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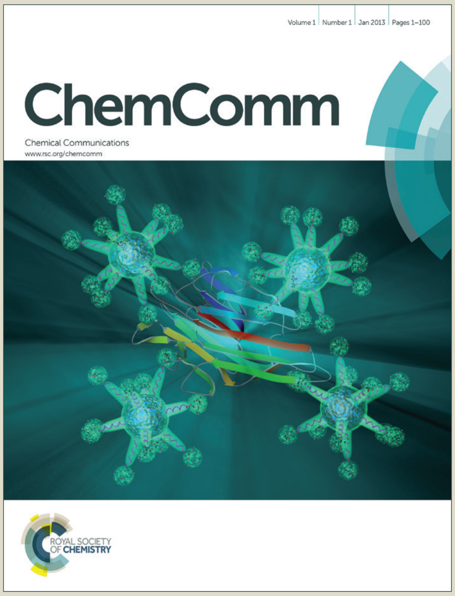

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Contamination-Free Solutions of Selenium in Amines for Nanoparticle Synthesis

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We present a first in providing versatile solutions of concentrated selenium within arrays of amines in a fast and low temperature manner without contaminants. These solutions allow the unprecedented opportunity to synthesize a variety of pure selenium and selenide nanoparticles as well as mixed chalcogen sulfoselenide compounds.

The chemical and physical properties of selenium lead to its value as in elemental and selenide materials with applications throughout electronics[1], solar cells,[2–8] light emitting diodes (LED),[9–11] and biology.[12,13] Nanoparticles from these materials range from elemental[1,13] to binary,[3,7,9,11,12,14] tertiary,[2,4–8,15] and quaternary[16,17] compounds and involve elements throughout the periodic table. For hot-injection nanoparticle synthesis, with the variety of metal precursors, reaction solvents, and temperatures it is surprising the singularity of the selenium source coming from dissolved/reacted selenium in trioctylphosphine (TOP).[3,4,10,11,18] TOP has limitations to use due to the cost, stability,[17] toxicity,[19] and optoelectronic degredation,[18] but more importantly the possibility of phosphorous incorporation and contamination of the final material under reaction conditions.[20,21]

Many attempts have been made to replace TOP as a medium for delivering selenium to these reactions, but each faces significant limitation. Organoselenide chemicals[5,12] are generally toxic and unstable. Soluble selenium in ethylenediamine[14] is limited by the low boiling point temperature of the solvent and general poor solubility . Oleylamine (OLA) used alone can only dissolve small quantities of selenium[4,6,7,22] and only at higher temperatures due to the relatively weak reducing ability of amines[23] unless coupled with a reducing agent like the alkali borohydrides[16,24,25] which then introduces boron and alkali ion contaminants to the system altering growth mechanisms[26] as well as electronic properties.

Herein we report a new route to create a solution of dissolved selenium, in high concentration, with the flexibility of a wide range of boiling points. This specific method was designed for the formation of pure selenide nanomaterials, due to the need for a homogeneous solution[8,11,22,27] to reproducibly generate controlled size nanoparticles. Although developed for this application, the flexibility of the approach enables possible tailor-made routes for other applications.

The process is based off our previous work where we were able to remove excess selenium from fouling selenide nanoparticles through post-synthesis dissolution of selenium in

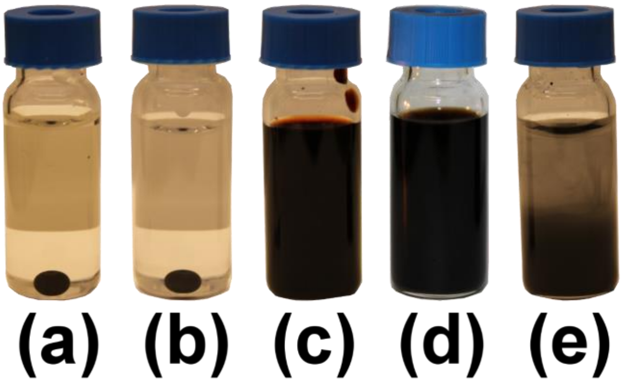

Fig. 1 Incorporating selenium into solution requires both a thiol and amine to be present initially. There is no observed dissolution when selenium is in either an amine (a) or thiol (b) only solvent. After combining both a thiol and amine together with the selenium (c) a dark red solution is formed. After the solution is formed, a post reaction removal of thiol and disulphide sulfur compounds (d) can be performed with maintained selenium solubility while removal of amine compounds (e) results in selenium precipitation.

$$2 \cdot R_1 - SH \rightarrow R_1 - S - S - R_1 + 2 \cdot H^+ + 2 \cdot e^- \tag{1}$$

$$Se_8 + 2 \cdot e^- \rightarrow Se_8^{2-} \tag{2}$$

$$2 \cdot R_2 - NH_2 + 2 \cdot H^+ \rightarrow 2 \cdot R_2 - NH_3^+ \tag{3}$$

$$Se_8^{2-} + 2 \cdot R_2 - NH_3^+ \rightarrow (Se_8^{2-})(R_2 - NH_3^+)_2 \tag{4}$$

Scheme 1 The proposed reaction mechanism that results in the dissolution of selenium in an amine and thiol solution relies on (1) the thiol-disulfide redox couple that enables (2) the reduction of selenium to its anionic form as well as (3) the protonation of the amine to form the ammonium ion. The complexation (4) of these two products results in a red and soluble version of selenium.

oleylamine by the addition of hexanethiol at room temperature and pressure[7]. Once dissolved, the selenium remains in the supernatant, and the nanoparticles can be successfully isolated. Liu et al[17] showed a similar dissolution route utilizing oleylamine and dodecanethiol and used it for the formation of nanoparticles.

The solution formed by mixing oleylamine with an alkylthiol and elemental selenium is homogenous and of a dark red color as depicted in Figure 1. The novelty is in the mixture of the two solvents since neither amines nor thiols alone readily dissolve selenium at room temperature (Fig 1 a and b), while in the combination of the two solvents directly results in this phenomenon (Fig 1 c).

Through the use of gas chromatography- mass spectroscopy (GCMS) we analyzed the solution formed from combining elemental selenium powder, ethanethiol, and oleylamine (see ESI† Fig S1). We report the evidence through GCMS of the presence of only four components: the oleylamine components and ethanethiol added initially, a diethyldisulfide formed in the reaction from the thiol, and elemental selenium in the allotropes Se_1 and Se_8. There is no evidence of an organo-selenium chemical formation, so selenium must exist in a weakly bound solvated or complexed form. The mechanism of dissolution (Scheme 1) depends on the reduction potential of the thiol to disulfide reaction[28] in a manner similar to results shown for borohydride[16,17,24,25] although it should be noted that the solution formed through thiol reducing agents is a dark red color rather than the colorless mixture observed when using borohydride;[25] thus suggesting a different end product, and potentially a different process.

The thiol oxidation and subsequent selenium reduction is enhanced by the basic environment[28] provided from the amine. Attempts to utilize non-amine bases did not result in dissolution though, and investigation of the final amine-thiol-selenium solution through infrared spectroscopy shows that the amine actively participates in stabilizing the final selenium anion (see ESI† Fig. S4). The lack of other compounds in the GCMS data implies that the selenium exists as a solvated complex hypothesized to be through a dissolution mechanism outlined in Scheme 1 where the final state is similar to that reported for dissolved sulfur in amine.[29] In the absence of oxidizing agents this solution is highly stable; we have successfully formed and stored solutions for more than three years without any observed precipitation.

Unfortunately, thiol and disulfide compounds are known to be active reactants in nanoparticle synthesis[30–32] and their copresence in solution during the reaction will directly result in sulfur contamination of the selenide nanoparticles through their incorporation. Our attempts to create cuprous-selenide nanoparticles through use of oleylamine and dodecanethiol show this contamination both in field emission scanning electron microscope (FE-SEM) based energy dispersive x-ray spectroscopy (EDS) (see ESI†) as well as powder x-ray diffraction (pXRD) depicted in Fig 2 as curve b. Although there are applications where contamination by a fellow chalcogen is advantageous,[8,15,33–36] it is still highly desirable to be able to consistently make pure selenide systems free from contamination and controllably add other chalcogens when desired.

In order to provide sulfur-free selenide solutions we successfully explored the options of removing the thiol and its disulfide post-dissolution.

As we explored the selenium dissolution mechanism we found that it is possible to dissolve selenium in many thiol and amine mixtures. To be precise, all combinations tested through the use of thiols ranging in size from C2-C16, and amines varied from C2-C24, showed positive selenium dissolution. Surprisingly, the amount of thiol needed is not a direct one to one stoichiometric ratio. Rather, when amine is provided in excess and chemicals are kept free from oxygen and other oxidizers, each thiol molecule added results in the dissolution of almost four selenium atoms. This gives insight to the mechanism shown in Scheme 1, as well as shows a first order reduction in sulfur content through utilizing less thiol initially.

With an array of solution options now available we tested the necessity of both components to stabilize the final selenium solution. This was done through utilizing two chemicals of dissimilar boiling points and then evaporating the more volatile component at elevated temperatures. For a volatile amine and nearly non-volatile thiol combination of butylamine and

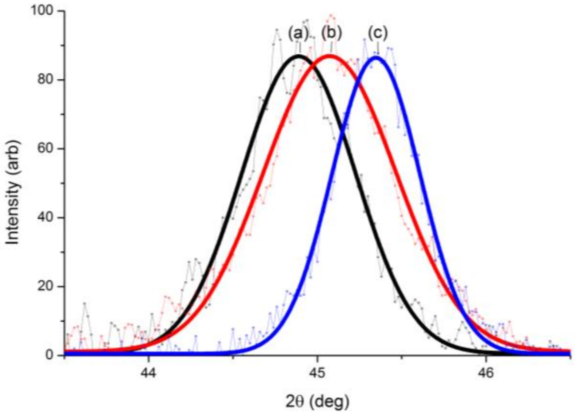

Fig. 2 pXRD data of the Cu_2Se 220 peak with overlaid Gaussian fits for: (a) Cu_2Se made from soluble selenium and removal of sulfur components (b) Cu_2Se nanoparticles made using soluble selenium in oleylamine and dodecanethiol showing sulfur incorporation into the lattice from the thiol and resulting shift in peak location (c) $Cu_2(S,Se)$ nanoparticles created by using mixed soluble sulfur and selenium. EDS data show the relative selenium content relative to total sulfur and selenium to be (a) 100%, (b) 86%, and (c) 59%. For additional details see ESI.†

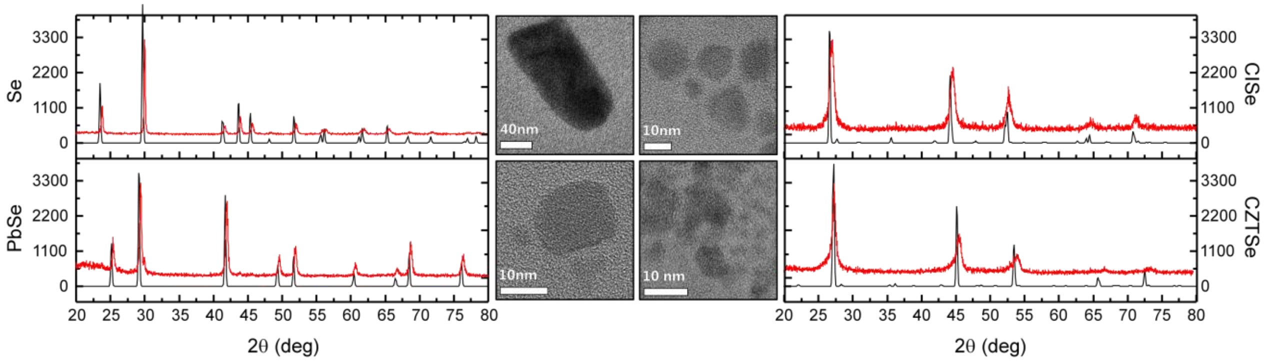

Fig. 3 TEM images and pXRD data of samples (red) and their respective bulk standard (black) of (counterclockwise from top left) selenium (PDF #01-086-2246), lead selenide (PbSe) (PDF #01-077-0245), copper-zinc-tin-selenide (CZTSe) (PDF #01-070-8930), and copper-indium selenide (CISe) (PDF #01-081-1936) nanoparticles without post synthesis size separation.

dodecanethiol, selenium promptly fell out of solution upon evaporation of the butylamine (Figure 1 part e). In the case of a volatile ethanethiol and nearly non-volatile oleylamine combination, the selenium stayed in solution (Figure 1 part d) even after removal of the ethanethiol.

Therefore, it is possible to create a solution of soluble selenium in amine, free from other contaminants, by introducing a post-dissolution thiol and disulfide removal step. This requires that the thiol used has dissimilar properties to the amine. We have developed two candidate pathways: either use a thiol that is significantly larger than the amine so that it can be separated from solution as a solid due to differences in the crystallization temperatures of the constituents, or utilize a thiol that is significantly smaller than the amine so that the thiol and disulfide formed can be removed in the vapor phase due to their higher relative volatilities. Oleylamine and other heavier amines are preferred over small alkylamines for most nanoparticle synthesis so our focus to date has been on developing the latter.

Ethanethiol was chosen due to being the lightest thiol readily available. Ethanethiol boils at roughly 35°C[37] and has high vapor pressure at lower temperatures to allow facile post reaction removal. Unfortunately the disulfide formed through selenium reduction is not as volatile. Pure phase diethyl disulfide has a normal boiling point around 154°C[37] and would require a higher temperature for complete removal from a liquid mixture as vapor. The higher temperatures required to remove the disulfide completely has resulted in visible deposition of volatized selenium on the sides of our condenser, and is deemed to be unsuitable. A secondary route is to reduce the pressure of the solution to enable removal of ethyl disulfide at lower temperatures. Ethyl disulfide has a room temperature vapor pressure of 5.7 mbar[37], while oleylamine has an estimated value several orders of magnitude smaller at close to 1 nanobar[37], and is kept from vaporizing. To completely extract the diethyl disulfide we raise the temperature under vacuum until we reach the normal refluxing temperature under vacuum for oleylamine, which in our lab set-up is ~120°C. Complete removal of all sulfur components is confirmed through GCMS (see ESI† Fig S1). Due to the reducing properties of amines,[23] the selenium-amine solution is stable in the absence of oxidizers even at high selenium concentrations exceeding 2.5 molar, and can be stored at room temperature for later use.

Utilization of this selenium source has shown success in making nanoparticles of selenide materials without any sulfur incorporation. For cuprous selenide nanoparticle synthesis the result is a noticeable change in pXRD (Fig 2a) as well as EDS† in comparison with the initial sulphur contaminated oleylamine-dodecanethiol solution (Fig 2b and ESI†).

As mentioned above, the selenium dissolution was successful with all thiols and amines utilized. The nature of the amine is not essential to the success of dissolution as primary, secondary, tertiary, and di-amines have all resulted in solvated selenium. The rate of dissolution is structure dependent with the faster reactions involving primary amines and the slower involve tertiary amines while diamines were observed to have a rate between tertiary and secondary. Smaller chain amines were also observed to be faster than heavier alkyl amines. These two aspects are expected for the nature of the dissolution proposed, and give greater strength to the hypothesis.

With the solution of dissolved selenium the formation of various selenide nanoparticles is easily accomplished. In addition to the cuprous selenide addressed above, we have successfully formed elemental selenium (Se), binary lead-selenide (PbSe), tertiary copper-indium-diselenide (CISe), and quaternary dicopper-zinc-tin-tetraselenide (CZTSe) nanomaterials as confirmed through pXRD, TEM, and EDS (Fig 3 and ESI†). Conditions for the individual nanoparticles have not been optimized, but the preliminary results are strong enough to show the validity of pure selenide nanomaterials free from contamination of phosphorous, boron, and even sulfur.

The value of the method is not only in the ability to form pure selenide materials, but also in the ability to controllably add sulfur into the solution and form a mixed chalcogen compound. The formation of mixed chalcogenide nanoparticles can be created through controlling the reactivity[8,16] of the individual components when utilizing hot injection from a homogenous mixture of the two components in solution. Our approach allows the dissolution of elemental sulfur powder in addition to selenium in an amine. By mixing sulfur and selenium powders to the desired ratios, dissolving them in oleylamine and ethanethiol mixtures, and then removing the organosulfide compounds from the resulting mixtures, we successfully created a solution that enabled the formation of controllable homogenous cuprous-sulfoselenide nanoparticles with a single peak in the pXRD spectra (Figure 2c).

To summarize, we have successfully engineered a novel method to form a homogenous solution of selenium in high concentrations without contamination from phosphorus, boron, or sulfur. The capability of this route shows the ability to utilize a reducing agent, and then remove that agent while maintaining the desired solubility. The potential of this technique has been shown through using volatile mercaptans, and the creation of a vast family of selenium and selenide nanoparticles as well as mixed chalcogen materials. Although selenium is the component of interest for this paper the feasibility of others utilizations should also be considered. The versatility of the process allows utilization of amines under a wide range of properties which allows greater flexibility in the design of synthesis routes than had been previously realized.

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Notes and references

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† Electronic Supplementary Information (ESI) available: including experimental details, FTIR data of solutions, EDS of all nanoparticles shown, as well as GC-MS of components. See DOI: 10.1039/b000000x/

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