Materials Based Sensing and Control

Dermot Diamond

INSIGHT Centre for Data Analytics, National Centre for Sensor Research, Dublin City University, Dublin 9, Ireland

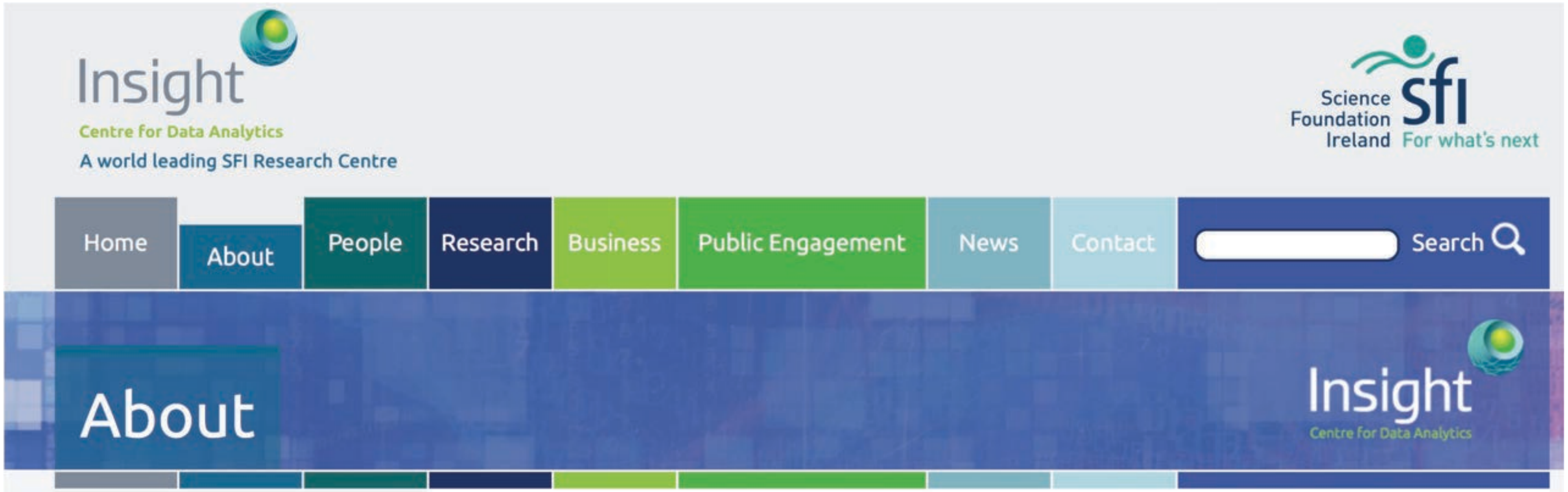
Invited Lecture Presented at

13th Electromaterials Science Symposium

Deakin University, Geelong, Australia

12 February 2019

The Insight Centre for Data Analytics



Insight is one of the biggest data analytics centres in Europe. It undertakes high-impact research, seeks to derive value from Big Data and provides innovative technology solutions for industry and society by enabling better decision-making.

With **€88 million (ca.50% Industry)** in funding, Insight has 400 researchers across areas such as connected health, decision analytics, social media analytics, smart cities and the semantic web.

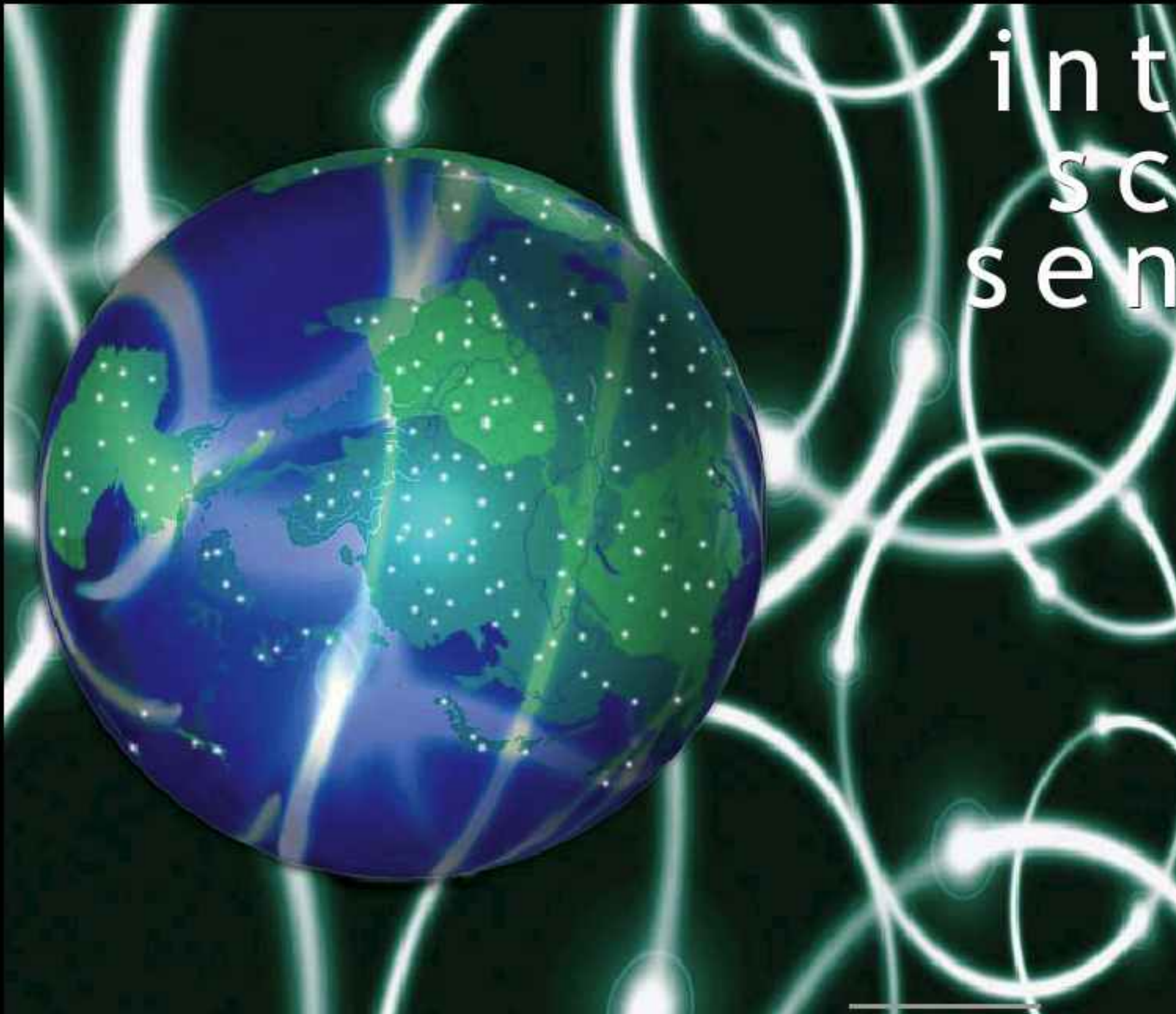
http://www.sfi.ie/sfi-research-centres/insight/

2nd Phase funding approved (ca. €50 million SFI) commencing autumn 2019

Internet of Things (IOT)

- Embedded ‘smartness’
  - Sensing (temperature, light-level, imaging, vibration)
  - Communications (wireless)
  - Power (10-year battery life-time, scavenging capacity)
- Awareness of
  - Surrounding environment
  - Internal (functional) condition
- **Bridging the Molecular and Digital worlds**
  - Emergence of ‘Internet of Analytical Things’, Internet of ‘Molecular Things’, ‘Internet of Biochemical Things’

Keynote Article: Anal. Chem., 76 (2004) 278A-286A



internet scale sensing

Dermot Diamond
Dublin City University
(Ireland)

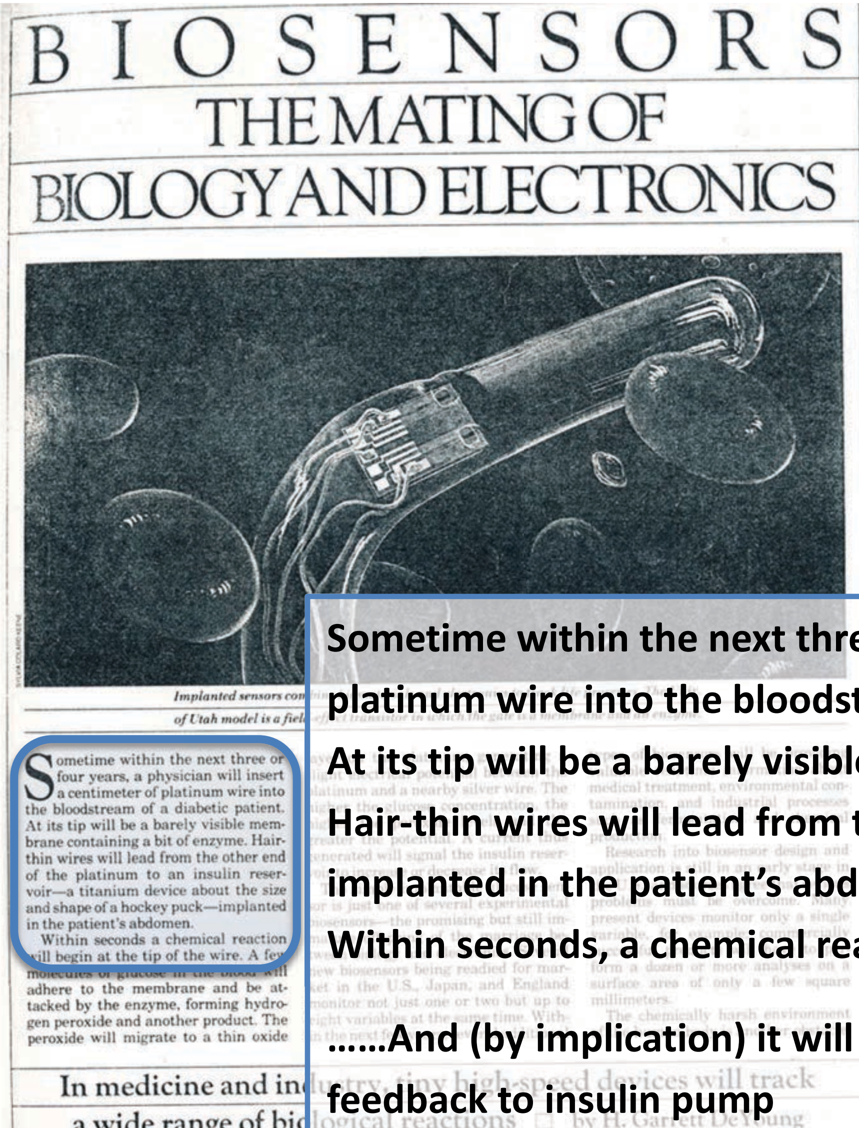
Incredible advances in digital communications and computer power have profoundly changed our lives. One chemist shares his vision of the role of analytical science in the next communications revolution.

Digital communications networks are at the heart of modern society. The digitization of communications, the development of the Internet, and the availability of relatively inexpensive but powerful mobile computing technologies have established a global communications network capable of linking billions of people, places, and objects. Email can instantly transmit complex documents to multiple remote locations, and websites provide a platform for instantaneous notification, dissemination, and exchange of information globally. This technology is now pervasive, and those in research and business have multiple interactions with this digital world every day. However, this technology might simply be the foundation for the next wave of development that will provide a seamless interface between the real and digital worlds.

The crucial missing part in this scenario is the gateway through which these worlds will communicate: How can the digital world sense and respond to changes in the real world? Analytical scientists—particularly those working on chemical sensors, biosensors, and compact, autonomous instruments—are

Ron Ambrosio & Alex Morrow, IBM TJ Watson

The (broken) promise of biosensors…..


BIOSENSORS
THE MATING OF BIOLOGY AND ELECTRONICS

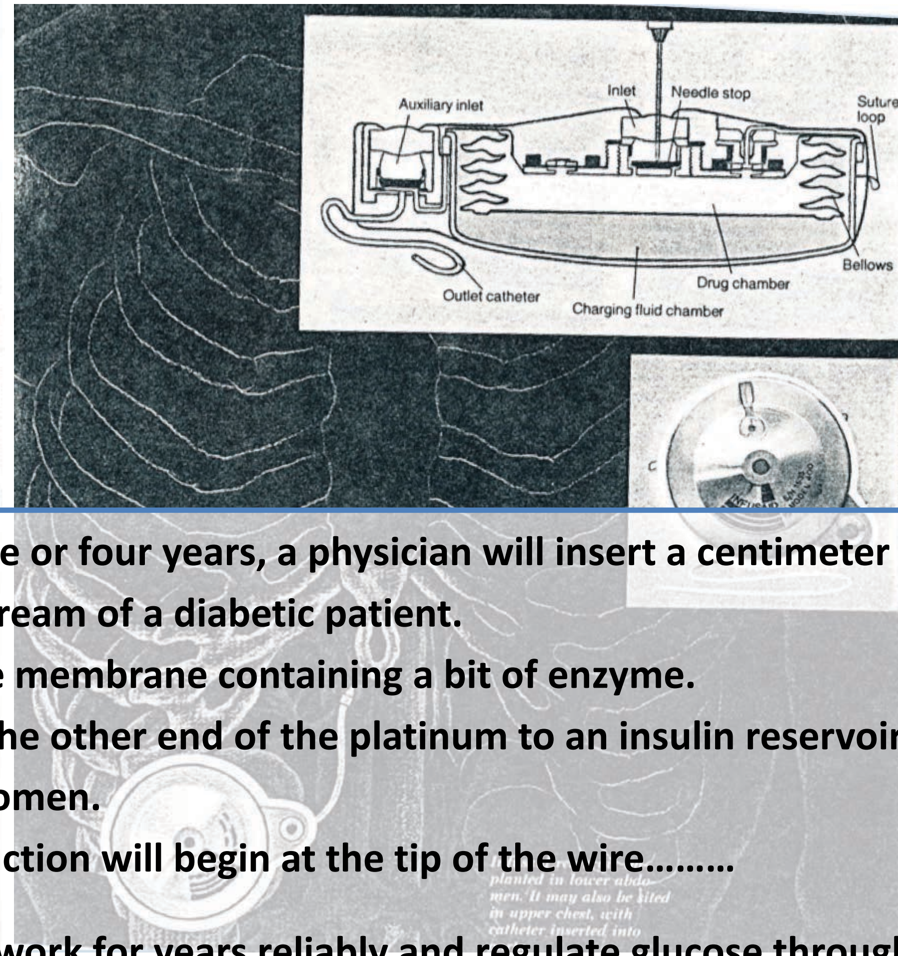
Implanted sensors co…
of Utah model is a fiel…

Sometime within the next three or four years, a physician will insert a centimeter of platinum wire into the bloodstream of a diabetic patient. At its tip will be a barely visible membrane containing a bit of enzyme. Hair-thin wires will lead from the other end of the platinum to an insulin reservoir—a titanium device about the size and shape of a hockey puck—implanted in the patient's abdomen.

Within seconds a chemical reaction will begin at the tip of the wire. A few molecules of glucose in the blood will adhere to the membrane and be attacked by the enzyme, forming hydrogen peroxide and another product. The peroxide will migrate to a thin oxide

In medicine and in… a wide range of bio…

High Technology, Nov. 1983, 41-49



Sometime within the next three or four years, a physician will insert a centimeter of platinum wire into the bloodstream of a diabetic patient.
At its tip will be a barely visible membrane containing a bit of enzyme.
Hair-thin wires will lead from the other end of the platinum to an insulin reservoir implanted in the patient's abdomen.
Within seconds, a chemical reaction will begin at the tip of the wire………

……And (by implication) it will work for years reliably and regulate glucose through feedback to insulin pump

After Ca. 40 years – Dominant Use Model is Finger Prick Sampling

- e.g. Diabetes: ca. 7% of world population
- USA: population 300 million
- Ca. 20 million diabetics
- Personal control of condition using finger prick test => blood sample + glucose biosensor

- Say four measurements per day = 80 million/day
- Per year = ca. 30 Billion measurements/yr
- Each sensor used ONCE

Adam Heller

Subcutaneous sampling of interstitial fluid using microneedles to access the fluid through the skin without causing bleeding

San Francisco Business Times; Tuesday, April 6, 2004

‘Abbott completes TheraSense acquisition’

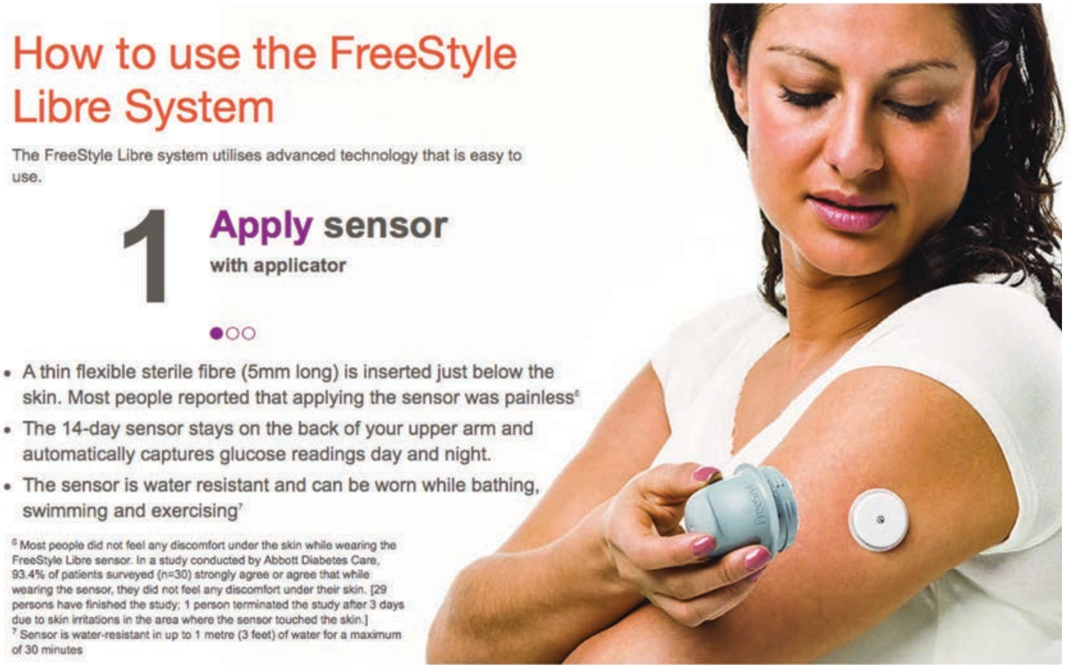
Abbott Laboratories said Tuesday it completed its $1.2 billion acquisition of Alameda-based TheraSense Inc. after a majority of shareholders approved the transaction a day earlier.

- **Abbott Press Release September 29, 2008**
- Abbott Park, Illinois — Adam Heller, Ph.D., a professor at the University of Texas in Austin who created the technology that led to the development of Abbott's FreeStyle Blood Glucose Monitoring Systems® and FreeStyle Navigator® Continuous Glucose Monitoring System, today received the 2007 National Medal of Technology and Innovation from President George W. Bush in an award ceremony at the White House.

Abbott Freestyle 'Libre'

The days of routine glucose testing with lancets, test strips and blood are over.[2]

Welcome to flash glucose monitoring!



- 'Small fibre' used to access interstitial fluid
- Data downloaded at least once every 8 hr via 1s contactless scan (1-4 cm)
- Waterproof to 1 metre
- Replace every 2 weeks

THE IRISH TIMES

Mon, Feb 11, 2019

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Abbott to add 500 new jobs at Donegal healthcare plant

US healthcare giant employs almost 3,000 people in the Republic

Mon, Jul 23, 2018, 15:35 | Updated: Mon, Jul 23, 2018, 20:33

Peter Hamilton

Abbott's Donegal site manufactures test strips used in its FreeStyle blood glucose-monitoring meters. Photograph: Tim Boyle/Bloomberg

US healthcare giant Abbott plans to create 500 jobs in Donegal as it expands its existing manufacturing facility there.

With nearly 3,000 employees across nine sites in the Republic, Abbott's operations here include manufacturing nutritional products and creating diagnostic tools for physicians.

Abbott Jobs

Macromolecules **1990,** *23,* 4372–4377

Synthesis, Characterization, and Properties of a Series of Osmium- and Ruthenium-Containing Metallopolymers

Robert J. Forster and Johannes G. Vos*

School of Chemical Sciences, Dublin City University, Dublin 9, Ireland

Received November 27, 1989; Revised Manuscript Received February 16, 1990

- **1989: Forster and Vos series of papers on Os/Ru bipy/PVP**
- **1990s: Heller develops foundational ideas**
- **2004: Abbott acquires Therasense ($1.2bn)**
- **2018: Abbott Jobs announcement**

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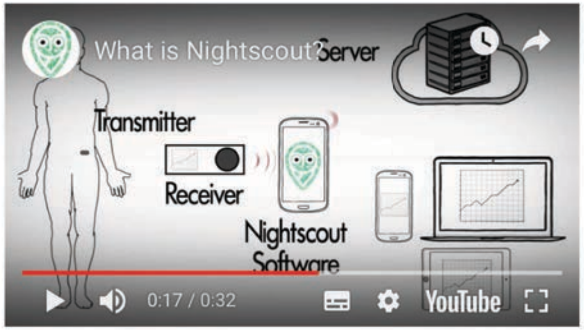
NIGHTSCOUT

#WeAreNotWaiting

http://www.nightscout.info https://www.dexcom.com

Welcome to Nightscout

What is the Nightscout project?



Nightscout (CGM in the Cloud) is an open source, DIY project that allows real time access to a CGM data via personal website, smartwatch viewers, or apps and widgets available for smartphones.

Nightscout was developed by parents of children with Type 1 Diabetes and has continued to be developed, maintained, and supported by volunteers. When first implemented, Nightscout was a solution specifically for remote monitoring of Dexcom G4 CGM data. Today, there are Nightscout solutions available for Dexcom G4, Dexcom Share with Android, Dexcom Share/G5 with iOS, and Medtronic. Nightscout also provides browser-based visualization for #openAPS users and Loop users. The goal of the project is to allow remote monitoring of a T1D's glucose level using existing monitoring devices.

Search ...

Disclaimer

All information, thought, and code described here is intended for informational and educational purposes only. Nightscout currently makes no attempt at HIPAA privacy compliance. Use of code from github.com is without warranty or support of any kind. Please review the LICENSE found within each repository for further details. **Use Nightscout at your own risk, and do not use the information or code to make medical decisions.**

Support Nightscout

Your contributions help the developers purchase test equipment, webspace, cables, and other tools that drive this project forward. Received donations are managed by The Nightscout Foundation. Click here to donate.

Please consult with your tax professional regarding deducting donations.

Nightscout

Developed by coders & engineers within the T1 Diabetes Community & friends

Developing APPs

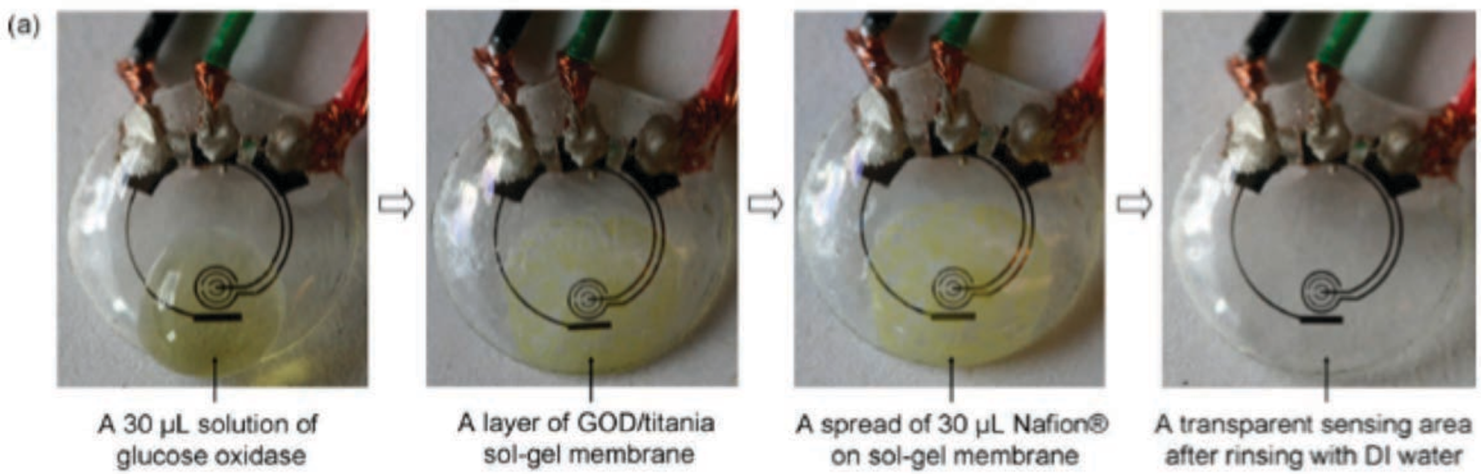
Accessing real-time data from diabetes monitors (Dexcon, wearable glucose sensors)

User groups formed, self-funded

Use disclaimers, no warranty, not for making therapeutic decisions

Google Contact Lens

H. Yao et al. / Biosensors and Bioelectronics 26 (2011) 3290–3296 3293



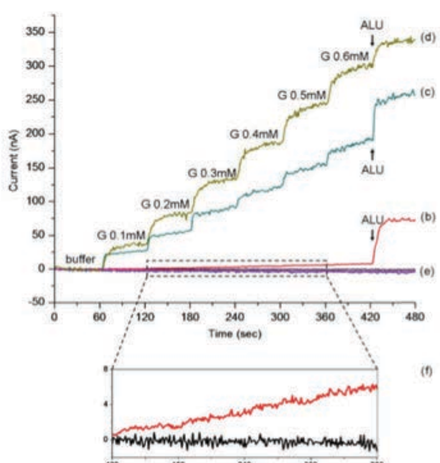
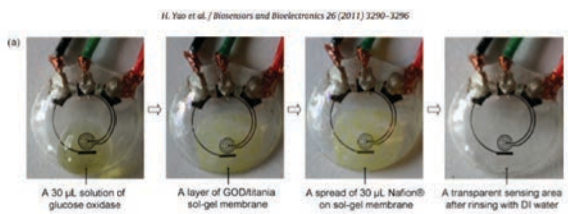


Fig. 2. Images of the sensor as it goes through surface functionalization and the related measured responses: (a) sequential images of sensor pre-treatment with GOD/titania/Nafion®; (b) measured amperometric response for the sensor just incubated with GOD; (c) measured amperometric response for the sensor prepared with GOD/titania sol-gel film; (d) measured amperometric response for the sensor prepared with GOD/titania/Nafion®; (e) three controls (signals for buffer) for the same pre-treatment of (b), (c), and (d); (f) the enlarged view of curve (b) and control of (b) for 120–360 s.



***A contact lens with embedded sensor for monitoring tear glucose level*, H. F. Yao, A. J. Shum, M. Cowan, I. Lahdesmaki and B. A. Parviz, *Biosensors & Bioelectronics*, 2011, 26**, 3290-3296.

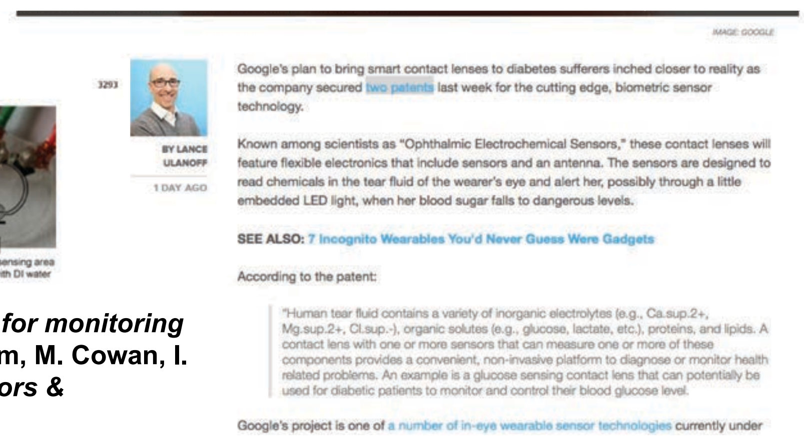


IMAGE: GOOGLE

BY LANCE ULANOFF

1 DAY AGO

Google's plan to bring smart contact lenses to diabetes sufferers inched closer to reality as the company secured two patents last week for the cutting edge, biometric sensor technology.

Known among scientists as "Ophthalmic Electrochemical Sensors," these contact lenses will feature flexible electronics that include sensors and an antenna. The sensors are designed to read chemicals in the tear fluid of the wearer's eye and alert her, possibly through a little embedded LED light, when her blood sugar falls to dangerous levels.

SEE ALSO: 7 Incognito Wearables You'd Never Guess Were Gadgets

According to the patent:

> "Human tear fluid contains a variety of inorganic electrolytes (e.g., Ca.sup.2+, Mg.sup.2+, Cl.sup.-), organic solutes (e.g., glucose, lactate, etc.), proteins, and lipids. A contact lens with one or more sensors that can measure one or more of these components provides a convenient, non-invasive platform to diagnose or monitor health related problems. An example is a glucose sensing contact lens that can potentially be used for diabetic patients to monitor and control their blood glucose level.

Google's project is one of a number of in-eye wearable sensor technologies currently under

http://www.gmanetwork.com/news/story/360331/scitech/technology/google-s-smart-contact-lenses-may-arrive-sooner-than-you-think

Contact Lens Biochemical Sensing

- **Contact lens use model is 24 hours**
- **Google (Verily) & Novartis (Alcon) announces research collaboration (2014)**

Project Abandoned November 2018
([https://www.bbc.com/news/technology-46262520)](https://www.bbc.com/news/technology-46262520)

"Our clinical work on the glucose-sensing lens demonstrated that there was insufficient consistency in our measurements of the correlation between tear glucose and blood glucose concentrations to support the requirements of a medical device," **Verily said.**

Verily did have some success in a controlled environment, but not in actual tests **because of the dynamic environment of the eye.**

'We are working closely with **Dexcom** to develop miniaturized continuous glucose monitors and with **Onduo**, our joint venture with **Sanofi**, to integrate continuous sensing into the care paradigm for people living with T2 diabetes.

ACS Nano Cover (9) 12 December 2015

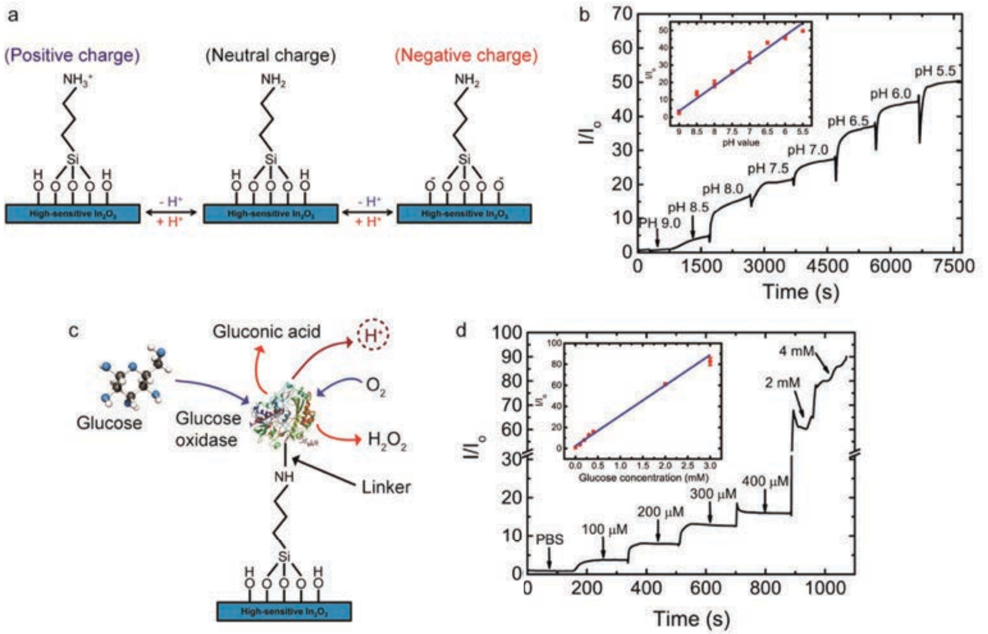
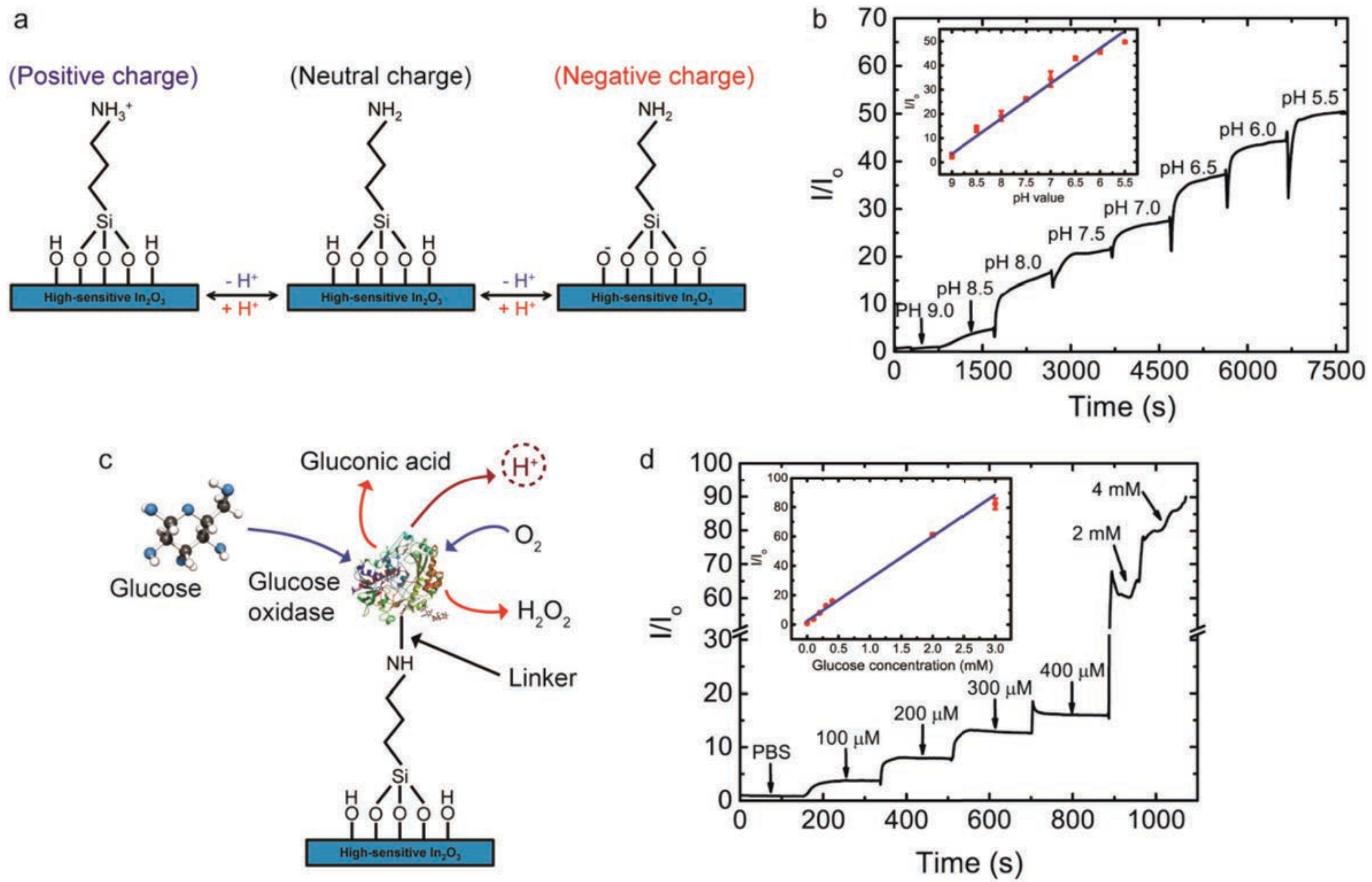


Figure 4. Chemical sensing *via* In_2O_3 FET-based conformal biosensors. (a) The pH-sensing mechanism occurs by protonation of In_2O_3 surface hydroxyl groups and primary amines of APTES at decreasing pH (increasing proton concentrations). (b) Representative responses of an In_2O_3 based FET biosensor to a biologically important pH range (pH 5.5−9). Inset shows data from five devices. (c) Enzymatic oxidation of D-glucose *via* glucose oxidase to produce gluconic acid and hydrogen peroxide. Protons are generated during this oxidation and protonation of the In_2O_3 surfaces is manifested. (d) Representative responses of In_2O_3 sensors to physiologically relevant D-glucose concentrations found in human diabetic tears (lower range) and blood (upper range). Inset shows data from five devices. Error bars represent standard deviations of the means.

- **Reference and counter electrodes are not integrated**
- **Glucose monitored via pH change caused by creation of gluconic acid**

Materials – great! Sensing - ????



- ‘CHEMFET’ configuration (same as 1984 paper) pH response not great
- Glucose sensor responds to pH – selectivity issue

Long-Term Continuous Monitoring.....

IEEE Trans. Biomed. Eng., 64 (9) 2017, 1982

1982 IEEE TRANSACTIONS ON BIOMEDICAL ENGINEERING, VOL. 64, NO. 9, SEPTEMBER 2017 EMB

Glucose Monitoring in Individuals With Diabetes Using a Long-Term Implanted Sensor/Telemetry System and Model

Joseph Y. Lucisano, *Member, IEEE*, Timothy L. Routh, *Member, IEEE*, Joe T. Lin, and David A. Gough*

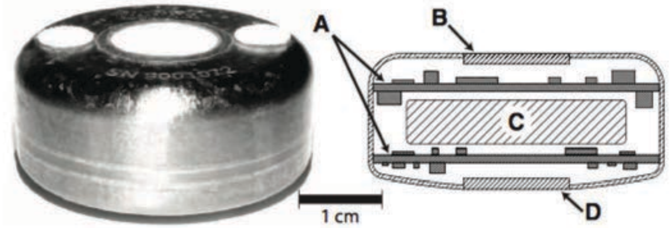


Fig. 1. Sensor array with integrated telemetry system before implantation. The implant is 3.4 cm in diameter and 1.5 cm thick. The top surface of the implant includes two polyester velour patches for tissue adhesion. Cross-sectional schematic view shows electronics modules (A), telemetry transmission portal (B), battery (C), and sensor array (D).

*

S=subject; C=clamp calibration expt (monthly)

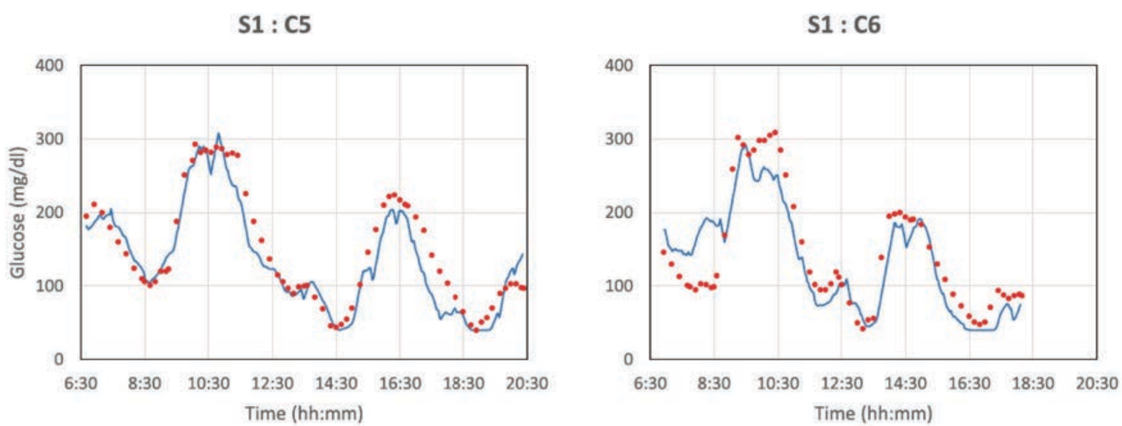


Fig. 2. Monthly glucose excursions created by controlled glucose and insulin infusions. Blue lines: transmitted sensor signals; red points: blood glucose samples from forearm venous catheter assayed with the YSI blood glucose analyzer. The maximal rate of glucose change was 3.66 mg/dl · min^{-1}, which is representative of most rapid anticipated excursions in clinical situations [14]. Signals were truncated electronically below 40 and above 400 mg/dl.

"Sensors are based on a membrane containing immobilized glucose oxidase and catalase coupled to oxygen electrodes and a telemetry system, integrated as an implant. **The devices remained implanted for up to 180 days, with signals transmitted every 2 min……"**

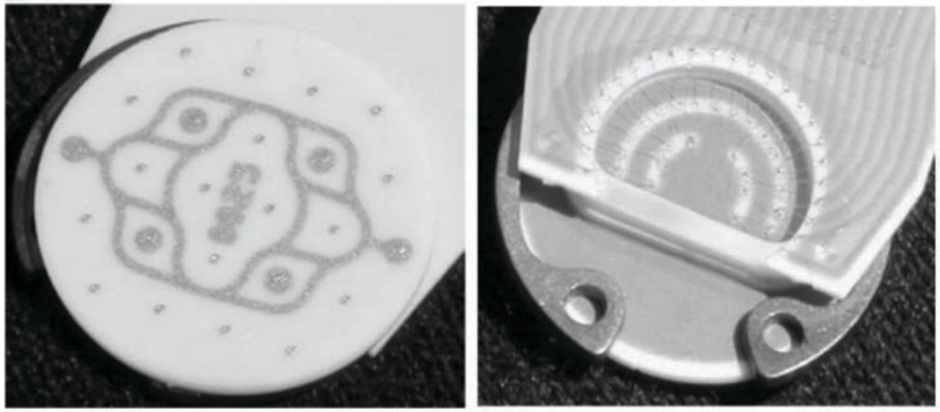
* **Sensor unit published previously (2010!!)**

D.A. Gough, L.S. Kumosa, T.L. Routh, J.T. Lin, J.Y. Lucisano, Function of an implanted tissue glucose sensor for more than 1 year in animals, Science Translational Medicine. 2 (2010) 42ra53–42ra53.

Based on electrode arrangement published previously - 2003!!

A

B

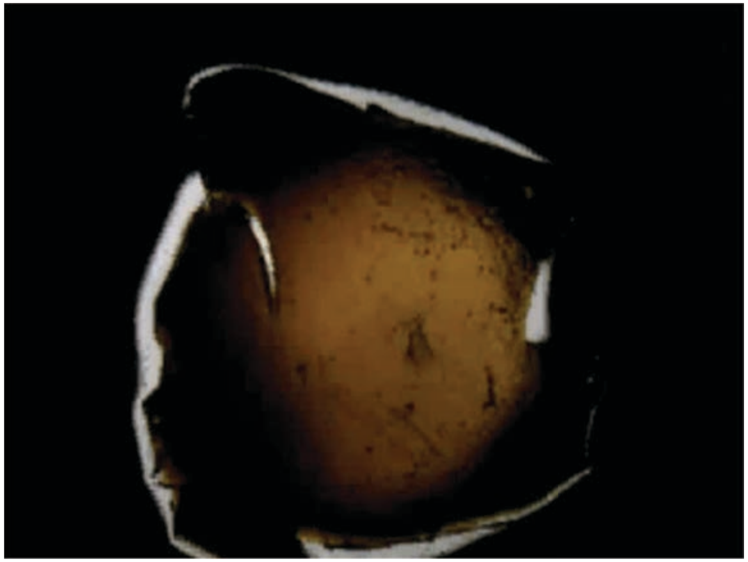


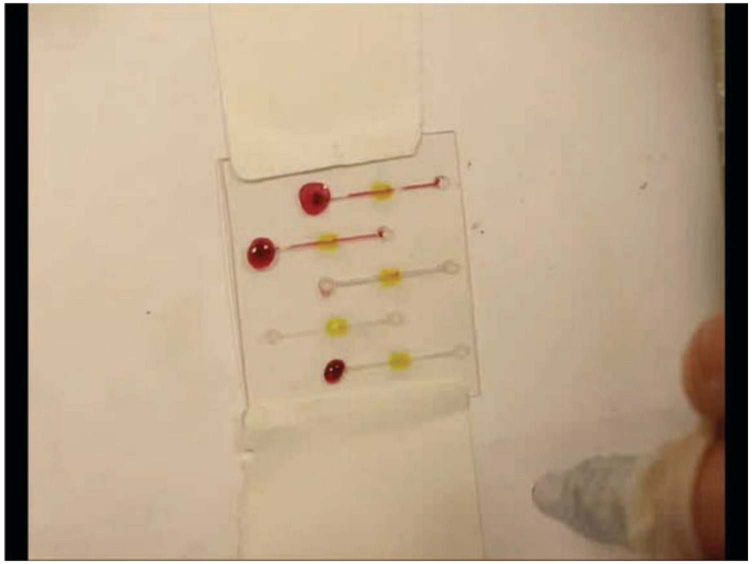
M.T. Makale, J.T. Lin, R.E. Calou, A.G. Tsai, P.C. Chen, D.A. Gough, Tissue window chamber system for validation of implanted oxygen sensors, American Journal of Physiology - Heart and Circulatory Physiology. 284 (2003) H2288–H2294. doi:10.1152/ajpheart.00721.2002.

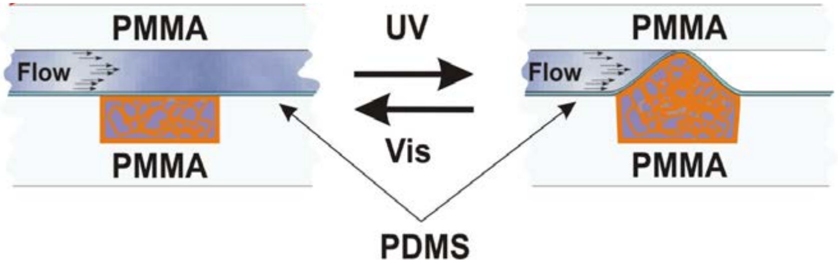
Based on enzyme electrode concepts published in 1985!!!!!!

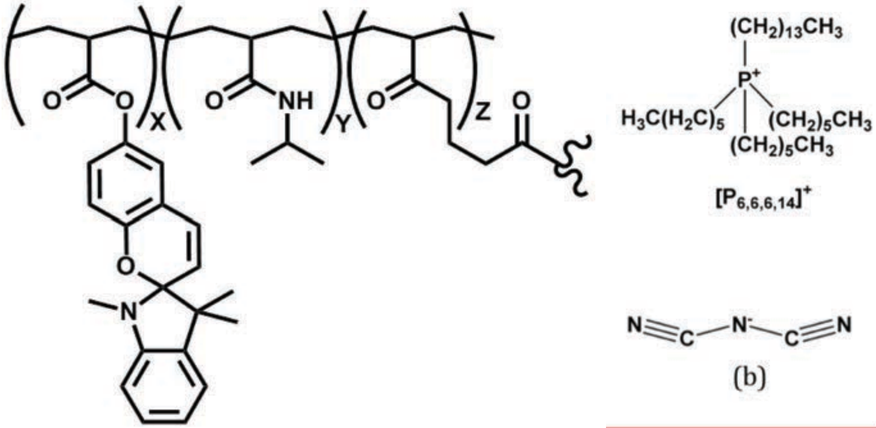
D.A. Gough, J.Y. Lucisano, P.H. Tse, Two-dimensional enzyme electrode sensor for glucose, Analytical Chemistry. 57 (1985) 2351–2357.

Photo-actuator polymers as microvalves in microfluidic systems









trihexyltetradecylphosphonium dicyanoamide $[P_{6,6,6,14}]^{+}[dca]^{-}$

Ionogel-based light-actuated valves for controlling liquid flow in micro-fluidic manifolds, Fernando Benito-Lopez, Robert Byrne, Ana Maria Raduta, Nihal Engin Vrana, Garrett McGuinness, Dermot Diamond, Lab Chip, 10 (2010) 195-201.

Experimental set up for PID Control

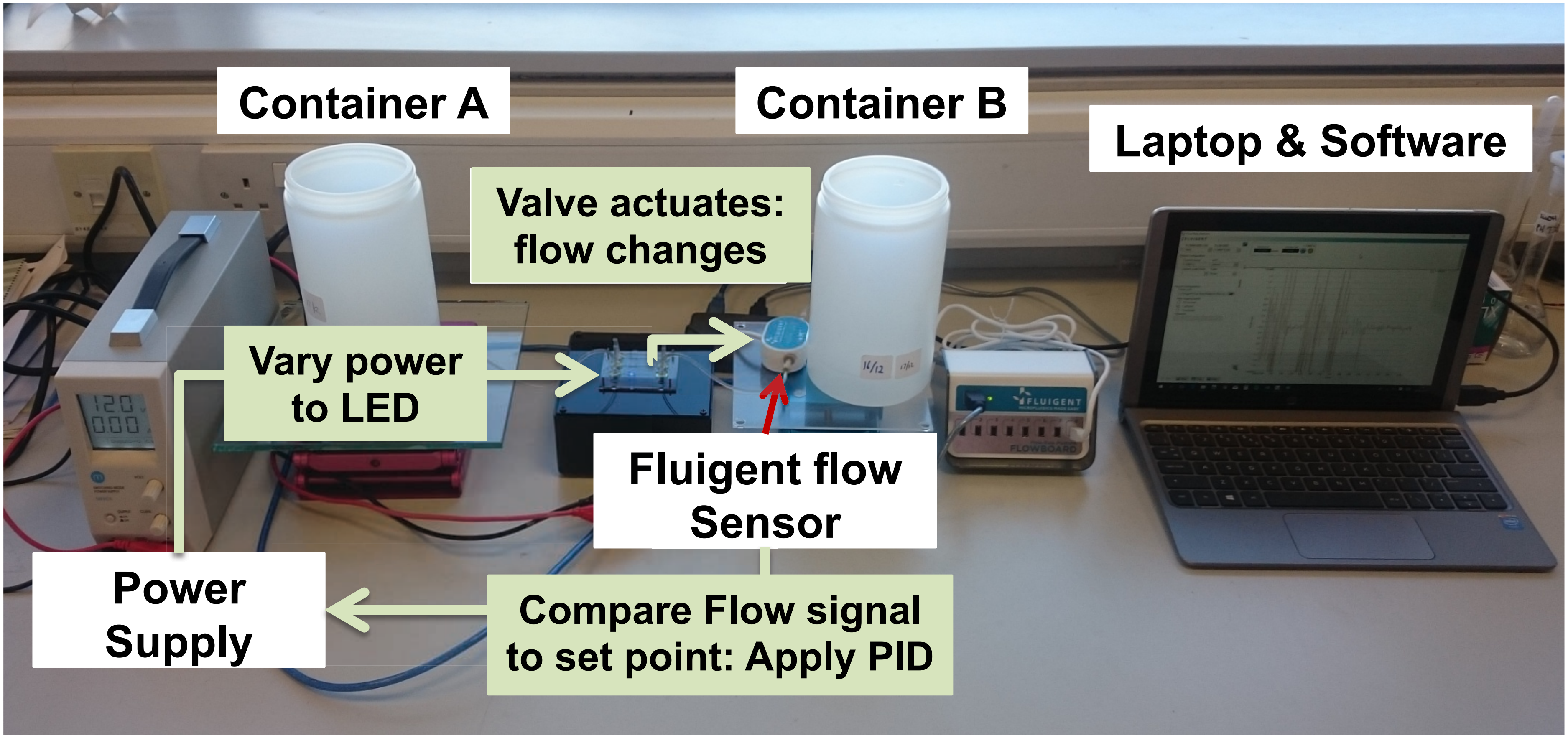
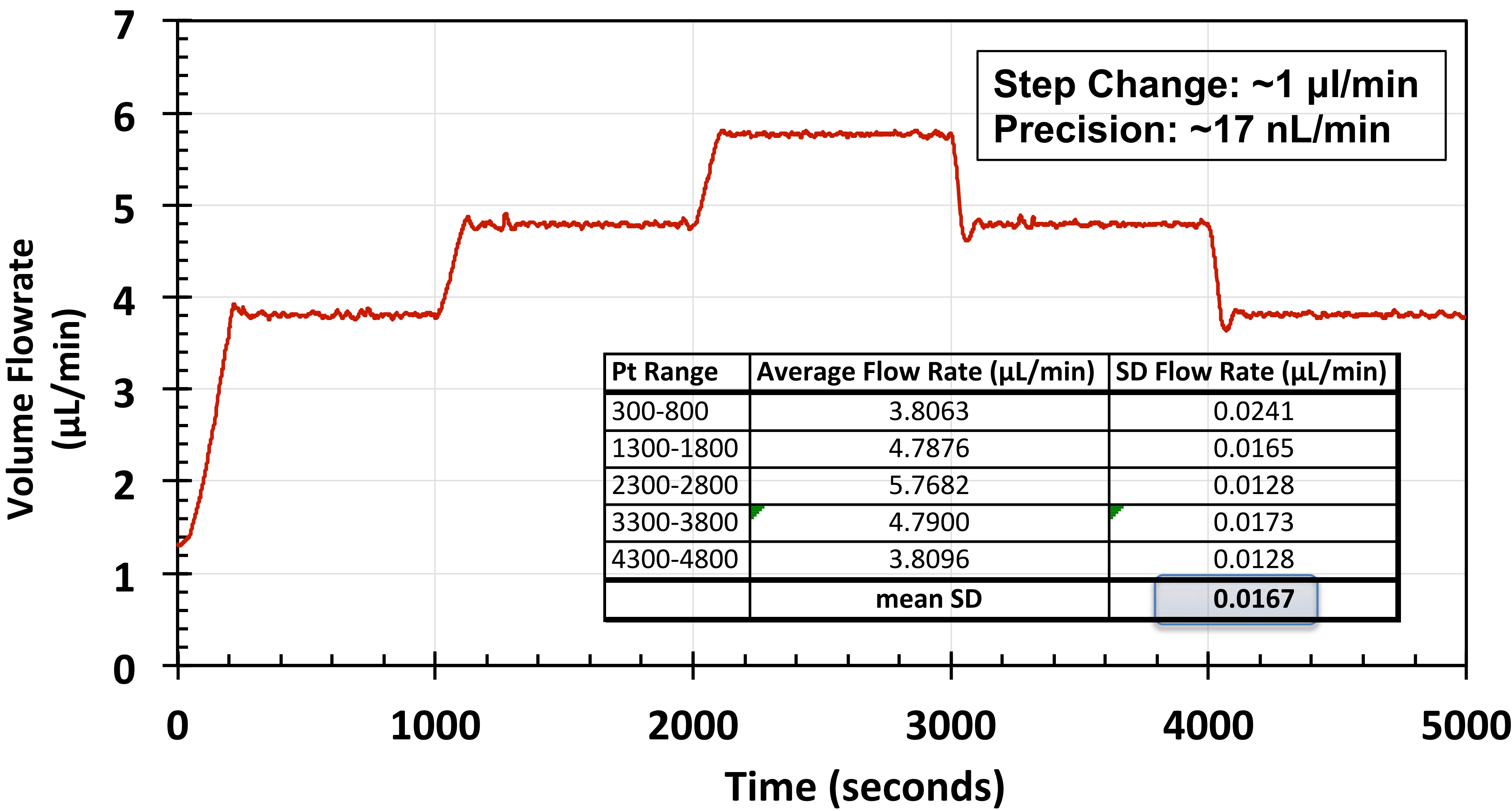


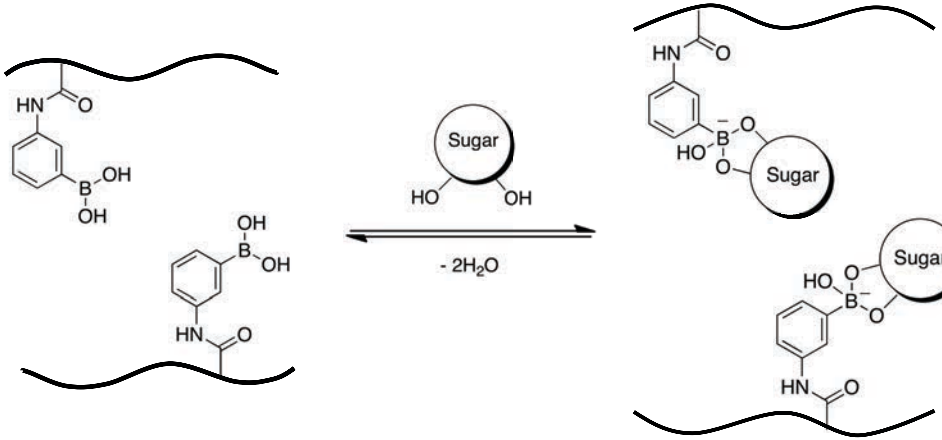
Photo-Controlled Flow Rate

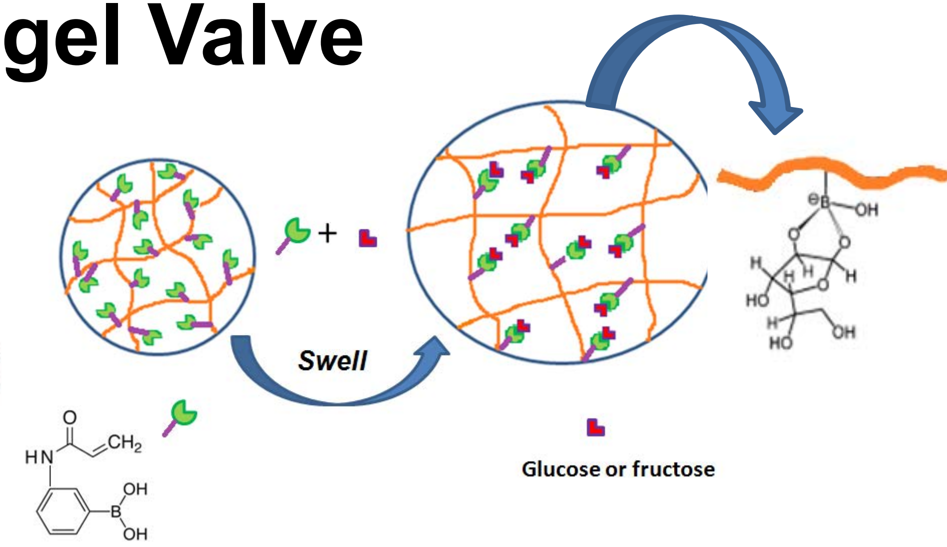


Pt Range	Average Flow Rate (µL/min)	SD Flow Rate (µL/min)
300-800	3.8063	0.0241
1300-1800	4.7876	0.0165
2300-2800	5.7682	0.0128
3300-3800	4.7900	0.0173
4300-4800	3.8096	0.0128
	mean SD	**0.0167**

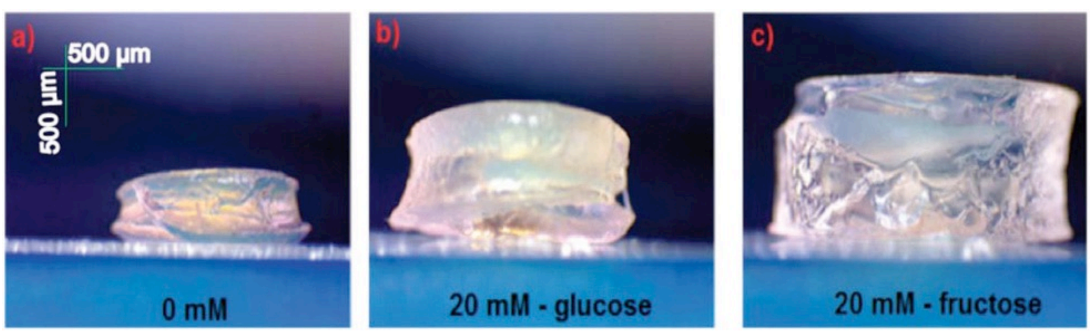
C. Delaney, P. McCluskey, S. Coleman, J. Whyte, N. Kent, D. Diamond, Precision control of flow rate in microfluidic channels using photoresponsive soft polymer actuators, LAB ON A CHIP. 17 (2017) 2013–2021. doi:[10.1039/c7lc00368d](10.1039/c7lc00368d).

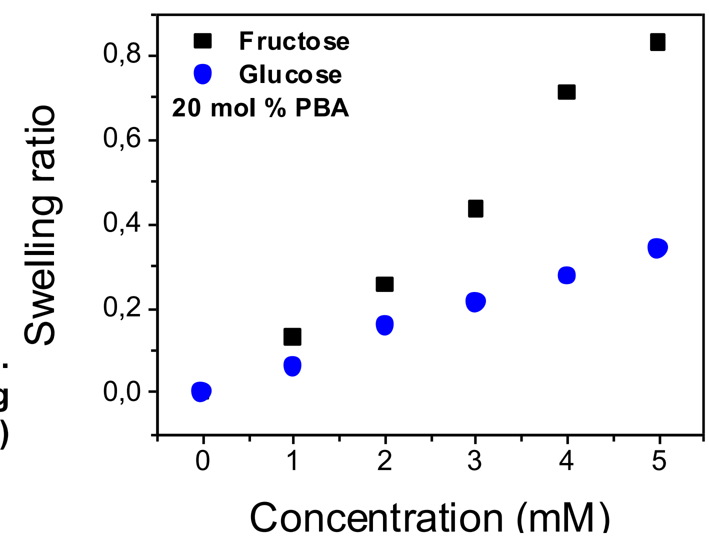
Forget Biosensors: Sugar-Responsive Soft Hydrogel Valve





Acrylamide-*co*-PBA Polymer

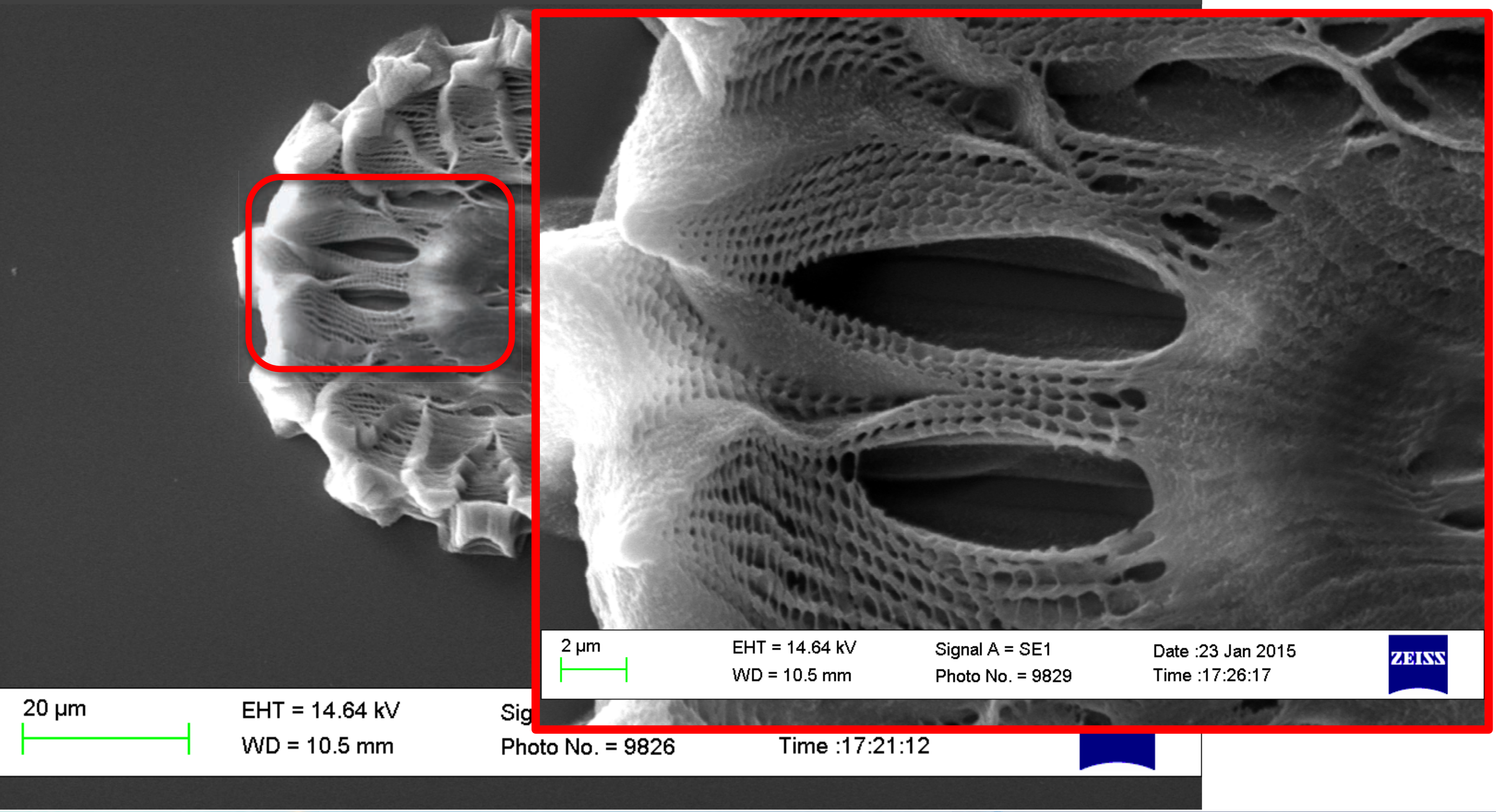




C.M. Daikuzono, C. Delaney, H. Tesfay, L. Florea, O.N. Oliveira, A. Morrin, D. Diamond, Impedance spectroscopy for monosaccharides detection using responsive hydrogel modified paper-based electrodes, Analyst. 142 (2017) 1133–1139. doi:10.1039/c6an02571d.

‘Daisy’ – Micro/Nano Scaled Porous Structure

A. Tudor, C. Delaney, H. Zhang, A.J. Thompson, V.F. Curto, G.-Z. Yang, M.J. Higgins, D. Diamond, L. Florea, Fabrication of soft, stimulus-responsive structures with sub-micron resolution via two-photon polymerization of poly(ionic liquid)s, Materials Today. 21 (2018) 807–816. doi:10.1016/j.mattod.2018.07.017.



February 8, 2019

www.nano-magazine.com
email announcing

'The graphene biosensor that could provide early lung cancer diagnosis'

'The wonder-material graphene could hold the key to unlocking the next generation of advanced, early stage lung cancer diagnosis'

nano
THE MAGAZINE FOR SMALL SCIENCE

Weekly News Round-up: The graphene biosensor that could provide early lung cancer diagnosis, plus much more.

MON, FEB 04

The graphene biosensor that could provide early lung cancer diagnosis

The wonder-material graphene could hold the key to unlocking the next generation of advanced, early stage lung cancer diagnosis.

Nanoscale, 2019, 11, 2476

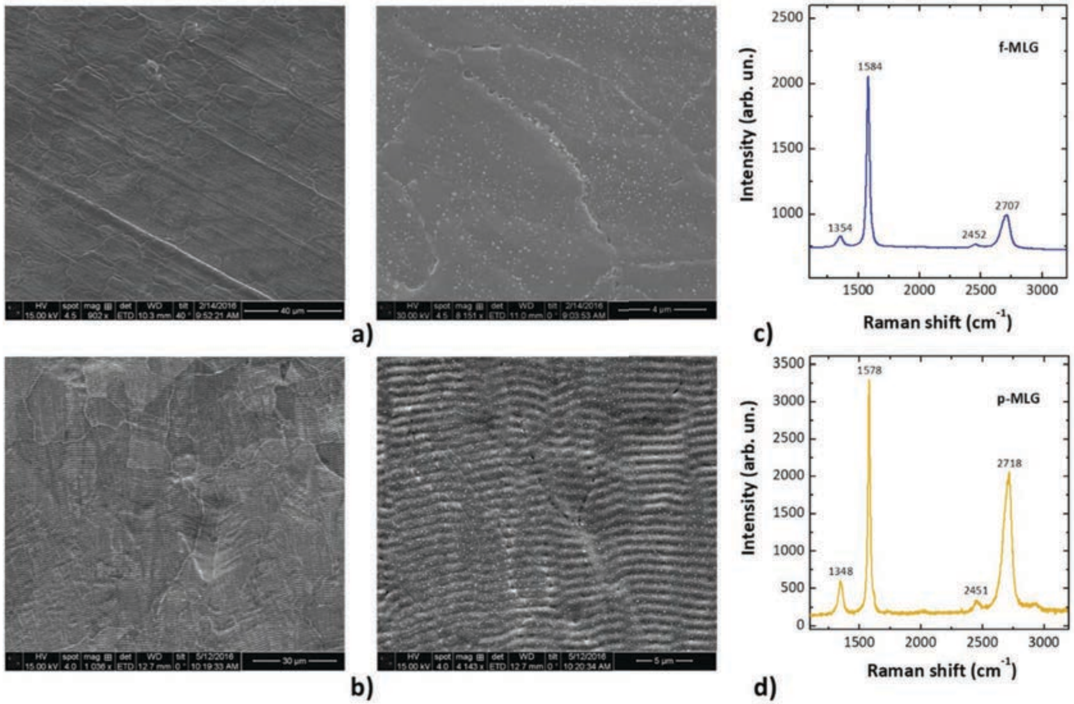


Fig. 2 Characterization of the graphene films. SEM images of the top view of the f-MLG (a) and p-MLG (b) samples on PVC. Raman spectra of the f-MLG (c) and p-MLG (d) performed using a 532 nm laser excitation system with a 40x microscope objective, and 10 s integration time for the single scan.

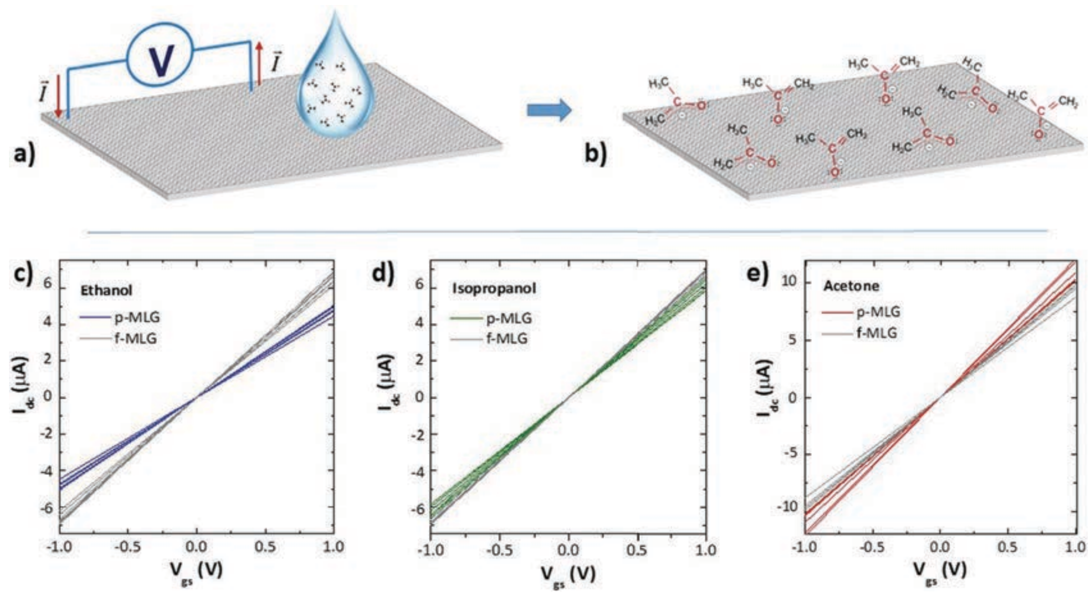
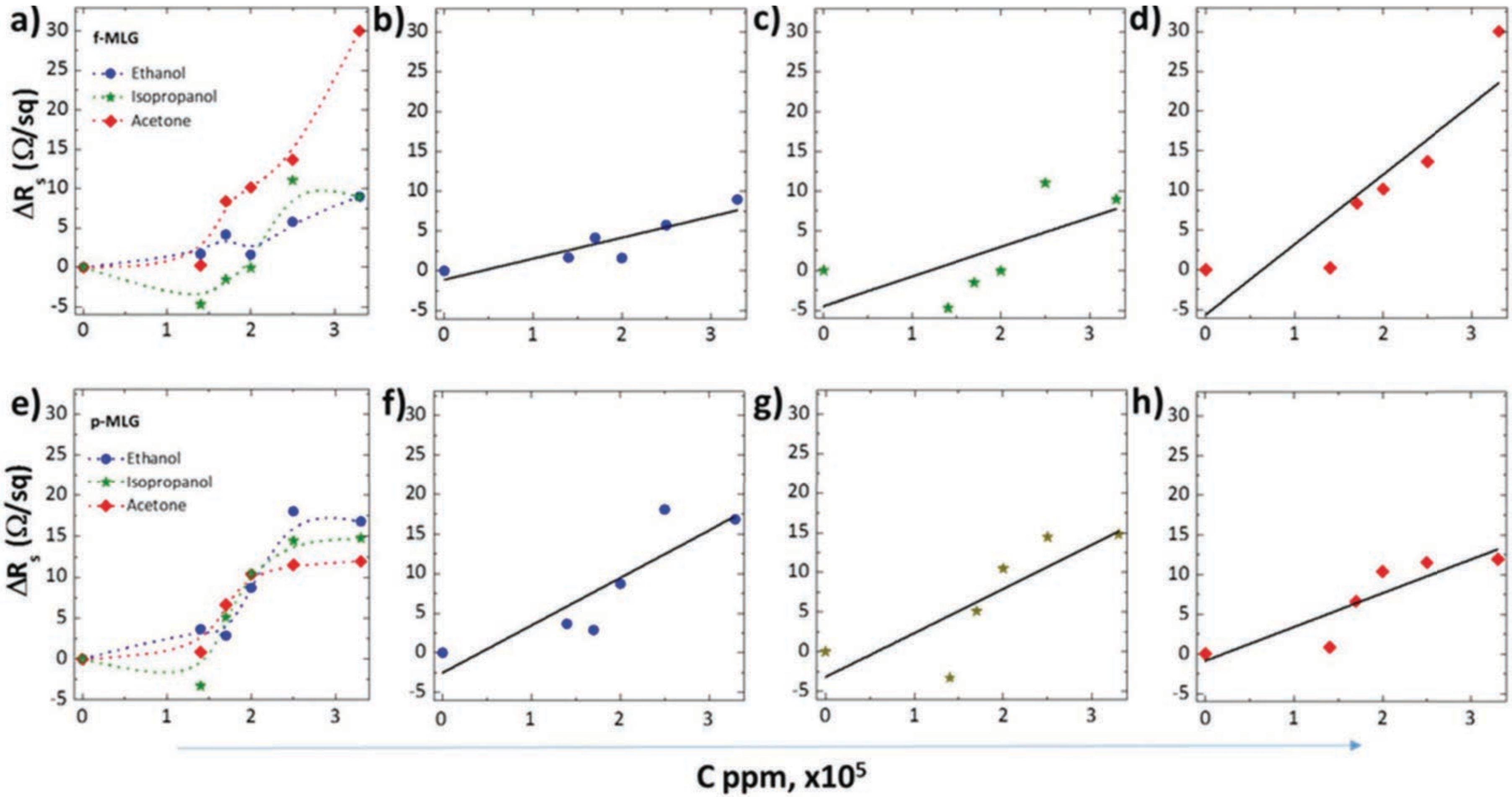


Fig. 3 The schematic representation of the two-point measurement concept (a) for the in situ electrical characterization of VOC-induced graphene electrodes (c, d); electron-induced reorientation of acetone while applying ±1 V (b).
The I_{dc} versus V_{gs} curves of the flat and patterned graphene electrodes influenced with exposure to **1.4–3.3x10^5 ppm** of VOC solutions: ethanol (c), isopropanol (d) and acetone (e).

Response Curves to ‘cancer marker’ VOCs in breath (e-Nose)

Fig. 4 Sensitivity identification of f-MLG (a) and p-MLG (e) electrodes at various concentrations of cancer marker solutions (ethanol – ●, isopropanol – ★, and acetone – ◆). Changes in the value of sheet resistance (ΔR_s) for f-MLG (b–d) and p-MLG (f–h) as a function of CM concentration.



Massive concentrations (0-30%!), no selectivity, bare graphene (no surface functionalization), no humidity studies…….

Merging of Materials, Devices and Data

Data and Information; IOT

Outside: On-Body

- Smart Bandages
- Sensorised Contact Lens
- platforms patches/watches
- Sensorised Splints/dentures
- Smart Textiles/Clothing

Inside: Implants/In-vivo

- Smart Stents
- Self-Aware Transplant
- Platforms and Implants
- Post-Operative IC (days)
- Medium term Convalescence (weeks)

Devices and Platforms

MATERIALS

Physics Chemistry Biology Engineering

(photonics, electronics, fluidics, 4D materials)

Thanks to…..

- NCSR, DCU
- Science Foundation Ireland & INSIGHT Centre
- Enterprise Ireland (IPP Shimmer, IPP TELLABs)
- Research Partners – academic and industry
- EU Projects: NAPES, CommonSense, Aquawarn, Holifab

MASK
Project no: 269302
Materials and Advanced Sensor Knowledge Exchange

Thanks for the invitation!

SEVENTH FRAMEWORK PROGRAMME
MARIE CURIE ACTIONS
MASK
Project no: 269302
Materials and Advanced Sensor Knowledge Exchange
NAPES
NEXT GENERATION ANALYTICAL PLATFORMS FOR ENVIRONMENTAL SENSING
COMMON SENSE
MARINE SENSORS - MARINE MONITORING
aquawarn

sfi DCU UCC OÉ Gaillimh NUI Galway UCD DUBLIN