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COMMUNICATION

Highly-photoluminescent ZnSe nanocrystals *via* a non-injection-based approach with precursor reactivity elevated by a secondary phosphine†Kui Yu,^{*a} Amy Hrdina,^a Xinguo Zhang,^{ab} Jianying Ouyang,^a Donald M. Leek,^a Xiaohua Wu,^c Menglian Gong,^b Diana Wilkinson^d and Chunsheng Li^e

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Highly-photoluminescent ZnSe quantum dots with 72% quantum yield and 22 nm full width at half maximum were synthesized with more reactive precursors *via* a non-injection approach with high synthetic reproducibility; ³¹P NMR provided insight into the formation mechanisms of ZnSe monomers.

Efforts on the development of synthetic approaches to colloidal semiconductor quantum dots (QDs) with high quality have been driven mainly by their technological potential. When the dimensions of the semiconductor nanocrystals (NCs) are similar to or smaller than the Bohr exciton radii of their corresponding bulk materials, quantum confinement effects arise.¹ Also, fundamental research such as that on their size-dependent properties demands high-quality NCs. The successful control of nucleation/growth with reactive precursors leads to high-quality NCs.

Zinc selenide (ZnSe) QDs are of special interest. With a wide bulk bandgap (2.7 eV or 460 nm) and a small Bohr radius (4.5 nm), they can be tuned to exhibit size-dependent fluorescence in the blue/near UV region.^{2,3} Hence, high-quality ZnSe NCs have significant potential in areas such as lasing and light-emitting diodes (LEDs). Also, they can offer cadmium-free and lead-free alternatives such as Mn-doped ZnSe NCs.

The synthesis of ZnSe QDs has been less established than that of CdSe and PbSe QDs. Mainly, a hot-injection approach was documented to produce ZnSe QDs exhibiting photoluminescence (PL) with quantum yield (QY) up to 50% and in a size range of 2.5–10 nm.⁴ The limited body of the literature on the synthesis of ZnSe NCs articulates the low reactivity of

the precursors used.^{4,5} The rational advance from the use of diethylzinc to zinc carboxylate salts is plausible. With *n*-tributylphosphine selenide (TBPSe) as a Se precursor, alkylamines were believed to be essential to activate the Zn salts in 1-octadecene (ODE) for the growth of high-QY ZnSe NCs at 310 °C. Without the use of amines, the resulting ZnSe NCs *via* a non-injection approach in ODE and with *n*-trioctylphosphine selenide (TOPSe) as a Se precursor were reported to exhibit low PL QY.⁵ Careful inspection reveals that these reported ZnSe QDs exhibited PL with noticeable red-side tails. Till now, the synthesis of high-quality ZnSe NCs still remains challenging.

Recently, secondary phosphine selenides, such as dibutylphosphine selenide (DBPSe) and dioctylphosphine selenide (DOPSe), were documented to be more reactive than tertiary phosphine selenides, such as TBPSe and TOPSe.⁶ Also, DBP and DOP were detected to be among the impurities in commercial TBP and TOP, respectively. However, with secondary phosphine selenides, such as diphenylphosphine selenide (DPPSe), the control of the sizes of (PbSe) QD was revealed to be not well understood.⁶

Here, we report on the development of a non-injection one-pot approach in ODE to synthesize highly-photoluminescent ZnSe NCs. Zinc oleate (ZnOA₂) was used as a Zn precursor, while TOPSe or DPPSe as a Se precursor. The reactivity difference of TOPSe made from commercial 90% and 97% TOP was investigated; the former was more reactive than the latter. The activation of ZnOA₂ with DPP was explored. Experimentally, the addition of DPP into a ZnOA₂ solution in ODE at 80 °C could be carried out before, during, or after the addition of a Se precursor. The temporal evolution of optical properties of the resulting NCs was monitored. The order of the DPP addition played a role when DPPSe was used but did not when TOPSe was used. Regarding the different experimental conditions in our non-injection approach, the corresponding formation mechanism of ZnSe monomers is discussed (Scheme 1). The present study on the use of DPP to improve the precursor reactivity in our non-injection-based approach to synthesize highly-emissive ZnSe NCs brings insight into the fundamental understanding of the monomer formation mechanism and the requirement for sizeable nucleation taking place at a relatively low reaction temperature with high reactivity precursors. Also, the present study offers

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† Electronic supplementary information (ESI) available: Experimental methods with details about ZnSe QD syntheses and the growth kinetics monitored, ³¹P NMR, XRD and TEM. See DOI: 10.1039/c1cc12237a

Scheme 1 Schematic drawing of the formation of the ZnSe monomer proposed with direct and indirect pathways for our syntheses.

conceptual methodology with high reactivity precursors to synthesize various highly-photoluminescent QDs with high quality, high particle yield, and high synthetic reproducibility.

Fig. 1 shows the temporal evolution of absorption of the ZnSe NCs from four batches with the feed molar ratio of 4Zn-to-1Se and [Se] 60 mmol kg⁻¹. Samples were taken at 80 °C and 20 °C intervals up to 280 °C. See Table S1 (ESI†) for experimental details and Fig. S1A (ESI†) for the comparison of same-growth samples from the four batches. Interestingly, nucleation took place at ~280 °C (Sample 11) for Batch left-top (SeTOP 97%), ~260 °C (Sample 10) for Batch left-bottom (SeTOP 90%), ~160 °C (Sample 5) for Batch right-top (SeTOP 90%–DPP), and ~100 °C (Sample 2) for Batch right-bottom (SeDPP). Obviously, such noticeable differences in nucleation/growth of the ZnSe NCs suggest an increase of the reactivity of the corresponding precursors.

For the left two SeTOP batches, intriguingly, SeTOP made from commercial 97% TOP was less reactive than that from 90% TOP. For the latter, the addition of DPP (Batch right-top) enhanced the reactivity further leading to an improved PL QY of Sample 11 (with 20 nm full-width half

maximum (FWHM)). It seems, accordingly, that the more the secondary phosphine (DOP or DPP), the faster the nucleation. The formation of high-quality CdSe NCs in TOP may share a similar cause.⁷

Collectively,^{6–9} we propose that there are two routes for the formation of ZnSe monomers (Scheme 1). One is direct between ZnOA₂ and phosphine selenide (such as TOPSe or DPPSe), the other is indirect with the activation of ZnOA₂ by a phosphine compound (such as DPP, DOP, or TOP) resulting in a Zn–P complex/intermediate, which in turn reacts with TOPSe or DPPSe.

For Batch SeTOP 97% and Batch SeDPP, the direct route might be active at ~280 °C and ~100 °C, respectively. For Batch SeTOP 90% and Batch SeTOP 90%–DPP, the indirect route might be active at ~260 °C and ~160 °C, respectively. Scheme S1A (ESI†) demonstrates the reactions proposed for the formation of the ZnSe monomer, while Scheme S1B (ESI†) presents the combination of the ZnSe monomers leading to nucleation/growth of ZnSe NCs.

For the three SeTOP solutions used in Fig. 1, the absence of DOPSe and DPPSe is suggested by ³¹P nuclear magnetic resonance (NMR, Scheme S2, ESI†), together with the presence of TOPSe. Such absence should be related to greater stability of TOPSe. Furthermore, for Fig. 1 Batch right-top, the possible formation of a Zn–P complex at ~80 °C could be suggested by ³¹P NMR (Scheme S3 (ESI†), performed with a mixture of ZnOA₂ and DPP). This activation temperature is lower than the apparent nucleation/growth temperature, which was ~160 °C. Accordingly, regarding the formation of high-quality ZnSe NCs, the addition of DPP, before or after the addition of SeTOP 90%, to a ZnOA₂ solution in ODE at ~80 °C should not matter. Fig. S1B (ESI†) demonstrated such an insensitivity, namely highly-synthetic reproducibility. It is reasonable that, for a non-injection-based approach with highly-synthetic reproducibility of high-quality NCs formed *via* the indirect route (Scheme 1), the temperature of addition should be lower than the temperature of nucleation.

When DPPSe was used as a Se precursor, the effect of the addition of DPP before, simultaneously, or after the addition of DPPSe to a ZnOA₂ solution in ODE at ~80 °C is demonstrated in Fig. S2A and B (ESI†). The temporal evolution of absorption of the ZnSe NCs suggests that the order of the addition of DPP and DPPSe affected the nucleation/growth of the resulting ZnSe NCs. When DPP was added before or with DPPSe, nucleation took place relatively fast with relatively obvious Ostwald ripening at the later growth stages, as compared to that when DPP was added after DPPSe. It seems reasonable that when DPP was added before or with DPPSe, the indirect route was activated; the reactivity of a Zn–P complex is higher than that of ZnOA₂, leading to faster nucleation/growth with more consumption of the monomer and thus more obvious Ostwald ripening at the later growth stages.

Furthermore, Fig. S2A and B (ESI†) present little difference between the two batches, one without DPP addition, the other with DPP addition but after DPPSe. When DPPSe was added, the quick consumption of DPPSe resulted in little DPPSe being available, and thus the following addition of DPP could

Fig. 1 Temporal evolution of absorption (offset) of the as-synthesized ZnSe NCs from four batches in ODE with SeTOP or SeDPP as a Se precursor, with or without DPP added.

Fig. 2 (left) Absorption (offset solid lines) and emission (normalized dashed lines) of the growing ZnSe NCs from a batch where DPPSe was added at 280 °C which was also the growth temperature. The growth periods are indicated. (right) Powder XRD patterns of one ZnSe QD ensemble (1) and bulk (2), with an inset of one high-resolution TEM image of a ZnSe QD ensemble and the scale bar of 5 nm.

no longer influence anymore the formation of the ZnSe monomer and nucleation/growth.

Overall, an increase of PL QY up to ~50% along with the growth of the four batches (Fig. S2, ESI†) is worthy of notice, together with the decrease of trap emission. When DPPSe was added at higher temperature such as 280 °C instead of 80 °C, as shown in Fig. 2 and Fig. S2C (ESI†), the resulting ZnSe NCs exhibited PL with little red-side tail and up to 72% QY. To the best of our knowledge, the QY value of 72% is a new record for colloidal ZnSe QDs. Such high quality may be the result of rapid nucleation at high temperature and long growth periods. Furthermore, when DPPSe was added at high temperatures, such as 200–280 °C, the non-injection approach exhibited excellent synthetic reproducibility. As shown in Fig. S2C (ESI†), the three ensembles from the three batches with the growth at 280 °C for 30 min exhibited similar emission peak positions and PL QY.

Powder X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to study purified ZnSe NCs. The XRD pattern (Fig. 2, right) reveals a zinc blende crystal structure. The inset TEM image and those shown in Fig. S3 (ESI†) suggest a narrow size distribution of ~3 nm NCs.

In conclusion, highly-photoluminescent ZnSe NCs were synthesized *via* a non-injection one-pot approach in ODE. A secondary phosphine, diphenylphosphine (DPP), was explored to promote the reactivity of ZnOA₂ in ODE, and was applied to form a Se precursor SeDPP. The reactivity of SeTOP made from commercial 90% TOP was found to be higher than that made from commercial 97% TOP. ³¹P NMR suggested the absence of DOPSe in our TOPSe solutions prepared but the presence of TOPSe and a small amount of DOP. When DPP was added into our TOPSe solutions, ³¹P NMR suggested the absence of DPPSe but the presence

of TOPSe and DPP. The order of DPP and TOPSe addition to a ZnOA₂ solution in ODE at 80 °C did not affect the nucleation/growth of the resulting ZnSe NCs. However, the order of DPP and DPPSe addition did. Such a difference was argued to be related to the fact that the reactivity of TOPSe is lower than that of DPPSe and there are two routes leading to the formation of the ZnSe monomer. One is a direct reaction between ZnOA₂ and TOPSe or DPPSe. The other is an indirect reaction between a Zn–P complex and TOPSe or DPPSe. The reactivity of the Zn–P complex (resulted from ZnOA₂ and DPP at ~80 °C) is higher than that of ZnOA₂. The present study brings insight into the fundamental understanding of the monomer formation mechanism and offers a conceptual approach to delightfully synthesize QDs with high quality and high synthetic reproducibility.

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