Supplementary Information

Enzymatic Biomineralization of Biocompatible CuInS$_2$, (CuInZn)S$_2$ and CuInS$_2$/ZnS Core-Shell Nanocrystals for Bioimaging

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**Table S3**. Lattice fitting of CuInS$_2$/ZnS nanocrystals shown in Figure 5 a) & c) to the chalcopyrite CuInS$_2$ structure.

Table S4. Lattice fitting of (CuInZn)S$_2$ nanocrystals shown in Figure 7 a) to the expected chalcopyrite structure.
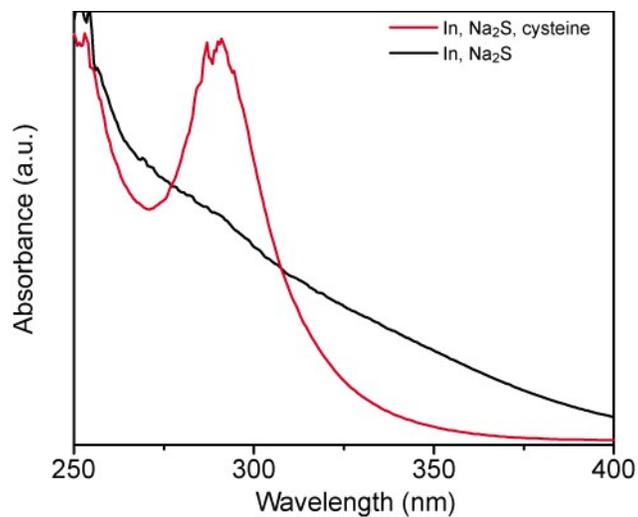
Figure S1. Absorbance spectrum with a peak at 290 nm of a buffered solution of 4 mM indium, 8 mM Na$_2$S with 8 mM cysteine (red) and without L-cysteine (black).
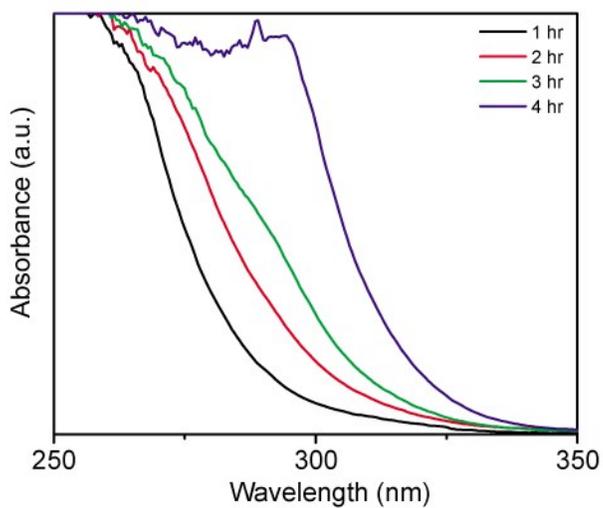

Figure S2. Absorbance spectrum of a buffered solution of 4 mM indium, 0.2 mg/mL CSE and 32 mM L-cysteine, showing faster growth of the peak at 290 nm relative to that in Figure 1(b).
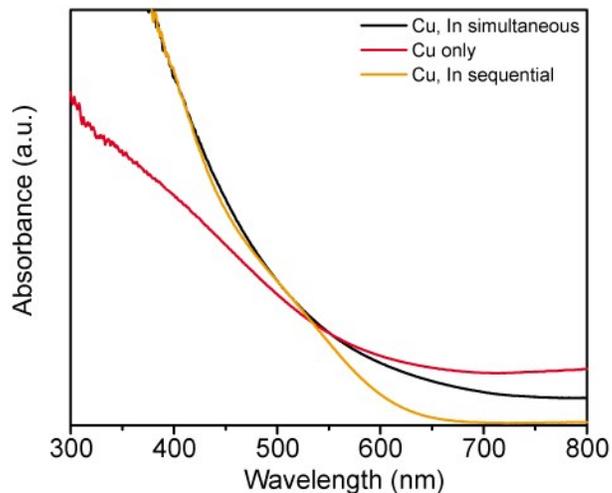
Figure S3. Absorbance spectra from a buffered solution of 0.2 mg/mL CSE and 32 mM L-cysteine with copper and indium incubated together (black line). This is compared to solutions incubated with only copper (red line) or pre-incubated with indium for 2 h before adding copper (yellow line). The resultant spectra indicate the nucleation of both $CuInS_2$ and Cu_{2-x} nanocrystals.

Table S1. Calculated band gap values for the various sols presented in Figure 2. Band gap values calculated using a Tauc plot.

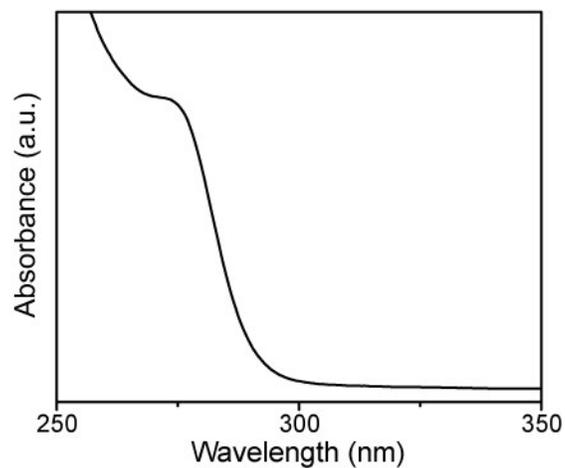| Sample	Band gap (eV)
16 mM cys 2 h	2.35
16 mM cys 4 h	2.33
32 mM cys 2 h	2.26
32 mM cys 4 h	2.04
32 mM cys 6 h	1.93
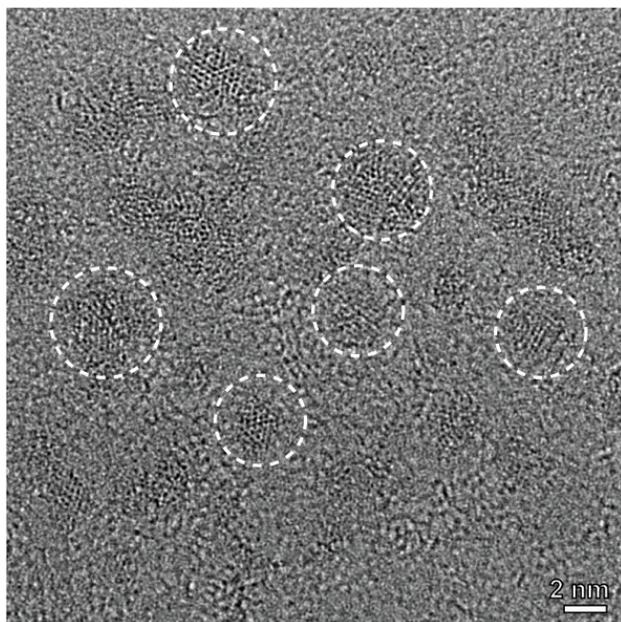
Figure S4. HRTEM image showing several CuInS$_2$ nanocrystals, with a mean size of 2.5 nm, from the 32 mM cysteine, 4 h In incubation sample whose optical properties are shown in Figure 2 b).

Table S2. Lattice fringe fitting of the CuInS$_2$ nanocrystal shown in Figure 3 a) to the chalcopyrite CuInS$_2$ structure. <x,y> denotes the angle between two intersecting planes x and y. Planes 1, 2 and 3 are identified in the FFT shown in Figure 3 b).

| Nanocrystal identification as tetragonal CuInS$_2$		
Figure 2(a): [10$\bar{3}$] projection		
	Measurement	Matching
Plane 1	d=2.92 Å	2.76 Å (020)
Plane 2	d=1.75 Å	1.81 Å (301)
Plane 3	d=1.49 Å	1.51 Å (321)
<1, 2>	89.1˚	90.0˚
<1, 3>	57.5˚	56.7˚
<2, 3>	31.6˚	33.3˚
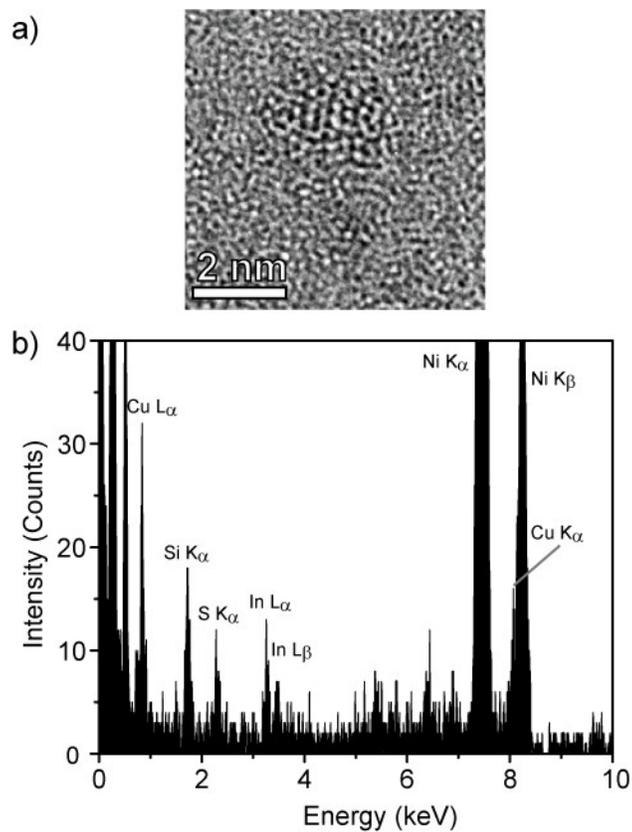
Figure S5. a) HRTEM phase contrast image of a 2 nm CuInS$_2$ nanocrystal and b) corresponding XEDS from single particle.

Figure S6. Absorbance spectrum a buffered solution of 1 mM Zn acetate, 8 mM cysteine, and 0.05 mg/mL CSE, showing an absorbance peak at 280 nm, demonstrating the formation of ZnS quantum dots.
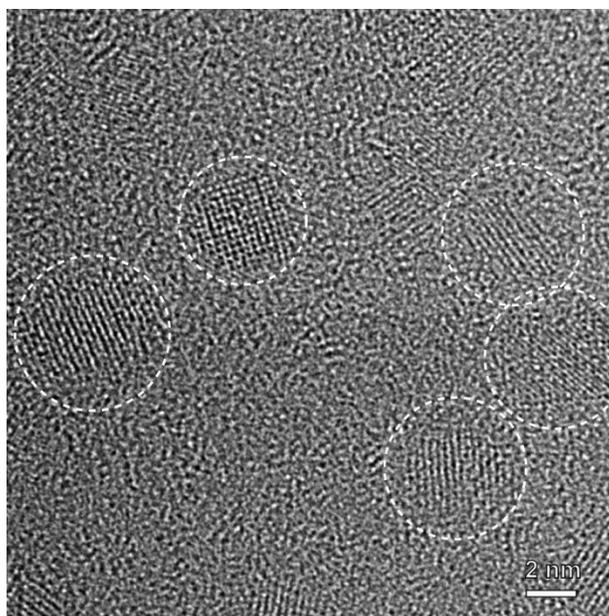
Figure S7. HRTEM phase contrast image showing several 4 nm CuInS/ZnS core-shell nanocrystals corresponding to core CuInS$_2$ formed from the pre-incubation of 32 mM cysteine with 4 mM In and 0.2 mg/mL CSE for 4 h, and then incubated with Zn acetate for 12 hours.

Table S3. Lattice fitting of CuInS$_2$/ZnS nanocrystals shown in Figure 5 a) & c) to the chalcopyrite CuInS$_2$ structure. <x,y> denotes the angle between two intersecting planes x and y. Planes are identified in Figure c) & d).

Nanocrystal Identification as chalcopyrite CuInS$_2$					
Figure 5 a,c): [010] projection			Figure 5 b,d): [010] projection		
	Measurement	Matching		Measurement	Matching
Plane 1	d=2.80 Å	2.78 Å (004)	Plane 1	d=2.82 Å	2.78 Å (004)
Plane 2	d=1.99 Å	1.96 Å (204)	Plane 2	d=1.96 Å	1.96 Å (204)
Plane 3	d=2.77 Å	2.76 Å(200)	Plane 3	d=2.83 Å	2.76 Å (200)
<1, 2>	45.6˚	45.2˚	<1, 2>	44.4˚	45.2˚
<1, 3>	89.6˚	90.0˚	<1, 3>	88.8˚	90.0˚
<2, 3>	44.7˚	44.8˚	<2, 3>	44.4˚	44.8˚

Table S4. Lattice fitting of (CuInZn)S$_2$ nanocrystals shown in Figure 7 a) to the expected chalcopyrite structure. <x,y> denotes the angle between two intersecting planes x and y. Planes are identified in Figure b).

Nanocrystal identification as chalcopyrite CuInS$_2$		
Figure 7(a): [02$\bar{1}$] projection		
	Measurement	Matching
Plane 1	d=2.75 Å	2.76 Å (020)
Plane 2	d=3.13 Å	3.19 Å (301)
Plane 3	d=3.16 Å	3.19 Å (321)
<1, 2>	54.5°	54.6°
<1, 3>	56.1°	54.6°
<2, 3>	69.4°	70.7°