

Supporting Information

Exploring different photocatalytic behaviors of $\text{Cd}_x\text{Zn}_{1-x}\text{Se}_y\text{S}_{1-y}$ gradient alloyed quantum dots via composition regulation

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1. Synthetic Procedures

1.1 Preparation of Cd_{0.14}Zn_{0.86}S blue QDs

(1) Preparation of Zn-oleate and Cd-oleate precursor 1

The Zn-oleate & Cd-oleate precursor solution were prepared by dissolving CdO of 128.4 mg (1 mmol) and Zn(acet)₂ of 1651.3 mg (9 mmol) in 8 mL of OA and 15 mL of ODE. The mixture was placed in a 100 mL three-neck flask and degassed for 90 mins under vacuum at 100 °C.

(2) Preparation of sulfur (S) precursor 1

To prepare the sulfur precursor 1, was dissolved sulfur (S) powder of 51.2 mg (1.6 mmol) in 3 mL ODE. The mixture was stirred at 230 °C for 4 mins and keep the temperature at 80 °C for 5 mins.

(3) Preparation of sulfur (S) precursor 2

The sulfur precursor 2 was prepared by dissolving 384 mg (12 mmol) of S powder in 6 mL TOP. The mixture was stirred at 170°C for 10 mins, and then keep the temperature at 140 °C.

(4) Preparation of Cd-oleate precursor 2

To prepare the Cd-oleate precursor, was dissolved CdO of 77.1 mg (0.6 mmol) in 0.9 mL OA and 8.1 mL ODE, mixing thoroughly. The mixture was degassed at 230°C for 90 mins, and then heated to 450°C untill solution transparent and clear.

(5) Synthesis of Cd_{0.14}Zn_{0.86}S blue QDs

In the inert gas environment, the Zn-oleate and Cd-oleate precursor 1 prepared in the first step was heated to 303°C, and then all the sulfur precursor 1 was quickly injected into the cationic precursor, leading to the rapid nucleation of Cd_xZn_{1-x}S. After 20 min of reaction, 3 mL of the sulfur precursor 2 and 6 mL of the Cd-oleate precursor 2 were added dropwise to the reaction solution with an injection rate of 3 mL/h and 10 mL/h by injection pump, respectively, at the elevated temperature of 300 °C. After 5 min of reaction, 2 mL of OAm was injected into the flask at the temperature of 180 °C for 5 min. When the reaction was finished, the solution was cooled down naturally to room temperature. The obtained QDs were repeatedly dissolved with toluene and anhydrous methanol, precipitated, and then purified by centrifugation three times.

1.2 Preparation of $\text{Cd}_{0.06}\text{Zn}_{0.94}\text{S}_{0.23}\text{Se}_{0.77}$ red QDs

(1) Preparation of Zn-oleate and Cd-oleate precursor

The Zn-oleate & Cd-oleate precursor solution were prepared by dissolving CdO of 102.7 mg (0.8 mmol) and $\text{Zn}(\text{acet})_2$ of 2201.8 mg (12 mmol) in 14 mL of OA and 15 mL of ODE. The mixture was placed in a 100 mL three-neck flask and degassed for 20 mins under vacuum at 100 °C.

(2) Preparation of selenium (Se) precursor 1

To prepare the selenium precursor 1, was dissolved selenium (Se) powder of 142.2 mg (1.8 mmol) in 4 mL TOP. The mixture was stirred at 150 °C for 30 mins and keep the temperature at 140 °C.

(3) Preparation of selenium and sulfur precursor 2

The selenium and sulfur precursor 2 was prepared by dissolving 19.2 mg (0.6 mmol) of S powder and 64.1 mg (0.2 mmol) of Se powder in 2 mL TOP. The mixture was stirred at 170°C and keep the temperature at 170 °C.

(4) Synthesis of $\text{Cd}_{0.06}\text{Zn}_{0.94}\text{S}_{0.23}\text{Se}_{0.77}$ red QDs

In the inert gas environment, the Zn-oleate and Cd-oleate precursor prepared in the first step was heated to 300°C, and then all the selenium precursor 1 was quickly injected into the cationic precursor, leading to the rapid nucleation of $\text{Cd}_x\text{Zn}_{1-x}\text{Se}$. After 10 min of reaction, 2 mL of the selenium and sulfur precursor 2 was added dropwise to the reaction solution with an injection rate of 4 mL/h by injection pump at the elevated temperature of 300 °C. After 30 min of reaction, 2 mL of OAm was injected into the flask at the temperature of 180 °C for 5 min. When the reaction was finished, the remaining purification steps were the same as blue QDs.

1.3 Preparation of $\text{Cd}_{0.05}\text{Zn}_{0.95}\text{S}_{0.5}\text{Se}_{0.5}$ green QDs

(1) Preparation of Zn-oleate and Cd-oleate precursor

The Zn-oleate & Cd-oleate precursor solution were prepared by dissolving CdO of 51.35 mg (0.4 mmol) and $\text{Zn}(\text{acet})_2$ of 1467.9 mg (8 mmol) in 10 mL of OA and 20 mL of ODE. The mixture was placed in a 100 mL three-neck flask and degassed for 30

mins under vacuum at 100 °C.

(2) Preparation of selenium and sulfur precursor **1**

The selenium and sulfur precursor **1** was prepared by dissolving 128 mg (4 mmol) of S powder and 641 mg (2 mmol) of Se powder in 4 mL TOP. The mixture was stirred at 170°C and keep the temperature at 170 °C.

(3) Preparation of sulfur (S) precursor **2**

To prepare the sulfur precursor **2**, was dissolved sulfur (S) powder of 158 mg (2 mmol) in 2 mL TOP. The mixture was stirred at 150 °C for 30 mins and keep the temperature at 140 °C.

(4) Synthesis of Cd_{0.05}Zn_{0.95}S_{0.5}Se_{0.5} green QDs

In the inert gas environment, the Zn-oleate and Cd-oleate precursor prepared in the first step was heated to 300°C, and then the selenium and sulfur precursor **1** was quickly injected into the cationic precursor, leading to the rapid nucleation of Cd_xZn_{1-x}Se_yS_{1-y}. After 15 min of reaction, 2 mL of the sulfur precursor **2** was added dropwise to the reaction solution with an injection rate of 3 mL/h by injection pump at the elevated temperature of 300 °C. After 30 min of reaction, 2 mL of OAm was injected into the flask at the temperature of 180 °C for 5 min. When the reaction was finished, the remaining purification steps were the same as blue QDs.

2. Photoelectrochemical Linear Sweep Voltammetry

In order to test the LSV curves of three QDs, the 20 wt% chitosan (CS) aqueous solution was employed to adhere the MPA capped Cd_xZn_{1-x}Se_yS_{1-y} gradient alloyed QDs on the FTO, which is served as photoelectrode. The electrolyte was 0.1 M AA solution, and the Pt plate and Ag/AgCl electrode were set as the counter electrode and reference electrode. The LSV curves were obtained under the visible light with a 300 W Xe lamp equipped by an AM 1.5G filter (Perfectlight, China), the power density of the light was measured to be 100 mW/cm². The potential range was set between -0.1 V to 0.1 V, and the scanning rate was 0.01 V/s.

3. Figures

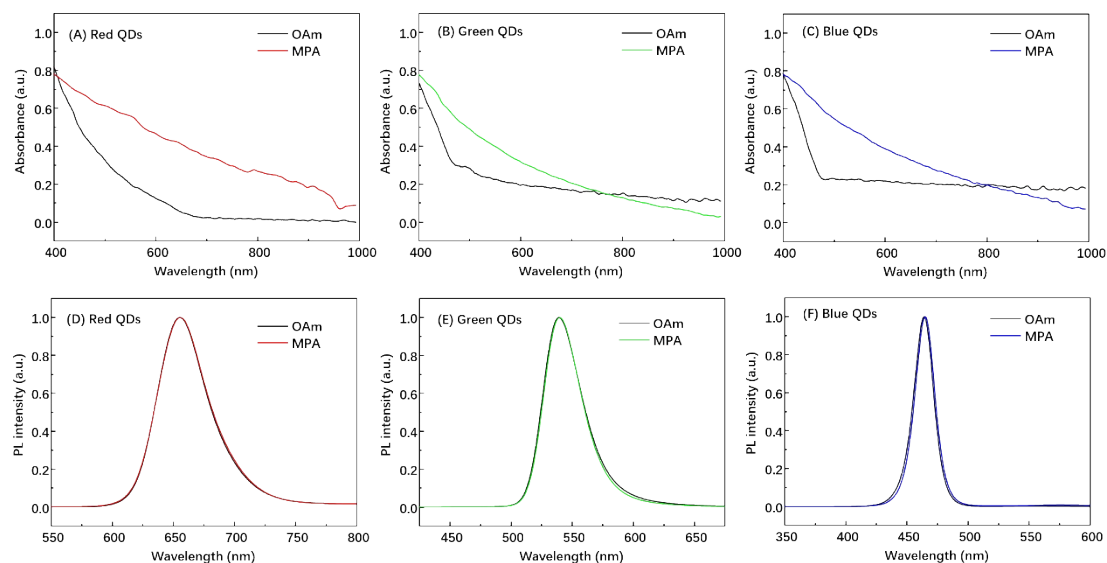


Fig. S1. The UV-Vis absorption and fluorescence spectra of the OAm and MPA capped QDs.

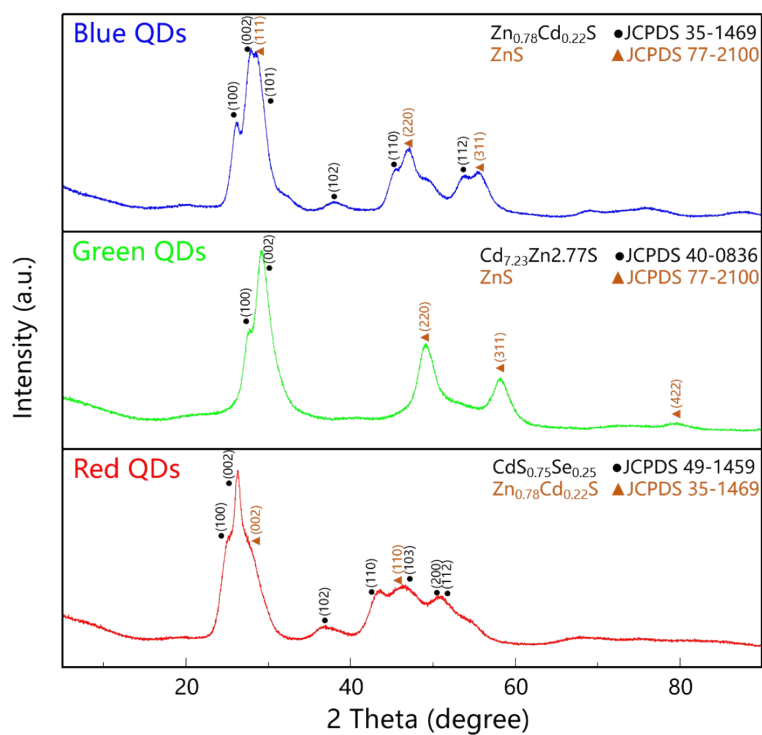


Fig. S2. XRD pattern of the blue, green and red QDs.

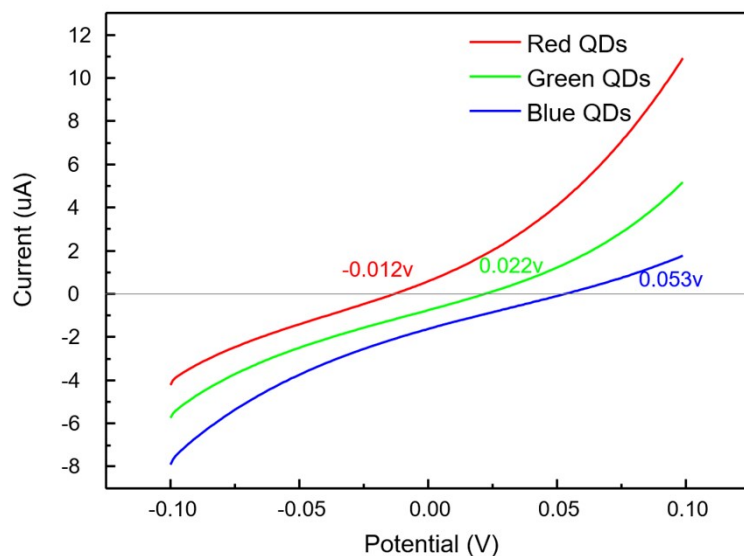


Fig. S3. Photoelectrochemical linear sweep voltammograms of the blue, red and green QDs under irradiation of visible light. The potential range was set between -0.1 V to 0.1 V (vs. Ag/AgCl), and the scanning rate was 0.01 V/s.

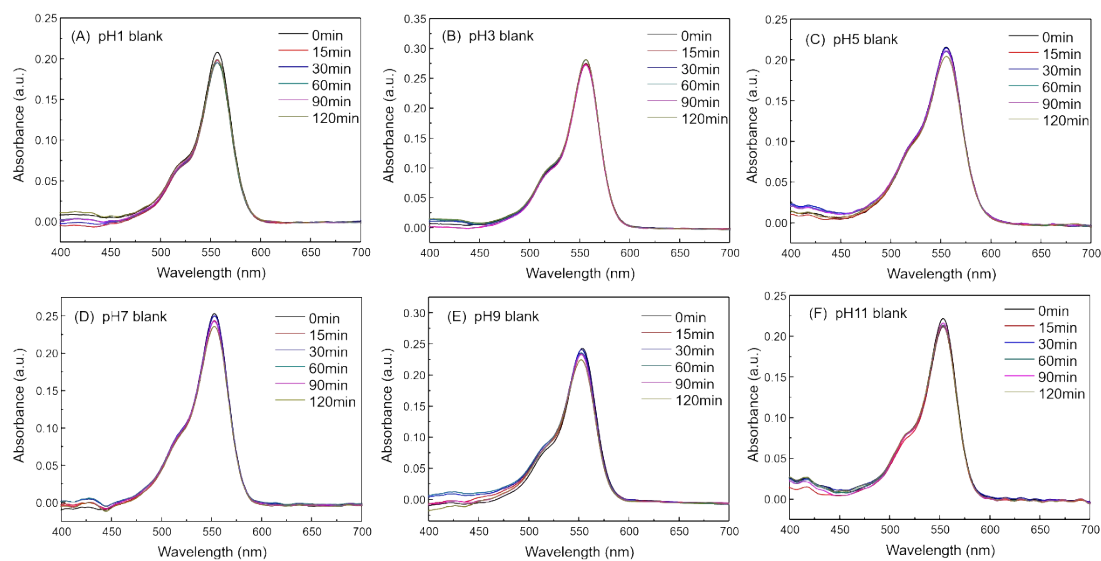


Fig. S4. Time dependent steady-state UV-vis absorption spectra of 20 mg/L RhB in 30 mL aqueous solution without QDs at different pHs upon irradiation of visible light.

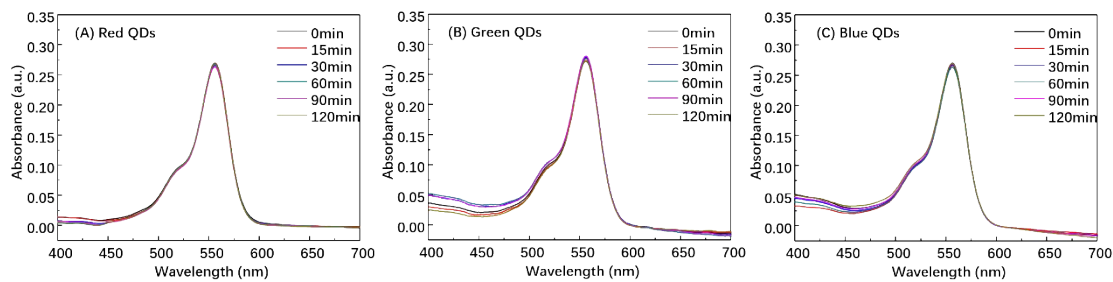


Fig. S5. Time dependent steady-state UV-vis absorption spectra of 3 mg red (A), green (B) and blue QDs (C) in 30 mL aqueous solution of 20 mg/L RhB in dark at pH=3.

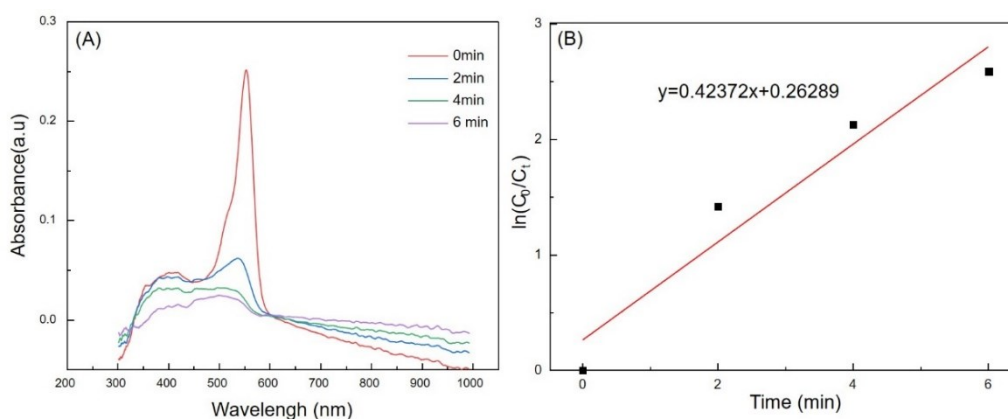


Fig. S6. (A) Time dependent steady-state UV-vis absorption spectra of 3 mg blue QDs in 30 mL aqueous solution of 20 mg/L RhB upon irradiation of visible light (pH=3). (B) The linear fitting result obtained by plotting $\ln(C_0/C_t)$ vs. time.

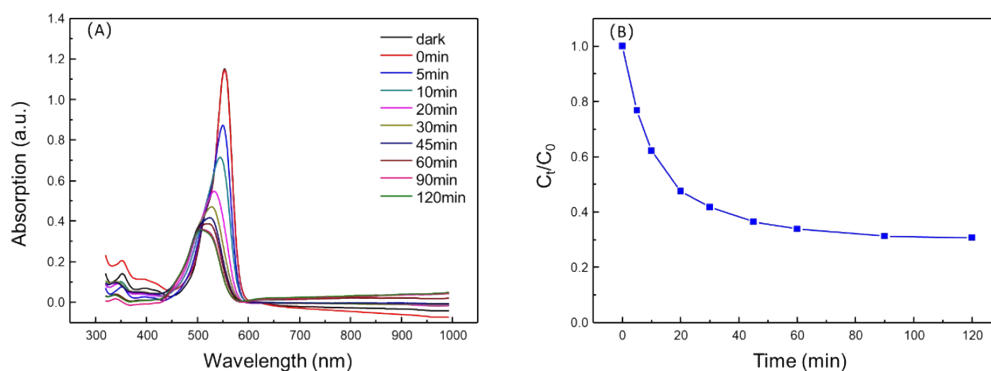


Fig. S7. (A) Time dependent steady-state UV-vis absorption spectra of 3 mg blue QDs in 30 mL aqueous solution of 120 mg/L RhB upon irradiation of visible light. (B) The Degradation ratio over time of it.

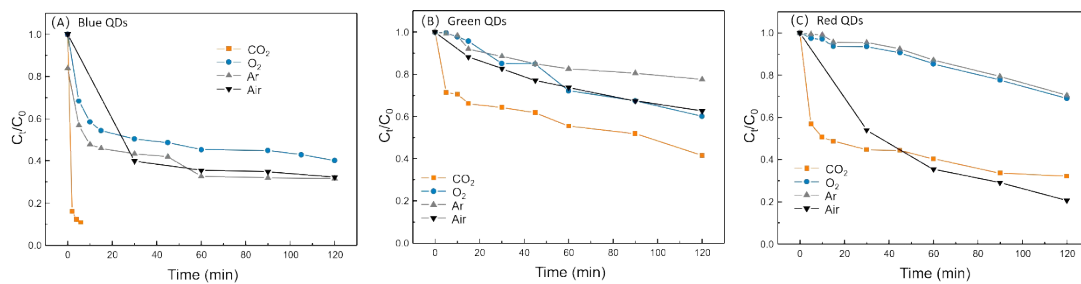


Fig. S8. Effect of different atmospheres on RhB degradation by blue (A), green (B) and red QDs (C).

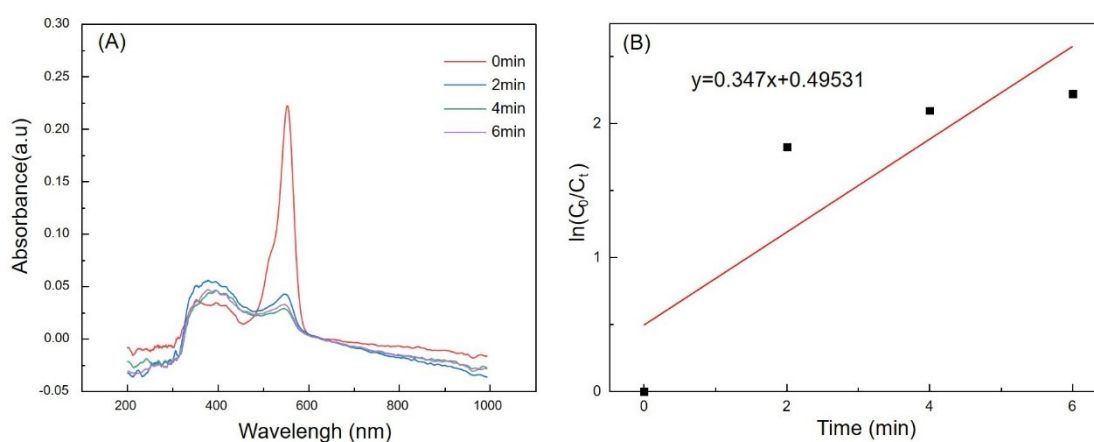


Fig. S9. (A) Time dependent steady-state UV-vis absorption spectra of 3 mg blue QDs in 30 mL aqueous solution of 20 mg/L RhB upon irradiation of visible light in the CO_2 atmosphere. (B) The linear fitting result obtained by plotting $\ln(C_0/C_t)$ vs. time.

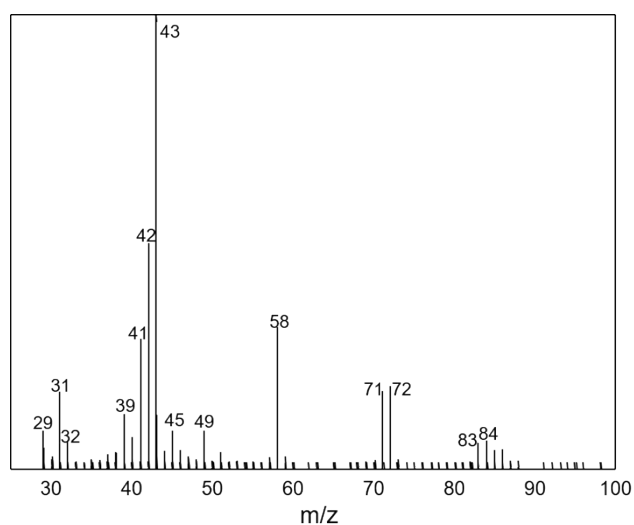


Fig. S10. The total ion current spectrum of GC-MS obtained from the photodegradation

products of 3 mg blue QDs in 30 mL aqueous solution containing 20 mg/L RhB upon irradiation of visible light in the CO₂ atmosphere. The formation of methanol, ethanol and acetone in the reaction, corresponding to the reduction product of CO₂, was identified by selecting m/z 31, 45 and 58 respectively.

Table S1 Quantitative results of EDS for blue QDs

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
S K	29.07	48.69	3494.18	4.48	0.2255016	1.1486	0.6706	1.0071
Cd L	19.32	9.23	958.52	2.71	0.1471497	0.8627	0.8823	1.0004
Zn K	49.29	40.50	1507.78	2.21	0.4812554	0.9683	0.9859	1.0228

Table S2 Quantitative results of EDS for green QDs

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
S K	19.66	34.99	2600.20	5.34	0.1349573	1.1662	0.5864	1.0040
Cd L	4.77	2.42	293.25	4.34	0.03618977	0.8759	0.8662	1.0006
Zn K	52.94	46.23	2090.07	2.15	0.5367671	0.9835	0.9933	1.0379
Se K	22.63	16.36	271.94	4.45	0.2031107	0.8987	0.9736	1.0257

Table S3 Quantitative results of EDS for red QDs

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
S K	8.50	18.14	1106.71	5.95	0.05682767	1.2204	0.5447	1.0061
Cd L	15.53	9.46	1019.35	2.79	0.124392	0.9173	0.8728	1.0004
Zn K	36.14	37.86	1551.09	2.45	0.3943276	1.0361	0.9864	1.0675
Se K	39.83	34.54	514.65	3.53	0.3804829	0.9517	0.9785	1.0258