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Supplementary Information[†]

Gas-Liquid Flow Synthesis of Zn₃N₂-Quantum Dots

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Figure S1: Fluorescence emission maxima as function of periodically added diethylzinc in a batchwise synthesis approach. Standard deviations results from four individual batches. The wavelength emission maximum increases logarithmitically at 225 °C and linearly at 190 °C.



Figure S2: Piping and Instrumentation Diagram of continuous Zn_3N_2 synthesis. Throughout production, the liquid precursor diethylzinc is flushed with inert gas and diluted in-line with the solvent 1-octadecene by means of a slit-interdigital static mixer. N_2 is applied in the pre-operating procedure to reach the reaction temperature and to obtain blank spectra of the gas-liquid mixture for baseline correction. Then, the gas flow is switched to NH_3 which is the second precursor. Its pipeline and gas mass flow meter are thermally insulated to prevent condensation before both reaction partners are brought together in a second static mixer (T-piece) to generate a gas-liquid segmented flow. For this purpose, all gas and liquid flow rates are recorded as well as the system pressure. A check-valve prevents possible damage to the instruments from reflux. The reaction solution then enters the hot and afterwards the cool zone before the fluorescence emission is recorded online at room temperature. Finally, the synthesis fractions are collected automatically under N_2 atmosphere.



Figure S3: Schematic flow-chart demonstrating input and output variables in a thermodynamic process simulation (top). Simulated ammonia gas mass flow as a function of room temperature, back pressure and water impurities (bottom). To dimension the reactor, the gas cylinder is considered as a heat exchange module with a specific surface of 0.064 m² derived from its actual shape. As input factors, an air circulation was considered of 1700 Nm³h⁻¹ within the fume hood. As a result, sufficient ammonia mass flows (> 100 ml/min) can be supplied by the employed gas cylinder (8.6 bar) as gas phase only (VF ~1). In detail, gas regulation (5 or 7 bar) has the major influence on the withdrawal amount in comparison to room temperature variations (20-24 °C) and water impurities (200 ppm).



Figure S4: Slit interdigital micromixer designed and manufactured as Fraunhofer IMM (Mainz, Germany) which was applied to adapt the liquid-liquid ratio of diethylzinc with 1-octadecene for inline-dilution.



Figure S5: Photo images of the gas-liquid interface after joining (top left), before heat reaction zone (top right) and within cooling zone (bottom). The size of the initial gas segments decreases towards the heat reaction zone and expands rapidly at reaction temperatures of 190- 225 °C. A dewetting behaviour becomes visible again after cooling the reaction medium within the water bath.



Figure S6: Offline fluorescence spectra as a function of excitation wavelengths (Ex) of technicalgrade oleylamine (top left), and two Zn_3N_2 QDs samples (middle and bottom). Zn_3N_2 nanocrystals can be clearly distinguished from technical-grade oleylamine which is used as surfactant. Latter exhibits emission maxima from 350-480 nm and their second order starting around 700 nm. In addition, a strong excitation dependency becomes visible indicating multiple fluorescence states and/or species. To completely avoid excitation of such species within technical-grade oleylamine, 455 nm was used as common excitation wavelength of Zn_3N_2 QDs samples for offline as well as online analysis. A less pronounced Ex-Em dependency also exists for blue emitting Zn_3N_2 QDs (middle) when using excitation wavelengths > 430 nm which decreases with nanoparticle growth and vanishes for QDs emitting at 580 nm or higher wavelengths (bottom).



Figure S7: Offline fluorescence spectra of the same Zn_3N_2 QDs sample as a function of time within. The emission maxima blueshifts when the sample is prepared and measured at atmospheric condition (top row). The peak position and intensity remain most stable within 1-octadecene and additionally dried toluene when prepared and sealed under inert gas condition (bottom row). In comparison, the initial signal intensity was found to be the highest within additionally dried toluene over time.



Figure S8: Residence time distribution (E(t), left axis) and sum distribution (F(t), right axis)at different total mass flow settings within the Zn_3N_2 tubular reactor based on Nile Red as a tracer material. Four average residence times were considered. One average residence time is similar to the batchwise synthesis approach (292 s $\approx 5 \text{ min}$).



Figure S9: TEM images of Zn_3N_2 nanocrystals (left), particle circularity results (right histograms) including their statistical analysis. Cyan lines indicate the objects suitable for analysis. The circularity decreases with increasing particle size (top to bottom) which indicates atomic addition to selective crystal facets in relation to the monomer amount available in solution.



Figure S10: Electron energy loss spectra of the same Zn_3N_2 sample: Zn (top left), N_2 (top right) and O_2 (bottom). EEL spectroscopy qualitatively confirms the presence of a Zn-N compound among the continuously fabricated 10 nm nanoparticles. The specific energy loss of oxygen was also detected as an indication of ZnO as a side product.



Figure S11: Full widths at half emission maximum (FWHM) at various emission wavelength of continuously synthesised Zn_3N_2 Quantum dots. FWHM increases with emission wavelength of the sample material.



Figure S12: Integrated fluorescence intensity as a function of absorbance at 480 nm (left) of four Zn_3N_2 quantum dots samples and Rhodamine 6G (Rh6G) as reference material. Corresponding fluorescence spectra (dotted line) and absorbance spectra (right). There is a linear correlation between the integrated intensity of the fluorescence emission signals and the absorbance value at 480 nm. As a result, quantum yields of the samples were determined to be circa 20 and 56% taking the error estimations into account. There is no clear exciton peak found within the absorbance spectra of differently coloured Zn_3N_2 quantum dots.



Figure S13: Photo image at UV-light of post-synthetic surface passivation using the same Zn_3N_2 sample and different surfactants, diluted aliquots in toluene (top row). Qualitatively, surfactants with higher Lewis base strength were found to enhance the photon efficiency (tributylphosphine, trioctylphosphine). The 1-octanol sample shows a blue shift in colour which indicates an etching effect, that is a decrease in nanoparticle size. Zn_3N_2 decomposes after addition of thiol-surfactants. Here, all surfactant materials were used without drying procedure.



Figure S14: Online fluorescence spectra of Zn_3N_2 quantum dots at different process parameter conditions during continuous synthesis. The raw and smoothed spectra are grey and red respectively. The second maximum at 760 nm and the shoulder at 658 nm are attributed to measurement artefacts since both are visible regardless of the sample material.