendency was found for I_{oc} (Table S5). These data indicate an improvement in the photo-response due to surface modification by QD@APDEMS.⁷⁶ The large current response under illumination indicates the high conductivity of the sample, which confirms the

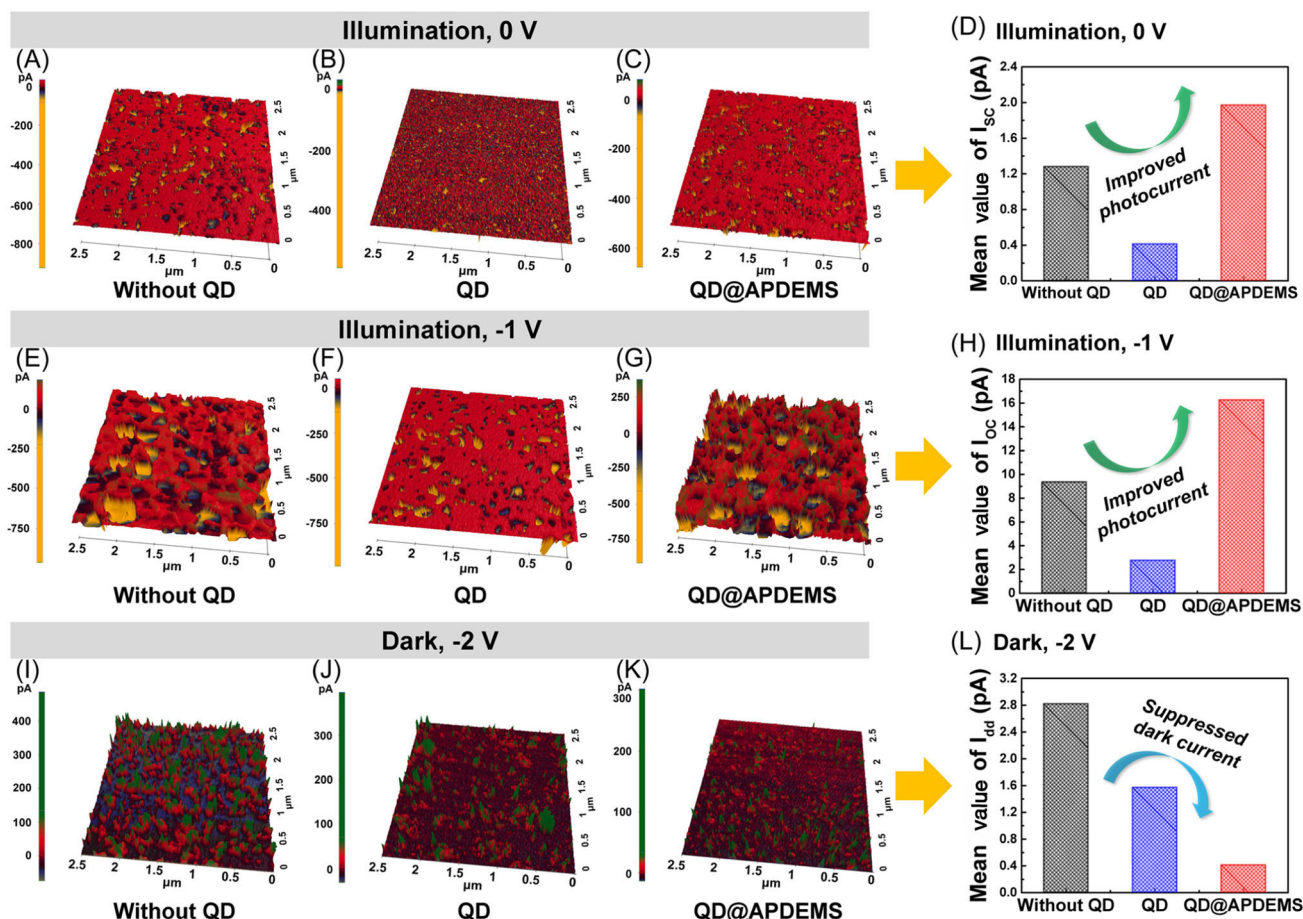


FIGURE 5 c-AFM images measured under (A–C) illumination at 0 V, (E–G) illumination at -1 V, and (I–K) in the dark at -2 V of perovskite films (A, E, I) without the QD, (B, F, J) with the QD, and (C, G, K) with QD@APDEMS. Summarized graph of the current signal measured under (D) illumination at 0 V, (H) illumination at -1 V, and (L) in the dark at -2 V.

improved charge-transfer properties for the film with QD@APDEMS.^{77–79} In contrast, the I_{dd} signal was the weakest for the film with QD@APDEMS, followed by the film with the QD and the film without the QD (Table S5). Overall, the tendencies of the current signals support the reduction in the dark current and increase in the photocurrent of the optimized devices (Figure 4).

The charge dynamics were examined to observe the effect of QD@APDEMS on the bulk perovskite photo-sensitive layer. PL measurements were conducted for the samples with different structures including a lower layer (Poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate); PEDOT:PSS) and with or without an upper layer (PC₇₀BM) (Figure 6A). In both cases with quenching layers, a reduced PL intensity was observed for the samples with QD@APDEMS, indicating enhanced charge transfer.⁸⁰ This was also supported by the lower value of E_{u} (Figure S5C). The trap density (N_{t}) was measured by SCLC (Figure 6B). To observe hole charge, hole-only devices were fabricated with MoO₃ as an electron-blocking layer (inset of Figure 6B). In the I - V curve, the trap-field-limit voltage (V_{TFL}) is the transition point between the Ohmic region and trap-field-limit region. The device without the QD had a V_{TFL} of 0.428 V, while the device with QD@APDEMS had a V_{TFL} of

0.338 V. N_{t} was calculated based on the obtained V_{TFL} from the graph using the following equation^{81–83}:

$$N_{\text{t}} = \frac{2\epsilon\epsilon_0}{qd^2} V_{\text{TFL}}, \quad (6)$$

where ϵ , ϵ_0 , and d are the dielectric constant, the permittivity of free space in a vacuum, and the film thickness, respectively. The lower N_{t} for the device with QD@APDEMS ($1.36 \times 10^{16}/\text{cm}^3$) compared with that of the device without the QD ($1.86 \times 10^{16}/\text{cm}^3$) demonstrated the trap passivation effect of QD@APDEMS. This was also supported by the shape of the recombination region in dark current density (Figure 4B). EIS was conducted in the dark at 0 V bias to compare the charge recombination tendency of the devices (Figure 6C). A much larger semicircle was observed for the device with QD@APDEMS compared with that of the device without the QD. The shunt resistance (R_{sh}) values related to the charge recombination⁸⁴ were 21.64 and 199.55 k Ω for the device without the QD and that with QD@APDEMS, respectively. The tendency of reduced charge recombination corresponded with the high current response of the film (Figure 5).^{85,86} This is attributed to the formation of a high-quality film after passivation with

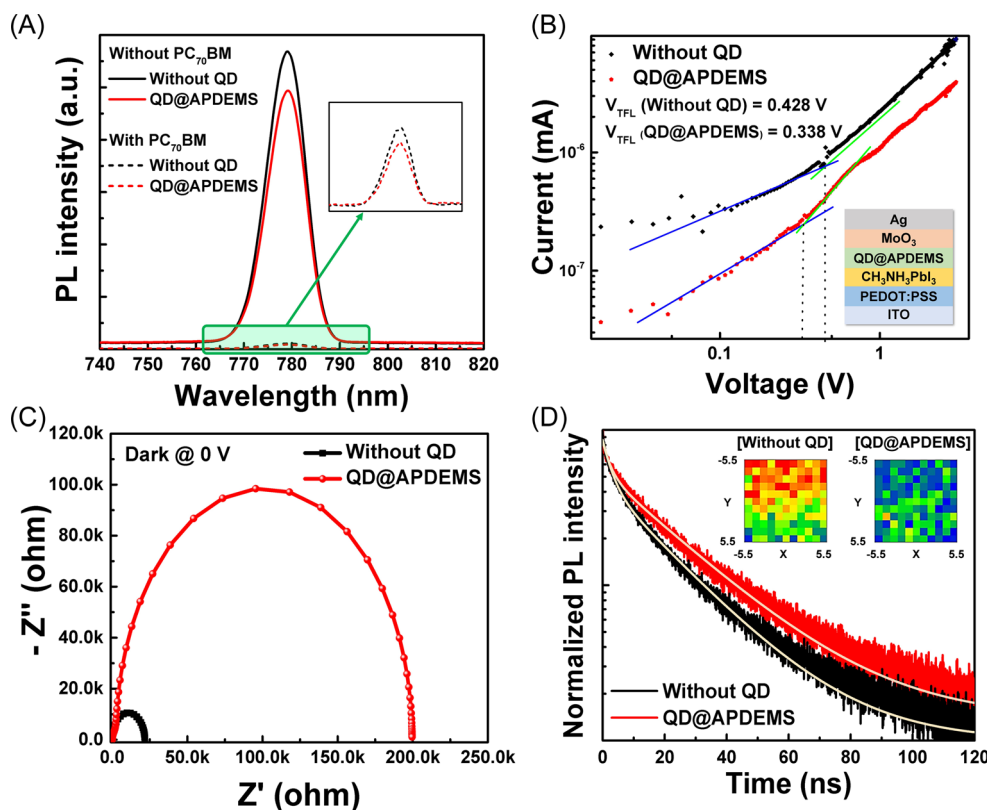


FIGURE 6 (A) PL spectra of the perovskite film with and without a PC₇₀BM layer. (B) SCLC results of CH₃NH₃PbI₃-based hole-only devices and the corresponding device structure (inset). (C) Impedance graph of CH₃NH₃PbI₃-based devices with and without a QD@APDEMS passivation layer in the dark with no applied bias. (D) Normalized TRPL decay spectra and corresponding maps (inset).

QD@APDEMS with larger grains and improved crystallinity (Figures 2 and 3). In addition, this was supported by the lower dark current density due to the deep HOMO level of QD@APDEMS (Figures 4B and S2).^{38,53,68}

TRPL was performed to evaluate the charge generation ability of the perovskite film with and without QD@APDEMS (Figure 6D). The lifetime of the charge carrier was calculated using a bi-exponential fitting equation⁸⁷:

$$A(t) = A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}}, \quad (7)$$

where A_1 and A_2 are the PL amplitudes of the short-life component and the long-life component, respectively. τ_1 (short-lived lifetime) originates from the bimolecular recombination and τ_2 (long-lived lifetime) reflects free carrier recombination.^{87,88} The bimolecular recombination specifically corresponds to the radiative recombination, which means that photogenerated excitons are not dissociated and then recombined inside the bulk.^{89–91} For each parameter, the values of A_1 and τ_1 were 37.15% and 2.45 ns, respectively, for the film with QD@APDEMS, which are lower than that of the film without the QD (A_1 : 47.75%, τ_1 : 2.86 ns). This suggests that the photogenerated excitons dissociate from the bulk and induce free charge generation.^{89–91} Accordingly, the relatively higher value of A_2 (62.85%) compared with A_1 was observed for the film with QD@APDEMS. In conclusion, the improved free charge-carrier generation property was confirmed due to the increased t_2 related to the free carrier recombination for the film with QD@APDEMS. The average lifetime (τ_{avg}) was 18.46 ns for the device without the QD and 22.77 ns for the device with QD@APDEMS (Table 3). The longer lifetime with QD@APDEMS indicated more efficient charge generation.⁹² This is also consistent with the increased PL intensity (Figure S15) with the addition of the QD@APDEMS layer for the same device structure. These results confirmed that the addition of QD@APDEMS reduced trap density and improved charge-carrier properties.

TABLE 3 Parameters obtained from the TRPL decay spectra shown in Figure 6D.

Condition	Without the QD	QD@APDEMS
A_1 (%)	47.75	37.15
A_2 (%)	52.25	62.85
τ_1 (ns)	2.86	2.45
τ_2 (ns)	20.45	24.00
τ_{avg} (ns)	18.46	22.77

4 | CONCLUSION

In this study, passivated QD@APDEMS was applied to the surface of a bulk $\text{CH}_3\text{NH}_3\text{PbI}_3$ photosensitive layer to enhance morphological and charge properties when used in a photodetector. Carbon-based silica shells were successfully synthesized using APDEMS silane ligands with hydrophobic terminal groups to improve the dispersibility and stability of QD@APDEMS. The synthesized QD and QD@APDEMS were compared and validated using optical analyses. The QD@APDEMS coating increased the surface hydrophobicity of the perovskite surface, which improved the interfacial affinity with hydrophobic PC_{70}BM . A low-defect film with a smoother morphology was achieved after the application of QD@APDEMS. The introduction of QD@APDEMS resulted in larger grains of photosensitive layers, leading to enhanced light absorption. This was due to the effect of the grain boundary interconnection via interaction with uncoordinated Pb^{2+} in grain boundaries. By passivating the grain boundaries, where various trap sites were distributed, hole charge-carrier injection and shunt leakage were stably suppressed. Also, the deep HOMO level of QD@APDEMS contributed to blocking the hole charge injection and reducing dark current density. Based on the reduced trap density, charge carrier showed better properties. Based on these results, the highly enhanced detectivity was achieved in the optimized condition.

In summary, carbon-based QD@APDEMS played the following roles in energy sensing devices: (1) promoted grain boundary interconnection via interaction with uncoordinated Pb^{2+} ; (2) created a hole charge injection barrier due to its deep HOMO level and wide band gap; and (3) enhanced charge-carrier dynamics. Thus, the application of multifunctional QD@APDEMS is an effective strategy for passivating the grain boundary and enhancing photo-sensing device performance.

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CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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