Supporting Information

Surface Passivation Enabled-Structural Engineering of I-III-VI_2 Nanocrystal Photocatalyst

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Table S1. The elemental composition of the samples obtained from In^{3+}-for-Cu^{+} cation exchange in Cu_7S_4 NCs under different reaction conditions. Determined by EDS analysis except otherwise specified.

Sample	Cu (atomic %)	In (atomic %)	S (atomic %)	Cu : In : S (molar ratio)
Pristine NCs[a]	63.6	0	36.4	3.49:///:2.00
In:Cu = 4:1	63.21	0	36.78	3.44:///:2.00
In:Cu = 2:1	23.23	27.02	48.25	0.96:1.12:2.00
In:Cu = 1:1	26.67	25.26	48.06	1.11:1.05:2.00
In:Cu = 0.5:1	36.43	19.47	44.10	1.65:0.88:2.00
In:Cu = 0.5:1[b]	27.46	24.04	48.49	1.13:0.99:2.00
In:Cu = 2:1, 0 min, 1 mL of 1-DDT	52.85	7.25	39.90	2.65:0.36:2.00
In:Cu = 2:1, 0 min, 1 mL of t-DDT	26.75	24.98	48.27	1.11:1.04:2.00
In:Cu = 1:1, 5 min, 50 μL of 1-DDT	26.10	25.54	48.36	1.08:1.06:2.00

a. The data are cited from our previous publication (ACS Appl. Mater. Interfaces 2019, 11, 27170).
b. The data were obtained by XPS elemental analysis.

Table S2. The elemental composition of the samples obtained from In^{3+}-for-Cu^{+} cation exchange in Cu_7S_4 or Cu_2S NCs (with In^{3+} to Cu^{+} ratio controlled at 2:1) under different reaction times. Determined by EDS analysis.

Sample	Cu (atomic %)	In (atomic %)	S (atomic %)	Cu : In : S (molar ratio)
Cu_2S 30min	55.58	2.99	41.43	2.68:0.14:2.00
Cu_7S_4 30min	54.09	3.53	42.37	2.55:0.17:2.00
Cu_2S 90min	38.16	19.17	42.66	1.79:0.90:2.00
Cu_7S_4 90min	27.57	22.73	49.69	1.11:0.91:2.00

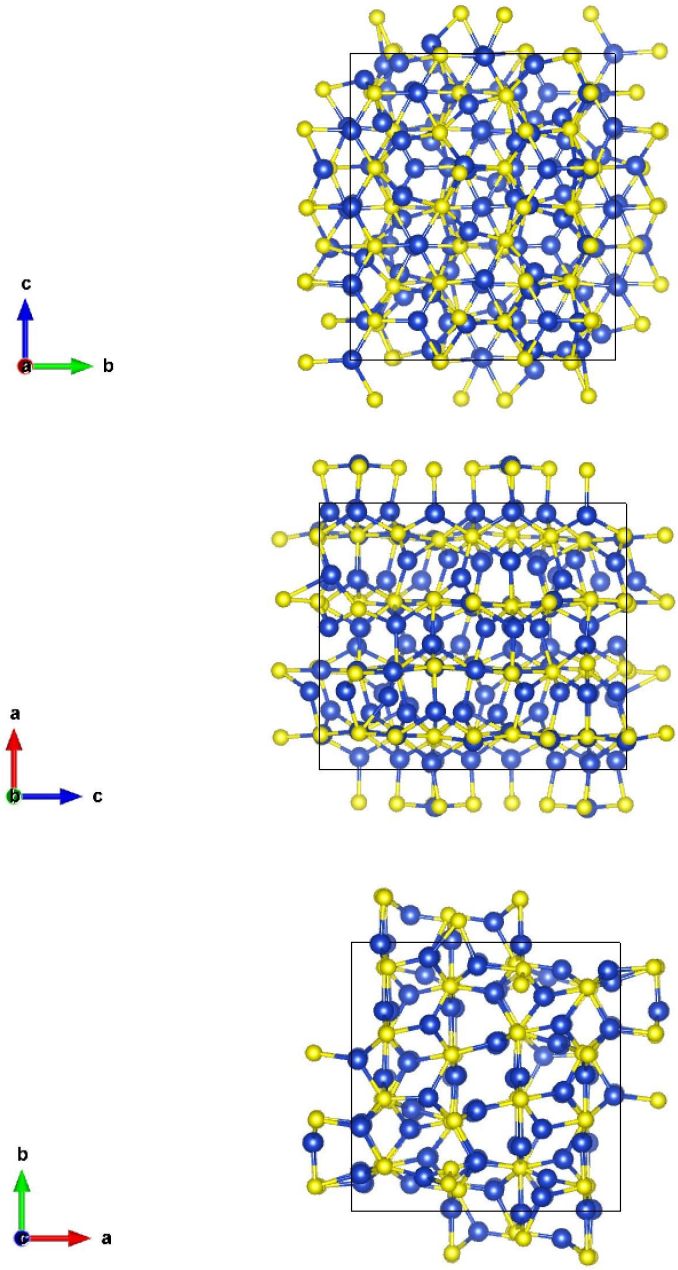

Figure S1. Schematic representation of the crystal structure of Cu_7S_4 viewed along the *a*-axis, *b*-axis and *c*-axis, respectively. Drawn by VESTA.

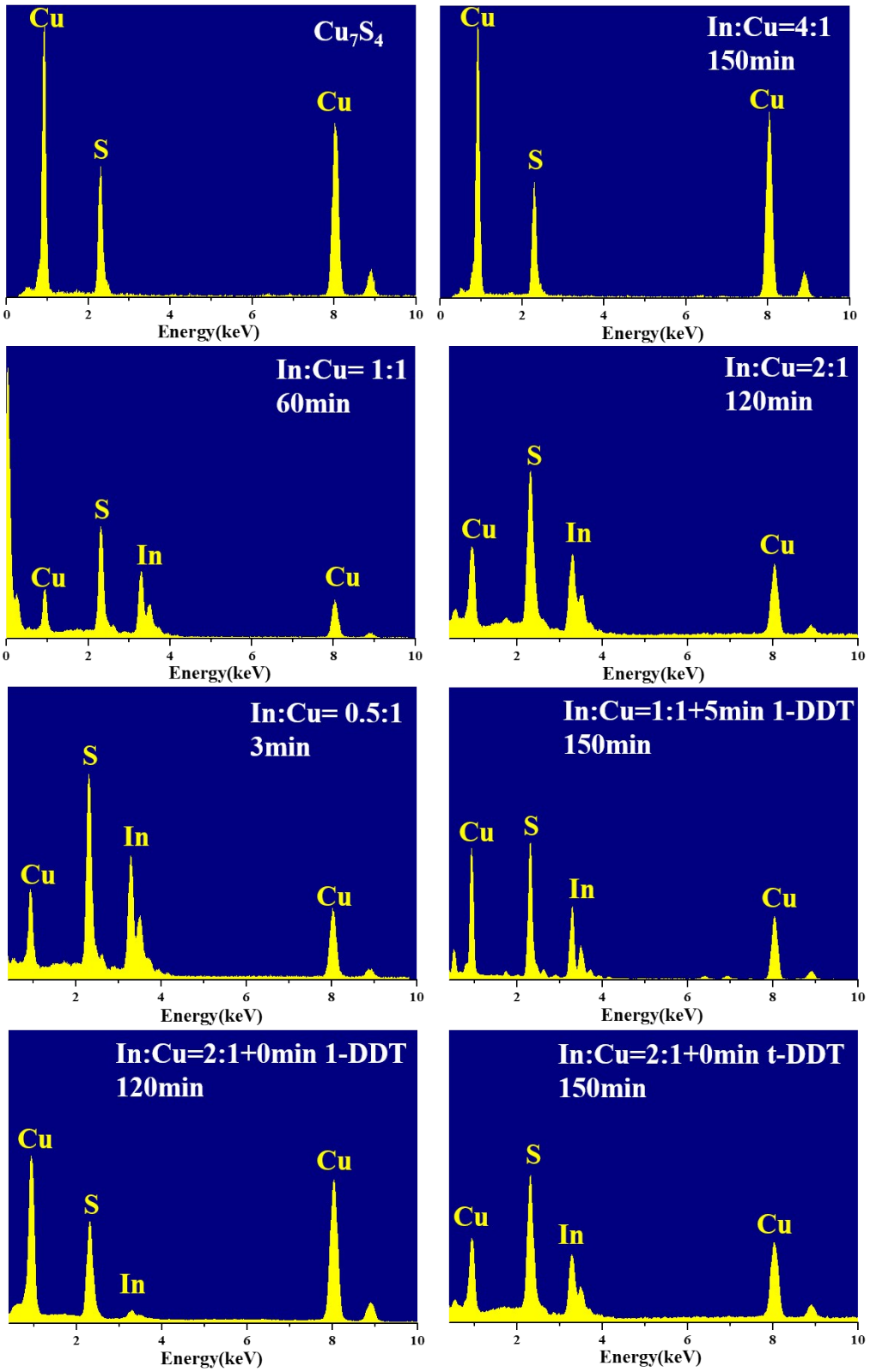

Figure S2. The EDS spectra of the pristine Cu_7S_4 NCs and the products derived from In^{3+}-for-Cu^{+} cation exchange in Cu_7S_4 NCs under different reaction conditions. The spectra were collected over a transmission electron microscope (FEI Tecnai G2 F20 S-Twin, an acceleration voltage of 200kV) equipped with an X-ray energy-dispersive spectroscopy detector.

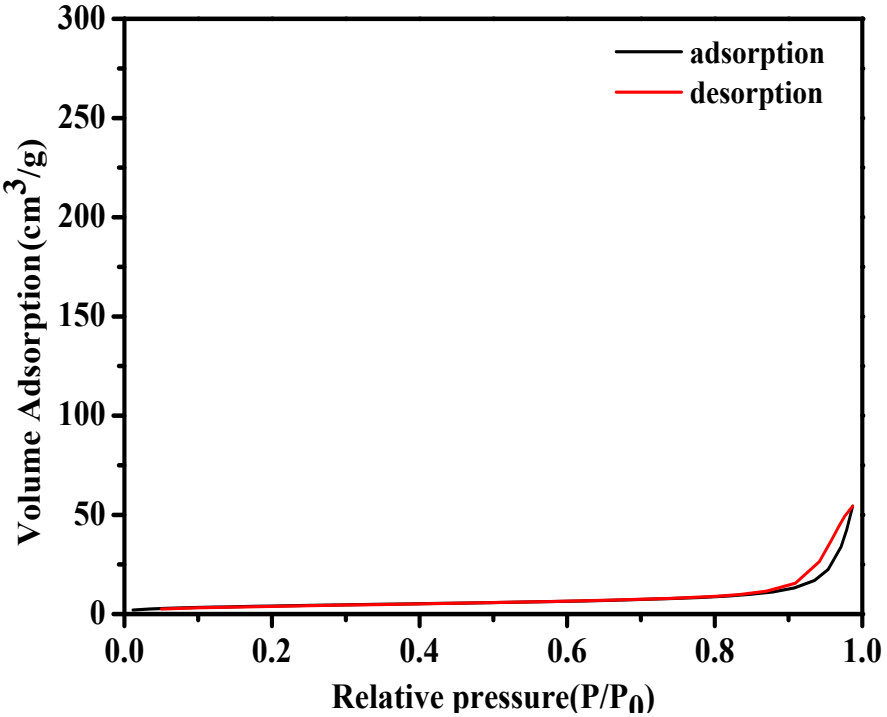

Figure S3. The N_2 absorption-desorption isotherms of pristine Cu_7S_4 NCs.

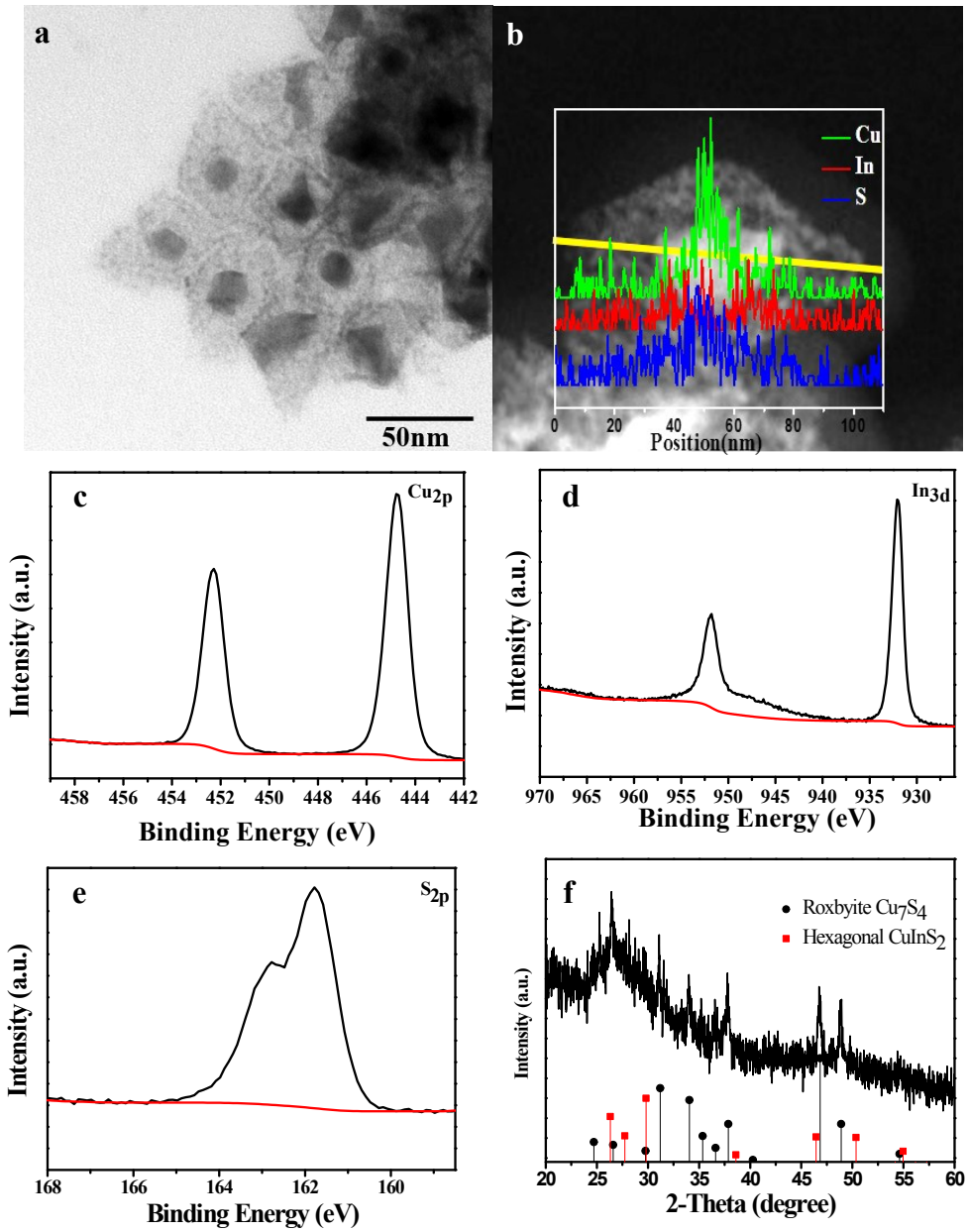

Figure S4. (a) The TEM image, (b) HAADF-STEM image (inset: the corresponding EDS line-scan profiles), (c-e) XPS spectra and (f) XRD pattern of the product derived from In^{3+}-for-Cu^{+} cation exchange in Cu_7S_4 NCs with the In^{3+} to Cu^{+} ratio controlled at 0.5:1.

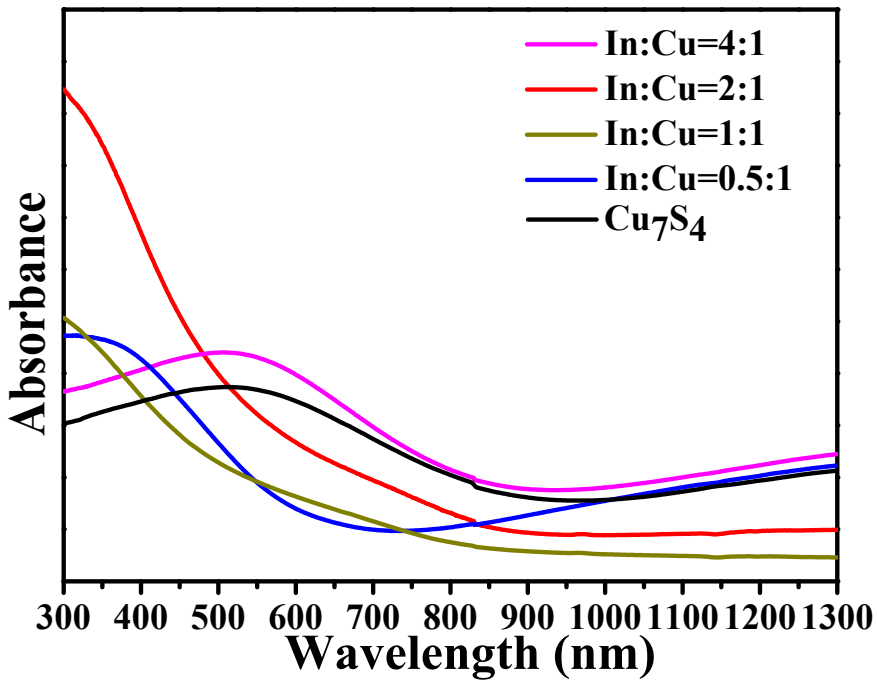

Figure S5. The UV-vis-NIR absorption spectra of Cu_7S_4 NCs and the products derived from In^{3+}-for-Cu^{+} cation exchange in Cu_7S_4 NCs under different reaction conditions.

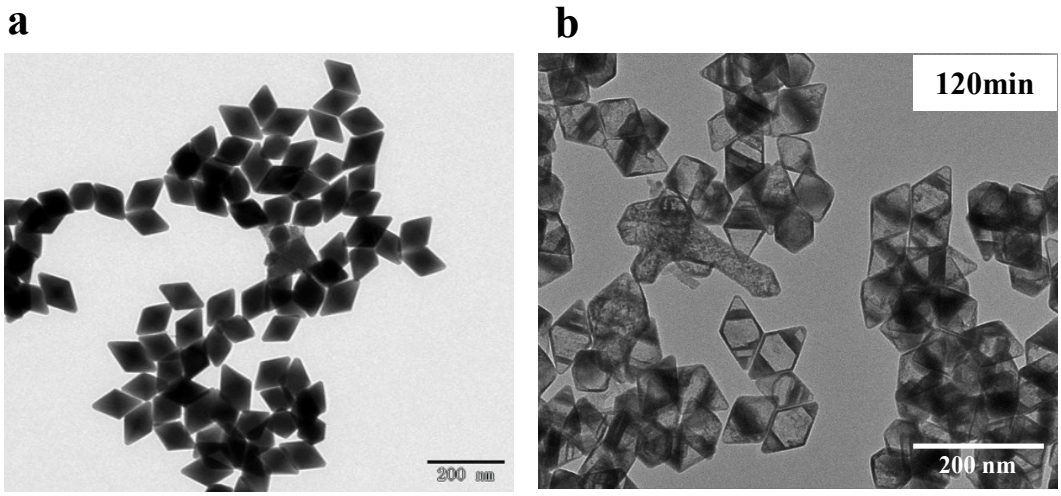

Figure S6. The TEM images of (a) pristine Cu_2S NCs and (b) the product (120 min) derived from In^{3+}-for-Cu^{+} cation exchange in Cu_2S NCs with the In^{3+} to Cu^{+} ratio controlled at 2:1.

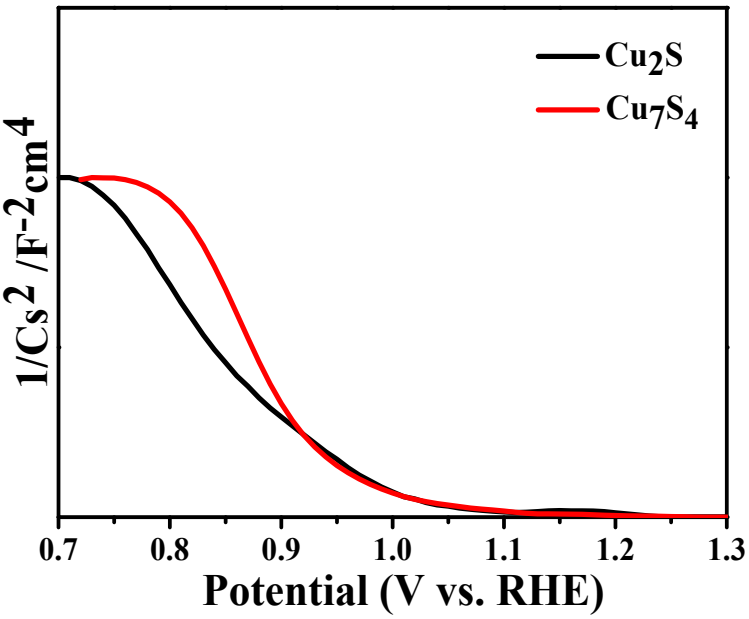

Figure S7. The Mott-Schottky curves of Cu_7S_4 and Cu_2S NCs.

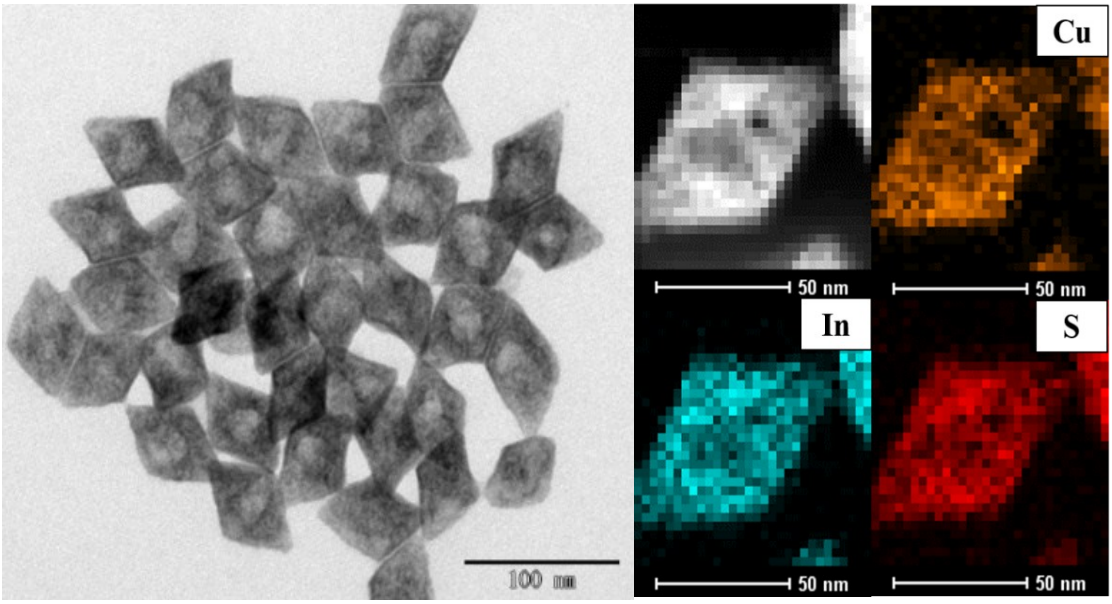

Figure S8. The TEM image, HAADF-STEM image and the corresponding STEM-EDS elemental maps for the product derived from In^{3+}-for-Cu^{+} cation exchange in Cu_7S_4 NCs under the condition where the In^{3+} to Cu^{+} ratio was controlled at 1:1 with the addition of 50 μL of 1-DDT into the system 5 min after initiation of the reaction.

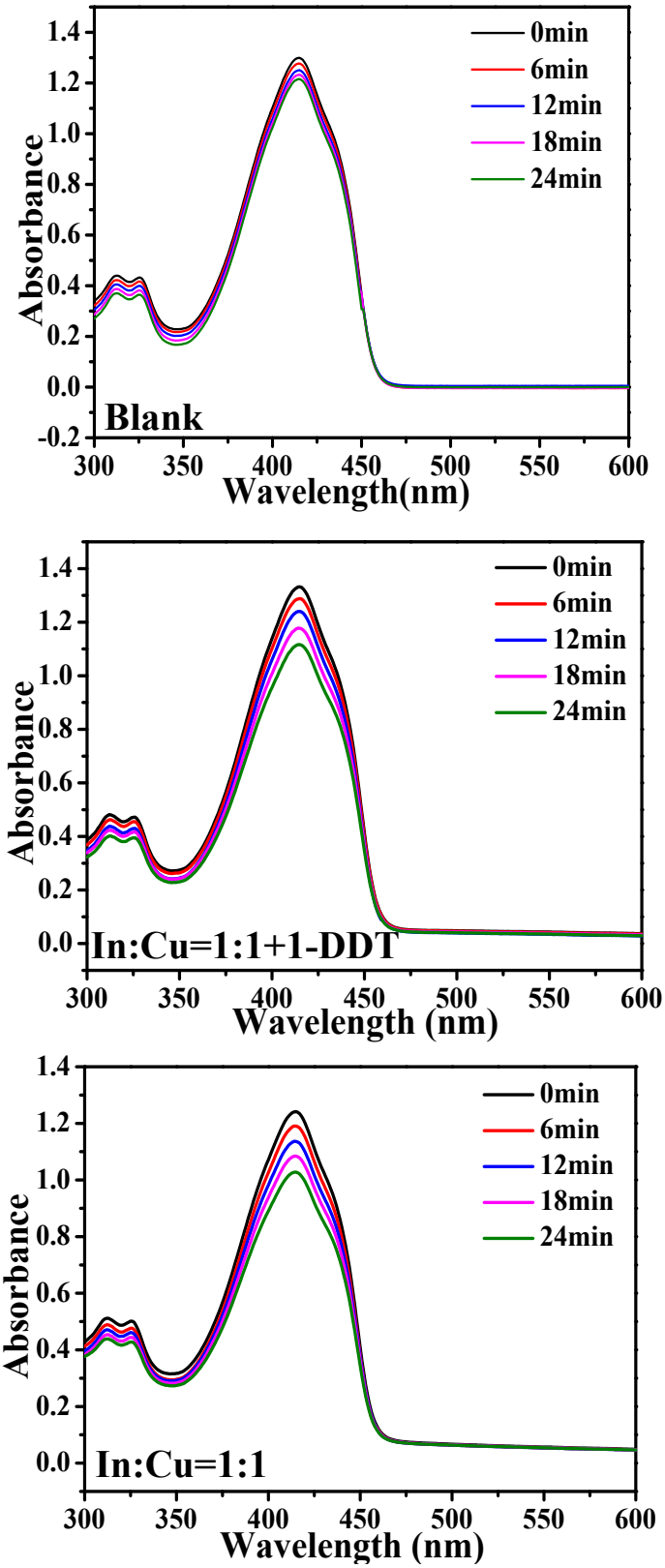

Figure S9. Normalized absorbance of the DPBF in the absence (blank) or presence of different $CuInS_2$ NCs that are obtained under varied reaction conditions. The decomposing of DPBF experiments were carried out under Xe lamp with 600 nm cutoff filter.