Supplementary Information

Highly Efficient Narrowed Emitting $AgIn_xGa_{1-x}S_2/AgGaS_2$ Quantum Dots via HF-Assisted One-Pot Synthesis Strategy and Their Light-emitting Diodes

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Table S1. Performance summary of Ag-In-S QDs with narrow band emission.

QDs	Year	FWHM [nm]	λ [nm]	PL QY [%]	Synthesis Method	Synthesis Step	ref
AIS/GaS_x	2018	28.6	585	28.8%	HU	two	1
AIS/GaS_x	2019	32	582	49.2%	HI	two	2
AIS/GaS_x	2022	~30	530-606	29%-40%	HI	two	3
AIS/GaS_x	2022	36	581	87.4%	HI	two	4
AIS/GaS_x/ZnS	2023	45	575	60%	HI	four	5
AIS/Ga-S-Se	2023	64	733	25	HI	two	6
AIS/AIGS/GS	2023	35	602	3%	HI	three	7
AIGS/GaS_x	2018	43-50	500-610	4%-28%	HU	two	8
AIGS/GaS_x	2021	32-42	498-602	28%-59%	HU	two	9
AIGS/GaS_x	2023	31-37	499-543	20%-75%	HI	two	10
AIGS/GaS_x	2023	31	532	55%	HI	two	11
AIGS/AGS	2023	30-55	468-610	50%-96%	HI	two	12
AIGS/Ga_2O_3	2023	44	563	58%	HU	one	13
AIGS/AGS		33	532	45%	HI	one	This work

HU: Heating Up / **HI:** Hot Injection

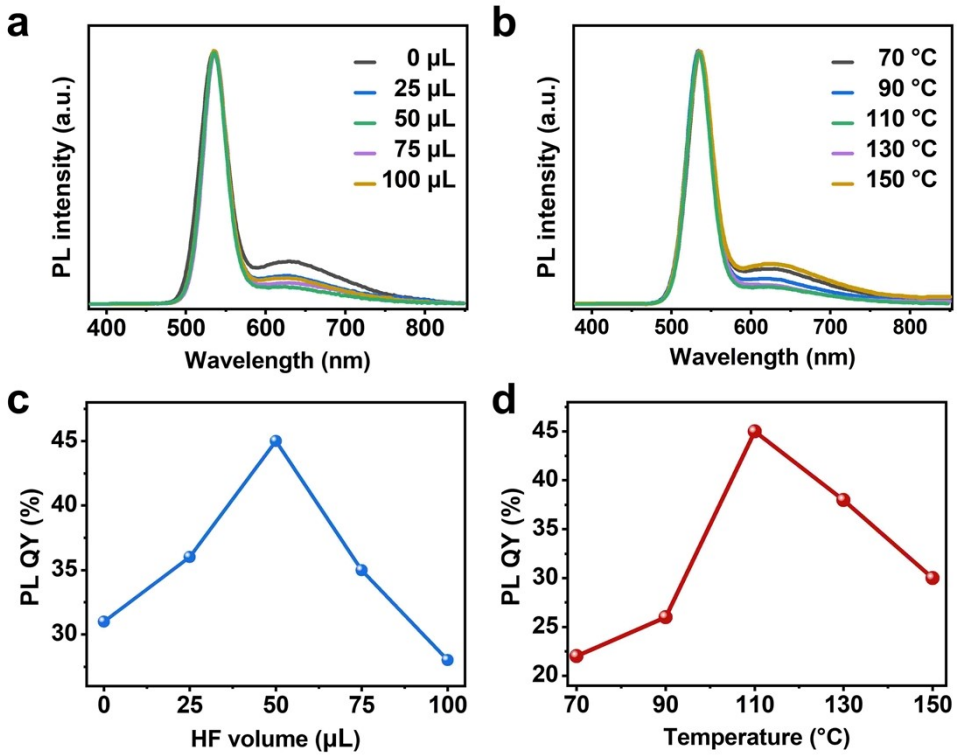

Figure S1. PL spectra of AIGS/AGS QDs with HF (3 wt%) treatment. PL spectra at different loading amounts (a) and PL spectra at different reaction temperatures (b) before AGS shell coating. The variation of PL QY of the AIGS/AGS QDs obtained at different loading amounts (c) and different reaction (d) temperatures.

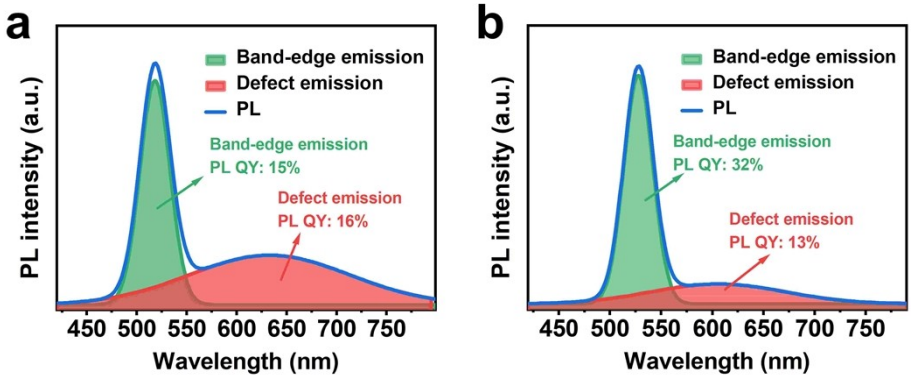

Figure S2. The ratio of band-edge emission and defect emission in the PL spectra of AIGS/AGS QDs (a) and AIGS/AGS-HF QDs (b).

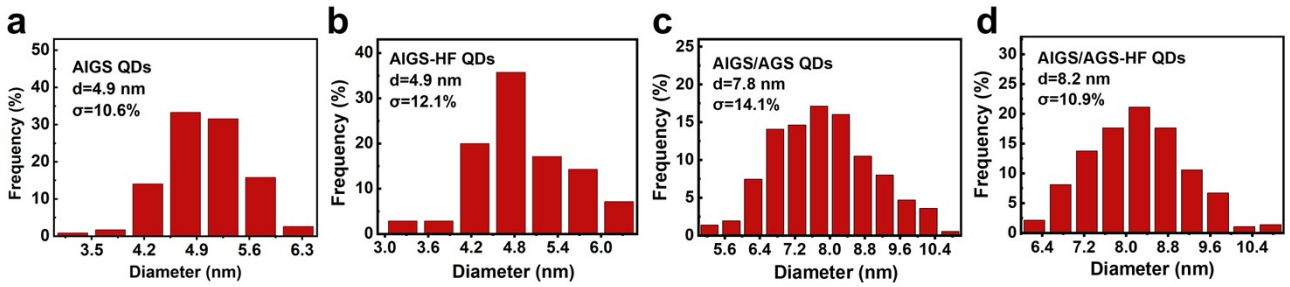

Figure S3. Size distribution histograms of (a) AIGS cores, (b) AIGS-HF cores, (c) AIGS/AGS QDs, and **(**d**)** AIGS/AGS-HF QDs.

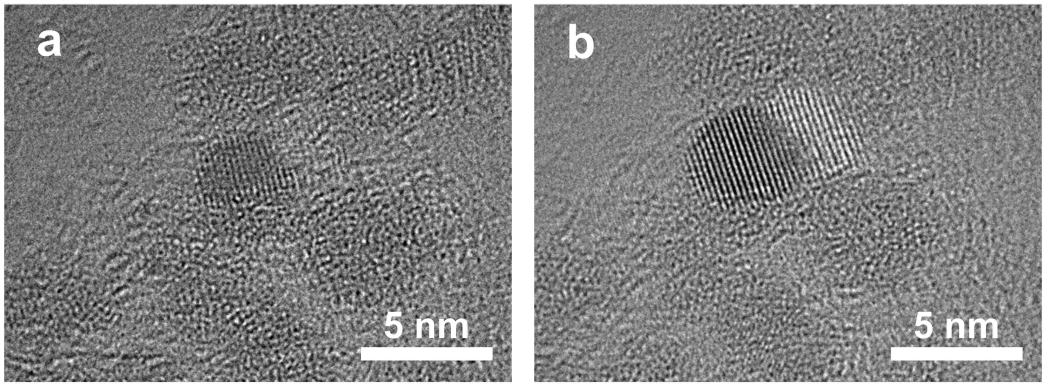

Figure S4. HRTEM images of AIGS cores before (a) and after (b) prolonged electron beam irradiation.

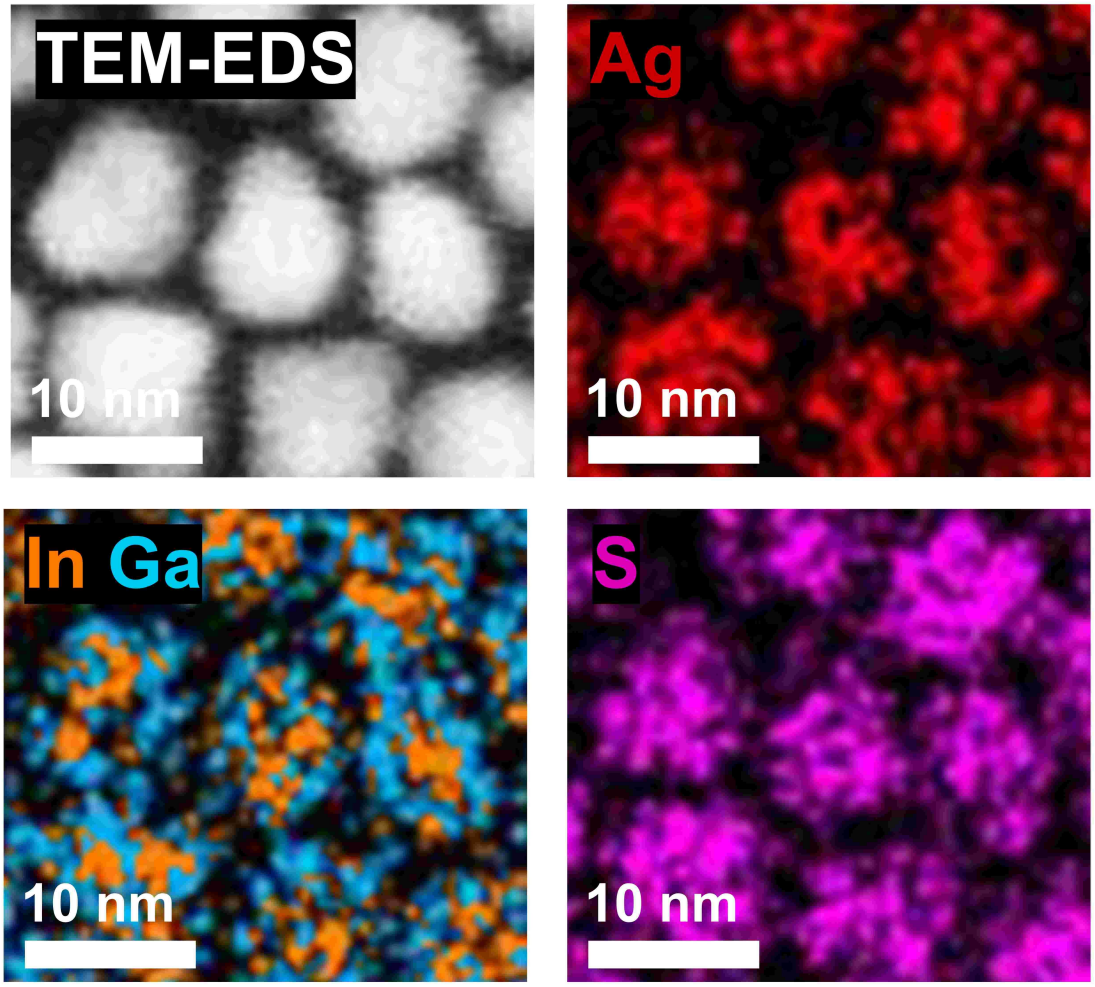

Figure S5. High-angle annular dark-field TEM image and EDS elemental mapping of Ag (red), In (orange), Ga (blue), and S (violet) for AIGS/AGS QDs.

Table S2. Composition ratios calculated from EDS data in atomic% in AIGS cores, AIGS-HF cores, and normalized ratios of AIGS-HF cores excluding the F element.

QDs	Ag	In	Ga	S	F
AIGS	20.2	16.3	23.3	40.2	0
AIGS-HF	20.4	16.2.	20.8	38.2	4.4
AIGS-HF (normalized)	21.3	16.9	21.8	40.0	/

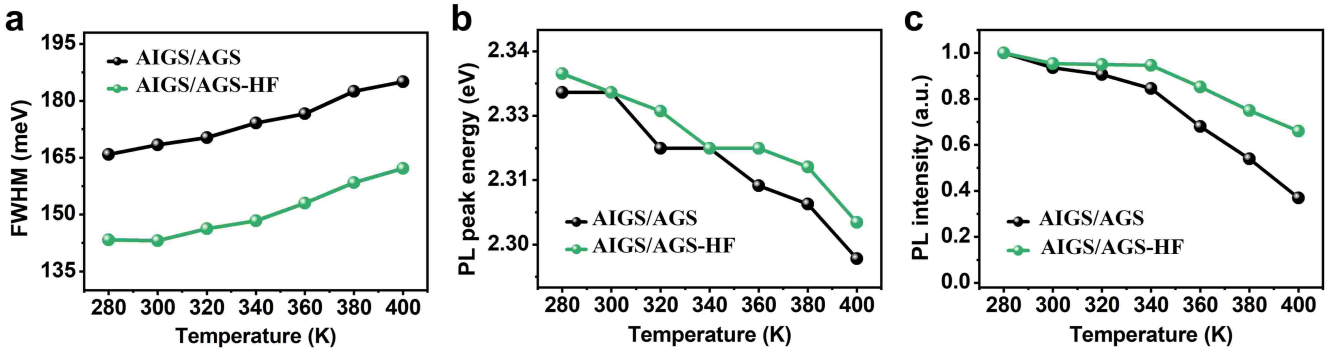

Figure S6. Variation in FWHM (a), PL peak energy (b) and PL intensity (c) with temperature of AIGS/AGS QDs and AIGS/AGS-HF QDs.

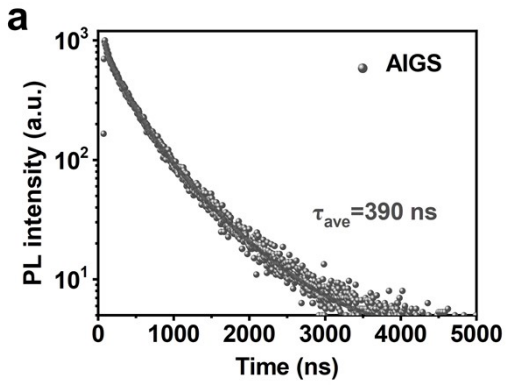

Figure S7. PL decay curve of AIGS cores.

Table S3. PL decay components of AIGS cores, AIGS/AGS QDs, and AIGS/AGS-HF QDs.

Sample	PL peak (nm)	A_1(%)	τ_1(ns)	A_2(%)	τ_2 (ns)	χ2	τ_{ave} (ns)
AIGS cores	669	50	89	50	445	0.99	390
AIGS/AGS QDs	532	85	24	15	130	0.99	77
AIGS/AGS -HF QDs	532	72	40	28	150	0.99	105

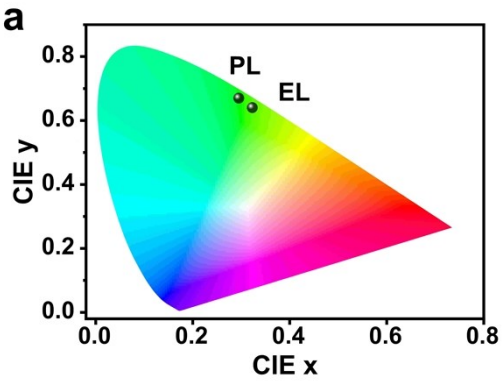

Figure S8. CIE coordinate of EL of QLED and PL of AIGS/AGS-HF QDs.

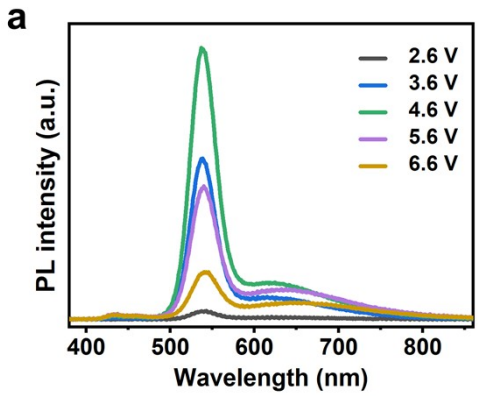

Figure S9. Electroluminescence (EL) spectra of the QLED at various voltages.

Table S4. Performance summary of green-QLEDs based on narrow-emitting I-III-VI QDs.

QDs	EL [nm]	FWHM [nm]	EQE [%]	V_{on} [V]	L_{max} [cd A^{-1}]	ref
AIS/GaS_x	570	44	0.54	2.8	60.3	14
AIGS/GaS_x	539	39		2.0	~10	15
AIGS/GaS_x	531	33	1.1	2.4	175	16
AIGS/GaS_x	529	32	1.5	2.4	57	11
AIGS/Ga_2O_3	563	49	0.65	3.2	~50	13
AIGS/AGS	535	36	0.75	2.2	2747	This work

References

1 T. Uematsu, K. Wajima, D. K. Sharma, S. Hirata, T. Yamamoto, T. Kameyama, M. Vacha, T. Torimoto and S. Kuwabata, Narrow Band-edge Photoluminescence from $AgInS_2$ Semiconductor Nanoparticles by the Formation of Amorphous III-VI Semiconductor Shells, *NPG Asia Mater.*, 2018, **10**, 713-726.

2 W. Hoisang, T. Uematsu, T. Yamamoto, T. Torimoto and S. Kuwabata, Core Nanoparticle Engineering for Narrower and More Intense Band-edge Emission from $AgInS_2/GaS_x$ Core/shell Quantum Dots. *Nanomaterials*, 2019, **9**.

3 T. Thi Thu Huong, N. T. Loan, T. D. T. Ung, N. T. Tung, H. Han and N. Q. Liem, Systematic Synthesis of Different-sized $AgInS_2/GaS_x$ Nanocrystals for Emitting the Strong and Narrow Excitonic Luminescence, *Nanotechnology*, 2022, **33**, 355704.

4 M. Tepakidareekul, T. Uematsu, T. Torimoto and S. Kuwabata, Encapsulation of $AgInS_2/GaS_x$ Core/shell Quantum Dots in In-fumarate Metal-organic Frameworks for Stability Enhancement, *CrystEngComm*, 2022, **24**, 3715-3723.

5 N. T. Loan, T. T. T. Huong, M. A. Luong, L. Van Long, H. Han, T. D. T. Ung and N. Q. Liem, Double-shelling $AgInS_2$ Nanocrystals with GaS_x/ZnS to Make Them Emit Bright and Stable Excitonic Luminescence, *Nanotechnology*, 2023, **34**, 315601.

6 N. Krobkrong, T. Uematsu, T. Torimoto and S. Kuwabata, Emission Tuning of $AgInS_2$-based Core/shell Semiconductor Quantum Dots with Type-II and Quasi-type-II Band Alignments, *Jpn. J. Appl. Phys.*, 2023, **62**, 061003.

7 N. T. Loan, T. T. T. Huong, M. A. Luong, L. Van Long, H. Han, T. D. T. Ung and N. Q. Liem, Double-shelling $AgInS_2$ Nanocrystals with GaS_x/ZnS to Make Them Emit Bright and Stable Excitonic Luminescence, *Nanotechnology*, 2023, **34**, 315601.

8 T. Kameyama, M. Kishi, C. Miyamae, D. K. Sharma, S. Hirata, T. Yamamoto, T. Uematsu, M. Vacha, S. Kuwabata and T. Torimoto, Wavelength-tunable Band-edge Photoluminescence of Nonstoichiometric Ag-In-S Nanoparticles via Ga^{3+} Doping, *ACS Appl. Mater. Interfaces*, 2018, **10**,

42844-42855.

9 W. Hoisang, T. Uematsu, T. Torimoto and S. Kuwabata, Luminescent Quaternary Ag(InxGa1-x)S2/GaSy Core/shell Quantum Dots Prepared Using Dithiocarbamate Compounds and Photoluminescence Recovery via Post Treatment, Inorg. Chem., 2021, 60, 13101-13109.

10 T. Uematsu, M. Tepakidareekul, T. Hirano, T. Torimoto and S. Kuwabata, Facile High-Yield Synthesis of Ag-In-Ga-S Quaternary Quantum Dots and Coating with Gallium Sulfide Shells for Narrow Band-edge Emission, Chem. Mater., 2023, 35, 1094-1106.

11 T. Uematsu, R. Izumi, S. Sugano, R. Sugano, T. Hirano, G. Motomura, T. Torimoto and S. Kuwabata, Spectrally Narrow Band-edge Photoluminescence from AgInS2-based Core/shell Quantum Dots for Electroluminescence Applications, Faraday Discuss., 2023, DOI: 10.1039/d3fd00142c.

12 H. J. Lee, S. Im, D. Jung, K. Kim, J. A. Chae, J. Lim, J. W. Park, D. Shin, K. Char, B. G. Jeong, J.-S. Park, E. Hwang, D. C. Lee, Y.-S. Park, H.-J. Song, J. H. Chang and W. K. Bae, Coherent Heteroepitaxial Growth of I-III-VI2 Ag(In,Ga)S2 Colloidal Nanocrystals with Near-unity Quantum Yield for Use in Luminescent Solar Concentrators, Nat. Commun., 2023, 14, 3779.

13 M. Tozawa, C. Miyamae, K. Akiyoshi, T. Kameyama, T. Yamamoto, G. Motomura, Y. Fujisaki, T. Uematsu, S. Kuwabata and T. Torimoto, One-pot Synthesis of Ag-In-Ga-S Nanocrystals Embedded in a Ga_2O_3 Matrix and Enhancement of Band-edge Emission by Na^+ Doping, *Nanoscale Adv.*, 2023, **5**, 7057-7066.

14 G. Motomura, K. Ogura, Y. Iwasaki, T. Uematsu, S. Kuwabata, T. Kameyama, T. Torimoto and T. Tsuzuki, Electroluminescence from Band-edge-emitting $AgInS_2/GaS_x$ Core/shell Quantum Dots, *Appl. Phys. Lett.*, 2020, **117**, 091101.

15 G. Motomura, Y. Iwasaki, T. Kameyama, T. Torimoto, T. Uematsu, S. Kuwabata and T. Tsuzuki, Green Electroluminescence Generated by Band-edge Transition in Ag-In-Ga-S/GaS_x Core/shell Quantum Dots, *ITE Trans. on MTA*, 2021, **9**, 222-227.

16 G. Motomura, T. Uematsu, S. Kuwabata, T. Kameyama, T. Torimoto and T. Tsuzuki, Quantum-Dot Light-emitting Diodes Exhibiting Narrow-Spectrum Green Electroluminescence by Using Ag-In-

Ga-S/GaS_x Quantum Dots, *ACS Appl. Mater. Interfaces*, 2023, **15**, 8336-8344.