



HAL
open science

Chemistry platform for the ultrafast continuous synthesis of high-quality III–V quantum dots

Baptiste Giroire, Garcia Alain, Samuel Marre, Thierry Cardinal, Cyril Aymonier

► **To cite this version:**

Baptiste Giroire, Garcia Alain, Samuel Marre, Thierry Cardinal, Cyril Aymonier. Chemistry platform for the ultrafast continuous synthesis of high-quality III–V quantum dots. *Chemistry - A European Journal*, 2021, 27 (51), pp.12965-12970. 10.1002/chem.202101802 . hal-03354280

HAL Id: hal-03354280

<https://hal.science/hal-03354280v1>

Submitted on 24 Sep 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Chemistry Platform for the Ultrafast Continuous Synthesis of High Quality III-V Quantum Dots.

B. Giroire,^[a] A. Garcia,^[a] S. Marre,^[a] T. Cardinal^[a] and C. Aymonier*^[a]

Abstract: A chemistry platform for the fast continuous synthesis of III-V quantum dots is demonstrated. III-nitride QDs are prepared using short residence times (less than 30 s) in a one-step continuous process with supercritical solvents. GaN QDs prepared *via* this route exhibit strong UV photoluminescence with a structuring of the emission signal at low temperature (5K), confirming their high quality. An example of metal site substitution is given with the synthesis of $\text{In}_x\text{Ga}_{1-x}\text{N}$ solid solution. A continuous bandgap shift towards lower energies is demonstrated when increasing indium content with strong photoluminescence signals from UV to visible. The chemistry platform proposed could be easily extrapolated to binary and ternary III phosphides or arsenides with the homologous V source.

III-V semiconductors have been well studied for the past 40 years due to their excellent optoelectronic properties^[1–4]. A wide range of applications can be achieved with bulk III-V semiconductors such as laser diodes (GaN^[5], GaInAsN/GaAs^[6,7]) and UV detection (GaN^[8], GaInP-AlInP-GaAs^[9], AlGaIn^[10]). Binary and ternary III-V have attracted increasing interest with the display of quantum confinement effect and size-related properties with decreasing particle diameter^[11,12]. III-V quantum dots (QDs) are excellent candidates for solid state lighting devices^[13] with a precise control of emission wavelengths from ultraviolet ((Al,Ga)N^[14]) to infrared (InAs^[15]). The current outlook for these systems includes their use in photonic waveguides^[16,17], their implementation in trace-gas or chemical sensing devices^[18–20] and their use as replacement for organic phosphors in OLED-like structures^[21–23]. III-V QDs are also amongst the best lead-free and cadmium-free candidates for bio-related applications^[24] such as bio-imaging^[25], bio-sensing^[26] and bio-integrated devices^[27]. However, the preparation of high quality III-V QDs with size and morphology control can be challenging compared to II-VI semiconductors^[28], especially CdSe, where size control^[28,29] and shape control have been widely demonstrated^[30,31]. Synthesis in supercritical fluids has been established as an efficient method for the continuous synthesis of nanomaterials of controlled size, crystallinity, morphology and composition due to precise control of the reaction media through a fine tuning of the experimental conditions^[32–36]. High quality II-VI QDs, exhibiting sharp excitonic emission, have already been fabricated using this approach, *i.e.* CdSe^[37,38] and ZnO^[39,40], with evidence of size-related optical properties. Moreover, the proof of concept for the continuous synthesis of III-V nanocrystals in supercritical fluids, demonstrating evidence of size dependence of the bandgap, was established in our previous work on GaN QDs from a single

source precursor^[41]. However, this approach lacks versatility for the fabrication of other III-V QDs such as phosphides, arsenides or ternary nitrides.

The most successful approach to prepare III-V semiconductors in solution-based processes is through the use of tris(trimethylsilyl) derivatives as the V source (*i.e.* TMS-As and TMS-P) mixed with III-halides^[42–45] as well as organometallic precursors^[46,47]. This chemistry has been reproduced in continuous microfluidic processes, primarily the synthesis of high quality InP QDs^[11,48].

Here, we propose a chemistry platform for an ultrafast continuous preparation of high quality III-V semiconductors with controlled size distribution and morphology *via* the gallium nitride model system. Nanosized GaN particles have been successfully prepared by reacting various gallium sources such as gallium halides^[49,50], azide^[51], and cupferronate (cup)^[52] with a nitrogen source (mostly ammonia). Beyond our previous works on the synthesis of GaN using a single source-Ga based precursor, we demonstrate in this report the use of double source precursors for the synthesis of III-nitride QDs in a continuous microscale process operated at supercritical conditions. Two types of gallium sources (Ga₃ or Ga(cup)₃^[52]) were considered along with two trimethylsilyl derivatives as nitrogen sources hexamethyldisilazane (HMDS) and (TMS)₃N. This approach has also been validated for $\text{In}_x\text{Ga}_{1-x}\text{N}$.

In a typical experiment, the gallium and nitrogen sources are injected in two separate lines using two Jasco PU 2080 plus high-pressure pumps operating at 150 bar and 1 mL·min⁻¹ (2 mL·min⁻¹ of total flow rate). The precursor concentration is fixed at 5 × 10⁻³ M for both the gallium source and the nitriding agent. The two precursors meet in a tee mixer (Figure 1) prior to entering the reactor set at a temperature of 350 °C. Under these conditions the residence time in the reactor is approximately 30 seconds. The products are collected continuously during the reaction and the GaN QDs are recovered after centrifugation of the collected solution.

[a] Dr. B. Giroire, Dr. A. Garcia, Dr. S. Marre, Dr. T. Cardinal, Dr. C. Aymonier
Institut de Chimie de la Matière Condensée de Bordeaux – UMR
5026
87, Avenue du Docteur Schweitzer, 33608 PESSAC cedex (France)
Email: cyril.aymonier@icmcb.cnrs.fr
Homepage: <http://www.icmcb-bordeaux.cnrs.fr>

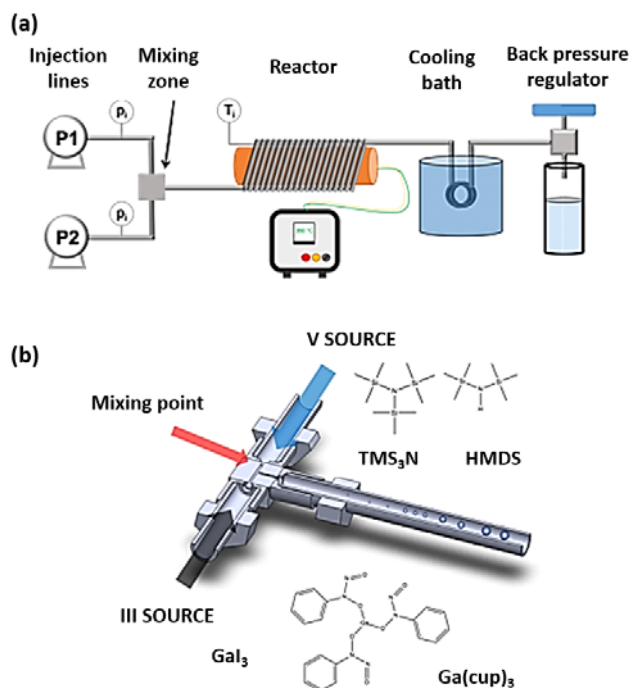


Figure 1 Schematic representation of a) the experimental set-up used for the continuous synthesis of III-V nanoparticles and b) enlargement of the mixing zone.

The materials prepared through the continuous supercritical toluene route from gallium cupferronate displayed similar morphologies for each nitrogen source, as shown by TEM analysis (Figure 2a and 2b), producing spherical aggregates, roughly 100 - 200 nm in width. In both cases, these aggregates are composed of small nanoparticles, 2.5 ± 0.7 and 2.6 ± 0.7 nm average size for the samples prepared from HMDS and TMS₃N, respectively. Particle size was determined from isolated NPs

located on the periphery of aggregates on more than 100 nanoparticles. The morphological similarities between the two samples can be explained by the use of the same hydrodynamic conditions as well as a similar reaction mechanism.

A completely different morphology is observed for the sample prepared with gallium iodide, as isolated particles and non-spherical aggregates are present in this sample. The average size of particles is estimated to be 3.5 nm. Additionally, a significantly lower yield is observed and the collected powder was insufficient to perform XRD characterization on this sample.

XRD patterns of the NPs prepared from Ga(cup)₃, shown in Figure 2c, are composed of two broad bands centered at $2\theta = 34.8$ and 60.8° , usually assigned to the formation of cubic GaN. However, the asymmetry and the width of the first peak could indicate a more complex structure with the presence of wurtzite and/or rocksalt arrangement in our sample. These patterns are in agreement with the formation of nanosized gallium nitride^[41,50,52-54]. The formation of gallium nitride particles was confirmed by X-ray photoelectron spectroscopy (XPS) analysis performed on the sample prepared from Ga(cup)₃ and HMDS (Figure 2d and 2e). The presence of Ga, C, In (support), O, and N was detected in the complete survey (available in supporting info). Ga2p_{3/2} and Ga2p_{1/2} signals are centered at 1145.39 and 1118.54 eV, respectively, in agreement with the formation of Ga-N bonds^[55]. No higher or lower energy contributions can be fitted on the Ga signal, confirming the absence of Ga-O or metallic Ga bonding^[55,56]. The N1s signal of nitrogen can be fitted with two contributions. The first, centered at 394.74 eV, is due to a Ga auger emission^[57] and the second, centered at 398.17 eV, corresponds to the nitride bonding energy (N³⁻)^[55].

The carbon C1s and O1s XPS signals spectra - available in supplementary information - exhibit contributions coming from post-synthesis surface contamination. The O1s signal is decomposed into two contributions at 530.3 eV and 532 eV. The lowest energy contribution can be assigned to surface OH groups or nitroso (N=O) groups^[58]. The highest energy signal can be

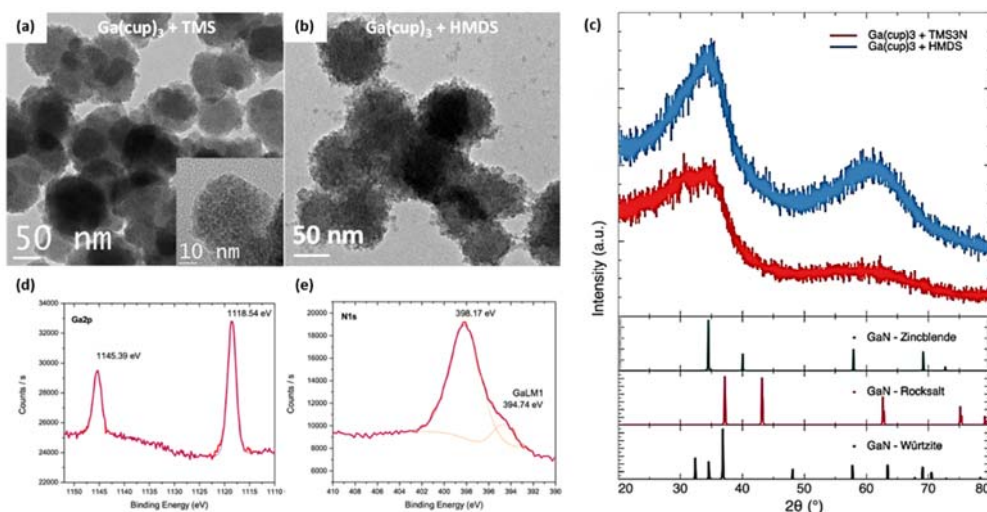


Figure 2 Characterization of GaN QDs obtained from Ga(cup)₃ in reaction with HMDS or TMS₃N. TEM pictures of materials prepared with a), b) Ga(cup)₃ in reaction with TMS₃N and HMDS, respectively and c) XRD patterns, d) XPS Ga2p and e) N1s signals of the sample prepared from HMDS.

attributed to the presence of C-O or C=O bonds^[58,59]. The formation of gallium oxide can be excluded since the Ga-O binding energy in Ga₂O₃ is expected around 531.0 eV^[57,60]. Room temperature photoluminescence (PL) spectra are shown in Figure 3a. Measurements were performed on solid samples (QDs drop-casted onto quartz slides). The excitation spectra are displayed in dotted line on the left-hand side and emission spectra are in plain line on the right-hand side of the Figure. Measurements were performed on solid samples (QDs drop-casted onto quartz slides) for the particles synthesized from gallium cupferronate or on particles in solution for the sample prepared from gallium iodide.

A strong UV emission, centered at 3.47 eV (357 nm) is measured for the sample elaborated from GaI₃ and TMS₃N upon excitation at $\lambda = 313$ nm, in agreement with the synthesis of quantum confined GaN particles^[53]. The lack of higher energy absorption in the excitation spectra is due to concurrent solvent (toluene) absorption. Both samples prepared from Ga(cup)₃ exhibit strong UV luminescence with an emission maximum (λ_{max}) centered at 325 nm (3.81 eV). Excitation spectra show numerous peaks around 280, 260 and a maximum at 230 nm. Upon excitation at these different energies, similar emission spectra - of matching intensities with their excitations - are obtained with the same λ max confirming their origin from the same emission center: GaN QDs. Emission maxima are strongly blue shifted (roughly of 0.55 eV) compared to bulk material (Würtzite, λ max = 370 - 390 nm^[61-63]) confirming the formation of quantum confined GaN particles expected from the size measured by TEM. The structuring of the excitation spectra could be correlated to a discretization of energy levels in the GaN band structure^[64]. Additionally, the narrow FWHM of the emission spectra (0.45 eV for the sample prepared from HMDS) is in accordance with the formation of well crystallized QDs with narrow size distribution^[53].

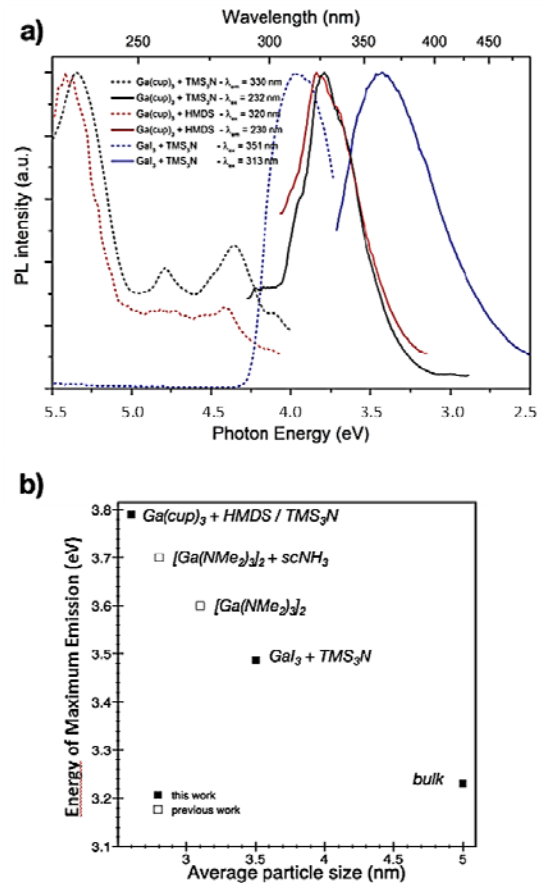


Figure 3 a) Room temperature PL spectra of samples prepared from gallium cupferronate with HMDS (red curve) and TMS₃N (black curve), spectra were collected from powder samples drop-casted onto a quartz slide and NPs prepared from GaI₃ and TMS₃N, spectra were collected in a toluene solution (blue curve) with excitation spectra in dotted line and emission spectra in plain line. b) Correlation between GaN particle size and energy of maximum emission of materials prepared from different routes.

The relationship between the GaN QDs size from this work and our previous study^[41] and their maximum energy emission is presented in Figure 3b. A strong relationship between the GaN QDs size and the emission maximum energy is evidenced by the sample prepared *via* various continuous supercritical routes.

Looking closer at both emissions spectra of the sample synthesized from Ga(cup)₃, the signal may be decomposed into three parts, with peaks at 310, 325 and 335 nm (3.99, 3.81 and 3.70 eV) for the sample synthesized with HMDS and at 315, 325 and 338 nm (3.93, 3.81 and 3.67 eV) for the sample prepared with TMS₃N. The structuring of the emission is further inspected by low temperature measurements performed on solid samples in a liquid helium cell, as shown in Figure 4.

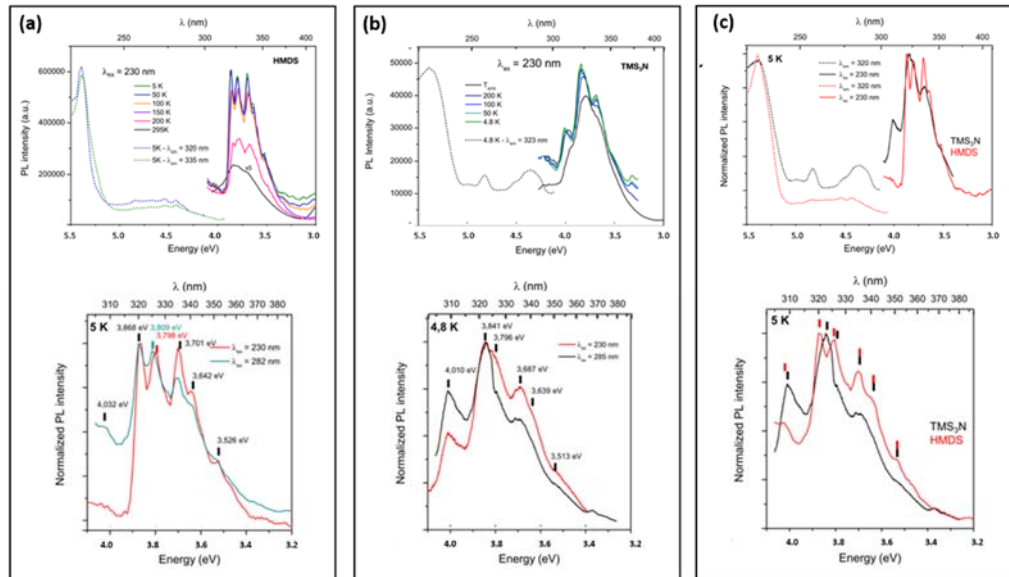


Figure 4 Low temperature PL measurements a) PL spectra from RT down to 5 K of GaN QDs prepared from HMDS (left) and comparison of spectra recorded at 5 K at $\lambda_{\text{exc}} = 230$ nm and 282 nm (right), b) PL spectra from RT down to 4.8 K of GaN QDs prepared from TMS₃N (left) and comparison of spectra recorded at 5 K at $\lambda_{\text{exc}} = 230$ nm and 285 nm and c) 5 K PL comparison between the two materials at $\lambda_{\text{exc}} = 230$ nm (left) and at $\lambda_{\text{exc}} = 280$ nm (right).

Upon decreasing the sample temperature, a finer structuring of both PL emissions occurs with six contributions clearly identified. A strong increase in PL intensity is observed with decreasing temperature. At 5 K, the QDs prepared from HMDS exhibit six major contributions centered at 4.032, 3.868, 3.800, 3.701, 3.642 and 3.526 eV. At 4.8 K, QDs produced from TMS₃N also present six major emission levels centered at 4.010, 3.841, 3.796, 3.687, 3.639 and 3.513 eV, regardless of the considered excitation wavelength. Both low temperature emission PL are composed of narrow FWHM emission levels, in agreement with the formation of small, well-dispersed NPs.

No change in emission is observed when a different excitation wavelength is employed. However, a significant change in energy level intensity ratio is noticed between the two excitation wavelengths for both samples. When excited at higher wavelength, closer to gap levels, an increase of higher energy emission level intensities coupled with a decrease of lower energy emission levels is observed. This behavior can be explained by differences in population density in gap levels that induce differences transition probabilities to the emission levels. To the authors' knowledge, this is the first example of PL structuring for GaN QDs prepared from wet chemistry.

All transitions are listed as a function of temperature and excitation wavelength in Figure 5. Transition energy differences with temperature and excitation wavelength are weak. A maximum difference of 0.064 eV is recorded for the first transition (at 4.01 eV, QDs from TMS₃N). Transitions of both samples are very close in energy (slightly higher for the sample prepared from HMDS), highlighted in Figure 5, implying similar electronic band structures for the QDs. The origin of the different energy levels is difficult to assess, though the higher energy levels may be attributable to free excitons, while the lower energy transitions may result from bound excitons and donor-acceptor pairs. Exciton-phonon coupling could be possible, but the change in

energy with temperature for any given transition is so miniscule that this hypothesis is discarded. Ultrafast spectroscopy is required to further investigate the nature of the different transitions.

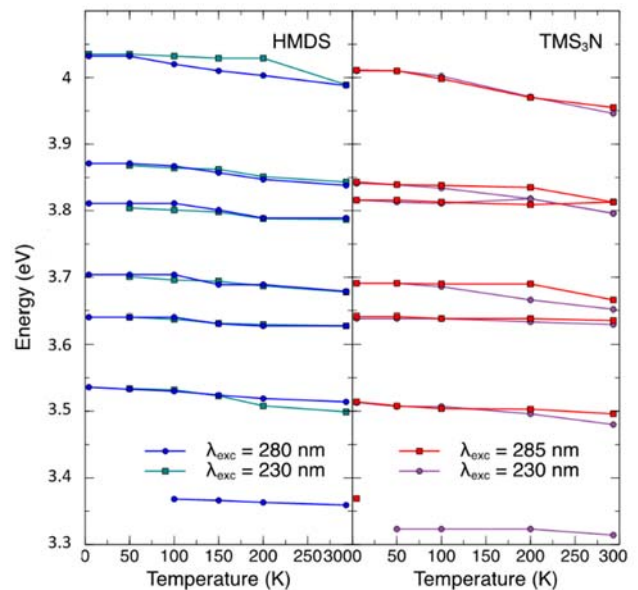


Figure 5 Transition energy positions of all listed contributions as a function of the temperature recorded at $\lambda_{\text{exc}} = 230$ nm and $\lambda_{\text{exc}} = 280$ or 285 nm for TMS₃N (right) and HMDS (left).

GaN QDs produced via our continuous supercritical route with gallium cupferronate in reaction with HMDS or TMS₃N exhibit a very similar band structure.

This result is a validation of the chemistry platform for the synthesis of high quality III-V QDs. To further demonstrate our approach, an example of metal site substitution is shown in Figure

6. QDs of the indium gallium nitride solid solution, up to 40% indium content, were prepared.

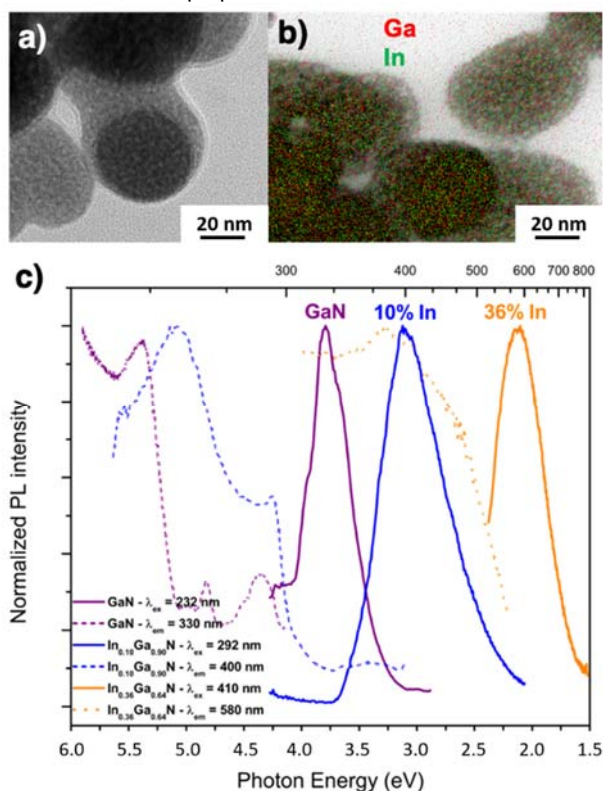


Figure 6 Characterization of InGaN samples: a), b) TEM and STEM pictures of $\text{In}_{0.36}\text{Ga}_{0.64}\text{N}$ sample and c) room temperature PL spectra of GaN, $\text{In}_{0.10}\text{Ga}_{0.90}\text{N}$ and $\text{In}_{0.36}\text{Ga}_{0.64}\text{N}$, with excitation spectra in dotted line and emission spectra in plain line.

The synthesis was performed in similar conditions as previously described. The mixture of metal cupferronate ($\text{In}_x\text{Ga}_{1-x}\text{cup}_3$, $x = 10$ and 40) was dissolved in anhydrous methanol and the nitrogen source (HMDS or TMS_3N) was injected in anhydrous cyclohexane. Reactions were performed at 400 °C and 140 bar. Morphologies similar to those observed with GaN (Figure 2) are obtained, with small NPs aggregated into nanospheres. An intimate mixing of both metals, as well as QD compositions approaching the desired targets are observed with STEM. The QDs are found to be $\text{In}_{0.10}\text{Ga}_{0.90}\text{N}$ and $\text{In}_{0.36}\text{Ga}_{0.64}\text{N}$ for the $\text{In}_{0.10}\text{Ga}_{0.90}\text{N}$ and $\text{In}_{0.40}\text{Ga}_{0.60}\text{N}$ samples, respectively, which are confirmed by photoluminescence. A continuous shift in excitation and emission spectra towards lower energies is observed with increasing indium content. Emission energies close to the theoretical values are measured, with a small shift towards higher energies that can be attributed to quantum confinement. The narrow FWHM of all emission spectra are in agreement with the preparation of QDs with a narrow size distribution.

In summary, we have demonstrated a fast, one-step continuous synthesis of III-V QDs using supercritical fluids. The flexible multi-source approach in the conditions employed allows for rapid precursor screening and precise control of experimental conditions, resulting in high homogeneity of the reaction medium, and therefore the obtained materials. GaN QDs synthesized *via*

this route from gallium cupferronate and trimethylsilyl derivatives (HMDS or TMS_3N) exhibit strong photoluminescence in the UV region, shifted towards higher energies than that of bulk GaN, highlighting the quantum confinement effect from the 2.5 nm nanoparticles. A structured PL signal with six major separate contributions is observed upon decreasing temperature in both samples, confirming the appeal of this approach for the preparation of high quality III-V QDs. The different energy levels could originate from various excitonic or trapped levels close to the QD bandgap. Moreover, a strong correlation between the QD size and their respective luminescence emission maxima has been demonstrated, further proving the quantum confinement effect of the as-prepared GaN QDs.

Additionally, metal site substitution was demonstrated with the preparation of InGaN samples. Intimate mixing of metals in the as-prepared particles was observed, which was confirmed by the change in their optical properties and bandgap, validating the proposed chemistry platform.

Thus, binary and ternary III phosphides and/or arsenides could be easily synthesized with a homologous V source using this approach.

Experimental Section

Gallium cupferronate - $\text{Ga}(\text{cup})_3$ was prepared from anhydrous gallium iodide - GaI_3 (99.999 %, Sigma Aldrich) - mixed with cupferron (97 %, Sigma Aldrich) in deionized water at 0 °C adapted from a previously reported procedure. The iodide and cupferron were carefully weighed and mixed into a septum-capped vial inside an argon-filled glovebox. The vial was then placed inside an ice bath where a fixed amount of cooled water was added through the septum. After the instantaneous precipitation of a large amount of white powder (gallium cupferronate), the solution was sonicated to ensure full conversion of precursors. The powder was then recovered by centrifugation and vacuum dried to remove all traces of water. The as-prepared white powder ($\text{Ga}(\text{cup})_3$) was dissolved in anhydrous toluene (99.8 %, Sigma Aldrich) and used for the synthesis of GaN QDs along with two different nitrogen sources hexamethyldisilazane - HMDS (≥ 99 %, Sigma Aldrich) - or tris(trimethylsilyl)amine - TMS_3N (98 %, Sigma Aldrich) - also dissolved in toluene. The 1.6 mL tubular reactor (Figure 1a) consisted of a two-meter long 316 L stainless steel tubing (1/16", 1 mm inside diameter) coiled around a heating cartridge (Acim Jouanin, 800 W, 230 V). The temperature of the system is regulated by a PID controller up to 450 °C and the pressure was adjusted using a back pressure regulator (Idex-hs, P-880) allowing a fine control of the pressure up to 345 bar. A cooling bath was placed upstream of the BPR to quench the reaction and to cool the solvent before exiting the system. All chemicals were handled without further purification.

Acknowledgements

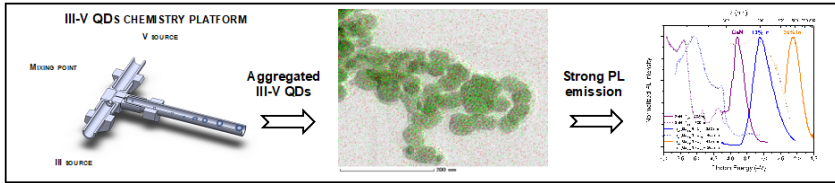
The authors would like to acknowledge the "Agence Nationale de la Recherche" (convention n° ANR-12-G8ME-0002-01), and the region Nouvelle-Aquitaine for their financial support.

Keywords: III-nitrides • quantum dots • nanoparticles • semiconductors • photoluminescence

- [1] I. Vurgaftman, J. R. Meyer, L. R. Ram-Mohan, *J. Appl. Phys.* **2001**, *89*, 5815–5875.
- [2] R. F. Davis, *Proc. IEEE* **1991**, *79*, 702–712.
- [3] S. Zhao, H. P. T. Nguyen, M. G. Kibria, Z. Mi, *Prog. Quantum Electron.* **2015**, *44*, 14–68.
- [4] J. Wu, W. Shan, W. Walukiewicz, *Semicond. Sci. Technol.* **2002**, *17*, 860–869.
- [5] S. Nakamura, S. Pearton, G. Fasol, *The Blue Laser Diode: The Complete Story*, **2013**.
- [6] M. O. Fischer, M. Reinhardt, A. Forchel, *IEEE J. Sel. Top. Quantum Electron.* **2001**, *7*, 149–151.
- [7] P. J. S. Heim, Z. F. Fan, S.-H. Cho, K. Nam, M. Dagenais, F. G. Johnson, R. Leavitt, *Electron. Lett.* **1997**, *33*, 1387.
- [8] S. J. Pearton, J. C. Zolper, R. J. Shul, F. Ren, *J. Appl. Phys.* **1999**, *86*, 1–78.
- [9] Y.-G. Zhang, C. Li, Y. Gu, K. Wang, H. Li, X.-M. Shao, J.-X. Fang, *IEEE Photonics Technol. Lett.* **2010**, *22*, 944–946.
- [10] K. Kishino, M. Yonemaru, A. Kikuchi, Y. Toyoura, *Phys. status solidi* **2001**, *188*, 321–324.
- [11] J. Baek, P. M. Allen, M. G. Bawendi, K. F. Jensen, *Angew. Chemie* **2011**, *123*, 653–656.
- [12] O. I. Micić, A. J. Nozik, *J. Lumin.* **1996**, *70*, 95–107.
- [13] J. J. Wierer, N. Tansu, A. J. Fischer, J. Y. Tsao, *Laser Photon. Rev.* **2016**, *10*, 612–622.
- [14] J. Brault, S. Matta, T.-H. Ngo, D. Rosales, M. Leroux, B. Damilano, M. Al Khalifioui, F. Tendille, S. Chenot, P. De Mierry, J. Massies, B. Gil, *Mater. Sci. Semicond. Process.* **2016**, *55*, 95–101.
- [15] D. Franke, D. K. Harris, O. Chen, O. T. Bruns, J. A. Carr, M. W. B. Wilson, M. G. Bawendi, *Nat. Commun.* **2016**, *7*, DOI 10.1038/ncomms12749.
- [16] S. Haffouz, K. D. Zeuner, D. Dalacu, P. J. Poole, J. Lapointe, D. Poitras, K. Mnamneh, X. Wu, M. Couillard, M. Korkusinski, E. Schöll, K. D. Jöns, V. Zwiller, R. L. Williams, *Nano Lett.* **2018**, *18*, 3047–3052.
- [17] V. Dolores-Calzadilla, B. Romeira, F. Pagliano, S. Birindelli, A. Higuera-Rodriguez, P. J. Van Veldhoven, M. K. Smit, A. Fiore, D. Heiss, *Nat. Commun.* **2017**, *8*, 1–8.
- [18] R. Wang, S. Sprengel, G. Boehm, R. Baets, M.-C. Amann, G. Roelkens, *Optica* **2017**, *4*, 972.
- [19] D. Heinz, F. Huber, M. Spiess, M. Asad, L. Wu, O. Rettig, D. Wu, B. Neuschl, S. Bauer, Y. Wu, S. Chakraborty, N. Hibst, S. Strehle, T. Weil, K. Thonke, F. Scholz, *IEEE J. Sel. Top. Quantum Electron.* **2017**, *23*, 15–23.
- [20] R. Wang, A. Vasiliev, M. Muneeb, A. Malik, S. Sprengel, G. Boehm, M.-C. Amann, I. Šimonyté, A. Vizbaras, K. Vizbaras, R. Baets, G. Roelkens, *Sensors* **2017**, *17*, 1788.
- [21] J. Lim, M. Park, W. K. Bae, D. Lee, S. Lee, C. Lee, K. Char, *ACS Nano* **2013**, *7*, 9019–9026.
- [22] Y. H. Won, O. Cho, T. Kim, D. Y. Chung, T. Kim, H. Chung, H. Jang, J. Lee, D. Kim, E. Jang, *Nature* **2019**, *575*, DOI 10.1038/s41586-019-1771-5.
- [23] F. Cao, S. Wang, F. Wang, Q. Wu, D. Zhao, X. Yang, *Chem. Mater.* **2018**, *30*, 8002–8007.
- [24] G. Xu, S. Zeng, B. Zhang, M. T. Swihart, K.-T. Yong, P. N. Prasad, *Chem. Rev.* **2016**, *116*, 12234–12327.
- [25] G. Fan, C. Wang, J. Fang, *Nano Today* **2014**, *9*, 69–84.
- [26] X. Li, X. Liu, *Nanoscale* **2017**, *9*, 7320–7341.
- [27] M. K. Choi, J. Yang, T. Hyeon, D.-H. Kim, *npj Flex. Electron.* **2018**, *2*, 10.
- [28] D. J. Norris, M. G. Bawendi, *Phys. Rev. B* **1996**, *53*, 16338–16346.
- [29] E. M. Chan, R. A. Mathies, A. P. Alivisatos, *Nano Lett.* **2003**, *3*, 199–201.
- [30] L. Li, J. Hu, W. Yang, A. P. Alivisatos, *Nano Lett.* **2001**, *1*, 349–351.
- [31] X. Peng, L. Manna, W. Yang, J. Wickham, E. Scher, A. Kadavanich, A. P. Alivisatos, *Nature* **2000**, *404*, 59–61.
- [32] S. Marre, K. F. Jensen, *Chem. Soc. Rev.* **2010**, *39*, 1183.
- [33] F. Cansell, C. Aymonier, *J. Supercrit. Fluids* **2009**, *47*, 508–516.
- [34] C. Aymonier, A. Loppinet-Serani, H. Reverón, Y. Garrabos, F. Cansell, *J. Supercrit. Fluids* **2006**, *38*, 242–251.
- [35] K. Byrappa, S. Ohara, T. Adschiri, *Adv. Drug Deliv. Rev.* **2008**, *60*, 299–327.
- [36] C. Aymonier, G. Philippot, A. Erriguible, S. Marre, *J. Supercrit. Fluids* **2018**, *134*, 184–196.
- [37] S. Marre, J. Park, J. Rempel, J. Guan, M. G. Bawendi, K. F. Jensen, *Adv. Mater.* **2008**, *20*, 4830–4834.
- [38] A. Chakrabarty, S. Marre, R. F. Landis, V. M. Rotello, U. Maitra, A. Del Guerso, C. Aymonier, *J. Mater. Chem. C* **2015**, *3*, 7561–7566.
- [39] Y. Roig, S. Marre, T. Cardinal, C. Aymonier, *Angew. Chemie Int. Ed.* **2011**, *50*, 12071–12074.
- [40] E. S. Ilin, S. Marre, V. Jubera, C. Aymonier, *J. Mater. Chem. C* **2013**, *1*, 5058.
- [41] B. Giroire, S. Marre, A. Garcia, T. Cardinal, C. Aymonier, *React. Chem. Eng.* **2016**, *1*, 151–155.
- [42] R. L. Wells, A. T. McPhail, S. Shafieezad, R. B. Hallock, C. G. Pitt, A. P. Purdy, *Chem. Mater.* **1989**, *1*, 4–6.
- [43] R. L. Wells, M. F. Self, A. T. McPhail, S. R. Aubuchon, R. C. Woudenberg, J. P. Jasinski, *Organometallics* **1993**, *12*, 2832–2834.
- [44] S. R. Aubuchon, A. T. McPhail, R. L. Wells, J. A. Giambra, J. R. Bowser, *Chem. Mater.* **1994**, *6*, 82–86.
- [45] A. A. Guzelian, U. Banin, A. V. Kadavanich, X. Peng, A. P. Alivisatos, *Appl. Phys. Lett.* **1996**, *69*, 1432–1434.
- [46] S. Xu, S. Kumar, T. Nann, *J. Am. Chem. Soc.* **2006**, *128*, 1054–1055.
- [47] D. Battaglia, X. Peng, *Nano Lett.* **2002**, *2*, 1027–1030.
- [48] J. Baek, Y. Shen, I. Lignos, M. G. Bawendi, K. F. Jensen, *Angew. Chemie Int. Ed.* **2018**, *57*, 10915–10918.
- [49] Y. Xie, Y. Qian, W. Wang, S. Zhang, Y. Zhang, *Science* (80-.). **1996**, *272*, 1926–1927.
- [50] G. Pan, M. E. Kordesch, P. G. Van Patten, *Chem. Mater.* **2006**, *18*, 5392–5394.
- [51] A. Manz, A. Birkner, M. Kolbe, R. A. Fischer, *Adv. Mater.* **2000**, *12*, 569–573.
- [52] K. Sardar, C. N. R. Rao, *Adv. Mater.* **2004**, *16*, 425–429.
- [53] F. Gyger, P. Bockstaller, H. Gröger, D. Gerthsen, C. Feldmann, *Chem. Commun.* **2014**, *50*, 2939–2942.
- [54] G. Pan, M. E. Kordesch, P. G. Van Patten, *Chem. Mater.* **2006**, *18*, 3915–3917.
- [55] S. Bhaviripudi, J. Qi, E. L. Hu, A. M. Belcher, *Nano Lett.* **2007**, *7*, 3512–3517.
- [56] M. Kumar, S. K. Pasha, T. C. S. Krishna, A. Pratap Singh, P. Kumar, B. Kumar Gupta, G. Gupta, *Dalt. Trans.* **2014**, *43*, 11855–11861.
- [57] W. Wei, Z. Qin, S. Fan, Z. Li, K. Shi, Q. Zhu, G. Zhang, *Nanoscale Res. Lett.* **2012**, *7*, 562.
- [58] Y. Chi, L. Zhao, Q. Yuan, X. Yan, Y. Li, N. Li, X. Li, *J. Mater. Chem.* **2012**, *22*, 13571–13577.
- [59] W. P. Yang, D. Costa, P. Marcus, *J. Electrochem. Soc.* **1994**, *141*, 2669–2676.
- [60] D. Y. Guo, Z. P. Wu, Y. H. An, P. G. Li, P. C. Wang, X. L. Chu, X. C. Guo, Y. S. Zhi, M. Lei, L. H. Li, W. H. Tang, *Appl. Phys. Lett.* **2015**, *106*, 42105.
- [61] D. Esken, S. Turner, C. Wiktor, S. B. Kalidindi, G. Van Tendeloo, R. A. Fischer, *J. Am. Chem. Soc.* **2011**, *133*, 16370–16373.
- [62] Y. Hori, X. Biquard, E. Monroy, D. Jalabert, F. Enjalbert, L. S. Dang, M. Tanaka, O. Oda, B. Daudin, *Appl. Phys. Lett.* **2004**, *84*, 206–208.
- [63] T. Kuykendall, P. Ulrich, S. Aloni, P. Yang, *Nat. Mater.* **2007**, *6*, 951–956.
- [64] A. M. Smith, S. Nie, *Acc. Chem. Res.* **2010**, *43*, 190–200.

Entry for the Table of Contents

COMMUNICATION



In this work, a III-V quantum dots chemistry platform is presented. III-nitrides QDs are prepared in short residence times in a one-step continuous process involving supercritical solvents. $\text{In}_x\text{Ga}_{1-x}\text{N}$ QDs fabricated via this platform exhibit strong photoluminescence with continuous bandgap shift towards lower energies measured when increasing indium content. The chemistry platform proposed could be easily transferred to other binary and ternary III-V systems source.

*B. Giroire, A. Garcia, S. Marre, T. Cardinal and C. Aymonier**

Page No. – Page No.

Chemistry platform for the ultra-fast and continuous synthesis of high quality III-V quantum dots.