

## Continuous supercritical route for quantum-confined GaN nanoparticles

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### Residence time calculation:

The residence time of the continuous reaction was determined using the following equation:

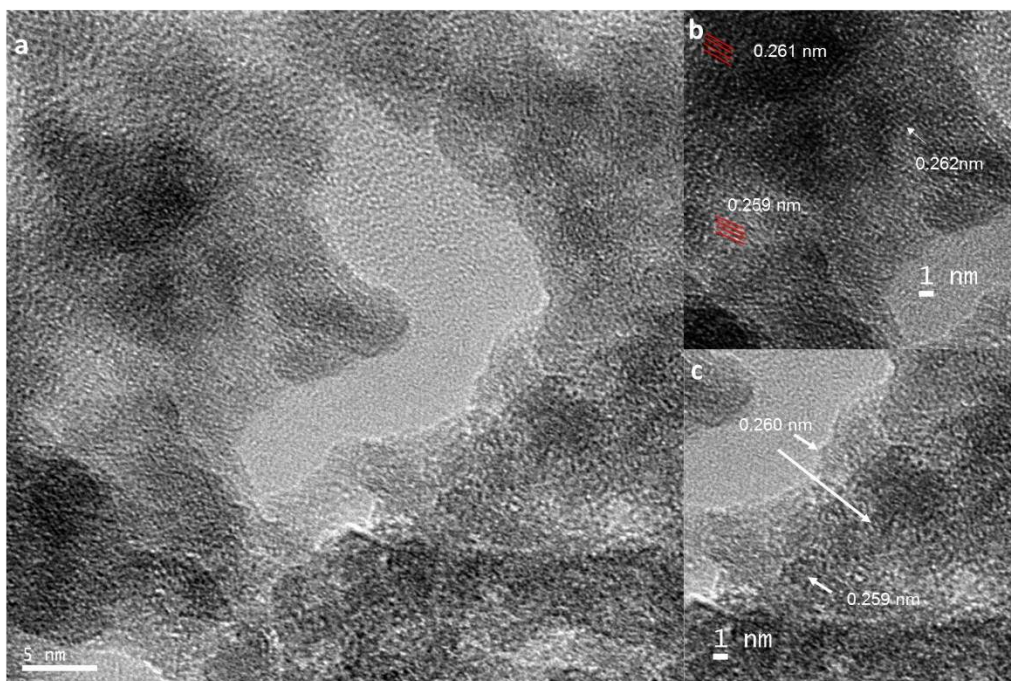
$$t_s = \frac{V_r * \rho_r}{Q_{pump} * \rho_{pump}}$$

Where  $t_s$  is the residence time in seconds (s),  $V_r$  is the volume of the reactor in  $m^3$ ,  $\rho_r$  is the density of the fluid in the reaction conditions in  $kg.m^{-3}$ ,  $Q$  is the flow rate of the fluid in  $m^3.s^{-1}$  and  $\rho_i$  is the density of the fluid at the working pressure and ambient temperature (25 °C) in  $kg.m^{-3}$ .

The fluid densities of both processes could be determined using REFPROP® from the NIST (National Institute of Standards and Technology).

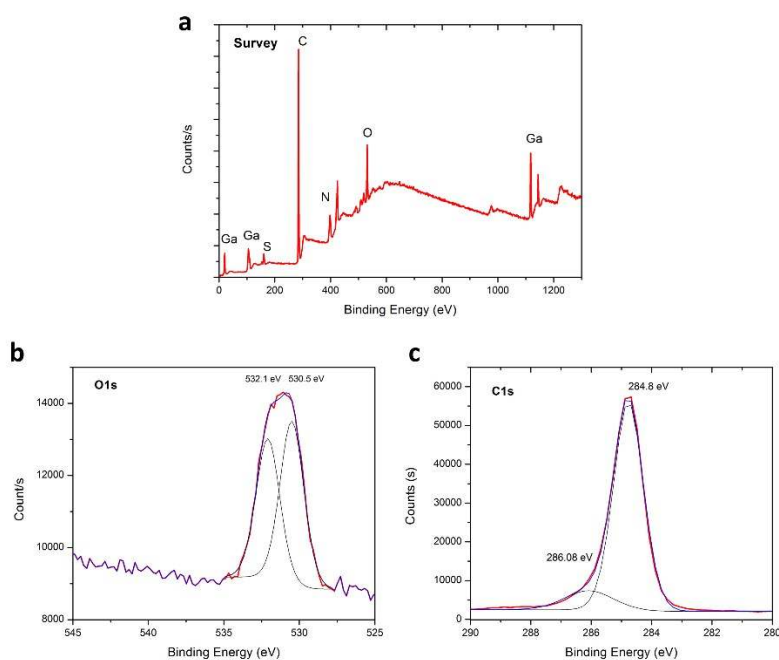
	$\rho_r$ (in $kg.m^{-3}$ )	$\rho_i$ (in $kg.m^{-3}$ )	$Q_{pump}$ ( $m^3.s^{-1}$ )
<b>Process 1</b> <b>(pure cyclohexane)</b>	366,97	786,01	$3,33 \times 10^{-8}$
<b>Process 2</b> <b>(hexane-ammonia mixture)</b>	99,87	664,40	$1,67 \times 10^{-8}$

The volume of the reactor is 1,571 mL ( $1,571 \times 10^{-6} m^3$ ) and was the same in both experiments. Using these values the residence times were estimated to be 22 seconds in process 1 and 14 seconds in process 2.



**Figure S1** a, b, c) HRTEM pictures of the as-prepared GaN NPs

Looking at HRTEM pictures lattice fringes of GaN NCs can be identified. A d-spacing of roughly 0.26 nm corresponding to the  $\langle 111 \rangle$  plane of cubic GaN can be measured as seen in Figure S1.



**Figure S2** a) XPS survey for as-prepared GaN QDs b, c) High Resolution XPS signals for b) O1s and c) C1s

The presence of  $\text{Ga}_2\text{O}_3$  was excluded from the narrow Ga3d signal centered at 19.7 eV;  $\text{Ga}_2\text{O}_3$  is expected to be centered at 20.5 eV or higher.<sup>1,4</sup>

Regarding the XPS of O1s, the broad O1s signal could be separated into two signals: one centered at 530.5 eV and a second one centered at 532.1 eV. O1s signal is expected to be centered at 531.2 eV

for Ga<sub>2</sub>O<sub>3</sub>.<sup>1</sup> The lower binding energy signal (530.5 eV) could be due to a form of doubly bonded oxygen at the surface Ga-O-N or C-O-N (air/moisture contamination).<sup>2</sup> The higher energy contribution, signature of -OH formation, could be due to water contamination, during sample exposition to air.<sup>3</sup>

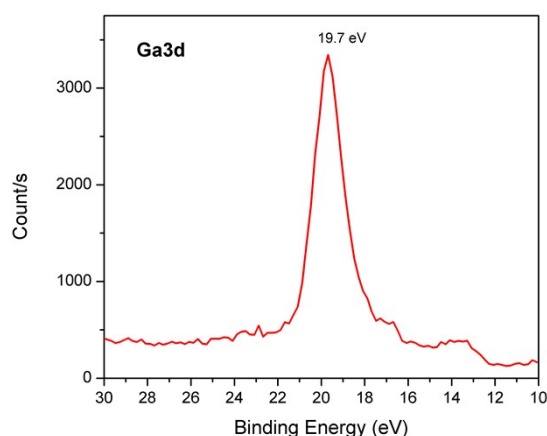
Finally we think that there is no lattice oxygen in our materials but possibly oxygen from some surface pollution.

XPS of N<sub>2</sub> is expected at much higher binding energies *i.e.* 403 eV reference <sup>5,6</sup>. The presence of N<sub>2</sub> in the system is improbable and the XPS signals do not show any N<sub>2</sub> signature.

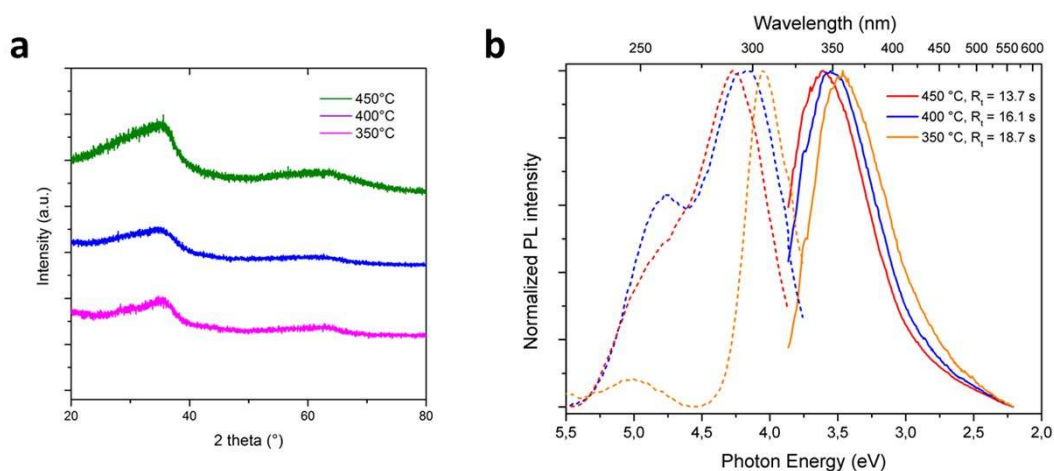
The contribution at 399.4 eV is in agreement with the formation of N-C bond. This signal was attributed to the surface state of our materials and to the presence of dimethylamine/trimethylamine byproduct in the reaction media that can act as a surface modifier. This assumption is supported by the FTIR spectra performed on the as-prepared NPs, where signatures corresponding to vibration of N-CH<sub>3</sub> were recorded.

Additional references were added for the 399.4 eV contribution due to C-N.<sup>7,8</sup> N-O species might also arise at high binding energies *i.e.* 402 eV,<sup>8,9,10</sup> but are not detected in our case.

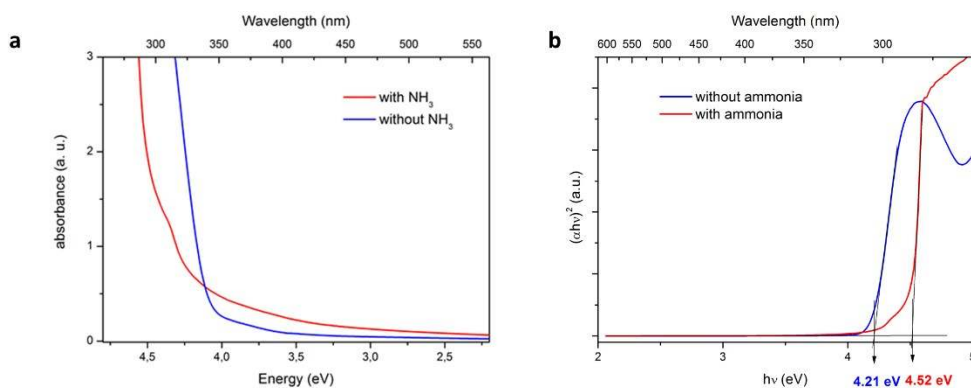
C1s signal is centered at 284.8 eV in agreement with the presence of sp<sup>2</sup> or sp<sup>3</sup> from elemental carbon due to the use of carbon tape during sample preparation (C-C bond).<sup>9,11</sup> The higher energy contribution around 286.1 eV could correspond to a sp<sup>3</sup>-C bound to a N atom.<sup>8</sup>



**Figure S3** Ga3d XPS signal of the GaN QDs prepared in supercritical cyclohexane at 400 °C & 150 bar



**Figure S4** a) XRD pattern and b) PL spectra of sample prepared in supercritical cyclohexane at 69 bar and 350, 400 and 450 °C



**Figure S5** a) UV-Vis absorption spectra of sample prepared in supercritical cyclohexane (in blue) and in the hexane-ammonia mixture (in red). b) Tauc Plot for optical bandgap determination of the as-prepared GaN quantum dots. Blue curve is for NPs prepared without ammonia, the red one is for NPs prepared with ammonia

The optical bandgap could be determined from the Tauc plot where the  $(\alpha h\nu)^{1/n}$  vs  $h\nu$  was fitted with  $n = \frac{1}{2}$  (for direct allowed transition). Bandgaps of 4.21 and 4.52 eV were determined, for particles prepared without ammonia (average size: 3.1 nm) and in presence of ammonia (average size: 2.8 nm), respectively. This measurement is in agreement with the preparation of quantum-confined cubic-GaN, and is an additional proof of size-related properties.

#### Reference

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