

Formation Mechanism and Excitonic Luminescence of Supercritical Fluid-Synthesized ZnO Nanoparticles

Supporting information

*Brian Dusolle^{†,‡}, Véronique Jubera[†], Evgeniy S. Ilin[†], Patrick Martin[#], Gilles Philippot[†],
Matthew. R. Suchomel[†], Bo B. Iversen[§], Samuel Marre[†], Cyril Aymonier^{†,*}*

[†] Univ. Bordeaux, CNRS, Bordeaux INP, ICMCB, UMR 5026, F-33600 Pessac Cedex, France

[‡] Univ. Bordeaux, CEA, CNRS, Bordeaux INP, IMS, UMR 5218, F-33405 Talence Cedex,
France

[#] Univ. Bordeaux, CNRS, CELIA, UMR 5107, F-33405 Talence Cedex, France

[§] Center for Integrated Materials Research, Department of Chemistry and iNANO, Aarhus
University, Aarhus, Denmark

*cyril.aymonier@icmcb.cnrs.fr

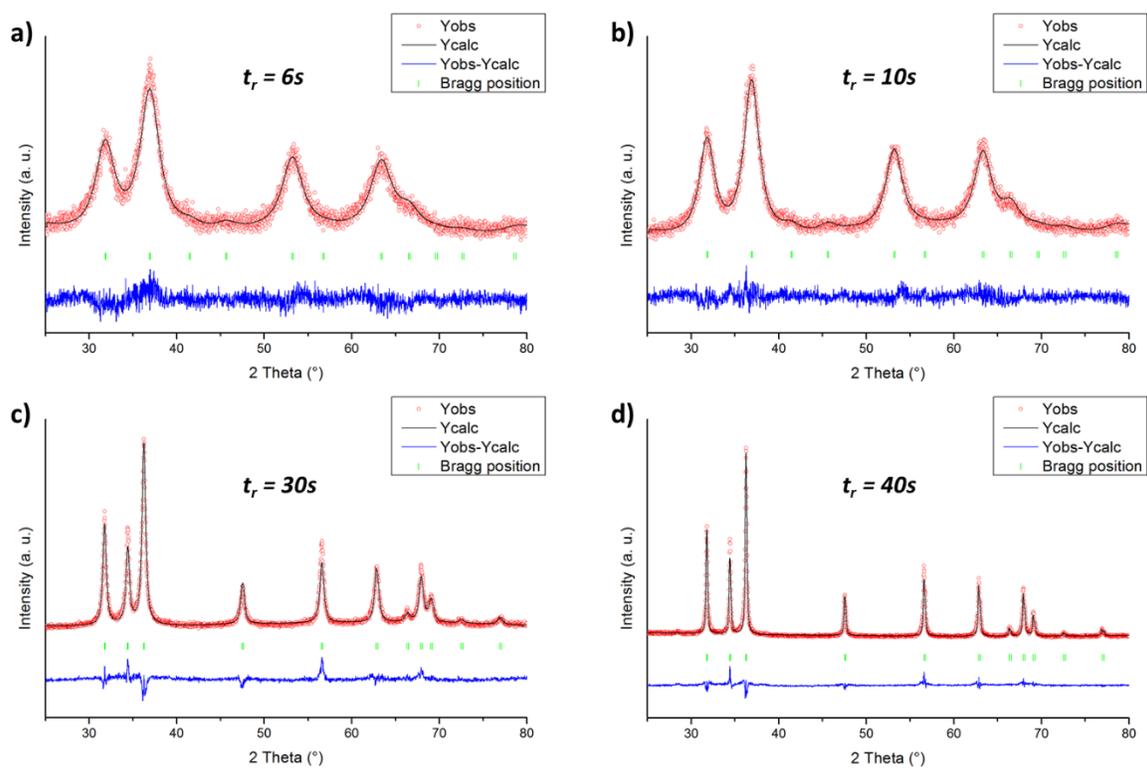


Figure S1 Plots of the final refinement cycle for samples at (a) 6 s, (b) 10 s, (c) 30 s and (d) 40 s residence time.

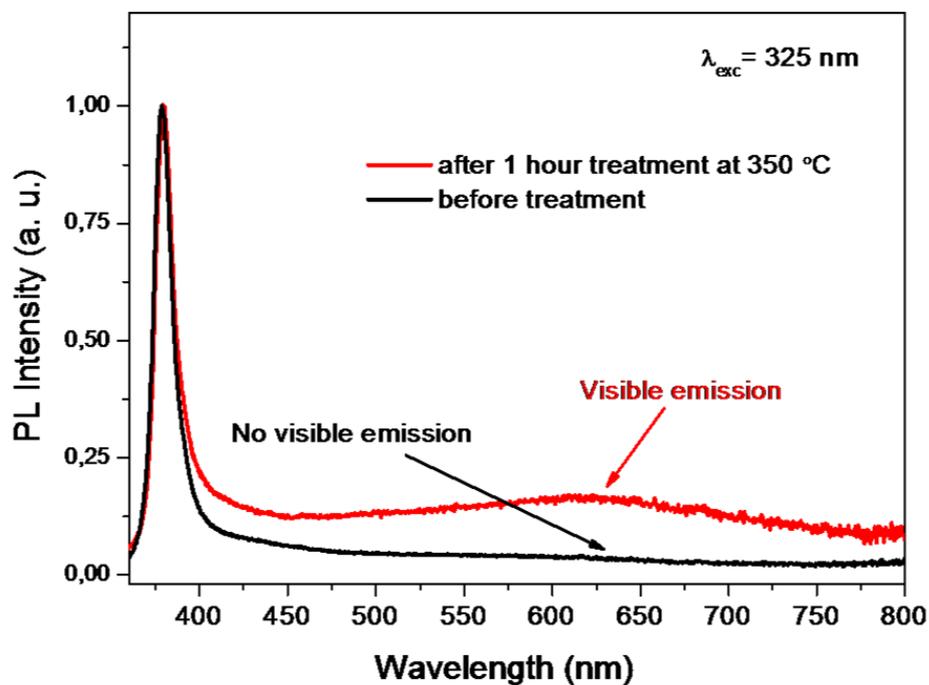


Figure S2 Normalized room temperature photoluminescence spectra of ZnO nanoparticles obtained at 40 s residence time in the presence of H_2O_2 , before and after heat treatment. *A one-hour heat-treatment at 350°C results in a total decomposition of the ZnO_2 phase and the appearance of a small visible contribution.*

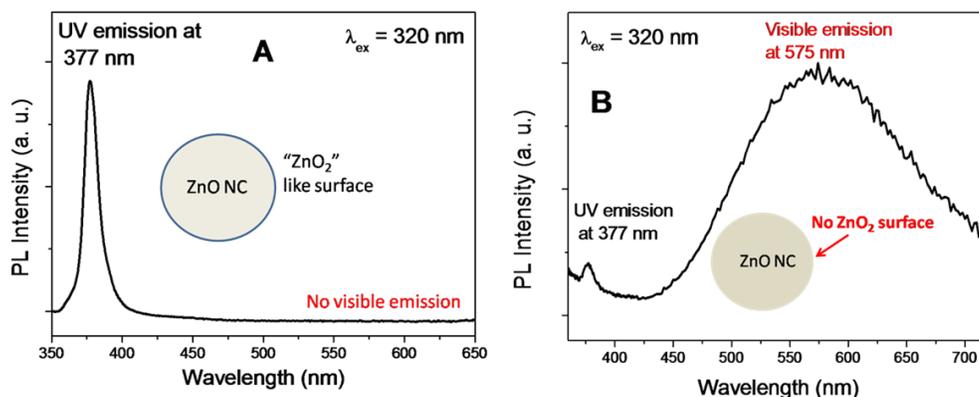


Figure S3 Room temperature photoluminescence spectra of ZnO nanoparticles obtained at 40 s residence time (A) in the presence of H_2O_2 and (B) without H_2O_2 . *A visible defect-related emission can be observed in the absence of H_2O_2 , in parallel to a strong decrease of the excitonic emission. Because the nucleation of ZnO particles comes from the decomposition of ZnO_2 , the use of H_2O_2 in the reaction medium is crucial not only to avoid the stabilization of oxygen vacancies within the core of the particles but also to neutralize surface defects.*

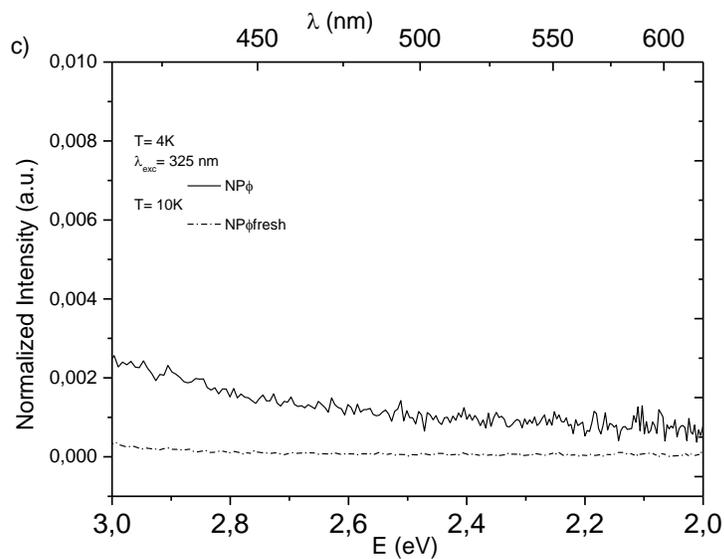


Figure S4 Excitation and emission spectra of ZnO nanoparticles performed at liquid Helium temperature. Zoom in the expected defect emission range. *The absence of any feature at this range is a testimony of a particularly pure excitonic emission.*

Table S1 Peaks' positions of UV emitting ZnO materials measured at low temperature and attribution.

ZnO shape	Ref.	Nature of PL emission							
		FX _C	FX _B	FX _A	D ⁰ X	A ⁰ X	TES	LO-DX	LO-FX
Nanorods	1		3.388	3.380	3.363				3.310
	2			3.376	3.364 3.360 3.359				
		3			3.377	3.351		3.326	
Nanowires	4				3.3737 3.3693 3.3645				
		5		3.366	3.3557 3.3586 3.3598				
	6			3.370	3.363 3.360				
	7			3.375	3.365				
	8,9			3.38	3.365	3.336		3.29 3.22 3.266 3.192	3.29
Films	10				3.360				
	11				3.364				
	12		3.384	3.377					3.25
	13				3.376 3.367 3.364 3.360 3.332		3.322		
		14				3.403 3.391 3.387			
	15			3.391	3.366				
16				3.357		3.32			
Single crystal	17			3.378	3.358 3.361 3.362 3.364 3.365 3.368				
		18	3.4335	3.3938	3.3773				
	19	3.4214	3.3830	3.4214					
	20			3.3772	3.3636 3.3614 3.3570		3.3220 3.3189 3.3137 3.3058		
		21		3.378	3.386				
NPØ	This work	FX _C	FX _B	FX _A	D ⁰ X	A ⁰ X → BSF	TES → FX _A - E ₂ high	LO-DX	LO-FX
			3.382	3.375	-	3.34	3.32 (FX _A - E ₂ high)	-	-

REFERENCES

- (1) Ahn, C. H.; Mohanta, S. K.; Lee, N. E.; Cho, H. K. Enhanced Exciton-phonon Interactions In Photoluminescence Of ZnO Nanopencils. *Appl. Phys. Lett.* **2009**, *94* (26), 261904. DOI: 10.1063/1.3159829.
- (2) Park, W. I.; Jun, Y. H.; Jung, S. W.; Yi, G.-C. Excitonic Emissions Observed In ZnO Single Crystal Nanorods. *Appl. Phys. Lett.* **2003**, *82* (6), 964–966. DOI: 10.1063/1.1544437.
- (3) Zhang, R.; Yin, P.-G.; Wang, N.; Guo, L. Photoluminescence And Raman Scattering Of ZnO Nanorods. *Solid State Sci.* **2009**, *11* (4), 865–869. DOI: 10.1016/j.solidstatesciences.2008.10.016.
- (4) Khranovskyy, V.; Glushenkov, A. M.; Chen, Y.; Khalid, A.; Zhang, H.; Hultman, L.; Monemar, B.; Yakimova, R. Crystal Phase Engineered Quantum Wells In ZnO Nanowires. *Nanotechnology* **2013**, *24* (21), 215202. DOI: 10.1088/0957-4484/24/21/215202.
- (5) Grabowska, J.; Meaney, A.; Nanda, K. K.; Mosnier, J.-P.; Henry, M. O.; Duclère, J.-R.; McGlynn, E. Surface Excitonic Emission And Quenching Effects In ZnO Nanowire/nanowall Systems: Limiting Effects On Device Potential. *Phys. Rev. B* **2005**, *71* (11), 115439. DOI: 10.1103/physrevb.71.115439.
- (6) Xing, G. Z.; Wang, D. D.; Yao, B.; Nien, A. Q. L. F.; Yan, Y. S. Structural Characteristics, Low Threshold Ultraviolet Lasing And Ultrafast Carrier Dynamics In High Crystalline ZnO Nanowire Arrays. *Chem. Phys. Lett.* **2011**, *515* (1-3), 132–136. DOI: 10.1016/j.cplett.2011.09.007.

- (7) Reparaz, J. S.; Güell, F.; Wagner, M. R.; Callsen, G.; Kirste, R.; Claramunt, S.; Morante, J. R.; Hoffmann, A. Recombination Dynamics In ZnO Nanowires: Surfaces States Versus Mode Quality Factor. *Appl. Phys. Lett.* **2010**, *97* (13), 133116. DOI: 10.1063/1.3496444.
- (8) Hamby, D. W.; Lucca, D. A.; Klopstein, M. J.; Cantwell, G. Temperature Dependent Exciton Photoluminescence Of Bulk ZnO. *J. Appl. Phys.* **2003**, *93* (6), 3214–3217. DOI: 10.1063/1.1545157.
- (9) Park, W. I.; An, S.-J.; Yi, G.-C.; Jang, H. M. Metal-organic Vapor Phase Epitaxial Growth Of High-quality ZnO Films On Al₂O₃(00.1). *J. Mater. Res.* **2001**, *16* (5), 1358–1362. DOI: 10.1557/jmr.2001.0190.
- (10) Park, W. I.; Yi, G.-C.; Jang, H. M. Metalorganic Vapor-phase Epitaxial Growth And Photoluminescent Properties Of Zn_{1-x}Mg_xO (0≤x≤0.49) Thin Films. *Appl. Phys. Lett.* **2001**, *79* (13), 2022–2024. DOI: 10.1063/1.1405811.
- (11) Li, L. M.; Li, C. C.; Zhang, J.; Du, Z. F.; Zou, B. S.; Yu, H. C.; Wang, Y. G.; Wang, T. H. Bandgap Narrowing And Ethanol Sensing Properties Of In-doped ZnO Nanowires. *Nanotechnology* **2007**, *18* (22), 225504. DOI: 10.1088/0957-4484/18/22/225504.
- (12) Makino, T.; Chia, C. H.; Tuan, N. T.; Segawa, Y.; Kawasaki, M.; Ohtomo, A.; Tamura, K.; Koinuma, H. Exciton Spectra Of ZnO Epitaxial Layers On Lattice-matched Substrates Grown With Laser-molecular-beam Epitaxy. *Appl. Phys. Lett.* **2000**, *76* (24), 3549–3551. DOI: 10.1063/1.126703.
- (13) Jung, S. W.; Park, W. I.; Cheong, H. D.; Yi, G.-C.; Jang, H. M.; Hong, S.; Joo, T. Time-resolved And Time-integrated Photoluminescence In ZnO Epilayers Grown On Al₂O₃(0001) By

Metalorganic Vapor Phase Epitaxy. *Appl. Phys. Lett.* **2002**, *80* (11), 1924–1926. DOI: 10.1063/1.1461051.

(14) Borysiewicz, M. A.; Wzorek, M.; Wojciechowski, T.; Wojtowicz, T.; Kaminska, E.; Piotrowska, A. Photoluminescence Of Nanocoral ZnO Films. *J. Lumin.* **2014**, *147*, 367–371. DOI: 10.1016/j.jlumin.2013.11.076.

(15) Ko, H. J.; Chen, Y. F.; Zhu, Z.; Yao, T.; Kobayashi, I.; Uchiki, H. Photoluminescence Properties Of ZnO Epilayers Grown On CaF₂(111) By Plasma Assisted Molecular Beam Epitaxy. *Appl. Phys. Lett.* **2000**, *76* (14), 1905–1907. DOI: 10.1063/1.126207.

(16) Chen, S. L.; Chen, W. M.; Buyanova, I. A. Dynamics Of Donor Bound Excitons In ZnO. *Appl. Phys. Lett.* **2013**, *102* (12), 121103. DOI: 10.1063/1.4798531.

(17) Park, W. I.; Yi, G.-C. Photoluminescent Properties Of ZnO Thin Films Grown On SiO₂/Si(100) By Metal-organic Chemical Vapor Deposition. *J. Electron. Mater.* **2001**, *30* (10), L32–L35. DOI: 10.1007/s11664-001-0127-7.

(18) Reynolds, D. C.; Look, D. C.; Jogai, B.; Litton, C. W.; Cantwell, G.; Harsch, W. C. Valence-band Ordering In ZnO. *Phys. Rev. B* **1999**, *60* (4), 2340–2344. DOI: 10.1103/physrevb.60.2340.

(19) Chichibu, S. F.; Sota, T.; Cantwell, G.; Eason, D. B.; Litton, C. W. Polarized Photoreflectance Spectra Of Excitonic Polaritons In A ZnO Single Crystal. *J. Appl. Phys.* **2003**, *93* (1), 756–758. DOI: 10.1063/1.1527707

(20) Reynolds, D. C.; Look, D. C.; Jogai, B.; Litton, C. W.; Collins, T. C.; Harsch, W.; Cantwell, G. Neutral-donor-bound-exciton Complexes In ZnO Crystals. *Phys. Rev. B* **1998**, *57* (19), 12151–12155. DOI: 10.1103/physrevb.57.12151.

(21) Liang, W. Y.; Yoffe, A. D. Transmission Spectra Of ZnO Single Crystals. *Phys. Rev. Lett.* **1968**, *20* (2), 59–62. DOI: 10.1103/physrevlett.20.59.