Supporting Information

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Photo- and Electroluminescence from Zn-Doped InN Semiconductor Nanocrystals

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**Figure S1.** (Top row) Photoluminescence excitation (PLE) spectra of (a) InZn_{0.5}N, (b) InZnN and (c) InZn_{2}N taken at 25 nm intervals across the emission spectrum. Dashed lines show the absorption and dashed dot lines the nanocrystal photoluminescence from which the PLE spectra were obtained. (Bottom row) The wavelength selected PL lifetime components obtained by fitting a tri-exponential decay to PL decay transients measured at 50 nm intervals across the emission from the materials shown above each panel.
Figure S2. (Top row) The PL spectral evolution as a function of nanocrystal growth time (at 240 °C) using a precursor stoichiometry of (a) In:Zn<sub>0.5</sub>, (b) In:Zn and (c) In:Zn<sub>2</sub>. Included is data from an aliquot taken at 225 °C to show the onset of photoluminescence during the heat up process (dot-dashed line). Below are images of the nanocrystal solutions under 365 nm excitation using a visible (top) and a NIR camera (bottom) left to right aliquots taken 225 °C and 1-40 min reaction solutions. (Bottom row) The PL peak positions (black squares) and FWHM (red triangles) as function of reaction time for the spectra presented.

Figure S3. (Top row) The PL lifetime decay of nanocrystal solutions with precursor stoichiometries of (a) In:Zn<sub>0.5</sub>, (b) In:Zn and (c) In:Zn<sub>2</sub> as a function of reaction time. (Bottom row) Extracted lifetimes using tri-exponential fitting (green, red and black squares) and corresponding QY (blue stars) for each sample.
Figure S4. TEM images of (a) InZn$_{0.5}$N, (b) InZnN and (c) InZn$_2$N NCs after 40 minutes growth. Scale bars 20 nm.

Figure S5. i) A HAADF-STEM micrograph of several InZnN nanoparticle after 40 minutes of growth showing crystal structure. Scale bar 5 nm ii) shows the Fourier transform of the nanocrystals highlighted in (i). iii) A table of the corresponding diffraction data for the reciprocal d-spacings, D spacings and angle between reflections in the Fourier transform of (ii). iv) and v) show the bulk lattice and simulated diffraction pattern for bulk hexagonal InN in the [100] direction utilizing the lattice constants of $^{[1]}$.
Figure S6. A HAADF-STEM micrograph of several InZnN nanocrystals extracted upon heating at 225 °C consistent with a hexagonal crystal structure. Scale bar 5 nm.

Figure S7. Powder X-ray diffraction patterns for InN and InZnN with a brief exposure to air and the corresponding literature InN,\textsuperscript{[1]} and Zn\textsubscript{3}N\textsubscript{2},\textsuperscript{[2]} as reference.

The main defects that are known to account for shifts in the InZnN XRD peaks are interstitial Zn, In substitution by Zn, N substitution by Zn, and also N vacancies.\textsuperscript{[3]} It has been predicted that Zn substitution of In and N vacancies are the most stable defect due to the lowest negative formation energy, whilst interstitial Zn, and N substitution by Zn, are considered to be metastable.\textsuperscript{[4]} Substitutional doping of In by Zn induces compressive strain reducing the overall lattice constant in that region, whilst substitution of N by Zn is tensile and causing lattice expansion.\textsuperscript{[3]} A combination of these defects would lead to the XRD patterns reported, however other interstitial defects can have varying effects depending on lattice position.\textsuperscript{[3,5]}
Figure S8. XRD of air exposed InZn$_{0.5}$N, InZnN and InZn$_2$N nanocrystals, (a) showing the corresponding literature diffraction values for (top) hexagonal InN,[1] (middle) anti-bixbyite Zn$_3$N$_2$[2]. (b) (top) Wurtzite Zinc oxide (middle), Indium oxide (bottom) ZnON as reported.[6,7] (*) Indicate reflections from the support.

Table S1. A comparison of the stoichiometry of alloyed NCs from the input precursor ratio to that determined by EDS and lab-based Al Kα XPS after a reaction time of 40 minutes. Stoichiometry normalized to Indium. (ND – not within detectable limits)
Figure S9. Depth-profiling SR-XPS of an InZn$_2$N nanocrystal sample after 5 minutes growth at 225 eV (top), 550 eV (middle) and 800 eV (bottom) kinetic energy corresponding to a sampling depth of 2.0 nm, 3.5 nm and 4.6 nm respectively. Depth profile results have been normalized to [In] = 1.0 such that the different peak heights represent the elemental concentrations relative to In. C 1s and O 1s magnitudes have been scaled down to a size comparable with other elements present.
**Figure S10.** Depth-profiling SR-XPS of an InZn$_2$N sample after 30 minutes growth at 225 eV (top), 550 eV (middle) and 800 eV (bottom) kinetic energy which correspond to a sampling depth of 2.0 nm, 3.5 nm and 4.6 nm respectively. Depth profile results have been normalized to [In] = 1.0 such that the different peak heights represent the elemental concentrations relative to In. C 1s and O 1s magnitudes have been scaled down to a size comparable with other elements present.
Table S2. Depth-profiling SR-XPS. A comparison of the stoichiometry normalized to In, as function of photo-excited electron kinetic energy of 225, 550 and 800 eV, corresponding to a sampling depth of 2.0 nm, 3.5 nm and 4.6 nm respectively, for an InZn$_2$N sample after reaction time of a) 5 minutes and b) 30 minutes. Due to the X-ray energy required and the monochromator range, the Zn 2p$_{3/2}$ peak was used to determine the relative composition at a kinetic energy of 225 eV whilst the 3s was utilized for 550 and 800 eV respectively and an experimentally determined cross section correction was applied. Stoichiometry normalized to Indium. (ND – not within detectable limits)

| KE (eV) | Sampling depth (nm) | In 3d | Zn 2p$_{3/2}$/3s | N 1s      | S 2p     | Na 1s   |
|---------|---------------------|-------|-----------------|-----------|----------|---------|
| 225     | 2.0                 | 1.0   | 1.3 ± 0.2       | 1.3 ± 0.1 | -        | 1.8 ± 0.2 |
| 550     | 3.5                 | 1.0   | 1.7 ± 0.2       | 1.8 ± 0.2 | 2.8 ± 0.2 | ND      |
| 800     | 4.6                 | 1.0   | 1.5 ± 0.3       | 1.7 ± 0.3 | 1.8 ± 0.4 | -       |

| KE (eV) | Sampling depth (nm) | In 3d | Zn 2p$_{3/2}$/3s | N 1s      | S 2p     | Na 1s   |
|---------|---------------------|-------|-----------------|-----------|----------|---------|
| 225     | 2.0                 | 1.0   | 2.0 ± 0.2       | 1.4 ± 0.1 | -        | 1.7 ± 0.1 |
| 550     | 3.5                 | 1.0   | 1.8 ± 0.2       | 1.0 ± 0.1 | 1.1 ± 0.1 | 0.8 ± 0.1 |
| 800     | 4.6                 | 1.0   | 2.0 ± 0.2       | 0.9 ± 0.1 | 1.0 ± 0.1 | -       |

Figure S11. SR-XPS spectra of the In 3d region at 225 eV (top), 550 eV (middle) and 800 eV (bottom) kinetic energy corresponding to a sampling depth of 2.0 nm, 3.5 nm and 4.6 nm respectively, illustrating an extra higher binding energy consistent with a hydroxylated/oxynitride In species towards the surface (225 eV) for an InZn$_2$N sample with a 5 minute growth time.
Figure S12. SR-XPS spectra of the N 1s region at 225 eV (top), 550 eV (middle) and 800 eV (bottom) kinetic energy corresponding to a sampling depth of 2.0 nm, 3.5 nm and 4.6 nm respectively, illustrating an extra higher binding energy consistent with a protonated N species at the surface (225 eV) for an InZn$_2$N sample with a 30 minute growth time.

Figure S13. TEM image of InZnN nanocrystals under 300 kV electron beam irradiation after 30 seconds (left) and 2 minutes (right) displaying signs of degradation within the electron-beam. Scale bar 20 nm.
**Figure S14.** A schematic representation of the initial and longer growth dynamics within the synthesis of InZnN NCs via NaNH$_2$ method. Highlighting initially the formation of an InN rich seed followed by Zn diffusion and growth. For later growth when NaNH$_2$ is depleted, the unbound Na becomes more important and diffuses into the NC.

| Sample            | In    | Zn    | Ga    | N     | S     |
|-------------------|-------|-------|-------|-------|-------|
| InZnN             | 1.0   | 0.7 ± 0.2 | -    | 0.3 ± 0.2 | 0.7 ± 0.2 |
| InZnN/ZnS         | 1.0   | 1.8 ± 0.2 | -    | 1.8 ± 0.2 | 1.5 ± 0.2 |
| InZnN/GaN         | 1.0   | 0.7 ± 0.2 | 0.2 ± 0.2 | 1.6 ± 0.2 | 0.7 ± 0.2 |
| InZnN/GaN/ZnS     | 1.0   | 3.8 ± 0.2 | 0.3 ± 0.2 | 1.6 ± 0.2 | 3.6 ± 0.2 |

**Table S3.** A comparison of the stoichiometry of the nanocrystals using EDS of an InZnN core grown to 30 minutes before shelling and with ZnS, GaN and GaN/ZnS shelling. Stoichiometry normalized to Indium.
Figure S15. (a) PL and EL spectra before and following correction for detector artefacts and smoothing. (b) Typical J-V sweep for the InZn$_2$N QDLEDs. Inset is a schematic of the energy band alignment for the device.

Figure S16 The instrument response function (IRF) of the TCSPC system was measured by placing a very diluted solution of milk as light scattering media in the sample holder and setting the detector at the excitation wavelength to record the time response of the experiment.

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