Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supplementary Information

Synthesis of $CuFeS_{2-x}Se_x$ – Alloyed Nanocrystals with Localized Surface Plasmon Resonance in the Visible Spectral Range

Patrycja Kowalik,[a,b] Piotr Bujak,*[,a] Mateusz Penkala,[c] Kamil Kotwica,[a] Angelika Kmita,[d] Marta Gajewska,[d] Andrzej Ostrowski,[a] Adam Pron[a]

[a]Warsaw University of Technology, Faculty of Chemistry, Noakowskiego 3, 00-664 Warsaw, Poland. *E-mail: piotrbujakchem@poczta.onet.pl
[b]Faculty of Chemistry, University of Warsaw, Pasteura 1 Str., PL-02-093 Warsaw, Poland
[c]Institute of Chemistry, Faculty of Mathematics, Physics and Chemistry, University of Silesia, Szkolna 9, 40-007 Katowice, Poland
[d]AGH University of Science and Technology, Academic Centre for Materials and Nanotechnology, al. Mickiewicza 30, 30-059 Kraków, Poland

Experimental

Materials

$CuCl_2 \times 2H_2O$ (99%), $FeCl_3 \times 6H_2O$ (97%), sodium oleate (99%), stearic acid (98%), diphenyl diselenide (98%), 1-dodecanethiol (DDT, 98%), oleylamine (OLA, 70%), 1,2-dichlorobenzene (DCB, 99%), 11-mercaptoundecanoic acid (MUA, 95%) were supplied by Sigma-Aldrich.

Synthesis of copper(II) oleate[1,2]

Copper(II) oleate was prepared by reacting $CuCl_2$ with sodium oleate. Sodium oleate (80 mmol, 29.7 g) and $CuCl_2 \times 2H_2O$ (40 mmol, 6,9 g) were dissolved in a mixed solvent composed of 80 mL of ethanol, 60 mL of water and 140 mL of hexane. The mixture was heated to 70 °C and then kept at this temperature for four hours. The organic layers containing the desired product was washed three times with 30 mL of water in a separatory funnel. After washing hexane layer was evaporated and the resulting product (copper(II) oleate) was recovered in a form of a green waxy solid. The content of the salt was determined by iodometric titration of copper. The copper(II) oleate content was 96.0% (10.0% calculated as copper).

Synthesis of iron(III) stearate[3]

Iron(III) stearate was prepared by reacting iron(III) hydroxide with stearic acid. Ammonium solution 25% (20 mL) was added drop-wise to a solution of 21.6 g $FeCl_3 \times 6H_2O$ (80 mmol) in 100 mL of water at 50 °C. The precipitate was separated by centrifugation (7000 rpm, 5 min), suspended in distilled water and centrifuged again. This step was repeated three more times. The as obtained iron(III) hydroxide was quantitatively transferred into a 500 mL flask equipped with a Dean-Stark trap, then 200 mL of toluene and stearic acid (68.3 g, 240 mmol) were added. The stirred mixture was heated to boiling. Distillation was carried out until the distillate no longer contained water. The resulting solid was filtered and dried under reduced pressure. The content of the salt was determined by complexometric titration of iron using EDTA and salicylic acid as an indicator. The iron(III) stearate weight content was 90.3% (6.2% calculated as iron).

Preparation of PhSeSePh/DDT precursor

156 mg (0.5 mmol) of diphenyl diselenide and 1.5 mL of DDT were loaded into a glass vial, which was then immersed in an ultrasonic bath. The mixture was sonicated at room temperature (for about 5 min) until a clear orange solution was formed.

Synthesis of $CuFeS_{2-x}Se_x$ nanocrystals

All operations were carried out under constant dry flow of argon. Copper(II) oleate (96.0%) (0.325 g, 0.5 mmol) and iron(III) stearate (90.3%) (0.500 g, 0.5 mmol) were mixed with 15 mL of OLA in a three-neck flask. The mixture was heated to 150 °C until a homogeneous green-brown solution was formed. Then, 1.5 mL of PhSeSePh/DDT precursor was quickly injected into the reaction solution. Upon injection, the color of the solution instantly changed to black. The temperature was raised to 180 °C, and the mixture was kept at this temperature for 60 minutes. After the mixture had cooled to room temperature, toluene (10 mL) was added, and the reaction mixture was centrifuged; the isolated precipitate consisting of organic waste and agglomerated particles was separated. The supernatant was treated with 30 mL of acetone, leading to the precipitation of the desired fraction of nanocrystals. The nanocrystals were separated by centrifugation (7000 rpm, 5 min), dried under a vacuum, and finally redispersed in toluene (or chloroform).

Ligand recovery

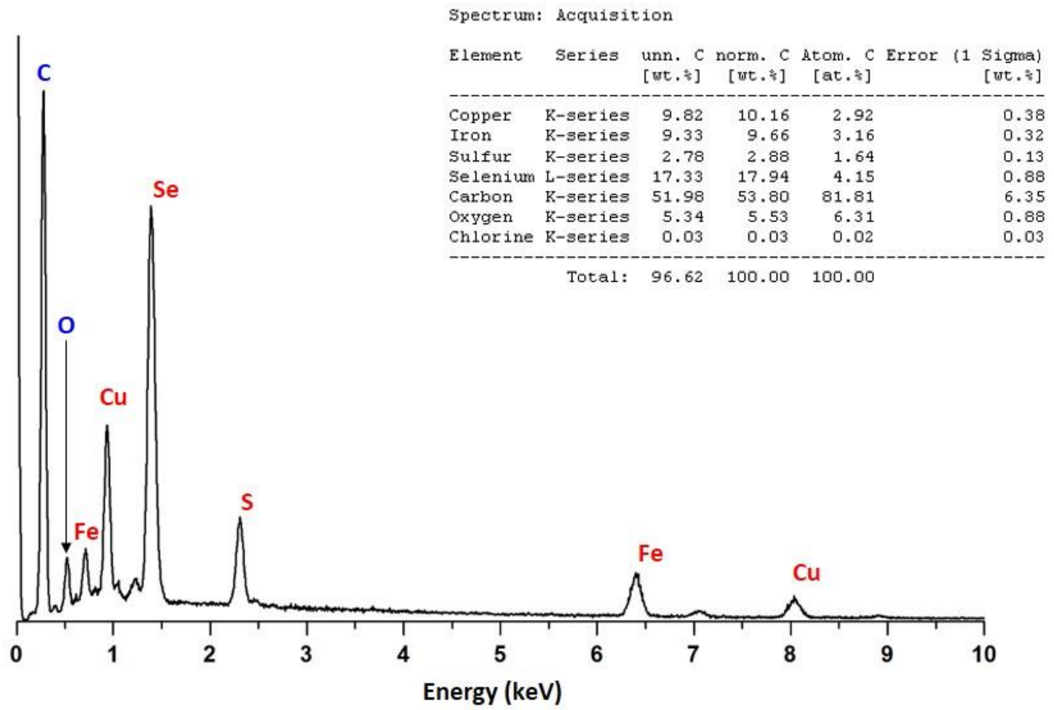
A colloidal solution of $CuFeS_{2-x}Se_x$ nanocrystals (~200 mg in 10 mL of choroform) and 10 mL of concentrated HCl were placed in a screw-capped ampule, which was immersed in an ultrasonic bath for 2 hours (and shaken every 30 minutes). Water (20 mL) was added, and the resulting mixture was centrifuged to achieve phase separation; the remaining solids were discarded. The organic phase was collected, and the aqueous phase was extracted with 15 mL of chloroform. The combined organic layers were washed twice with water, evaporated, and dried under reduced pressure to afford a black oil.

Ligand exchange for 11-mercaptoudecanoic acid

0.5 g (2.29 mmol) of 11-mercaptoundecanoic acid and 0.1 g (2.5 mmol) of NaOH were dissolved in 10 mL of water and transferred to a three-neck flask. Separately, $CuFeS_{2-x}Se_x$ nanocrystals, prepared as described above, were dissolved in 10 mL of toluene and then injected into the first solution. The as-obtained mixture was heated at 50 °C for 8 h under an argon atmosphere. After the mixture was cooled to room temperature and nanocrystals were precipitated by adding acetone and then collected by centrifugation (7000 rpm, 10 min). The nanocrystals were redispersed in 10 mL of water.

Characterization methods

Elemental analysis was carried out with a multichannel Quantax 400 energy-dispersive X-ray spectroscopy (EDS) system with a 125 eV xFlash Detector 5010 (Bruker) using a 15 kV electron beam energy. X-ray powder diffractograms were recorded at room temperature on a Bruker D8 Advance diffractometer equipped with a LYNXEYE position-sensitive detector using Cu Kα radiation ($\lambda = 0.15418$ nm). The data were collected in the Bragg-Brentano ($\theta/2\theta$) horizontal geometry (flat reflection mode) between 10° and 70° (2θ) in a continuous scan, using 0.04° steps at 960 s/step. The incident-beam path in the diffractometer was equipped with a 2.5° Soller slit and a 1.14° fixed divergence slit, whereas the path of the diffracted beam was equipped with a programmable antiscatter slit (fixed at 2.20°), a Ni β-filter, and a 2.5° Soller slit. The sample holder was rotated at an angular speed of 15 rpm. The data were collected under standard conditions (temperature and relative humidity). TEM analysis was performed on a Zeiss Libra 120 electron microscope operating at 120 kV. High-resolution images were acquired by a Tecnai TF20 X-TWIN (FEI) microscope operated at 200 kV. UV-vis-NIR spectra were registered using a Cary 5000 (Varian) spectrometer. ^{1}H NMR spectra were recorded on a Bruker (400 MHz) spectrometer and referenced with respect to tetramethylsilane (TMS) and solvents.



```
Spectrum: Acquisition

Element   Series   unn. C norm. C Atom. C Error (1 Sigma)
                   [wt.%]  [wt.%]  [at.%]          [wt.%]
---------------------------------------------------------
Copper   K-series   9.82   10.16    2.92             0.38
Iron     K-series   9.33    9.66    3.16             0.32
Sulfur   K-series   2.78    2.88    1.64             0.13
Selenium L-series  17.33   17.94    4.15             0.88
Carbon   K-series  51.98   53.80   81.81             6.35
Oxygen   K-series   5.34    5.53    6.31             0.88
Chlorine K-series   0.03    0.03    0.02             0.03
---------------------------------------------------------
           Total:  96.62  100.00  100.00
```

Figure S1. Energy-dispersive spectrum of $Cu_{1.00}Fe_{1.08}S_{0.56}Se_{1.42}$ nanocrystals.

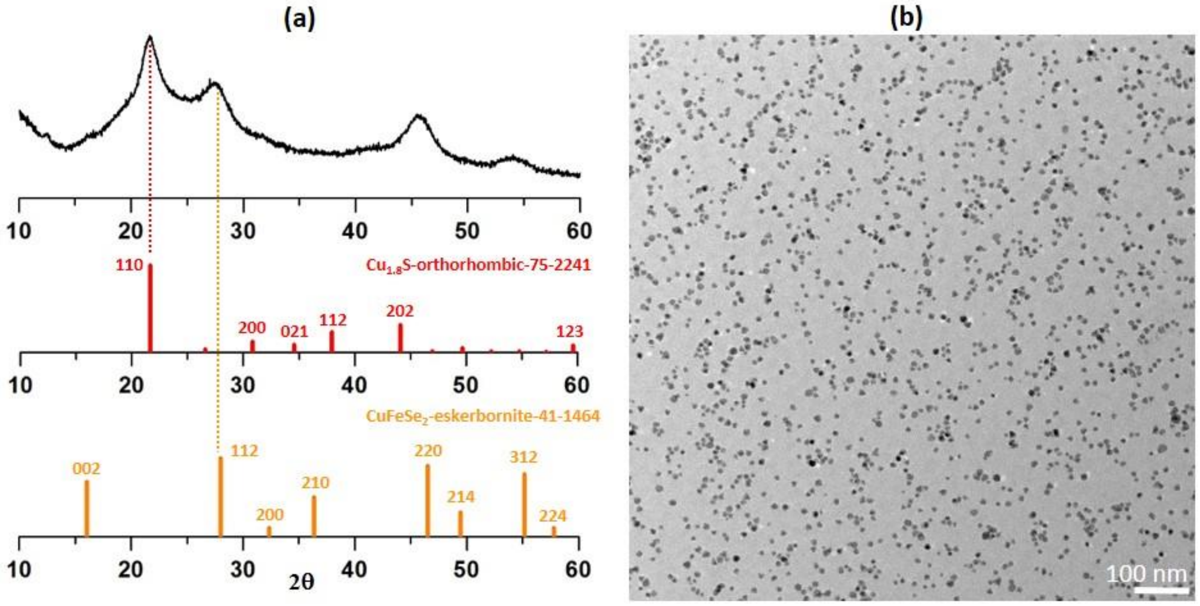


Figure S2. X-ray diffractogram (a) and TEM image (b) of the Cu$_{1.8}$S-CuFeSe$_2$ nanocrystals obtained for copper(II) oleate, iron(III) stearate and PhSeSePh/DDT using ODE as solvent.

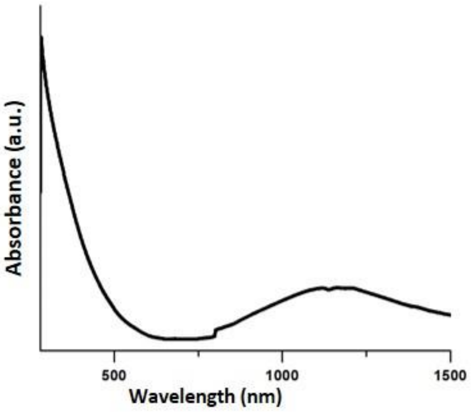


Figure S3. UV-vis-NIR spectrum (in chloroform) of the Cu$_{1.8}$S-CuFeSe$_2$ nanocrystals obtained for copper(II) oleate, iron(III) stearate and PhSeSePh/DDT using ODE as solvent.

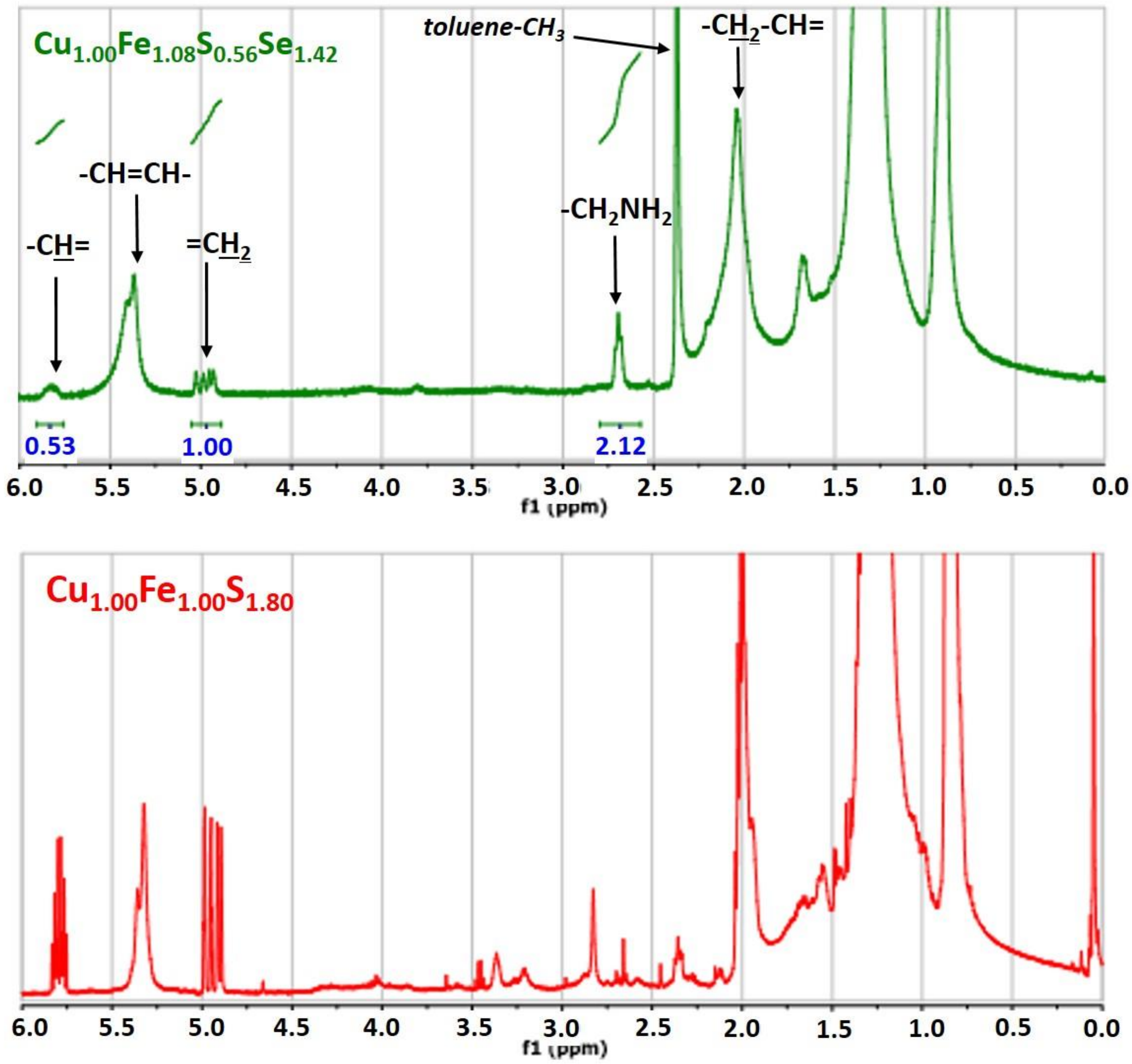


Figure S4. ^{1}H NMR spectra of organic residue from alloyed **$Cu_{1.00}Fe_{1.08}S_{0.56}Se_{1.42}$** **(a)** and **$Cu_{1.00}Fe_{1.00}S_{1.80}$** **(b)** nanocrystals.

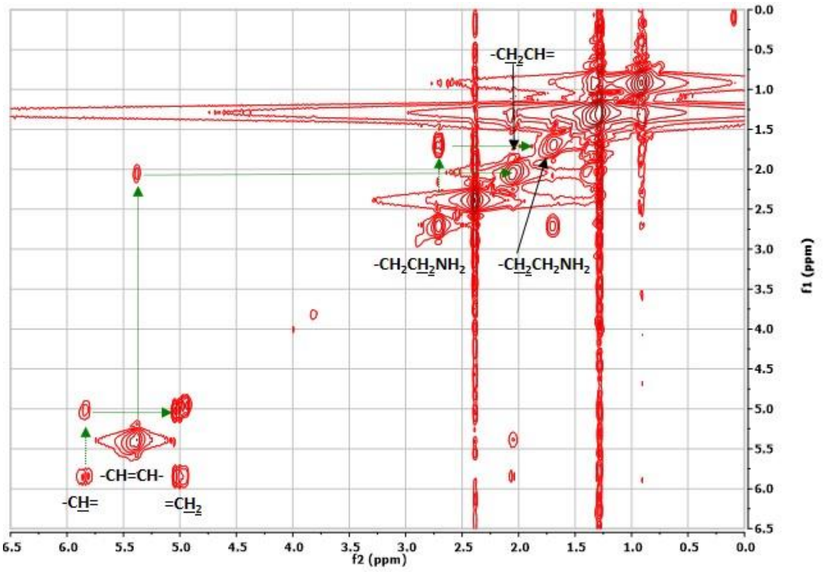


Figure S5. 1H-1H COSY spectrum of organic residue from alloyed $\mathbf{Cu_{1.00}Fe_{1.08}S_{0.56}Se_{1.42}}$ nanocrystals.

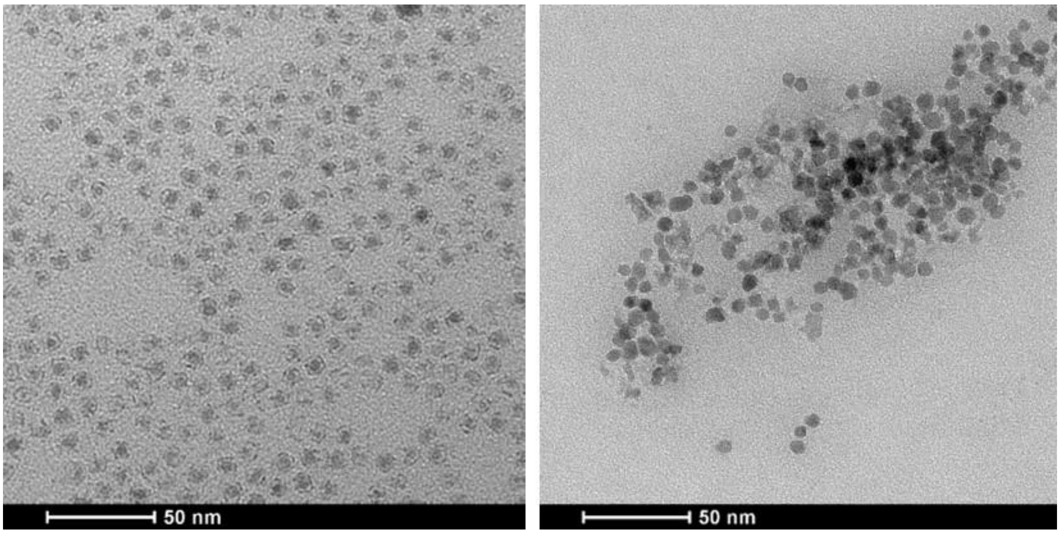


Figure S6. TEM images of $\mathbf{Cu_{1.00}Fe_{1.08}S_{0.56}Se_{1.42}}$ nanocrystals before (a) and after (b) the exchange of initial capping ligands for 11-mercaptoundecanoic acid (MUA).

References

(1) J. Park, K. An, Y. Hwang, J.-G. Park, H.-J. Noh, J.-Y. Kim, J.-H. Park, N.-M. Hwang, T. Hyeon, *Nat. Mater.*, 2004, **3**, 891-895.

(2) J.-J. Wang, Y.-Q. Wang, F.-F. Cao, Y.-G. Guo, K.-J. Wan, *J. Am. Chem. Soc.*, 2010, **132**, 12218-12221.

(3) G. Gabka, P. Bujak, A. Ostrowski, W. Tomaszewski, W. Lisowski, J.W. Sobczak, A. Pron, *Inorg. Chem.*, 2016, **55**, 6660-6669.