

Supporting Information

Chemical etching with tetrafluoroborate: a facile method for resizing of CdTe nanocrystals under mild conditions

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1 Experimental Procedures

Materials

Sodium tetrafluoroborate (NaBF_4 , $\geq 98.0\%$) and cysteamine (95%) were purchased from Sigma-Aldrich. Aluminum telluride (Al_2Te_3 , 99.5%) was purchased from CERAC Inc.. Cadmium perchlorate hexahydrates ($\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, 99%) and Rhodamin 6G were purchased from Acros Organics. Unless otherwise noted, all reagent-grade chemicals were used as received, and Millipore water ($18.2 \text{ M}\Omega \cdot \text{cm}$) was used in the preparation of all aqueous solutions.

Preparation of CdTe nanocrystals

CdTe nanocrystals stabilized by cysteamine were prepared in water, as described previously.¹ In a typical synthesis, 2.35 mmol $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ is dissolved in 125 mL of degassed water, and 5.7 mmol cysteamine is added. Under stirring, H_2Te gas (generated by the reaction of 0.46 mmol Al_2Te_3 lumps with 15-20 mL of 0.5 M H_2SO_4) is passed through the solution together with a slow nitrogen flow for ~ 20 min. CdTe precursors are formed at this stage which is accompanied by a change of the solution color from colorless to dark red. After refluxed at 100°C about 30 h or 45 h, CdTe nanocrystals with fluorescence peak at 588 nm or 618 nm could be obtained respectively. The mole concentration of CdTe nanocrystals was determined as a procedure reported by Peng et al.²

Chemical etching and purification of nanocrystals

The chemical etching of CdTe nanocrystals was performed in air under neutral condition. A solution of NaBF₄ was directed added into CdTe nanocrystals at room temperature. The final concentrations of CdTe nanocrystals and NaBF₄ were $\sim 10^{-6}$ M and 0.4 M, respectively. The mixture was kept in the dark. After etching for a period, the mixture can be added with identical volume of isopropanol and CdTe nanocrystals with desired size could be isolated by centrifugation at 6869 g for 10 min.

Characterization

UV/Vis absorption and fluorescence spectra were recorded on a Shimadzu UV-Vis 1601 spectrophotometer and a Hitachi FL 2500 fluorescence spectrophotometer, respectively. The absorption spectra were obtained by scanning the wavelength at intervals of 0.5 nm in the range of 300-800 nm. The fluorescence spectra were obtained by wavelength scan in the range of 430-700 nm at an excitation wavelength of 400 nm. The excitation and emission slit widths were set at 2.5 nm and 5.0 nm, respectively. PMT voltage was set at 700V. The room-temperature fluorescence quantum yields (QY) of nanocrystals were calculated by comparing the integrated emission area to that of Rhodamine 6G in methanol assuming its fluorescence QY as 95%.

Cd(II) concentration was measured with potentiometric stripping voltammetry on an electrochemical workstation (Model CHI-660, Shanghai Chenhua Apparatus Company, China). Working electrode is a form of thin mercury film on glassy carbon. A calomel electrode and a platinum wire were used as the reference and counter electrode, respectively. Electro deposition potential and deposition time were -1.2 V and 120 s, respectively. After a 20 s rest period (without stirring), stripping was performed by scanning the potential from -1.2 to -0.3 V.

High resolution transmission electron microscopy (HRTEM) was performed on a JEOL-JEM 3010 microscope operating at an accelerating voltage of 300 kV. The size distribution histograms were obtained by measuring a large number of individual CdTe nanocrystals on enlarged photographs.

XPS measurements were performed for analyzing the surface chemical bonding in the nanocrystals. Samples of CdTe nanocrystals were isolated by centrifugation and then dehydrated by vacuum freeze-drying. XPS were performed on a XSAM800 X-ray Photoelectron Spectrometer (Kratos Ltd, UK) with Mg K α (1253.6eV) as excitation source. The average resolution for the experiment was 0.9 eV. The spectrum fitting was performed using XPS Peak Fitting Software.

The Cd/ Te ratios of nanocrystals were determined by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, Thermo Scientific, IRIS Advantage1000). Prior to analysis, the CdTe nanocrystals were isolated by centrifugation and then dissolved in 15% HNO₃ solution.

2 Experimental Results

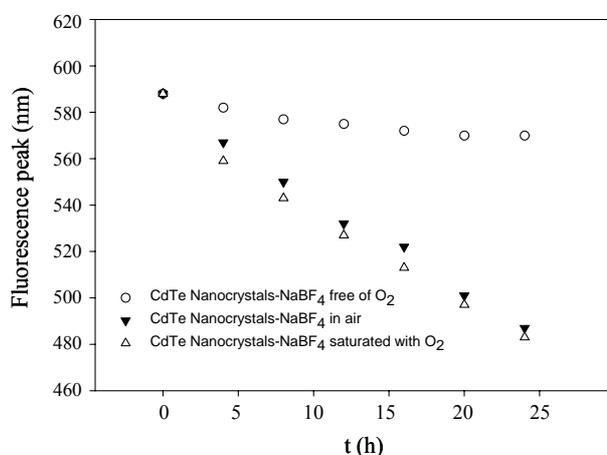


Figure S1. The effect of oxygen on the blue shift rate of fluorescence peaks of CdTe nanocrystals with the initial fluorescence peak at 588 nm. The etching was performed at room temperature under neutral condition. The concentrations of CdTe nanocrystals and NaBF₄ were $\sim 10^{-6}$ M and 0.4 M, respectively.

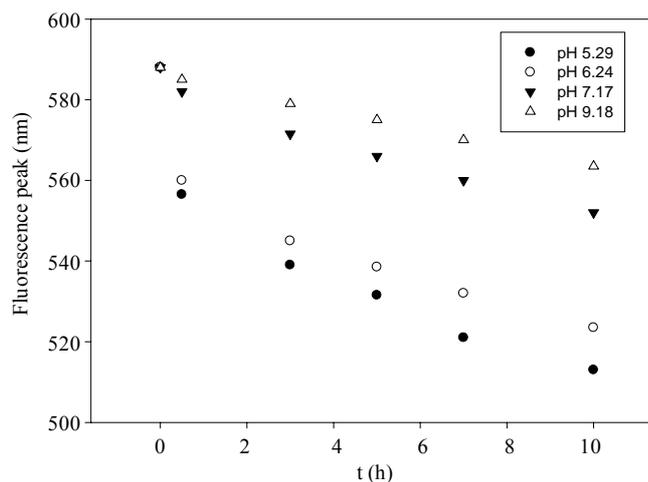


Figure S2. The effect of pH on the blue shift rate of fluorescence peaks of CdTe nanocrystals. The initial fluorescence peak of nanocrystals was 588 nm. The concentrations of CdTe nanocrystals and NaBF₄ were $\sim 10^{-6}$ M and 0.4 M, respectively.

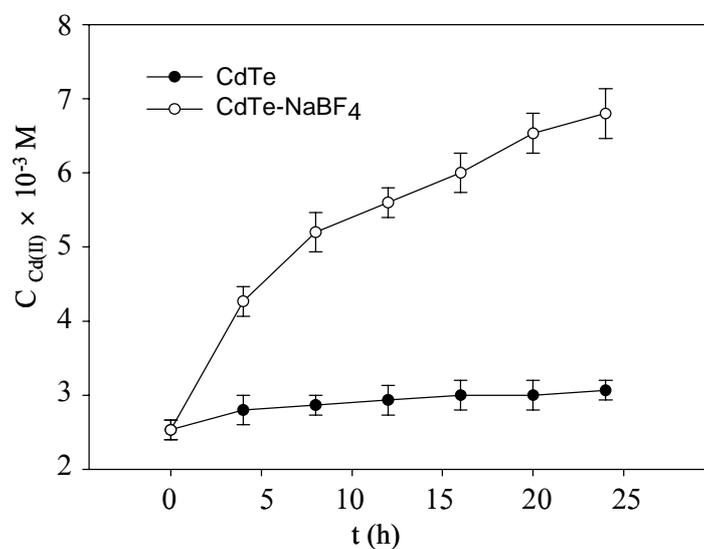


Figure S3. Evolution of Cd(II) concentration in CdTe nanocrystals solution without (filled circle) and with (hollow circle) tetrafluoroborate. Cd(II) was determined by potentiometric stripping voltammetry. Experimental conditions: $E_d = -1.2$ V, $t_d = 240$ s.

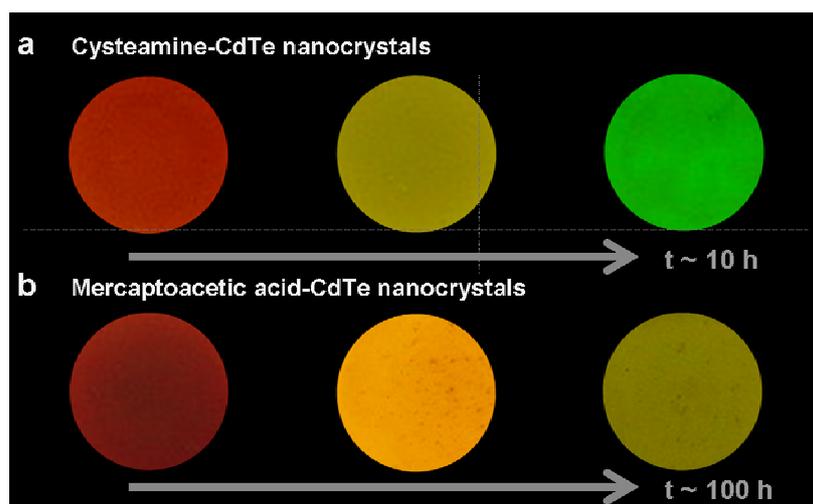


Figure S4. Evolution of cysteamine-CdTe (a) and mercaptoacetic acid-CdTe (b) nanocrystals solution added with 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid at room temperature in air. The CdTe nanocrystals were illuminated at 365 nm with a UV lamp.

According to Ref. 3 and 4, F1s component S1 (686.8 eV) was originated from F in NaBF₄ (Figure S4a). As shown in Figure S4b, component S2 (684.2 eV) for CdTe nanocrystals etched with NaBF₄ in air has a chemical shift of 2.6 eV with respect to component S1, which was attributed to Cd-F bonds on the surface of nanocrystals.

According to Ref. 3 and 4, Te3d component S3 (572.4 eV) was originated from Te in CdTe (Figure S4c). As shown in Figure S4d, component S4 (575.9 eV) for CdTe nanocrystals etched with NaBF₄ in air has a chemical shift of 3.5 eV with respect to component S3, which was attributed to Te-O bonds on the surface of nanocrystals.

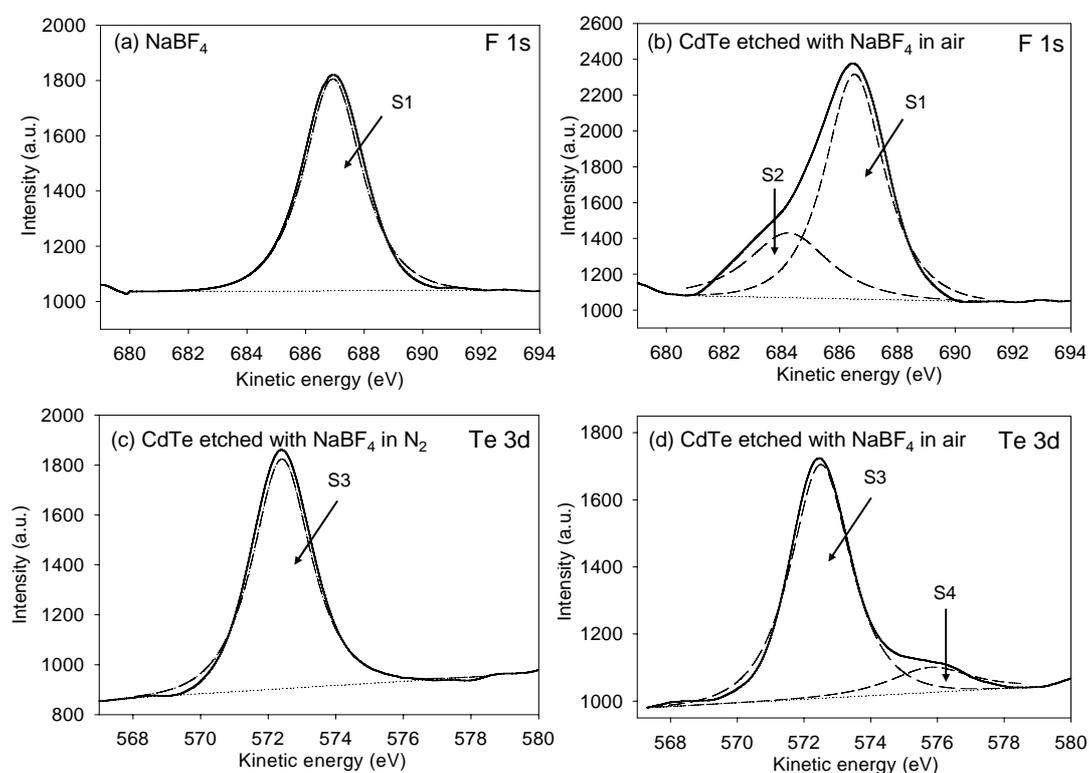


Figure S5. F1s photoelectron spectra of NaBF₄ (a) and CdTe nanocrystals after etching with NaBF₄ in air (b), Te3d photoelectron spectra of CdTe nanocrystals after etching with NaBF₄ in nitrogen (c) and in air (d). Curving fitting (dotted lines) was performed using XPS Peak Fitting Software. The spectra were fitted with Voigt functions with a combined polynomial and Shirley-type background. The chemical etching was performed for 12 h at room temperature under neutral condition. The concentrations of CdTe nanocrystals and NaBF₄ were $\sim 10^{-6}$ M and 0.4 M, respectively.

Table S1. The effect of various anion ions on the fluorescence peaks of CdTe nanocrystals^a

ions	$\Delta\lambda$ (nm)		ions	$\Delta\lambda$ (nm)	
	4 h	24 h		4 h	24 h
BF ₄ ⁻	-32	-110	HPO ₄ ²⁻	2	5
F ⁻	-12	-12	citrate	2	-4
Cl ⁻	0	1	HCO ₃ ⁻	2	3
I ⁻	5	8	B ₄ O ₇ ²⁻	1	2
oxalate	-4	-8	EDTA	quenched	
acetate	-9	-10	HS-	quenched	

^a EDTA: ethylene diamine tetra acetic acid; $\Delta\lambda$ defined the shift of fluorescence peak. The “quenched” means that no fluorescence signal was detected. All the anion ion solutions were prepared from their sodium salts. The concentrations of the salts were set 0.4 M, except that oxalate, B₄O₇²⁻, and EDTA were 0.3 M, 0.04 M and 0.02 M, respectively. All the solution was adjusted to neutral.

Table S2. Atomic contents of purified nanocrystals obtained after different etching times^a

Etching time/ h	Cd (mM)	Te (mM)	Cd/ Te
0	15.41	11.97	1.29
8	11.30	8.78	1.29
16	11.22	8.59	1.31
24	9.48	7.19	1.32

^a The concentrations of CdTe nanocrystals and NaBF₄ were $\sim 10^{-6}$ M and 0.4 M, respectively. Samples of CdTe nanocrystals were isolated by centrifugation and then dissolved in 15% HNO₃.

References

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- 3 J. F. Moulder, W. F. Stickle, P. E. Sobol and K. D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy*, Perkin- Elmer Corp., Eden Prairie, MN, USA, 1992.
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