

Electronic Supplementary Information

Poly acrylic acid-b-polystyrene -passivated CsPbBr₃ perovskite quantum dots with high photoluminescence quantum yield for light- emitting diodes

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Supporting Experimental Section

Materials

Lead (II) bromide (PbBr_2 , 99.9%), cesium bromide (CsBr , 99.999%), N, N-Dimethylformamide (DMF, > 99.8%), oleic acid (technical grade, 90%), and oleylamine (OAm, technical grade, 90%) were purchased from Aladdin Industrial Corporation, China. Hexane and toluene were purchased from Shanghai Titan Scientific Co., Ltd. All the reagents are directly used without further purification. Polyacrylic acid-b-polystyrene ($\text{PAA}_{24}\text{-b-PS}_{206}$ and $\text{PAA}_{24}\text{-b-PS}_{285}$) block copolymers were synthesized via sequential atomic transfer radical polymerization (ATRP) as previously reported^[1,2].

Synthesis of CsPbBr_3 PQDs and $\text{CsPbBr}_3@$ PAA-b-PS PQDs

The precursor solution was obtained by first dissolving PbBr_2 (0.4 mmol) and CsBr (0.4 mmol) in DMF (10 mL), followed by the adding of OAm (0.5 mL) and OA (1 mL) into the mixture. Then, it was stirred for half an hour to obtain a clear solution. After that, 0.25 mL precursor solution was quickly added into 5 mL toluene under vigorous stirring at 1500 rpm for 30 s to synthesize pure CsPbBr_3 PQDs. $\text{CsPbBr}_3@$ PAA-b-PS PQDs were synthesized by adding PAA-b-PS block polymer toluene solution into obtained fresh pure CsPbBr_3 PQDs under vigorous stirring at 1500 rpm to achieve ligands exchange. A bright green solution could be immediately observed.

Fabrication of white light-emitting diodes (WLEDs)

The green $\text{CsPbBr}_3@$ PAA-b-PS PQDs powder and $\text{K}_2\text{SiF}_6:\text{Mn}^{4+}$ phosphors were encapsulated into the epoxy resin adhesive. Then, the above mixture was put on the top of the red emissive layer. The optical properties of the fabricated white LED were evaluated by a temperature programmed LED optoelectronic analyzer with an integrating sphere spectroradiometer system (Everfine, ATA-500, Hangzhou, China). The white LED was operated under a current of 20 mA.

Supplementary Figures

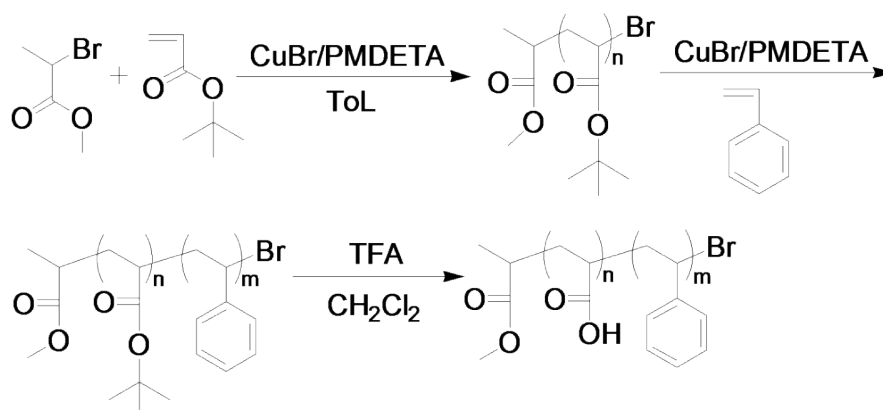


Fig. S1. Preparation of PAA-b-PS by sequential atom transfer radical polymerization (ATRP). Polyacrylic acid-b-polystyrene (PAA₂₄-b-PS₂₀₆ and PAA₂₄-b-PS₂₈₅) block copolymers were synthesized via sequential atomic transfer radical polymerization (ATRP) as previously reported. Initially, tert-Butyl acrylate (tBA) was polymerized using CuBr complexed by N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA) as the catalyst and methyl 2-bromopropionate (MBP) as the initiator. Furthermore, styrene was polymerized using the same catalyst and PtBA as the macroinitiator. Finally, hydrolysis led to the corresponding PAA-b-PS.

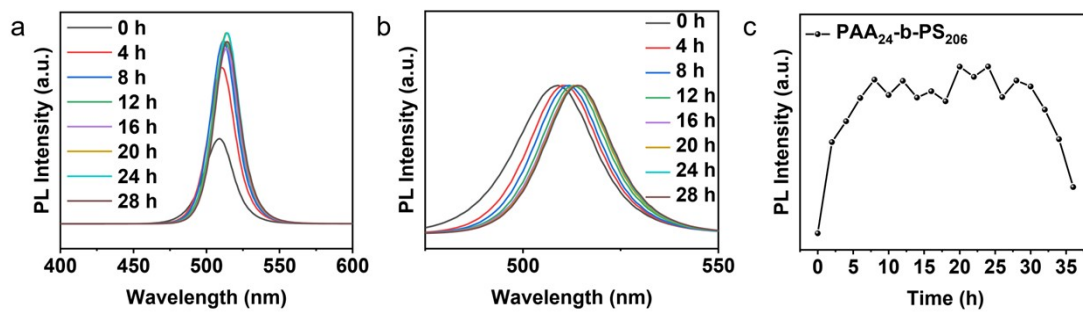


Fig. S2. (a) PL spectra of CsPbBr₃@PAA₂₄-b-PS₂₀₆ PQDs for different reaction times. (b) PL spectra of CsPbBr₃@PAA₂₄-b-PS₂₀₆ PQDs with different reaction times. (c) Variation of PL intensity with CsPbBr₃@PAA₂₄-b-PS₂₀₆ PQDs at different reaction times.

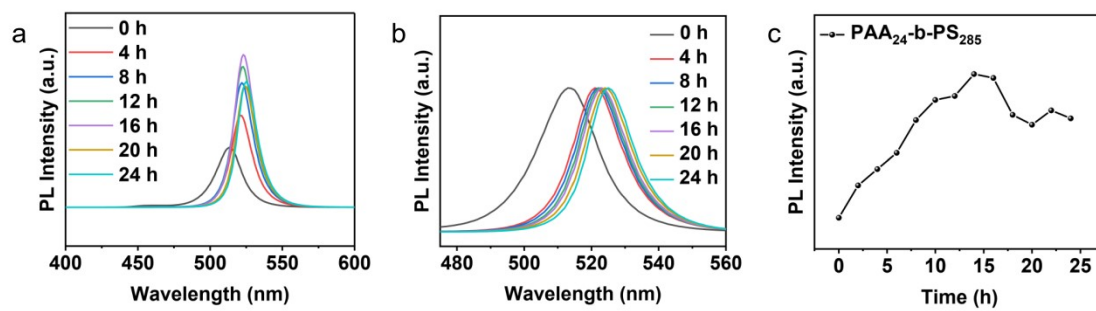


Fig. S3. (a) PL spectra of CsPbBr₃@PAA₂₄-b-PS₂₈₅ PQDs for different reaction times. (b) PL spectra of CsPbBr₃@PAA₂₄-b-PS₂₈₅ PQDs with different reaction times. (c) Variation of PL intensity with CsPbBr₃@PAA₂₄-b-PS₂₈₅ PQDs at different reaction times.

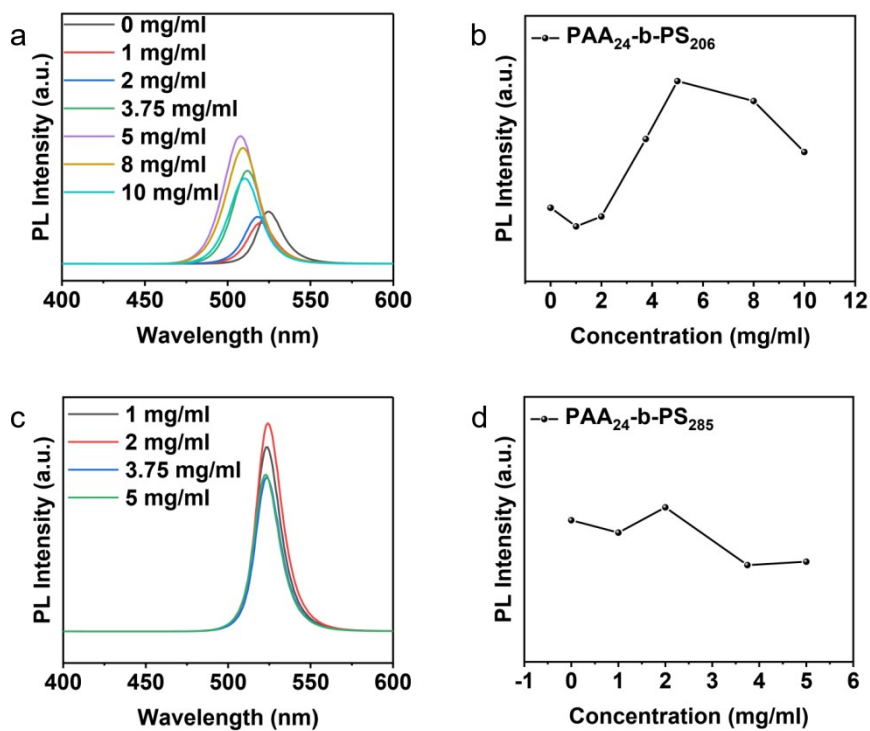


Fig. S4. (a) PL spectra of CsPbBr₃@PAA₂₄-b-PS₂₀₆ PQDs with different concentrations. (b) Variation of PL intensity with CsPbBr₃@PAA₂₄-b-PS₂₀₆ PQDs concentrations. (c) PL spectra of CsPbBr₃@PAA₂₄-b-PS₂₈₅ PQDs with different concentrations. (d) Variation of PL intensity with CsPbBr₃@PAA₂₄-b-PS₂₈₅ PQDs concentrations.

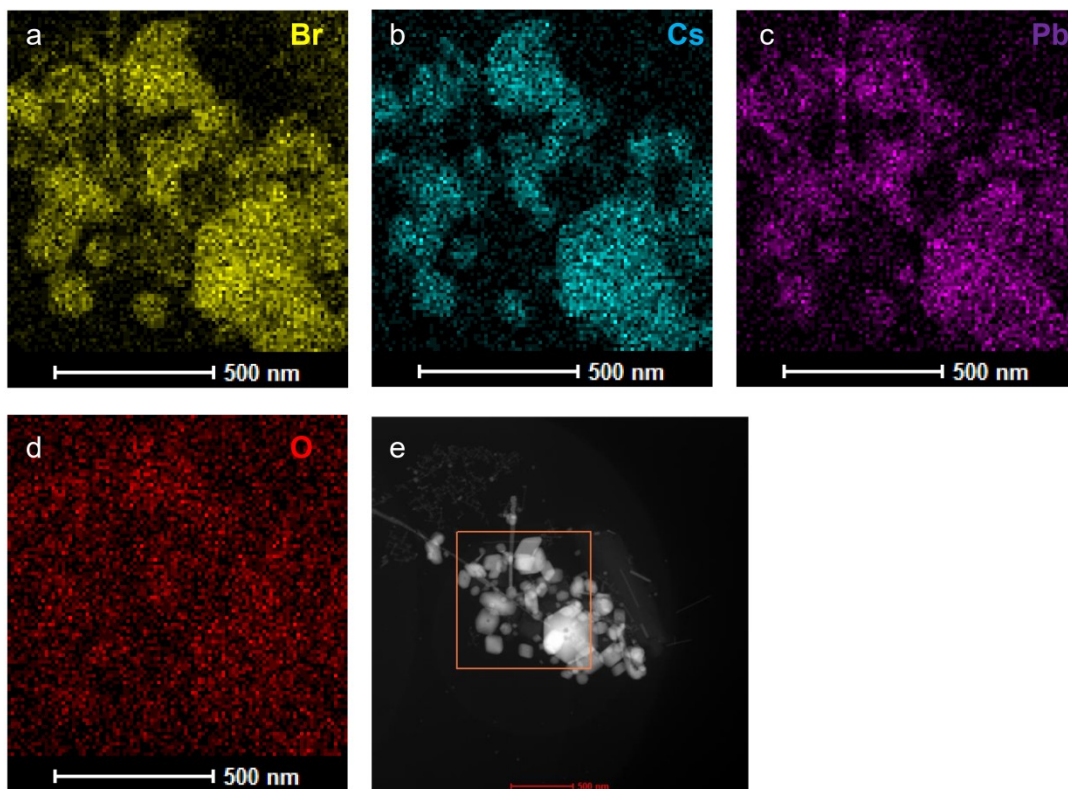


Fig. S5. EDX elemental mappings of (a) Br (yellow), (b) Cs (blue), (c) Pb (purple), and (d) O (red). (e) High-angle annular dark-field scanning TEM.

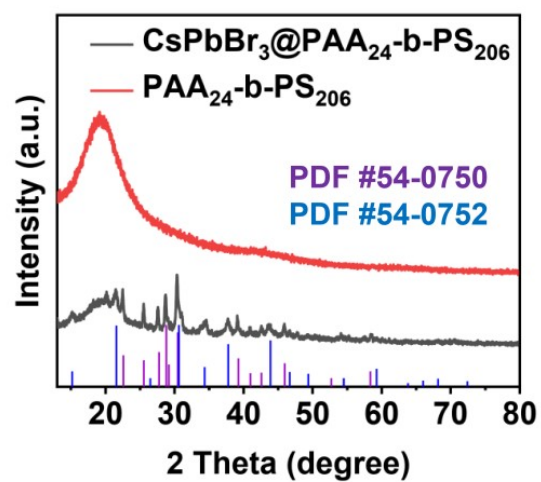


Fig. S6. XRD patterns of CsPbBr₃@PAA₂₄-b-PS₂₀₆ PQDs (black line) and PAA₂₄-b-PS₂₀₆ (red line).

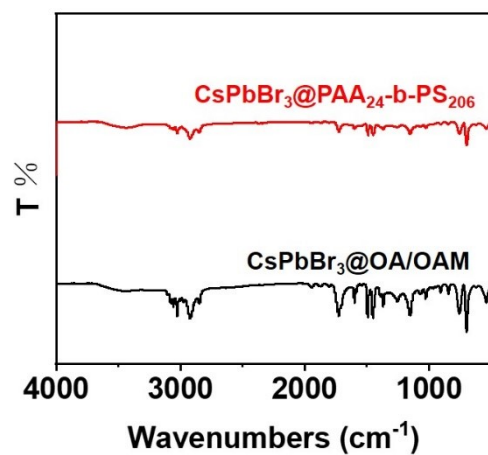


Fig. S7. FTIR images of CsPbBr₃@PAA₂₄-b-PS₂₀₆ PQDs (red line) and CsPbBr₃@OA/OAM PQDs (black line) after reaction for 24 hours.

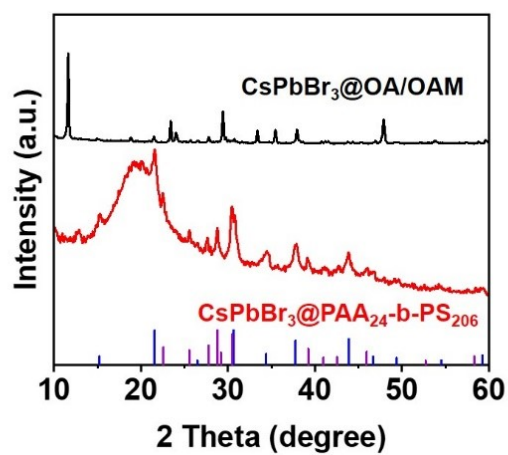


Fig. S8. XRD patterns of CsPbBr₃@PAA₂₄-b-PS₂₀₆ PQDs (red line) and pristine CsPbBr₃ PQDs (black line) after immersion in ethanol for 2 days.

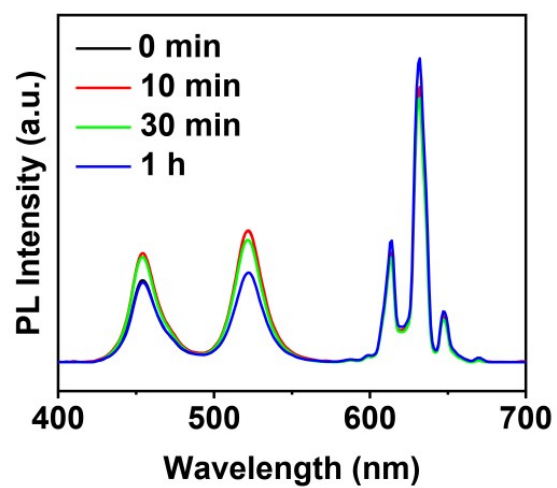


Fig. S9. White light-emitting diodes (WLEDs) PL images with different light times.

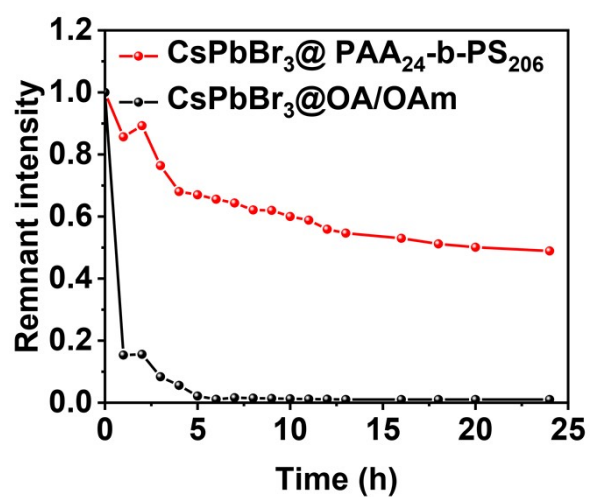


Fig. S10. Remnant PL values of CsPbBr₃@OA/OAM and CsPbBr₃@PAA₂₄-b-PS₂₀₆ PQDs in water.

Table S1. Polymers and PQDs used in PQDs/polymer nanocomposites.

Polymer/monomer		PQDs	PLQY (%)	Ref.
Poly acrylic acid- <i>b</i> -polystyrene	PAA- <i>b</i> -PS	CsPbBr ₃	95	This work
Polystyrene	PS	CsPbX ₃	75	[3]
			44	[4]
			25	[5]
			68	[6]
			34	[7]
			48	[8]
			27	[9]
			79	[10]
Poly (ethylene glycol)	PEG	CsPbX ₃	41	[11]
Poly (ethylene oxide)	PEO	CsPbBr ₃	60	[12]
Poly (vinylidene fluoride)	PVDF	CsPbBr ₃	65	[13]
Poly (methyl methacrylate)	PMMA	CsPbX ₃	54	[14]
			45	[15]
Poly (lauryl methacrylate)	PLMA	CsPbBr ₃	86	[16]
Poly(vinylpyrrolidone)	PVP	CsPbX ₃	55	[17]
			24	[18]
Poly (lactic acid)	PLA	CsPbX ₃	90	[19]
Poly (maleic anhydride- <i>alt</i> -1-octadecene)	PMAO	CsPbX ₃	88	[20]
			69	[21]
			88.8	[22]
Poly (isobutylene- <i>alt</i> -maleic anhydride)	PIMA	CsPbBr ₃	80	[23]
Ethyl cellulose		CsPbBr ₃	37.2	[24]
Diphenylvinylphosphine-styrene copolymer	PDPEP- <i>co</i> -PS	CsPbBr ₃	90	[25]
Polystyrene- <i>block</i> -poly-2-vinylpyridine	PS- <i>b</i> -P2VP	CsPbX ₃	51	[26]
Poly (divinylbenzene)	PDVB	CsPbBr ₃	60	[27]
Poly (ethylene vinyl acetate)	PEVA	CsPbBr ₃	40.5	[28]
Star-like poly(acrylic acid)- <i>block</i> -polystyrene	PAA- <i>b</i> -PS	CsPbBr ₃	91.4	[29]
			71	[30]
Star-like polystyrene- <i>block</i> -poly (acrylic acid)- <i>block</i> -polystyrene	PS- <i>b</i> -PAA- <i>b</i> -PS	CsPbBr ₃	67	[30]
Poly (ethylenimine)	PEI	CsPbBr ₃	75	[31]
			85	[32]
Polyimide	PI	CsPbBr ₃	88.1	[33]
Poly (2-(dimethylamino)ethylmethacrylate)	PDMAEMA	CsPbBr ₃	60	[34]

Table S2. Comparisons with the CsPbBr₃ QDs-based WLEDs reported previously.

Samples	PLQY (%)	CCT (K)	CRI	CIE coordinates (X, Y)	Ref.
CsPbBr ₃ @PAA ₂₄ -b-PS ₂₀₆ ⁺	95	5464	65.5	(0.3333, 0.3396)	This work
K ₂ SiF ₆ :Mn ⁴⁺ (KSF) phosphors					
CsPbBr ₃ @ZrO ₂ + CaAlSiN ₃ :Eu ²⁺	80	4743	NA	(0.351, 0.346)	[35]
CsPbBr ₃ @SiO ₂ + Ag-In-Zn-S	75	3689	91	(0.4037, 0.411)	[36]
CsPbBr ₃ : Na + KSF phosphors	85	6652	75.2	(0.31, 0.33),	[37]
CsPbBr ₃ /PMAO + nitride phosphors	88.8	3320	NA	(0.390, 0.332)	[38]
CsPbBr ₃ + KSF phosphors	93	4574	85	(0.34, 0.31)	[39]
CsPbBr ₃ AeroPQDs + KSF phosphor	75.6	6500	NA	(0.31, 0.33)	[40]

References

- [1] Y. Kang, T. A. Taton, *Angew. Chem. Int. Ed.* 2005, 44, 409–412.
- [2] T. Azzam, A. Eisenberg, *Angew. Chem. Int. Ed.* 2006, 45, 7443–7447.
- [3] S. N. Raja, Y. Bekenstein, M. A. Koc, S. Fischer, D. Zhang, L. Lin, R. O. Ritchie, P. Yang, A. P. Alivisatos, *ACS Appl. Mater. Interfaces* 2016, 8, 35523.
- [4] Y. C. Wong, J. De Andrew Ng, Z. K. Tan, *Adv. Mater.* 2018, 30, 1800774.
- [5] S. Pathak, N. Sakai, F. Wisnivesky Rocca Rivarola, S. D. Stranks, J. Liu, G. E. Eperon, C. Ducati, K. Wojciechowski, J. T. Griffiths, A. A. Haghighirad, A. Pellaroque, R. H. Friend, H. J. Snaith, *Chem. Mater.* 2015, 27, 8066.
- [6] Y. Wei, X. Deng, Z. Xie, X. Cai, S. Liang, P. a. Ma, Z. Hou, Z. Cheng, J. Lin, *Adv. Funct. Mater.* 2017, 27, 1703535.
- [7] Y. Wang, J. He, H. Chen, J. Chen, R. Zhu, P. Ma, A. Towers, Y. Lin, A. J. Gesquiere, S. T. Wu, Y. Dong, *Adv. Mater.* 2016, 28, 10710.
- [8] H. Liao, S. Guo, S. Cao, L. Wang, F. Gao, Z. Yang, J. Zheng, W. Yang, *Adv. Opt. Mater.* 2018, 6, 1800346.
- [9] H. Zhang, X. Wang, Q. Liao, Z. Xu, H. Li, L. Zheng, H. Fu, *Adv. Funct. Mater.* 2017, 27, 1604382.
- [10] H. Kim, S. So, A. Ribbe, Y. Liu, W. Hu, V. V. Duzhko, R. C. Hayward, T. Emrick, *Chem. Commun.* 2019, 55, 1833.
- [11] Q.-B. Yan, N. Bao, S.-N. Ding, *J. Mater. Chem. B* 2019, 7, 4153.
- [12] Y. Ling, Y. Tian, X. Wang, J. C. Wang, J. M. Knox, F. Perez-Orive, Y. Du, L. Tan, K. Hanson, B. Ma, H. Gao, *Adv. Mater.* 2016, 28, 8983.
- [13] P. Liang, P. Zhang, A. Pan, K. Yan, Y. Zhu, M. Yang, L. He, *ACS Appl. Mater. Interfaces* 2019, 11, 22786.
- [14] A. Pan, J. Wang, M. J. Jurow, M. Jia, Y. Liu, Y. Wu, Y. Zhang, L. He, Y. Liu, *Chem. Mater.* 2018, 30, 2771.
- [15] K. Ma, X.-Y. Du, Y.-W. Zhang, S. Chen, *J. Mater. Chem. C* 2017, 5, 9398.
- [16] J. Tong, J. Wu, W. Shen, Y. Zhang, Y. Liu, T. Zhang, S. Nie, Z. Deng, *ACS Appl. Mater. Interfaces* 2019, 11, 9317.
- [17] L. Zhang, X. Yang, Q. Jiang, P. Wang, Z. Yin, X. Zhang, H. Tan, Y. M. Yang, M. Wei, B. R. Sutherland, E. H. Sargent, *Nat. Commun.* 2017, 8, 15640.
- [18] J. Hai, H. Li, Y. Zhao, F. Chen, Y. Peng, B. Wang, *Chem. Commun.* 2017, 53, 5400.
- [19] L. Rao, Y. Tang, C. Yan, J. Li, G. Zhong, K. Tang, B. Yu, Z. Li, J. Z. Zhang, *J. Mater. Chem. C* 2018, 6, 5375.

- [20] M. Meyns, M. Perálvarez, A. Heuer-Jungemann, W. Hertog, M. Ibáñez, R. Nafria, A. Genç, J. Arbiol, M. V. Kovalenko, J. Carreras, A. Cabot, A. G. Kanaras, *ACS Appl. Mater. Interfaces* 2016, 8, 19579.
- [21] D. Baranov, G. Caputo, L. Goldoni, Z. Dang, R. Scarfiello, L. De Trizio, A. Portone, F. Fabbri, A. Camposeo, D. Pisignano, L. Manna, *Chem. Sci.* 2020, 11, 3986.
- [22] H. Wu, S. Wang, F. Cao, J. Zhou, Q. Wu, H. Wang, X. Li, L. Yin, X. Yang, *Chem. Mater.* 2019, 31, 1936.
- [23] S. Wang, L. Du, Z. Jin, Y. Xin, H. Mattoussi, *J. Am. Chem. Soc.* 2020, 142, 12669.
- [24] Y. H. Song, J. S. Yoo, B. K. Kang, S. H. Choi, E. K. Ji, H. S. Jung, D. H. Yoon, *Nanoscale* 2016, 8, 19523.
- [25] W. Yang, L. Fei, F. Gao, W. Liu, H. Xu, L. Yang, Y. Liu, *Chem. Eng. J.* 2020, 387, 124180.
- [26] S. Hou, Y. Guo, Y. Tang, Q. Quan, *ACS Appl. Mater. Interfaces* 2017, 9, 18417.
- [27] T. Xuan, J. Huang, H. Liu, S. Lou, L. Cao, W. Gan, R.-S. Liu, J. Wang, *Chem. Mater.* 2019, 31, 1042.
- [28] Y. Li, Y. Lv, Z. Guo, L. Dong, J. Zheng, C. Chai, N. Chen, Y. Lu, C. Chen, *ACS Appl. Mater. Interfaces* 2018, 10, 15888.
- [29] Y. J. Yoon, Y. Chang, S. Zhang, M. Zhang, S. Pan, Y. He, C. H. Lin, S. Yu, Y. Chen, Z. Wang, Y. Ding, J. Jung, N. Thadhani, V. V. Tsukruk, Z. Kang, Z. Lin, *Adv. Mater.* 2019, 31, 1901602.
- [30] S. Pan, Y. Chen, Z. Wang, Y.-W. Harn, J. Yu, A. Wang, M. J. Smith, Z. Li, V. V. Tsukruk, J. Peng, Z. Lin, *Nano Energy* 2020, 77, 105043.
- [31] G. Jiang, C. Guhrenz, A. Kirch, L. Sonntag, C. Bauer, X. Fan, J. Wang, S. Reineke, N. Gaponik, A. Eychemüller, *ACS Nano* 2019, 13, 10386.
- [32] W. Yin, M. Li, W. Dong, Z. Luo, Y. Li, J. Qian, J. Zhang, W. Zhang, Y. Zhang, S. V. Kershaw, X. Zhang, W. Zheng, A. L. Rogach, *ACS Energy Lett.* 2021, 6, 477.
- [33] J. Zhang, P. Jiang, Y. Wang, X. Liu, J. Ma, G. Tu, *ACS Appl. Mater. Interfaces* 2019, 12, 3080.
- [34] A. Pan, L. Yan, X. Ma, Y. Wu, Y. Zhang, G. Zhou, L. He, *J. Alloys Compd.* 2020, 844, 156102.
- [35] Q. Mo, C. Chen, W. Cai, S. Zhao, D. Yan, Z. Zang, *Laser & Photonics Rev.* 2021, 15, 2100278.
- [36] H. Guan, S. Zhao, H. Wang, D. Yan, M. Wang, Z. Zang, *Nano Energy* 2020, 67, 104279.
- [37] S. Li, Z. Shi, F. Zhang, L. Wang, Z. Ma, D. Yang, Z. Yao, D. Wu, T. Xu, Y. Tian, Y. Zhang, C. Shan, X. Li, *Chem. Mater.* 2019, 31, 3917–3928.
- [38] H. Wu, S. Wang, F. Cao, J. Zhou, Q. Wu, H. Wang, X. Li, L. Yin, X. Yang, *Chem. Mater.* 2019, 31, 1936-1940.
- [39] H. Xu, J. Wang, T. Xuan, C. Lv, J. Hou, L. Zhang, Y. Dong, J. Shi, *Chem. Eng. J.* 2019, 364, 20.
- [40] Z. Li, C. Song, J. Li, G. Liang, L. Rao, S. Yu, X. Ding, Y. Tang, B. Yu, J. Ou, U. Lemmer, G. Gomard, *Adv.*

Mater. Technol.2020,5, 190094.