Supplementary information

Zn, Cd and Hg doping of $AgInS_2$ quantum dots - efficient strategy to modify nonlinear absorption

Rafał Kosman, [a] Dominika Wawrzyńczyk,[b] Marcin Nyk, [b] Mirosława Pawlyta,[c] Oleksii Bezkrovnyi[a] and Bartłomiej Cichy *[a]

[a] *Polish Academy of Sciences, Institute of Low Temperature and Structure Research, Okólna 2, 50-422 Wrocław, Poland*

[b] *Wroclaw University of Science and Technology, Faculty of Chemistry, Institute of Advanced Materials, Wybrzeże Wyspiańskiego 27, 50-370 Wroclaw, Poland*

[c] *Silesian University of Technology, Institute of Physics – Centre for Science and Education, Konarskiego 22B, 44-100 Gliwice, Poland*

Corresponding author Bartłomiej Cichy e-mail: b.cichy@intibs.pl

1. Structure and morphology analysis

Table s1. d-spaces for $AgInS_2$ with orthorhombic and tetragonal structure.

Orthorhombic $AgInS_2$ (a=6.9972Å; b=8.2733 Å. c=6.6939 Å)		Tetragonal $AgInS_2$ (Chalcopyrite structure) (a=5.8760 Å; b=5.8760 Å. c=11.2007 Å)	
hkl	**d-space. A**	**hkl**	**d-space. A**
110	5.3526	101	5.2034
011	5.2039	112	3.3469
111	4.1857	103	3.1513
020	4.1467	200	2.9380
120	3.5609	004	2.8002
200	3.5086	202	2.6017
002	3.3570	211	2.5584
210	3.2223	213	2.1489
121	3.1438	105	2.0932
201	3.1006	220	2.0775
211	2.9034	204	2.0270
112	2.8363	301	1.9294
220	2.6713		
022	2.6019		
130	2.5567		
031	2.5499		
221	2.4810		
122	2.4388		
202	2.4185		
131	2.3957		
212	2.3213		
310	2.2449		
230	2.1658		
013	2.1543		
311	2.1283		
222	2.0878		
040	2.0683		
231	2.0606		
113	2.0590		
132	2.0362		

320 140	2.0317 1.9840		

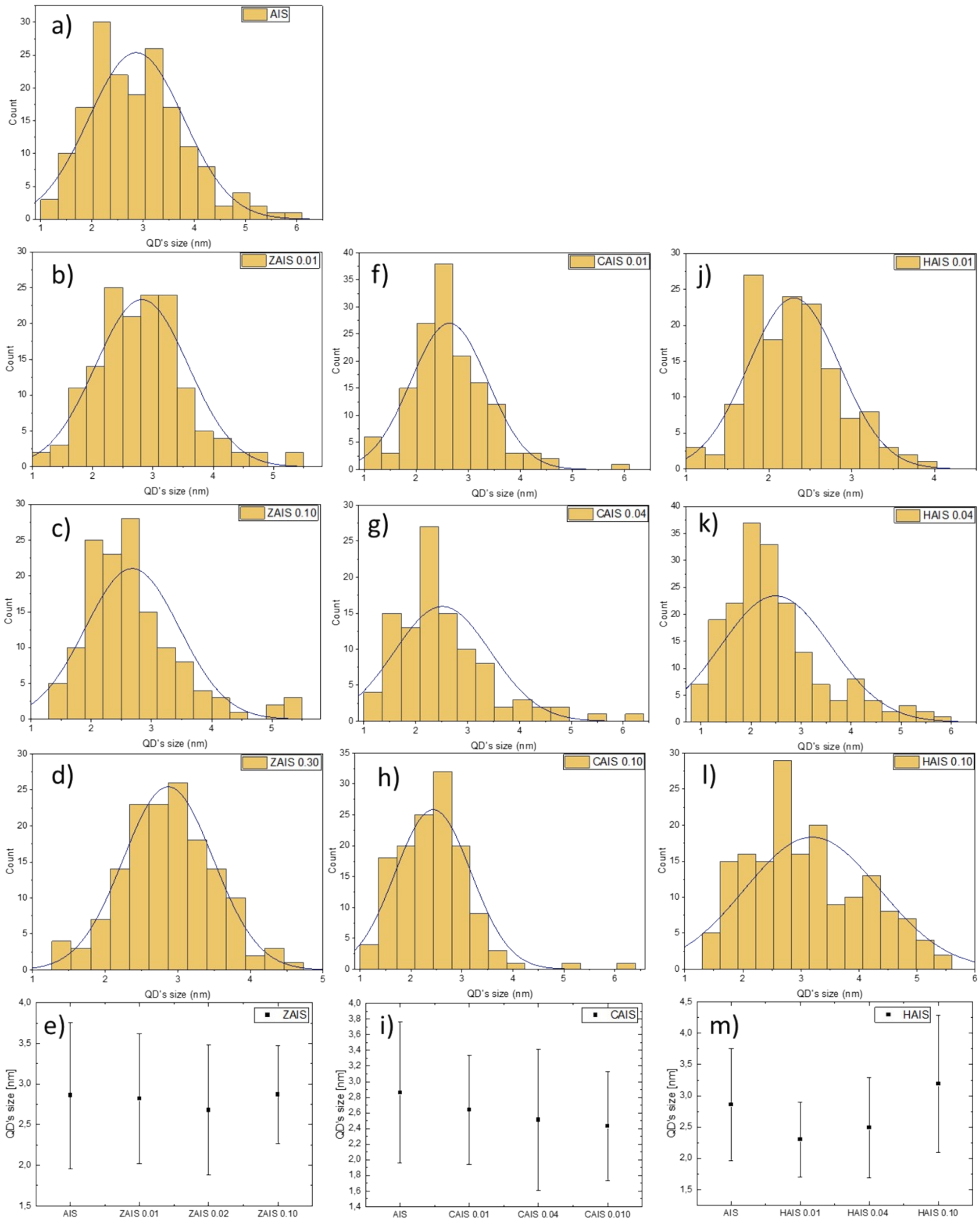

Fig s1 Histogram with distribution size of AIS (a). ZAIS (b-d). CAIS (f-h) and HAIS (j-l). Graphs of calculated average size values with errors (e)for ZAIS (i) for CAIS and (m) for HAIS.

2. Chemical composition analysis - ICP

Table s2 The percentage of the forming elements i.e., Ag, In and S, as well as the dopant elements in all the tested samples. Results obtained in ICP method.

	Zn (%)	Cd (%)	Hg (%)	Ag (%)	In (%)	S (%)
AIS	0	0	0	21.57	26.72	51.7
HAIS 0.01	0	0	1.04	21.29	26.54	51.65
HAIS 0.04	0	0	4.26	21.56	24.76	51.55
HAIS 0.10	0	0	10.66	19.02	22.71	52.93
CAIS 0.01	0	1.08	0	21.59	26.13	51.74
CAIS 0.04	0	4.34	0	20.75	25.34	51.74
CAIS 0.10	0	10.86	0	18.68	24.06	51.83
ZAIS 0.01	1.1	0	0	21.46	26.19	51.8
ZAIS 0.10	10.58	0	0	19.82	22.61	52.28
ZAIS 0.30	32.88	0	0	15.53	18.24	49.79

3. **Analysis of spectroscopic properties**

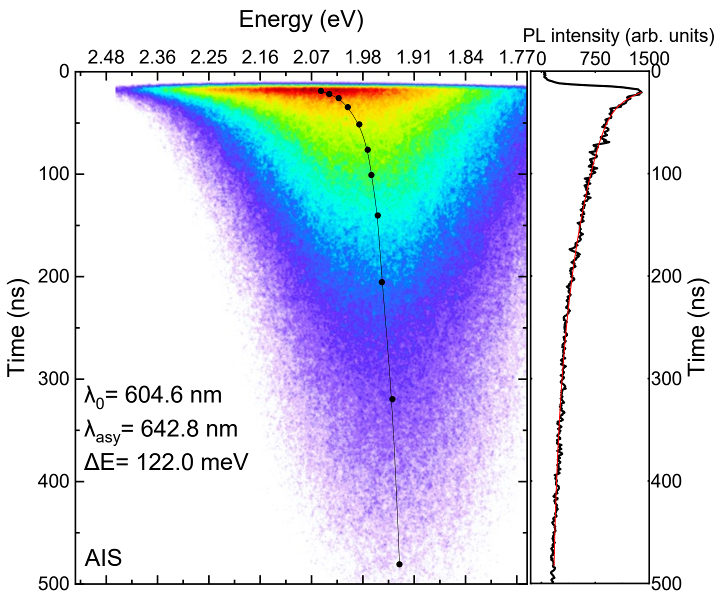

Fig s2. Time resolved luminescence spectra of pristine $AgInS_2$ quantum dots. On the spectra was showed the emission maximum at t_0 and t_{asy} and was determined the energy shift (ΔE) between this value. Was marked the change of the emission maximum over time on the spectra. The decay time shown in the side chart was calculated for the wavelength in the asymptotic (λ_{asy}) position with used bi-exponential model $I(t) = A_1 e^{-1/\tau_1} + A_2 e^{-1/\tau_2}$.

Table s3 Spectroscopic property analysis data QDs maximum of emission band, Full width at half maximum (FWHM), quantum yield (QY) and decay time appropriate for maximum emission in T=0 ns and asymptotic maximum.

	Maximum of emission [nm]	FWHM [nm]	QY [%]	Decay time In T_0		Decay time In T_0	
				T_0 [ns]	Δτ [ns]	T_{asy} [ns]	Δτ [ns]
AIS	670	168	5.93 ±0.42	35.64	1.10	58.60	1.18
ZAIS 0.01	666	165	5.26 ±0.38	23.76	0.37	62.67	1.05
ZAIS 0.10	658	152	4.82 ±0.36	26.29	0.75	44.11	1.42
ZAIS 0.30	630	148	3.42 ±0.21	39.95	1.72	19.91	0.87
CAIS 0.01	620	137	2.59 ±0.06	23.34	0.53	38.59	0.53
CAIS 0.04	590	134	1.03 ±0.07	21.11	0.51	35.84	0.81
CAIS 0.10	574	127	0.55 ±0.04	19.85	0.48	26.52	0.82
HAIS 0.01	645	150	2.78 ±0.19	21.85	0.52	75.92	4.44
HAIS 0.04	660	160	3.52 ±0.25	24.06	0.54	9.35	0.56
HAIS 0.10	700	178	3.76 ±0.25	25.63	0.39	47.26	0.93

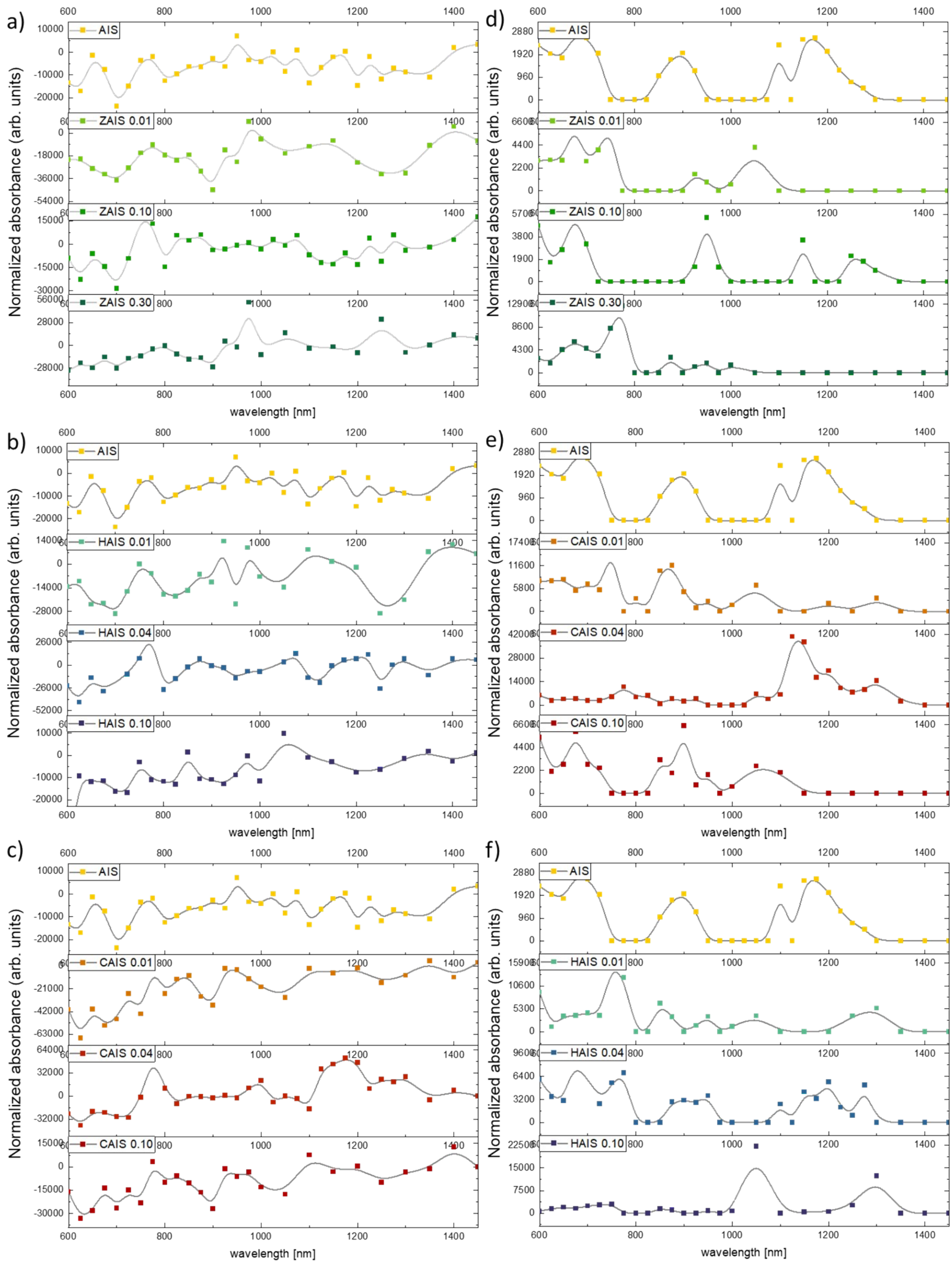

Fig. S3 Data of two photon absorption for (a-c) close (real part) and (d-f) open (imaginary part) Z-scan aperture.

Spectra of the TPFE upon beam splitted in two arms irradiation with the femtosecond tunable laser system: a Quantronix Integra-C Ti:sapphire regenerative amplifier producing ~130 fs, 800 nm pulses of 1 mJ energy per pulse with 1 kHz frequency and a Quantronix Palitra-FS optical parametric amplifier for wavelength tuning between 600 and 1500 nm, were obtained with two fiber optic spectrographs (Ocean Insight Flame and Ocean Optics QE Pro-FL). A sample and reference (*Rhodamine 610*) for the measurements is placed in a two 4-way cuvette holders A i B with fiber collimating lens and the spectra are collected at an angle of 90° to the laser beam. Here, the unknown 2PA cross section can be determined from the relation [N.S. Makarov, J. Campo, J.M. Hales, J.W. Perry, Opt Mater Express 1 (2011) 551-563]:

$$\sigma_2 = \sigma_{2,ref} \cdot \frac{c_{ref}}{c} \sqrt{\frac{I_A \quad I_B}{I_{ref,A} I_{ref,B}}} \cdot \frac{\eta_{ref}}{\eta}$$

the ratio:

$$\frac{\eta_{ref}}{\eta} = \frac{f(\lambda)_{ref} \quad 1-10^{-OD_{sample}}}{1-10^{-OD_{ref}} \qquad f(\lambda)}$$

where

$f(\lambda)$ stands for fluorescence signal at specific wavelength λ, excited in low concentration solutions (OD<0.1) via one photon excitation, which can be obtained with regular spectrofluorimeter, the K factor of the emission collection efficiency on the refractive index of sample and reference is identical for one- and two-photon excitation, and therefore cancels out in the final expression for the σ_2 expression. The $\sigma_{2,ref}$ values were taken from the work of Makarov et al.[N. S. Makarov, M. Drobizhev, and A. Rebane, Opt. Express 16, 4029 (2008)]. The proposed method eliminates the need to determine the fluorescence quantum yield of the sample and reference, as it allows measurement of emission from samples at a common specified wavelength.

Table s4. The values of TPA measured by TPEE method

Sample	AIS	ZAIS 0.01	ZAIS 0.10	ZAIS 0.30	CAIS 0.01	CAIS 0.04	CAIS 0.10	HAIS 0.01	HAIS 0.04	HAIS 0.10
Wavelength [nm]	σ_2 [GM]*									
850	117	294	9.7	44	115	12.0	24.1	107	38.9	245
900	9.2	88	2.1	9.9	30.4	2.9	7.5	2.3	11.7	72.4
950	2.6	7.5	0.83	3.6	6.7	0.44	3.9	5.1	2.2	11.8
1000	1.2	15.7	0.56	6.0	17.7	0.70	10.4	1.2	3.7	9.9
1050	0.79	107	1.1	20	23.0	1.2	14.5	15.8	1.4	161
1100	1.8	1.2	2.6	4.3	8.4	0.77	4.3	5.2	4.0	16.3
1150	0.87	3.4	0.69	0.39	1.7	0.10	0.37	0.65	0.44	3.0
1200	0	0.99	0	0.13	0.63	0	0.18	0.27	0	0
1250	0	0	0	0	0	0	0	0	0	0

* calculated based on TPEE experiment