11th International conference "Nanotechnologies and nanomaterials", Bukovel, 16–19 August 2023

Synthesis and characterization of colloidal Ag–(In,Ga)–S semiconductor nanocrystals

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INTRODUCTION

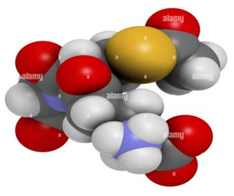
Research interest towards I–III–VI colloidal semiconductor nanocrystal (NCs) is caused by their non-toxicity and the possibilities of size variation of their bandgap in a broad range, high luminescence efficiency, high photocatalytic activity, and possible applications in biology and medicine as well as in light sources and photovoltaic elements. Much less studied are gallium containing Ag–(In,Ga)–S NCs. To our knowledge, no studies of size-selected Ag–(In,Ga)–S NCs have been presented so far. Here we report on the synthesis and characterisation of size-selected quaternary non-stoichiometric Ag–(In,Ga)–S NCs obtained at mild conditions in the presence of glutathione (GSH) from aqueous solutions with different [In]:[Ga] molar ratios in the reaction mixture.

SYNTHESIS OF Ag–(In,Ga)–S NANOCRYSTALS

Ag–(In,Ga)–S NCs were obtained following the method by Raevskaya *et al.* for Ag–In–S [*J. Phys. Chem. C* 2017, 121, 9032] with some modifications.

aqueous solutions $AgNO_3$ + GSH + NH_4OH + $InCl_3$ + $GaCl_3$+ Na_2S (in desired proportions)
at intense stirring ↓ aging for 30 min at 90–95 ^oC ↓
luminescent Ag–In(Ga)–S quantum dots

Glutathione (GSH) → was used as a stabilizer.



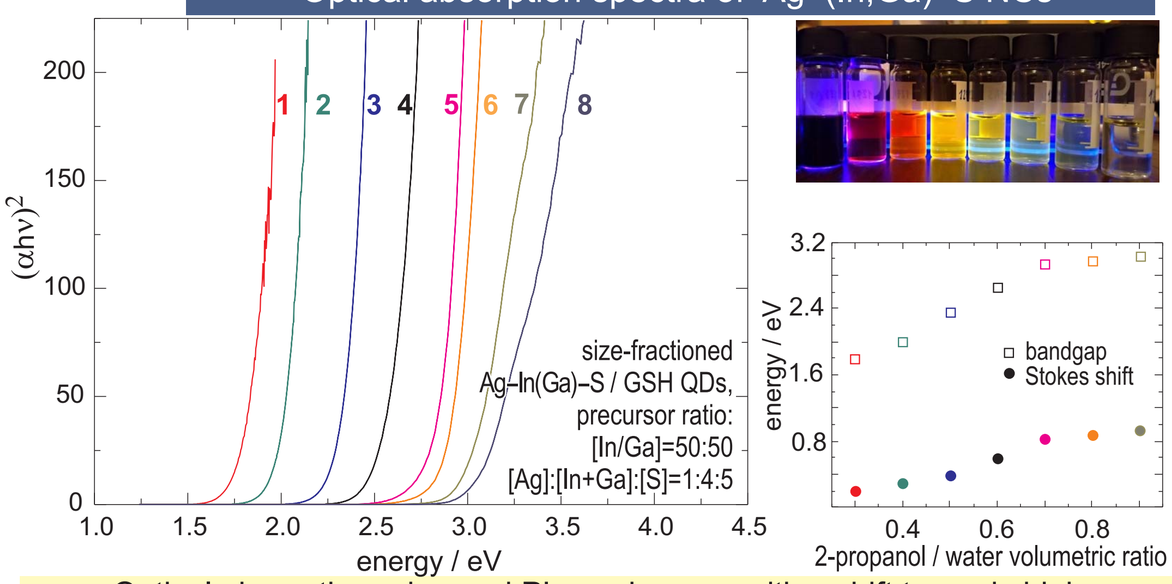
Size-selective fractioning: precipitation in the presence of isopropanol by centrifugation (4000 rpm, 5 min)

CHARACTERISATION TECHNIQUES

XPS measurements: ESCALAB 250Xi XPS Microprobe (Thermo Scientific) photoelectron spectrometer, Al Kα X-ray source (hν = 1486.68 eV).
X-ray diffraction: Rigaku Smartlab, Cu Kα radiation, Bragg-Brentano and parallel-beam geometries
Optical absorption spectra: Cary 50 spectrophotometer (Varian) with a Xe pulse lamp source and dual Si diode detectors.
PL measurements: Black Comet CXR-SR spectrometer (StellarNet) with diode excitation (λ_{exc} = 390 nm)

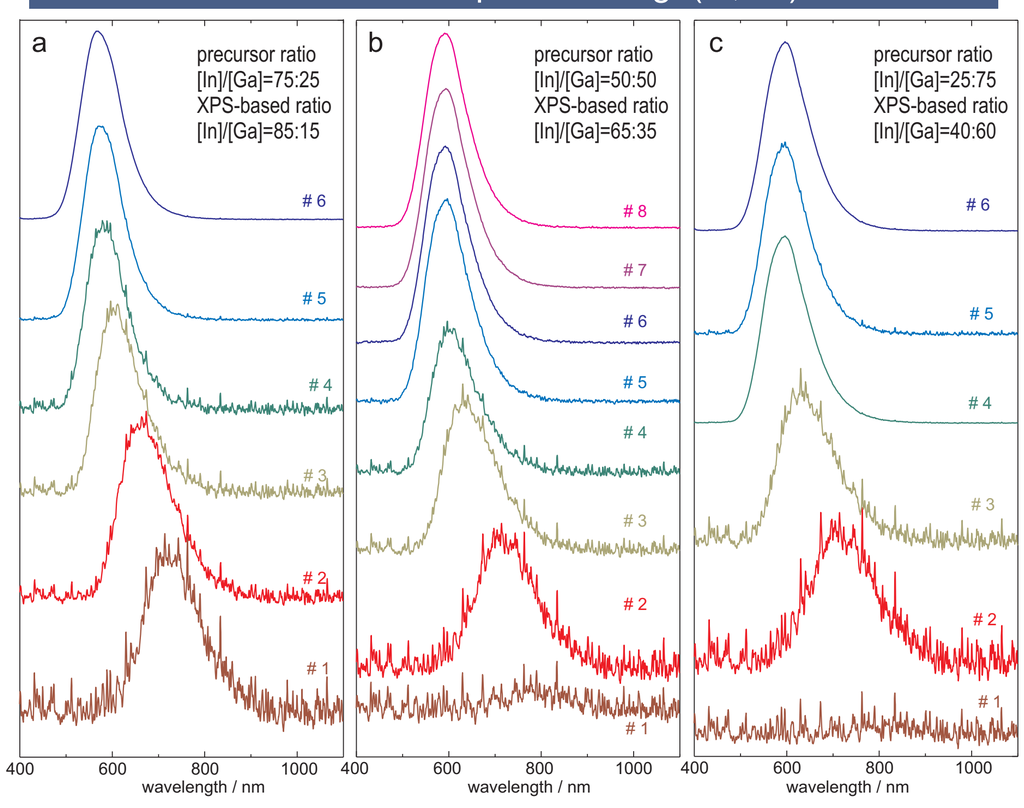
RESULTS AND DISCUSSION

Optical absorption spectra of Ag–(In,Ga)–S NCs



Optical absorption edge and PL maximum position shift towards higher energies with NC size decrease.

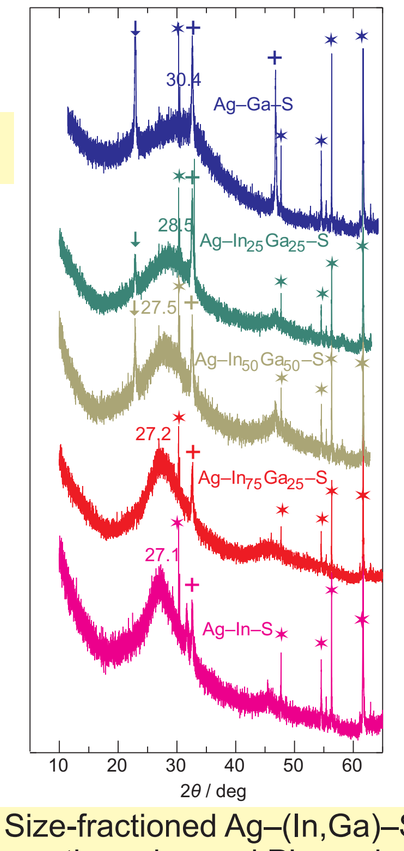
Photoluminescence spectra of Ag–(In,Ga)–S NCs



XPS-determined chemical composition of Ag–(In,Ga)–S NCs

Sample	Ag (at. %)	In at. %)	Ga (at. %)	S (at. %)
Ag–($In_{75}Ga_{25}$)–S, fraction 1	15.7	24.0	5.2	55.1
Ag–($In_{75}Ga_{25}$)–S, fraction 2	11.0	24.8	4.8	59.4
Ag–($In_{50}Ga_{50}$)–S, fraction 1	18.9	19.9	8.0	53.2
Ag–($In_{50}Ga_{50}$)–S, fraction 2	9.9	14.4	8.1	67.6
Ag–($In_{25}Ga_{75}$)–S, fraction 1	11.4	13.0	19.0	56.6
Ag–($In_{25}Ga_{75}$)–S, fraction 2	12.3	13.3	16.0	58.4
Ag–Ga–S, fraction 1	23.9	–	26.3	49.8
Ag–Ga–S, fraction 2	20.0	–	30.3	49.7
Ag–Ga–S, fraction 3	6.5	–	36.2	57.3

X-ray diffraction



Such broad XRD peaks are characteristic for small NCs.

Average Ag–(In,Ga)–S NC size *L* determined from the width of the XRD maxima β (the Scherrer equation)

$$\beta(2\theta) = K\lambda / L\cos\theta$$

is 2 nm.

XRD maximum position for Ag–In–S (27.1^o) corresponds to diffraction from (112) planes of tetragonal (chalcopyrite type) phase of $AgInS_2$ (JCPDS 00-025-1330).

With In→Ga substitution, the XRD maximum shifts upward. At transition to Ag–Ga–S its stepwise change is observed, and the maximum position (~30^o) is untypical for tetragonal $AgGaS_2$ (~28^o). It most likely corresponds to a metastable orthorhombic, rhombohedral, or cubic (rocksalt type) phase of $AgGaS_2$.

CONCLUSIONS

❶ Ag–(In,Ga)–S NCs capped with GSH were synthesised from aqueous solutions at different [In]/[Ga] molar ratios in the reaction mixture.
❷ Size-fractioned Ag–(In,Ga)–S NCs series revealed clear size-dependent shift of the absorption edge and PL maximum position,
❸ Chemical composition of the Ag–(In,Ga)–S NCs exhibited lower Ga content than that in the reaction mixture.
❹ Ag–(In,Ga)–S NCs (except Ag–Ga–S) possess tetragonal (chalcopyrite type) crystal structure.
❺ Average size of Ag–(In,Ga)–S NCs is about 2 nm.

ACKNOWLEDGEMENTS

The authors are grateful to A.I. Pogodin, Ya.I. Lopushanska, and O.P. Kokhan for their assistance. Y.M. Azhniuk is grateful to TU Chemnitz for the funding of his research stay at the university. Ye.I. Havryliuk is gratedul to the Alexander von Humboldt foundation.