Supporting Information

Tunable Ionic Conductivity and Photoluminescence in Quasi-2D $CH_3NH_3PbBr_3$ Thin Film Incorporating Sulphur Doped Graphene Quantum Dots

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Experimental Section

Chemicals:

N, N- Dimethyl sulfoxide (DMSO), Dimethylformamide (DMF, anhydrous 99.8%), benzylamine, and Poly(3-hexylthiophene) (P3HT) were brought from Sigma-Aldrich. Methylammonium bromide (CH3NH3Br, 99.9%) was purchased from Tokyo Chemical Industry (TCI). SGQD was synthesized in the laboratory in DMF solvent.

Synthesis of SGQDs

SGQDs were synthesized using previously reported bottom-up technique with minor modifications [1][2]. In this, 2.0 g of citric acid and 300 μL of 3-marcaptopronic acid were mixed and subjected to thermal carbonization at 200 °C for 10 minutes. The resultant orange colour viscous liquid was mixed into 15 mL DMF and stirred for another 20 minutes. To remove unreacted precursors and large particles, the obtained mixture comprising SGQDs was purified using a standard syringe filter with pore size of 0.22 μm. The final solution was stored in a refrigerator at 4 °C until further use and characterizations.

Perovskite film preparation and perovskite-electrolyte device fabrication

For thin fabrication, the $CH3NH_3PbBr_3$ precursor solution was prepared according to our previously reported articles. In this, MABr and PbBr2 were mixed in molar ratio of 1.05:1 in co-solvent of DMF and DMSO (7:3 by volume ratio). The concentration of perovskite precursor was 0.6 M. For SGQDs treated perovskite films, we have incorporated the SGQDs precursor solutions (1 V%) into the perovskite precursor. This SGQDs incorporated perovskite solution was spin-coated on TiO_2-coated FTO substrates at 4500 rpm for 40 s in the controlled humidity chamber with a relative humidity of 25–30%. During the spin coating process, antisolvent was dripped after 5 s. Finally, these films were annealed at 100 °C for 20 min. For interfacial study, we have fabricated a FTO/TiO_2/perovskite/electrolyte device geometry. We

have used tetrabutylammonium hexafluorophosphate (TBAPF6) electrolyte in DCM solvent (0.1M).

Characterizations

Structural and morphological characterizations of both films were performed using X-ray diffractometry (XRD, D8-ADVANCE) and field emission scanning electron microscopy (FE-SEM, QUANTA 200 FEG). In XRD, Cu Kα = 1.54 Å source in the (2θ) angle range 5–70° was used. Electrochemical impedance measurements of perovskite-electrolyte devices were performed by Zahner Electrochemical Workstation under dark condition at various applied bias 0.0 – 1.0 V. In this, 20 mV ac amplitude from 100 mHz to 1 MHz frequency range was varied to measure impedance measurements.

References:

[1]. Kadian, S., Manik, G., Kalkal, A., Singh, M., & Chauhan, R. P. (2019). Effect of sulfur doping on fluorescence and quantum yield of graphene quantum dots: An experimental and theoretical investigation. ***Nanotechnology***, 30(43), 435704.

[2] Kadian, S., Tailor, N. K., Chaulagain, N., Shankar, K., Satapathi, S., & Manik, G. (2021). Effect of sulfur-doped graphene quantum dots incorporation on morphological, optical and electron transport properties of CH3NH3PbBr3 perovskite thin films. ***Journal of Materials Science: Materials in Electronics***, 1-12.

SGQDs

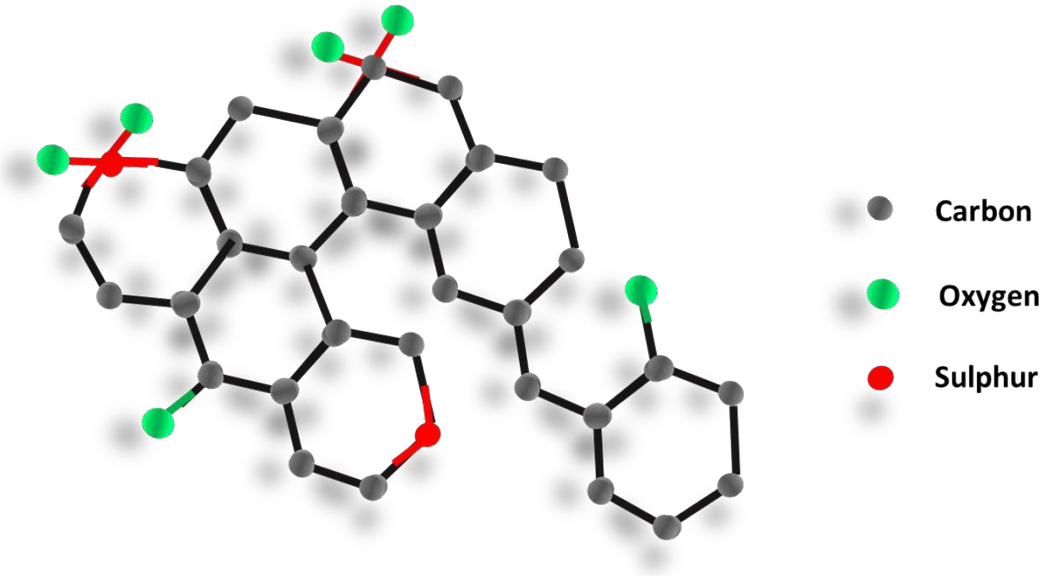

Figure S1. Structure of sulphur doped GQDs.

FESEM Analysis

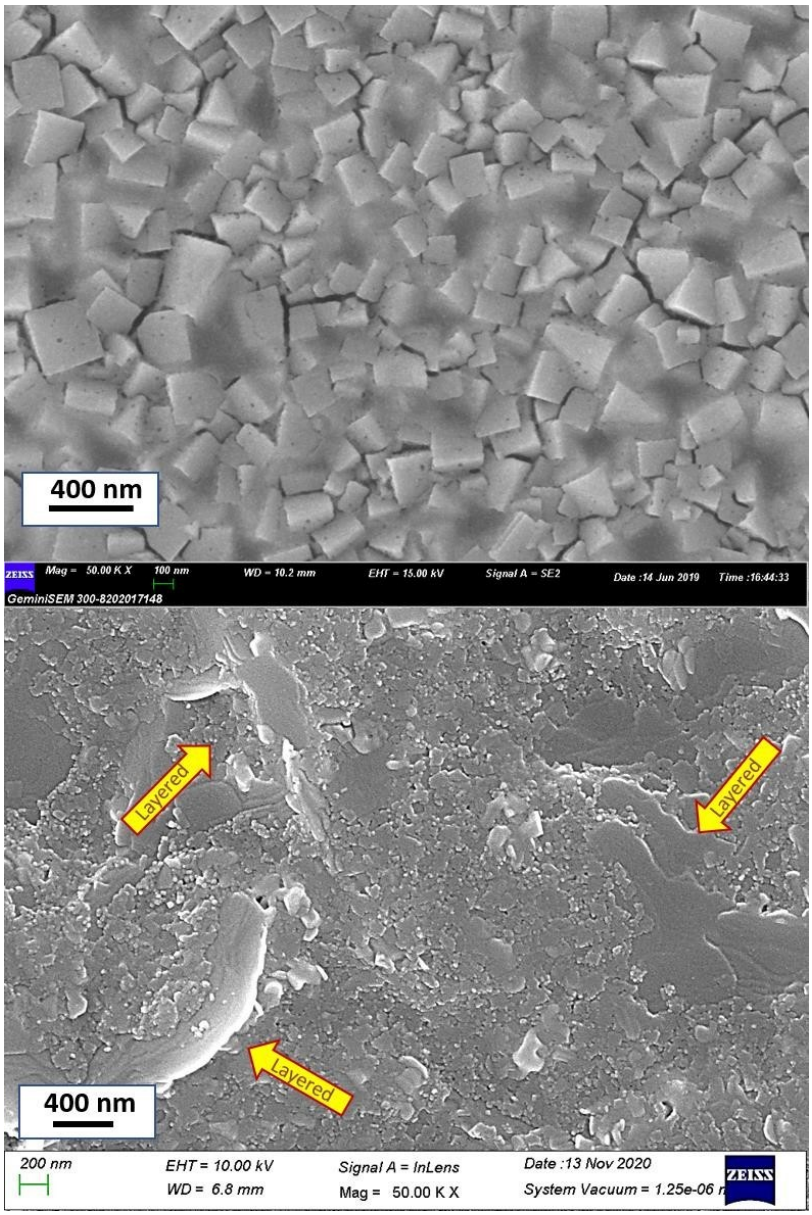

Figure S2. The top-view surface morphology of pristine MAPbBr3 film and SGQDs treated MAPbBr3 film. SGQDs treated perovskite film shows layered structures which further confirm the formation of 2D layered structure with 3D bulk.

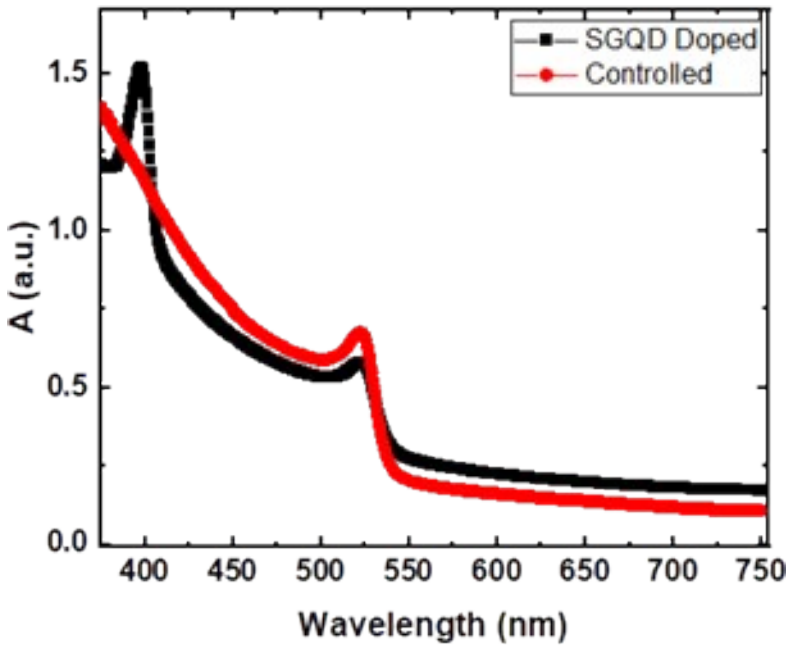

Figure S3. Absorption spectra of 3D perovskite and 2D/3D mixture perovskite films.

Wavelength dependent PL

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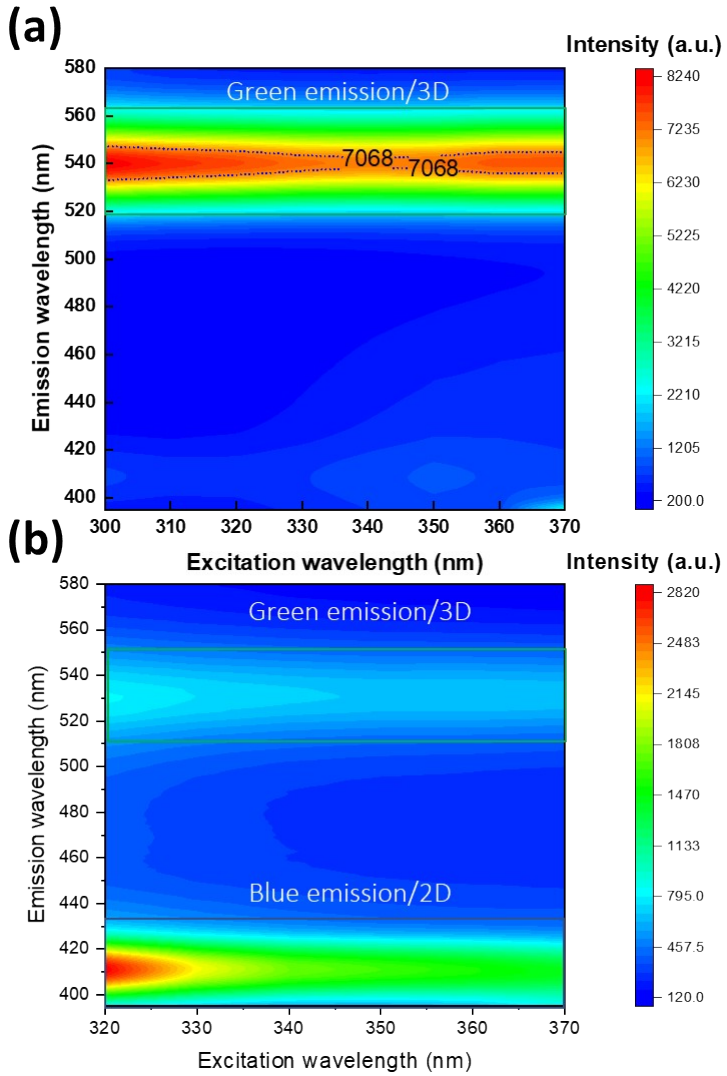

Figure S4. Wavelength dependent photoluminescence (PL) spectra of 3D perovskite and 2D/3D mixture perovskite films.

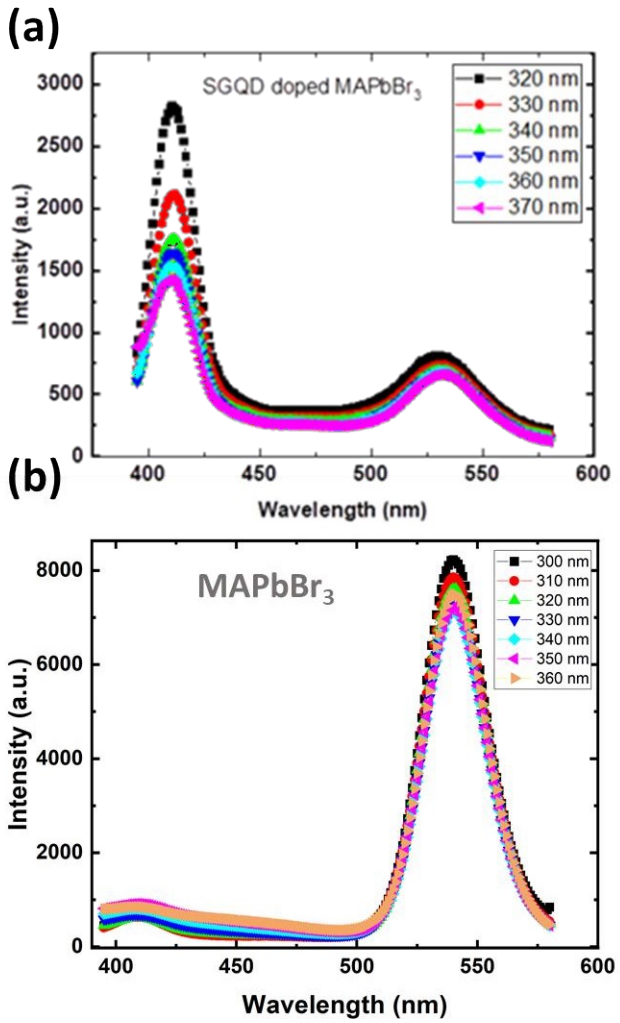

Figure S5. Wavelength dependent photoluminescence (PL) line spectra of 3D perovskite and 2D/3D mixture perovskite films.

Device Geometry

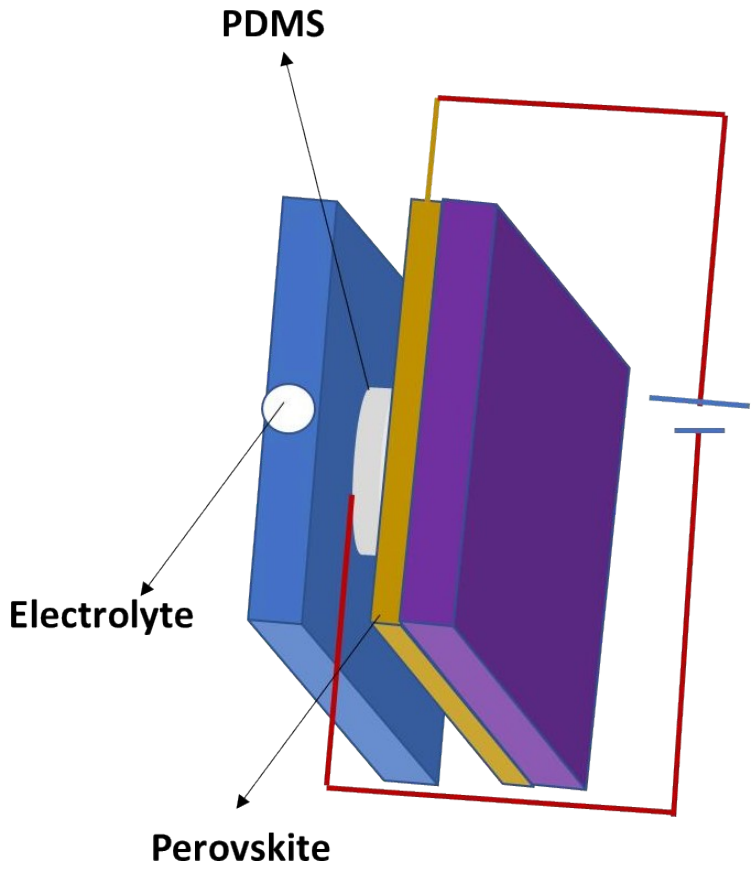

Figure S6. Device geometry of perovskite-electrolyte structure.

Diffusion Coefficient

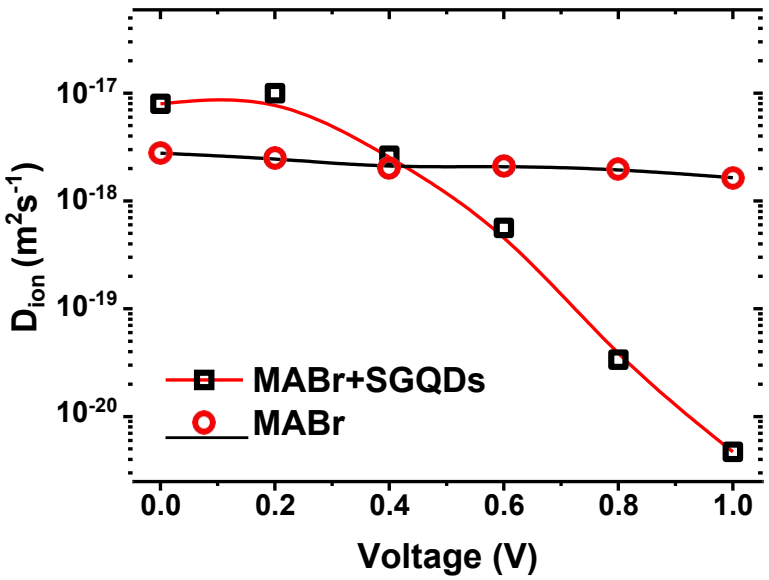

Figure S7. Diffusion coefficients of both devices at different voltages.

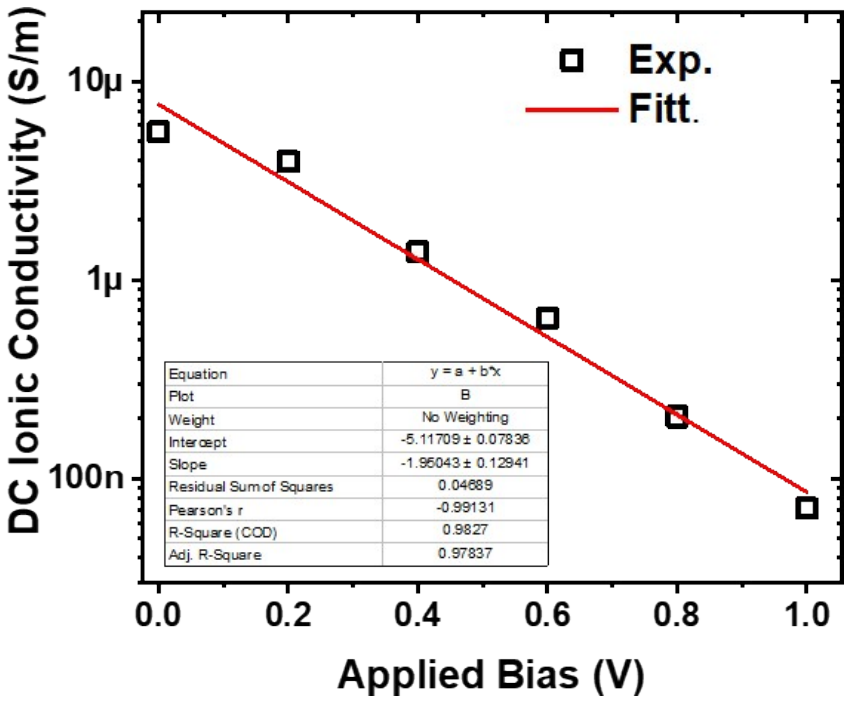

Figure S8. Exponential fitting of DC ionic conductivity of SGQDs treated perovskite-electrolyte devices.

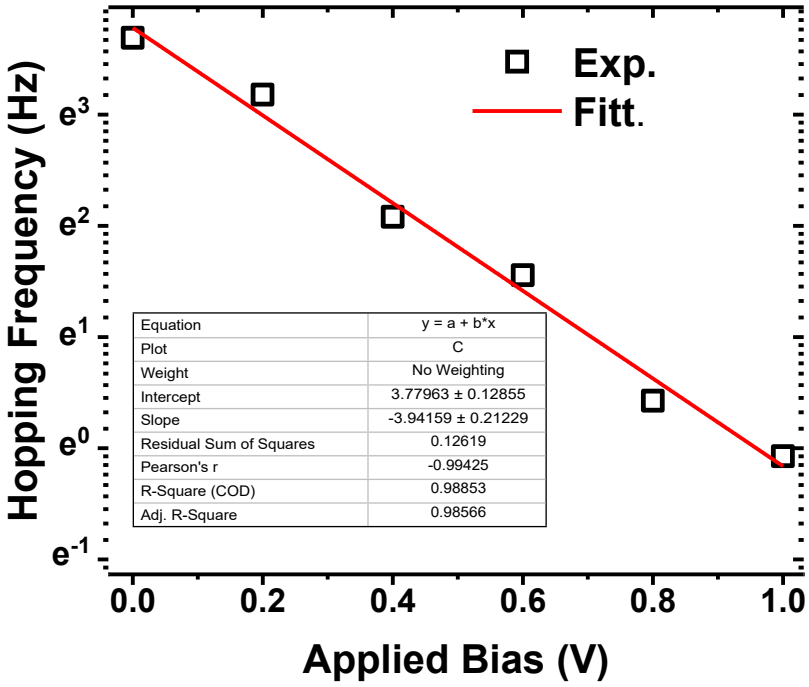

Figure S9. Exponential fitting of hopping frequency of SGQDs treated perovskite-electrolyte devices.