Next-Gen Ion-Sensing Tech for Multiplex Element Monitoring and e-Tongue Apps

次世代離子感測技術於多通道元素監測與電子舌應用

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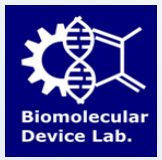
第十五屆農畜產品品質非破壞性檢測技術國際學術研討會

2019/11/19 (二) 國立臺灣大學



Outlines of This Talk

1. How Sensor and AI Tech Reshape Agriculture?
2. R&Ds of Intelligent Biosensing Systems
3. R&Ds of Next-Gen. Ion Sensing Technology
4. Smart Multiplex Ion Detection for Hydroponics
5. Smart Electronic Tongue for Machine Taste
6. Concluding Remarks

Biomolecular Device Lab.

1. Reshape Agri with Sensors and AI

A Robot Farmer w/ CCD Sensor and AI

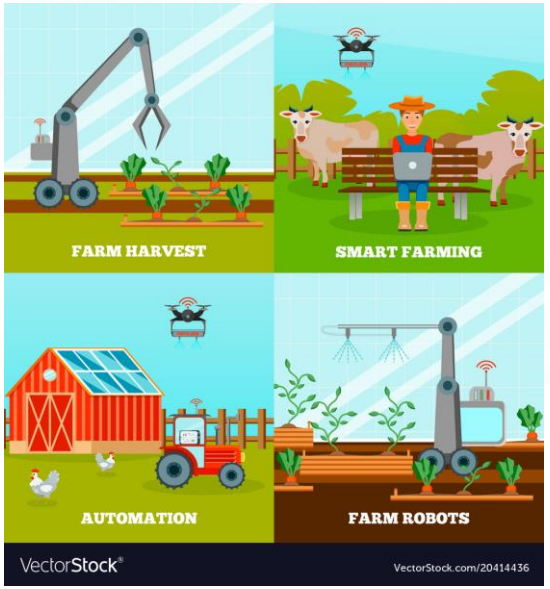
MIT Technology Review

New autonomous farm wants to produce food without human workers

Down on a new robot farm, machines tend rows of leafy greens under the watch of software called “The Brain.”

Biomolecular Device Lab.

Logics of Smart Agri 4.0 w/ Sensors & AI



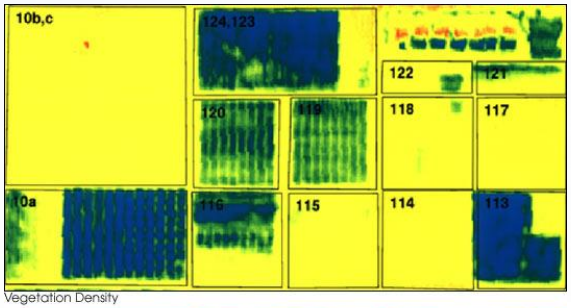
- Interconnection
- Information transparency
- Technical assistance
- Decentralized decisions

http://www.fao.org/family-farming/detail/en/c/897026/

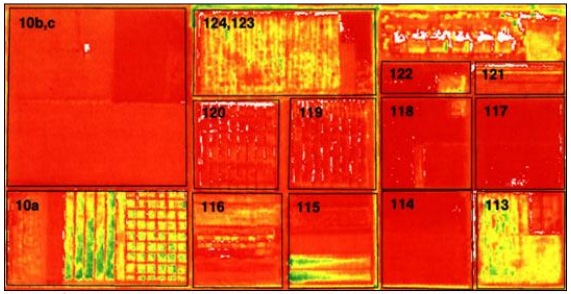
Sensors → Data → Analysis → Information → Service

nowadays AI algorithms

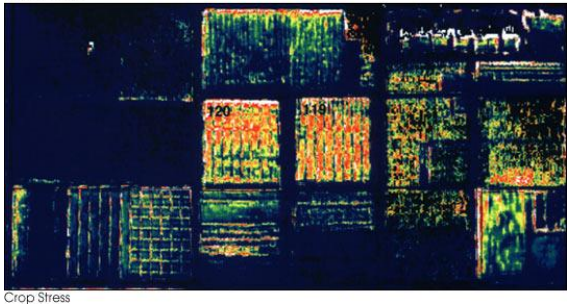
Machine Vision Reshapes Agri with High-Content & Precise Information



Vegetation Density



Water Deficit



Crop Stress

False-color images demonstrate remote satellite sensing for precision farming.

A sensor on a tractor's canopy that records light reflection of crops, calculates fertilisation recommendations and then varies the amount of fertilizer spread

Pteryx UAV, a civilian UAV for aerial photography and photo mapping with roll-stabilised camera head

https://en.wikipedia.org/wiki/Precision_agriculture

Chemical/Bio-Sensors Needed for "Smarter" Agri. Especially When Seeing ISN'T Believing

Soil Elements

Hydroponics

Aquaculture

Beverages & Drinks

Coffee Flavors

Clinical Samples

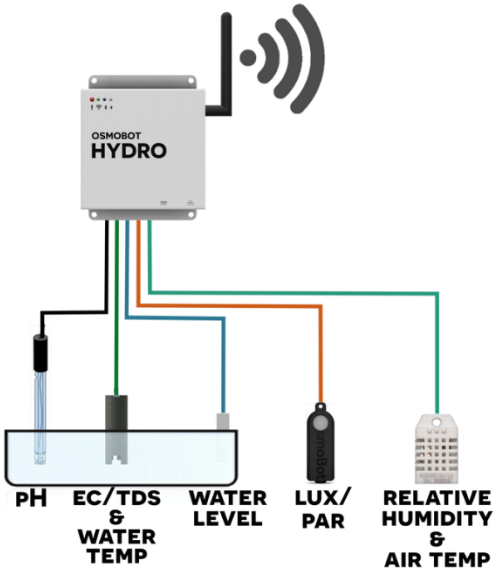
(contains images from the Internet)

Bio/Chemical Sensor Challenge: Limited, Costly Options for AI-Driven Agri.

1. Physical Sensors:
   - **Temperature sensor**
   - Image sensor
   - Illuminance sensor
   - **Electrical conductivity meter**
2. Chemical Sensors:
   - **pH meter**
   - Humidity sensor
   - **Ion-selective electrodes (ISEs)**
3. Instrumental Analysis:
   - Spectrophotometer
   - HPLC
   - AA and ICP-MS

(contains images from the Internet)

Sensors for Nutrient Monitoring



2. Intelligent Biosensing Systems - From Biomed to Smart Agri.

Overview of the R&D Activities at an Intelligent Biosensing Lab, NTU BME

(former Biomolecular Device Lab since 2005)

We innovate intelligent bio-sensing systems with fusion of frontier electrochemistry, biochemistry, nano-devices and "SMART" tech.

https://chenlinchi.wixsite.com/ibslab

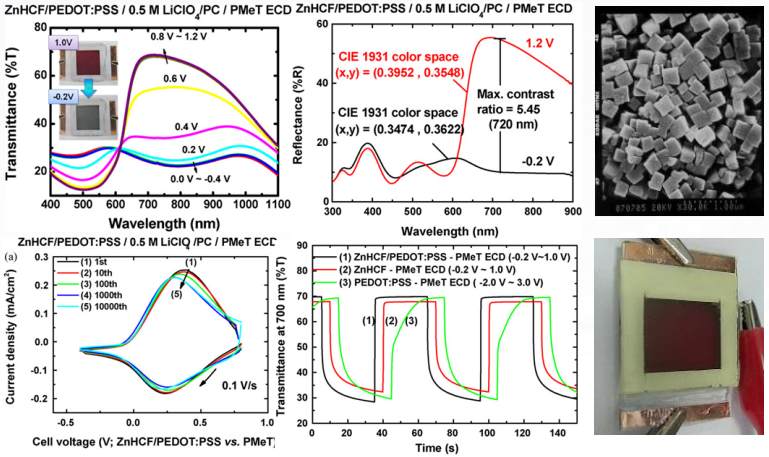
Scopus

ID: 7409439070

Biomolecular Device Lab.

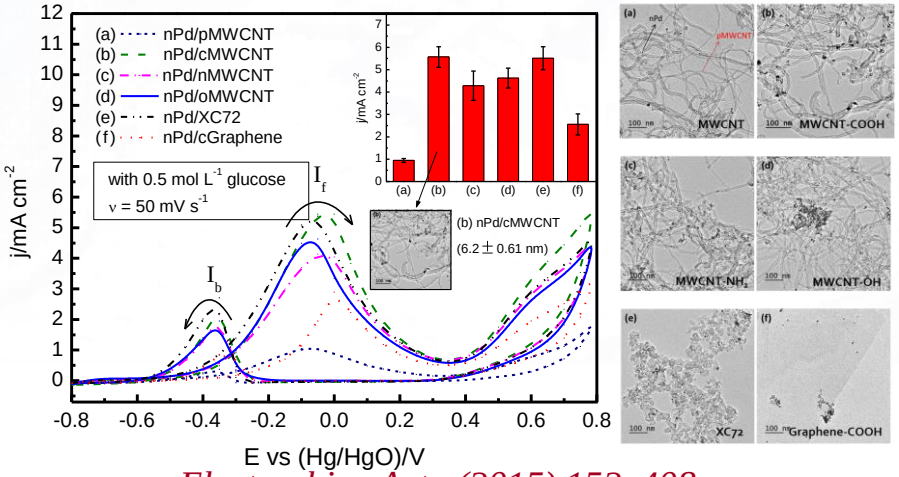
From Nanomaterials to Sensor Materials

High ΔR Electrochromic Display



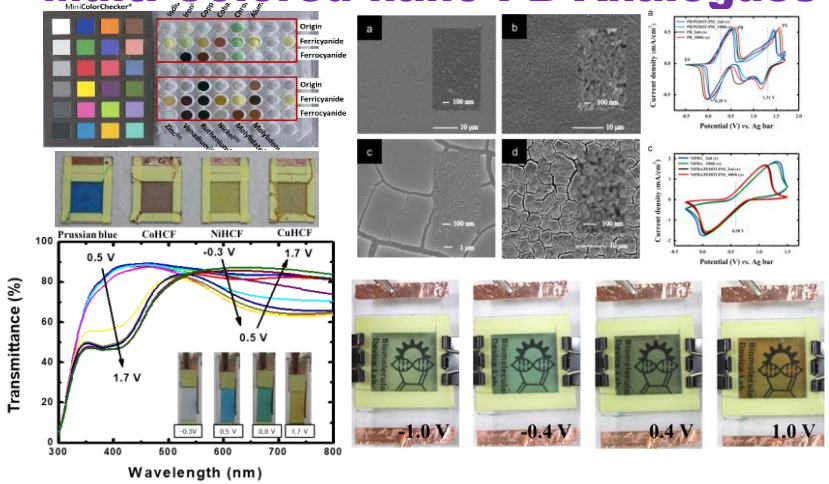
Electrochim. Acta (2010) 55, 3966

nPd/Functionalized MWCNT for GOR



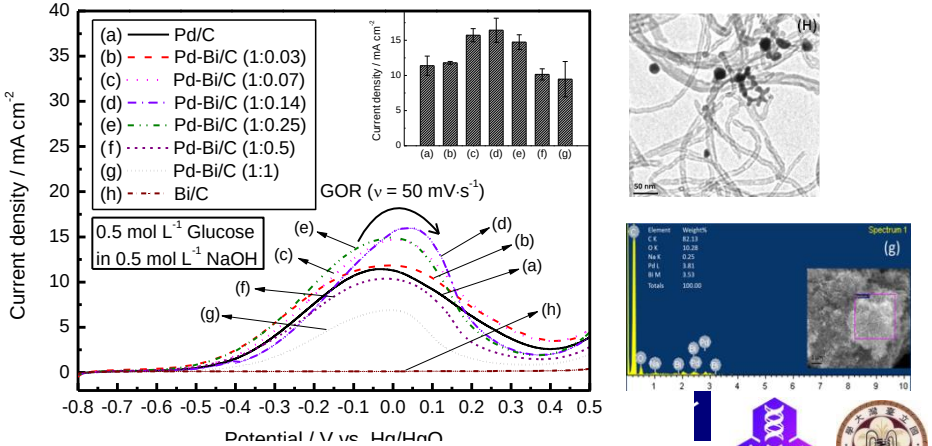
Electrochim. Acta (2015) 152, 408

Multi-Colored nano-PB Analogues



Sol. Energy Mater. Sol. Cell. (2016) 145, 26

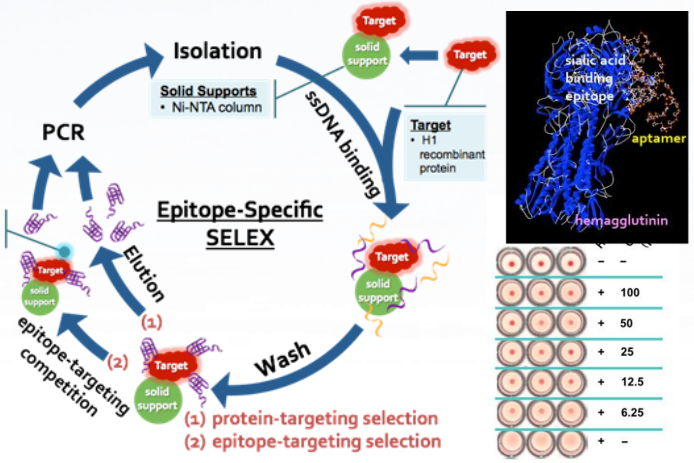
Binary Palladium–Bismuth Nanocatalyst



J. Power Sources (2015) 287, 323

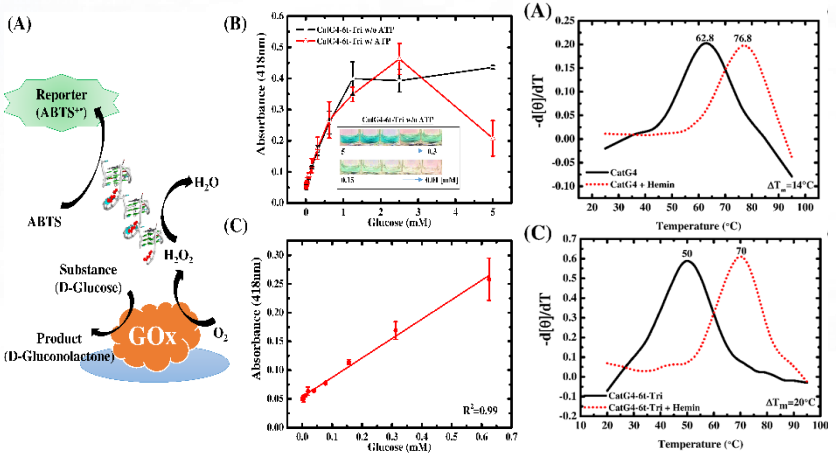
Artificial Evolution of DNA Aptamers

Epitope-Specific SELEX for H1



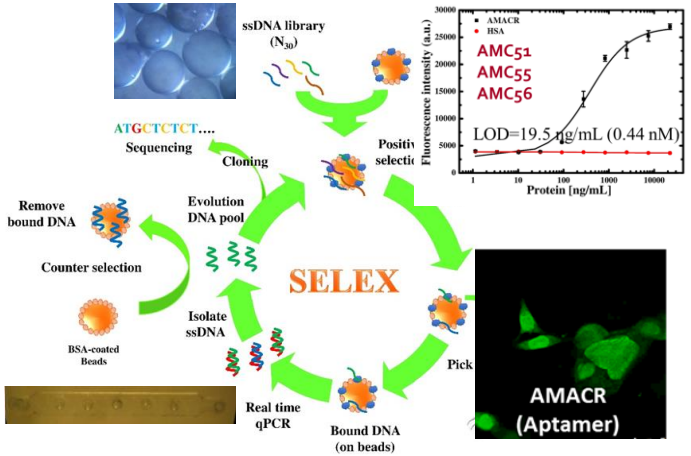
Chem. Commun. (2014) 50, 8719

Artificial HRP DNAzyme Design



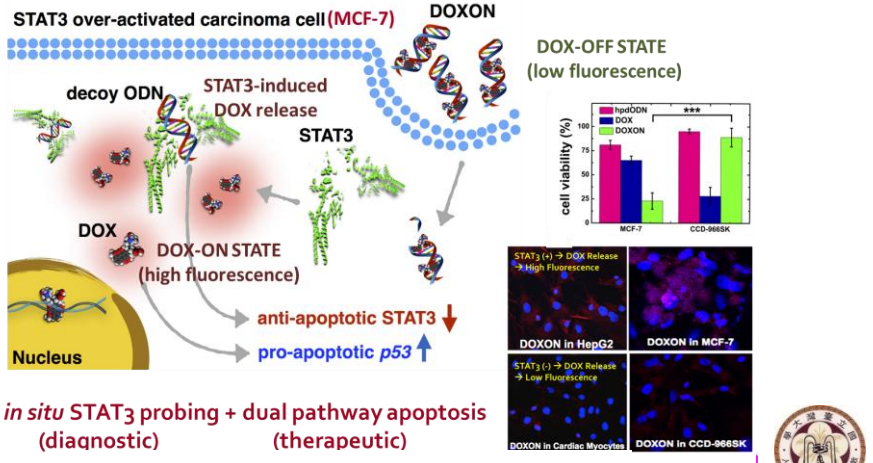
Anal. Chim. Acta (2015) 856, 96

Single-Bead SELEX for AMACR



Biosens. Bioelectron. (2014) 62, 106

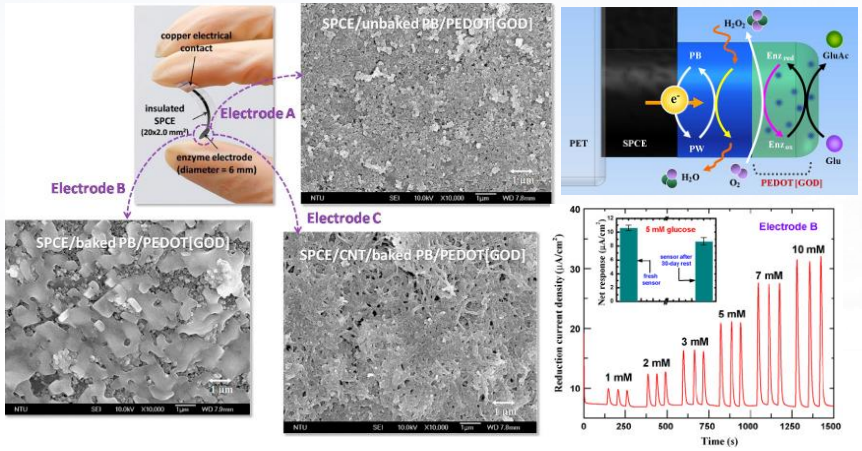
Intracellular Targeted Theranostics



Chem. Commun. (2015) 50, 13309

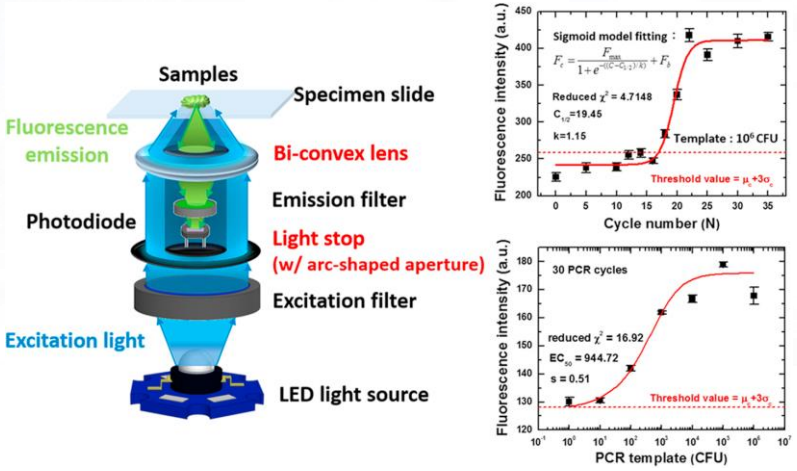
Nano-Biosensor and Biochip Platforms

Reusable Enzymatic Glucose Sensor



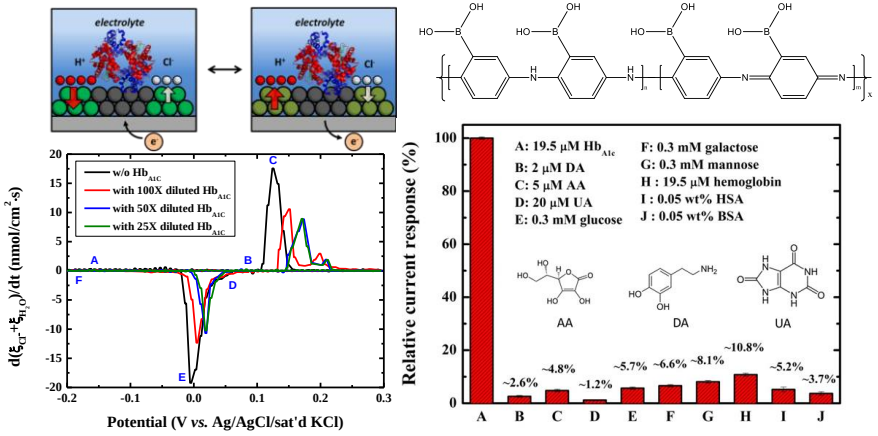
Biosens. Bioelectron. (2009) 24, 2015

Confocal Epifluorescent DNA Sensor



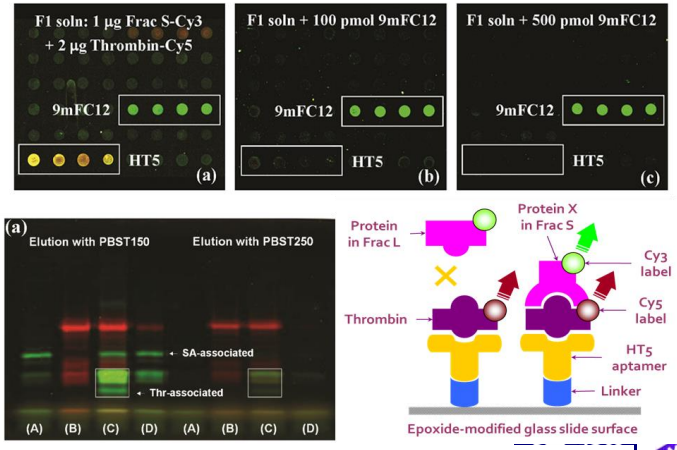
Biosens. Bioelectron. (2018) 100, 71

Label-free Ion-Flux Immunosensor



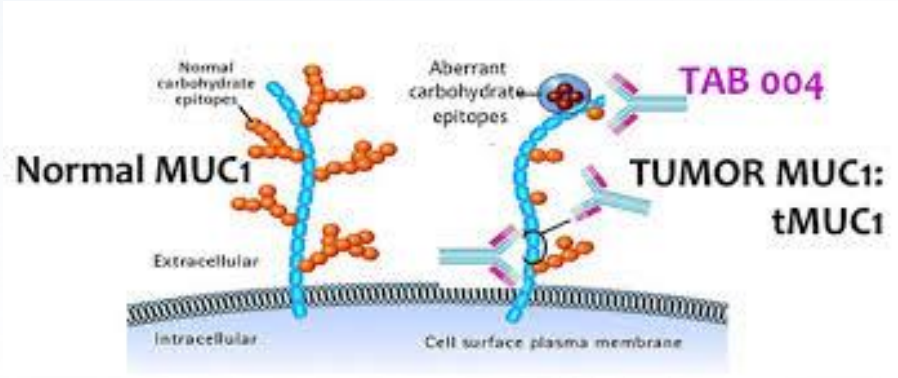
Biosens. Bioelectron. (2015) 63, 317

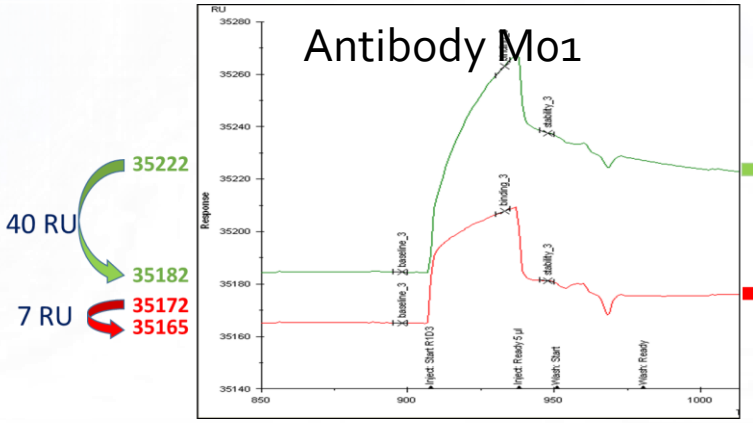
Aptamer Chip for Protein Detection

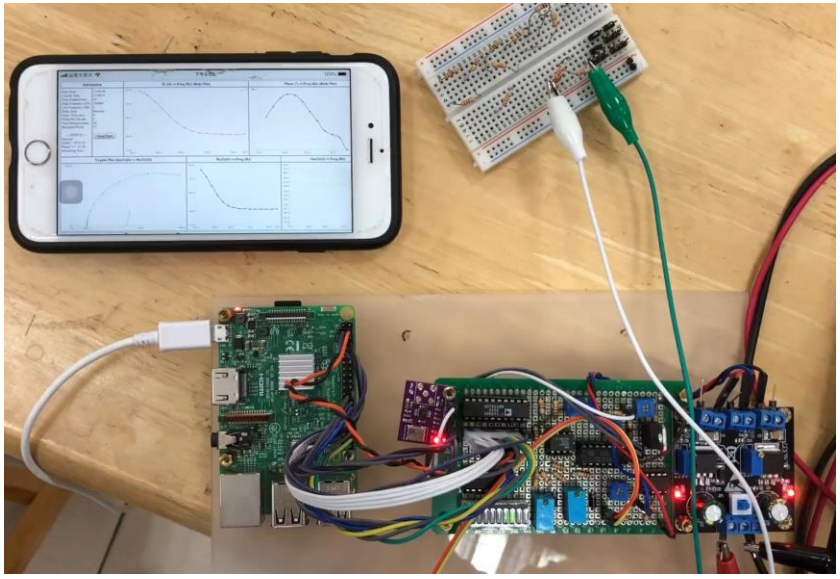


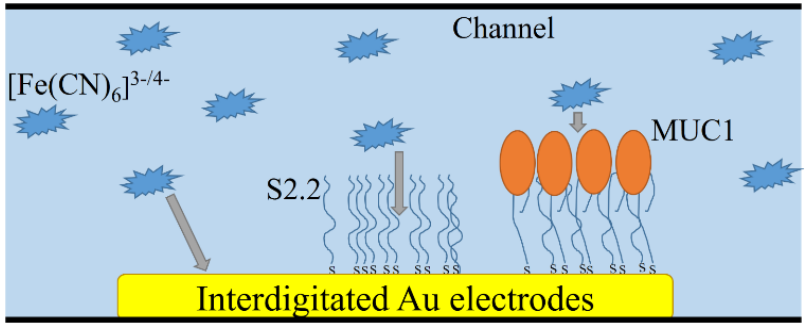
Biosens. Bioelectron. (2013) 42, 248

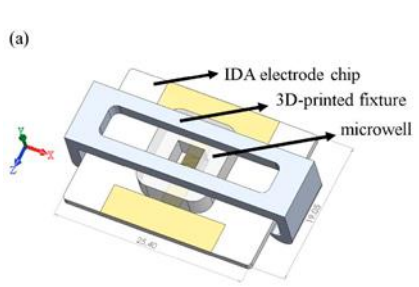
On the Smartphone-assisted Diagnostics

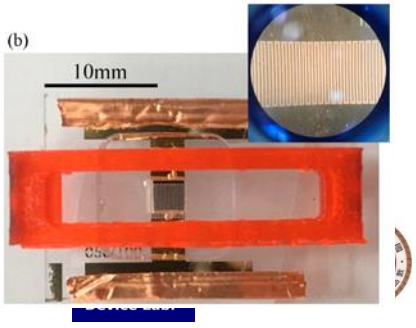










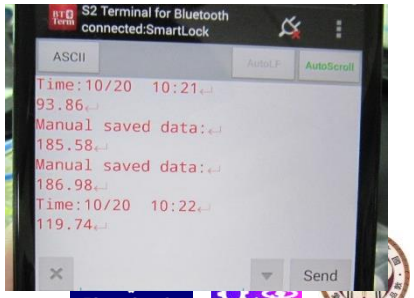


From Biochip to Smart Cancer Diagnostics

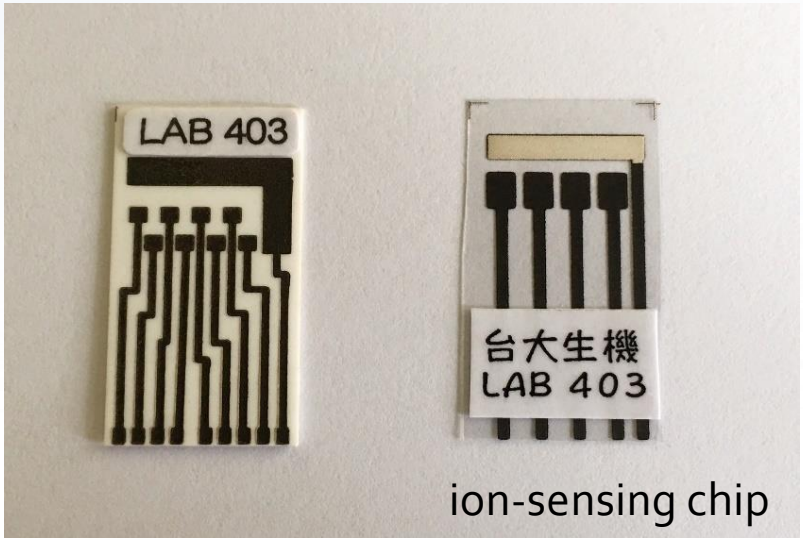
Ion-Sensing Project for Plant Factory

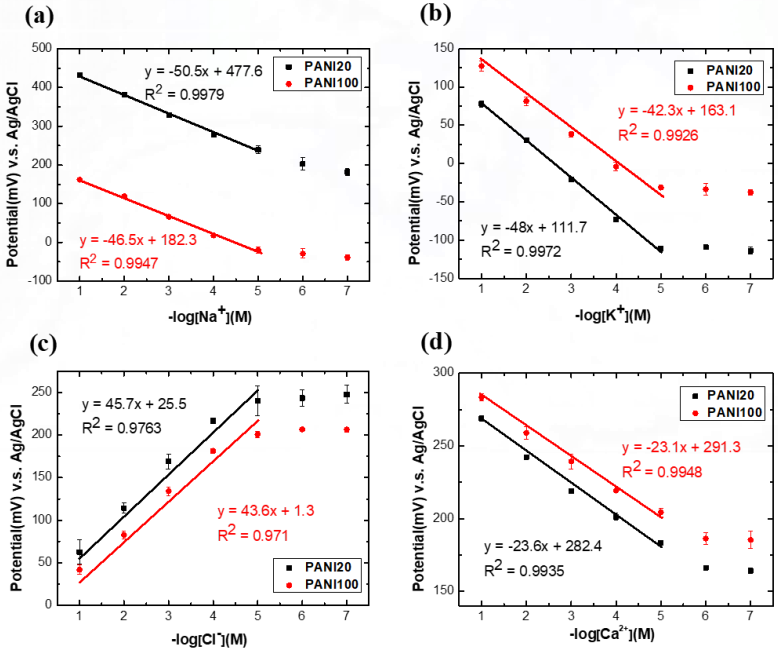
1. Ion-selective electrodes (ISEs) available but
   - costly (500-1k USD per ISE)
   - bulky (like a pH meter)
   - not for real-time monitoring
2. To date, a EC (mS/cm) meter is used to monitor a sum ion effect.
3. Need new ISEs capable of
   - **low cost** → SPCE-based
   - **miniaturization** → all-solid-state
   - **informative** → all elements
   - **real-time monitoring** → stability
   - **IoT** → smartphone sensing

NTU BME's ISE Tech R&Ds (since 2010 in LC Chen's Lab)



Next-Generation Ion-Sensing Chip & Smart Multiplex Ion Detection





1. Detectable Elements: NO_3^-, NH_4^+, **Na^+, K^+, Cl^-, Ca^{2+}**, Mg^{2+}, SO_4^{2-}, HPO_4^{2-}, H^+
2. Detection range: $10^{-1} \sim 10^{-5}$ M
3. Solid-contact ISE array w/ a wireless detection module
4. Smartphone APP real-time reading

(Taiwan Patent Pending)

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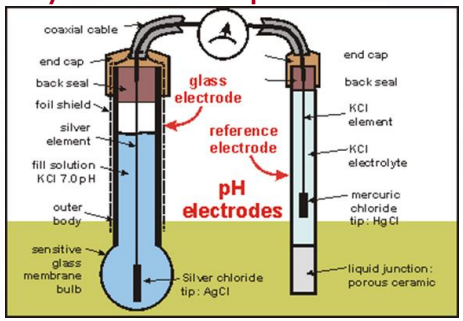
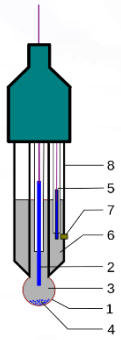
3. Techs behind Next-Gen. Ion Sensing

Evolution of Ion Sensors: From a pH Glass Electrode to a Solid-Contact ISE

High material cost, bulky, not possible for ISE array-on-a-chip

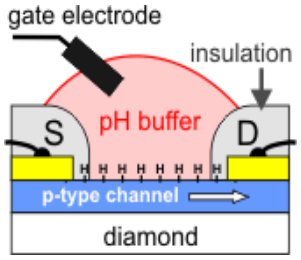
1. **First-Gen. ISEs (1950s-1960s)**
   - pH glass electrode*
   - inner solution-type ISE*
   (required Ag/AgCl, internal soln)

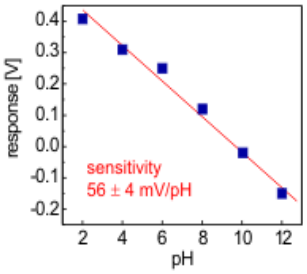


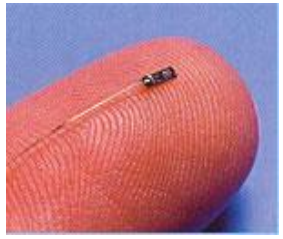


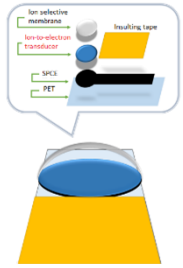
2. **Second-Gen. ISEs (1970s-1980s)**
   - ion-selective field effect transistor (ISFET)*
   - coated wire electrode (ISE)
   - ISE array (electronic tongue) *

(contains images from the Internet)









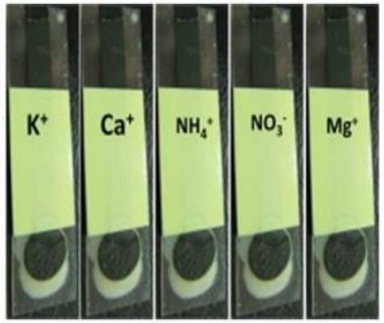
3. **Third-Gen. ISEs (1990s-now)**
   - thin-film electrode
   - **solid-contact ISE***

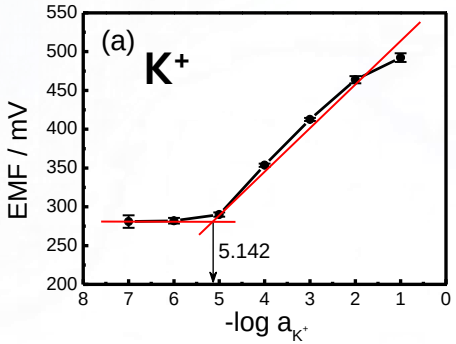
Anal. Chem., 1992, 64 (21), pp 2496–2501

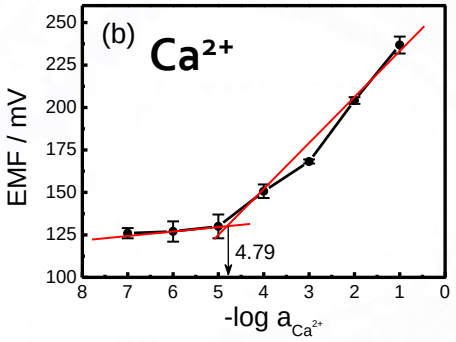
Low material cost, miniaturized, possible for ISE array-on-a-chip

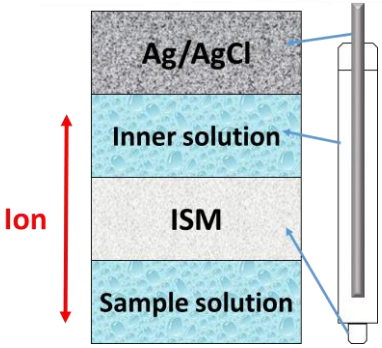
Biomolecular Device Lab.

Solid-Contact: Size and Cost Advantages

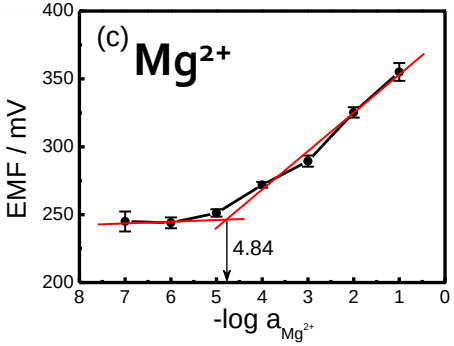


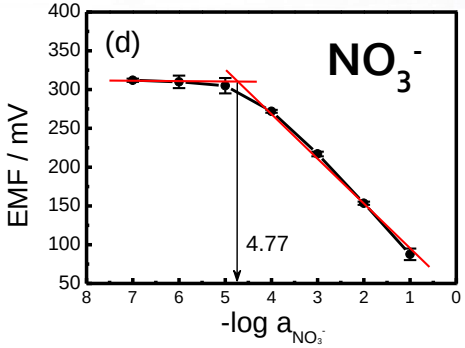




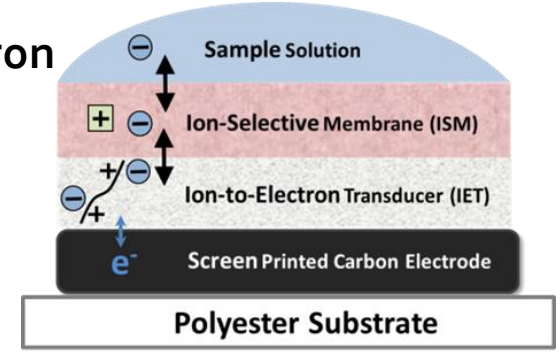


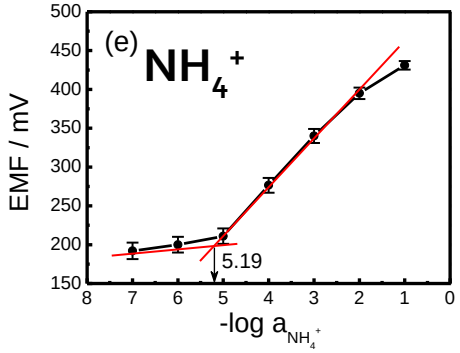
Use a **solid contact** to replace the inner reference solution

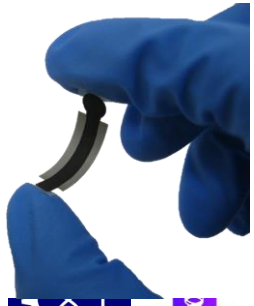




ion-to-electron transducer = solid contact

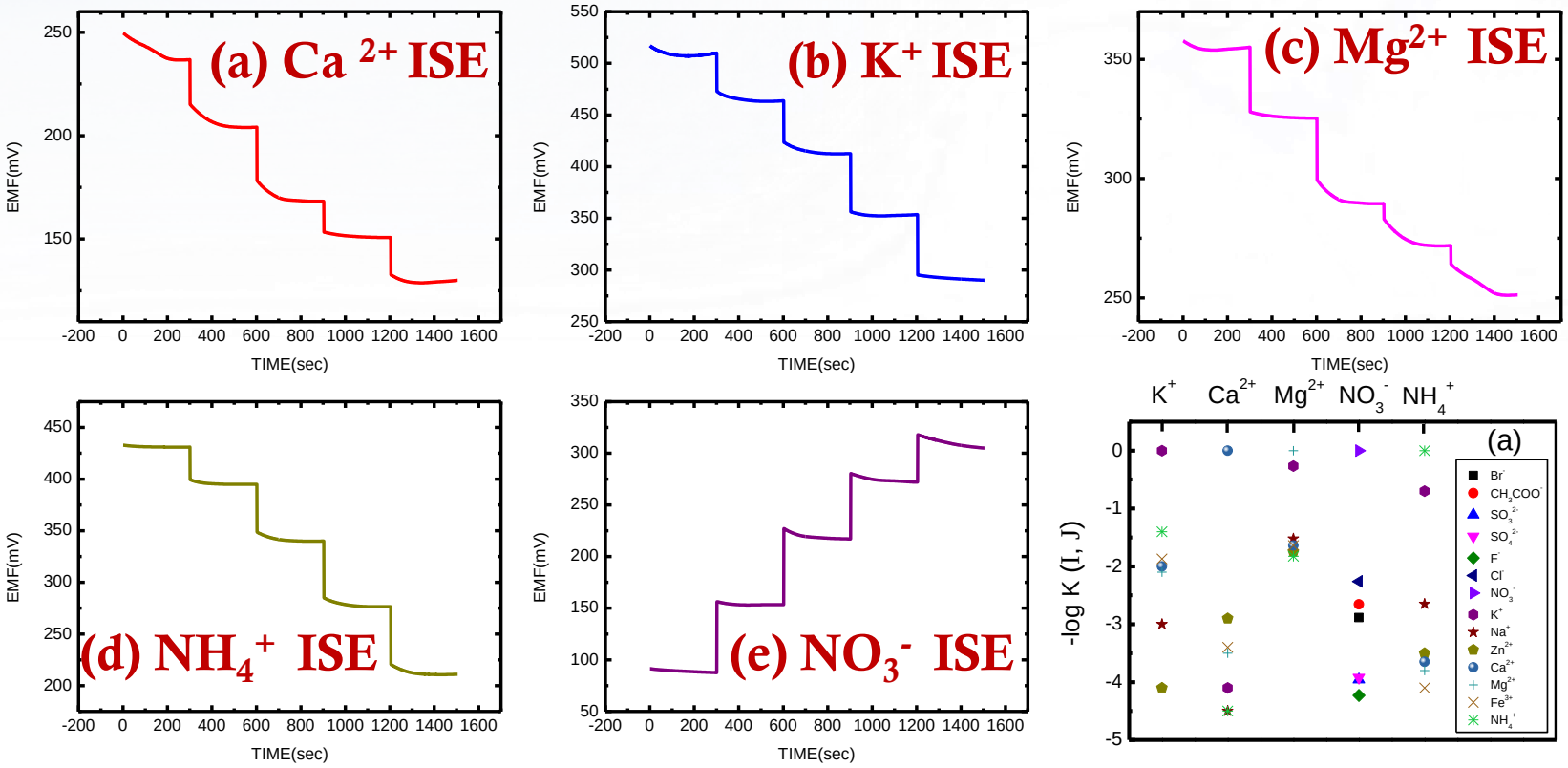






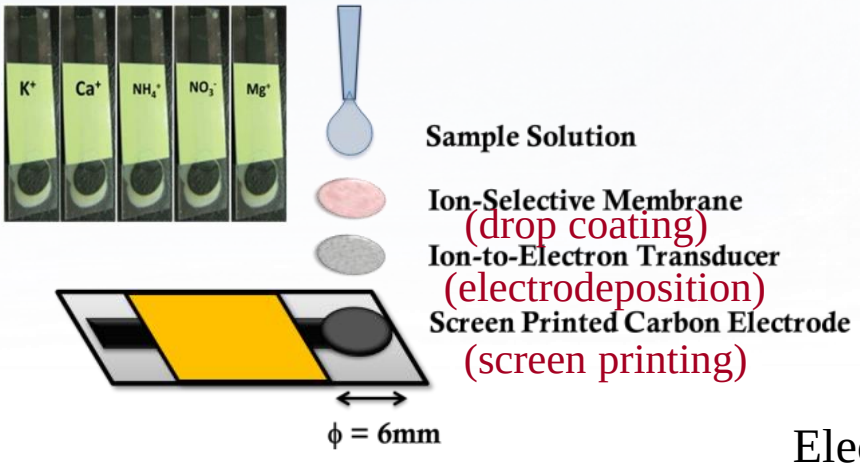
Biomolecular Device Lab.

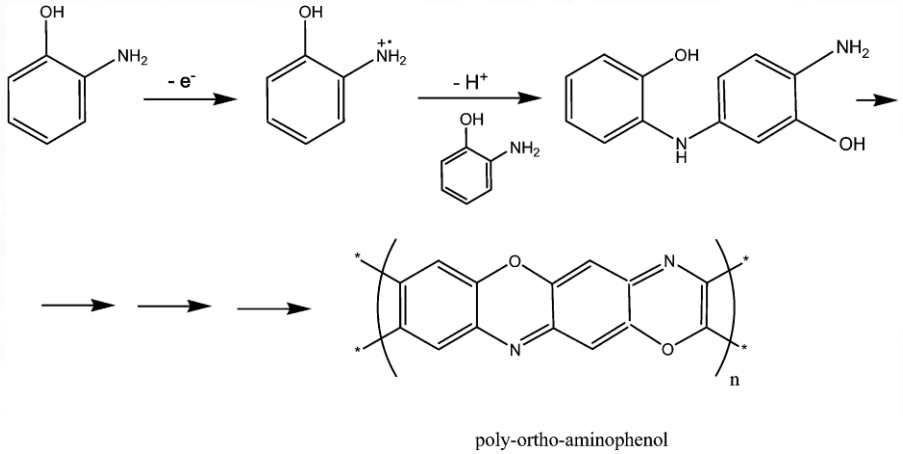
Fast Response & Satisfactory Selectivity



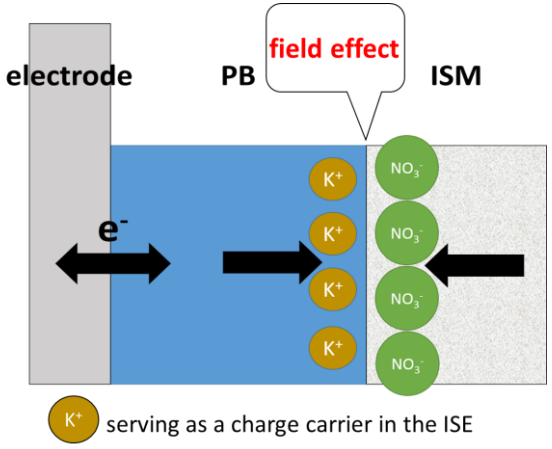
The ISE response time is *ca.* 10-30 s to attain a steady potential reading (±0.5 mV) for concentrations ranging from 0.1 to 10^{-5}M. And ion selectivity is as good as that of an inner solution-type ISE.

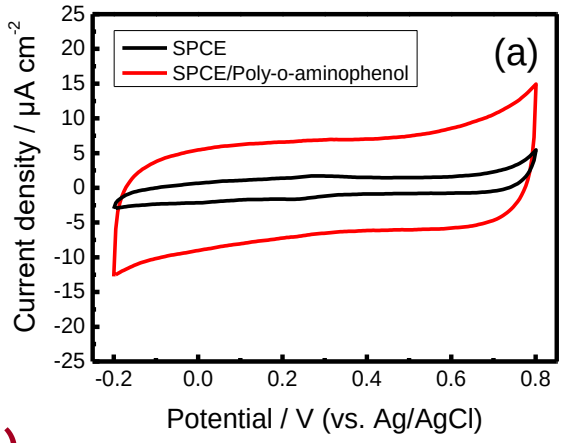
Solid Contact – What, Why, & How?

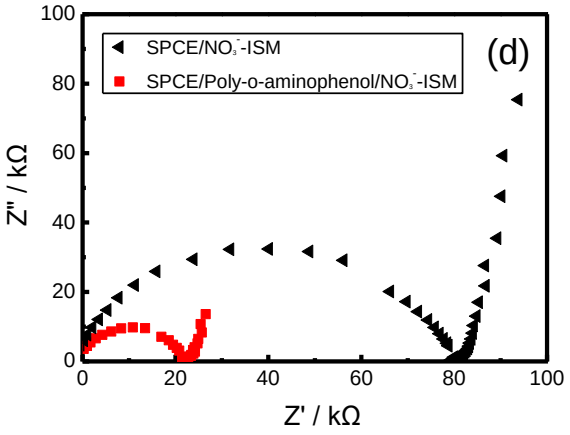




Electrodeposition of **poly-o-aminophenol (POAP)** as a solid contact layer for ion-to-electron transduction



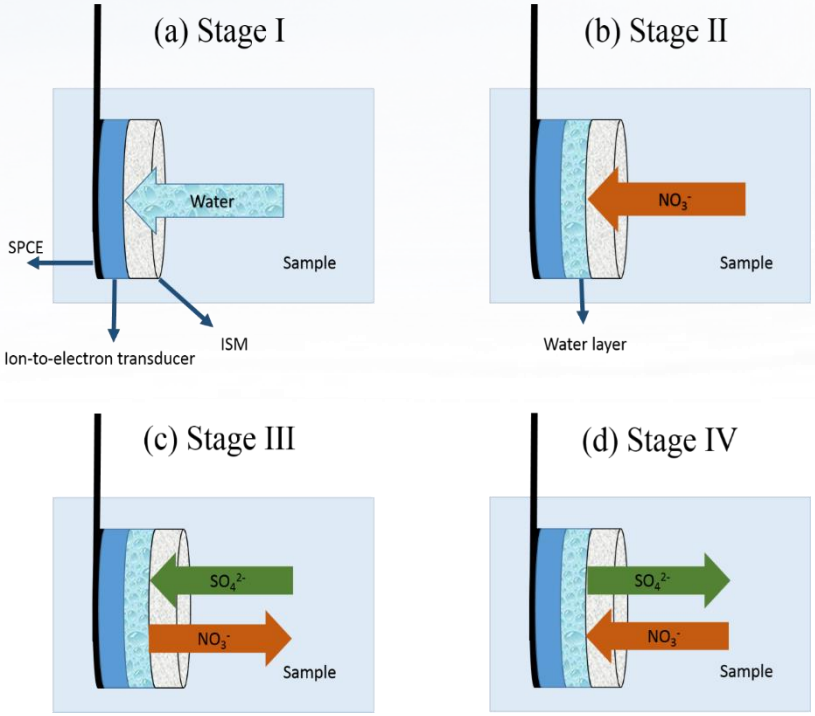


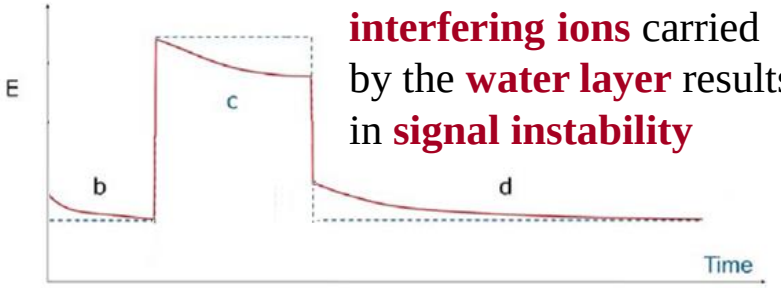


E = fn (field effect) = fn ([ion])

Solid contact contributes C_{dl} and reduces R_{ct}

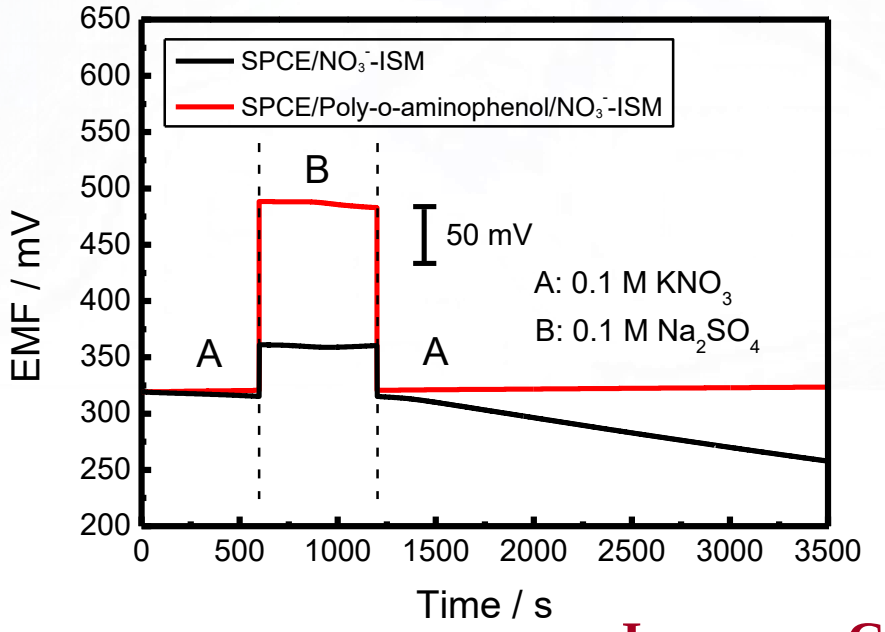
Reduces "Water-Layer Interference" besides "Ion-to-Electron Transduction"





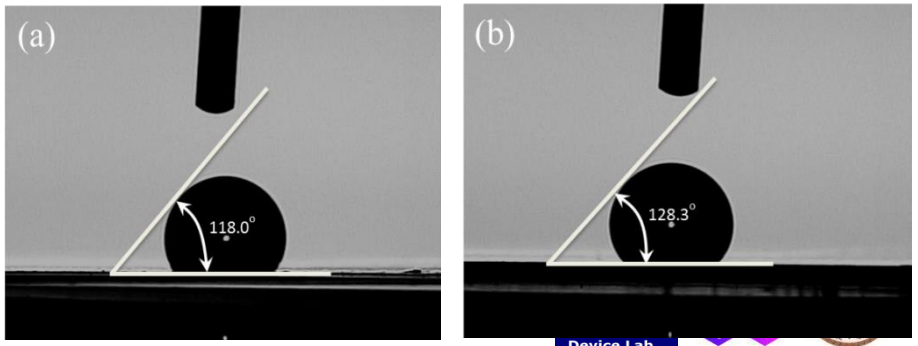
interfering ions carried by the **water layer** results in **signal instability**

Ref.: Lindner and Gyurcsanyi, 2009



Increases CA

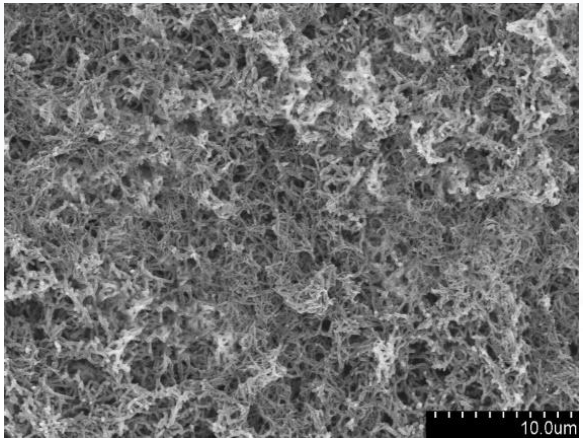
SPCE **SPCE/POAP**



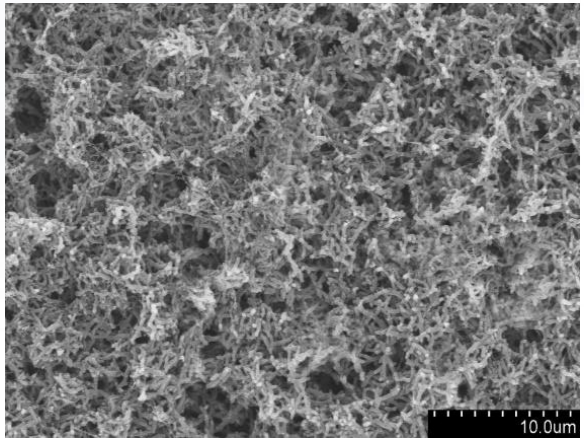
Device Lab.

Surface Morphology Ctrl of PANI SC

(a) PANI10

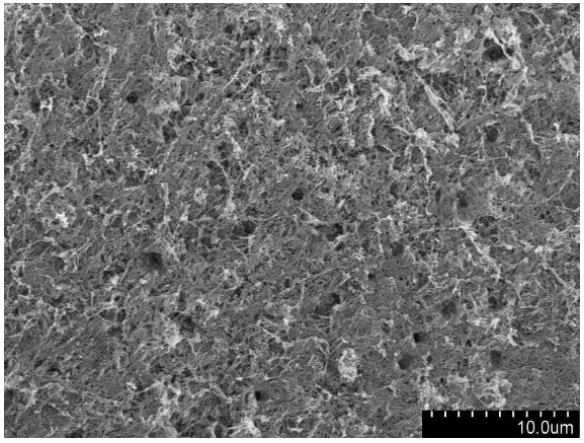


(b) PANI20

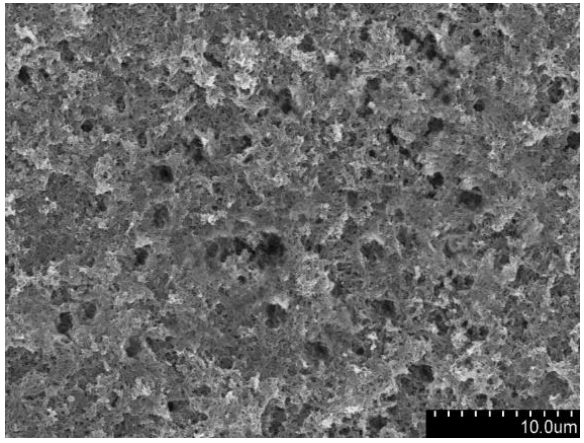


Nano-fibrous PANI surface

(c) PANI50



(d) PANI100

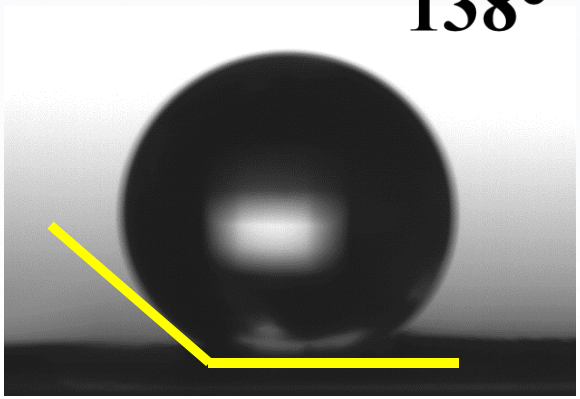


Flat-sheet PANI surface

Biomolecular Device Lab.

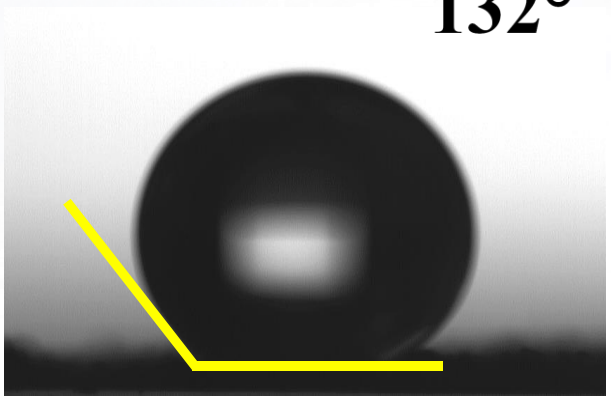
Hydrophobicity vs. Surface Morphology

(a)



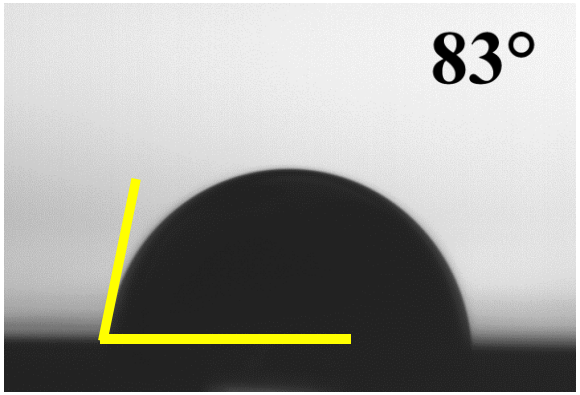
PANI10

(b)



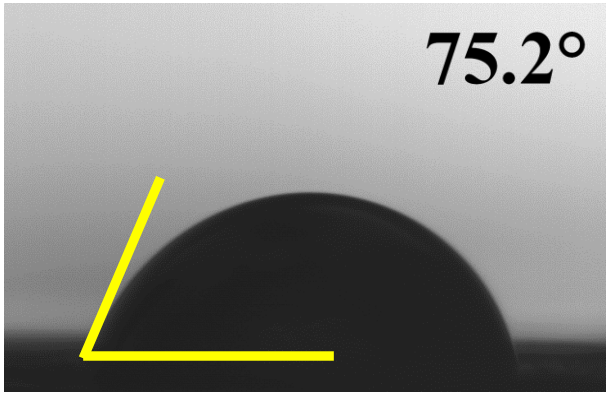
PANI20

(c)

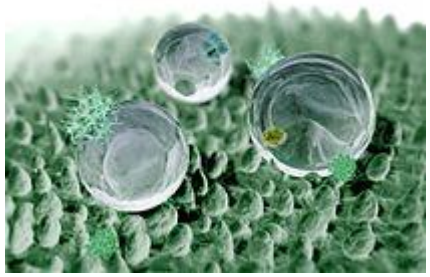


PANI50

(d)



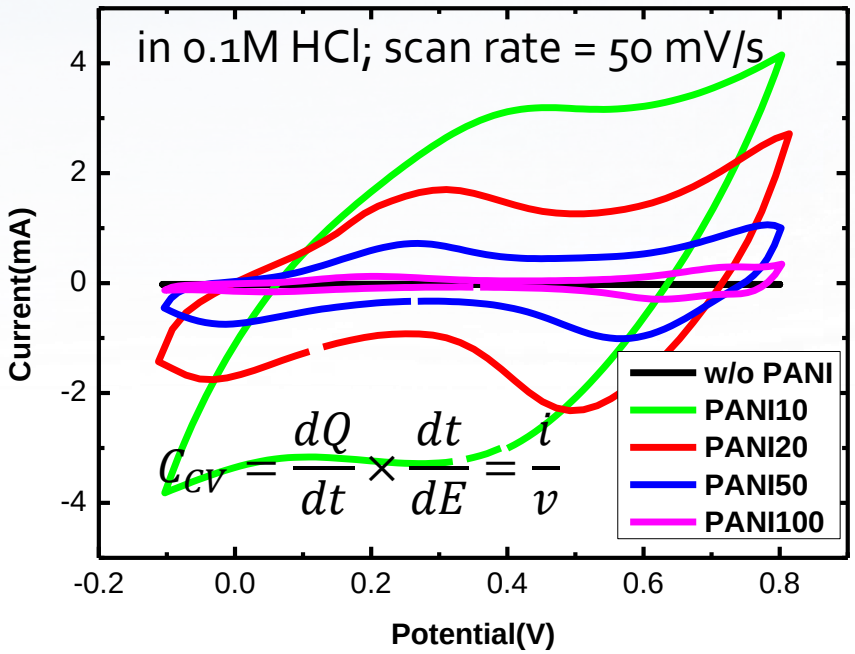
PANI100

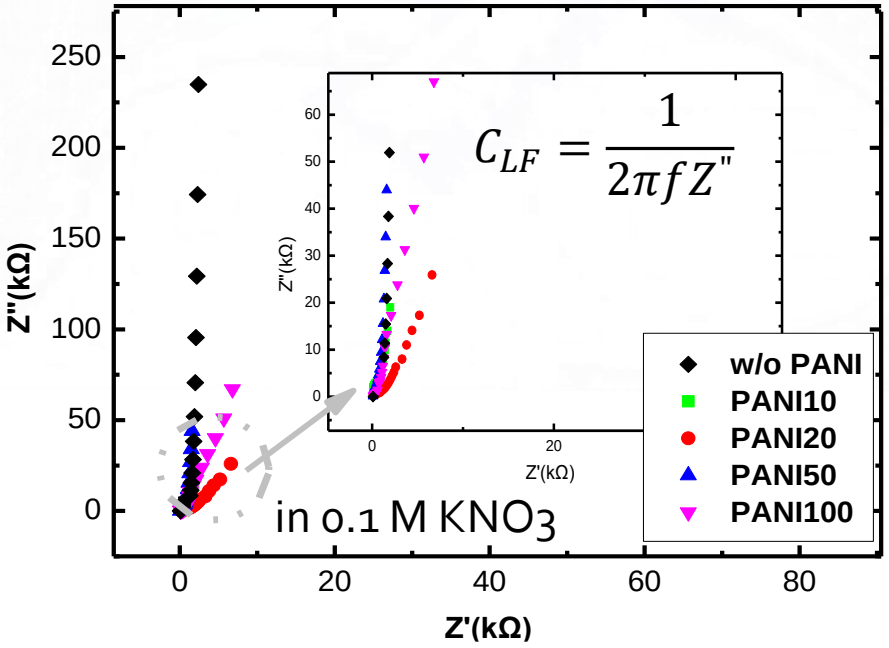


nano lotus effect

Biomolecular Device Lab.

Pseudo-capacitance Ctrl of PANI SC





Pseudo-capacitance est. from CV:

- **SPCE alone: 4.28 x 10^1 μF**
- **PANI10: 4.61 x 10^3 μF**
- PANI20: 2.47 x 10^3 μF
- PANI50: 9.46 x 10^2 μF
- **PANI100: 2.19 x 10^2 μF**

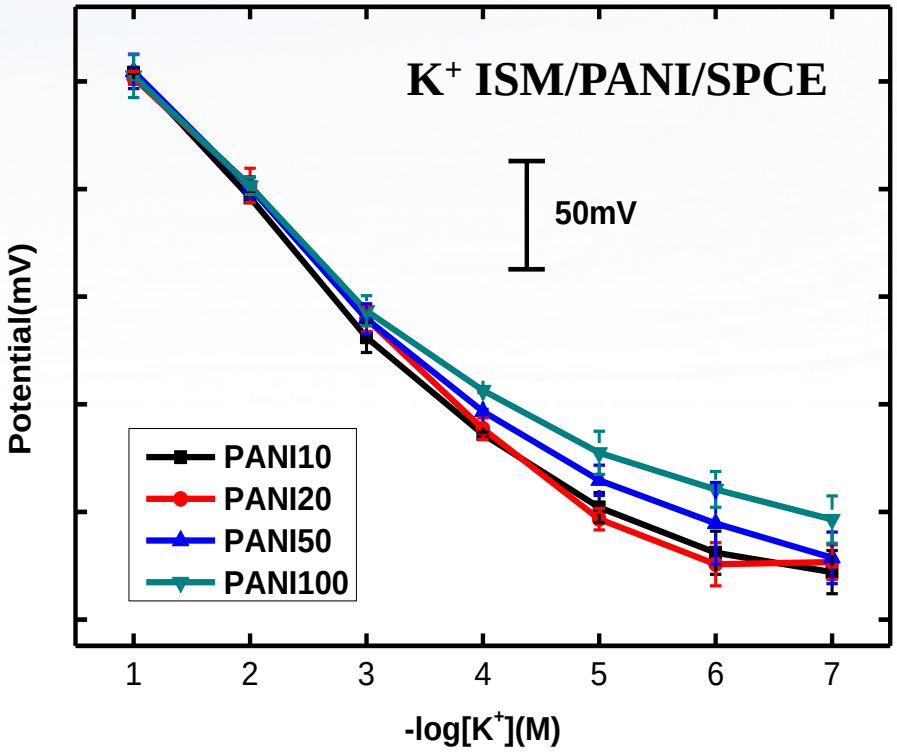
100-fold

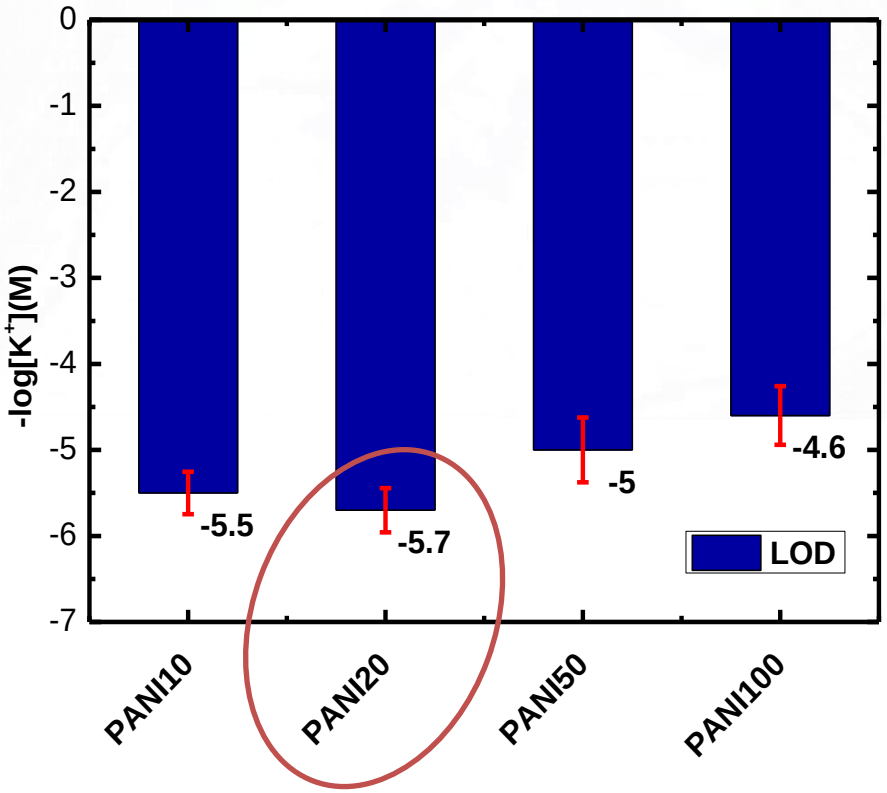
20-fold

Pseudo-capacitance est. from EIS:

- SPCE alone: 6.78 x 10^1 μF
- PANI10: 8.03 x 10^2 μF
- PANI20: 6.15 x 10^2 μF
- PANI50: 3.62 x 10^2 μF
- PANI100: 2.36 x 10^2 μF

ISEs of Different PANI Solid Contacts





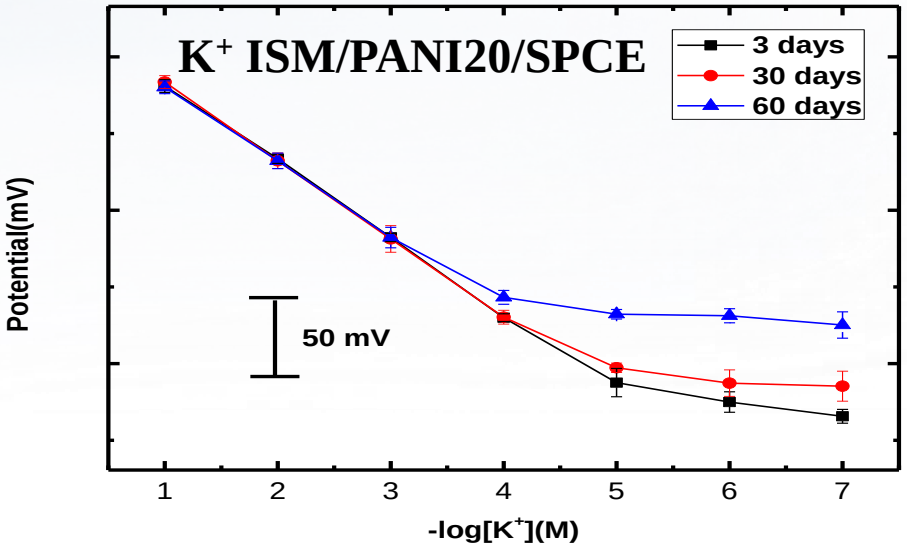
SEN (mV/dec) between 10^{-1} and 10^{-5} M

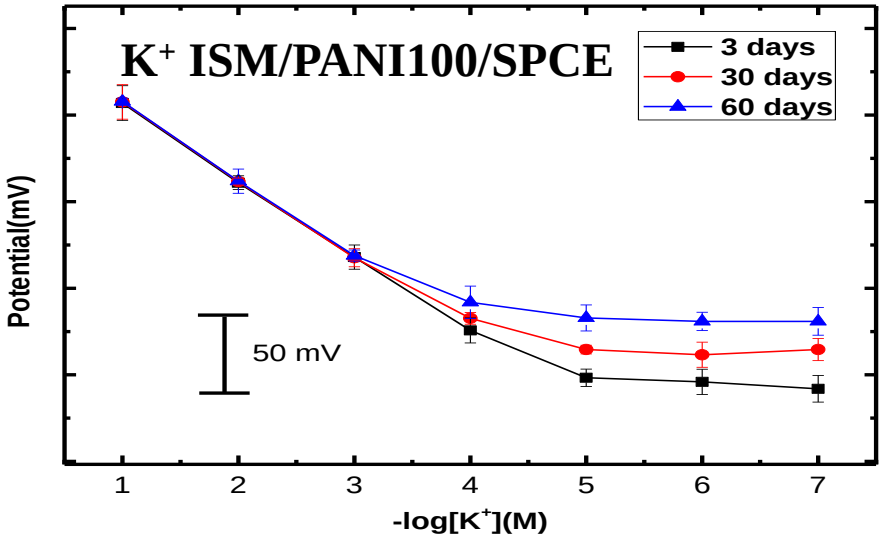
- PANI10: 51.4 mV/decade
- **PANI20: 52.3 mV/decade**
- PANI50: 48.5 mV/decade
- PANI100: 44.6 mV/decade

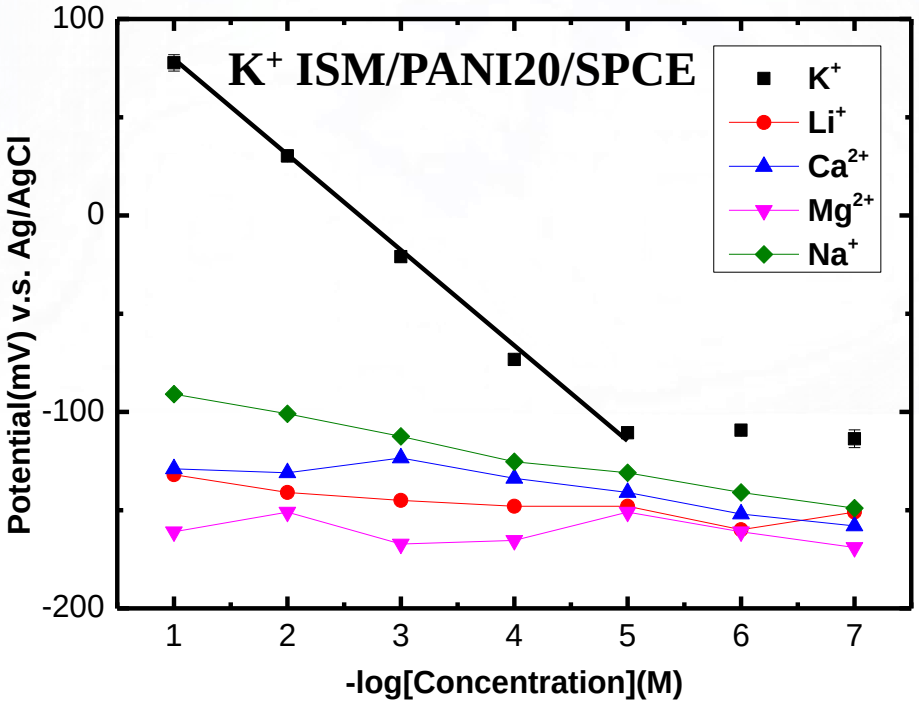
Performance of PANI solid contact: PANI20* ~ PANI10 > PANI50 > PANI100

Biomolecular Device Lab.

Lifetime/Selectivity of PANI20 K^+-ISE





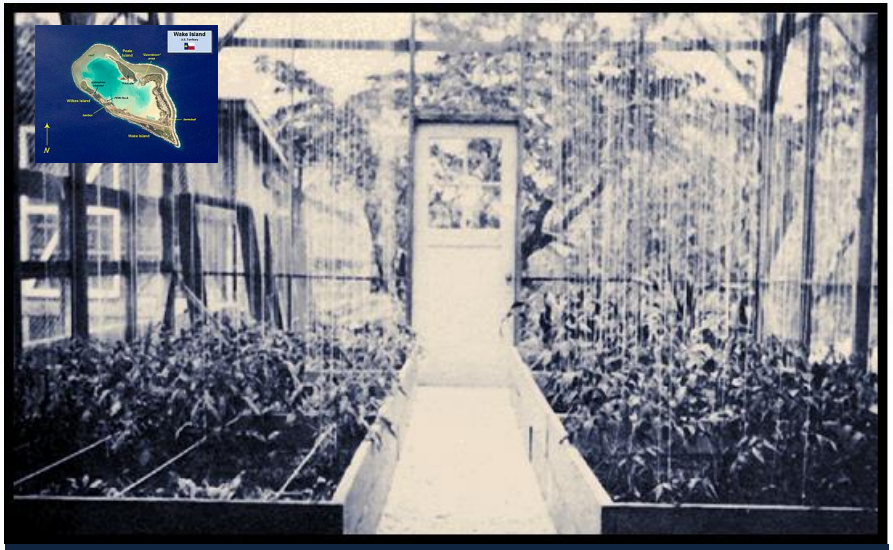


1. PANI20 shows better stability than PANI100
2. > 30 day stability
3. Ideal ion selectivity

Biomolecular Device Lab.

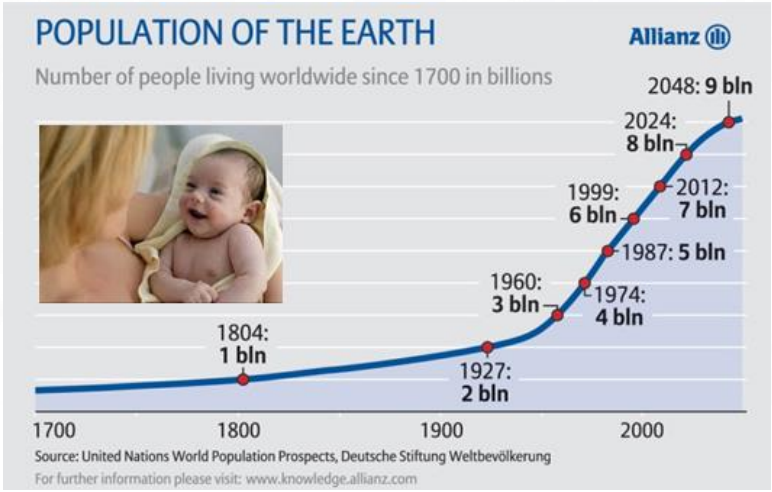
4. Multiplex Ion Monitoring for Hydroponics / Plant Factory

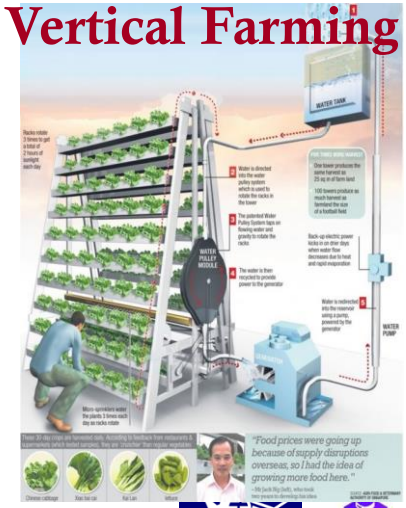
From Hydroponics to Vertical Farming



One of the earliest success hydroponics occurred on Wake Island, a rocky soil-less atoll in the Pacific Ocean, in the 1930s. This Pan American Airlines refueling stop used hydroponics to grow their own vegetables for their crew members and passengers.

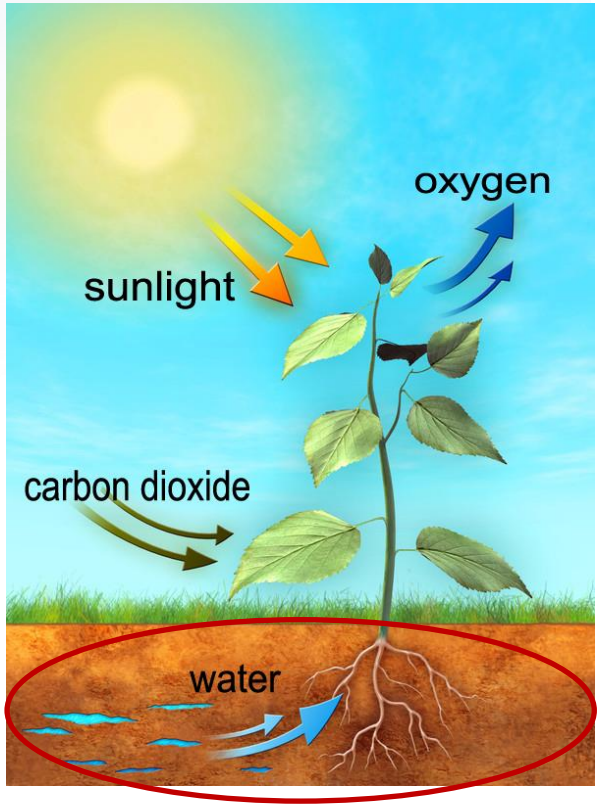
(Website Materials)





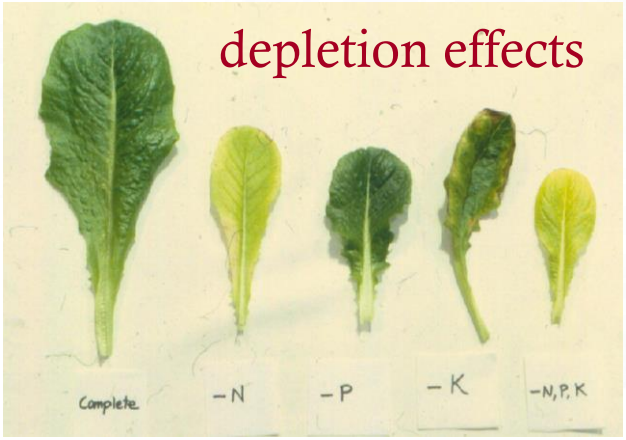
Biomolecular Device Lab.

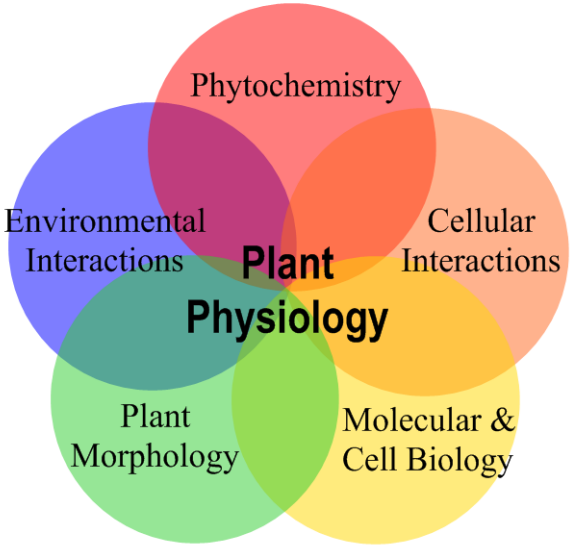
Plant Physiology and Plant Nutrition



replaced by nutrient solution (hydroponics)

Nutrient	Ions Absorbed by Plants
Structural elements	
Carbon, C	CO_2
Hydrogen, H	H_2O
Oxygen, O	O_2
Primary nutrients	
Nitrogen, N	NO_3^-, NH_4^+
Phosphorus, P	$H_2PO_4^-$, HPO_4^{-2}
Potassium, K	K^+
Secondary nutrients	
Calcium, Ca	Ca^{+2}
Magnesium, MG	Mg^{+2}
Sulfur, S	SO_4^{-2}
Micronutrients	
Boron, B	$H_2BO_3^-$
Chlorine, Cl	Cl^-
Ccbalt, Co	Co^{+2}
Copper, Cu	Cu^{+2}
Iron, Fe	Fe^{+2}, Fe^{+3}
Manganese, Mn	Mn^{+2}
Molybdenum, MO	MoO_4^{-2}
Zinc, Zn	Zn^{+2}



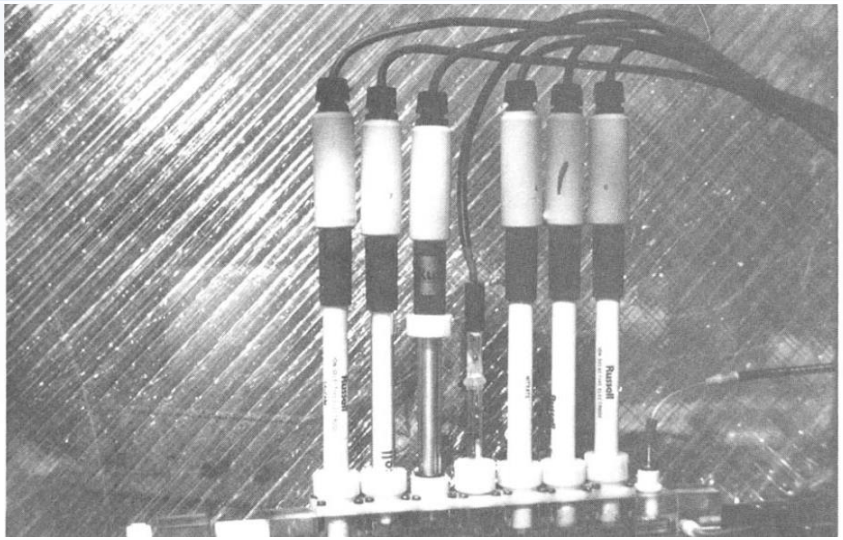


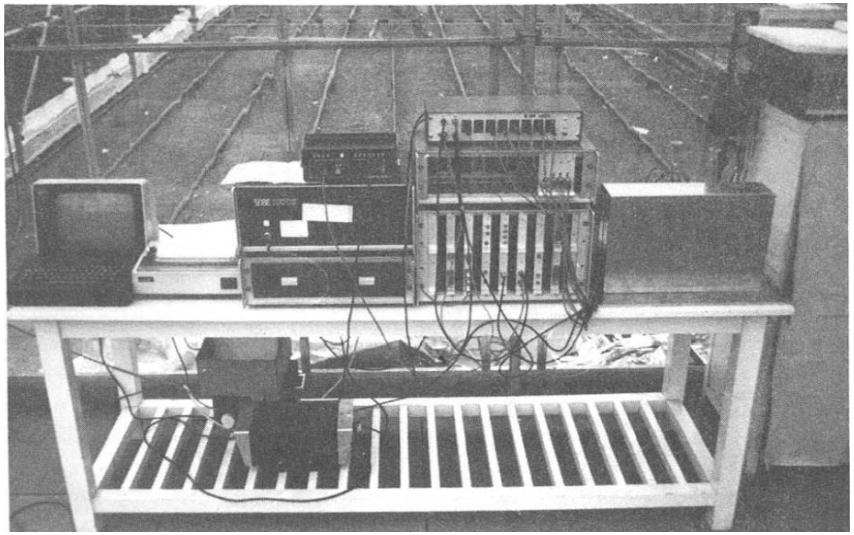
nutrients for plant growth exist in ion forms and they are essential for plant health and growth

(contains images from the Internet)

Albery et al., Biosensors 1(1985) 369-397

Use of First-Gen ISEs for Hydroponics





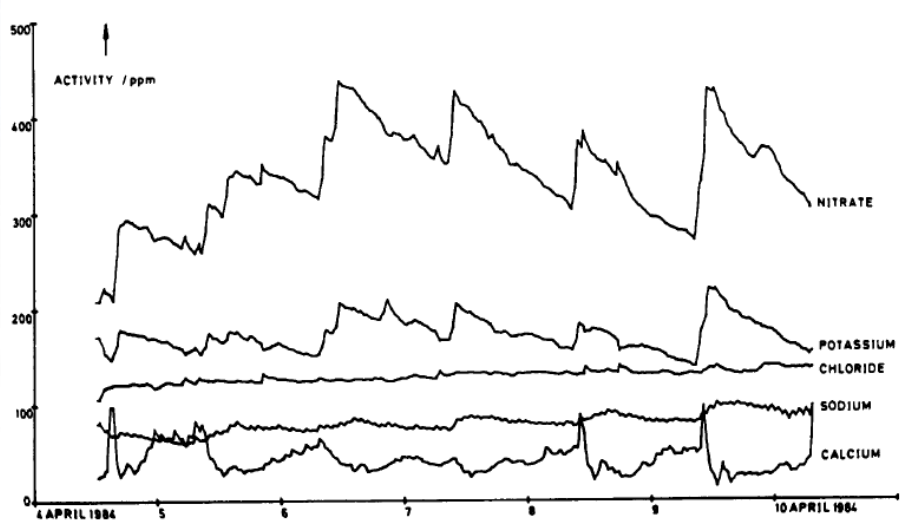
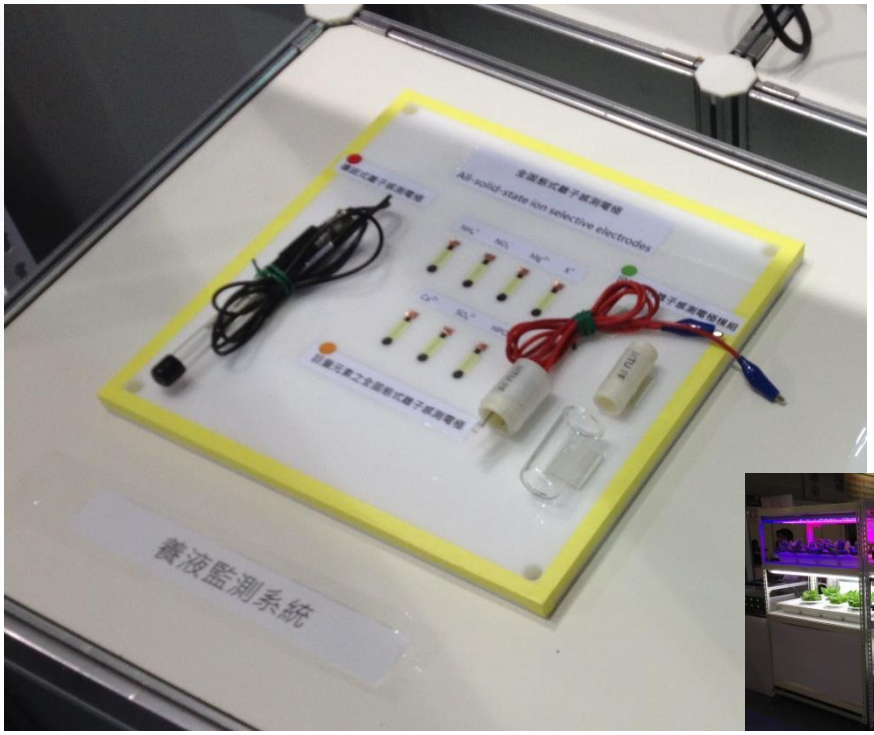


Fig. 10. Results from the ANFA showing changes in ion activity over a period of a week.

Automated nutrient film analyzer:

- Svanberg team, ICST (London)
- Tomato hydroponic growing
- ISEs + microprocessors
- 6 ions: NO_3^-, K^+, Ca^{2+}, Cl^-, Na^+, H^+
- One-week continuous monitoring

Biomolecular Device Lab.



NEW Ion-Sensing Total Solutions for Smart Agriculture with 3rd Gen ISEs

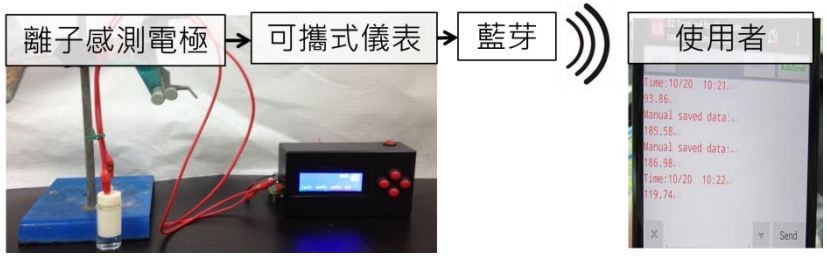
離子感測電極:

傳統式

http://www.test-cn.com/

全固態式

離子	靈敏度 (mV/decade)	感測極限 (μM)
硝酸根	55.3 ± 1.1	16.9
銨根	55.8 ± 1.0	6.45
鉀	55.0 ± 0.8	7.2
鈣	26.7 ± 0.6	16.2
鎂	26.1 ± 0.8	14.4
硫酸根	29.3 ± 1.3	32.36
磷酸氫根	32.9 ± 0.9	12.59



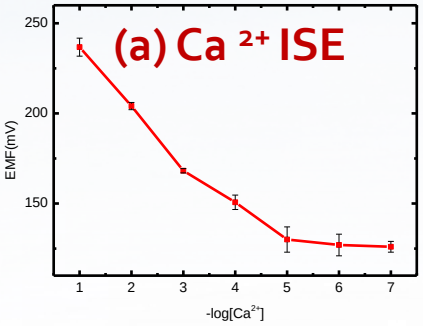
20150616-18 光電展/植物工廠展 (台北南港世貿展覽館)

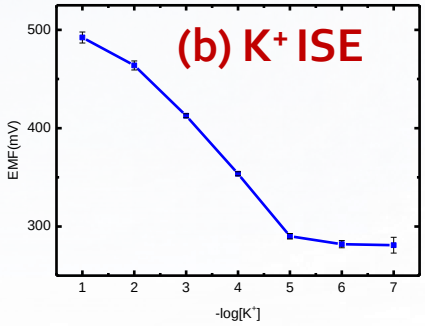
2015 Taiwan Plant Factory and Agriculture Facility Expo

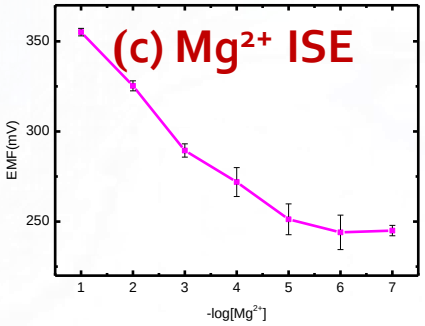
(Taiwan Patent Granted)

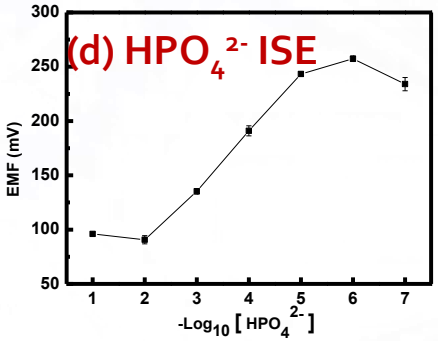
Biomolecular Device Lab.

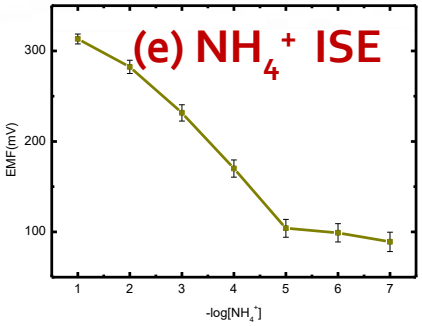
Applications to Macro-nutrient Detection

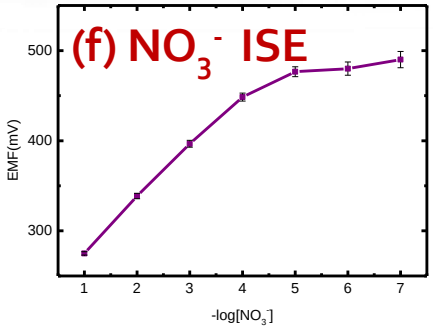


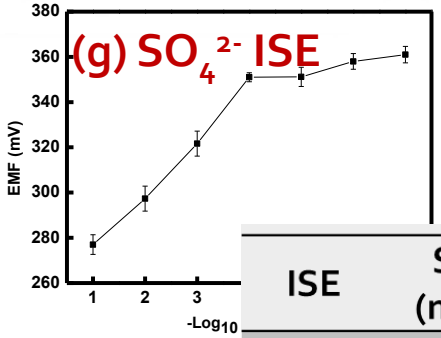










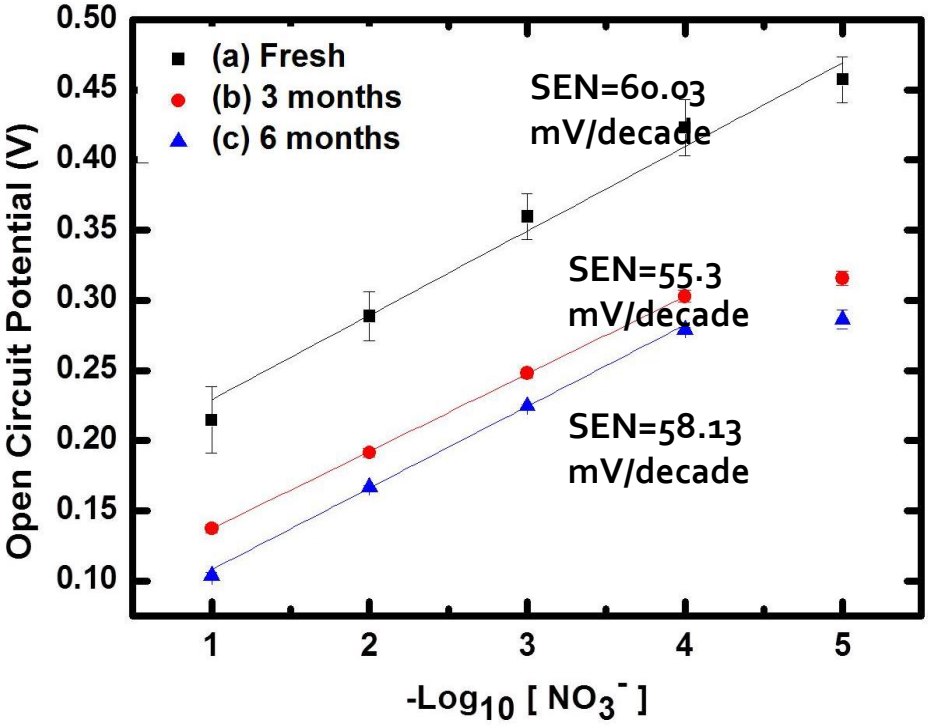


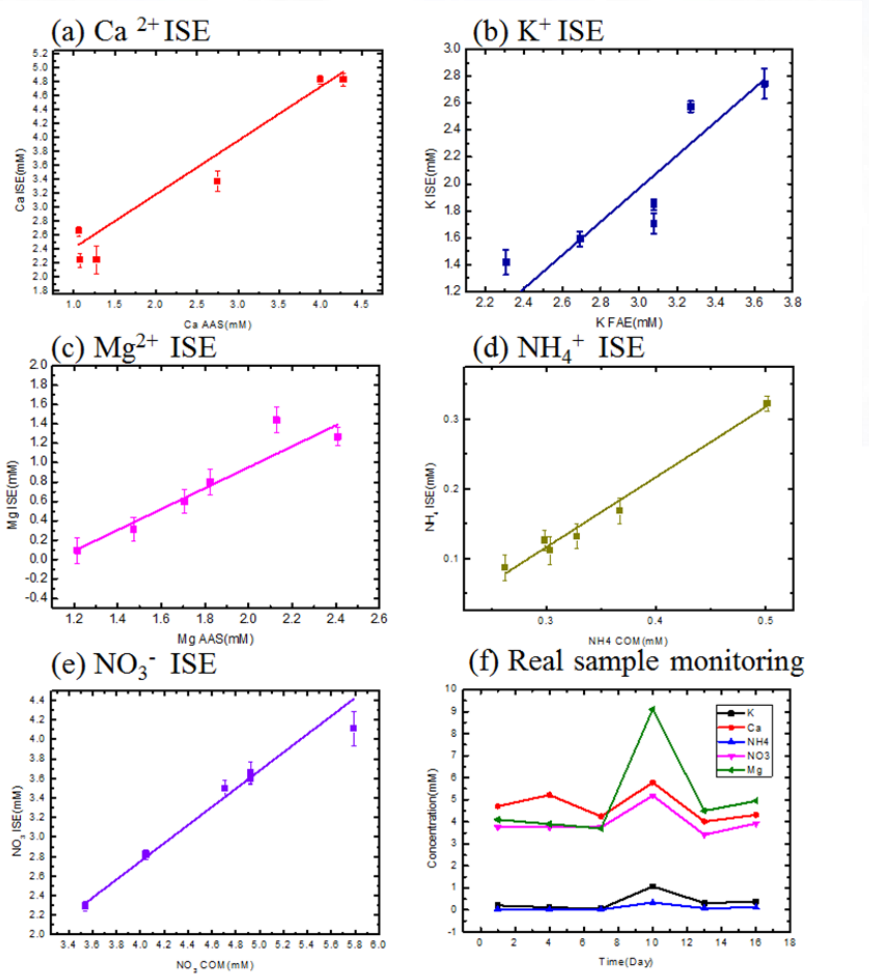
$$E_M = E^0 + \frac{RT}{zF} \ln a_I(aq)$$

Theoretical SEN = (59.1/z) mV/log C at 25 °C (298 K)

ISE	Sensitivity (mV/decade)	Detection limit (mM)
NO_3^-	55.3	0.0169
NH_4^+	55.8	0.00645
Ca^{2+}	26.7	0.0162
K^+	55.0	0.00724
Mg^{2+}	26.1	0.0144
SO_4^{2-}	29.3	32.36
HPO_4^{2-}	32.9	12.59

Lifetime and Reliability Test

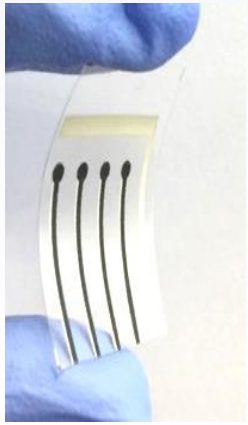




- ISE lifetime greater than 6 months
- $R^2 = 0.99$ wrt standard methods or commercial ISEs
- detect real samples in a plant factory

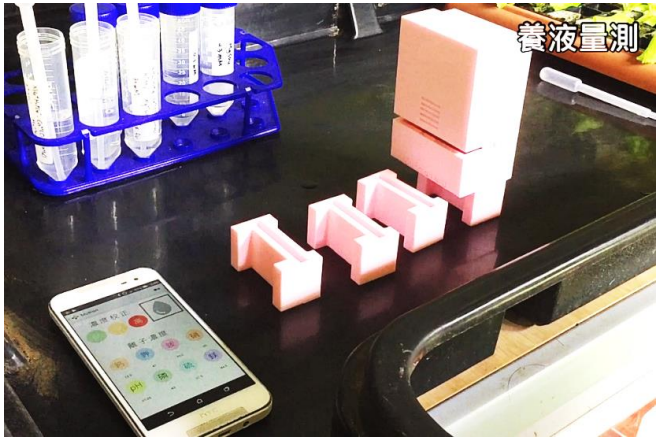
Biomolecular Device Lab.

Smart Multiplex Ion Detection (MID)

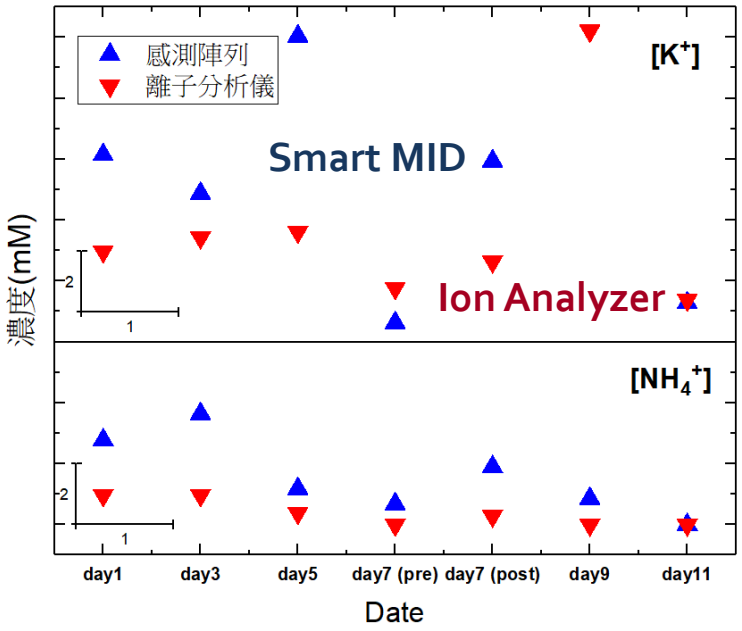


Multi-ion sensor chip (Yen, 2017)

Bluetooth smart sensing module & APP (Pan and Cheng, 2017)



Hydroponic sample measurement in the NTU plant factory with Smart MID

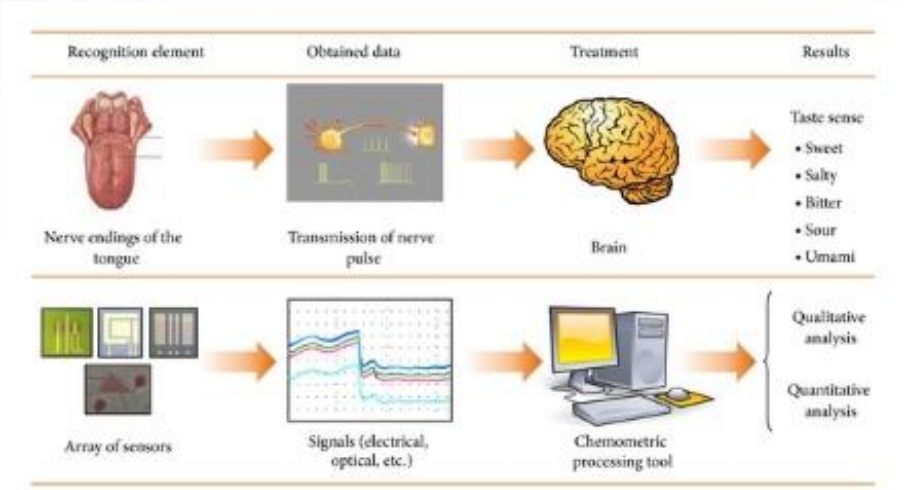


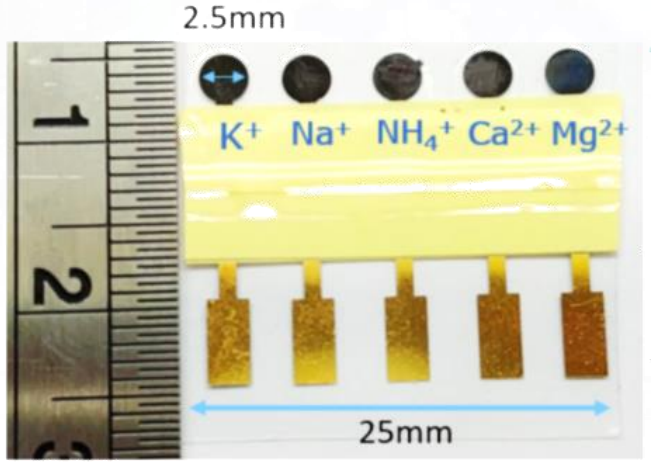
Nutrient monitoring results during hydroponic cultivation

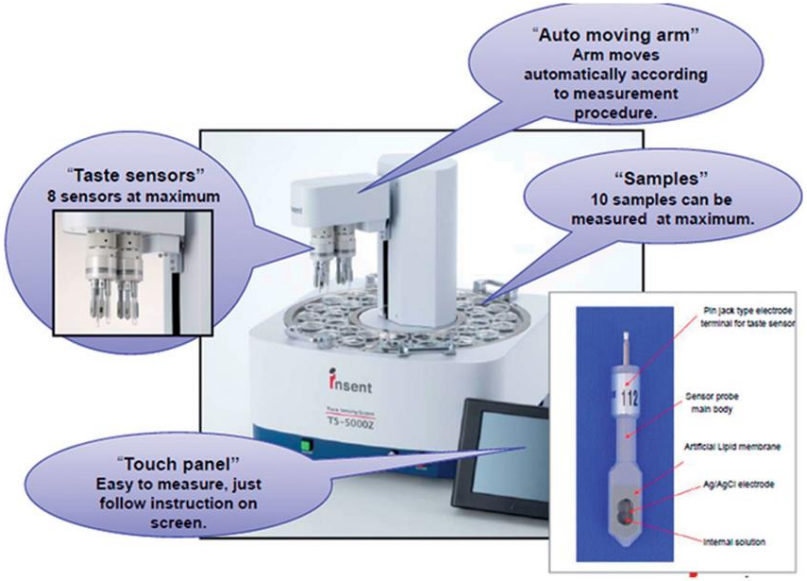
Device Lab.

5. ISE e-Tongue Chip Application

From MID to New Electronic Tongue (eT)



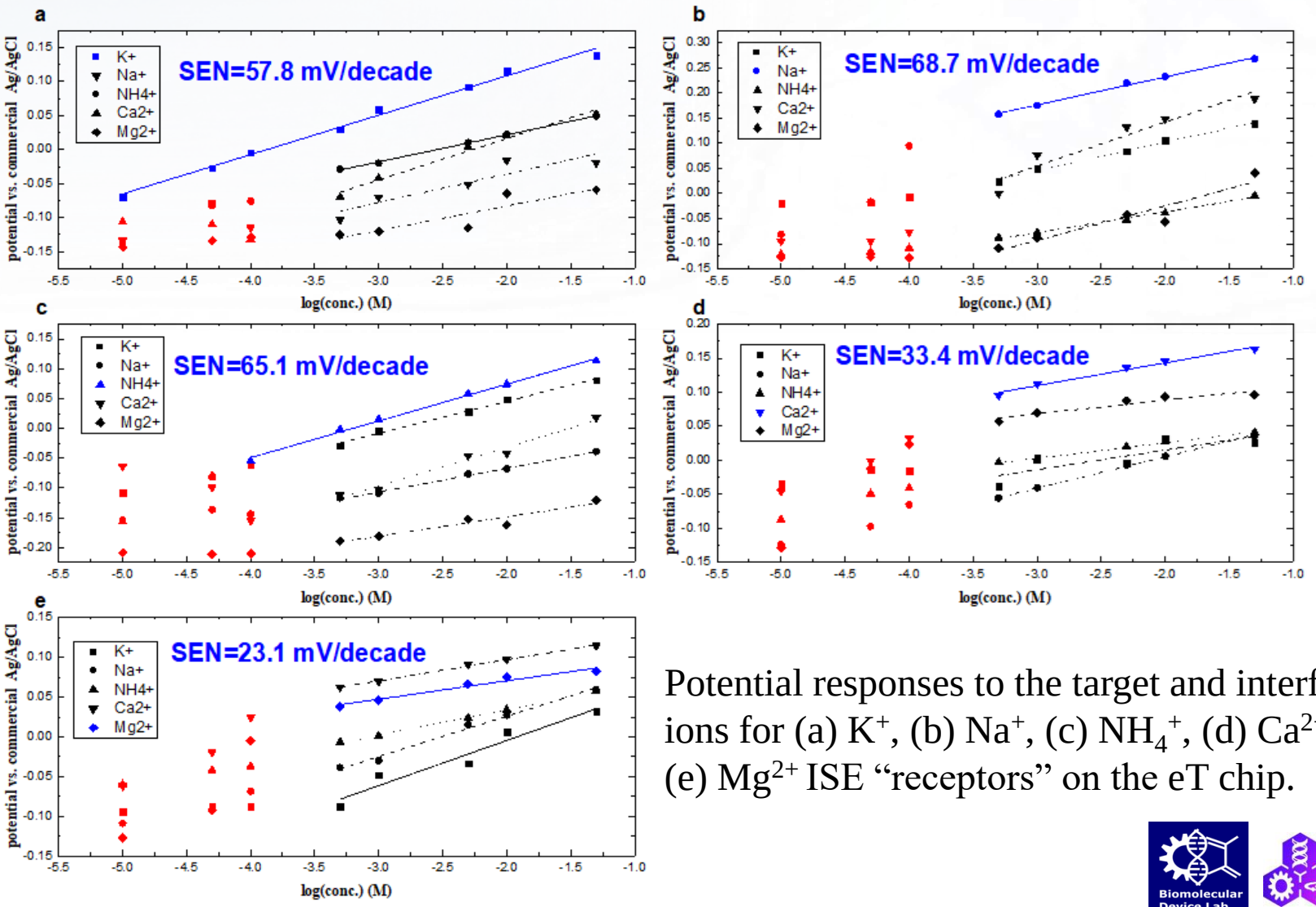




Rationales for an ISE chip as a novel eT

1) Each ion-selective electrode (ISE) unit can serve as a "taste" receptor.
2) Most salty & sour tastes results from ions, so do some bitter tastes.
3) Ionphores can cross react with sweet and bitter molecules.
4) ISEs are more reproducible & stable than conducting polymer electrodes.
5) Low cost & compatible with Smart tech.

SEN and SEL Check for ISE "Receptors"



Potential responses to the target and interfering ions for (a) K^+, (b) Na^+, (c) NH_4^+, (d) Ca^{2+}, and (e) Mg^{2+} ISE "receptors" on the eT chip.

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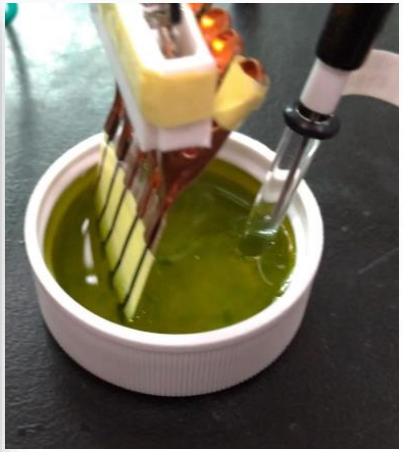
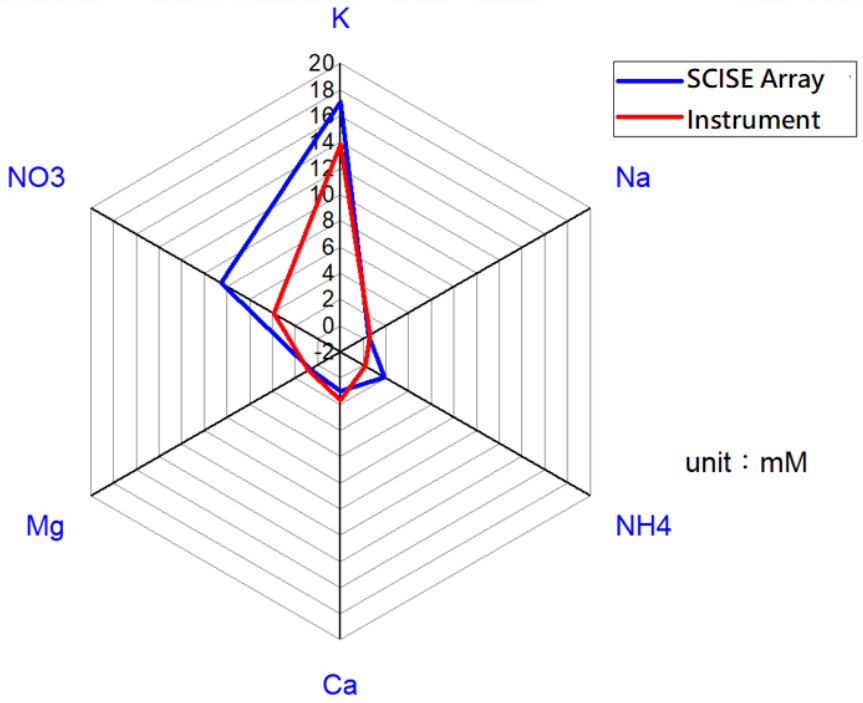
Taste of a Lettuce Juice with the eT Chip



- **Taste exp. with the ISE eT chip**

1. ISE chip calibration with high & low-conc. standard solutions.
2. Taste the sample: 4 gram of lettuce juice + 20 ml of DIW.
3. Covert potential signals to concentrations.

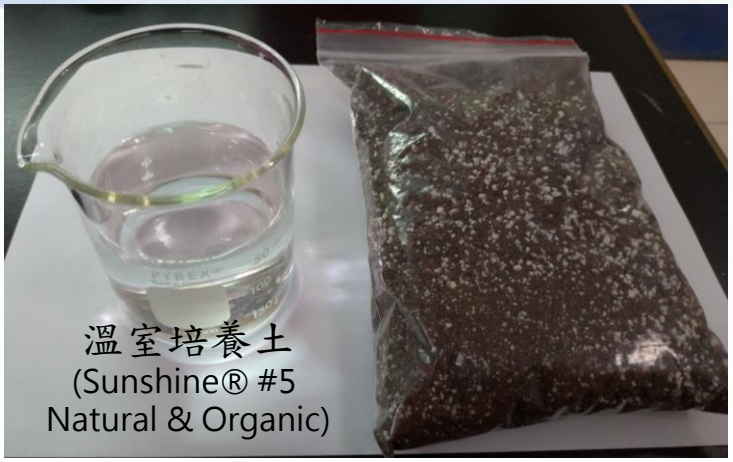
- Control exp. of sample measurements by an ion analyzer for K^+, Na^+, $NH4^+$, Mg^{2+}, Ca^{2+} and a spectrophotometer assay for NO_3^-.

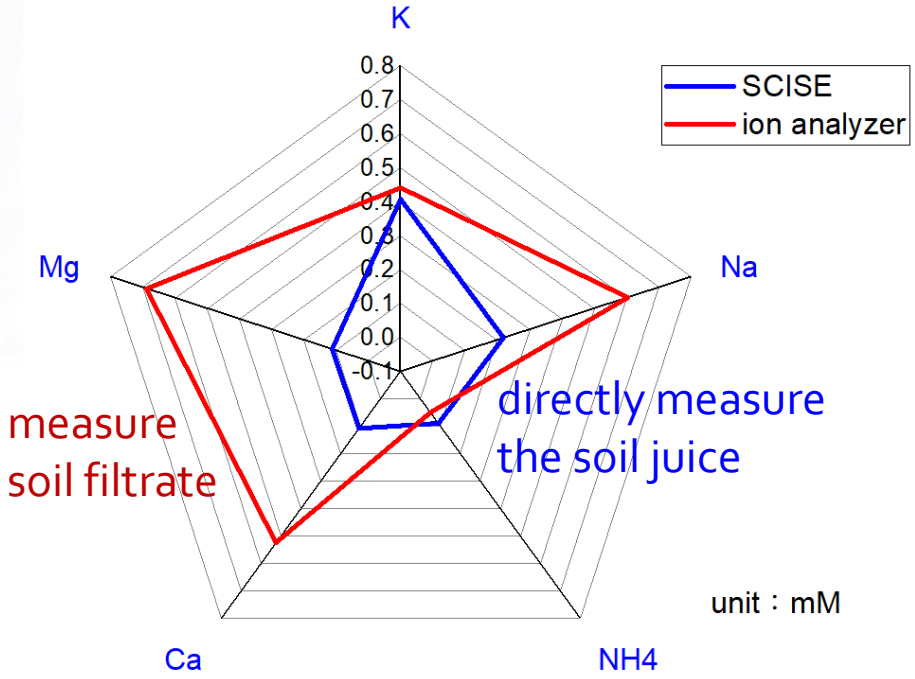


The major “tastes” of a lettuce juice is nitrate and potassium ion.

Biomolecular Device Lab.

Taste of a Soil Sample with the eT Chip



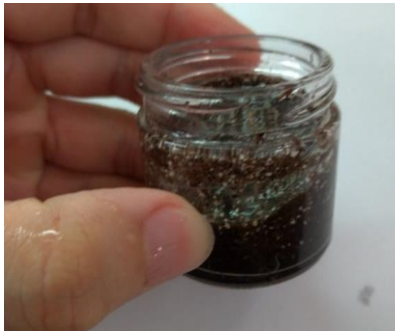


- 實驗步驟- ion sensing chip

1.校正:量測高/低濃度標準液
2.量測樣本:混合土壤與去離子水，濃度為0.1 g/ml　不需過濾
3.將量測訊號換算成濃度

- 實驗步驟- ion analyzer (離子分析儀)

1.製備樣本:混合土壤與去離子水，濃度為0.1 g/ml
2.將樣本離心與過濾(0.25 mm)
3.將樣本注入儀器量測



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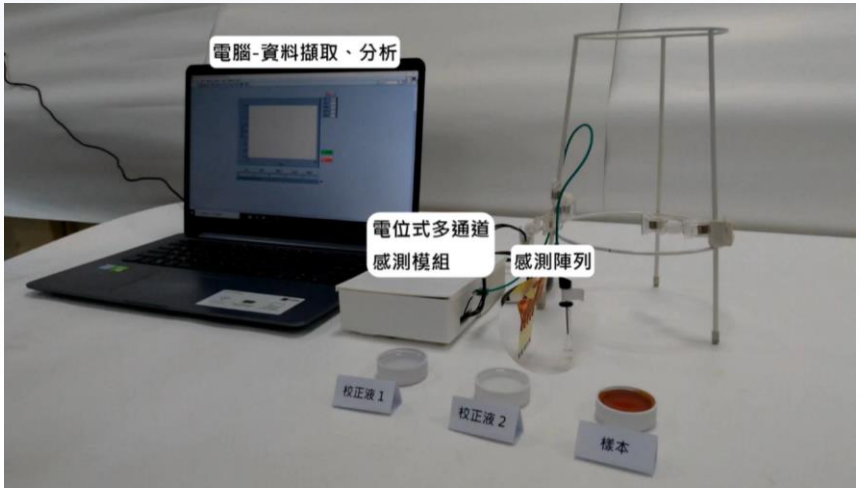
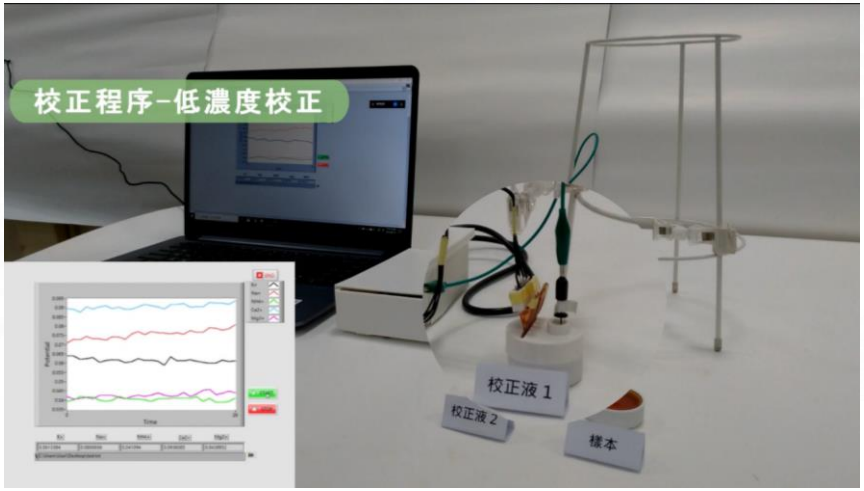
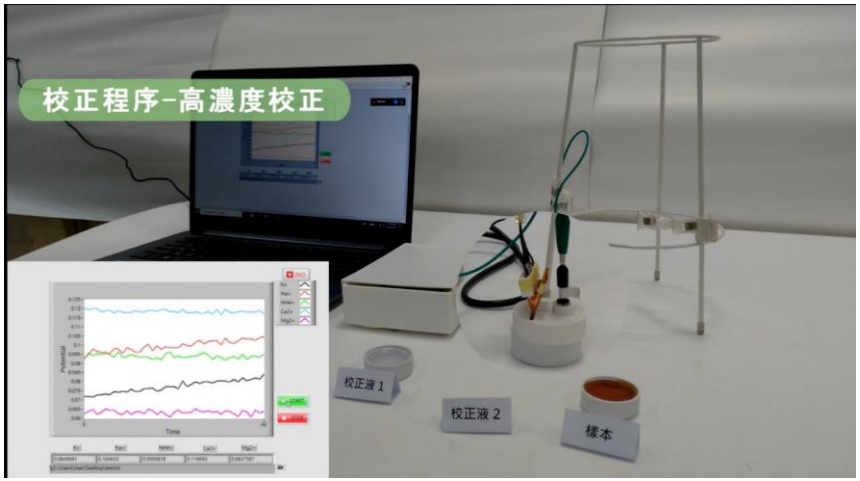
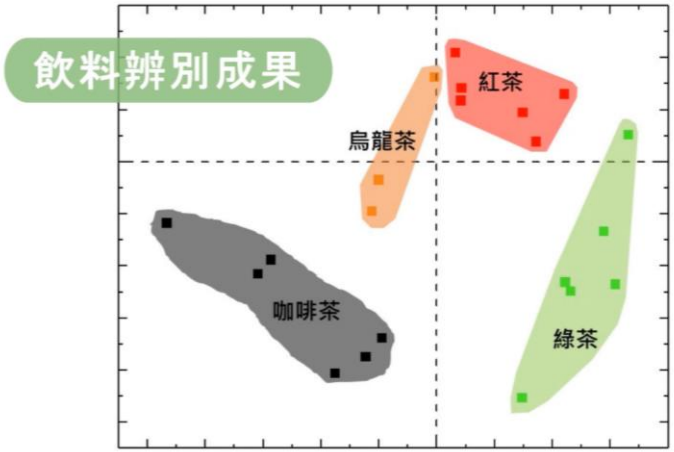
From Taste of Ions to Taste of Flavors









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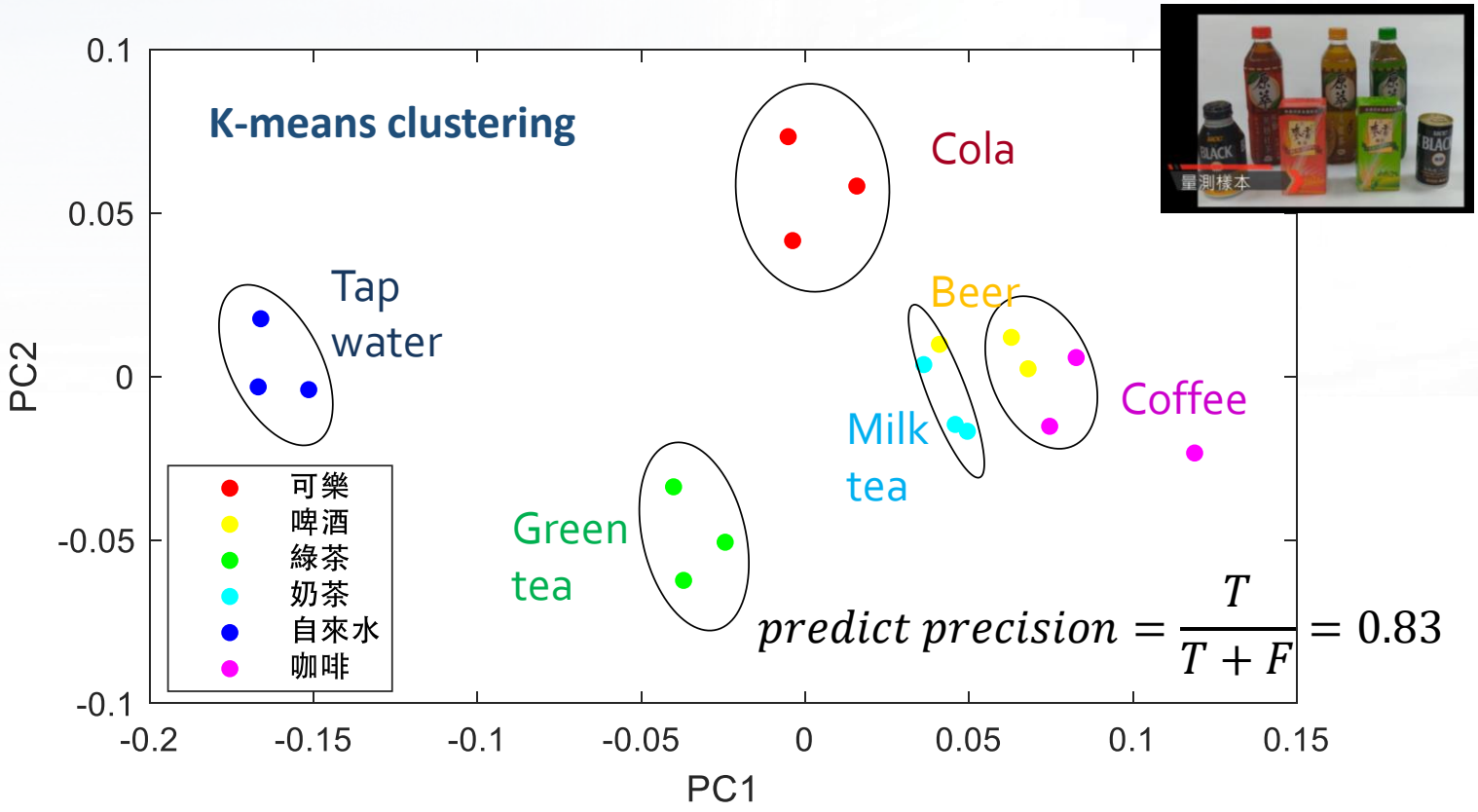
eT Taste for Beverage Discrimination



PCA plots for commercial drinks “tasted” with the eT.
Different colors represents different drinks.
The ellipses are depicted to discriminate clusters.

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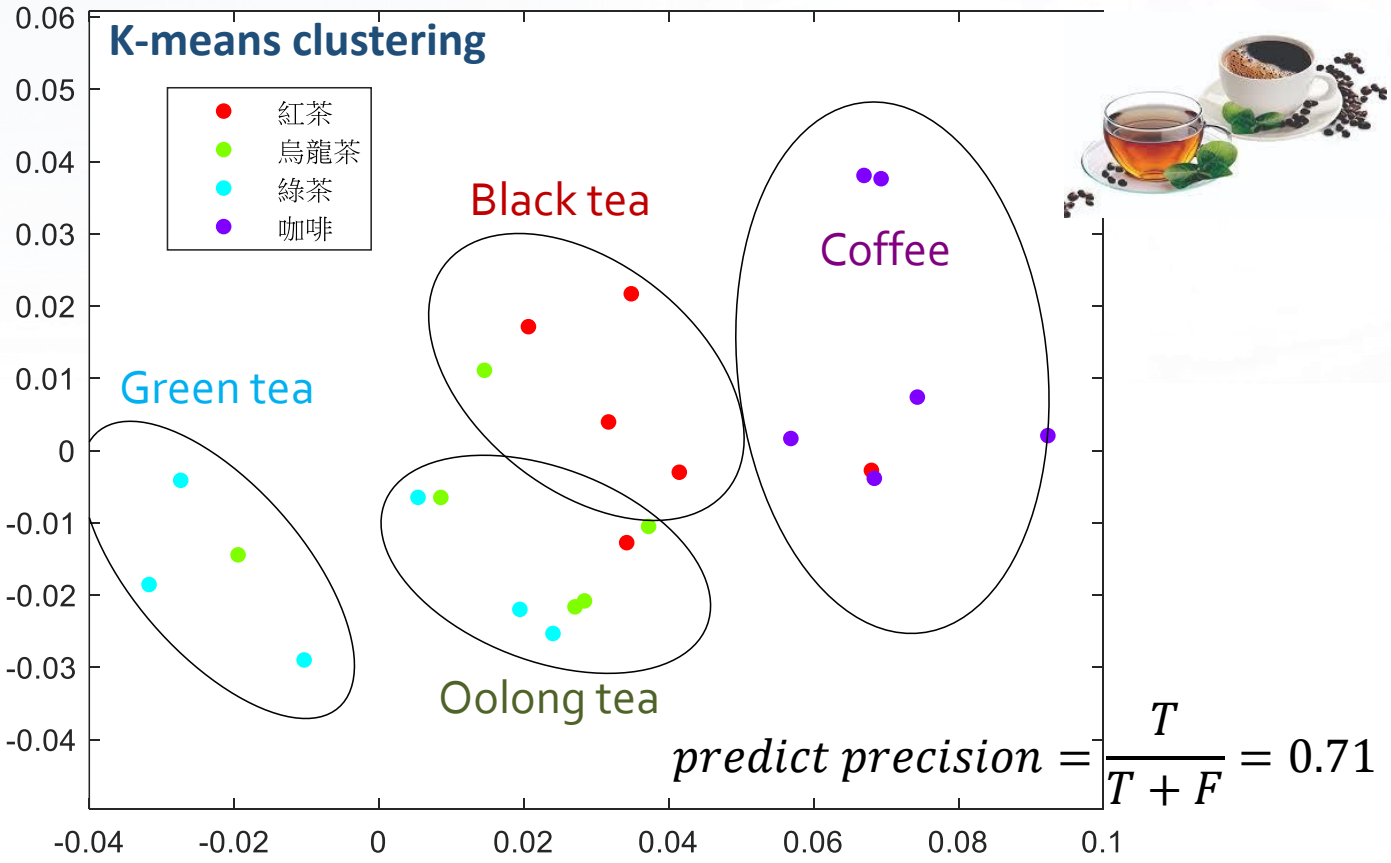
Discrimination between Teas and Coffee



PCA plots for the brewed teas and coffee "tasted" with the eT.
Different colors represents different drinks.
The ellipses are depicted to discriminate clusters.

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6. Concluding Remarks

Concluding Remarks

1. Sensors providing reliable, real-time, high-content chemical information (e.g., ion composition, taste, & smell) have great potentials in the era of AI-driven agriculture.
2. Fusion of frontier electrochemistry, biochemistry, device science and smart technology shows benefits in R&Ds of intelligent chemical/bio-sensing systems for agriculture.
3. The third generation of ISE uses a solid-contact layer to covert an ion concentration into a potential signal, which has the advantages of cost, size, and arraying on a chip.

Concluding Remarks (Cont'd)

4. Smart multiplex ion detection for element monitoring during hydroponic cultivation can be attained with the ISE array chip, a Bluetooth module and smartphone APP.
5. Preliminary studies show that the solid-contact ISE arrays can be used as a novel electronic tongue chip, which not only can sense the "ion taste" of vegetable and soil samples but also can discriminate beverages and tastes between teas and coffee.
6. We look forward to collaborations with smart agriculture experts to drive our intelligent biosensing systems into realistic applications.

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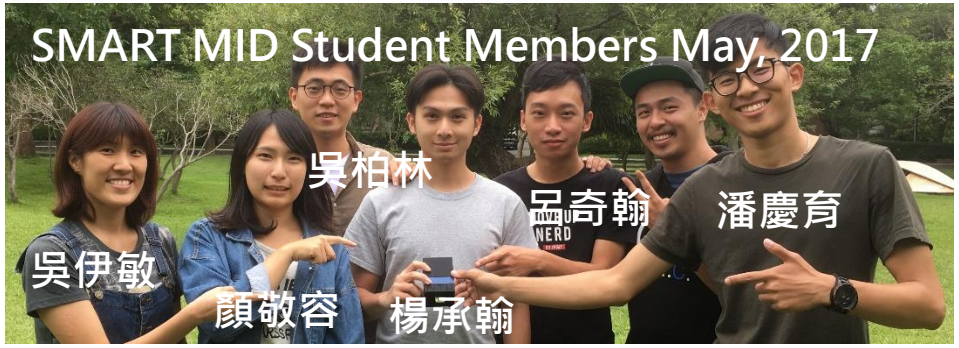
Special Thanks to Prof. Tzong-Chi Cheng, Prof. Wei Fang, and Prof. Jian-Zhang Chen and SMART MID Team



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