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Supporting Information

Halogen ions doping mediated exciton states modulation in MoS_2 quantum dots for fluorescence tuning and optical anti-counterfeiting

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Content

1 Formula and calculation

1.1 Calculation of Relative dielectric constant at optical frequency

$n = \sqrt{\varepsilon_r \mu_r}$

n: Refractive index; μ_r: Relative permeability, the relative permeability is about 1 for inorganic materials; ε_r: relative dielectric constant. The refractive index of KF, KCl, KB and KI aqueous solution (25mM) was measured as 1.3321,1.3321,1.3320 and 1.333 by an Abbe refractometer. The relative dielectric constant of KF, KCl, KBr and KI aqueous solution was calculated 1.7745, 1.7745,1.7742, and 1.7769.

1.2 Lorentz formula for PL spectra fittings

As we know, B and A exciton emissions are normally present in the PL spectrum of single-layer MoS_2 due to the spin-orbit-splitting at the K-point in the valence band. [1] In addition, A^- trions and defect-bound excitons are also commonly observed in MoS_2 with high charge carrier and defect density. [2] PL spectra of all samples were well fitted by the following Lorentz formula:

$$y = y_0 + \frac{I_B}{\left[\frac{2(E-E_B)}{W_B}\right]+1} + \frac{I_A}{\left[\frac{2(E-E_A)}{W_A}\right]+1} + \frac{I_{A^-}}{\left[\frac{2\left(E-E_{A^-}\right)}{W_{A^-}}\right]+1} + \frac{I_{DX_A}}{\left[\frac{2\left(E-E_{DX_A}\right)}{W_{DX_A}}\right]+1}$$

Where I_B, E_B and W_B are the intensity, the energy position, and the full width at half-maximum (fwhm) of B exciton, respectively. I_A, E_A and W_A are the intensity, the energy position, and the full width at half-maximum (fwhm) of A exciton,

respectively. I_{A^-}, E_{A^-} and W_{A^-} are the intensity, the energy position, and the full width at half-maximum (fwhm) of trion exciton A^-, respectively. I_{DX_A}, E_{DX_A} and W_{DX_A} are the intensity, the energy position, and the full width at half-maximum (fwhm) of Defect-bound exciton DX_A, respectively.

2 Figures and Tables

2.1 Figures

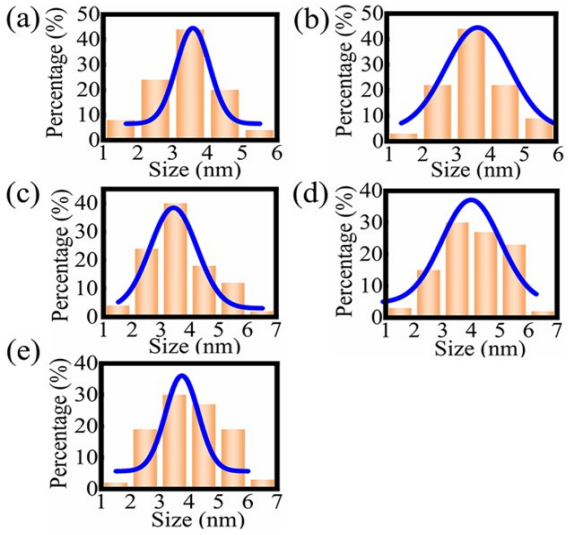

Fig. S1. Size distributions of MoS_2 QDs (a), F-MoS_2 QDs (b), Cl-MoS_2 QDs (c), Br-MoS_2 QDs (d), and I-MoS_2 QDs (e).

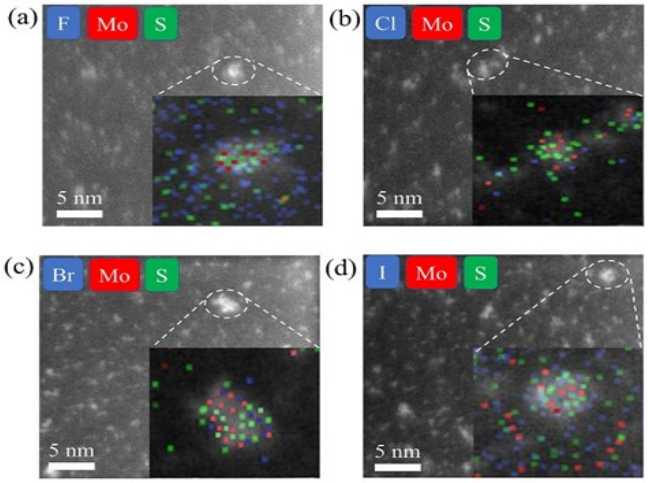

Fig. S2. HRTEM-mapping of F-MoS_2 QDs (a), Cl-MoS_2 QDs (b), Br-MoS_2 QDs (c) and I-MoS_2 QDs (d).

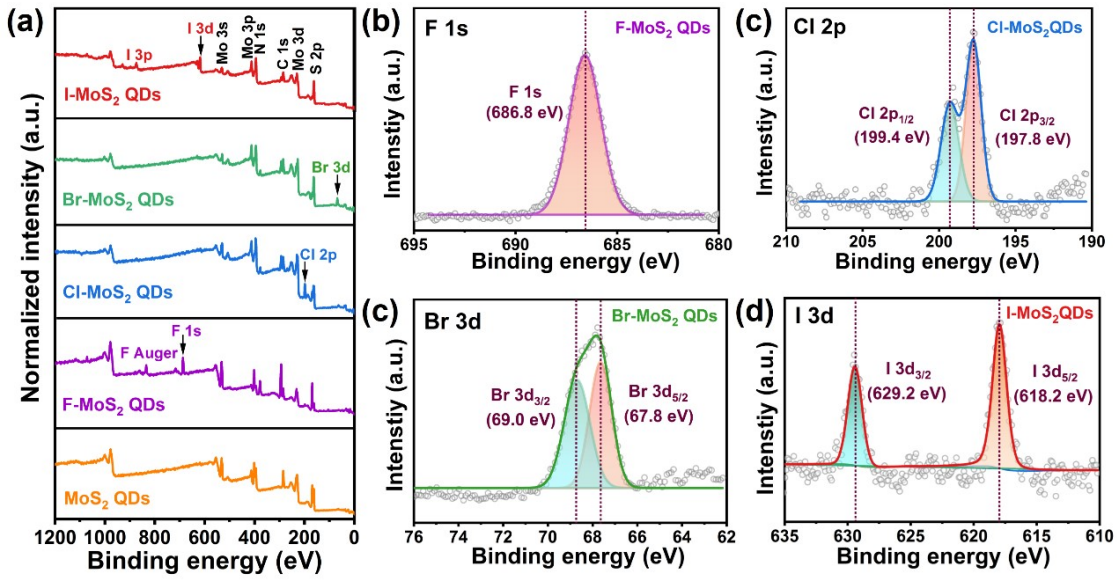

Fig. S3. XPS survey spectra (a) and high-resolution XPS spectra for halogen implanted in MoS_2 QDs with F (b), Cl (c), Br (d), and I (e).

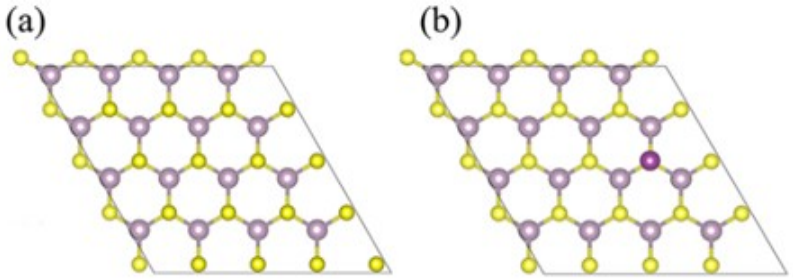

Fig. S4. Optimized geometries for MoS_2 QDs (a) and X-MoS_2 QDs in the top (b) bright yellow spheres denote S element, lavender spheres: Mo element, purple spheres: halogen element. Isosurface of charge-density difference of F-MoS_2 QDs (c), Cl-MoS_2 QDs (d), Br-MoS_2 QDs (e), and I-MoS_2 QDs (f). The khaki and cyan distribution respectively represent electron accumulation and depletion. Isosurface was set as 6×10^{-4} $e^{-1}Å^3$.

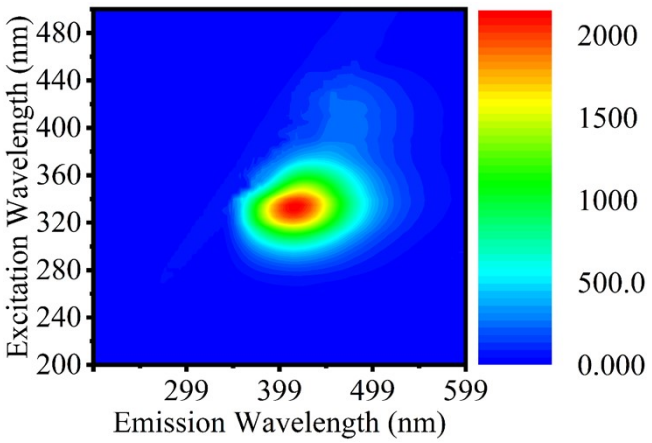

Fig. S5. PLE intensity map of the excitation spectra for MoS_2 QDs.

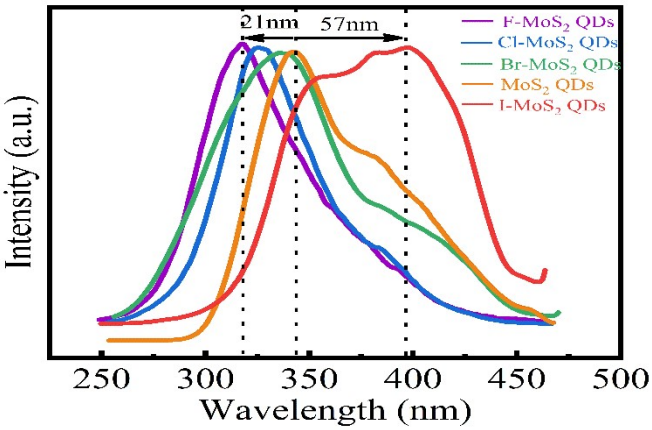

Fig. S6. Photoluminescence excitation spectra (PLE) of all of the MoS_2 QDs samples (from left to right: F-MoS_2 QDs, Cl-MoS_2 QDs, Br-MoS_2 QDs, MoS_2 QDs and I-MoS_2 QDs).

Fig. S7. Digital photos of the MoS_2 QDs under the excitation of 365nm UV lamp. From left to right: F-MoS_2 QDs, Cl-MoS_2 QDs, Br-MoS_2 QDs, MoS_2 QDs, I-MoS_2 QDs.

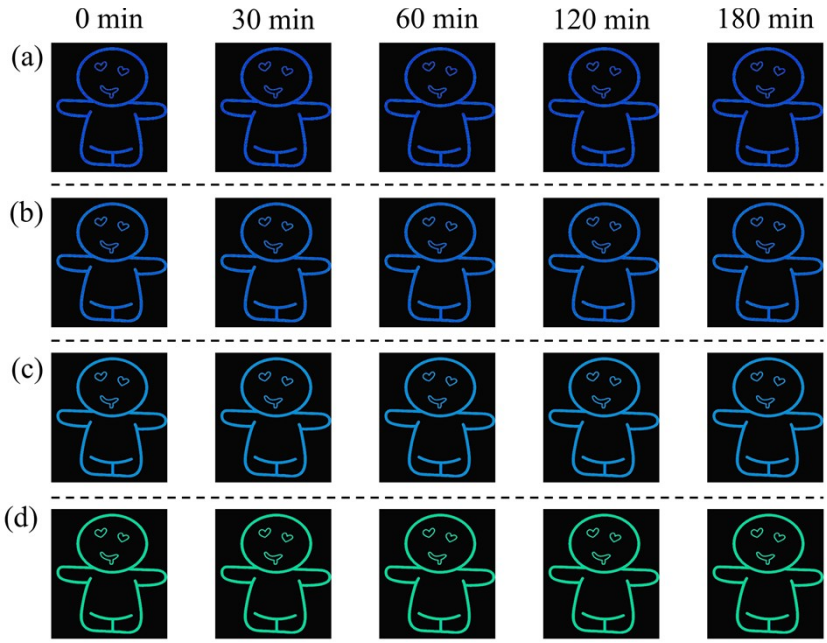

Fig. S8. Printed patterns under the irradiation of 365 nm UV lamp for different time: 0, 30, 60, 120 and 180 min. The 1st - 4th rows of images show respectively the patterns printed by F-MoS_2 QDs (a), Cl-MoS_2 QDs (b), Br-MoS_2 QDs (c) and I-MoS_2 QDs inks.

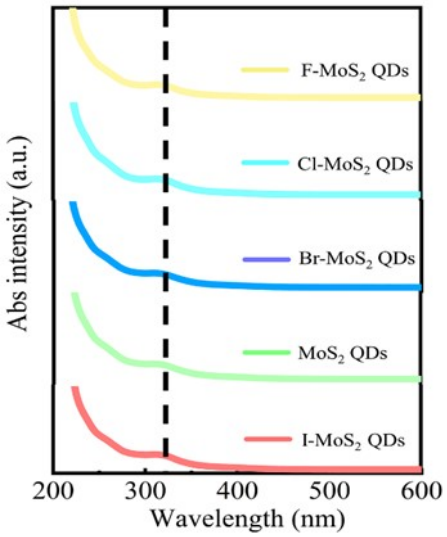

Fig. S9. Absorption spectra of MoS2 QDs and X-MoS2 QDs.

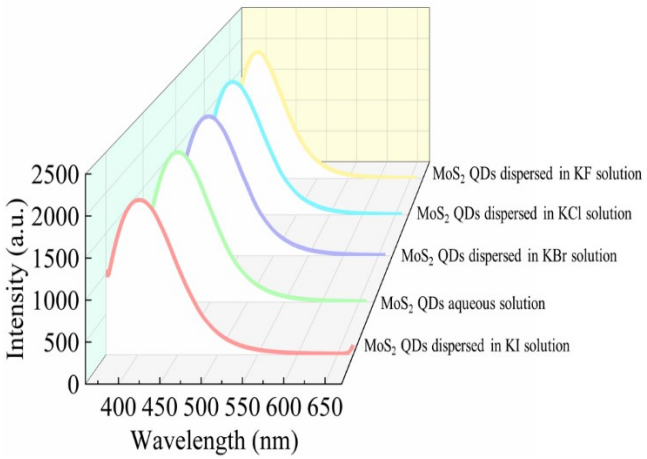

Fig. S10. PL spectra of MoS_2 and MoS_2 QDs dispersed in potassium halides solution at room temperature.

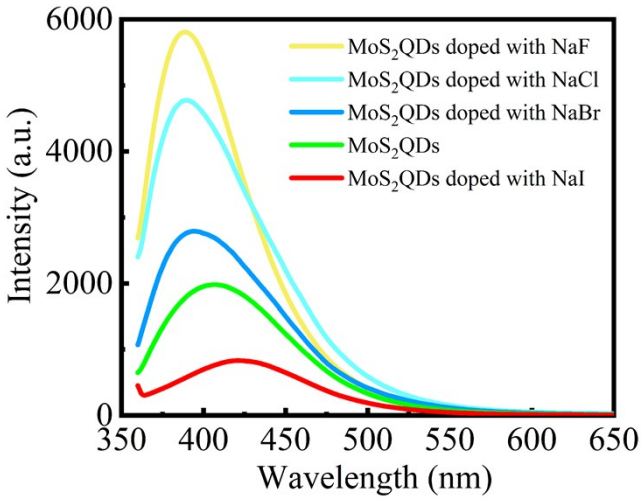

Fig.S11. PL spectra of MoS_2 QDs in-situ doped using sodium halides as dopant

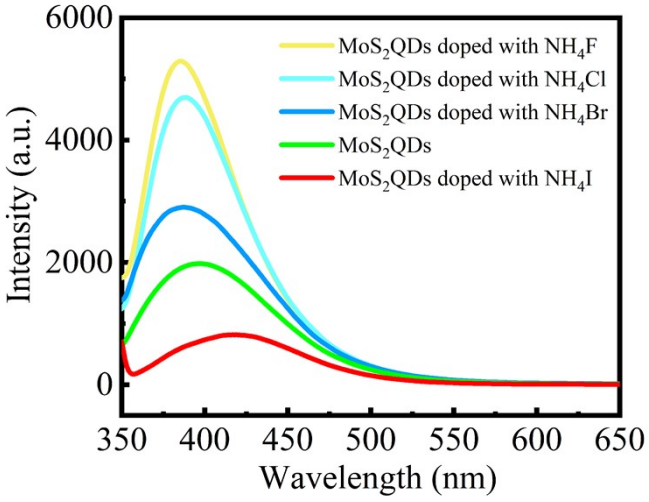

Fig. S12. PL spectra of MoS_2 QDs in-situ doped using different ammonium halide as dopant

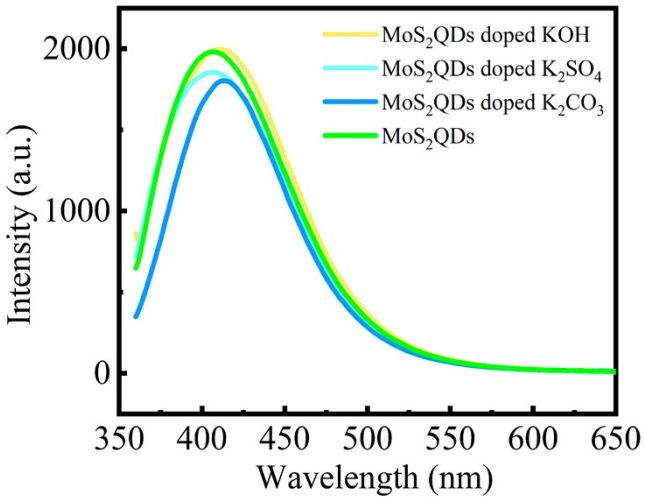

Fig. S13. PL spectra of MoS_2 QDs in-situ doped using different potassium salts as dopant

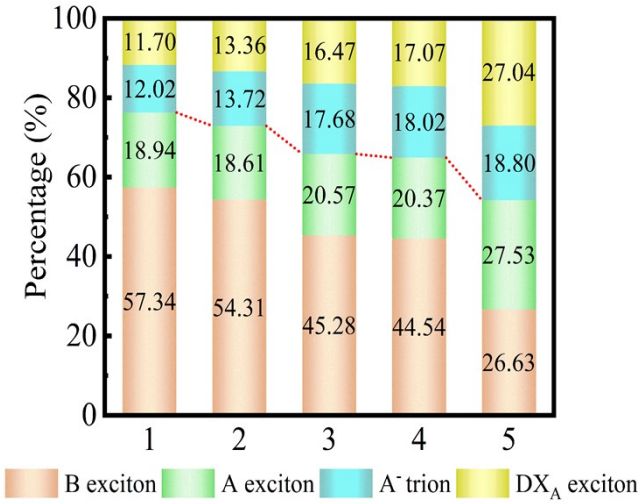

Fig. S14. Weight of B, A exciton, A^- tiron, and DX_A exciton of MoS_2 QDs undoped and dopped with different halogens (1-5 denote F-MoS_2 QDs, Cl-MoS_2 QDs，Br-MoS_2 QDs, MoS_2 QDs，I-MoS_2 QDs, respectively) with the same concentration (25 mM).

2.2 Tables

Table S1. Optical parameters of MoS_2 QDs with and without doping with halogen ions

QDs	Abs (nm)	PL (nm)	FWHM (nm)	PLQY (%)
MoS_2 QDs	322	407	90	6.4 %
F-MoS_2 QDs	321	387	58	36.3 %
Cl-MoS_2 QDs	321	389	62	32.2 %
Br-MoS_2 QDs	323	395	75	20.2%
I-MoS_2 QDs	324	422	98	4.8 %

Table S2. Fitting results of PL spectra of MoS_2 QDs without and with doping different halogen ions

Samples	Exciton type	Peak position (nm)	Area	Spectral weight
F-MoS_2 QDs	B	385.00	49.63	57.34
	A	415.01	16.39	18.94
	A^-	445.00	10.52	12.15
	DX_A	460.01	10.01	11.57
Cl-MoS_2 QDs	B	385.00	41.18	54.31
	A	415.01	14.11	18.61
	A^-	445.00	10.40	13.72
	DX_A	460.00	10.13	13.36
Br-MoS_2 QDs	B	385.03	42.86	45.28

	A	415.33	19.47	20.57
	A^-	445.33	16.74	17.68
	DX_A	460.33	15.59	16.47
	B	385.03	40.98	44.54
MoS_2 QDs	A	415.33	18.74	20.37
	A^-	445.31	16.58	18.02
	DX_A	460.33	15.70	17.07
	B	385.01	25.86	26.63
I-MoS_2 QDs	A	415.03	26.73	27.53
	A^-	445.05	18.25	18.80
	DX_A	460.61	26.26	27.04

Table S3 Lifetime of exciton decay dynamics of MoS_2 QDs and X- MoS_2 QDs

Smaple	τ_1 /ns	A1	τ_2/ns	A2	τ_{ave} /ns
F-MoS_2 QDs	5.90	6361.90	32.72	0.93	5.90
Cl- MoS_2 QDs	6.71	2263.70	38.81	0.68	6.70
Br- MoS_2 QDs	8.00	832.30	56.01	0.18	8.10
MoS_2 QDs	8.21	673.13	64.72	0.14	8.30
I- MoS_2 QDs	9.64	246.80	91.40	0.12	10.00

3. Reference

1 K. F. Mak, K. He, C. Lee, G. H. Lee, J. Hone, T. F. Heinz and J. Shan, *Nat. Mater.,* 2013, **12**, 207–211.

2 K. Greben, S. Arora, M. G. Harats and K. I. Bolotin, *Nano Lett.*, 2020,**20**,2544–2550.