



# Colloidally stable selenium@copper selenide core@shell nanoparticles as selenium source for manufacturing of copper–indium–selenide solar cells



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## ABSTRACT

Selenium nanoparticles with diameters of 100–400 nm are prepared via hydrazine-driven reduction of selenious acid. The as-prepared amorphous, red selenium (*a*-Se) particles were neither a stable phase nor were they colloiddally stable. Due to phase transition to crystalline (trigonal), grey selenium (*t*-Se) at or even below room temperature, the particles merged rapidly and recrystallized as micron-sized crystal needles. As a consequence, such Se particles were not suited for layer deposition and as a precursor to manufacture thin-film CIS (copper indium selenide/CuInSe<sub>2</sub>) solar cells. To overcome this restriction, Se@CuSe core@shell particles are presented here. For these Se@CuSe core@shell nanoparticles, the phase transition *a*-Se → *t*-Se is shifted to temperatures higher than 100 °C. Moreover, a spherical shape of the particles is retained even after phase transition. Composition and structure of the Se@CuSe core@shell nanostructure are evidenced by electron microscopy (SEM/STEM), DLS, XRD, FT-IR and line-scan EDXS. As a conceptual study, the newly formed Se@CuSe core@shell nanostructures with CuSe acting as a protecting layer to increase the phase-transition temperature and to improve the colloidal stability were used as a selenium precursor for manufacturing of thin-film CIS solar cells and already lead to conversion efficiencies up to 3%.

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## 1. Introduction

Thin-film solar cells represent an important alternative to crystalline silicon solar cells. Here, the most efficient thin-film technology is related to CuInSe<sub>2</sub> (CIS: copper indium selenide) with record values above 20% if gallium is incorporated as well (CIGS: copper indium gallium selenide) [1]. Conventionally, CIS/CIGS layers are deposited by applying high-vacuum techniques. Besides thermal co-evaporation of the relevant elements, including selenium, sequential processes are often used, where typically Se is deposited by thermal evaporation as a thin top coating on a layer stack of Cu-/In-/Ga-containing precursors [2]. In a second step, these layers are chemically converted in a thermal process at 550–600 °C – called “selenization” – into the desired chalcopyrite structure of the CIS/CIGS absorber. Ideally the Se cap acts as a sufficient Se source during the annealing step. Usually, an additional

treatment in harmful H<sub>2</sub>S atmosphere is applied during the heating step to increase the electronic quality of the absorber layer [3].

In recent years, vacuum-free deposition of suitable precursor pastes has attracted increasing attention in view of low-cost high-throughput production of CIS thin-film solar cells [4,5]. One possibility for paste formulation is to use nanoparticles, which have already been reported for elemental metals (Cu, In, CuIn/Cu<sub>11</sub>-In<sub>9</sub>) [6–8], metal oxides [9], and metal selenides (CuInSe<sub>2</sub>, Cu<sub>2</sub>Se/CuSe, In<sub>2</sub>Se<sub>3</sub>) [10–13]. For reaching high efficiencies, the precursor layers were always annealed in a selenium vapour atmosphere to compensate for a possible loss of selenium during the heating step or to reach denser polycrystalline layers. So far, only conventional sources of selenium were investigated, either as an evaporated capping layer or as additional selenium vapour in the gas phase. The use of inks containing Se nanoparticles is, however, a kind of a missing link. The availability of colloidally stable Se inks would allow avoiding vacuum-techniques and gas-phase deposition completely. Ideally, just a simple heat treatment of the as-deposited particulate metal and selenium precursor layers could generate dense and crystalline CIS layers. This option is however hampered due to the room-temperature phase transition of selenium (31 °C

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for bulk-Se) [14]. As a consequence, Se particles are of limited colloidal stability in suspension and show rapid agglomeration and merging of particles, followed by re-crystallization of large crystal needles. Such Se particles are not suitable for layer deposition and manufacturing of thin-film solar cells.

In the following, we report on the synthesis of Se particles that are capped by CuSe to form Se@CuSe core@shell nanostructures. Based on this newly introduced CuSe capping, the phase-transition temperature of elemental selenium is shifted to >100 °C. As a result, colloidal stable suspensions of Se particles could be obtained and were manufactured - together with Cu<sub>11</sub>In<sub>9</sub> nanoparticles - in a first conceptual study via a vacuum-free process to CIS thin-film solar cells. The strategy of repelling the Se phase transition and increasing the colloidal stability by metal selenide cappings, more generally, can also be interesting for application of Se particles in mechanical sensors, electrical rectifier, xerography, or tumour therapy [15,16].

## 2. Experimental section

### 2.1. Materials, synthesis and thin-film deposition

**General considerations:** Selenious acid (H<sub>2</sub>SeO<sub>3</sub>, 98%), hydrazine monohydrate (N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O, 98%), copper(II) acetate (Cu(CH<sub>3</sub>COO)<sub>2</sub>, 98%) and polyvinylpyrrolidone (PVP, M<sub>w</sub> = 40,000) were purchased from Sigma-Aldrich. Diethylene glycol (DEG, C<sub>4</sub>H<sub>10</sub>O<sub>4</sub>, 99%) was obtained from Alfa Aesar. All chemicals were of analytical grade and used as received.

**Synthesis of Se@CuSe core@shell nanoparticles:** In a typical recipe, N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O (10–40 mmol, Table 1) and 200 mg PVP were added to 50 ml of DEG in a three-necked flask. This mixture was dispersed to form a homogeneous solution by constant stirring (solution I). Solution I was then cooled to 0 °C with an ice bath. Thereafter, 0.8 mmol of H<sub>2</sub>SeO<sub>3</sub> in 3 ml of DEG (solution II) were injected into the precooled solution I. The reaction was allowed to proceed for different periods of time (*t*, Table 1). The gradual colour shift from a colourless solution to an orange suspension allows following the course of the reaction even by the naked eye. Finally, all residual N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O in the reaction solution was removed by vacuum distillation for 30 min at 0 °C, followed by 150 min at room temperature. Thereafter, 0.04 mmol of Cu(CH<sub>3</sub>COO)<sub>2</sub> dissolved in 3 ml of DEG (solution III) were added dropwise. The addition of Cu(CH<sub>3</sub>COO)<sub>2</sub> again resulted in a colour change, from orange via orange-red to brick-red. Detailed information regarding the experimental parameters of the synthesis is listed in Table 1. Finally, the suspensions were diluted with demineralised water and the Se@CuSe core-shell nanoparticles were collected via centrifugation, washed three times with demineralised water, and then redispersed in demineralised water for further analysis and treatment.

**Preparation and processing of Se@CuSe inks:** Suitable suspensions of Se@CuSe nanoparticles were obtained by redispersing the as-

prepared powders in ethanol with a solid load of typically 200 mg ml<sup>-1</sup>. These precursor inks were prepared right before layer deposition in order to prevent particle agglomeration over time. Layer deposition was done via doctor blading, using an Erichsen film applicator and an adjustable blade by Zehntner, on Molybdenum covered sodalime-glass substrates of 1 mm thickness. Two different strategies were applied: Scenario 1 – Se@CuSe nanoparticles were co-dispersed with Cu<sub>11</sub>In<sub>9</sub> nanoparticles in ethanol and deposited thereafter to form a mixed Se@CuSe/Cu<sub>11</sub>In<sub>9</sub> nanoparticle film. Scenario 2 – Alternatively, a Cu<sub>11</sub>In<sub>9</sub> layer was deposited first, followed by a stacked layer of the Se@CuSe nanoparticles on top of the Cu<sub>11</sub>In<sub>9</sub> particle film. The synthesis of the Cu<sub>11</sub>In<sub>9</sub> nanoparticles was performed as described in [8].

**Selenization of thin-films and solar cell preparation:** To convert the precursor films to chalcopyrite-type CIS absorber layers, selenization of the thin-films was performed in a tube furnace at 550 °C, eventually in nitrogen-diluted selenium vapour, as described in [8]. The CIS absorber layers were further treated by selective KCN etching to remove undesired binary CuSe phases, which would typically lead to shunted cell behaviour due to its good conductivity. The CIS absorber layers were finally completed by a wet-chemically processed CdS buffer layer, a sputtered ZnO buffer layer (*i*-ZnO) and a transparent ZnO:Al front-contact layer to obtain functional solar cells using standard procedures as described in [17].

### 2.2. Materials characterization and analytical tools

**Dynamic light scattering (DLS)** was performed with a Nanosizer ZS from Malvern Instruments (equipped with a He-Ne laser emitting at 633 nm), detection via non-invasive back-scattering at an angle of 173 °, 256 detector channels, polystyrene cuvettes). For analysis, the as-prepared Se@CuSe nanoparticles were redispersed in demineralised water by ultrasonic treatment for 15 min.

**Scanning electron microscopy (SEM)** was performed on a Zeiss Supra 40 VP, using an acceleration voltage of 20 kV and a working distance of 2 mm to analyse the size distribution and shape of the Se@CuSe nanoparticles. All samples were prepared by evaporating a single drop of a dispersion of the as-prepared Se@CuSe nanoparticles in demineralised water at room temperature in air. The thin-film morphology of precursor layers, selenized layers and completed solar cells were studied with a XL30 SFEQ Sirion from FEI Company, using a 5 kV acceleration voltage and working distances of 5.9, 4.3 and 3.4 mm.

**Scanning transmission electron microscopy in the high-angle annular dark-field mode (HAADF STEM)** was conducted with an aberration-corrected FEI Titan<sup>3</sup> 80–300 at 300 kV. Samples for STEM were prepared by evaporating water-based suspensions on an amorphous carbon (Lacey-) film copper grid.

**EDXS line profiles** were recorded with an FEI Titan<sup>3</sup> 80–300 microscope by applying a drift-correction routine via cross correlation of several images, which yields a local precision better than

**Table 1**  
Experimental conditions to adjust the mean size of Se@CuSe core@shell nanoparticles.

Sample	N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O (mmol)	H <sub>2</sub> SeO <sub>3</sub> (mmol)	$\frac{c(\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O})}{c(\text{H}_2\text{SeO}_3)}$ <i>r</i> *	Reaction time <i>t</i> * (min)	Cu(Ac) <sub>2</sub> (mmol)	Average diameter (nm)**
A	10	0.8	13	90	0.04	410(90)
B	20	0.8	25	90	0.04	310(63)
C	20	0.8	25	75	0.04	179(48)
D	20	0.8	25	30	0.04	162(48)
E	40	0.8	50	30	0.04	100(27)
F	40	0.8	50	30	0.16	105(29)

(\*: Molar ratio of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O and H<sub>2</sub>SeO<sub>3</sub>).

(\*): Reaction time of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O and H<sub>2</sub>SeO<sub>3</sub>.

(\*\*): Mean diameter according to DLS).

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