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Bis((dialkylamino)alkylselenolato)metal complexes as precursors for microwave-assisted synthesis of semiconductor metal selenide nanoparticles of zinc and cadmium in the ionic liquid [BMIm][BF_4]

Karsten Klauke [a], Björn Hahn [a], Kai Schütte [a], Juri Barthel [b], Christoph Janiak [a,*]

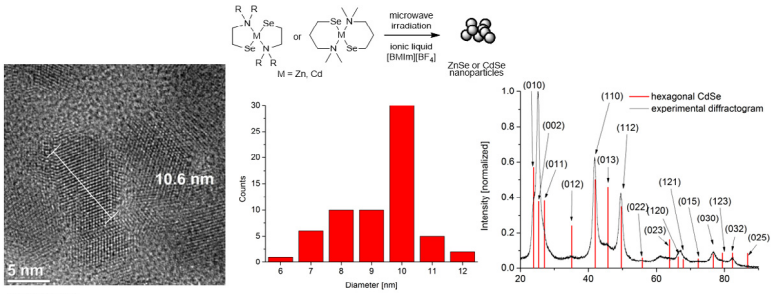
[a] Institut für Anorganische Chemie und Strukturchemie, Heinrich-Heine Universität Düsseldorf, Universitätsstraße 1, D-40225 Düsseldorf, Germany

[b] Gemeinschaftslabor für Elektronenmikroskopie RWTH-Aachen, Ernst-Ruska-Centrum für Mikroskopie und Spektroskopie mit Elektronen, D-52425, Jülich, Germany

HIGHLIGHTS

- (Dialkylamino)alkylselenolates as new single-source precursors for ZnSe and CdSe-NPs.
- ZnSe- and CdSe-NPs were obtained by microwave irradiation of precursor/IL suspensions.
- Obtained particles were mostly spherical, crystalline and only slightly agglomerated.
- No further stabilizing agents needed and no formation of metal fluorides observed.
- For ZnSe the particle diameter was 4–7 nm, while for CdSe the diameter was 10–19 nm.

GRAPHICAL ABSTRACT



Synopsis:
Bis(dialkylamino)alkylselenolates are novel single-source precursors for ZnSe and CdSe-nanoparticles by microwave irradiation of precursor/IL dispersions.

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ABSTRACT

Based on (dimethylamino)ethyldiselenide, (diethylamino)ethyldiselenide and (dimethylamino)propyldiselenide six different bis(dialkylamino)alkylselenolates with zinc and cadmium were decomposed by microwave irradiation in the ionic liquid (IL) 1-butyl-3-methyl-imidazolium tetrafluoridoborate ([BMIm][BF_4]) to give the respective metal selenide nanoparticles. In comparison to common methods like the hot injection method attention was paid how variations of the ligand system and different decomposition times affect the nanoparticle synthesis with respect to size, shape, crystallinity and crystal phase. The decomposition of the single-source zinc and cadmium precursors in the fluorous IL led mostly to spherical, crystalline and only slightly agglomerated nanoparticles. No formation of ZnF_2 or CdF_2 was observed which is different from the known dual-source synthesis. In case of the zinc precursors, hexagonal and cubic ZnSe with a particle diameter between 4–7 nm were obtained, whereas in case of the cadmium precursors hexagonal CdSe with an average particle diameter of 10–19 nm were prepared. An increase in decomposition time from 5 to 15 min at 250 °C mostly led to similar results concerning the particle size and crystal phase which is different from the hot injection method, thereby suggesting that the IL has a decisive role for nanocrystal growth and stabilization. No further stabilizing agents were necessary to reproducibly prepare ZnSe or CdSe particles with an average diameter below 10 or 20 nm,

* Corresponding author. Fax: +49 0 211 8112287.
E-mail address: janiak@uni-duesseldorf.de (C. Janiak).

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respectively. All dispersions of the metal selenide nanoparticles in [BMIm][BF_4] were characterized by high resolution transmission electron microscopy (HR-TEM), energy dispersive X-ray spectroscopy (EDX) and X-ray powder diffraction (PXRD).

1. Introduction

One of the emerging areas of nanotechnology is the field of semiconductor nanoparticles, whose interesting properties have attracted much attention in the past few decades. One of the most important concepts in relation to semiconductor nanoparticles is the quantum confinement which describes the particle-size-depended discretization of the electronic energy levels. Among others this has direct influence on the thermoelectric and optoelectric properties the material. Therefore, due to various possible applications especially II–VI and IV–VI semiconductors such as ZnSe, CdSe or PbSe belong to the best studied systems of this class of materials. They can be used in LEDs, photovoltaics, biological imaging, thermoelectric devices or single-electron transistors [1–11]. In terms of selenium-containing semiconductor nanoparticles a wide variety of starting materials is known [1,12–14]. In the literature metal selenide nanoparticles are mostly prepared by a dual-source approach from the reaction of different metal salts like MSO_4 or $M(OAc)_2$ and Na_2SeO_3 [1,15]. The metal complexes of aminoalkylselenoles like selenocysteamine for example have proven to be excellent single-source precursors for the preparation of metal selenide nanoparticles. Most of these complexes are air and moisture stable solids with moderate decomposition temperatures and are easily synthesized through cleavage of the respective diselenide (Scheme 1) [12–14].

One of the main goals of nanomaterial science is to develop economically and environmentally efficient methods for the design of novel nanostructured materials, preparation of thin films and highly dispersed systems, as well as the fabrication of functional nanostructures. Common methods for the synthesis of semiconductor nanoparticles include ball milling and chemical vapor deposition processes as well as precipitation methods. In wet chemical precipitation, sterically demanding stabilizing agents like hexadecylamine (HDA) or trioctylphosphine oxide (TOPO) have to be used to stabilize the nanoparticles and to prevent agglomeration. Another notable fact is, that in other methods like the classical hot injection method the particle size increases drastically with the reaction time, except when working in non-coordinating solvents like 1-octadecene, where the final size is quickly reached and remains stable for long time [1].

Due to their unique physicochemical properties ionic liquids, especially room temperature ionic liquids like 1-butyl-3-methylimidazolium tetrafluoridoborate, [BMIm][BF_4], have recently received attention as media for the synthesis of different types of nanoparticles [16–21] and inorganic materials [22,23] such as metal oxides including ZnO [24] or CuO semiconductor nanoparticles [25,26], metal chalcogenides [27,28], polynuclear metal complexes [29–31]. Among others, the properties of ILs include a high dielectric constant, polarity, thermal stability and a negligible vapor pressure. The stabilization of nanoparticles in ionic liquids is based on the integration of the particles in the network-like structure of the ionic liquid by weakly coordinating interactions, resulting in an enhancement of the repulsive energy [32–34]. Furthermore, through choice of the anion and cation, ionic liquids can be specifically designed for different tasks. Accordingly, a variety of different techniques and methods has been employed, including solvothermal [35–38], sol–gel [39–41], electrodeposition [42,43] and radiation assisted syntheses [44–50]. However, reports about the preparation of semiconductor nanoparticles in ionic liquids are quite rare [15,27,51,52]. There are gaps, for example in the selection of suitable precursors and methods, as well as in the investigation of the growth and shape-determining processes. Although ionic liquids are still expensive, their recycling makes progress and ILs are often considered a "green" alternative to classical organic solvents due to their less-harmful nature [53]. Therefore, we describe here for the first time the microwave assisted decomposition of single-source (alkylamino)alkylselenolates precursors of zinc and cadmium (**1**–**6**) in an ionic liquid, here [BMIm][BF_4]. Initial attempts to form MSe from metal acetate hydrates and bis(dialkylamino)alkyldiselenides in a dual-source approach yielded samples where the X-ray powder diffraction pattern showed the formation of MSe (M = Zn or Cd), albeit together with MF_2 impurities from the reaction with the BF_4^- anion of the IL (Figure S1 in Suppl. Mater.). In the literature the formation of MF_2 impurities is prevented through the use of non-fluoride containing ILs, such as [BMIm][$EtSO_4$] [15].

In this work we test the single-source approach to prevent the formation of metal fluorides from BF_4^- in the fluorous IL. Different from most other methods like the hot injection method we show that variations in ligand system of the precursor and different decomposition times do not affect the nanoparticle synthesis in the IL. Also, no further stabilizing agents are needed to reproducibly prepare MSe particles with average diameters of less than 20 nm.

2. Results and discussion

2.1. Precursor compounds

The synthesis of the bis((dialkylamino)alkylselenolato)metal(II) compounds is depicted in Scheme 1 and follows the literature [12,13,54].

2.2. Thermogravimetric analysis of Zn complexes *1–3*

The thermogravimetric analysis of the prepared bis((dialkylamino)alkylselenolato)zinc(II) complexes (**1**–**3**) (Fig. 1) verifies their decomposition temperature of about 250 °C, which corresponds to similar zinc selenolate complexes in the literature [13]. The residual mass (Δm) is close to the expected values for ZnSe ($\Delta m_{\text{theor.}}$), as shown in Table 1. Also formation of ZnSe as decomposition product was positively identified by X-ray powder diffraction of the residues (Figure S2 in Suppl. Mater.). The diffraction patterns showed the formation of either hexagonal or cubic ZnSe (Table 1).

2.3. ZnSe-NPs in [BMIm][BF_4]

Dispersions of pure ZnSe nanoparticles in [BMIm][BF_4] were obtained by suspending a defined amount of the respective precursor in the ionic liquid and then decomposing it via microwave assisted heating for 5 or 15 min at 250 °C as shown in Scheme 2.