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Electronic Supplementary Information

Mn²⁺-Doped Zn-In-S Quantum Dots with Tunable Bandgaps and High

Photoluminescence Properties

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QDs	PL QY/(%)	Peak/(nm)	Lifetime/(ms)	Band gap/(eV)	Ref.
Mn:ZnS	> 50	590	1.71	~3.7	1
Mn:ZnS	> 50	585	0.37 ~3.7		2
Mn:CdS	not	580-620,	not mentioned	~2.7	2
	mentioned	tunable	not mentioned		3
Mn:ZnSe	35	590	0.38	~2.7	4
Mn:ZnSSe	~60	~595	not mentioned	~2.9	5
MnS/ZnS/CdS	68	580	0.68	2.6-3.1, tunable	6
Mn:ZnCdS	30	580	not mentioned	2.7-3.9, tunable	7
Mn:CuInZnS	45	600	2.12	~2.7	8
Mn:CdInS	17	630	1.1	2.8-3.7, tunable	9
Mn:CdZnSe	~25	580	~0.6	~3.1	10
Mn:CuInS/ZnS	66	610	3.78	~2.7	11
Mn:Zn-In-S	56 600	4.2	2.88-3.68,	The present work	
		UUU	4.2	tunable	The present work

Table S1. Optical Properties of typical Mn²⁺-doped QDs in the reported works

precursor injection times							
Zn precursor injection times	A_1	$\tau_1/(ms)$	A_2	$\tau_2/(ms)$	$\tau_{ave}/(ms)$	PL QY(%)	
0	0.57	0.08	0.41	0.31	0.25	5	
1	0.82	0.52	0.17	2.44	1.45	21	
2	0.77	0.65	0.23	3.82	2.66	45	
3	0.52	0.72	0.44	4.89	4.27	56	

Table S2. Fitting parameters of PL dynamics of Mn²⁺ doped Zn-In-S QDs with different Zn

3



Figure S1. Typical PL spectra of Mn²⁺ doped Zn-In-S QDs before (black line, CHCl₃ dispersions) and after (red line, aqueous dispersions) ligand exchange. The inset shows the digital photographs of the Mn²⁺ doped Zn-In-S QDs dissolved in CHCl₃ (left) and water (right) excited at 365 nm.



Figure S2. The linear extrapolation of $(\alpha hv)^2 vs$ photon energy of Mn²⁺ doped Zn-In-S QDs under different nominal Zn/In precursor ratios.



Figure S3. Typical EDX spectra of Mn²⁺ doped Zn-In-S QDs under different nominal Zn/In precursor ratios



Figure S4. Typical TEM images of the Mn doped Zn-In-S QDs with nominal Zn/In precursor molar ratios of 7/3 (a,), 5/5 (b,), 4/6 (c,), and 3/7(d), indicating that the particle sizes are almost kept a constant regardless of various Zn/In precursor ratios introduced.

Table S3. Chemical Compositions of Mn²⁺ doped Zn-In-S QDs under different nominal Zn/In precursor ratios

Nominal Zn/In Ratios for Mn:ZnInS cores	Nominal Zn/In Ratios for Mn ²⁺ -doped QDs	Real Zn/In Ratios	S /atom.%	Zn /atom.%	In /atom.%	Mn /atom.%	Mn ²⁺ doping Concentration/ %
10/0	10/0		60.84	37.55	0	1.61	4.1
7/3	88/12=7.3	3.5	60.81	28.86	8.21	2.12	5.4
5/5	80/20=4	1.25	57.26	22.55	17.95	2.24	5.2
4/6	76/24=3.2	0.89	54.03	20.4	22.83	2.74	5.9
3/7	72/28=2.6	0.68	58.91	14.20	22.97	2.92	7.1

Nominal Mn ²⁺ Doping Concentration / %	S /atom.%	Zn /atom.%	In /atom.%	Mn /atom.%	Real Mn ²⁺ doping Concentration / %
1.5	75.23	19.31	4.72	0.74	3.1
3	83.97	11.24	4	0.79	5.2
4.5	77.05	15.25	6.48	1.22	5.6
6.5	74.03	18.32	6.12	1.53	6.3
7.5	80.92	12.34	5.32	1.42	8.1
9	70.55	19.62	7.32	2.51	9.3

Table S4. Chemical Compositions of Mn²⁺ doped Zn-In-S QDs under different nominal Mn²⁺ doping concentrations.



Figure S5. Typical absorption and PL spectra of Mn²⁺-doped Zn-In-S (red lines) and undoped Zn-In-S QDs (blue lines).

References

- 1. J. Zheng, W. Ji, X. Wang, M. Ikezawa, P. Jing, X. Liu, H. Li, J. Zhao and Y. Masumoto, *J. Phys. Chem. C* 2010, **114**, 15331-15336.
- 2. B. B. Srivastava, S. Jana, N. S. Karan, S. Paria, N. R. Jana, D. D. Sarma and N. Pradhan, *J. Phys. Chem. Lett.*, 2010, **1**, 1454-1458.
- 3. A. Nag, R. Cherian, P. Mahadevan, A. V. Gopal, A. Hazarika, A. Mohan, A. S. Vengurlekar and D. D. Sarma, *J. Phys. Chem. C* 2010, **114**, 18323-18329.
- 4. Z. Fang, P. Wu, X. Zhong and Y.-J. Yang, Nanotechnology 2010, 21, 305604.
- 5. R. Zeng, T. Zhang, G. Dai and B. Zou, J. Phys. Chem. C 2011, 115, 3005-3010.
- 6. S. Cao, J. Zheng, J. Zhao, L. Wang, F. Gao, G. Wei, R. Zeng, L. Tian and W. Yang, *J. Mater. Chem. C* 2013, 1, 2540-2547.
- 7. K. Jong-Uk, L. Myung-Hyun and Y. Heesun, *Nanotechnology* 2008, 19, 465605.
- 8. G. Manna, S. Jana, R. Bose and N. Pradhan, J. Phys. Chem. Lett. 2012, 3, 2528-2534.
- J. Lin, Q. Zhang, L. Wang, X. Liu, W. Yan, T. Wu, X. Bu and P. Feng, *J. Am. Chem. Soc.* 2014, 136, 4769-4779.
- 10. A. Hazarika, A. Pandey and D. D. Sarma, J. Phys. Chem. Lett. 2014, 5, 2208-2213.
- 11. S. Cao, C. Li, L. Wang, M. Shang, G. Wei, J. Zheng and W. Yang, Sci. Rep. 2014, 4, 7510.