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Fraunhofer IISB FutureIOT

# Printed Ion-Selective Sensors for Precision Agriculture

## 4th Joint BfR/Fraunhofer Symposium on Nanotechnology
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IOT

# Overview

- Research Project “FutureIOT”
- Sensor Networks for Soil Monitoring
  - Motivation
  - Vision
- Sensors
- Communication
- Summary and Outlook

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# FutureIOT – Smart Networks for Cities and Agriculture

- Bavarian research project FutureIOT (Partners from industry (24) and academia (10), >4 M€) covers the entire IoT value chain:
  - Sensors
  - Communications
  - Localization
  - Data Security
  - IoT Platforms
- Smart agriculture as a vertical topic
  - Soil monitoring
  - Cattle tracking

# Motivation and Vision

- Contamination of ground water with nitrate
  - Caused by leaching of mineralized N-fertilizer
  - Critical situation in „red areas“
    - More restrictions/limitations for farmers
    - Frequently nitrate soil control measures

Vision:

- **cost-effective, simple and continuous monitoring** of nutrient supply in soils
- basis for demand-based fertilization

# Research Approaches 1/2

- R&D towards sensor nodes for continuous, local acquisition of soil parameters
- Integration with IoT systems
- Continuous monitoring of nitrogen content in soil by electrochemical sensors
  - Combination of IISB proprietary sensors for nitrate and ammonium
  - Integration with electronic system
  - Connection to IOT platform
- ➢ Portable measurement equipment for on-site and real-time determination of $N_{min}$ content

# Research Approaches 2/2

- Wireless radio transmission out of soil
  - Use of commercially available sensors for soil humidity and conductivity
  - Data transfer from different soil depths by Low Power Wide Area Network (LPWAN) technology
  - Connection to IOT platform
- ➢ Buried measurement equipment for on-site and real-time determination of soil parameters

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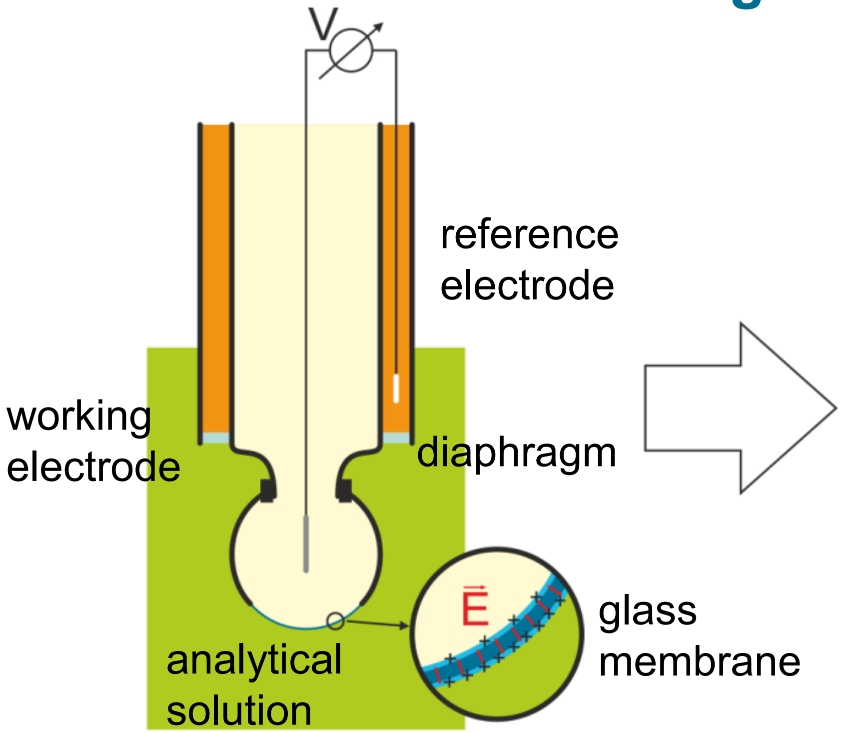
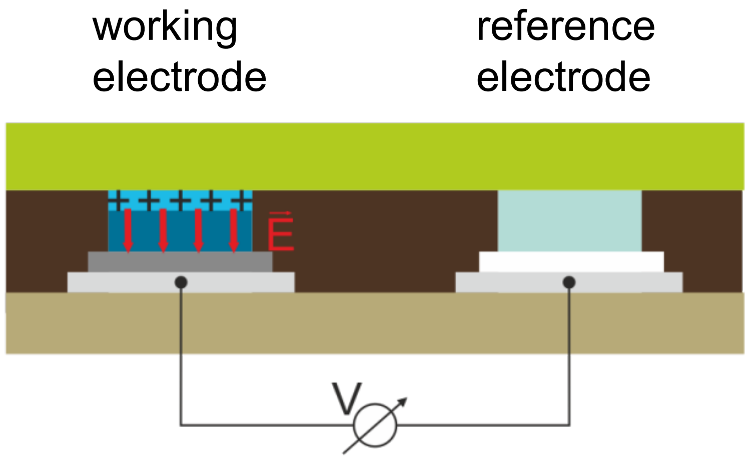
# NITROGEN SENSORS

# Printed Ion Sensors – Working Principle



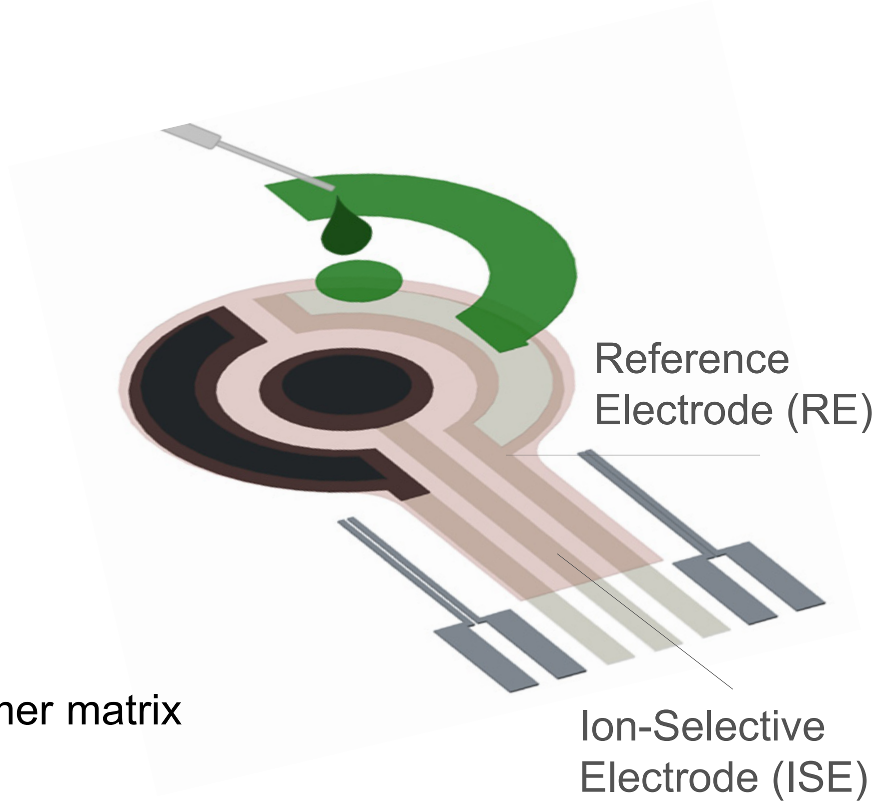

glass electrode




printed planar ion sensor

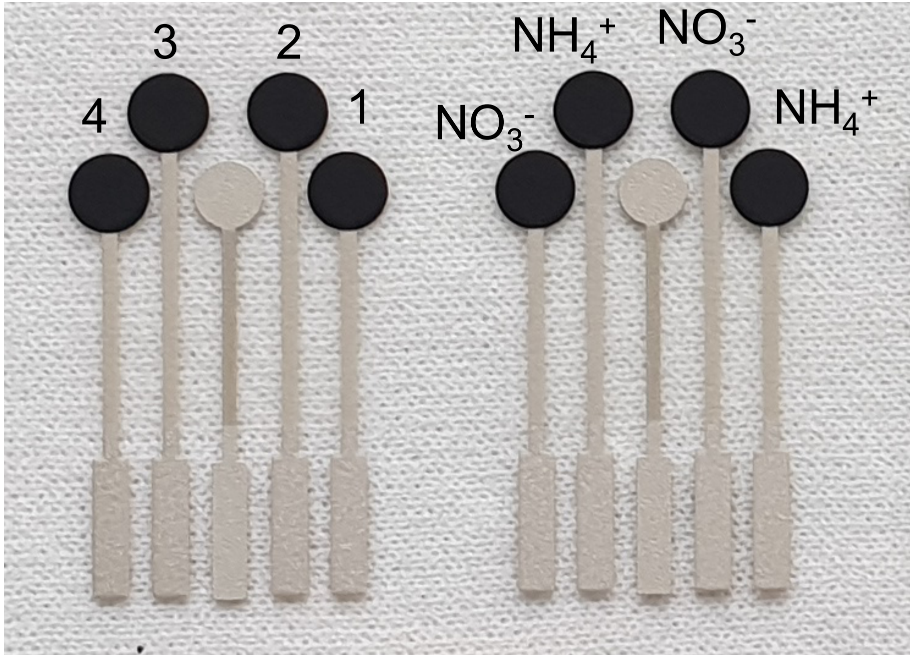
# Sensor Fabrication

- Screen-printed sensor electrodes
  - Working electrode (ISE): silver (Ag), carbon (C)
  - Reference paste (RE): silver/silver chloride (Ag/AgCl)
  - Polymer encapsulant
- **Substrate: PET, PEN, PI**
  - Layer annealing: 130 °C, 5 to 15 min
- **Functionalization of RE and ISE**
  - ISE: drop-casting of ionophore in polymer matrix
  - Functionalized RE



# Multisensors for $NH_4^+$ and $NO_3^-$ Ions

- Parallel measurement of $NO_3^-$ and $NH_4^+$
- Working electrodes:
  - AE1 & 3 for $NH_4^+$
  - AE2 & 4 for $NO_3^-$
  - optional: $K^+$, $Cl^-$, $Na^+$
- tailored functionalization is possible



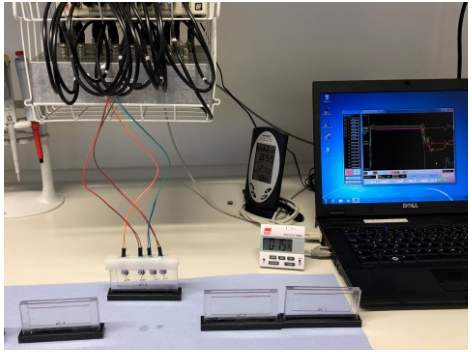
# Printed Ion Sensors - Characterization

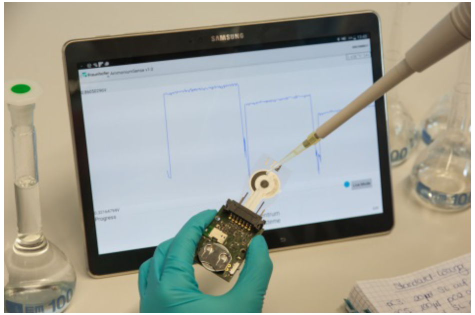
- Laboratory setup
  - parallel testing (up to 15 devices)
  - variation of target concentration
- Potentiometric response
  - Following Nernst equation

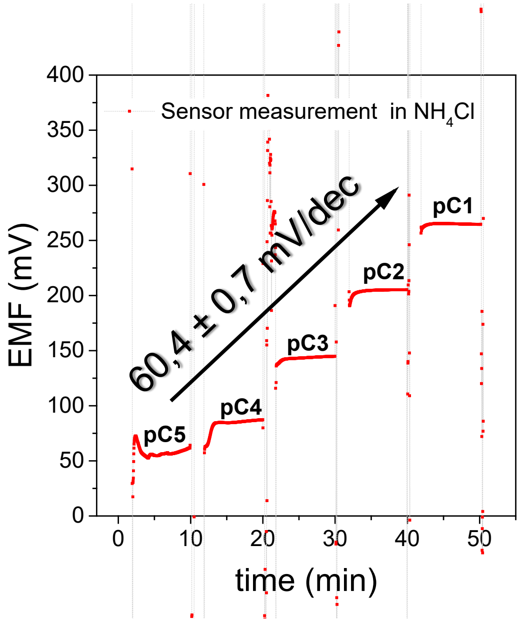
$$E = E_0 + 2.303 \frac{RT}{F z_i} \log(a_i)$$

ideally 59.2 mV/decade

- High resolution, direct read-out





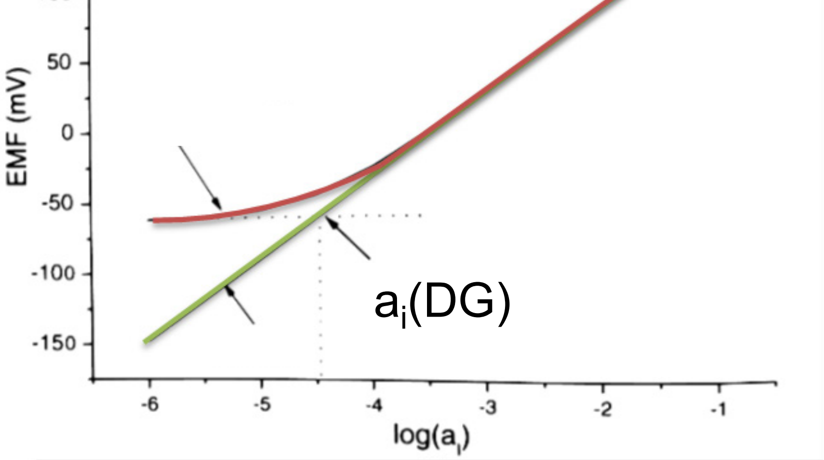


# Cross-sensitivity against $Cl^-$

- Test solutions
  - pC7 until pC1 $NH_4NO_3$ standards preparation and pC2 oder pC3 $CaCl_2$ addition
- 0,01mol/l $CaCl_2$ –solution
  - $\log(K_{ij})$= -2,6 ± 0,06
  - $K_{ij}$= 0,0028 ± 0,0004 ($K_{ij}$ <1)
- 0,001mol/l $CaCl_2$-solution
  - log ($K_{ij}$)= -1,9 ± 0,12
  - $K_{ij}$= 0,024 ± 0,004 ($K_{ij}$ <1)
- $K_{ij}$ <1 means: sensors are more selective against primary than against secondary (interfering) ion ($Cl^-$)

## Fixed Interference Method

$$\log(K_{ij}) = \left(\frac{a_i(DG)}{a_j}\right)^{\frac{z_i}{z_j}}$$

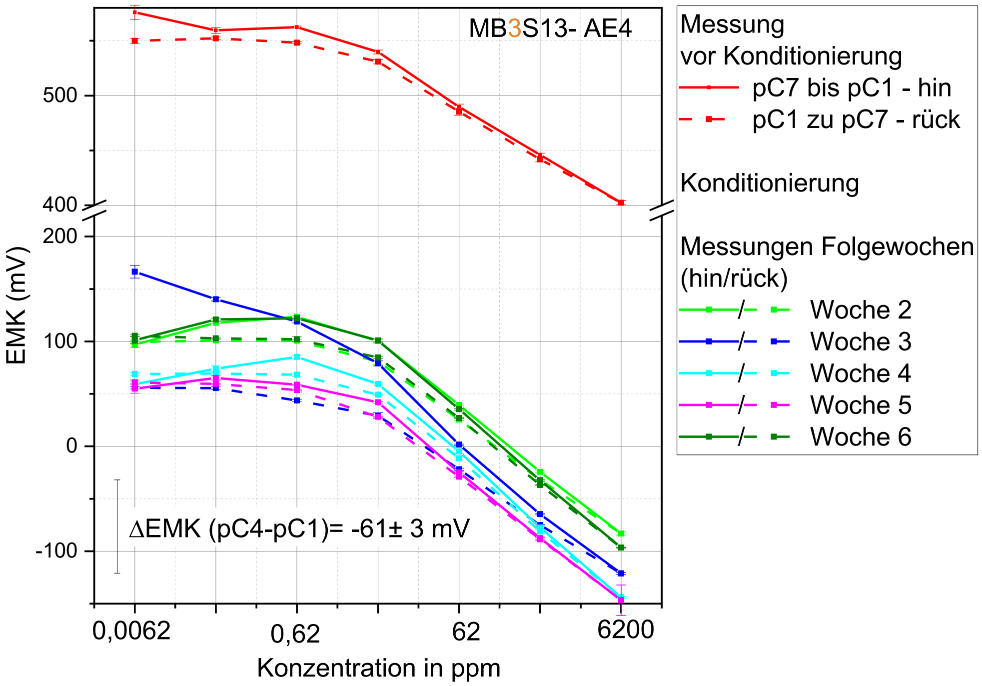



* G. Schwedt, T. C. Schmidt, O.J. Schmitz „Analytische Chemie - Grundlagen, Methoden und Praxis“ WILEY-VCH Verlag GmbH & Co. KGaA, 3.Auflage (2016)

# Long Term Stability

- **Preconditioning in $NH_4NO_3$**
- Nitrate sensors applied for 6 weeks potentiometric mesurement

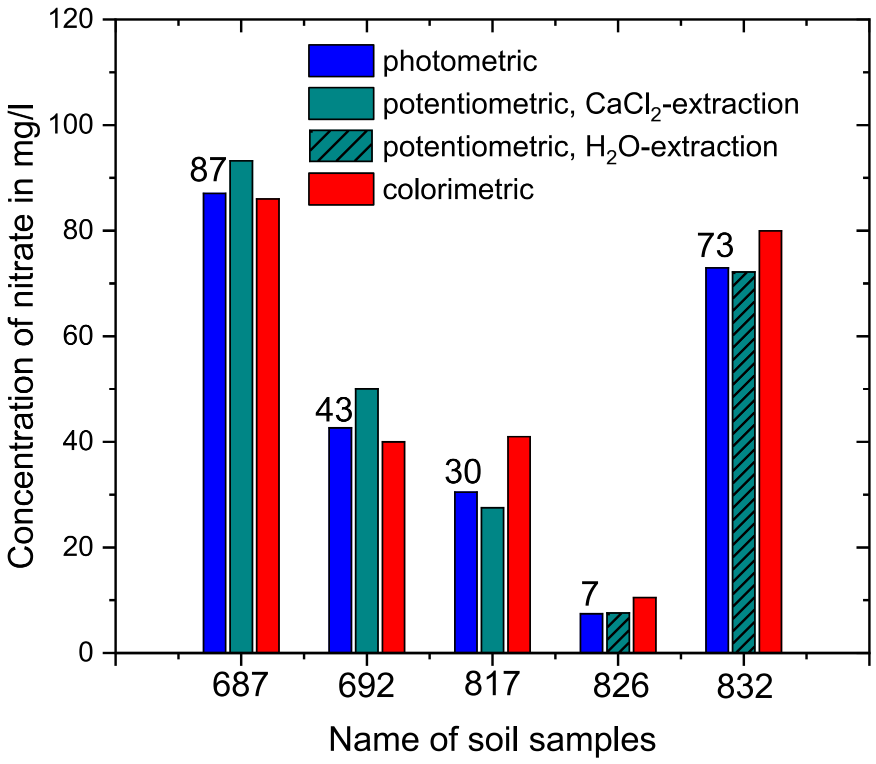
- Nitrate range from pC7 →0,0062 ppm until pC1→ 6200ppm
- Nernstian gradient of -61 mV/dec, excellent linearity for > 6,2 ppm
  - curve drift can be suppressed by developed contitioning routine



# Nitrate Content in Soil Samples

- Real-time space-resolved monitoring of nitrate concentration in agri- and horticulture
  - Fast response time
  - Low preparation effort
- Benchmarking against state-of-the-art or approved techniques
  - Photometry (spectroscopic)
  - Colorimetry (test strip)

$NO_3^-$ :
in <5min similar values like photometric values from test lab (t~24 hrs.)



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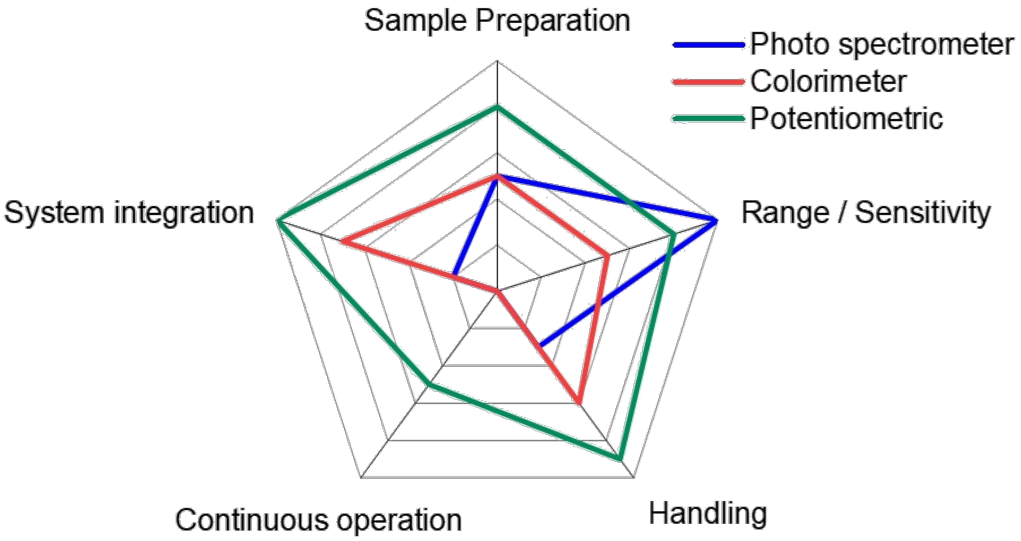


# Radio Transmission out of soil

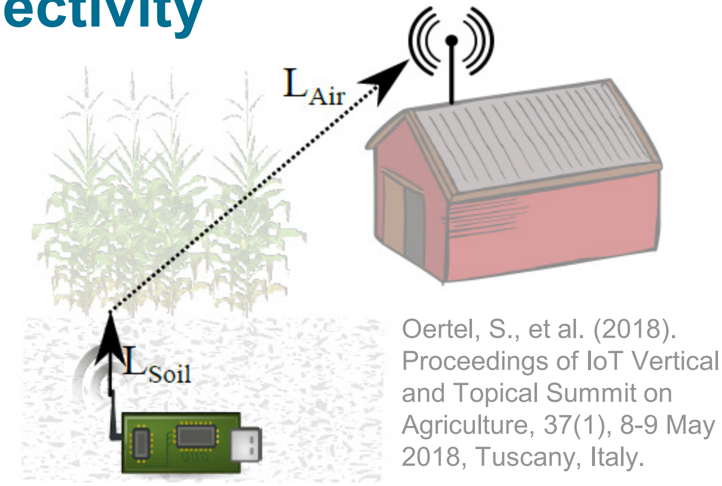
# Soil-Dashboard

- Continuous data transfer from soil
  - Use of commercially available sensors for humidity and conductance
  - Data transfer out of different soil depths
  - Transfer with Low Power Wide Area Network (LPWAN) technology
  - Optimal transmission frequency


*Different kind of soil sensors for soil humidity and temperature*

# LPWAN for Reliable Underground Connectivity

- Sensors to be buried within the soil will require
  - Autonomous operation over years using tiny batteries
  - Robust communication schemes for overcoming the high path-loss within the soil
- LPWANs are a new communication approach that covers the requirements, as they are optimized for
  - Very high maximum coupling loss → soil attenuation
  - Very low complexity → low cost and low energy
- FutureIOT developed LPWAN sensing nodes based on ETSI TS 103 357; > 5 km of comms ability



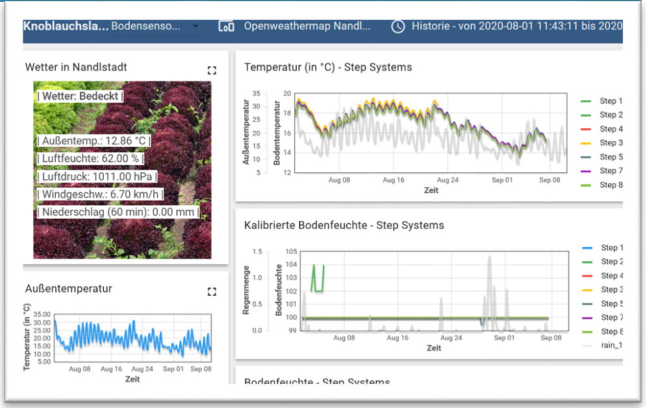

Oertel, S., et al. (2018). Proceedings of IoT Vertical and Topical Summit on Agriculture, 37(1), 8-9 May 2018, Tuscany, Italy.

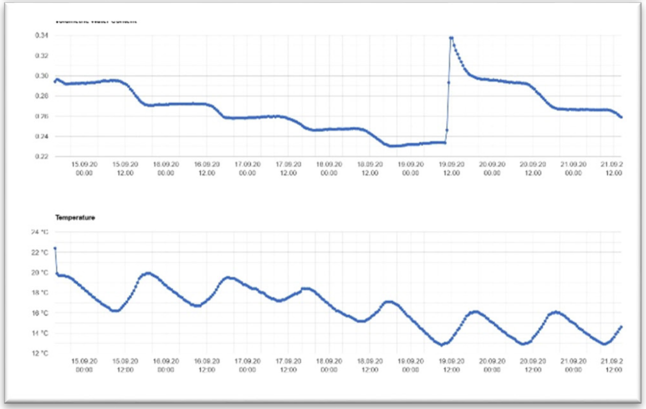
Images: Fraunhofer IISB Humidity soil sensor with data transfer via LPWAN, Display at App

# Summary and Future Work

- New soil monitoring solutions for agriculture
  - Development of nitrogen sensors, similar results to certified test lab
  - Long-term stable and reproducible nitrate and ammonium sensors
  - Feasibility of LPWAN transmission from soil proven
  - IoT platform in operation
- Adaption of sensor systems for prospective agricultural applications
  - Fixed base technology
  - Customizable based on customer requirements

*IoT Platform for soil humidity, temperature and further important data*



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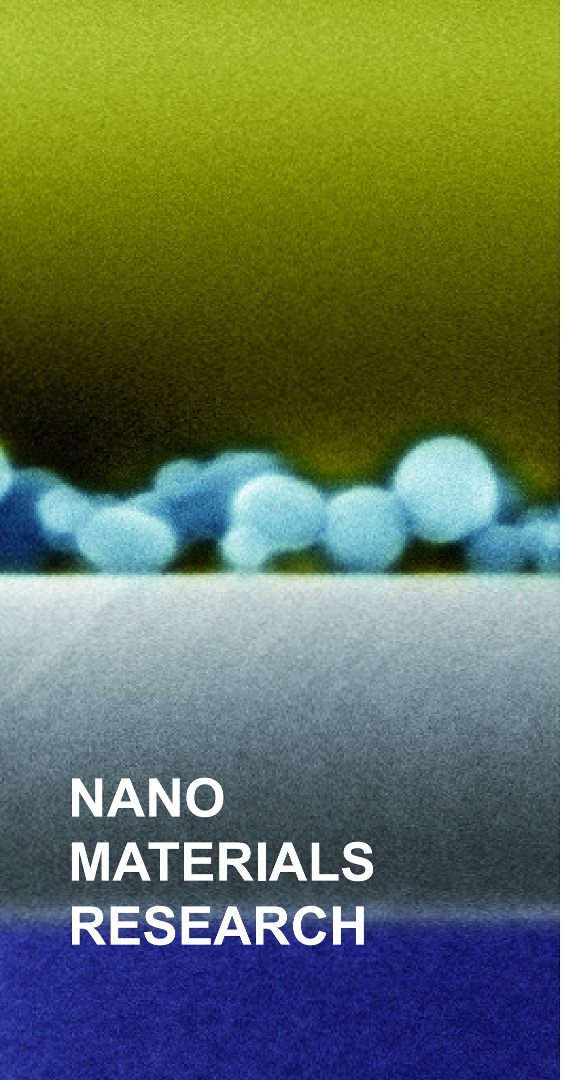
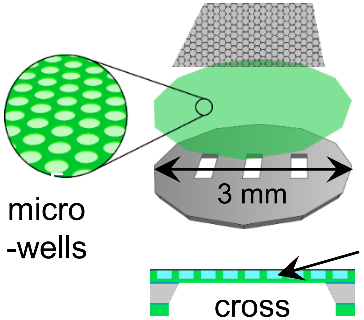
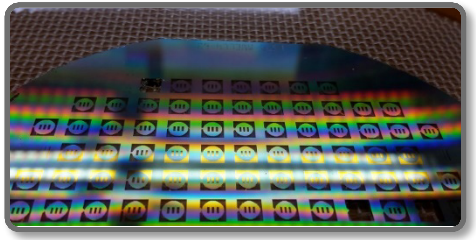
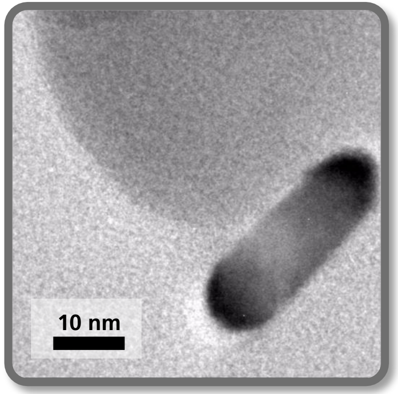


# NANO MATERIALS RESEARCH

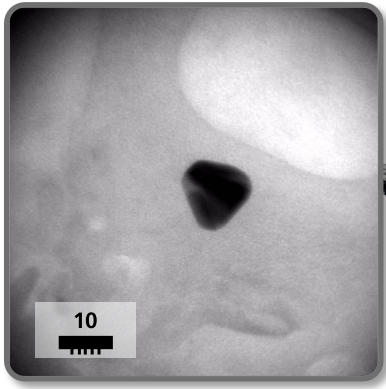


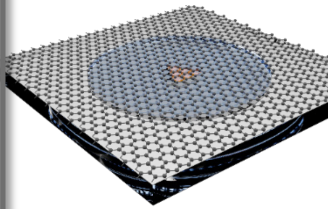

*Hutzler et al., Nano Lett. 2018, 18, 7222–7229; Adv. Mater. Interfaces, 345, p. 1901027*






**Core shell growth of nanoparticles**



**Interface reaction pathways**

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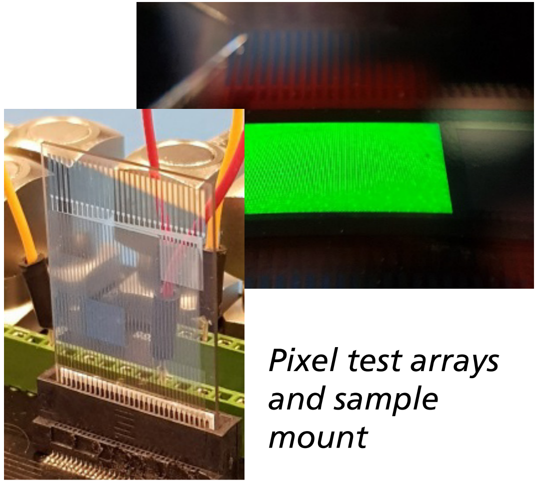
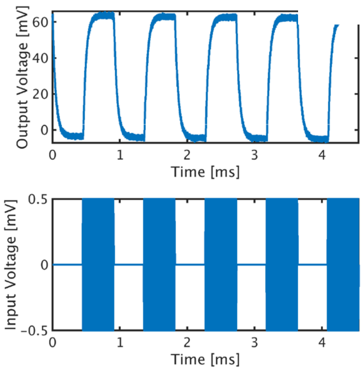
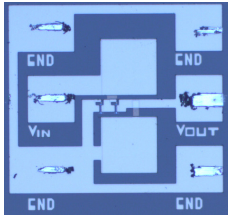
# ACTIVE MATRICES AND ADVANCED TFTs



*Pixel test arrays and sample mount*

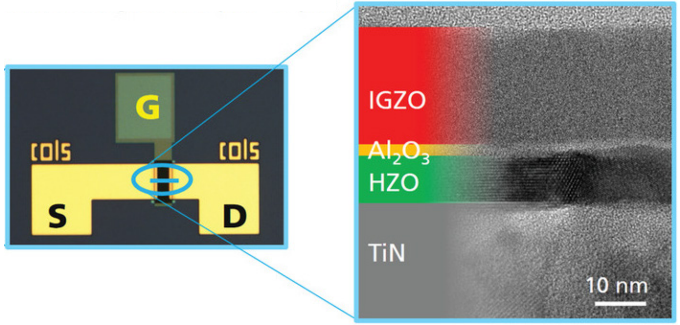


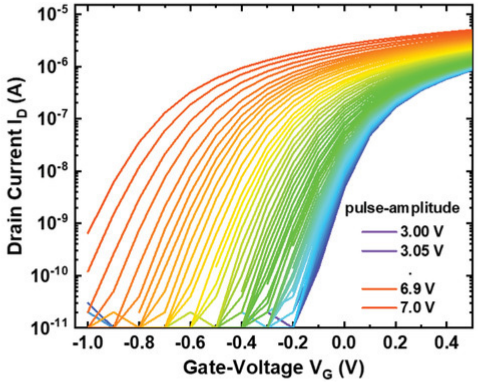




*metal oxide rf circuits (OOK demodulator)*

Ferroelectric TFTs

TEM X-section of channel region




Lehninger et al. | DOI:10.1002/aelm.202100082