Determination of the Molar Extinction Coefficient of Colloidal Selenium for Optical Characterization of Stabilized Nanoparticulate Dispersions

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Abstract
To prepare fully printed copper-indium-diselenide solar-cell-absorbers it is necessary to have well defined and printable precursor-inks. In this work, the synthesis and different approaches for the colloidal stabilization of Selenium (Se) nanoparticles are presented, which should ultimately serve as a selenium source for CISe absorbers. The produced particles were stabilized with different concentrations of Polyvinylpyrrolidone (PVP) and micelles (TX100) respectively. The resulting suspensions were analyzed in aspect of particle size and colloidal stability using dynamic light scattering (DLS). It was shown, that both approaches lead to stable colloidal suspensions with ca. 80 - 100 nm particle size. The PVP stabilized suspension stays stable for four weeks at a Zeta potential of > 35 - 25 mV whereas the TX100 stabilized suspension was only short-time-stable due to loss in Zeta potential over time. UV/VIS spectroscopy and Lambert-Beer’s law were used to determine the concentration of Se in the dispersion. The molar extinction coefficient \( \epsilon \) of colloidal selenium was calculated to be \( 1.44 \times 10^3 \text{ l/(mol·cm)} \) for \( \epsilon (\text{Se}) \) respectively \( 2.63 \times 10^7 \text{ l/(mol·cm)} \) for \( \epsilon (\text{Se-NP}) \pm 9 \% \) in both cases.

Highlights
- Evaluation of PVP vs. TX100 micelles as particle stabilizer
- Determination of Se concentration in dispersion via UV/VIS spectroscopy
- Determination of molar extinction coefficient of colloidal Selenium

Introduction
CuInSe₂ (CISe) materials have become very attractive as absorber layer for thin film solar cells, due to a suitable band gap, a high extinction coefficient and good materials stability [1-5]. Different approaches to produce CISe via co-evaporation, pulsed Laser deposition or sputtering have been reported [6-8]. Due to process complexity and the problem of scaling up the process various non-vacuum approaches have been suggested: the Selenium integrated at a temperature of ~ 450°C [9]. This procedure holds highly toxic H₂Se and is potentially explosive, due to free hydrogen. Therefore the preparation of a solid Se film via sputtering, electrochemical deposition or evaporation has been considered [10-14]. So far, these approaches lead to a poor intermixture of Se and Cu-In [15]. Recent research was conducted on all-printable precursors using bimetallic Cu-In nanoparticles [16]. Such precursors may be mixed and subsequently printed, leading to a well distributed (Cu+In):Se ratio. A method to precisely monitor and tune the molar composition of the dispersion and in particular the Se content would be beneficial.

In the present work the optical transmission of Se dispersions in combination with Lambert-Beer’s law is used to determine the concentration of Se in the dispersions. To apply the Lambert-Beer’s law accurately, knowledge about the molar extinction coefficient is necessary. However, hardly any data are available in literature for nanoparticulate Se dispersions. To determine the molar extinction coefficient of colloidal Se we have prepared a series of Cu-In + Se dispersions with varying Se concentrations. To determine the (Cu+In):Se ratio, layers were deposited and characterized using energy dispersive X-ray spectroscopy (EDX). In parallel optical transmission/extinction of the Se dispersion was determined by UV/VIS spectroscopy. Using Lambert-Beer’s law the molar extinction coefficient was deduced from the experimentally determined Se concentration and optical absorbance.

A commonly used synthesis route of Se nanoparticles is to

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precipitate Se-NP at room temperature and ambient pressure conditions from a Na₂SeSO₃ solution by adding HCl [17,18]. Various approaches to stabilize Se nanoparticles have been investigated to prevent agglomeration [19-21]. In this work, the stabilization of chemically synthesized Se-NP is achieved by using Polyvinylpyrrolidone (PVP) and Triton x100 Micelles (TX100) respectively. The concentrations of PVP and TX100 were varied for different syntheses and the resulting particles were analyzed using dynamic light scattering (DLS) for mean particle size and Zeta potential measurements. Using the above mentioned UV/VIS spectroscopy and Lambert-Beer’s law to determine the Se concentration a relatively simple, time saving and reliable method was implemented in the deposition process of well defined, fully printable Se precursors. A scheme of the desired experimental process can be seen in figure 1.

**Experimental**

\( \text{Na}_2\text{SO}_3 \) (≥ 98.0%, dehydrated, Sigma Aldrich), Se powder (≥ 99.5%, Sigma Aldrich), Polyvinylpyrrolidone (PVP, 10000 g/mol, Fluka Analytical), Polyethylene-glycol-tert-ocytophenyl-ether micelles (TX100) (Triton x100, laboratory grade, Sigma Aldrich), Hydrochloric acid (HCl) (Merck, 37% fuming) and Trisodium-citrate (Merck, 37% fuming) and Trisodium-citrate (Merck, dehydrated) were used as received without further purification for the experiments. Cu-In particles for the determination of the Molar Extinction Coefficient of Colloidal Selenium for Optical Characterization of Stabilized Nanoparticulate Dispersions. Int J Nanoparticles Nanotech 2:006

\( \text{Se} + \text{HCl} \rightarrow \text{Se}^+ \text{Cl}^- \)

The nanoparticles were fabricated from a 0.127 mol/l Na₂SeSO₃ solution [17]. This solution was prepared by dissolving 15.0 g of Na₂SO₃ in 200 ml of deionized water at a temperature of 80°C under constant stirring. To prevent evaporation of the solvent, a water cooled reflux condenser was attached. Once the solution was clear 2.0 g of Se powder were added. Referring to Stroyuk et al. [18] the following reaction takes place forming Na₂SeSO₃.

\( \text{Na}_2\text{SO}_3 + \text{Se} \rightarrow \text{Na}_2\text{SeSO}_3 \)

The solution was stirred at 80°C for 24 hours before being used as storage-batch-solution for the nanoparticle synthesis itself.

Several syntheses were carried out using different concentrations of PVP and TX100 respectively. Concentrations of 0.675 - 2.7 mmol/l for PVP and 2 - 63.3 mmol/l for the TX100 were implemented. For the syntheses with PVP, 0.306 - 1.225 g trisodium-citrate was added as an acidic buffer. For all syntheses, the respective stabilizer was first dissolved in 65.0 ml deionized water for PVP or in 25.0 ml for TX100 so fewer micelles achieve the desired concentrations. AVWR pH 100 mobile pH-meter with temperature sensor was attached to measure the pH to ~10 and the temperature significantly above room temperature. The reaction solution was then kept stirring until it cooled down to room temperature naturally. To initialize the Se nanoparticle precipitation, HCl was added successively in 5 ml steps until the pH reached a value of ≤ 0.5. The solution turned from clear to an orange-red murky solution in every performed synthesis. The solution was stirred for 1 hour after which the pH reached ca. -0.05. Subsequently, the solution was centrifuged at 12500 rpm for 20 minutes at 10 °C to extract the nanoparticles. After washing the Se-NP with 100 ml deionized water, thus re dispersing them, the dispersion was neutralized using the pH-meter and 1 M NaOH solution and centrifuged again. For further experiments and the application as printable Se precursor for thin-film CISe solar-cells the nanoparticles were concentrated and stored in dispersion. For the characterization of the nanoparticles 30 μl of the particle solution was placed in a 10x10 mm² cuvette and diluted with 3 ml of deionized water.

**Se nanoparticle characterization**

The size, size distribution and Zeta potential of the particles in the diluted dispersions were determined by Dynamic Light scattering (DLS) using a MALVERN Zetasizer Nano ZS. Differently stabilized samples were measured over a time period of 4 weeks storage to observe aging stability of both stabilizers.

To determine the concentration c of Se in the syntheses, 20.0 ml of a Se dispersion was mixed with 100.00 mg Cu-In Nanoparticles, and analyzed using energy dispersive X-ray spectroscopy (EDX) with an accelerating voltage of 20 kV in a Jeol JSM 6400 Scanning Electron Microscope.

The transmission of freshly synthesized, PVP-stabilized
dispersions was measured between 350 nm and 750 nm using a Perkin Elmer Lambda 950 UV/VIS spectrometer. For the measurement 30 µl of the respective Se nanoparticle dispersion was placed in a 10 × 10 mm² cuvette and diluted with 3 ml of deionized water. To reduce scattering effects and to use the measurements as a potential cross reference to determine the Se concentration, the measurement was conducted in an integrating sphere.

For the determination of particle morphology scanning electron microscopy (SEM)-images were taken, using a Zeiss FESEM ultra 55 with an acceleration voltage of 5 kV.

**Results and Discussion**

**Particle stabilization**

After several preliminary tests to optimize the different stabilizer concentrations, the characterizations were conducted on samples prepared with 1.35 mmol/l PVP or 63.3 mmol/l TX100. Other samples with lower concentrations agglomerated within a very short time and therefore were not investigated. To control colloidal stability the Zeta potential was measured over a time of 4 weeks (Figure 2).

The Zeta potential stays below -30 mV during the first week of storage. After four weeks, the TX100 stabilized particles agglomerate and do not remain colloidal because of the Zeta potential decrease to -1.6 mV. The PVP stabilized particles however remain stable which is reflected by a Zeta potential of -20 mV after four weeks of storage.

This could be explained by the stabilization principle of the respective stabilizer. Polymers, such as PVP, attach themselves to the particles leading to a permanent chemically bound hull. Micelles however form an electrostatic cage around the particles due to a energetically favorable balance between enthalpy and entropy. The Se particles however seem to be able to migrate through the micelle membrane leading to particle growth. Therefore this stabilization principle is apparently not convenient for Se nanoparticles over a longer period of time since the tendency of particle growth and agglomeration seems to be stronger than the electrostatic shielding of the micelles. In conclusion, the protecting layer of PVP seems to be much more impermeable, which is supported by the relating growth mechanisms shown by Shin et al. Therefore the following experiments to find out the molar extinction coefficient of colloidal selenium was performed with PVP stabilized dispersions.

**Particle size**

The particle size was determined with DLS by measuring the prepared samples over a period of four weeks (Figure 3). The freshly prepared and immediately measured PVP stabilized particles had size of ~80 nm with an obvious size distribution between 30 and 110 nm. All other PVP stabilized particles had a size of ~100 nm and a much smaller size distribution. The micelle stabilized particles also had a size of ~100 nm when measured freshly after preparation and after 1 week of storage. After 4 weeks of storage however, they showed an increase of size to ~450 nm.

Apparently, the PVP stabilized particles are much smaller at the beginning of the precipitation and grow until the equilibrium between growth tendency and stabilization is reached. The growth mechanisms of PVP stabilized particles has been well investigated by different research groups. The reason why the micelles do not show a size shift after being freshly synthesized could be explained with the critical micelle concentration (cmc). The used concentrations are all above the cmc which means, the shielding hull of the micelles have already formed and the particles can grow within them.

To confirm these results and to show the morphology of the synthesized particles, SEM pictures were taken. Particles stabilized with PVP (Figure 4) are spherical and fairly distributed particles.
which maintain this shape even after 4 weeks of storage time. However, the particles are rather sensitive concerning the stability of their shape. When applying higher acceleration voltages, the particles start to sinter. This effect intensifies with longer storage time. This is attributed to a decrease in particle stability over time, most likely due to particle ripening.

The same effect can be observed for the TX100 stabilized particles (Figure 5) but with an even higher tendency to sinter under the SEM. However, the structure was more spattered and the agglomeration/ripening process was much faster which can be seen after 4 weeks of storage. The particles are clustered to big µm sized structures and even form large needle like structures that start to become visible after the first week of storage. This can be explained by the assumed loss of colloidal stability due to the lack of stabilization potential of the micelles.

**Optical properties**

Due to their higher colloidal stability and application potential, only the PVP stabilized Se particles were evaluated concerning their optical properties. The objective was to look for a correlation between UV/VIS extinction behavior and particle concentration. According to the Lambert-Beer-Law the extinction $E$ is defined as:

$$E = -\log T = \varepsilon \cdot c \cdot d$$  \hspace{1cm} (1)

$T$ being the measured transmission, $\varepsilon$ the molar extinction coefficient, $c$ the concentration of Se and $d$ the path length which the light travels through the material, with our measurement setup 10 mm. To our best knowledge and literature search, there are no values for the molar extinction coefficient $\varepsilon$ for colloidal Se available so far. By rearranging the Lambert-Beer’s law it can provide $\varepsilon$, if the concentration is given:

$$\varepsilon = -\frac{\log T}{c \cdot d}$$  \hspace{1cm} (2)

To determine the concentration $c$, a mixture of Se and Cu-In nanoparticles was prepared and analyzed using EDX. Since we used well defined amount of Cu-In, it can be used as a reference to determine the Se amount in the mixture. Table 1 shows the atomic ratios of four samples.

| Sample no. | Mean ratio Cu in At.% | Mean ratio In in At.% | Mean ratio Se in At.% | Calculated Se yield in mg |
|------------|-----------------------|-----------------------|-----------------------|---------------------------|
| 1          | 31.50                 | 30.70                 | 37.74                 | 140.22                    |
| 2          | 33.24                 | 37.09                 | 29.66                 | 89.13                     |
| 3          | 32.07                 | 39.00                 | 28.93                 | 79.82                     |
| 4          | 31.22                 | 36.48                 | 32.30                 | 99.65                     |

Table 1: Atomic ratios of different Se synthesis mixed with Cu-In nanoparticles measured via EDX.

Figure 4: SEM pictures of Se particles, stabilized with PVP after 1 week (A,B) and 4 weeks (C,D) of storage. In the pictures B and D, a footprint of sintermarks can be seen where the picture with higher magnification was taken.
Apart from sample 1, the ratios are relatively constant, although sample preparations and syntheses were the same. In conclusion, we have a theoretical Se input of 250.00 mg and a mean particle outtake of 102.21 mg, leading to a mean efficiency for the synthesis of 41%. This value is rather low since there was no obvious loss of particles during the preparation. It could result from an incomplete conversion of selenium into particles. This aspect is due for further investigation and research, for the synthesis to become more efficient.

After determination of the concentration the transmission was measured using UV/VIS spectroscopy inside an integrating sphere. Figure 6 shows the absorbance of samples 1-4 and a reference sample that contained no Se nanoparticles.

The absorbance of sample 1 is significantly higher than the other three which was expected due to the higher amount of Se. Sample 2 shows less absorbance than sample 3, although it has a larger amount of Se in dispersion. The reference sample without Se nanoparticles does not show any influence on absorbance.

From the shape of the UV/VIS spectra it is possible to draw conclusions about the particle size as smaller particles show a steeper curve and more total absorbance in the shown wavelength range than larger particles [26]. Sample 2 therefore has slightly larger particles than the others, sample 1 has the smallest particles. However all samples were freshly synthesized and are expected to show a particle size distribution similar to the one seen in Figure 3 (PVP, fresh) with a particle size of ca. 80 nm. Depending on the time that passed between synthesis and measurement, the size distribution had slightly changed, and interferes with the concentration dependence, especially when the concentration is only changed a little bit. Larger particles or agglomerates appear as a lower concentrated dispersion than smaller and dispersed particles.
The molar extinction coefficient $\varepsilon$ of colloidal Se at this specific wavelength is calculated (Table 2) by taking the concentration of each dispersion and the respective extinction at a wavelength of 400 nm and insert all values into the Lambert-Beer law (equation 2). Moreover the amount of substance of the selenium colloids (80 nm diameter) was calculated for each sample to determine the extinction coefficient of the colloids. The sample thickness was the standard 10 mm cuvette.

The calculations lead to an average value for $\varepsilon$ of 1.44 $\times$ 10³ l/(mol·cm) and the fit passes through the origin, thus satisfying the Lambert-Beer law.

The deviation error could result from measurement errors in the UV/VIS spectrometer and/or impurities in the samples. Another source of error could be the fact, that the stabilizer is still attached to Se-NP. Moreover the particle size plays an important role for the UV/VIS measurements, showing a blue shift of the UV/VIS spectra. But the polymers and micelles in absence of surfactant assistance synthesis and spectroscopic characterization of selenium nanoparticles in ambient conditions. Nanotechnology: 19.

Conclusions

Se nanoparticles were synthesized by preparing a solution of Na$_2$SeSO$_3$ and then precipitated from that batch solution using HCl. The Se nanoparticles were stabilized with PVP and TX100, which led to well dispersed suspensions. DLS measurements showed that both approaches generated particle sizes of about 80 - 100 nm with relatively low size distribution. Additionally, DLS revealed a high Zeta potential for both stabilization approaches of > 35 mV indicating a good stability of the dispersions. However, compared to TX100 stabilized particles, PVP stabilized particles showed a better stability with almost no change in size and Zeta potential during a storage period of 4 weeks. The TX100 samples destabilized during this aging period, resulting in the loss of Zeta potential and leading to bigger particles of around 450 nm. The stability and size of the particles were also investigated by taking SEM images of freshly prepared samples and after four weeks of storage. Stabilization with PVP led to stable spherical particles while stabilization with TX100 led to rather scattered, less stable particles which had a tendency of coagulation and formation of Se needles.

For any further processing of Se nanoparticles, especially for application as Se source for printable CIS absorbers, it is necessary to know the concentration of the dispersion. A new and rather simple approach of determining the concentration by applying UV/VIS spectrometry and Lambert-Beer’s law has been developed. EDX measurements have been conducted to measure the concentration in different Se dispersions. By measuring the transmission of these samples, the Lambert-Beer law was applied to determine the molar extinction coefficient of Se, which was calculated to be 1.44 $\times$ 10³ l/(mol·cm) for $\varepsilon$ respectively 2.63 $\times$ 10⁷ l/(mol·cm) for $\varepsilon$ (Se-NP) ± 9 % in both cases. This allows to determine the Se concentration in dispersions in a very quick and simple fashion. It herewith allows to adjust the exact desired ratios in mixtures of Se with other particles or different dispersions. The experiments also revealed that the described synthesis has an efficiency of ca. 40 %.

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