

**EuroNanoForum 2019**  
**June 12-14, 2019, Bucharest, Romania**

**PILLAR 4 – NANO for EU RE-INDUSTRIALIZATION**

**Nanomembranes and Hollow Nanoparticles  
based on Gallium Nitride**

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# Outline

- 1. Introduction. The importance of GaN**
- 2. GaN hollow nanoparticles and their biomedical applications**
- 3. GaN ultrathin membranes and photonic crystals on their basis**
- 4. GaN microtubes with nanometer-thick walls**
- 5. Flexible three-dimensional hybrid nanoarchitectures**
- 6. Conclusions**

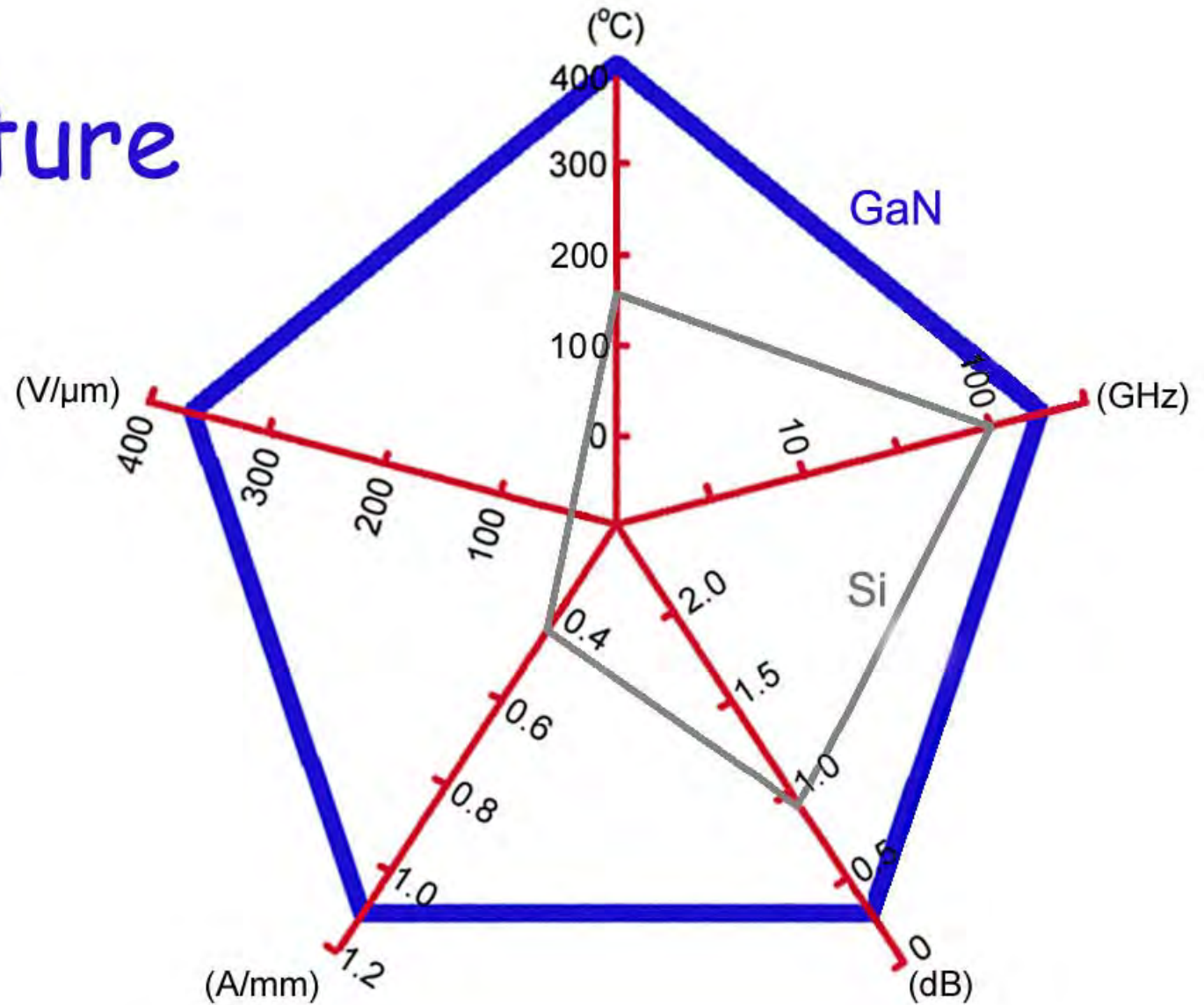
**Why GaN is so important?**

# Advantages of GaN versus Si

Temperature

Voltage

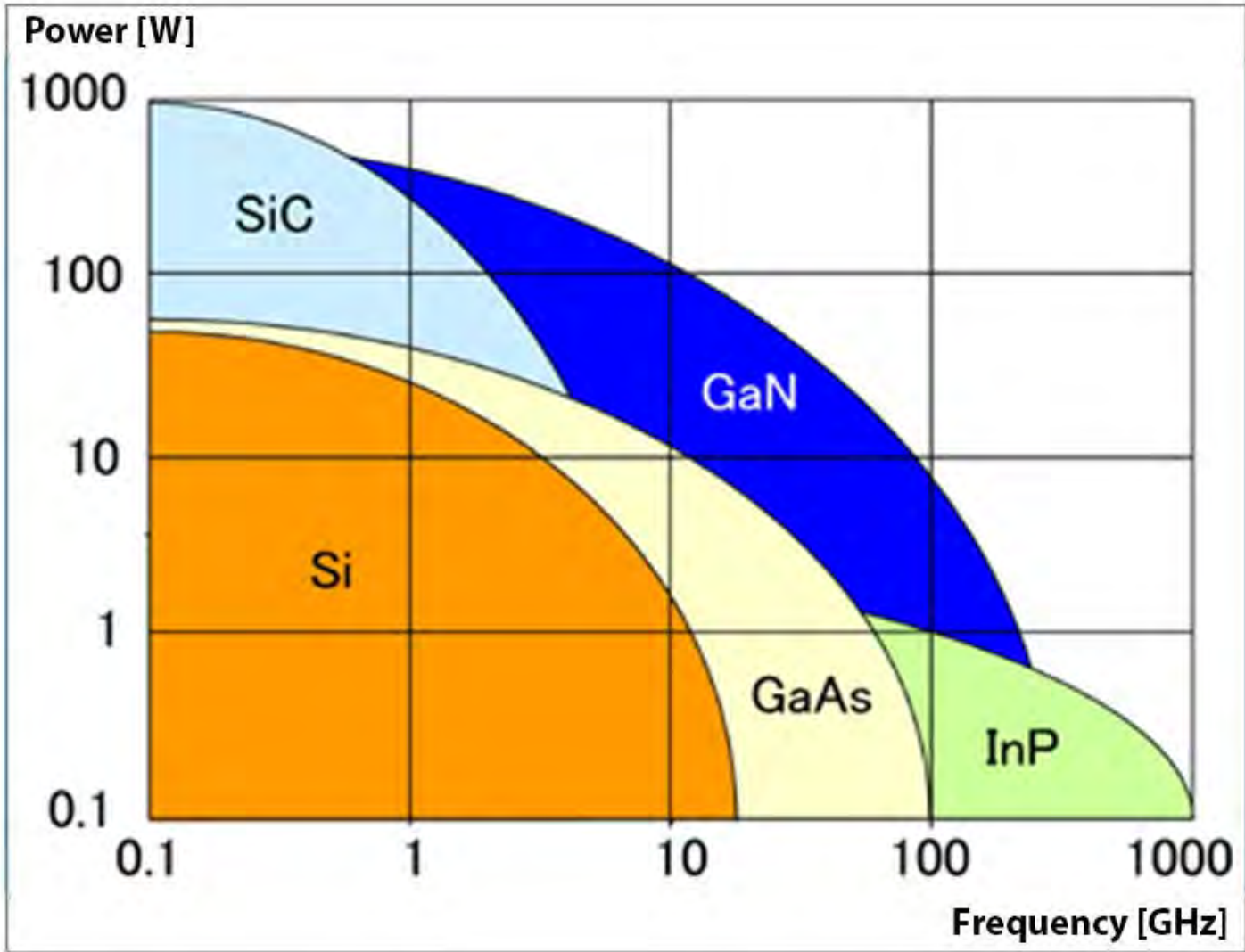
Current



[http://www.gansystems.com/why\\_gallium\\_nitride\\_new.php](http://www.gansystems.com/why_gallium_nitride_new.php)



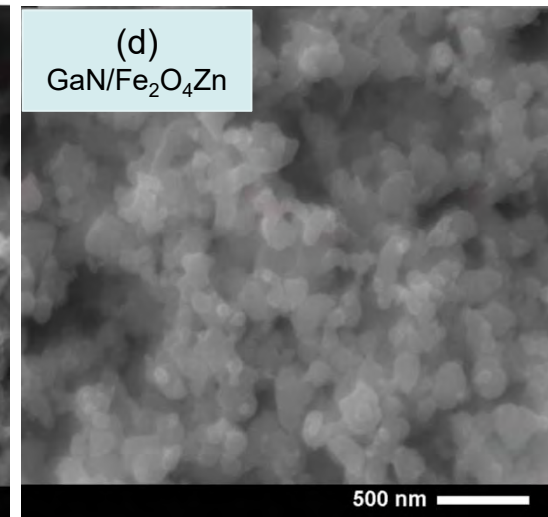
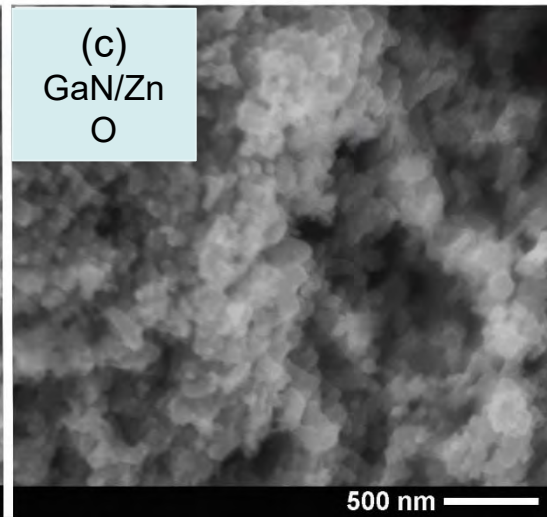
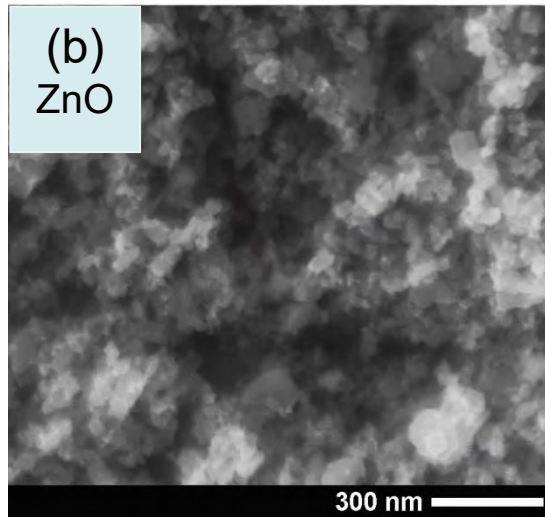
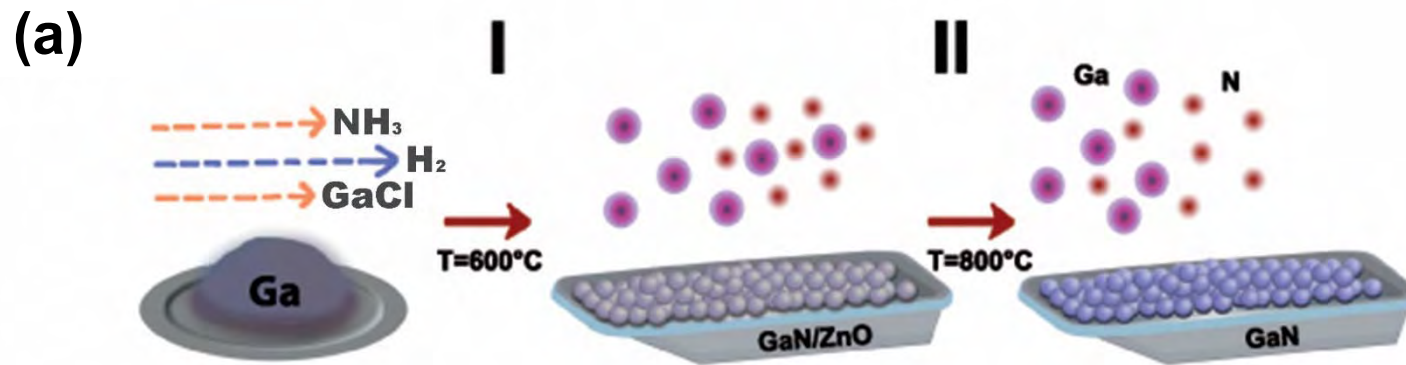
# Advantages of Gallium Nitride



Robert Dwilinski. AMMONO: [www.slideserve.com/jane/outstanding-quality-gallium-nitride-gan-enabler-for-new-industries](http://www.slideserve.com/jane/outstanding-quality-gallium-nitride-gan-enabler-for-new-industries)

# **GaN nanoparticles and their biomedical applications**

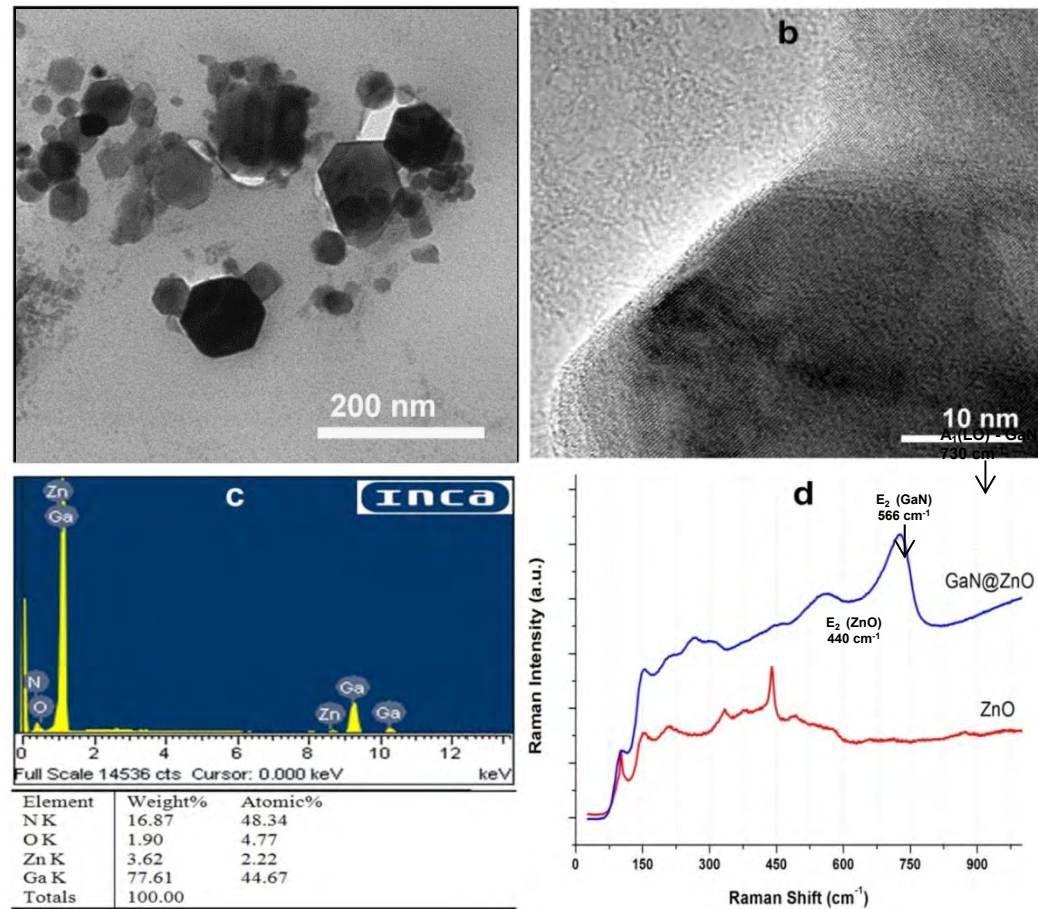
# Synthesis of GaN nanoparticles



(a) - schematic representation of synthesis process of GaN nanoparticles using ZnO and Fe<sub>2</sub>O<sub>4</sub>Zn sacrificial layer. SEM pictures presented in (c) and (d) show the morphology of the resulted nanoparticles, which does not differ from the initial ones depicted in (b)

**T. Braniste et al, Beilstein J. Nanotechnol. 7, 1330–1337 (2016).**

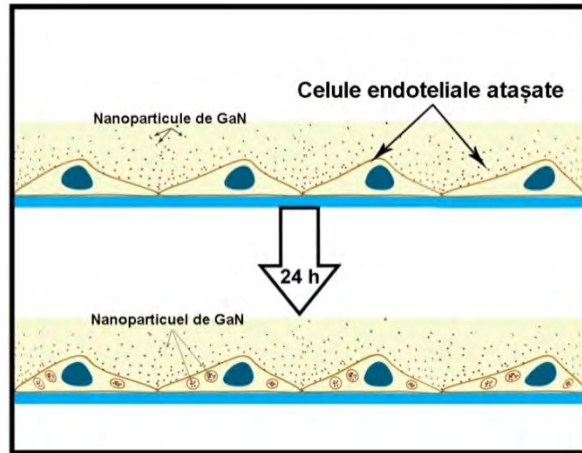
# Characterization of GaN nanoparticles synthesized on ZnO



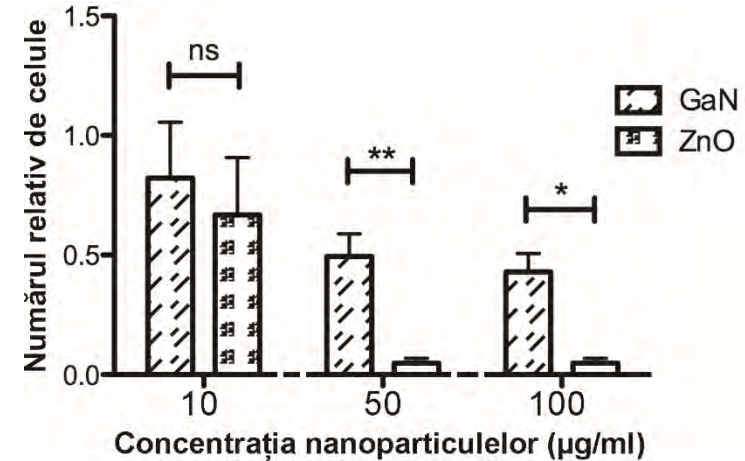
TEM pictures of GaN nanoparticles grown on ZnO (a) and HRTEM of a single nanoparticle (b); EDX analysis is presented in (c) and comparative Raman measurements in (d) confirm the GaN growth and ZnO decomposition.



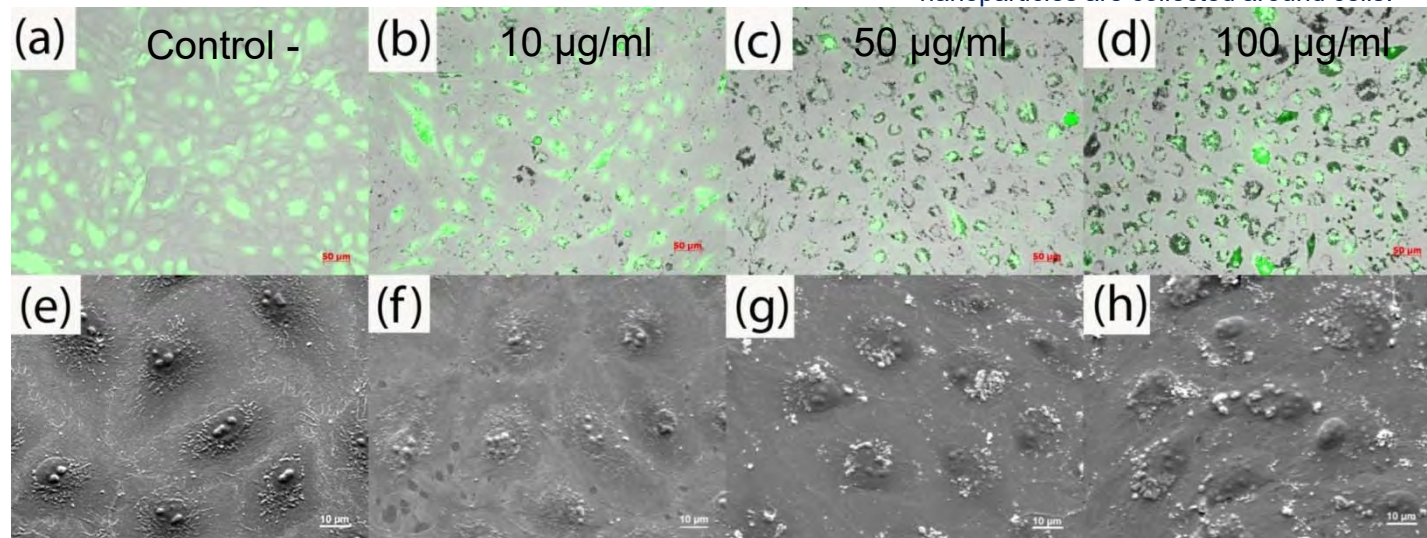
# The interaction of free floating nanoparticles and living endothelial cells



Experimental concept



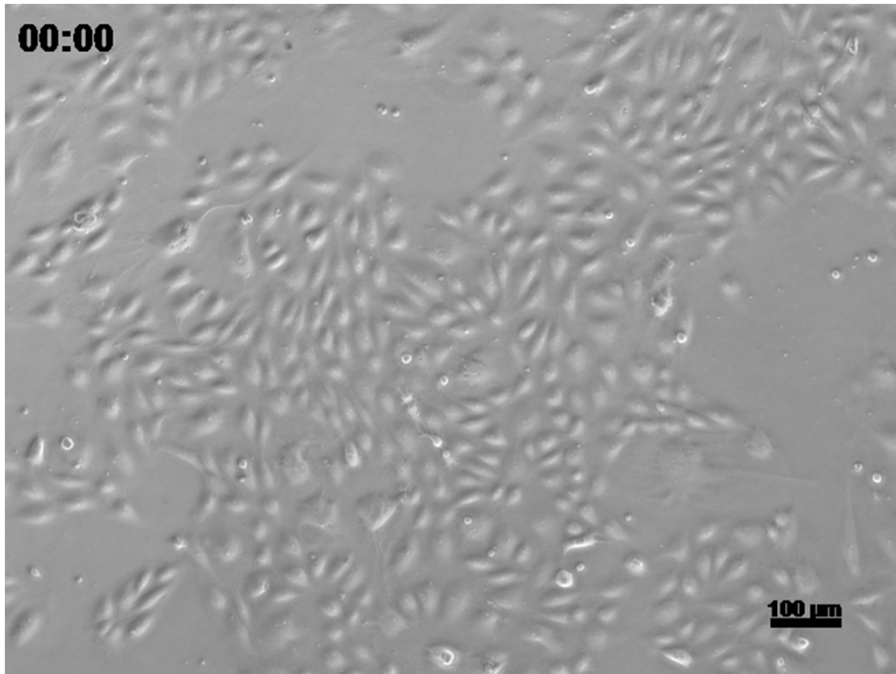
After 3 days of incubation of Endothelial Cells with NPs, we can observe that high concentrations of ZnO NPs are very toxic for cells, while by increasing the concentration of GaN NP cells are slowed down in the development and the nanoparticles are collected around cells.



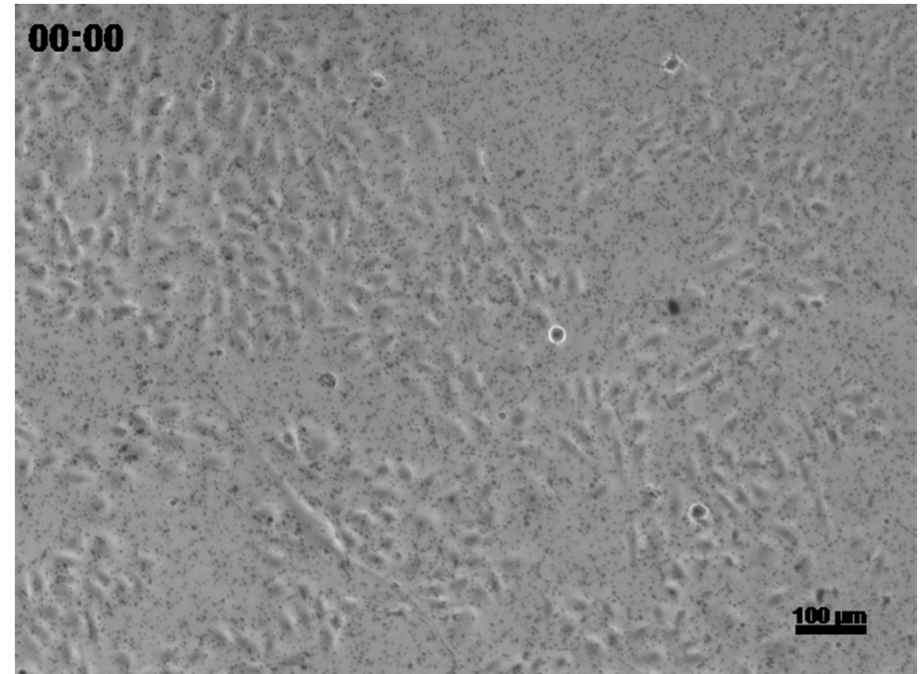
Nanoparticles distribution in endothelial cells culture after three days of cultivation of porcine aorta endothelial cells and GaN NPs. Optical views are presented in pictures (a) – (d) and SEM images are in (e) – (h). The concentration of GaN nanoparticles is 10 μg/ml for (b) and (f), 50 μg/ml for (c) and (g), and 100 μg/ml for (d) and (h). Images (a) and (e) represent the positive control of cells in EGM2

# Uptake of GaN nanoparticles by endothelial cells

Endothelial cells in the control group



Endothelial cells incubated with GaN nanoparticles (50  $\mu\text{g/ml}$ ).



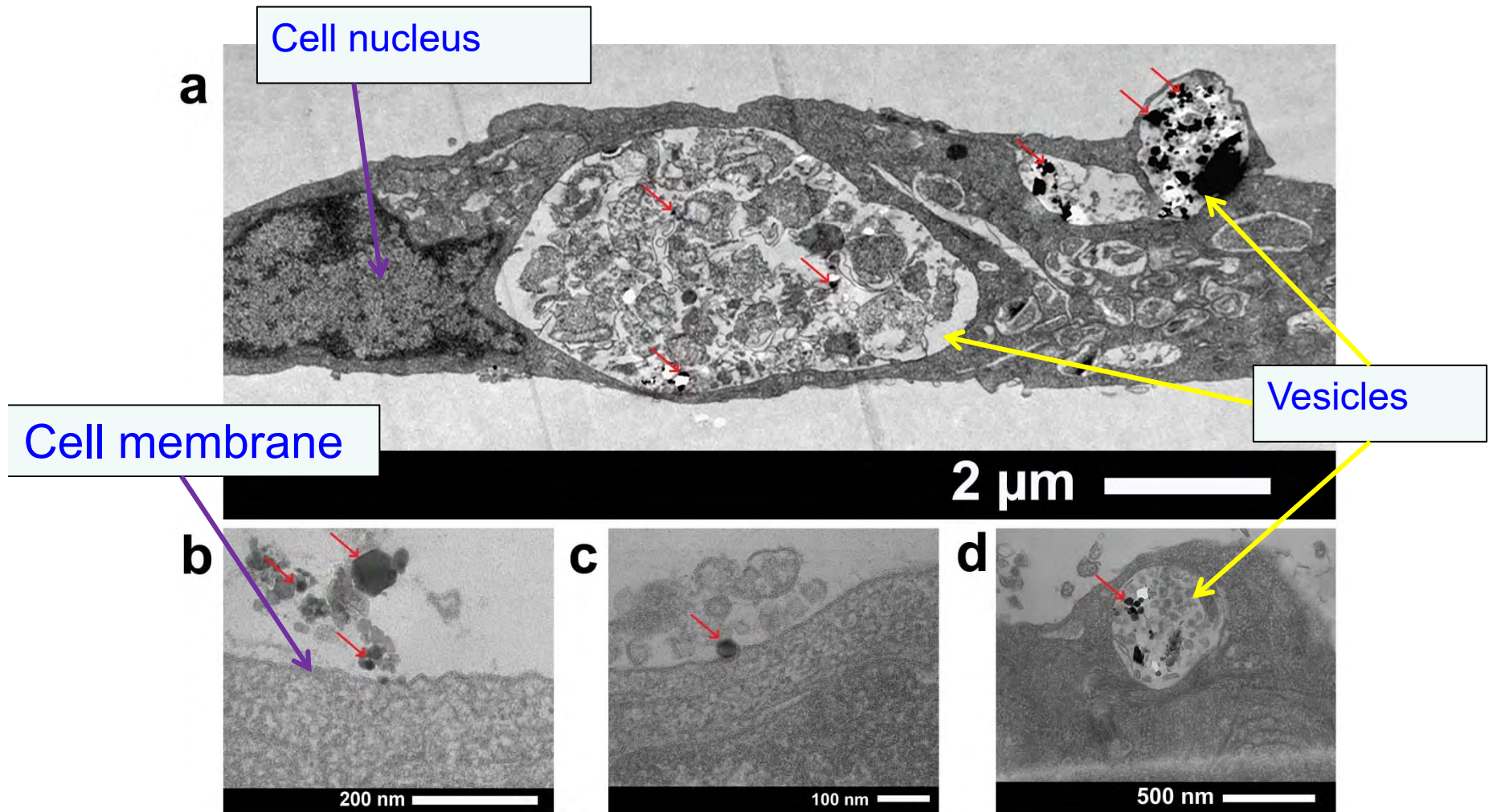
The cells were found to collect the nanoparticles surrounding them, nevertheless the mobility and the proliferation activity of endothelial cells are not affected by the presence of GaN nanoparticles in the medium.

**Note:** The investigations were performed for 20 h, one picture being shot every 10 min.

T. Braniste *et al*, *Beilstein J. Nanotechnol.* 7, 1330–1337 (2016).



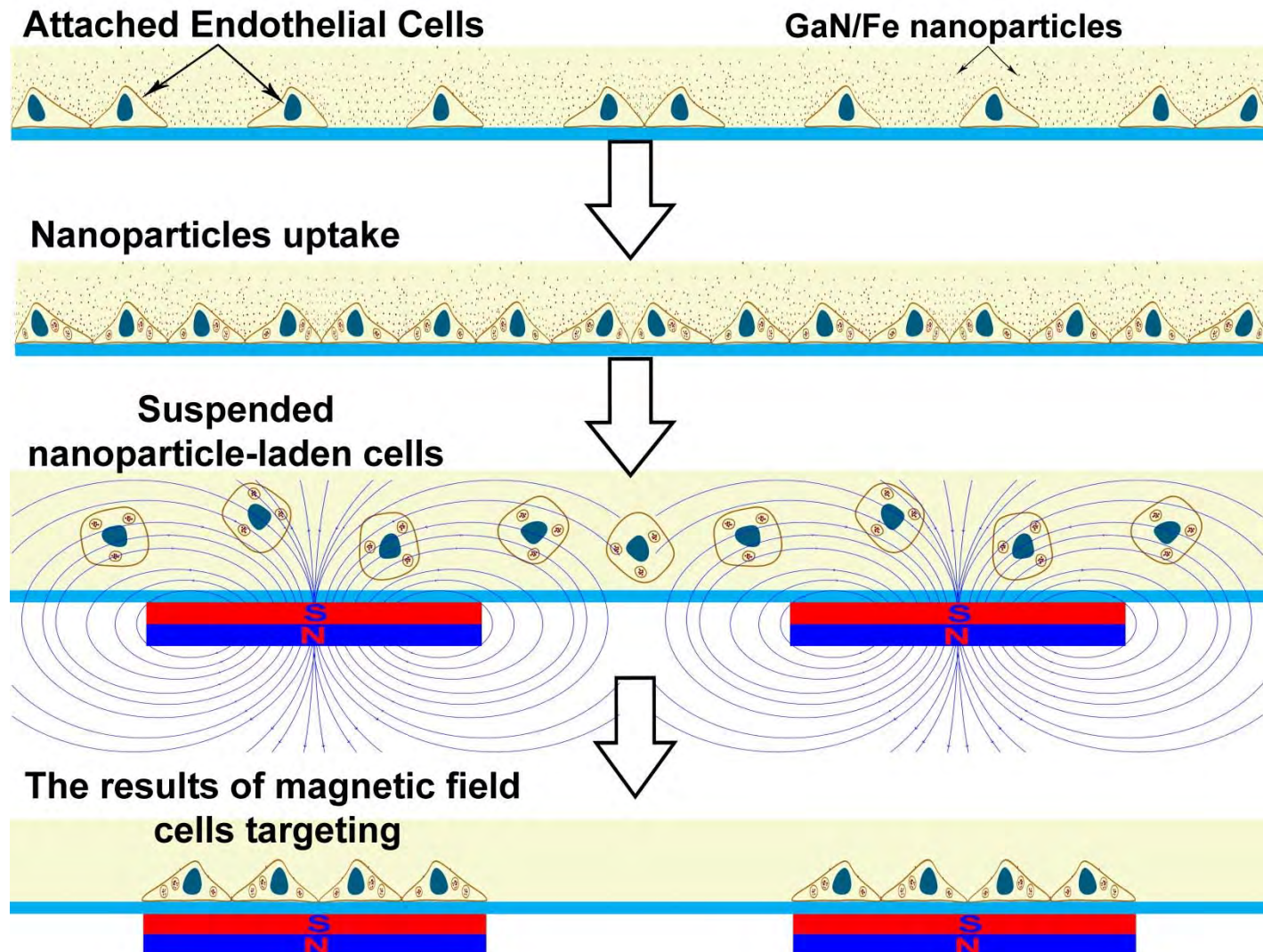
# Uptake of nanoparticles by endothelial cells and localization in vesicles determined by TEM investigations



TEM pictures taken from a endothelial cell incubated with GaN/Fe nanoparticles.

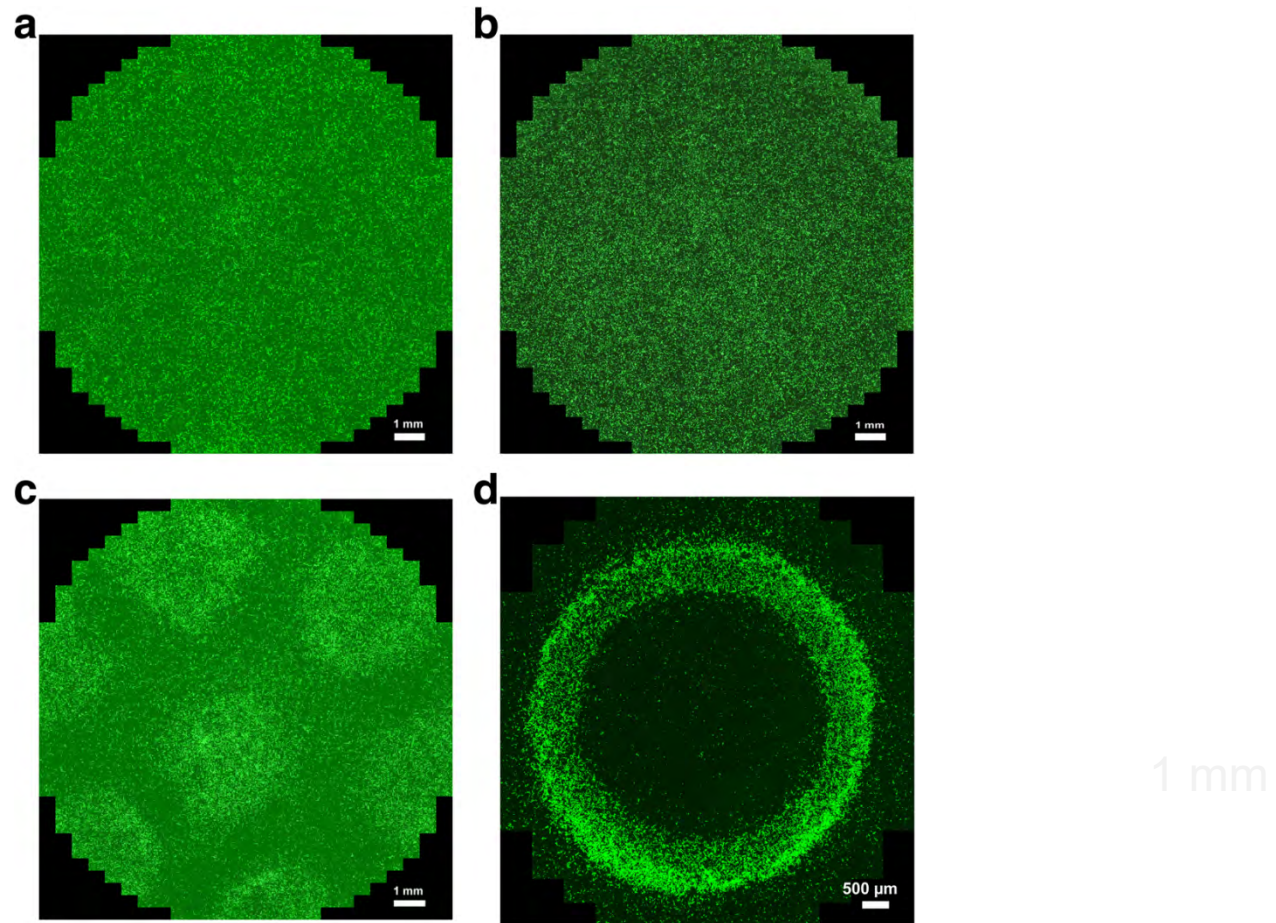
**T. Braniste et al, *Nanoscale Research Letters* 12, 486 (2017).**

# Magnetic guiding of endothelial cells targeted with nanoparticles





# Magnetic guiding of endothelial cells targeted with nanoparticles



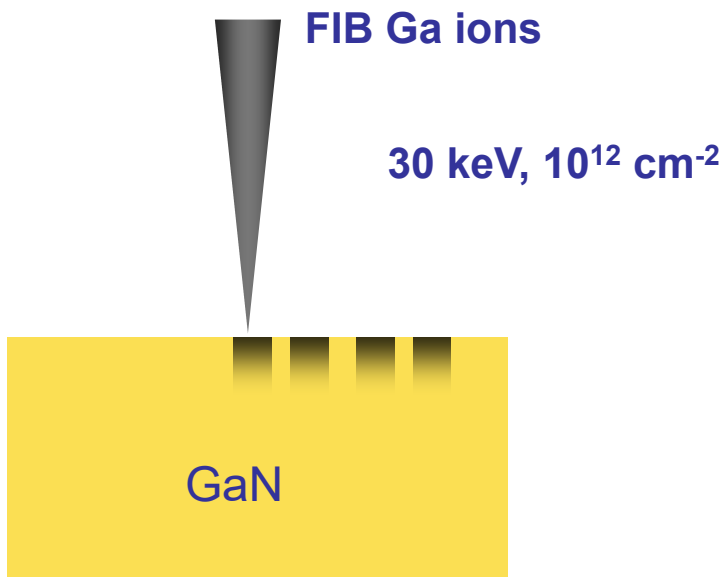
Fluorescence pictures of endothelial cells targeted with GaN/Fe nanoparticles and incubated in control groups (a,b) and in magnetic field gradients (c,d) and. After few hours of incubation a non-uniform distribution of cells exposed to magnetic field could be notified, while cells targeted with nanoparticles and incubated in normal conditions (without magnetic field) are distributed uniformly on the surface of culture plate.

**T. Braniste *et al*, *Nanoscale Research Letters* 12, 486 (2017).**

# GaN ultrathin membranes

# Surface Charge Lithography

Direct Writing of Negative Charge  
+  
Photoelectrochemical Etching

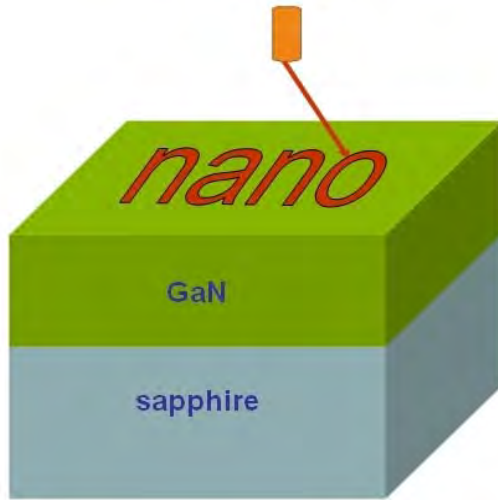


Gold Medal,  
Pittsburgh

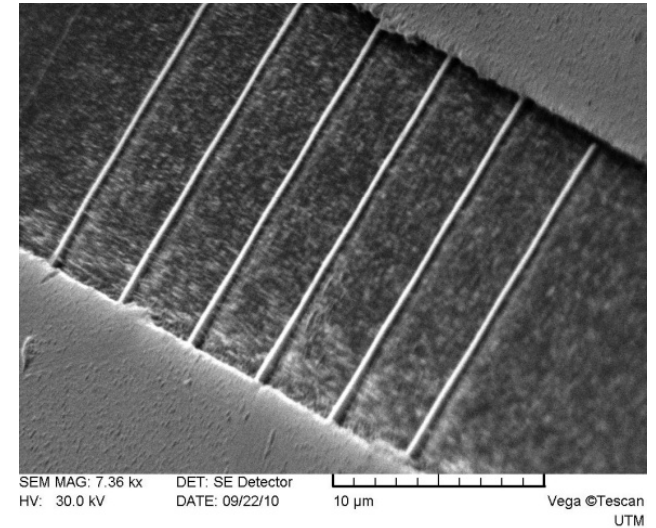
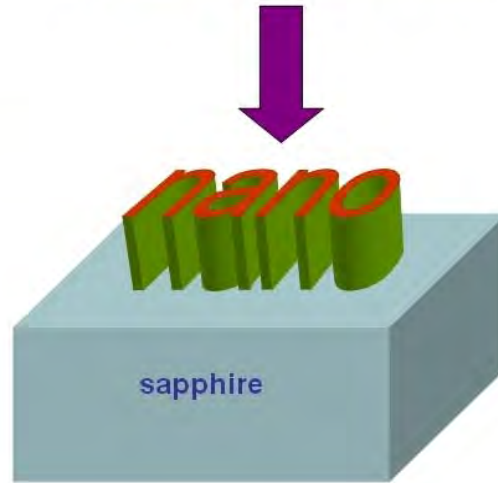


# GaN nanostructures

Low energy ion beam direct writing

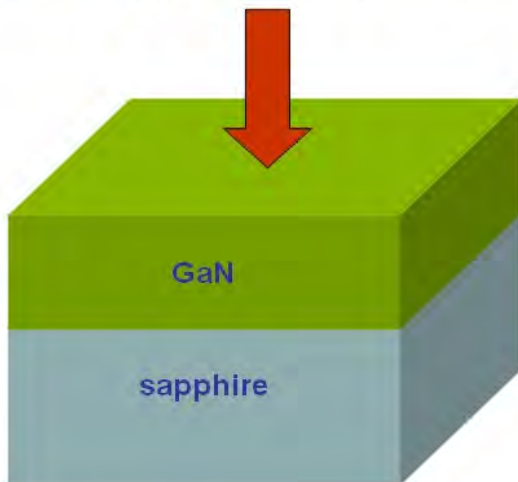


Photoelectrochemical etching

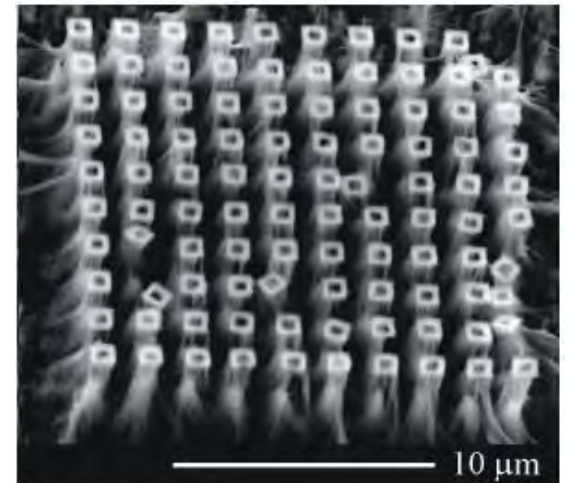
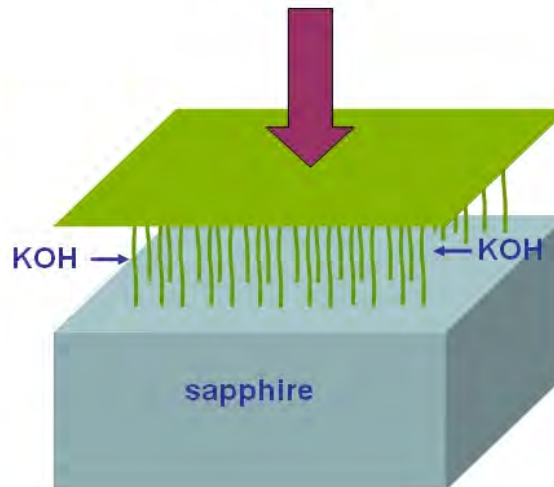


# GaN ultrathin membranes

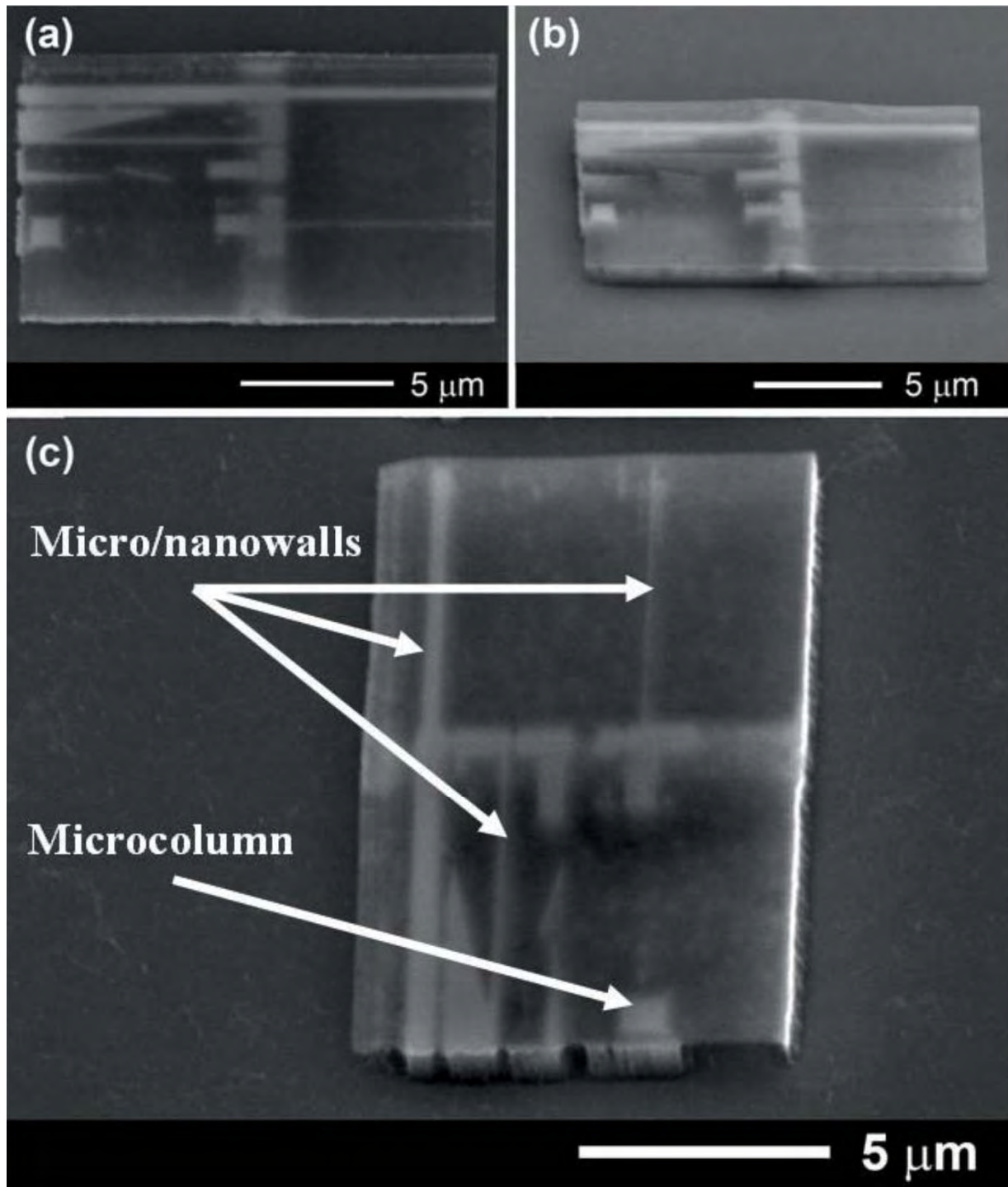
Low energy / low dose ion treatment



PEC etching







Design and  
maskless  
fabrication  
of suspended  
membranes

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- RELATED STORIES**
- ▶ Nano-roof reveals dislocations (Jan 2011)
  - ▶ Temperature orders TiO2 nanotubes (Apr 2010)
  - ▶ Salty water puts metal nanotubes in order (Jun 2008)
  - ▶ Gallium nitride nanopylarids resist radiation (May 2007)

- RELATED LINKS**
- ▶ Ion Tiginyanu

- RESTRICTED LINKS**
- ▶ *Physica Status Solidi - Rapid Research Letters* DOI: 10.1002/pssr.201206020

**TECHNOLOGY UPDATE**

Apr 12, 2012

**Surface writing produces designer nanostructures**

A new way to fabricate 3D nanostructures from gallium nitride using a focused ion beam (FIB) has been developed by researchers in Moldova, Australia, Germany and France. The technique, which involves directly writing a negative charge on the surface of GaN with the FIB and then photoelectrochemically etching the sample, allows ultrathin membranes and supporting nanocolumns to be fashioned in a controlled way. GaN is a large-bandgap semiconductor widely used in electronics applications such as high-temperature, high-power electronics and optoelectronics for light-emitting diodes and lasers. The material is also piezoelectric, so bridge-like GaN membranes might even find use in applications like nanoelectromechanical systems (NEMS).

**NANO HIGHLIGHTS**

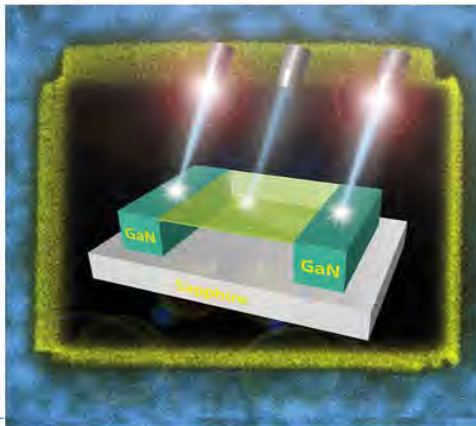
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**NANOTECHNOLOGY**

September 2011

**HEADLINES BY E-MAIL**

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Making GaN 3D nanostructures

Ion Tiginyanu and colleagues of the Moldova Academy of Sciences and Technical University of Moldova recently put forward a new way to make nanometre-thin membranes of gallium nitride hanging over a network of GaN threading-dislocation "whiskers" that act as a support. Their fabrication technique was based on etching away highly crystalline material from the GaN bulk epilayers, leaving behind only the negatively charged dislocation networks and a thin surface film to which the dislocations remain attached.

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ISSN 1862-6254  
 Phys. Status Solidi RRL  
 6 - No. 4 April  
 A37-A50, 145-186  
 (2012)

**physica status solidi rrl**

www.pss-rapid.com

**rapid research letters**

**4**  
**2012**

High dose ion beam treatment

High dose ion beam treatment

Low dose

**Design and maskless fabrication of ultrathin suspended membranes of GaN**

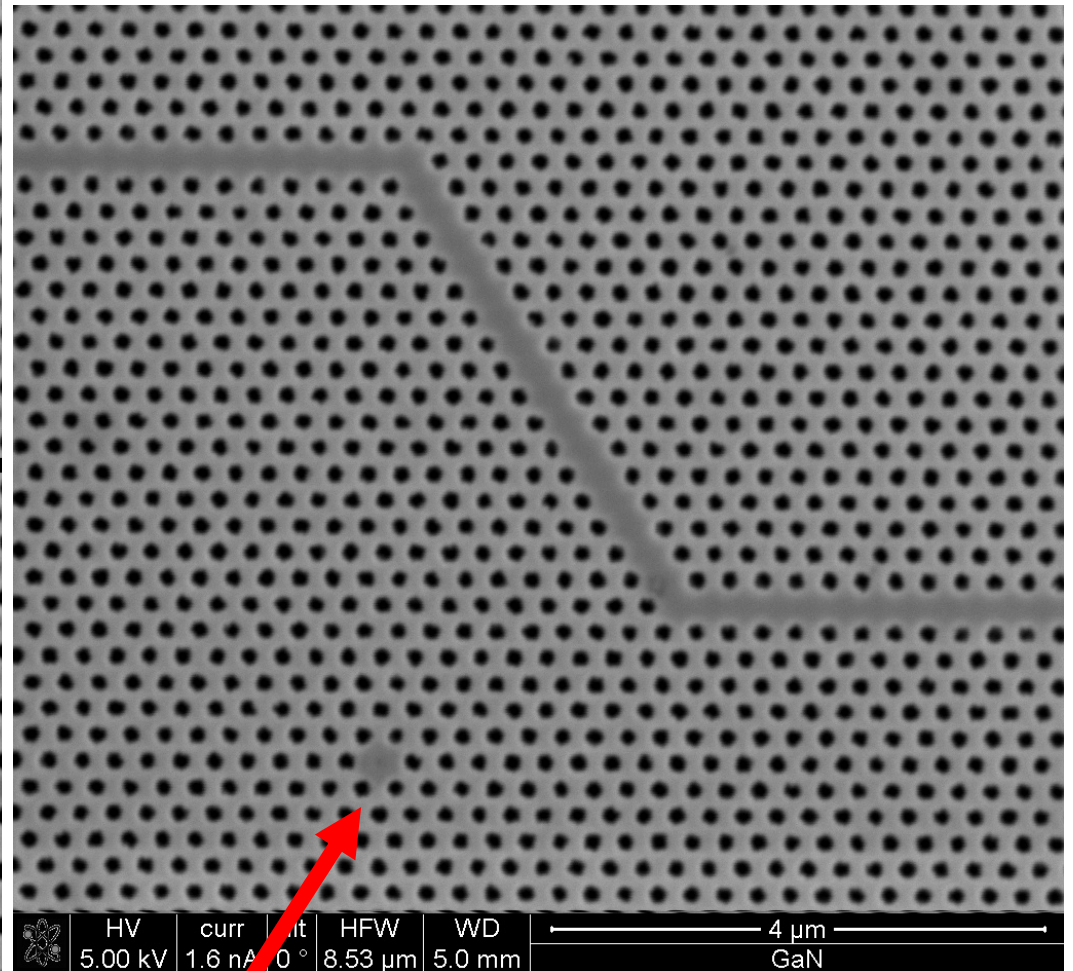
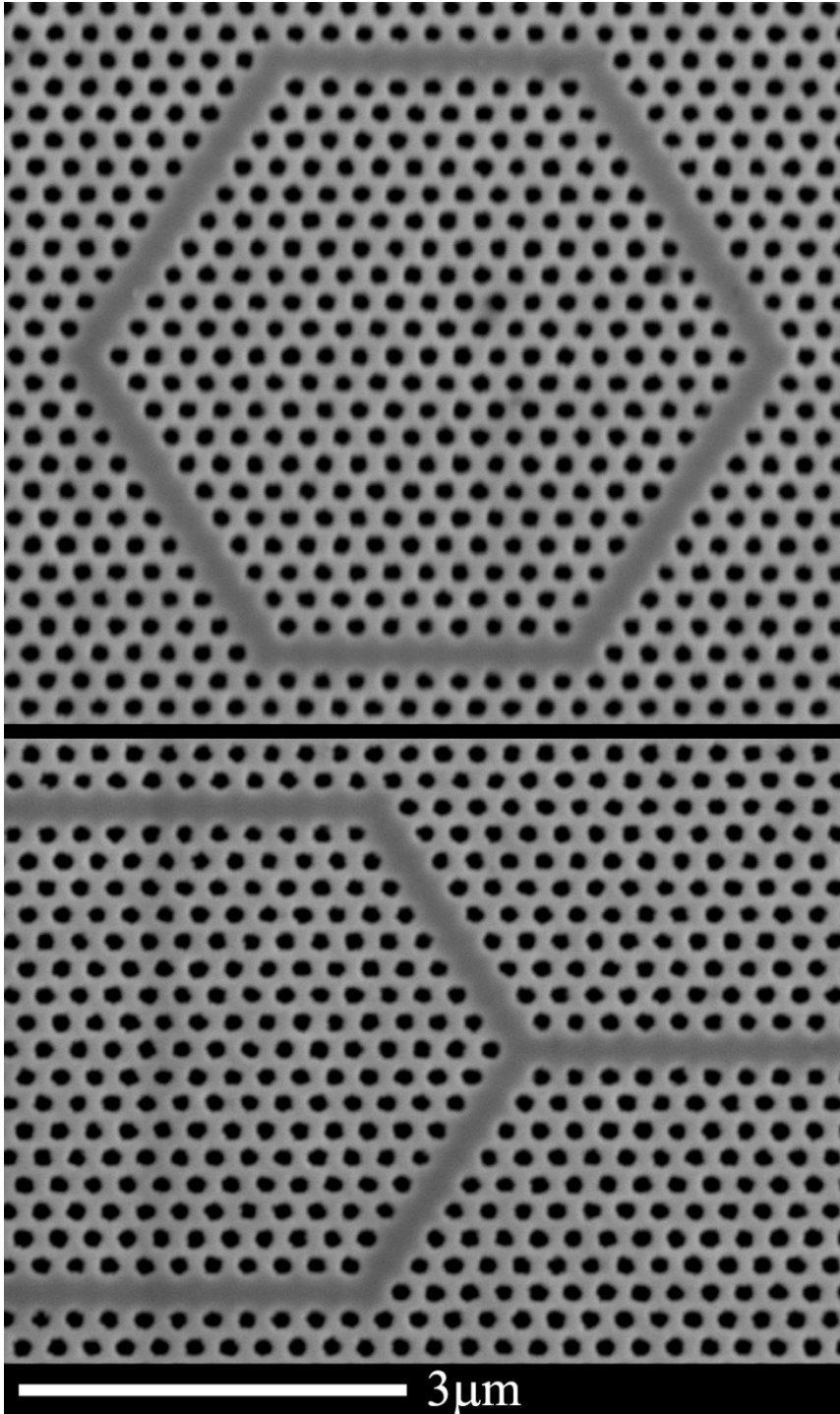
I. M. Tiginyanu, V. Popa, M. A. Stevens-Kalceff, D. Gerthsen, P. Brenner, and D. Pavlidis

**WILEY-VCH**

**Physica Status Solidi – RRL, Vol. 6, no 4, pp. 148-150 (2012).**



# GaN ultrathin photonic crystals

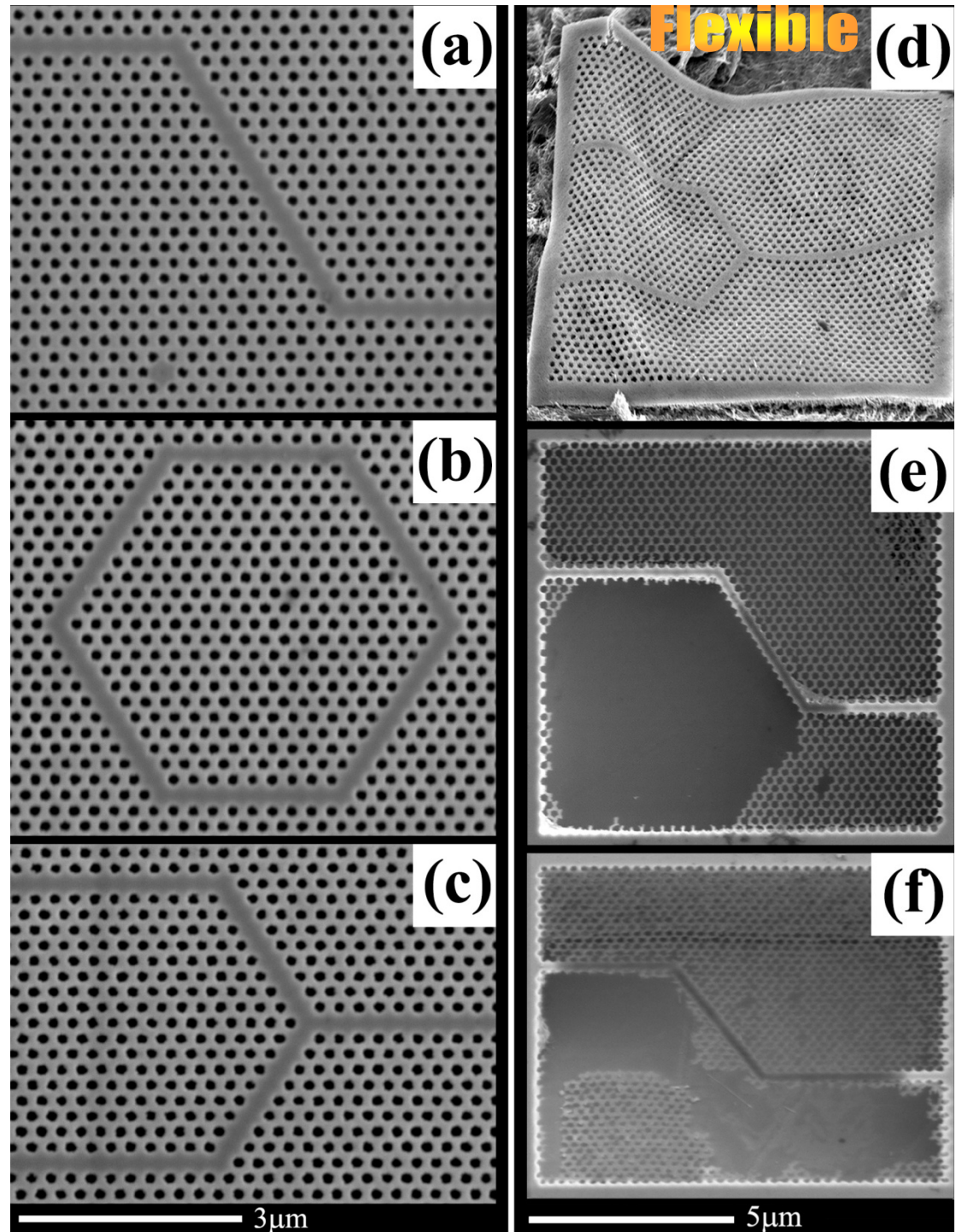


Absence of one hole

# GaN-based Flexible Photonic Structures

**15-nm thick**

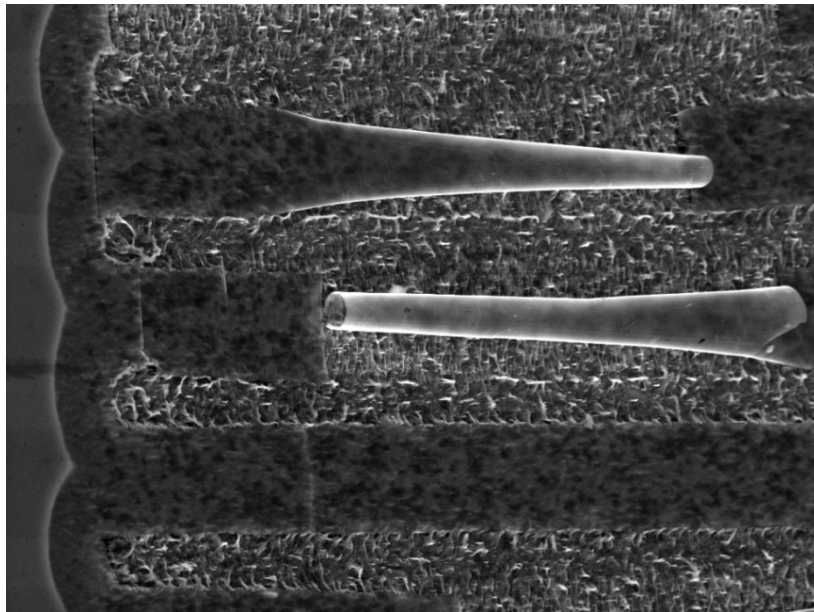
*Journal of Nanoelectronics  
and Optoelectronics, Vol. 9,  
no 2, pp. 271-275 (2014).*



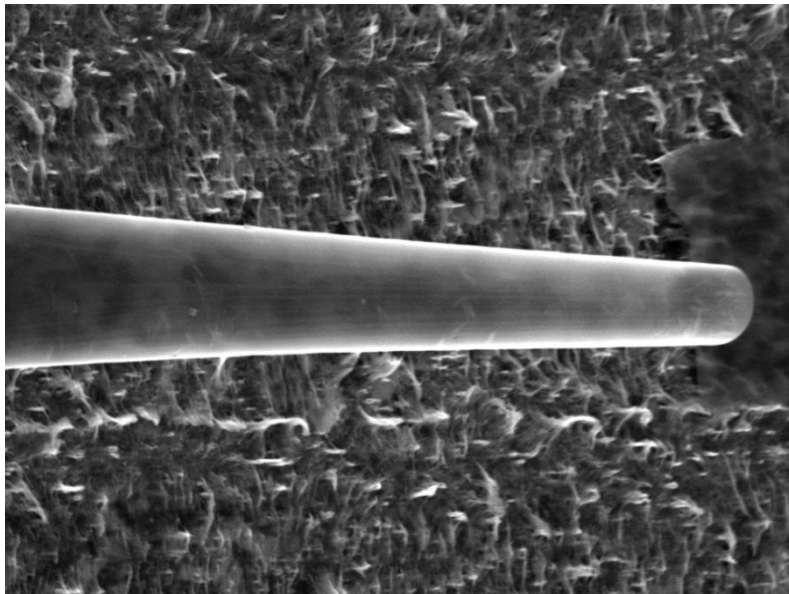


# Strain-induced self-rolled-up GaN microtubes

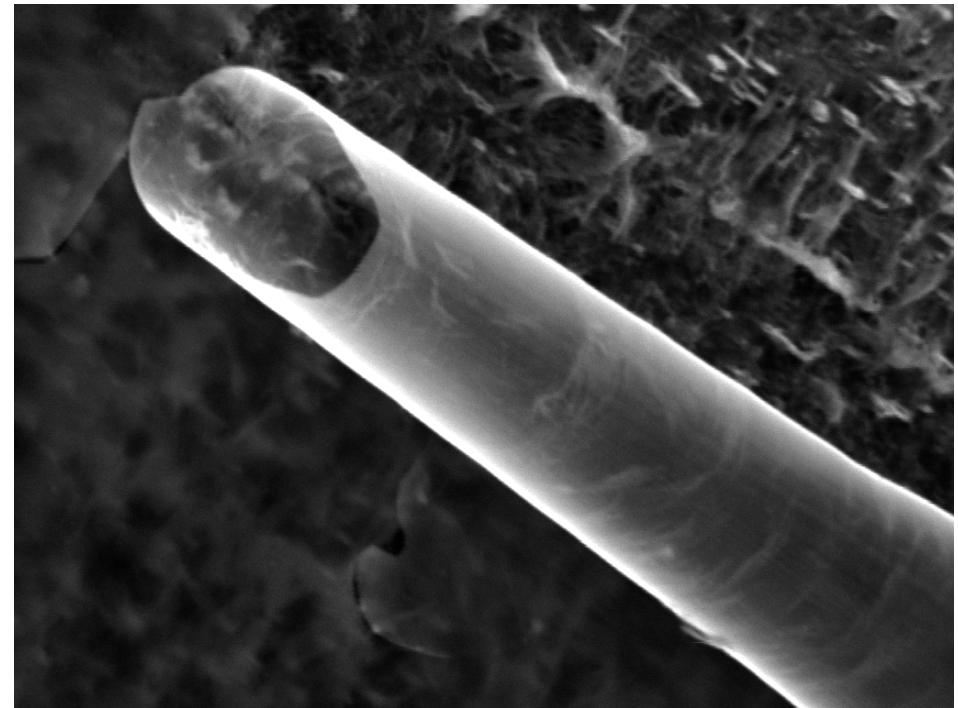
as promising structures for  
the development of  
microengines



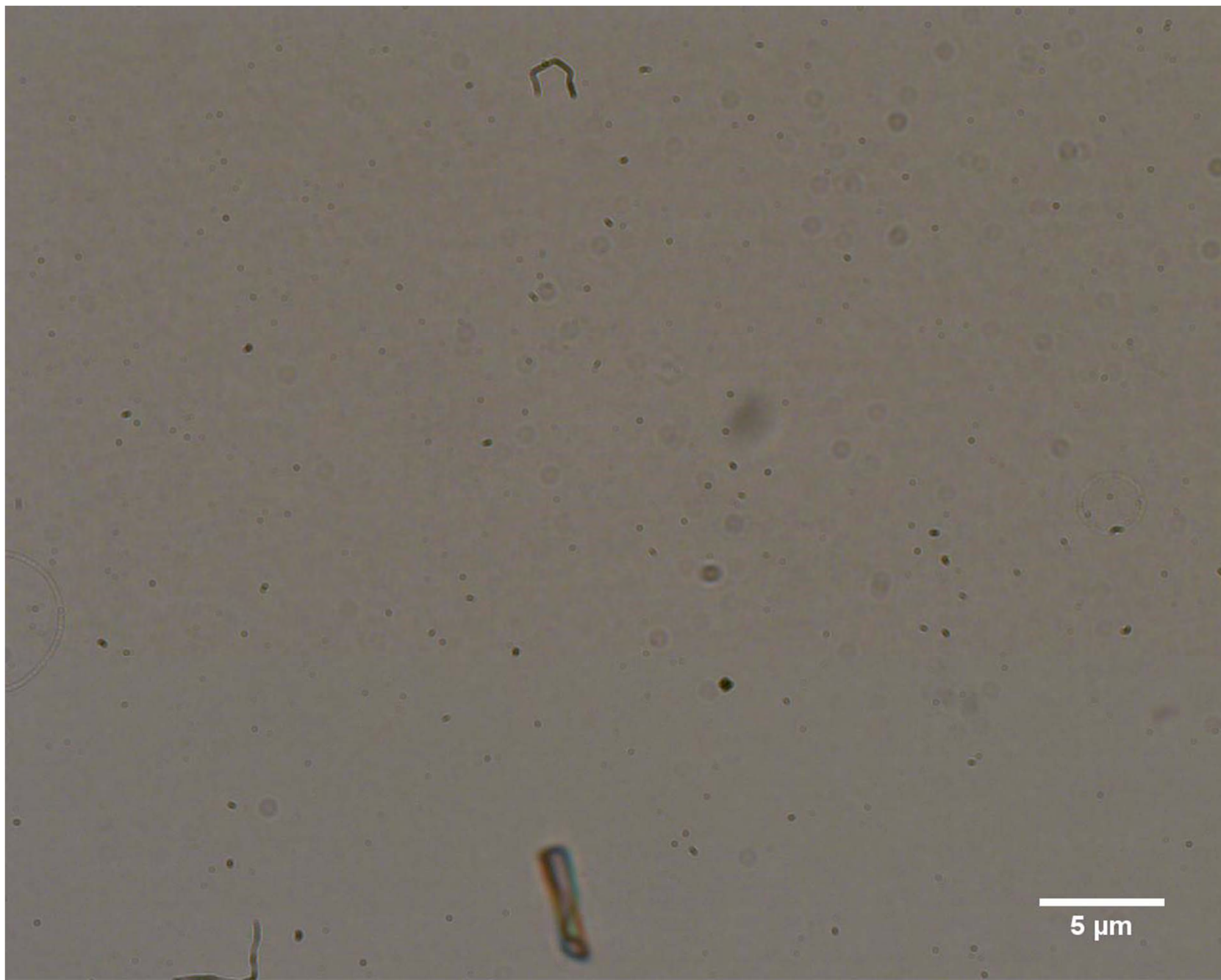
SEM MAG: 2.17 kx DET: SE Detector  
HV: 30.0 kV 50  $\mu$ m Vega ©Tescan  
UTM



SEM MAG: 5.68 kx DET: SE Detector  
HV: 30.0 kV 10  $\mu$ m Vega ©Tescan  
UTM

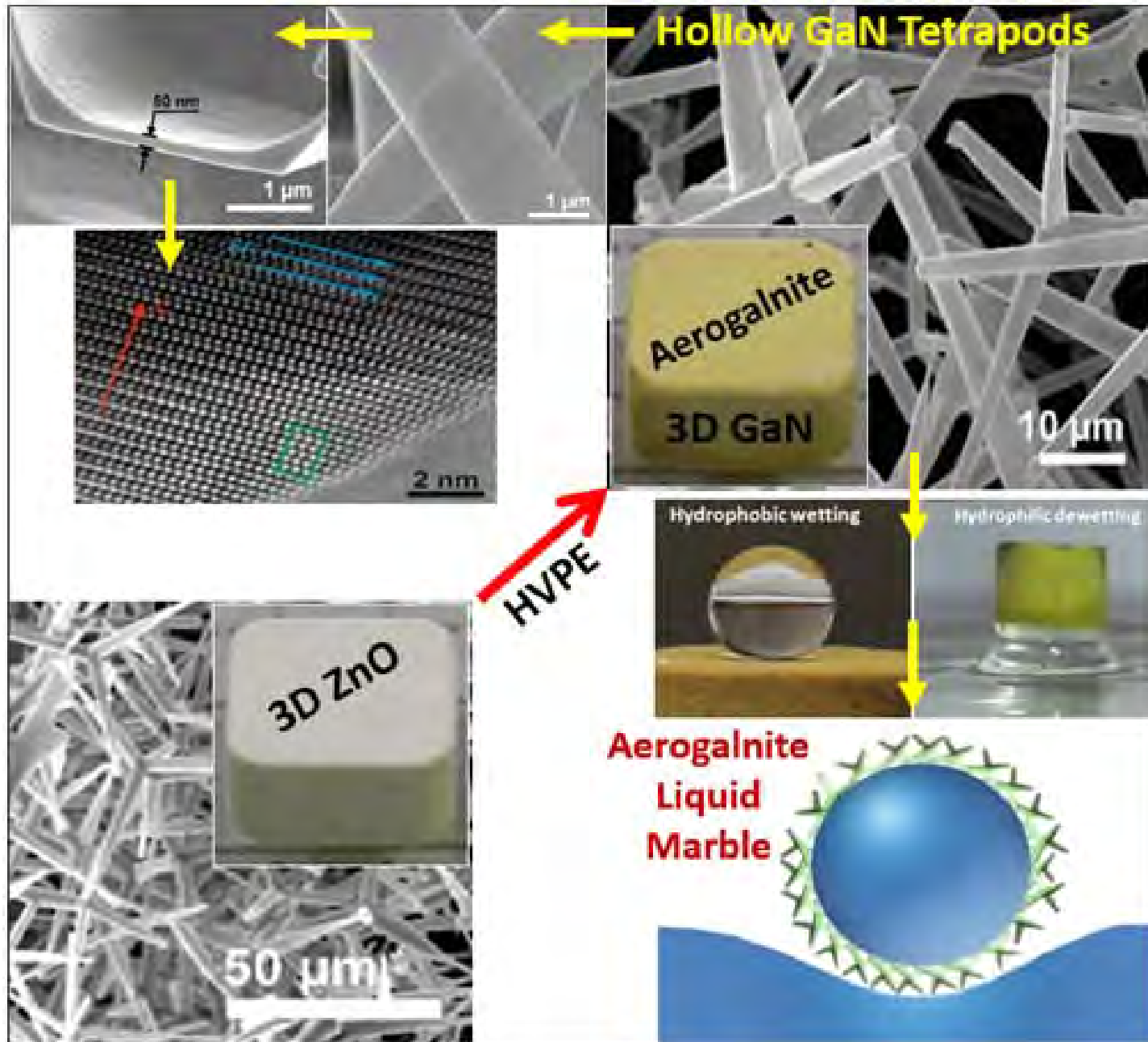


SEM MAG: 10.66 kx DET: SE Detector  
HV: 30.0 kV 10  $\mu$ m Vega ©Tescan  
UTM



**Aerogalnite**  
**(Aero-GaN)**

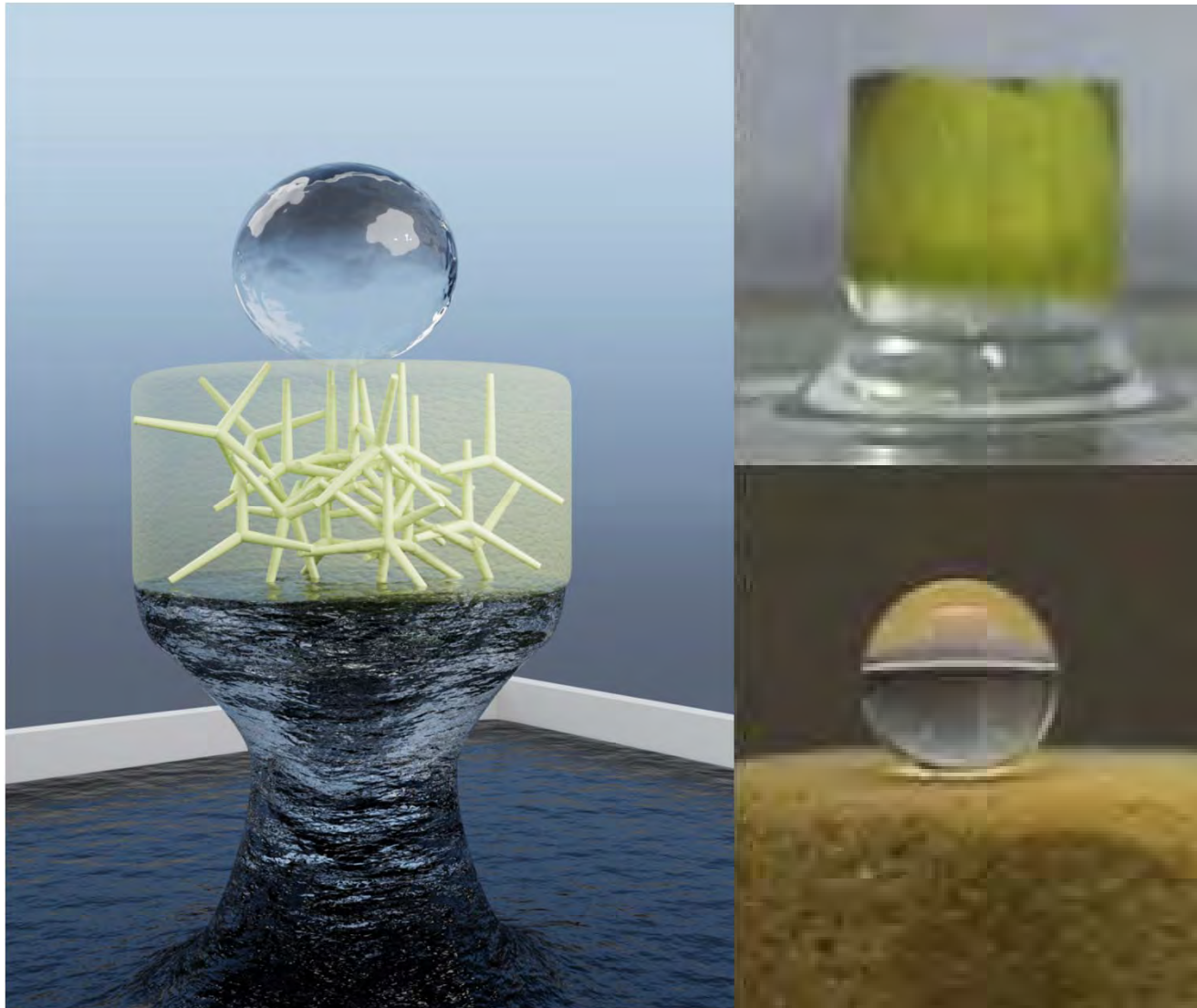
# Aero-GaN





# Physics World

<https://physicsworld.com/a/hydrophobic-or-hydrophilic-aero-gallium-nitride-is-both/>

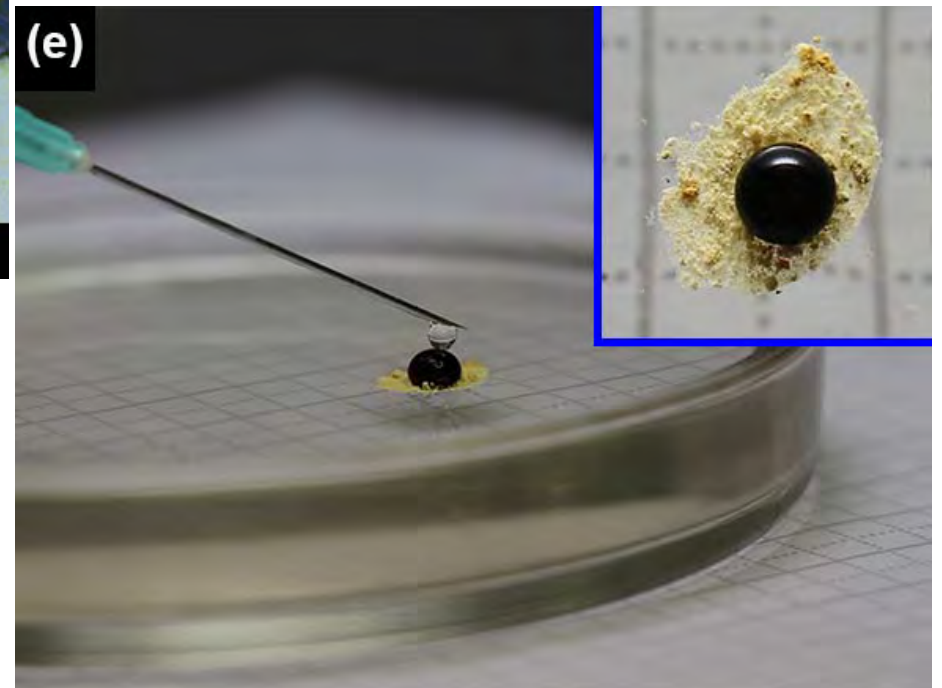
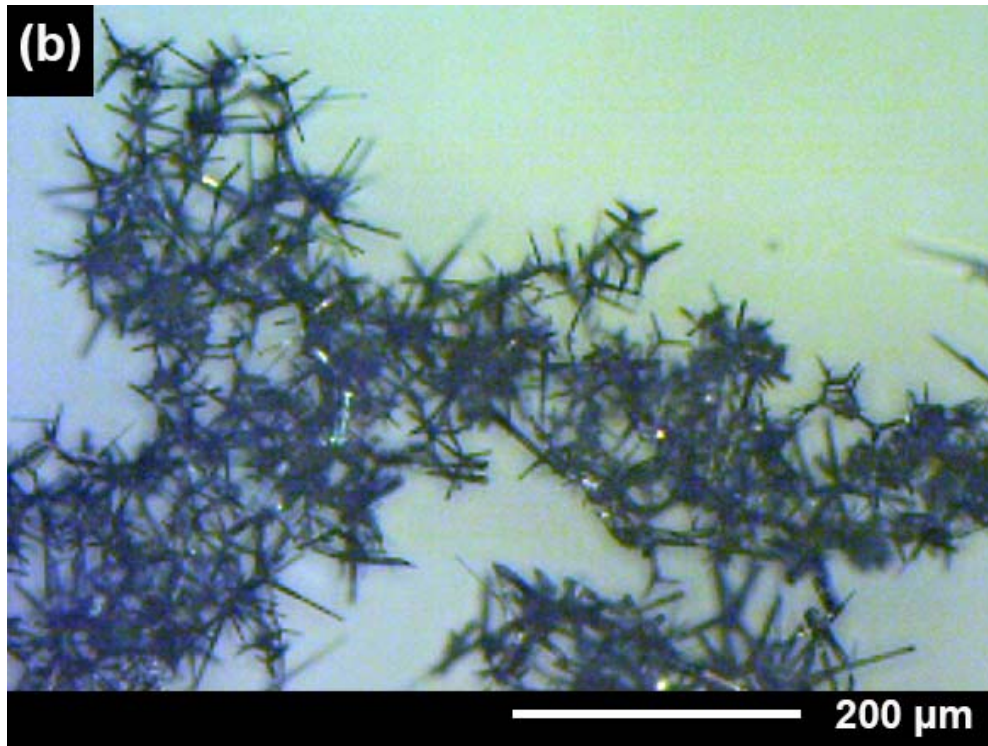


**Hydrophilic  
dewetting**

**Hydrophobic  
wetting**

I. Tiginyanu, T. Braniste *et al* Nano Energy, Vol. 56, pp. 759-769 (2019).

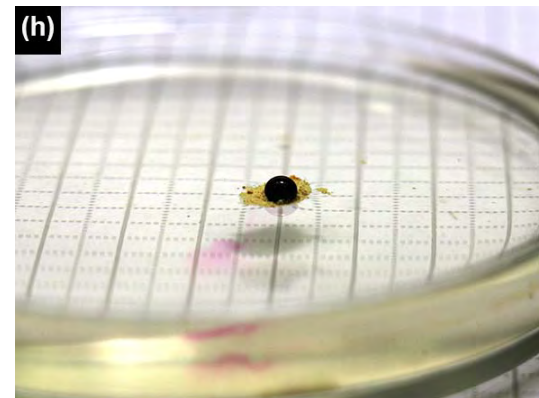
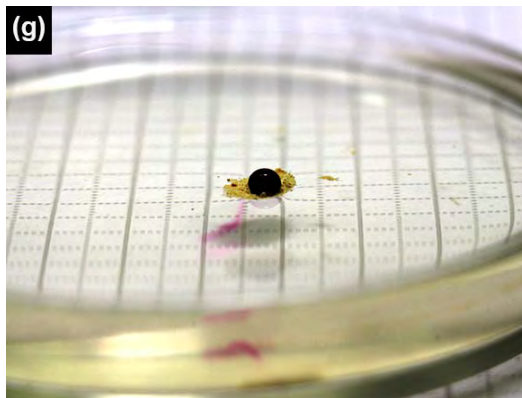
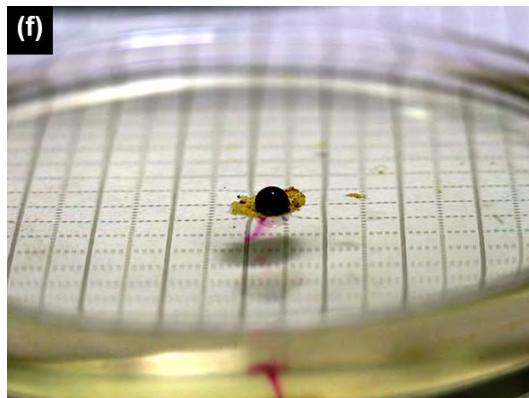
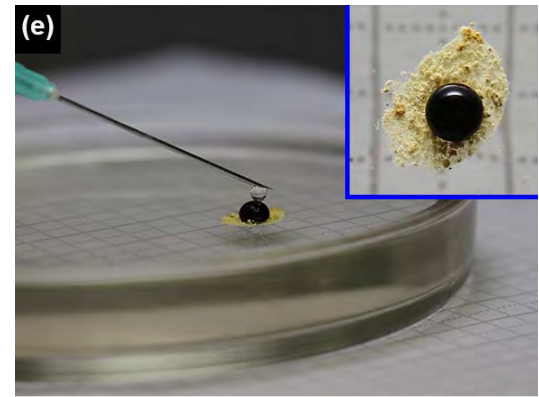
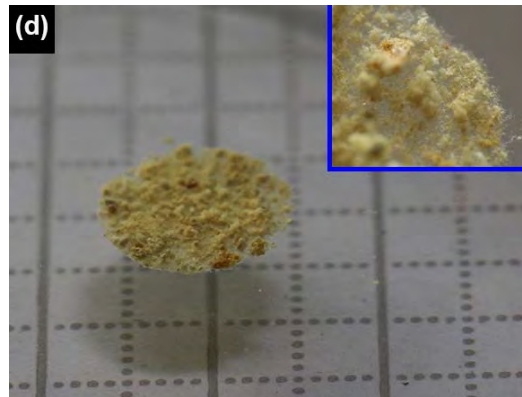
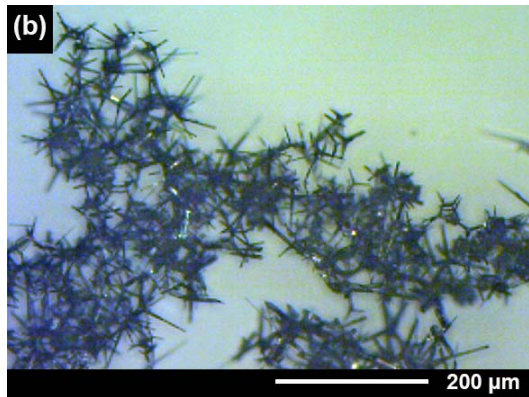
# Weaving GaN floating carpets







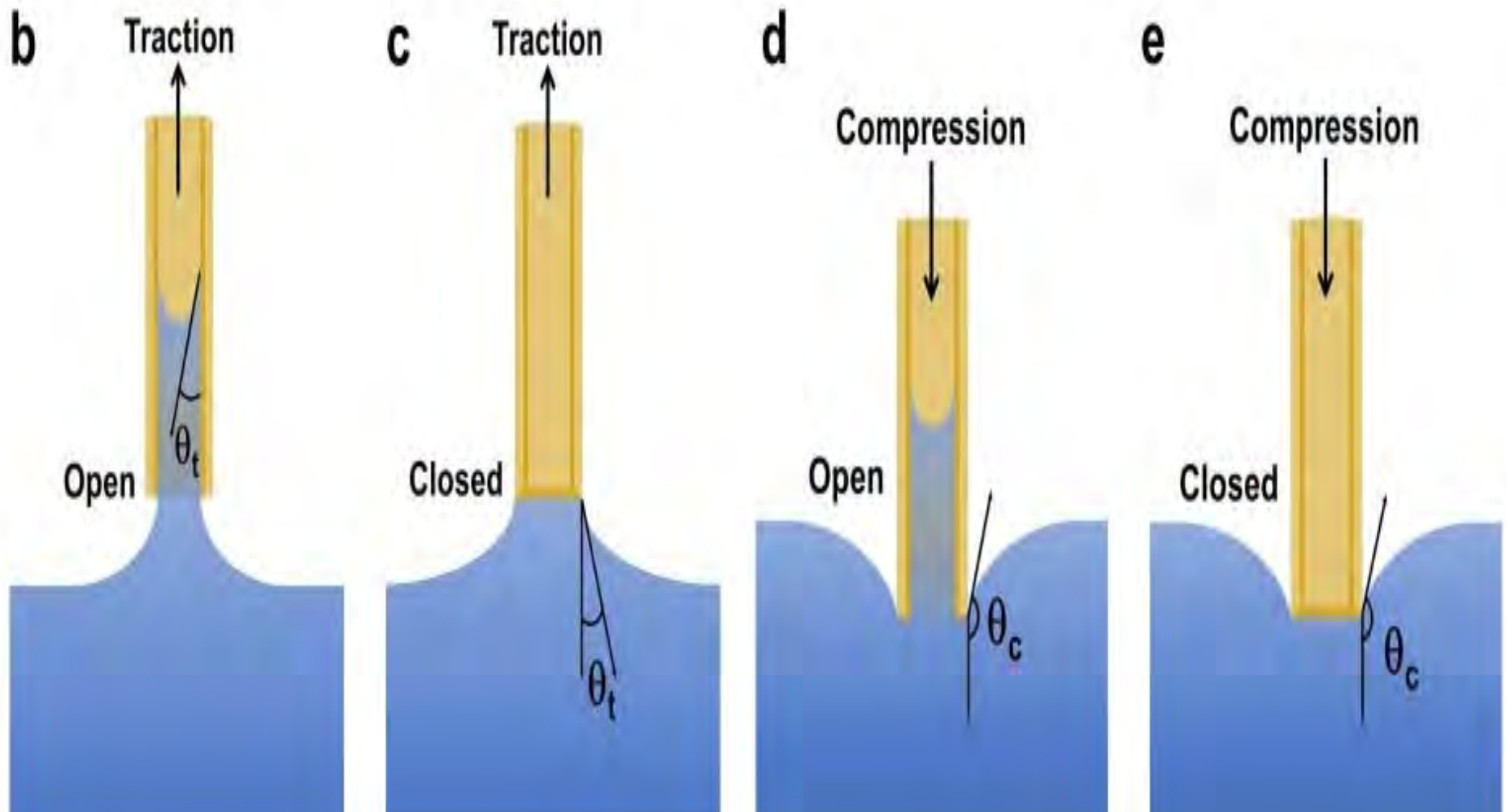
# Weaving GaN floating carpets and their use as self-healing rafts



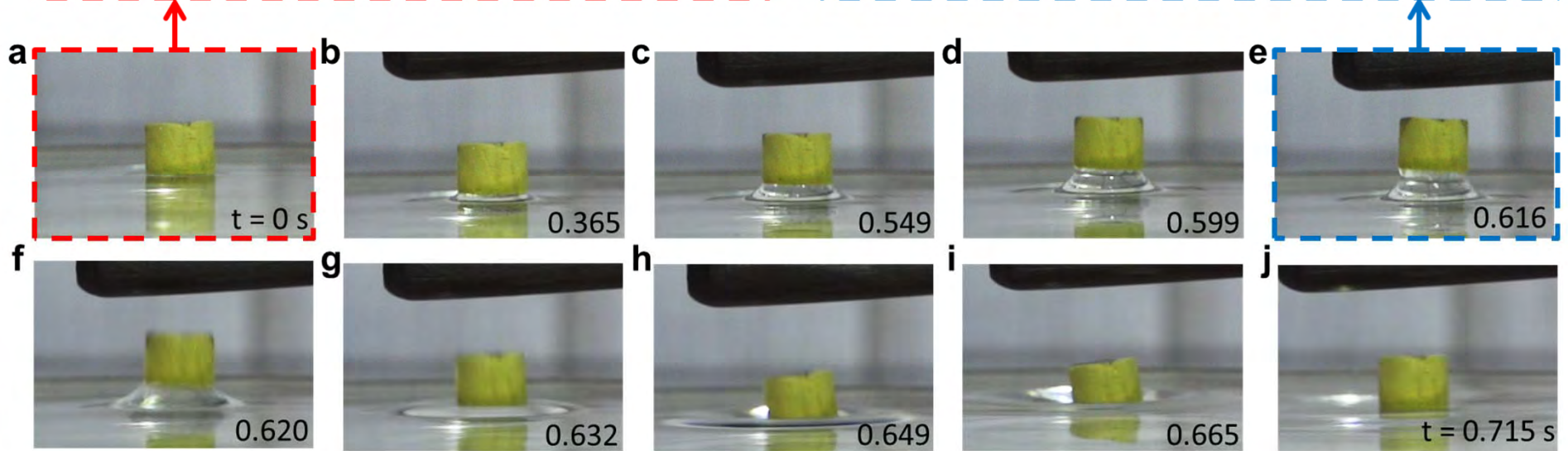
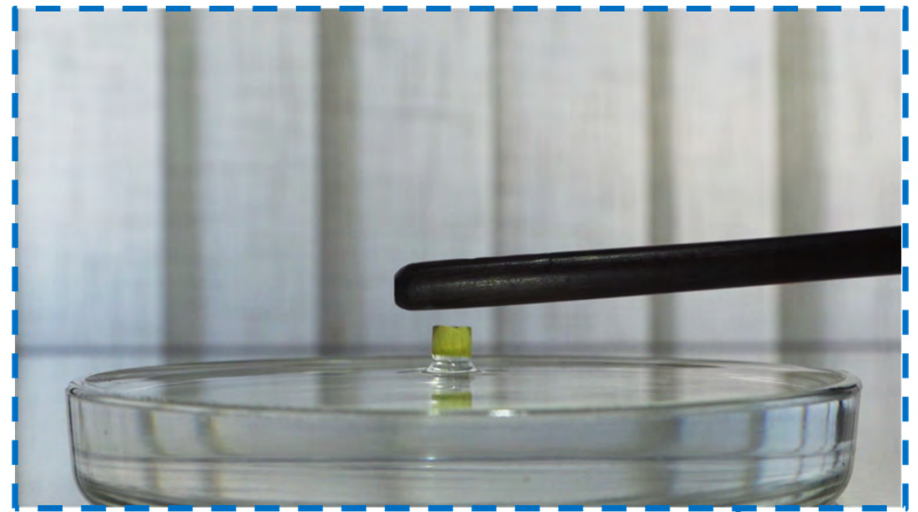
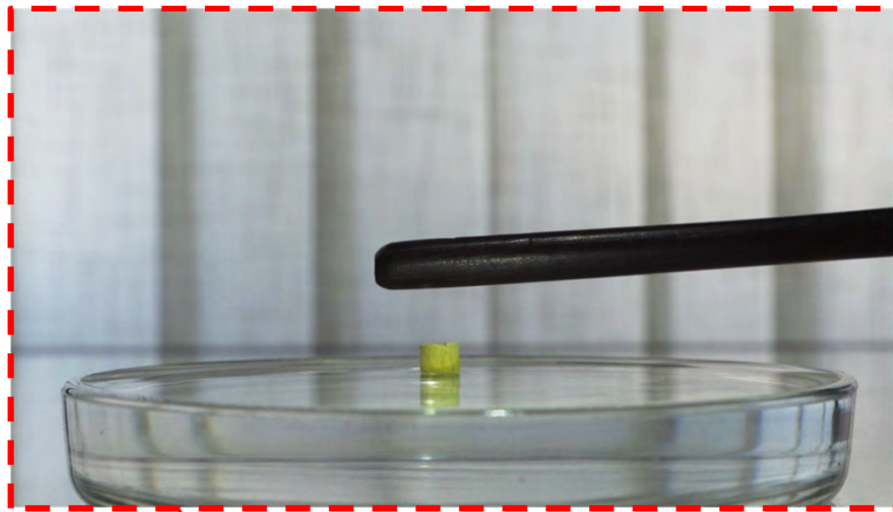
I. Tiginyanu, T. Braniste *et al* Nano Energy, Vol. 56, pp. 759-769 (2019).



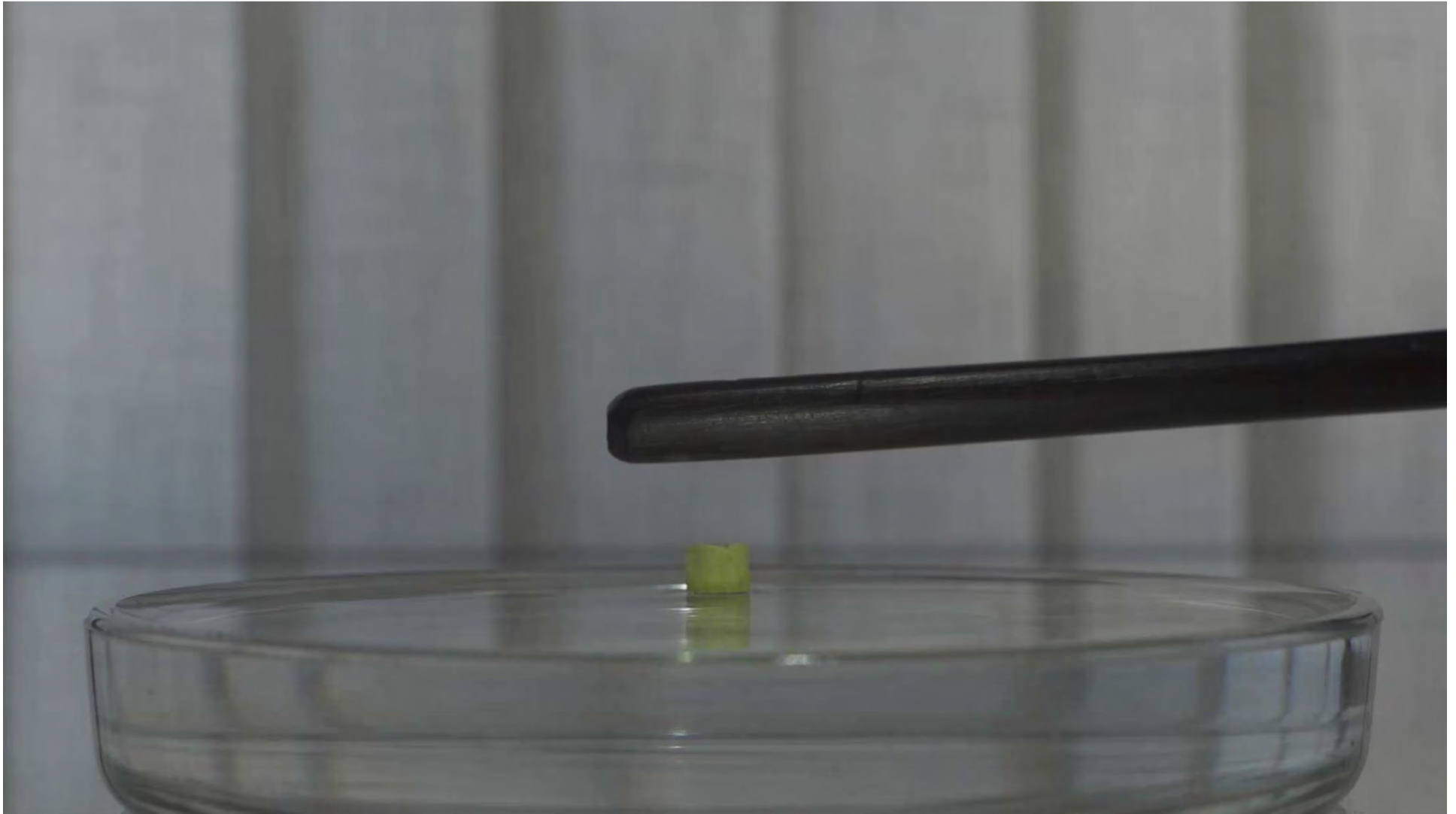
# Hydrophilic-hydrophobic nature



# Demonstration of hydrophilic dewetting



# Demonstration of hydrophilic dewetting



# Rotating liquid marbles

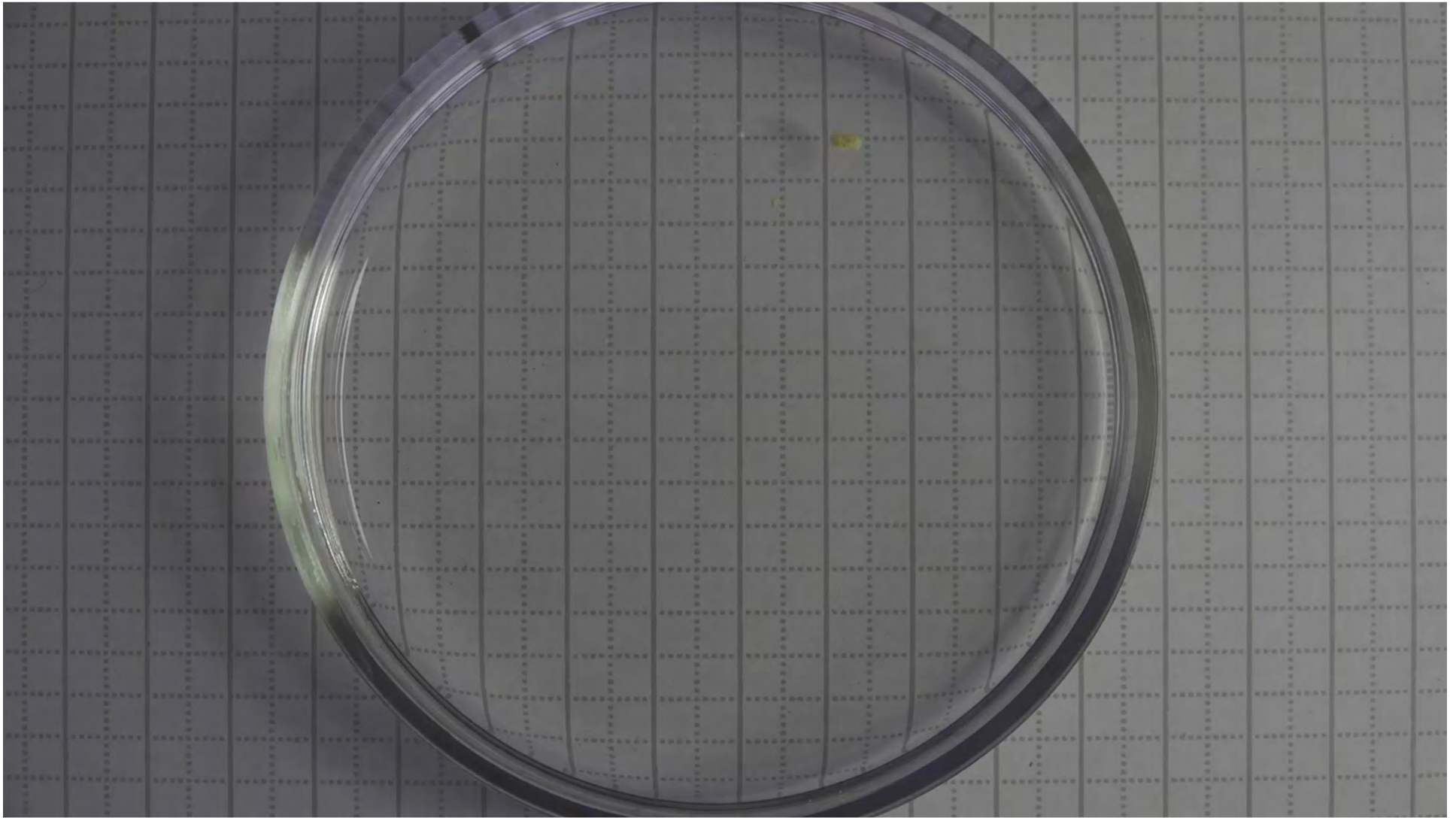


Ion Tiginyanu, Tudor Braniste, Daria Smazna, Mao Deng, Fabian Schütt, Arnim Schuchardt, Marion A. Stevens-Kalceff, Simion Raevschi, Lorenz Kienle, Nicola Puglo, Yogendra K. Mishra, Rainer Adelung, Self-organized and self-propelled aero-GaN with dual hydrophilic-hydrophobic behaviour, *Nano Energy* 56, 759-769 (2019).





# Rotating liquid marbles



# Consortium NanoMedTwin

<b>Technical University of Moldova</b>	<b>Moldova</b>
<b>Hannover Medical School (MHH)</b>	<b>Germany</b>
<b>Royal Institute of Technology (KTH)</b>	<b>Sweden</b>
<b>University of Bristol (UNIVBRIS)</b>	<b>UK</b>
<b>Joint Research Centre (JRC)</b>	<b>Italy Belgium</b>
<b>EFPC Ltd (EFPC)</b>	<b>Israel</b>



# Project objectives

1. **Promotion of the links between NANO and BioMedicine fields (multidisciplinarity)**
2. **Training of a new generation of highly-skilled researchers**
3. **Developing a strategic programme focusing on the field of nanomaterials for biomedical applications, establishing links with medical institutions in Moldova and building of capacities for the promotion of technology transfer**
4. **Extending networking and collaboration and creation of capacities for broader participation of NCMST and other linked research groups in Moldova with the Horizon 2020 Programme and future FP9 Programme**



# The International Conference on Nanotechnologies and Biomedical Engineering



ICNBME-2011

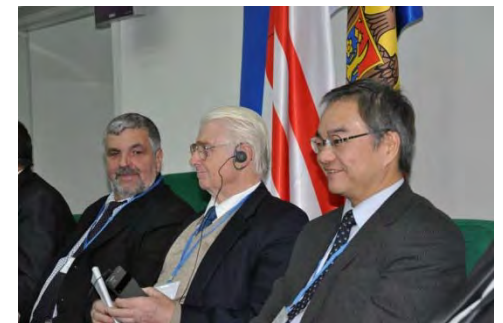
ICNBME-2013

ICNBME-2015

ICNBME-2019



Conference site: <http://www.icnbme.sibm.md/>

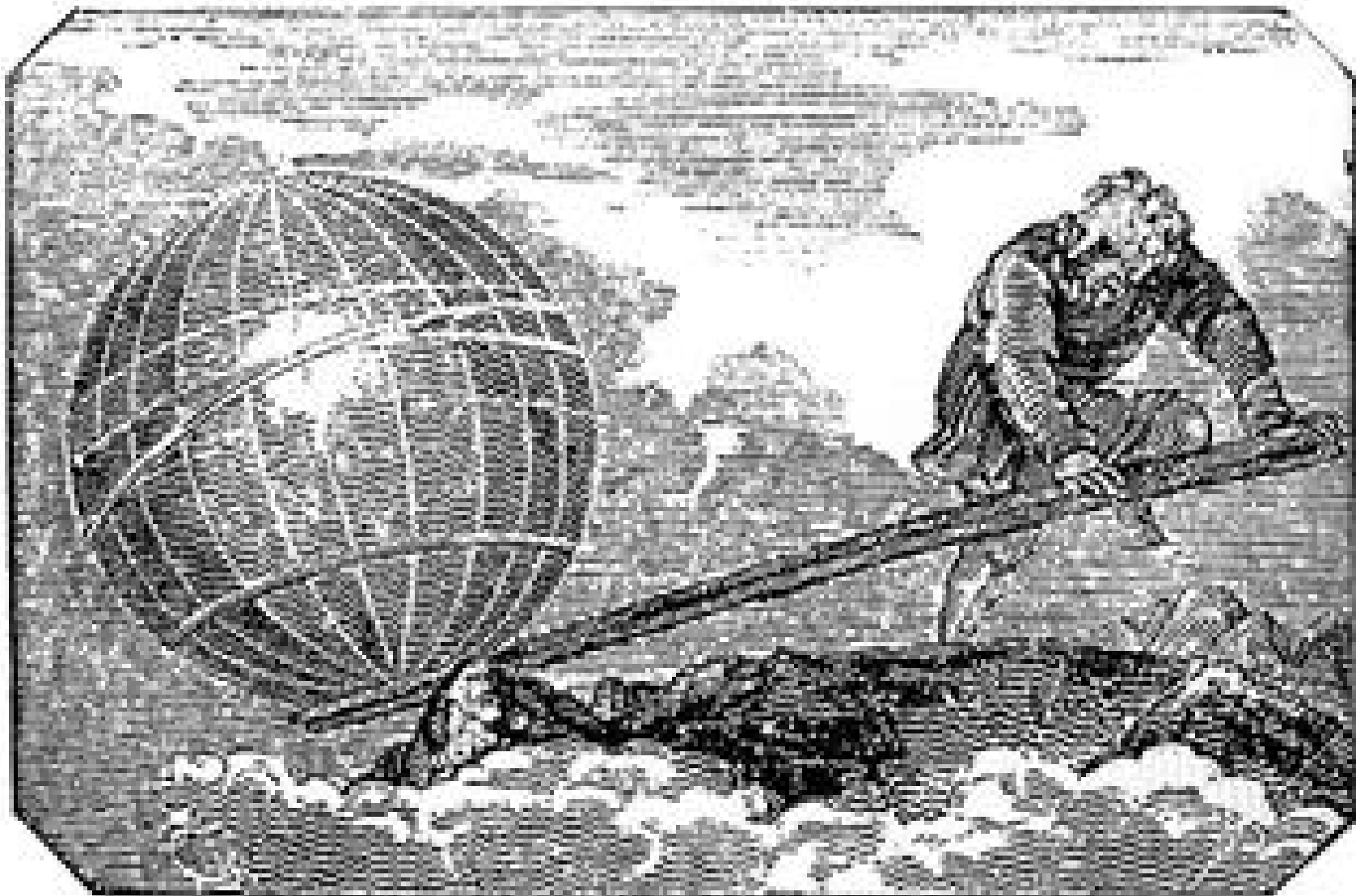




# Conclusions

- **GaN hollow nanoparticles were developed and their biocompatibility and uptake by living cells have been demonstrated;**
- **GaN-based ultrathin membranes as well as flexible two-dimensional photonic crystals with embedded waveguides, beam splitters and ring resonators have been fabricated;**
- **GaN-based microtubes with ultrathin walls and flexible three-dimensional architectures have been developed for biomedical and microfluidic applications.**

# Knowledge moves the world



Thank you

for your kind  
attention!