

Supporting Information

Spontaneous Alloying of Ultrasmall Non-Stoichiometric Ag-In-S and Cu-In-S Quantum Dots in Aqueous Colloidal Solutions

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Table S1. XRD peak positions, FWHMs, and average size d of QDs estimated using the Scherrer equation from the parameters of (220) and (312) peaks

QD type	2 θ /FWHM (112)	2 θ /FWHM (220)	2 θ /FWHM (312)	d , nm
AIS	26.93/4.76	45.17/4.27	52.72/4.40	2.0 \pm 0.1
CIS	27.52/6.03	46.60/4.66	54.35/4.20	1.8 \pm 0.1
CAIS	27.32/6.04	46.06/4.36	53.68/4.54	2.0 \pm 0.1

AIS+CIS	27.09/5.88	45.77/4.36	53.28/4.56	2.0 ± 0.1
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Table S2. Evolution of PL parameters of the 1:1 concentrated mixture of colloidal CIS and AIS QDs kept at 25 °C for different times

Time, min	E_{PL} , eV	I_{PL} , arb. un.	w_{PL} , meV
3	2.00	100	325
9	1.99	98	320
15	1.99	95	320
80	1.98	77	335
180	1.98	52	345
360	1.95	41	365

Notes: determination uncertainty is 0.01 eV for E_{PL} , 1 for I_{PL} , 5 meV for w_{PL} .

Table S3. Evolution of PL parameters of the 1:1 mixture of colloidal CIS and AIS QDs diluted by a factor of 1000 and kept at 25 °C for different times

Time, min	E_{PL} , eV	I_{PL} , arb. un.	w_{PL} , meV
4	2.0	100	320
11	1.99	91	320
15	1.99	83	325
32	1.98	82	330
82	1.98	78	330
108	1.97	77	335
134	1.97	76	335
300	1.96	66	345

Notes: determination uncertainty is 0.01 eV for E_{PL} , 1 for I_{PL} , 5 meV for w_{PL} .

Table S4. Evolution of PL parameters of the 1:1 concentrated mixture of colloidal CIS and AIS QDs kept at 96-98 °C for different times

Time, min	E_{PL} , eV	I_{PL} , arb. un.	w_{PL} , meV
1	1.98	100	340
2	1.92	51	380
6	1.85	43	345
9	1.83	39	335
12	1.81	35	330
15	1.80	33	330
18	1.79	32	325
21	1.77	26	320

Notes: determination uncertainty is 0.01 eV for E_{PL} , 1 for I_{PL} , 5 meV for w_{PL} .

Table S5. Evolution of PL parameters of the 1:1 mixture of colloidal CIS and AIS QDs diluted by a factor of 1000 and kept at 96-98 °C for different times

Time, min	E_{PL} , eV	I_{PL} , arb. un.	w_{PL} , meV
1	1.99	100	360
4	1.93	97	360
7	1.91	95	355
10	1.89	94	350
15	1.87	85	340
20	1.85	84	330
25	1.84	82	320
30	1.83	73	320
40	1.81	67	315
60	1.79	52	310

Notes: determination uncertainty is 0.01 eV for E_{PL} , 1 for I_{PL} , 5 meV for w_{PL} .

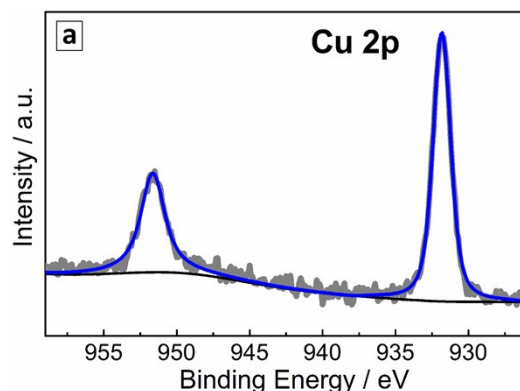


Figure S1. (a) X-ray photoelectron spectrum of GSH-capped CIS QDs in the range of copper 2p electron binding energies (gray solid line). Black line is a baseline, blue solid line - fitting of the experimental spectrum.

Description of the XPS setup and fitting procedure. XPS studies were performed using an ESCALAB™ 250Xi X-ray Photoelectron Spectrometer Microprobe (Thermo Scientific). For XPS measurements the colloids were drop-casted on Au/Si substrate and dried under vacuum. The spectra were acquired under excitation of a 650 μm spot with a monochromized Al K_{α} (1486.6 eV) X-ray source and a pass energy of 20 eV (spectral resolution of 0.5 eV). During the XPS measurement, the sample was flooded with low kinetic energy (about 0.1 eV) electrons to prevent possible charging. Spectra deconvolution and quantification were performed using the Thermo Scientific™ Avantage Software. The authors thankfully acknowledge Dr. Volodymyr Dzhagan (TU Chemnitz) for his help in acquiring XPS spectra.

Analysis of the XPS copper 2p range. The copper 2p range shows a doublet at 931.8/951.7 eV (Fig. 2c). The positions of peaks and the distance between them (19.9 eV), indicate that copper is present in the sample solely as Cu(I) typically found in metal sulfides [1-4]. Additionally, the absence of any features around 934/954 eV as well as any satellite peaks of paramagnetic Cu^{2+} species at 940-945 eV confirm that copper is present in the GSH-capped CIS/ZnS NCs as Cu(I) [1-4].

References.

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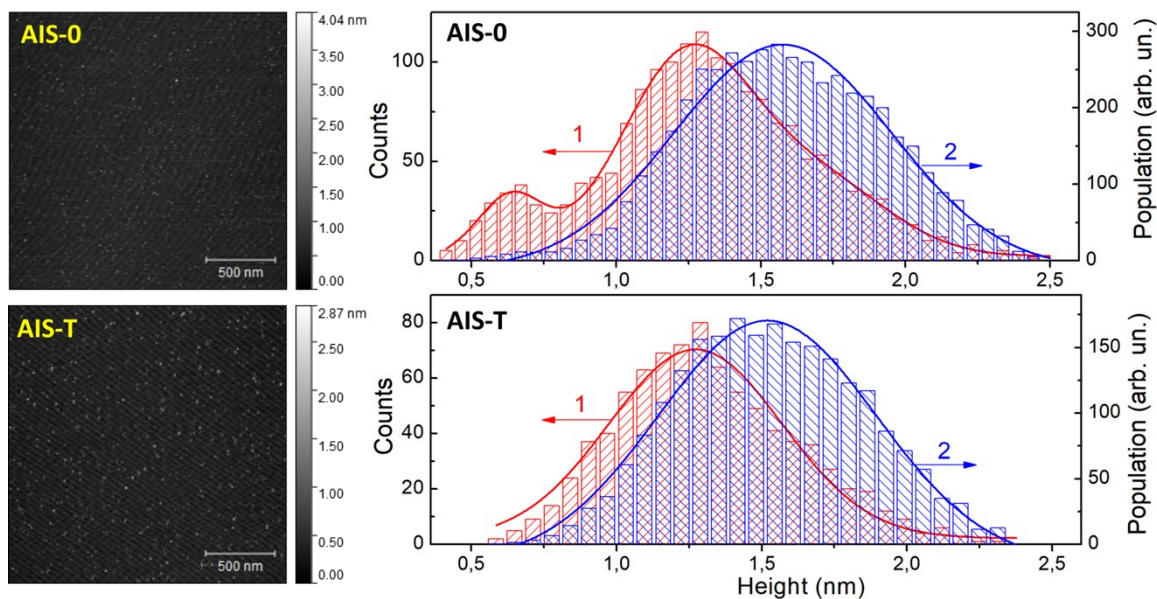


Figure S2. AFM images (left panel) and size distributions (right panel) of aqueous colloidal GSH-capped AIS QDs kept at room temperature (AIS-0) and at 96-98 °C (AIS-T). QD size (height) distributions are numerical (1) and volumetric (2).

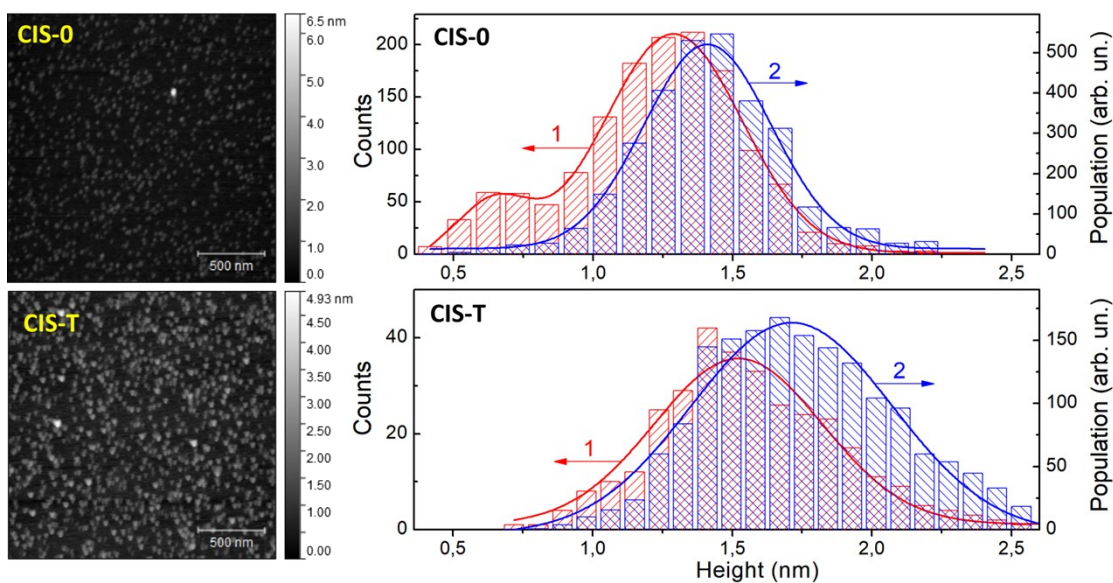


Figure S3. AFM images (left panel) and size distributions (right panel) of aqueous colloidal

GSH-capped CIS QDs kept at room temperature (CIS-0) and at 96-98 °C (CIS-T). QD size (height) distributions are numerical (1) and volumetric (2).

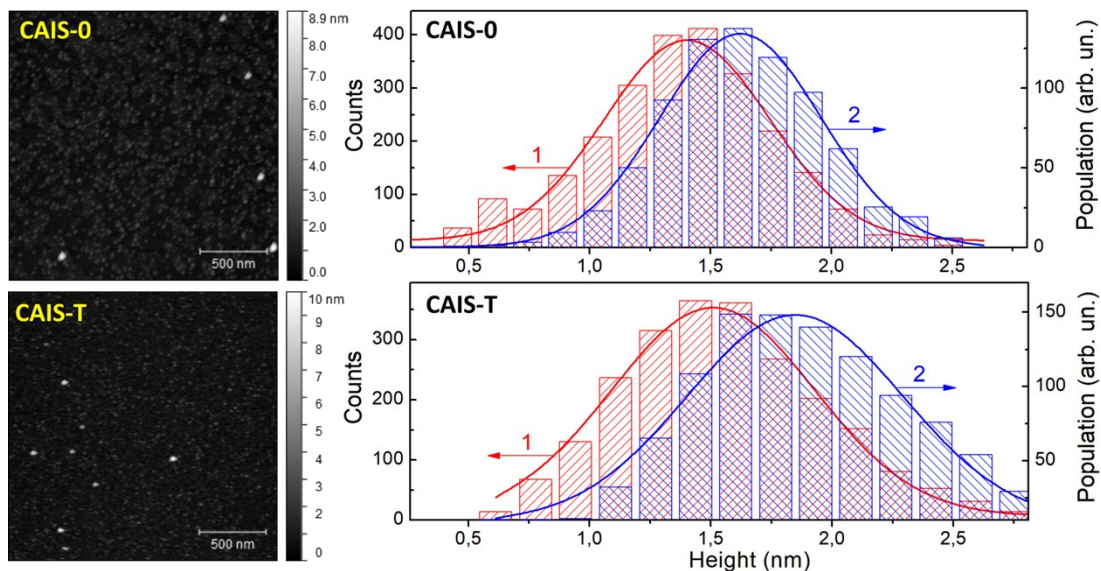


Figure S4. AFM images (left panel) and size distributions (right panel) of aqueous colloidal GSH-capped CAIS QDs (Cu:Ag = 1:1) kept at room temperature (CAIS-0) and at 96-98 °C (CAIS-T). QD size (height) distributions are numerical (1) and volumetric (2).

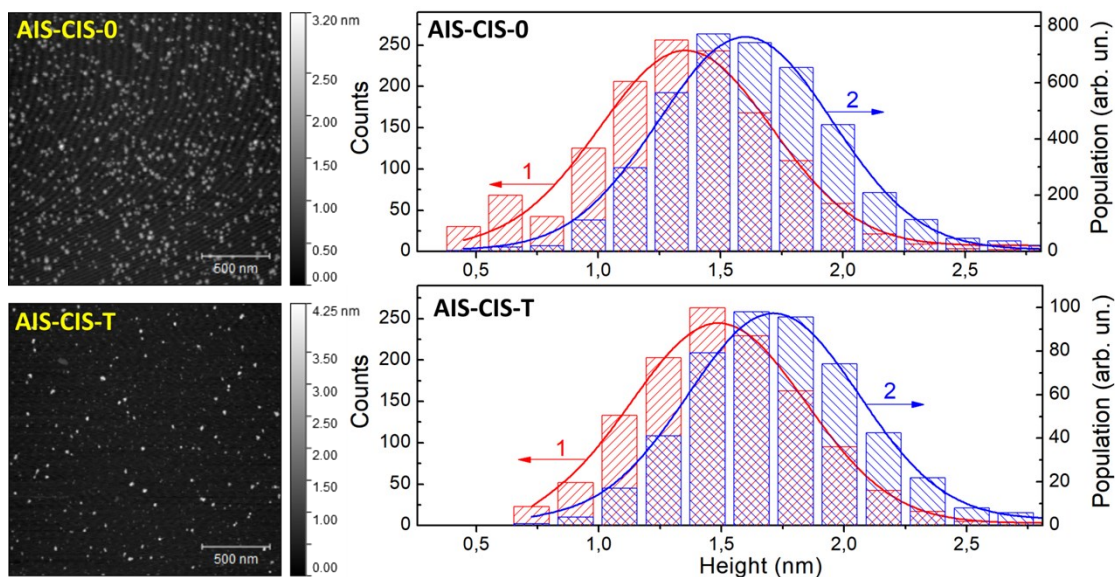


Figure S5. AFM images (left panel) and size distributions (right panel) of a mixture of aqueous colloidal GSH-capped AIS and CIS QDs (AIS:CIS = 1:1 v/v) kept at room temperature (AIS-CIS-0) and at 96-98 °C (AIS-CIS-T). QD size (height) distributions are numerical (1) and volumetric (2).

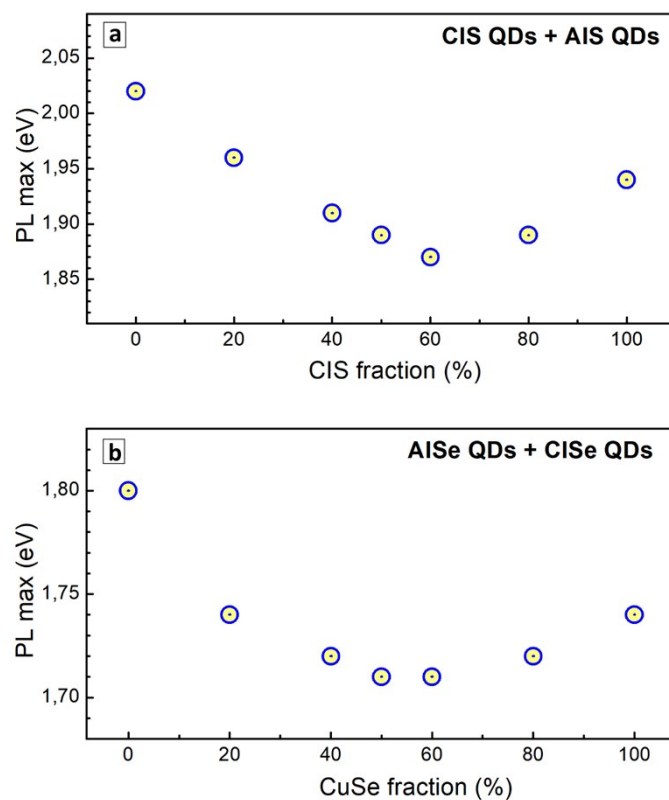


Figure S6. PL band maximum position of the products of spontaneous alloying of aqueous CIS and AIS QDs (a) and aqueous CISe and AISe QDs (b) at room temperature for 24 h.