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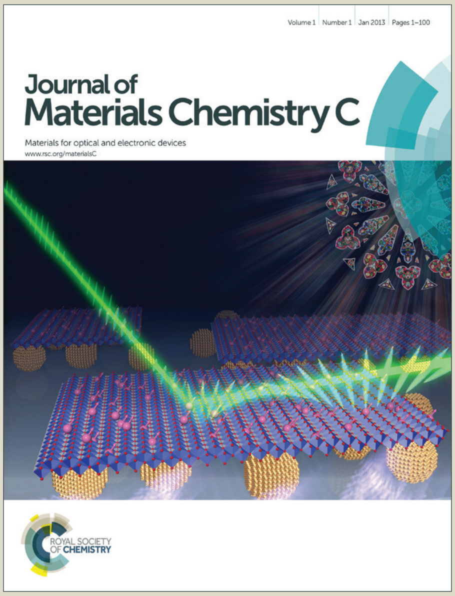

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COMMUNICATION

Synthesis of Widely Tunable and Highly Luminescent Zinc Nitride Nanocrystals

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Zinc nitride nanocrystals have been prepared from the reaction between ammonia and diethylzinc at 225°C. The peak photoluminescence wavelength can be tuned from below 500 nm to above 1100 nm and photoluminescence quantum yields greater than 50% have been measured. TEM and XRD analysis confirm the formation of Zn_3N_2 nanocrystals.

Since the first reports of size tunable optoelectronic properties of semiconductor nanocrystals,[1] multidisciplinary research in this field has grown rapidly. The rise of this technology has been driven by the use of synthetic chemical methods to produce a wide range of nanomaterials with precise control over their composition, structure and optical properties. The unique properties of semiconductor nanocrystals have led to the demonstration of wide ranging applications[2], including displays[3], photovoltaic cells[4], biological labels[5] and light emitting devices.[2,3] Even though excellent device performance has already been achieved with known semiconductor nanocrystals such as CdSe,[6] PbS,[7] and InP,[8] there are opportunities in many application areas for nanocrystals composed of alternative materials that provide even larger functional property ranges and do not contain scarce or toxic elements. One such promising material is Zn_3N_2; a narrow direct band gap II-V compound semiconductor that has only been intermittently investigated. The precise band gap energy of Zn_3N_2 is subject of debate, with the majority of the literature reporting a band gap around 1 eV,[9, 10] although values of up to 3.2 eV have been reported.[11] Thin films of Zn_3N_2 have been made by a variety of non-solution chemical methods including sputtering,[10] pulsed laser deposition,[11] metal organic vapour deposition[12] and molecular beam epitaxy.[13] In addition to thin films, powders,[9] hollow balls[14] and nanowires[15] have been made by similar methods. Recently there has been interest in Zn_3N_2 due to its application in the formation of p-type nitrogen-doped zinc oxide thin films.[16]

Here, we demonstrate the synthesis of colloidal emissive zinc nitride nanocrystals and report on their corresponding optical and structural properties. Our approach to chemically synthesizing zinc nitride nanocrystals uses the reaction of diethylzinc with ammonia gas in the presence of a capping agent (oleylamine). The synthesis method is as follows; a mixture of 1-octadecene (30 ml) and oleylamine (1 ml) is heated to 225°C while ammonia gas is bubbled though the solvent at a rate of 5 ml/min. Portions of diethylzinc (102 µl, 1.0 mmol) are rapidly injected into the reaction mixture at 5 minute intervals. After each addition the nanocrystals grow over the course of several minutes as evidenced by a visible bathochromic shift in the absorption of the reaction. After this initial colour change, the colour stabilizes at a slightly longer wavelength. The addition of more diethylzinc causes further growth of the nanocrystals and no signs of the nucleation of additional nanocrystals were observed. We found that this stepwise method enables accurate control of the growth of nanocrystals with a wide range of emission colours. While the reaction can also be performed with a single, larger addition of diethylzinc, we find that with that approach we are unable to produce either the smallest or largest nanocrystals effectively. Photoluminescence across the entire visible spectrum is clearly observed when samples removed from this reaction are diluted with toluene and illuminated with a 365 nm-UV lamp (Fig. 1).

Fig. 1 – Toluene solutions of oleylamine capped Zn_3N_2 nanocrystals sampled at different reaction times excited with a 365nm lamp

During the course of the reaction the shift to longer wavelengths in the absorption spectra and the photoluminescence (PL) emission peak maximum observed (Fig. 2) indicates the emission is from nanocrystals in the strong quantum confinement regime and that their size is increasing as the reaction proceeds. The synthesis method was used to produce nanocrystals over a very wide range of emission wavelengths, extending from below 500 nm to above 1100 nm (Fig. 5). The upper emission wavelength limit is consistent with a zinc nitride bulk band gap of ~1.0-1.1 eV. Photoluminescence quantum yields (PLQYs) were measured using standard methods[17] employing nile red[18] as a reference (PLQY 70% in 1,4-dioxane). PLQYs of 52%, 42%, 40% and 35% were measured for samples with emission maxima at 566 nm, 617 nm, 651 nm and 700 nm respectively when excited at 460 nm. The Stokes shift is hard to measure accurately due to the lack of a well-defined band-edge absorption feature, but we estimate it to be ~0.5 eV. Similarly large Stokes shifts have been observed in other II-V semiconductor nanocrystals such as zinc phosphide.[19] For further optical and structural characterisation, three solutions of nanocrystals with different emission wavelengths were prepared (Figs. 2-4). PL emission peaks at 585 nm, 752 nm and 1073 nm are observed (Fig. 2). The full width half-maximum of the emission peaks of these three samples (117, 163 and 282 nm) is indicative of a relatively large size distribution of nanocrystals, which can also contribute to the Stokes shift. More precise control of the nanocrystal growth mechanism should reduce this size distribution and is the subject of future work.

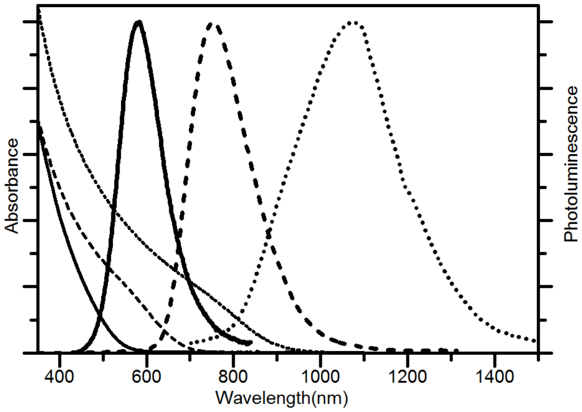

Fig. 2 – Absorption (thin lines) and emission (thick lines) spectra of Zn_3N_2 nanocrystals with mean diameters (TEM, Fig. 4) of 2.1±0.4 nm (solid lines), 4.6±2.3 nm (dashed lines) and 7.1±2.0 nm (dotted lines).

The nanocrystals were readily purified by precipitation with alkyl nitriles; full details can be found in the † ESI. Powder X-ray diffraction (XRD) θ-2θ measurements were performed on thin films of these materials deposited on amorphous silicon wafers; the samples were protected with a thin (25 µm) layer of Kapton® film to prevent photo-oxidation of the samples. A Bruker D2 Phaser diffractometer was used to measure diffraction patterns of the three samples (Fig. 3). Scherrer broadening is apparent in the diffraction peaks due to the finite domain size of the nanocrystals and agrees well with the observed changes in the optoelectronic spectra observed during nanocrystal growth. The expected reflections for Zn_3N_2 with an anti-bixbyite crystal structure [PDF 35-0762] are clearly observed, such as those originating from the (004) and (440) lattice planes, although some reflections are either very weak or missing altogether ((321) and (332)). This may be due to preferential alignment of the (100) and (110) planes of the nanocrystals parallel to the plane of the film prepared for the XRD measurements. XRD measurements on nanocrystalline Zn_3N_2 synthesised using the same approach, but without oleylamine showed very good agreement with all expected reflections for Zn_3N_2 (see ESI, † Fig. S1).

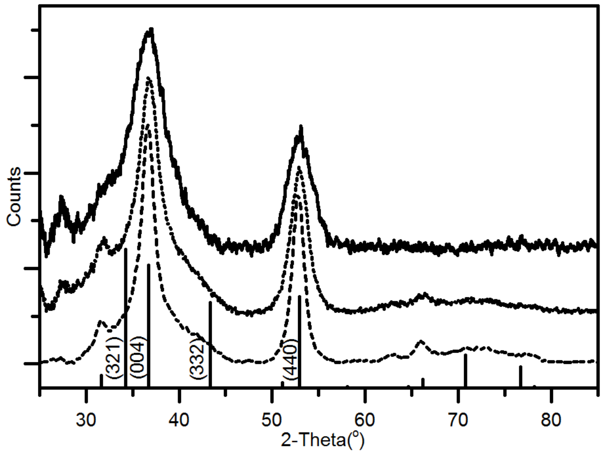

Fig. 3 – Powder X-ray diffraction patterns of Zn_3N_2 nanocrystals with peak emission in solution at 585 nm (solid line), 752 nm (dotted line) and 1073 nm (dashed line). Sticks show the peaks reported for Zn_3N_2 with an anti-bixbyite crystal structure [PDF 35-0762].

To further study the structure of the nanocrystals toluene solutions of the purified samples were drop cast onto ultra-smooth carbon or lacy carbon grids for analysis by transmission electron microscopy (TEM). Representative images are presented in Fig. 4 together with histograms illustrating the size distribution of the three samples. The TEM images support the size tuning observed in the XRD patterns and expected from the optical spectra. The histograms clearly show a plurality of similarly sized nanoparticles in each sample. For the smallest nanocrystals we observed small aggregates containing 5-10 individual nanocrystals (Fig. 4c). The mean sizes obtained from analysis of these images are in broad agreement with those calculated from Scherrer analysis of the (440) peak in the corresponding XRD patterns. High resolution TEM images of two representative crystals are shown in Figs. 4d and 4f together with the corresponding FFT patterns (Figs. 4e and 4g). Analysis of the FFT patterns indicate plane spacings of {004} 2.52 Å, {440} 1.72 Å, {444} 1.42 Å and {408} 1.09 Å, which are in good agreement with the expected spacings for Zn_3N_2 (2.44 Å, 1.73 Å, 1.41 Å and 1.09 Å).

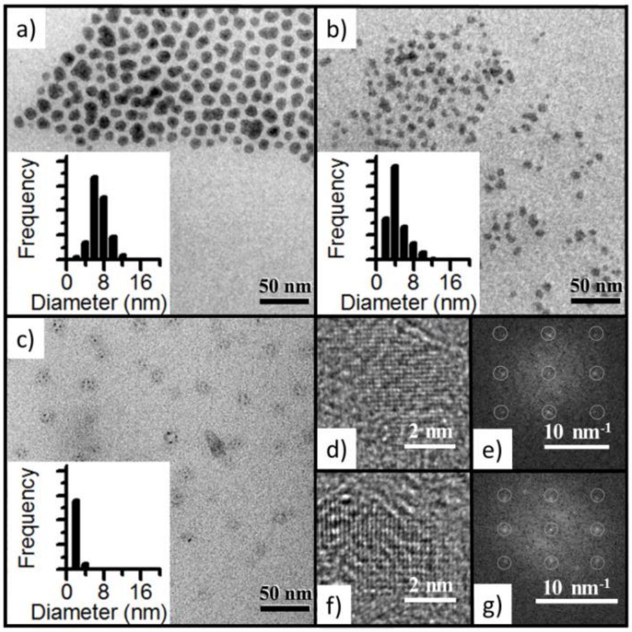

Fig. 4 – TEM images of the Zn_3N_2 nanocrystals with peak emission in solution at 1073 nm (a), 752 nm (b) and 585 nm (c); High resolution images observed along the [211] (d) and [110] (f) zone axes and corresponding FFT (e and g). The circles show the expected positions of the spots in the FFT patterns.

Unfortunately our attempts to obtain energy dispersive X-ray spectroscopy (EDX) data from the particles were hampered by their poor stability under the electron beam (see ESI, † Fig. S2) but elemental analysis gave a Zn:N atomic ratio of 3.0:2.1 which is in good agreement with that expected for Zn_3N_2.

Having successfully synthesised highly emissive zinc nitride nanocrystals we studied the effect of changing the reaction parameters on the synthesis. Initially we altered the flow rate of ammonia gas while leaving the other parameters unchanged. As can be seen in Fig. 5, reducing the ammonia flow resulted in larger nanocrystals being formed and conversely greater ammonia flows led to the formation of smaller particles. This behaviour is likely a result of altering the quantity of nanocrystals which nucleate during the initial stages of the reaction. With lower flow rates fewer nanocrystals nucleate so these grow larger after the addition of a given quantity of diethylzinc. Being able to control the degree of nucleation enables large quantities of nanocrystals of any given size to be produced. We have also investigated how the size of the individual diethylzinc injections affects the progress of the reaction. In this case large injections (2.0 mmol) have a similar effect to reducing the ammonia flow rate, whereas smaller injections (0.5 mmol) produce smaller nanocrystals (see ESI, † Fig. S3). This provides an alternative method to control the amount of nucleation. From a mechanistic viewpoint these observations suggest that the ratio of diethylzinc to ammonia controls the point at which nanocrystal growth commences. In cases where there is an excess of diethylzinc (large injections or low ammonia flow) nanocrystal growth starts sooner than in cases where less diethylzinc is present. More studies are planned to further investigate this fascinating reaction.

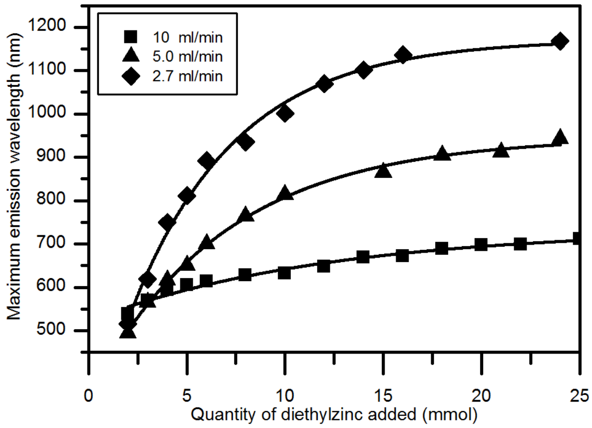

Fig. 5 – Effect of ammonia flow rate on the growth of Zn_3N_2 nanocrystals with the addition of diethylzinc – solid lines are a guide to the eye.

Conclusions

In conclusion, we have demonstrated for the first time the synthesis of highly luminescent zinc nitride nanocrystals. The method described uses cheap and readily available starting materials. The resulting nanocrystals are highly emissive and benefit from an extremely wide wavelength tuning range covering much of the visible and NIR spectrum, with the emission wavelength being easily controlled through the quantity of diethlyzinc employed. Considering that other nanocrystal materials often contain toxic or rare elements, zinc nitride nanocrystals, with such a wide tunable range, offer advantages in a number of applications, including solar cells, LEDs, displays and sensors.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Detailed experimental procedures, XRD patterns of zinc nitride prepared without oleylamine ligands, additional TEM images and details of effect of diethylzinc injection size on nanocrystal growth. See DOI: 10.1039/c000000x/

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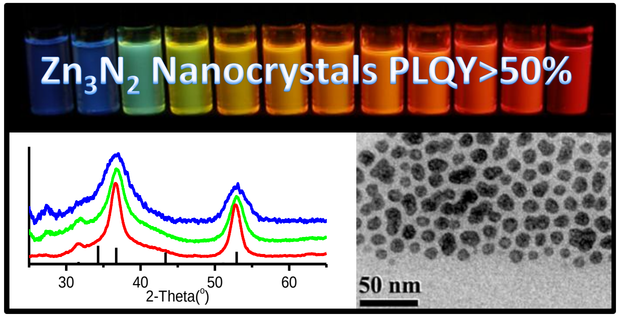

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