Dalton Transactions

PAPER

RSCPublishing

View Article Online View Journal

Cite this: DOI: 10.1039/c3dt50757b

Received 20th March 2013, Accepted 18th April 2013 DOI: 10.1039/c3dt50757b

www.rsc.org/dalton

Introduction

The formation of sterically stabilized colloidal nanocrystals from metalorganic complexes in reaction mixtures containing metalorganic precursors has seen a tremendous evolution over the last 20 years.¹ Introduced by Murray et al.² and Brust et al.³ to make cadmium chalcogenide and gold nanocrystals, respectively, the approach was rapidly extended to the synthesis of nanocrystals of various metals, metal oxides and semiconductor materials.⁴ Apart from this versatility, improvements of the method led to an excellent control over the nanocrystal size, resulting in colloidal suspensions with size dispersions of 5% or less. Moreover, the use of specific ligands during the synthesis enabled nanocrystals with a variety of shapes to be grown, including cubes,^{5,6} rods,^{7,8} multipods^{9,10} and platelets,¹¹ and it proved possible to form heterostructures, where, e.g., a second material is grown as a shell around initial core nanocrystals.^{8,12} Next to this, the synthetic approach resulted in dispersed nanocrystals with a welldefined and adjustable surface chemistry.¹³ This gives access to extensive post-synthesis processing, including the formation of nanocrystal assemblies by solution-based deposition techniques, such as spin coating and inkjet printing,¹⁴ and the chemical functionalization of nanocrystals to make them active towards biomolecules or analytes.¹⁵ As a result, applications of colloidal nanocrystals are actively explored in diverse fields such as biolabeling and biosensing,¹⁵ photovoltaics16 and opto-electronics.17-19

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In the case of semiconductor materials, the combination of synthetic control and a suitability for solution-based processing leads to roughly two types of applications. First, quantum confinement leads to a size-dependence of the opto-electronic properties, most notably the band gap, of semiconductor nanocrystals once their dimensions are reduced to ≈10 nm or less.²⁰ With size dispersions of 5% or less, this leads to materials having a well-defined onset wavelength for light absorption and a narrow light emission spectrum, both easily tunable by the nanocrystal size. In the case of CdSe and InP, for example, saturated emission colors can be obtained throughout the visible spectrum, while the bandgap of PbS or PbSe can be adjusted in the infrared,²¹ e.g., to reach the optimum range for photovoltaic energy conversion. As a result, the use of these materials extends from lighting^{22,23} and display¹⁷ applications to luminescent labeling,^{15,24} photodetection^{25,26} and photovoltaics.^{16,27} Second, dispersions of semiconductor nanocrystals can be seen as precursors for the formation of semiconductor thin films by solution-based processes. Especially in the field of thin film photovoltaics, various studies have addressed the formation of absorber layers, including CdTe,²⁸ Cu(In,Ga)(S,Se)₂ (CIGS)²⁹ or Cu₂ZnSn- $(S,Se)_4$ (CZTS)³⁰ by depositing colloidal nanocrystals, followed by a heat treatment to densify the resulting nanocrystal film. For both types of application, metal selenides are a widely used class of materials. In the case of light emission, CdSebased heteronanocrystals have been the most widely used nanocrystals, while ZnSe forms a so-called type 2 heterostructure with CdS that is useful in lasing applications.³¹ The use of CIGS and CZTS as absorber materials in thin film photovoltaics, on the other hand, raises interest in all metal selenide nanocrystals from Cu, In, Ga, Zn and Sn or the relevant ternary and quaternary combinations thereof.

Synthesis of metal selenide colloidal nanocrystals

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We describe the synthesis of metal selenide nanocrystals, including CdSe, ZnSe, CuInSe₂ and Cu₂(Zn,Sn)-

Se₄, by the hot injection of selenium powder dispersed in a carrier solvent. Since this results in a fast and

high yield nanocrystal formation, we argue that the approach is well suited for the low cost, large

by the hot injection of selenium powder

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volume production of nanocrystals.

With the increasing use of colloidal nanocrystals, the volume and concomitantly, the cost of production have become the subject of intense research.^{32–35} Apart from issues

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of synthesis methodology, this involves a search for alternative precursors that can reduce various aspects of the synthesis cost, such as reagent cost, the need for protective atmosphere, purification cost, waste management, etc. In the case of metal selenide nanocrystals, the initial CdSe synthesis for example was based on dimethyl cadmium and trioctylphosphine selenide (TOP-Se) or bis-trimethylsilyl selenide as the cadmium and selenium precursors, respectively.² While dimethyl cadmium was quickly replaced by cadmium carboxylate or cadmium phosphonate complexes,^{36,37} few alternatives have been developed for the selenium precursor. An example is the use of elemental selenium dissolved in a solvent such as octadecene (ODE) at elevated temperature, either using a hot injection or a heating-up approach.^{38,39} Whereas elemental selenium is cheap and easy to handle, the formation of CdSe nanocrystals based on this so-called ODE-Se precursor is slow and does not allow - opposite to TOP-Se based syntheses - for the full yield synthesis of CdSe NCs with different sizes. In fact, although expensive and oxidation prone, phosphine selenides such as TOP-Se remain widely used Se precursors for the synthesis of metal selenide nanocrystals, including - next to CdSe – for example ZnSe,⁴⁰ CuInSe₂^{41,42} and Cu₂(Zn,Sn)Se₄.⁴³

Here, we introduce the direct injection of Se powder - heterogeneously dispersed in a carrier solvent such as ODE - as an alternative precursor for the synthesis of colloidal metal selenide nanocrystals. Taking the synthesis of CdSe as a first example, we show that this injection initiates a fast reaction leading to the formation of CdSe nanocrystals with an 80-90% reaction yield within 5-10 minutes. Moreover, the reaction can be executed under air without compromising the quality of the end product. In a second step, we show how the same approach can be extended to the formation of nanocrystals of ZnSe, and various binary, ternary and quaternary selenides of the CIGS and CZTS materials family, including CuInSe₂, the binary compounds Cu₂Se and In₂Se₃ and Cu₂ZnSnSe₄. Also here, we typically find that the injection of Se powder initiates a fast (<10 min) and almost complete conversion of the precursors into nanocrystals. Using various literature examples, we show that the typical features of the reaction following the hot injection of selenium powder, i.e., fast and high yield conversion, contrast with current synthesis methods where elemental selenium is used. Based on this, we argue that the approach presented here is well suited for the high volume, low cost synthesis of metal selenide nanocrystals.

Experimental

All nanocrystal syntheses have been executed as described in the respective sections. After synthesis, nanocrystal purification is achieved by standard precipitation methods using methanol or methanol–isopropanol mixtures as the nonsolvent and toluene as the solvent. The quantitative analysis of the reaction development is based on the weight of the reaction mixture and of the different aliquots taken. The amount of product formed in the aliquots is either determined using

UV-Vis absorption spectroscopy⁴⁴ (CdSe) or X-ray fluorescence spectroscopy (CuInSe₂). The final reaction yield is obtained from the amount of unreacted precursors as determined using XRF in the supernatant after purification of the reaction product. For UV-Vis analysis (Perkin-Elmer lambda 950), published sizing curves and absorption coefficients are used.⁴⁵ For quantitative XRF analysis (Rigaku NEX CG), UltraCarry's® have been used to measure the liquid samples. A series of standard samples, in the same range of concentrations as the supernatant and the particle solutions, have been made making use of chloride salts and selenious acid solutions. The X-ray fluorescence intensities have been used to make a calibration curve and subsequently determine the concentration of the elements in the samples. X-ray diffraction (XRD) measurements were carried out using a Thermo scientific ARL X'TRA model on dried dispersions dropcast on silica substrates. Transmission electron microscopy (TEM) micrographs were acquired using a Cs-corrected Jeol 2200 FS microscope. Rutherford backscattering spectrometry (RBS) was performed as described before.46 RBS samples were made by spincoating a thin layer of nanocrystals on silicon. Quantitative ¹H nuclear magnetic resonance (NMR) spectra were taken as described before.⁴⁶ NMR samples were prepared by dissolving a known amount of QDs in toluene- d_8 .

Results

CdSe nanocrystals

For a standard CdSe nanocrystal synthesis, a mixture of CdO (0.4 mmol), a carboxylic acid (CA) such as myristic acid (MA, 1.2 mmol) and ODE (10 mL) is heated up to 270 °C under air, resulting in the dissolution of CdO by the formation of a cadmium carboxylate complex. The reaction is initiated by the injection of Se powder (0.2 mmol, 200 mesh), heterogeneously dispersed in 1 mL of ODE. To uniformly distribute the Se powder over the carrier liquid, the mixture is permanently stirred before injection, yet no attempt was made to dissolve the Se powder by heating. Upon injection, the black color of the Se powder disappears and, leaving the reaction mixture at 260 °C, it gradually changes color from yellow to orange to red within a few minutes time. Fig. 1a shows a TEM micrograph of the product obtained after 5 minutes of reaction followed by successive precipitation/redispersion steps. Here, we first use a methanol-isopropanol mixture as the non-solvent and a toluene-oleic acid (OA) mixture as the solvent, followed by two more precipitation/redispersion steps using methanol and toluene as the respective non-solvent and solvent. The micrograph clearly shows the formation of quasi-spherical nanoparticles, which have according to X-ray diffraction (see Fig. 1b) the crystal structure of zinc blende CdSe.

To follow the reaction development, we took aliquots of the reaction mixture that were quantitatively analysed using UV-Vis absorption spectroscopy to obtain the amount n_{CdSe} of CdSe formed and the nanocrystal diameter d_{NC} .⁴⁴ As shown in Fig. 1c, the absorption spectra show the succession of peaks

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Fig. 1 (a) TEM micrograph of CdSe nanocrystals as formed by the injection of a Se powder into a solution of cadmium myristate, myristic acid and octadecene. Scale bar: 10 nm. (b) X-ray diffractogram of the CdSe nanocrystals thus formed. The vertical lines indicate the most important reflections of zinc blende CdSe. (c) Normalized absorption spectra of purified aliquots taken at the indicated time after starting the reaction by the injection of a Se powder. (d) Time development of the amount of CdSe and the average nanocrystal diameter d_{NC} as calculated from the absorption spectra shown. The dashed line indicates the 100% yield level, corresponding to 0.2 mmol of the injected Se.

characteristic of size quantization in semiconductor nanocrystals. The red shift of these features - most notably the longest wavelength peak related to the band gap transition - reflects the nanocrystal growth as a function of time, from ≈ 2.6 nm after 5 s to \approx 3.1 nm after 5 min (see Fig. 1d). Importantly, the red shift of the absorption features stops within 5 min of reaction time, where $d_{\rm NC}$ attains a constant value for a reaction yield of \approx 80%. Hence, we conclude that the injection of Se powder into a mixture of ODE, a cadmium carboxylate and excess CA leads to the rapid and almost complete conversion of the Cd and Se precursors into CdSe nanocrystals. Moreover, the size dispersion of the resulting nanocrystal suspensions as determined from the full width at half maximum of the first absorption feature and the diameter histogram as obtained from TEM micrographs - amounts to 5-6% or less. This is comparable to the numbers obtained using TOP-Se as a Se precursor,⁴⁴ yet it is significantly better than the phosphine-free approaches described in the literature.^{38,39} Similar results are obtained when executing the reaction in a saturated hydrocarbon such as hexadecane.

Over the last 5 years, a detailed picture of CdSe nanocrystals synthesized in the presence of carboxylic or phosphonic acids has emerged, where a Cd excess in the nanocrystal core is charge balanced by anionic ligands, such as carboxylates or phoshonates and phosphonic acid anhydrates.¹³ Since a different Se precursor is used here and the reaction is carried out under air, it makes sense to investigate whether the same structural model applies to the CdSe nanocrystals formed here. Fig. 2a shows the solution ¹H NMR spectrum of a dispersion of CdSe nanocrystals in toluene- d_8 , after a purification process as mentioned above. In line with NMR spectra published in the literature,^{46,47} the broad resonances are characteristic of bound OA moieties, while no indication is given for residual free CA. By integrating the methyl resonance (labelled as 5 in Fig. 2a), we obtain a ligand density - OA plus possibly residual MA – of 3.4(2) nm⁻². To compare this with a possible Cd excess, we use Rutherford backscattering spectrometry to determine the Cd : Se ratio. From the Z^2 weighted intensity of the backscattered intensity on Se and Cd nuclei, we calculated a Cd: Se ratio of 1.22(5). This leads to a $Cd^{2+}:CA^{-}$ ratio of



Fig. 2 ¹H NMR spectrum of 3.1 nm CdSe nanocrystals synthesized as outlined in the text, followed by a purification using a toluene–oleic acid mixture as the solvent in the first precipitation/resuspension step. The different resonances are attributed to OA protons as indicated. (b) Rutherford backscattering spectrum showing the (blue) intensities and (red) integrated intensities related to backscattering with selenium and cadmium nuclei. (c) (red) Absorption and (blue) lumines-cence spectra of 2.8 nm CdSe nanocrystals synthesized as outlined in the text yet using 0.2 mmol of Cd and 0.1 mmol of Se.

1.9(4), *i.e.*, in line with literature results on CdSe nanocrystals synthesised in the presence of carboxylic or phosphonic acids, our approach yields non-stoichiometric nanocrystals where the charge related to the Cd excess is balanced by the carboxylate ligands. To finish the analysis of the CdSe nanocrystals made here, Fig. 2c shows a photoluminescence (PL) spectrum of 2.8 nm CdSe nanocrystals formed as described here. In line with the low size dispersion, the PL is spectrally narrow – a full width at half maximum of 25–30 nm is typically obtained – with a PL quantum yield of about 5%. We thus conclude that the synthesis method introduced here leads – even under air – to CdSe nanocrystals with state-of-the-art properties in terms of surface chemistry and basic optical properties.

ZnSe nanocrystals

The method developed for the synthesis of CdSe nanocrystals is with minor changes extendable to the formation of ZnSe NCs. Although ZnO can be used as the initial Zn precursor, we obtained better results in terms of size dispersion using zinc carbonate basic, *i.e.*, $Zn_5(CO_3)_2(OH)_6$. In a typical synthesis, 0.08 mol of $Zn_5(CO_3)_2(OH)_6$ is dissolved in a mixture of OA (1.2 mmol) and ODE at 270 °C, followed by the injection of Se powder (0.2 mmol) using 1 mL ODE as a carrier liquid. Again, after purification of the reaction mixture similar to the one used for CdSe, a TEM analysis shows the formation of nanocrystals with an average diameter of 3.4 nm that correspond according to XRD to zinc blende ZnSe (see Fig. 3a and 3b, respectively). Although the major part of the nanocrystals thus formed appears as quasi-spherical, a fraction of them has a more elongated shape.

Also for the ZnSe synthesis, the absorption spectra of reaction mixture aliquots are instrumental in analyzing the development of the reaction. Although less pronounced than in the case of CdSe nanocrystals, all spectra show the absorption peak characteristic of the band gap transition in ZnSe nanocrystals (see Fig. 3c). Since no sizing curve – linking the wavelength of the absorption peak to $d_{\rm NC}$ – is available in the literature for ZnSe, Fig. 3d represents the peak wavelength as a

function of the reaction time. It follows that the ZnSe nanocrystals grow larger with time, to reach a final diameter within 8 minutes. At that moment, the reaction yield, as determined by analyzing the supernatant after first purification of the reaction mixture, amounts to \approx 90%.

CuInSe2 and its binary compounds

For the synthesis of CuInSe₂ (CISe) nanocrystals, we start from a mixture of Cu(acac)₂ (2 mmol) and In(acac)₃ (2 mmol) in oleylamine (OLA) (16 mL). After flushing the mixture for 1 hour with nitrogen at 110 °C, its temperature is raised to 240 °C, leading to a color change from blue to brown to brown-red at 240 °C. At this temperature, Se powder (4.1 mmol), heterogeneously dispersed in ODE (8 mL), is swiftly injected, after which the reaction mixture turns black immediately. Fig. 4a shows a TEM micrograph and an XRD diffractogram of the product collected when stopping the reaction after 10 min. Clearly, quasi-spherical nanocrystals with a mean diameter of about 7 nm are formed with a crystal structure that corresponds to that of chalcopyrite CuInSe₂ (Fig. 4b). A more detailed view on the reaction development follows from the analysis of aliquots, taken at different times after the Se injection. The UV-Vis absorption spectra of the aliquots taken in the first 5 min of the reaction clearly show the infrared absorption band characteristic of the plasmon resonance of Cu_xSe_v nanocrystals (see Fig. 4c).⁴⁸ From 10 min on, the infrared absorption is absent, and we notice no difference with subsequent absorbance spectra. In line with the TEM and XRD analyses, this indicates that the formation of CISe is finished at about 10 min. Further analysis of the aliquots using XRF provides more information on the synthesis development (Fig. 4d). For these measurements, we first precipitated the quantitative aliquots. Since for all aliquots, the supernatant contained little Cu, In and Se, the precipitated powder was redispersed and subjected to a second precipitation step using a minimum amount of non-solvent (so-called size selective precipitation). This is meant to precipitate larger nanocrystals (denoted as NCs in Fig. 4d), leaving behind possible precursor



Fig. 3 (a) TEM micrograph of ZnSe nanocrystals as formed by the injection of Se powder into a solution of zinc oleate, oleic acid and octadecene. Scale bar: 10 nm. (b) X-ray diffractogram of the ZnSe nanocrystals thus formed. The vertical lines indicate the most important reflections of zinc blende ZnSe. (c) Normalized absorption spectra of purified aliquots taken at the indicated time after starting the reaction by the injection of Se powder. (d) Time development of the position of the first absorbance peak.

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Fig. 4 (a) TEM micrograph of CulSe nanocrystals formed by the injection of Se powder into a solution of $Cu(acac)_2$ and $In(acac)_3$ in oleylamine after 10 min of reaction time. Scale bar: 10 nm. (b) X-ray diffractogram of the CISe nanocrystals thus formed. The vertical lines indicate the most important reflections of chalcopyrite CulnSe₂. (c) Normalized absorption spectra of aliquots taken at the indicated time after the Se injection. The different spectra are offset for clarity. (d) Time development of the amount of (blue dots) Cu and (red dots) In in the precipitate – indicated as NC – and of (red circles) In and (green circles) Se in the supernatant – indicated as SN – after the second, size selective precipitation step of the respective aliquots.

complexes or small nanocrystals in the supernatant. Doing so, we find that the amount of Cu collected in the precipitate remains constant, equal to the 2 mmol of Cu used in the reaction. On the other hand, most of the In is initially recovered in the supernatant. Since the supernatant contains little Se and no Cu, this is most likely as an In complex, and not as small indium selenide nanocrystals, as previously observed by Kar *et al.*⁴⁹ During the first 5 minutes, the amount of In in the precipitate gradually increases, at the expense of the In in the supernatant. This points toward a gradual incorporation of In into the Cu_xSe_y nanocrystals, with a concomitant transformation of the initially formed Cu_xSe_y into CISe.

 Cu_{2-x} Se nanocrystals are obtained in a similar fashion. In this case, 2 mmol of $Cu(acac)_2$ is dissolved in 20 mL of OLA. This mixture is flushed with nitrogen at 110 °C during 1 hour, after which the temperature is increased to 200 °C to obtain a brown mixture. At this point, 1.5 mmol of Se dispersed in 1.5 mL of ODE is injected, leading to a color change to greenbrown. The mixture is allowed to react at 200 °C for 30 min, after which the reaction mixture is cooled down and the nanocrystals are separated using a similar procedure as shown above. TEM analysis of the reaction product (Fig. 5a) shows 8 nm nanocrystals with various shapes. In the XRD pattern, we can see that the reflections occur at angles in between those expected for Cu₂Se and Cu_{1.8}Se, indicating the formation of a Cu_{2-x}Se phase (see Fig. 5b). By chemical analysis of the supernatant after precipitating the nanocrystals, a chemical yield of 90–95% is obtained.

We follow a comparable approach to synthesize In_2Se_3 nanocrystals. To prevent the possible formation of indium oxide, we start by dissolving 2 mmol $InCl_3$ in 20 mL of OLA. This mixture is flushed with nitrogen at 110 °C for 1 hour, after which the temperature is increased to 200 °C. At this point, Se powder (3.1 mmol) dispersed in 3 mL of ODE is injected into the reaction mixture. The color of the mixture changes from yellow-red to dark red in the course of a minute. After leaving the reaction mixture at 200 °C for 1 hour, the nanocrystals are collected by cooling down the synthesis and



Fig. 5 (a) TEM micrograph of $Cu_{2-x}Se$ nanocrystals formed by the injection of Se powder into a solution of $Cu(acac)_2$ in oleylamine after 1 hour of reaction time (see the text). Scale bar: 10 nm. (b) X-ray diffractogram of the $Cu_{2-x}Se$ nanocrystals thus formed. The vertical lines indicate the most important reflections of chalcopyrite Cu_2Se and $Cu_{1.8}Se$ as a reference. (c) TEM micrograph of In_2Se_3 nanocrystals formed by the injection of Se powder into a solution of $In(acac)_3$ in oleylamine after 1 hour of reaction time (see the text). Scale bar: 10 nm. (d) X-ray diffractogram of the In_2Se_3 nanocrystals thus formed. The vertical lines indicate the most important reflections of In_2Se_3 as a reference.

using standard centrifugation methods. The TEM micrograph in Fig. 5c confirms the formation of nanocrystals with a size below 10 nm, yet the resulting particles are difficult to image. Nevertheless, the XRD pattern confirms the formation of crystalline In_2Se_3 , with no impurity phases present (Fig. 5d). The yield of the reaction, using the same procedure as for $Cu_{2-x}Se$ nanocrystals, was calculated as 80–85%.

Cu₂ZnSnSe₄ nanocrystals

We extended the method developed for the synthesis of CISe nanocrystals with minor changes to the formation of kesterite $Cu_2(Zn,Sn)Se_4$ (CZTSe) nanocrystals. In this case, a solution of Cu, Zn and Sn salts in 10 mL of OLA where in this case, Cu(acac)₂ (3 mmol), zinc acetate [Zn(Ac)₂·2H₂O, 1.5 mmol] and tin chloride [SnCl₄·5H₂O, 1 mmol] have been used - was heated up to 260 °C under vigorous stirring, after which 3 mmol of Se powder is injected using 2 mL of OLA as a carrier liquid. After the injection, the temperature is reduced to 240 °C and the reaction is stopped after 30 minutes. The final product is purified by successive precipitation/redispersion steps. Here, we first use ethanol as the non-solvent and a toluene-OLA mixture as the solvent, followed by two more precipitation/redispersion steps using ethanol and toluene as the respective non-solvent and solvent. The TEM micrograph in Fig. 6a shows that this procedure results in relatively polydisperse nanocrystals with irregular shapes and typical dimensions in the 10-30 nm range. The reflections in the X-ray diffractogram recorded on these nanocrystals correspond to those of kesterite Cu₂(Zn,Sn)Se₄.

To analyze the time development of the reaction in more detail, we took quantitative aliquots that were studied using UV-Vis absorbance spectroscopy and elemental analysis. In this case, only the absorption spectrum of the first aliquots, taken after 15 and 30 s, shows the infrared absorbance indicative of Cu_xSe_y nanocrystal formation⁴⁸ whereas little further changes in the spectra are observed after 2 minutes. This picture is confirmed by XRF analysis, which shows that within

30 s, all the injected Se has reacted to form nanocrystals poor in Sn and Zn. As the reaction proceeds, first the amount of Sn and next the amount of Zn incorporated into the nanocrystals increase to reach their final levels after about 8 min. Overall, we find that this results in CZTSe nanocrystals that are rich in Sn and poor in Zn.

Discussion

In the literature, elemental selenium has been used by various authors for the synthesis of metal selenide nanocrystals as an alternative for phosphine based selenium precursors or bis(trimethylsilyl)selenide. In the case of CdSe, this involves the injection in a reaction mixture of a cadmium carboxylate and excess carboxylic acid in ODE of a solution made by dissolving selenium in octadecene (ODE-Se) by heating at ≈200 °C for up to 2 hours.³⁸ Alternatively, CdSe nanocrystals can also be formed by the gradual heating up of this entire reaction mixture, including the selenium powder.39 However, both approaches result in relatively slow reactions. Injection of ODE-Se for example results in the formation of CdSe nanocrystals with a 20-40% yield after 30 minutes.⁵⁰ Similarly, CuInSe₂ nanocrystals have been synthesized using the combination of metal salts and elemental selenium as precursors and OLA as the ligand. Also here, all reagents are either mixed at low temperature, followed by a gradual heating-up of the reaction mixture^{51,52} or selenium is dissolved prior to injection in OLA by prolonged heating at elevated temperature.⁵³ In both approaches the reaction mixture is left at elevated temperatures for one to four hours. Although little is known about the yield or the yield development of these reactions, it indicates that this heating-up results - similar to the case of CdSe - in a relatively slowly reacting Se precursor. A very similar approach, based on the injection of selenium dissolved in OLA, has been described for the synthesis of Cu_{2-x}Se nanocrystals.⁴⁸ Although in this case, the reaction time was limited to 15 minutes, no information is provided on the concomitant reaction yield.



Fig. 6 (a) TEM micrograph of CZTSe nanocrystals formed by the injection of Se powder into a solution of Cu, Zn and Sn salts in oleylamine after 32 min of reaction time (see the text). Scale bar: 50 nm. (b) X-ray diffractogram of the CZTSe nanocrystals thus formed. The vertical lines indicate the most important reflections of chalcopyrite CZTSe. (c) Normalized absorption spectra of aliquots taken at the indicated time after the Se injection. The different spectra are offset for clarity. (d) Time development of the amount of (green circles) Se, (blue dots) Cu, (red squares) Sn and (red circles) Zn in the precipitate after the second, size selective precipitation step of the respective aliquots.

The results shown here indicate that for all these syntheses, state-of-the-art metal selenide nanocrystals can be obtained by injecting the selenium powder into the reaction mixture at elevated temperature using a carrier liquid. Opposite to heating-up approaches or the injection of dissolved selenium species, this typically initiates a rapid and high yield conversion of the precursors into nanocrystals. Moreover, the procedure can be extended to the formation of ZnSe, In₂Se₃ and CZTSe nanocrystals, where in all cases close to full yield is obtained. It is worth mentioning that only a few synthesis procedures for In₂Se₃ and CZTSe nanocrystals have been reported in the literature. It has been shown that prolonged heating of InCl₃ and elemental Se in OLA leads to cubic-phase InSe nanowires,⁵⁴ whereas In-Se nanosheets have been obtained using selenourea as a selenium precursor⁵⁵ and In₂Se₃ nanocrystallites have been obtained using solvothermal methods.⁵⁶ In the case of CZTSe, the use of a TOP-Se based selenium precursor has been shown to yield CZTSe nanocrystals,⁴³ albeit with a considerable Zn deficiency. A similar lack of Zn incorporation was found for an alternative approach based on SeO₂ as a selenium precursor.35

In the context of the CdSe synthesis using Se dissolved in octadecene, Bullen et al. have addressed the reactivity of this selenium precursor as a function of the preparation conditions.⁵⁰ They found that dissolution at a lower temperature and for a shorter time yields a more reactive precursor. This result was interpreted in terms of a vulcanization process where ODE molecules are first bridged by short Se chains and later on by single Se atoms. Since we obtain similar results in the case of the CdSe synthesis using either ODE or hexadecane as a solvent, it appears that the reactive selenium species formed after the injection of selenium powder is rather a dissolved selenium species that precedes these vulcanization reactions. This conclusion is corroborated by the observation that when a twofold excess of selenium relative to cadmium is used, 50% of the unreacted selenium is recovered as selenium powder when stopping the reaction after 8 minutes. In the case of the CISe and CZTSe synthesis, the highly reactive selenium species resulting from the injection of selenium powder forms a $Cu_x Se_y$ compound in which either In or Sn and Zn are incorporated in a later stage of the reaction to form CISe and CZTSe, respectively. In the case of CISe, this Cu_xSe_y formation has been described before by Kar et al.,49 who used a heating-up procedure. However, in their case, the CuSe formation extends over a large part of the 1 hour heating-up time, while upon injection of Se powder, we find that all CuSe is formed within the first 10-15 s of the reaction.

The combination of a fast and high yield reaction with low cost precursors makes the approach proposed here well suited for larger scale nanocrystal synthesis. An additional asset of the approach is the possibility to inject large quantities of selenium using only a small volume of carrier solvent. This enables synthesis conditions to be used where a large amount of nanocrystals is produced using a relatively small amount of solvent. Without attempting any optimization, the CISe and CZTSe syntheses described here produce for example 10–15 mg and 25–40 mg of nanocrystals per mL of solvent, respectively.

Conclusions

We describe the hot injection of elemental selenium powder, heterogeneously dispersed in a carrier liquid for the synthesis of various metal selenide nanocrystals. As compared to the existing synthesis procedure that makes use of elemental selenium, e.g., to form CdSe, CuInSe₂ and Cu_{2-x}Se, this leads to a fast and close to full yield conversion of precursors into nanocrystals. Moreover, as exemplified by the case of CdSe nanocrystals, the materials thus formed have state-of-the-art properties in terms of size dispersion, surface chemistry and optical properties. In addition, the method can be extended to the formation of ZnSe, In2Se3 and CZTSe nanocrystals materials for which little or no low-cost routes have been described - which again results in a fast and close to full yield reaction. Based on these results, we conclude that the hot injection of selenium powder is a versatile approach for the synthesis of metal selenide nanocrystals that allows for their large volume, low cost production.

Acknowledgements

ZH acknowledges Ghent University (IOF StarTT project 'Selene'), the FWO-Vlaanderen (research project G.0760.12) and the Belgian Science Policy Office (BelSPo) (IAP7.35, photonics@be) for funding this research. SF acknowledges the IWT-Vlaanderen (Agency for Innovation by Science and Technology in Flanders) for a scholarship.

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