

Cu₂ZnGeSe₄ Nanocrystals: Synthesis and Thermoelectric Properties

Supporting Information

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Chemicals; Copper (I) chloride (reagent grade, 97%), Zinc Oxide (99.9%), 1-octadecene (ODE, 90%), oleic acid (OA, $\geq 99\%$), hexadecylamine (HDA, tech. 90%) were purchased from Aldrich. Germanium (IV) chloride (99.9999 %) and Selenium (IV) oxide (99.8%) was purchased from Strem. n-Tetradecylphosphonic acid was purchased from PCI Synthesis. Chloroform, isopropanol and ethanol were of analytical grade and obtained from various sources. All chemicals were used as received without further purification.

All synthesis were carried out using standard airless techniques: a vacuum/dry argon gas Schlenk line was used for the synthesis and a argon glove-box for storing and handling air and moisture-sensitive chemicals.

Selenium solution: Selenium (IV) oxide (6.67g, 60mmol) was dissolved under argon atmosphere at 190° in 75ml of 1-octadecene. The mixture was stirred additionally at 190 °C for 5 hours to obtain a perfectly clear brownish orange solution.

Synthesis of Cu₂ZnGeSe₄ NCs: Copper (I) chloride (50 mg, 0.50 mmol), Zinc oxide (41 mg, 0.50 mmol), hexadecylamine (242-1694 mg, 1-7mM), n-Tetradecylphosphonic acid (33mg, 0.1mmol) were dissolved in 10 ml ODE. The solution was heated under argon flow to 200 °C and maintained at this temperature during 1h to remove water and other low-boiling point impurities. Afterwards, the mixture was cooled down to 150 °C and Germanium (IV) chloride (54 mg, 0.50 mmol) dissolved in dried ODE was injected. Following the Ge injection we observe a clear blueish solution. The solution is kept at this temperature for an additional

30 minutes and finally heated to the reaction temperature. The selenium solution (4 mL, 3 mM) was rapidly injected through a septum into the reaction flask. In order to reduce the dropping in the temperature, selenium solution was previously heated up at 180 °C. Following the injection, the temperature dropped to around 260 °C and then slowly recovered to 295°. The solution was kept at a temperature between 260 and 295 °C for 5 min and then quickly cooled down. The formation of $\text{Cu}_2\text{ZnGeSe}_4$ could be qualitatively followed by the color change of the mixture from an initial light yellow to green and eventually black color of the solution containing the $\text{Cu}_2\text{ZnGeSe}_4$ NCs. 3 mL of oleic acid were added to the mixture during the cooling at ~70 °C to replace the weakly bound HDA. The crude solution was mixed with 10 ml of chloroform and sonicated for 5 minutes. The $\text{Cu}_2\text{ZnGeSe}_4$ nanoparticles were isolated by centrifugation at 4000 rpm during 5 minutes. The black precipitate was redispersed in chloroform (~20 ml) and sonicated for 5 minutes. Then the product was additionally precipitated by adding isopropanol (~10 ml) and centrifuging. The NCs were redispersed in chloroform (~5 ml) and stored for further use.

Preparation of Pellets: The same synthesis procedure was scaled up for the production of a few grams of nanoparticles. In the scaled-up synthesis procedure, 6 times larger amounts of all precursor, surfactant and solvent were used. The nanocrystals were thoroughly washed by multiple precipitation and re-dispersion steps. The final nanoparticles could not be redispersed in organic solvents, proving the high degree of surfactant removal. Washed nanocrystals were dried out from solution under argon atmosphere. Afterward, the nanocrystals were heated to 500 °C for 1 hour under an Ar flow inside a tube furnace. The annealed nanoparticles were ground into fine powder and then hot pressed under a pressure of 40 MPa at 500 °C for 5 min into 12 mm pellets. The hot pressing was carried out in a Rapid Hot Press (RHP) system (Aaron D. LaLonde, Teruyuki Ikeda, and G. Jeffrey Snyder, REVIEW OF SCIENTIFIC INSTRUMENTS 82, 025104 (2011)). In this system, the heat is provided by an induction coil operated in the RF range applied directly to a graphite die acting as a susceptor. This set up configuration allows increasing temperature at a similar rate than Spark Plasma Sintering (SPS). However, during RHP only the die body is heated inside the induction coil enabling faster cooling of the die and chamber. In our conditions, we increase temperature from room temperature to 500 °C in around 3 minutes under a load of 40 MPa. The density of the pressed pellets was in the range 92-96 % of theoretical value, measured by weight/volume.

Electrical conductivity and Thermopower Measurements:

The Seebeck coefficient was measured by using a static DC method. Electrical resistivity data were obtained by standard four-probe method. Both Seebeck coefficient and electrical resistivity

were measured simultaneously by using LSR-3 equipment (LINSEIS) in the range between room temperature up to 450 °C, under helium atmosphere.

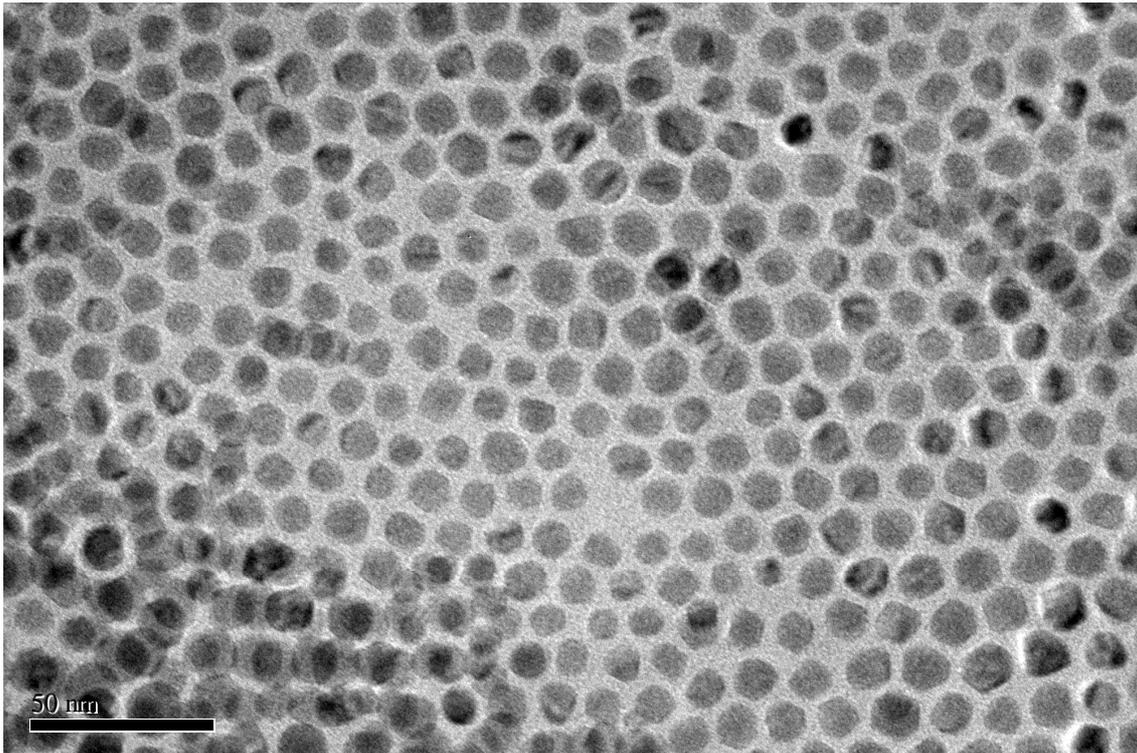
Thermal diffusivity measurement:

Thermal conductivity measurements were obtained from flash diffusivity measurements, using the mass density and the Dulong-Petit approximation for the specific heat capacity ($C_p = 0.34 \text{ J}\cdot\text{g}^{-1}\text{K}^{-1}$). The thermal conductivity was calculated as $\kappa = DC_p d$, where D is the thermal diffusivity, C_p is the heat capacity, and d is the density.

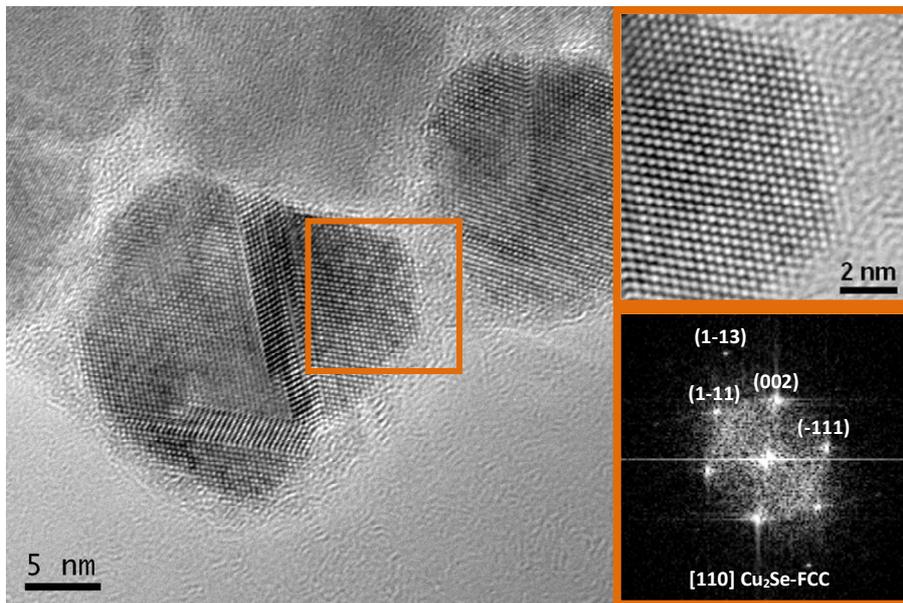
NCs formation mechanism

Nanocrystals were characterized by HRTEM, EDX and EELS. This set of characterization techniques revealed the compositional evolution of the nanoparticles with reaction time: upon injection, Cu_2Se spherical nanocrystals with the Berzelianite cubic structure (JCPDS 01-088-2043; space group, Fm3m) rapidly nucleated. The amounts of Zn and Ge detected by the EDX and EELS analysis were attributed to the presence of complexes of these elements on the surface of the nanocrystals. Moreover, the excess of selenium detected was also attributed to the unreacted species surrounding the nanoparticles. It should be pointed out here that the purification of these early-formed Cu_2Se nanocrystals was not an easy task as a result of the large amount of unreacted complexes covering the nanoparticles. During the first few minutes of reaction, Zn and Ge ions gradually entered into the nanocrystal structure, extending the unit cell along the c-axis into the double supercell characteristic of a tetragonal-symmetry structure with I42m space group (JCPDS 01-070-7623). After 5 min of reaction at 295 °C, the obtained nanoparticles already had the stoichiometric chemical composition: $\text{Cu}_2\text{ZnGeSe}_4$.

Images S3 and S4 display the compositional maps of different nanoparticles. In all the cases, it could be appreciate that Cu and Se are in the center of the particle with a strong signal, however Zn and Ge always are weaker in signal and appear everywhere, even where there is no particle. We attribute this effect to the unreacted complex.



S 1. TEM image of the nanoparticles after 10 s reaction time at 295°C.

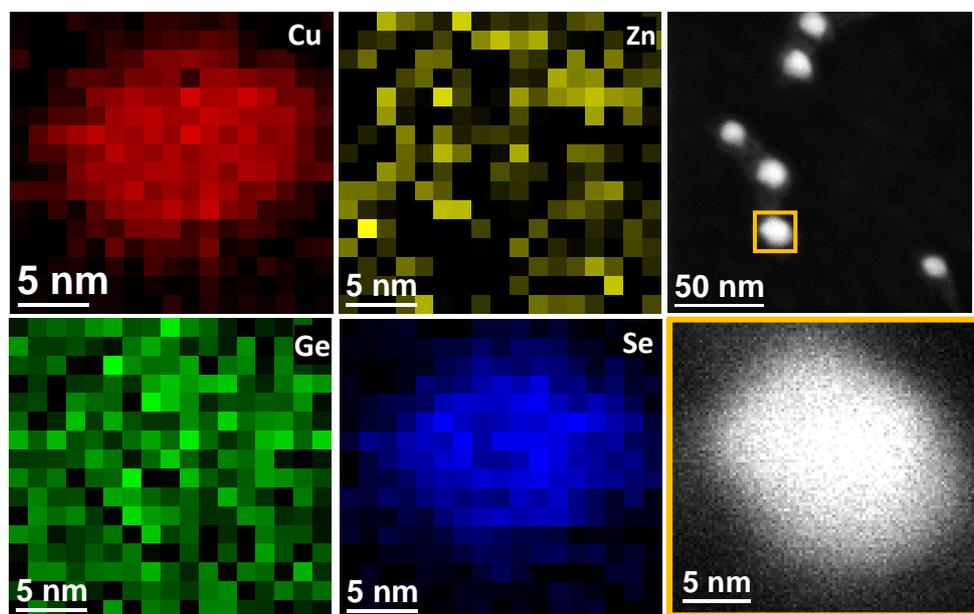


S 2. HRTEM image of the nanocrystals obtained after 10 s reaction time at 295 °C

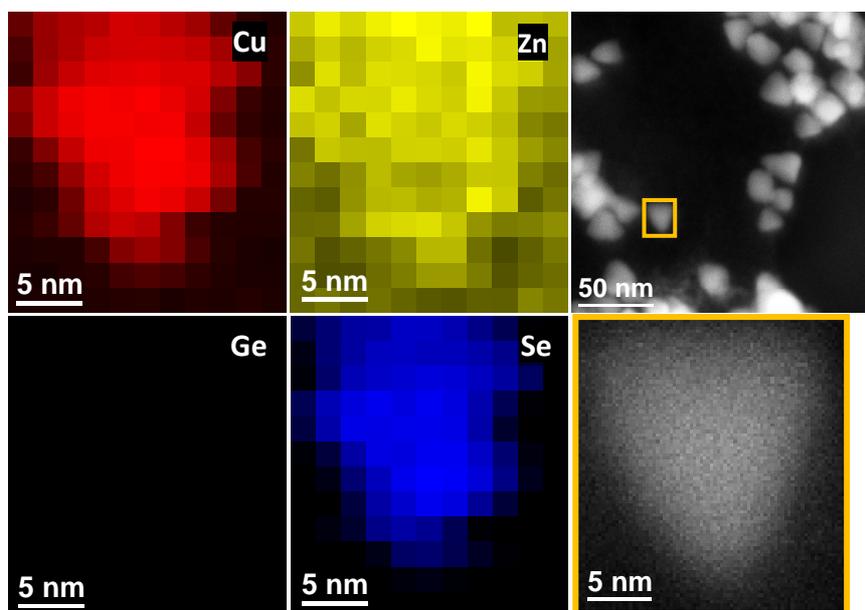
Table S1. Elemental composition measured by EDX and EELS of the $\text{Cu}_2\text{SnGeSe}_4$ nanoparticles obtained after 10 s and 300 s after the injection at 295 °C

	EDX (atomic %)	EELS (atomic %)
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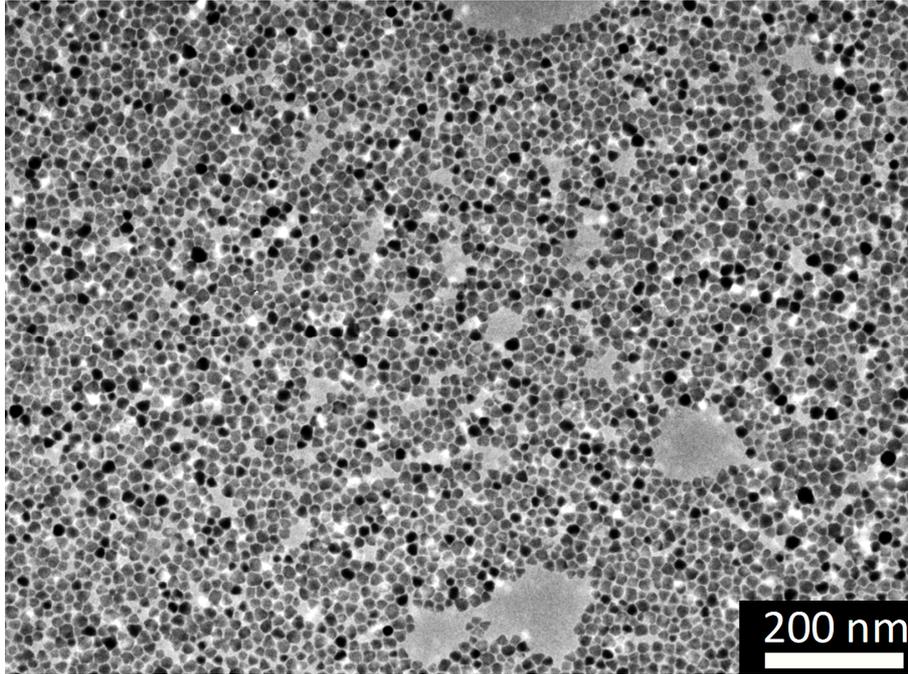
<i>Reaction time</i>	<i>10 s</i>	<i>300 s</i>	<i>10 s</i>	<i>300 s</i>
<i>Cu</i>	48	25	46	30
<i>Zn</i>	2	12	4	13
<i>Ge</i>	1	13	0	14
<i>Se</i>	49	50	50	43



S 3. HAADF image of a few and single nanoparticles and Cu, Zn, Ge and Se compositional maps of the same single particle obtained after 10 s



S 4. HAADF image of a few and single nanoparticles and Cu, Zn, Ge and Se compositional maps of the same single particle obtained after 10 s



S 5. Representative TEM micrograph of 13 ± 1 nm CZGS nanoparticles.