Gold nanowires as future low power sensors

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Nanotechnology Group

27th October 2011

Ireland's EU Structural Funds Programmes 2007 - 2013
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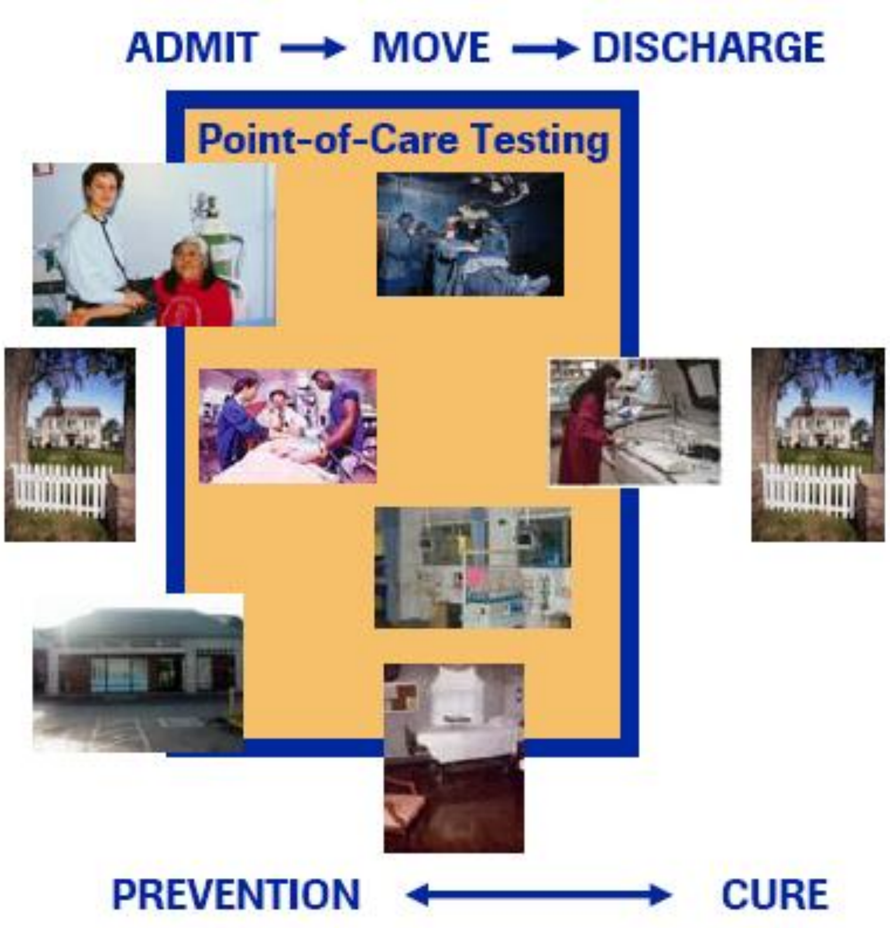
UCC
Coláiste na hOllscoile Corcaigh, Éire
University College Cork, Ireland

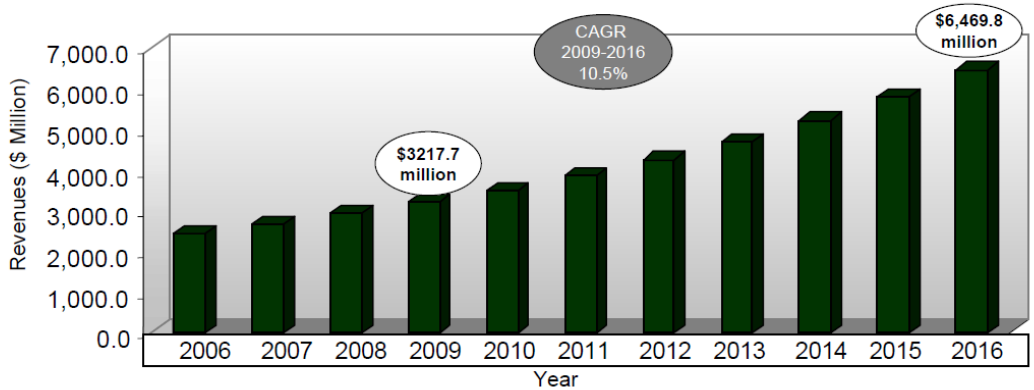
Health Care Trends

- On-site testing
  - From the hospital to GP to home.
- Tests answering urgent questions:
  - Acute and chronic disease.
  - Rapid diagnosis
  - Therapeutic monitoring.
- Specific test needs
  - Fast & cheap
  - Simple to use
  - Reliable and reproducible results.
  - Simultaneous measurement
  - **Free from expensive Fluorescent Labels.**
- New markets opening up



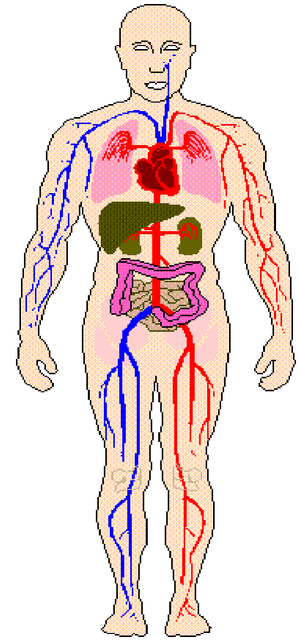
Global Biosensor Market Revenue Forecast

Point of Care (POC) Biosensor Market: Revenue Forecasts (World), 2006-2016



Note: All figures are rounded; the base year is 2009. Source: Frost & Sullivan

- Revenues in POC market expected to reach $6.5b by 2016



POC market requirements:

- Convenient, easy to use and low maintenance requirements
- Low cost (few cent – few dollars)
- Provide rapid (<5 min), robust analysis
- Detection limits same or better than clinical environment
- Low power - disposable

- **Nanosensor devices offer a potential solution to these needs**

Abbott i-STAT portable clinical analyser

- Blood gases
- Electrolytes
- Hematology
- Coagulation
- Cardiac Markers

http://www.abbottpointofcare.com

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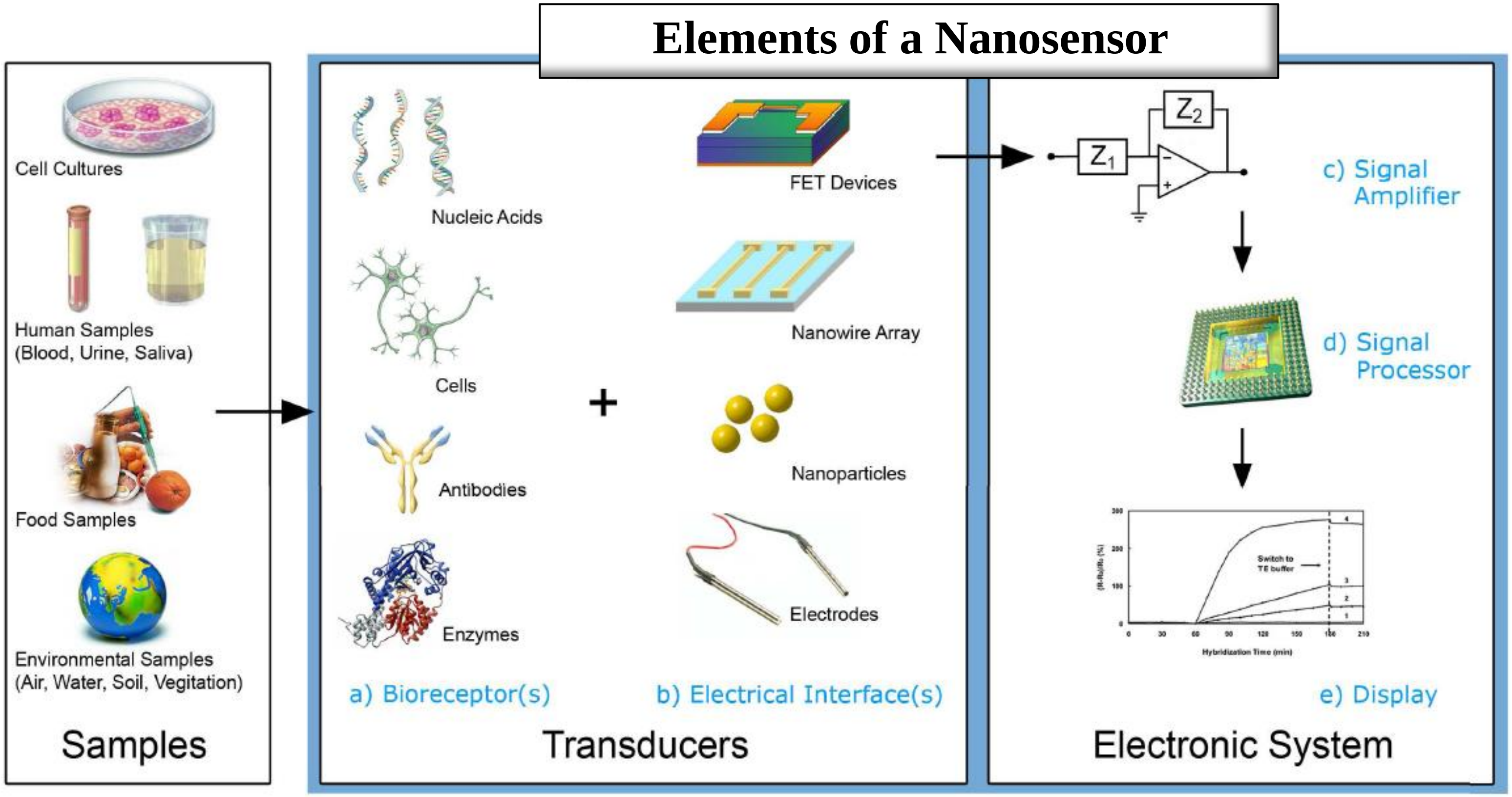

At the nanoscale:

- Sensor elements are of similar length scales to analytes
  - Lower limits of detection
  - Increased sensitivity & selectivity

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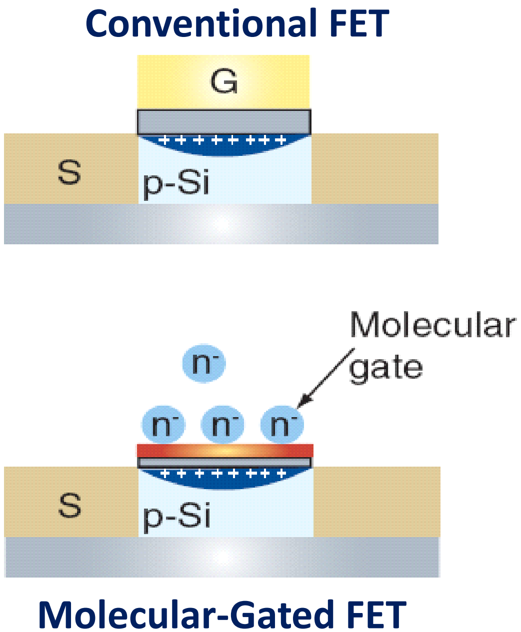
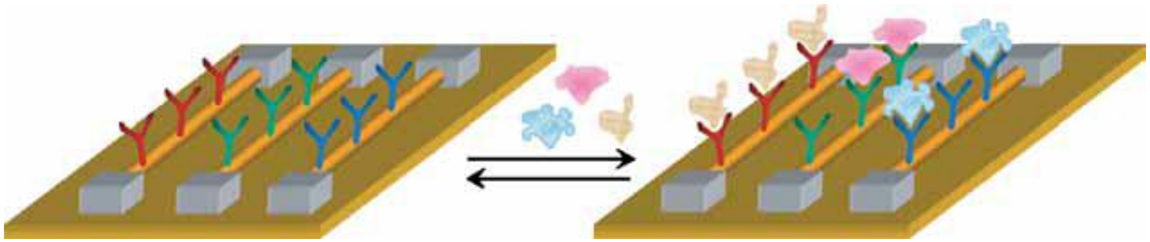
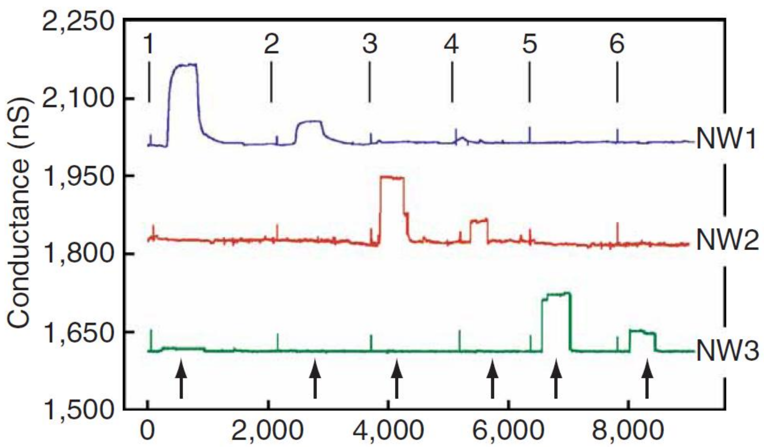
On-Chip Label Free Nanosensing: SOA





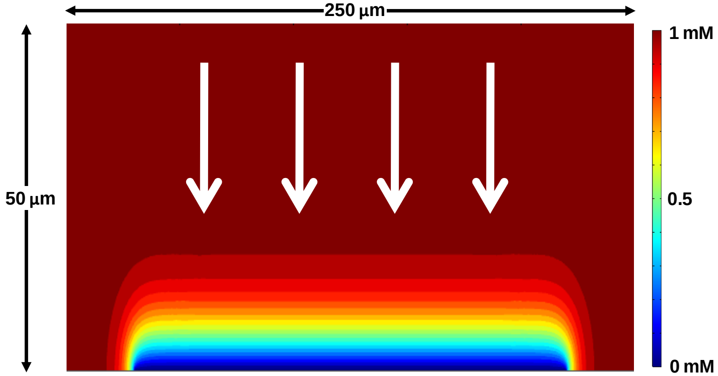


- **Dominant paradigm:** FET based sensing approaches (Si NW / CNTs).
- Highly sensitive detection of biomolecule including DNA, Viruses demonstrated (Vista Therapeutics).
- Complex fabrication approaches ➔ limited industrial take-up.
- Sometimes require for high back gate applied voltages (10 – 25 V).

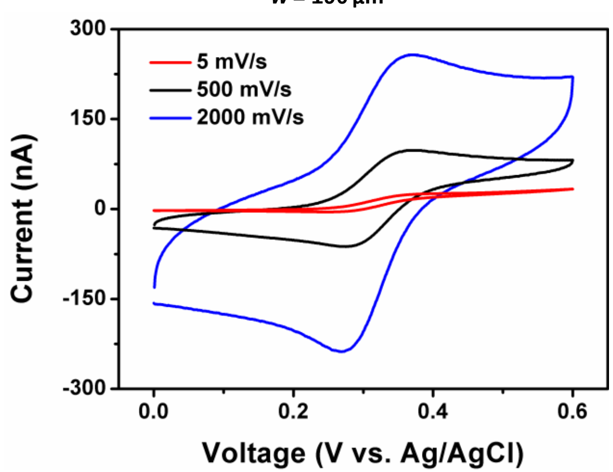
Lieber C. et al.
Nature Biotech. 23 (2005) 1294

Electroanalysis at the Nanoscale

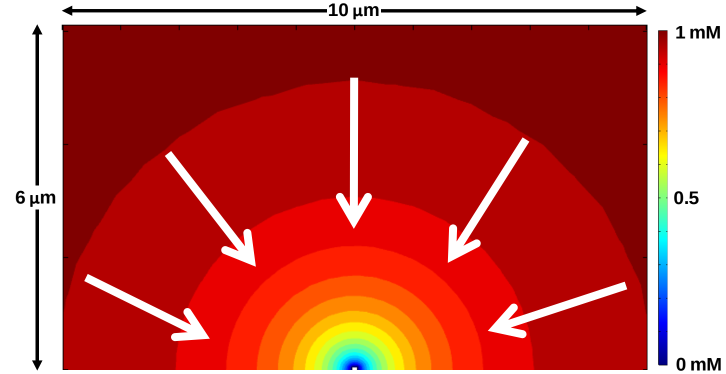
Planar Diffusion



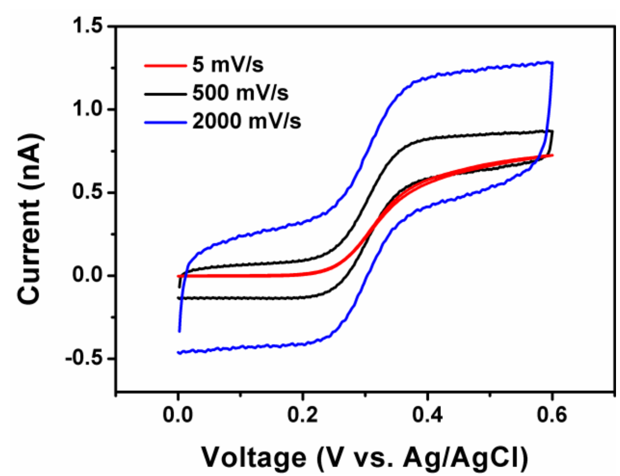
Micro-square Electrode:
w = 190 µm



Radial Diffusion



Single Nanowire:
w = 100 nm, *h* = 50 nm



- At the nanoscale, radial analyte diffusion profiles dominate:
  - Increased in mass transport, improved current density → Higher S/N ratios
  - Steady-state measurements enable analysis at faster time intervals

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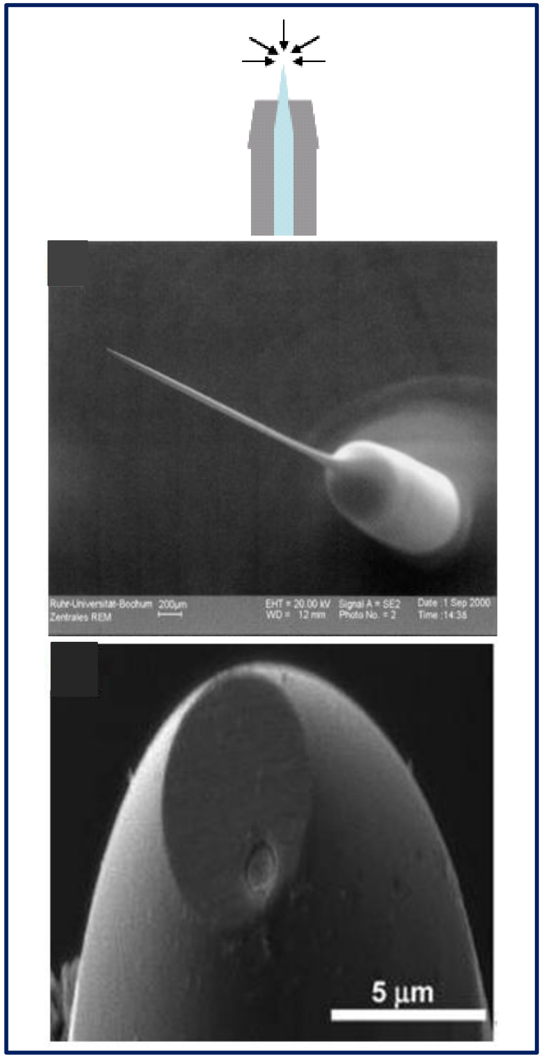
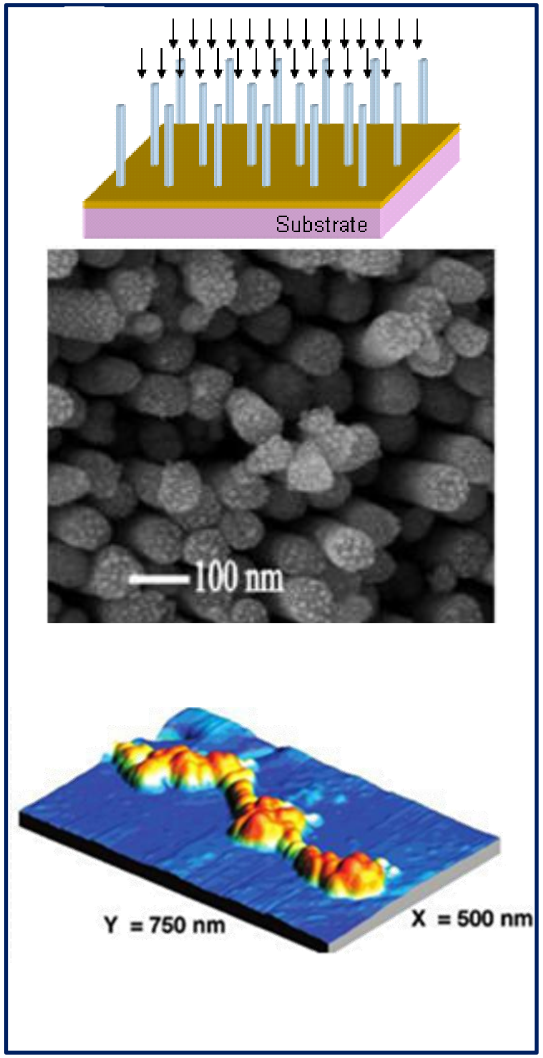
State Of Art – Nanoscale Electrodes

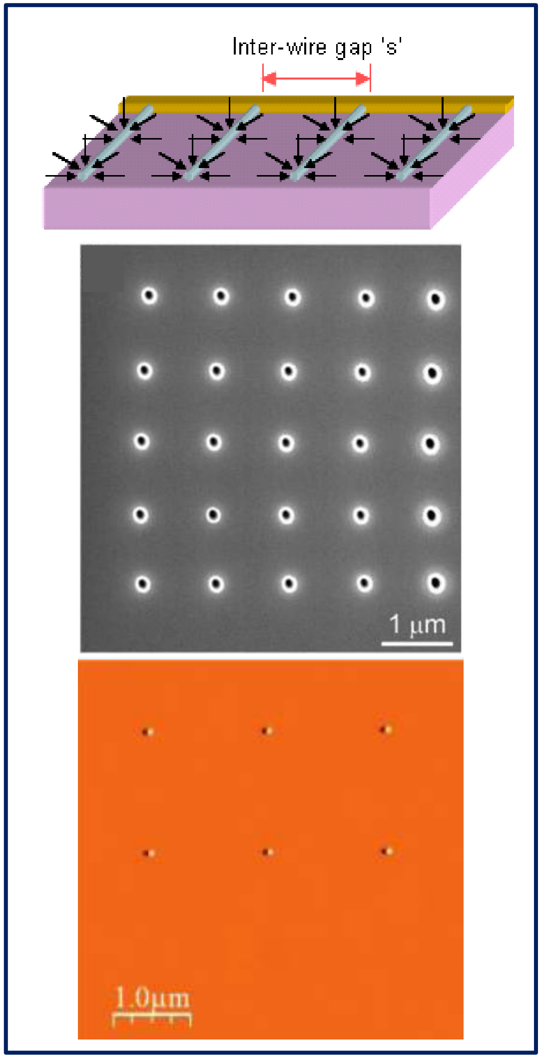
Single Nanoelectrodes



Nanoelectrode Ensembles



Nanoelectrode Arrays



Tyndall National Institute

Nanowires for sensing

Generation 1

- Single NW Electrode
- Bottom Up Approach
- Facile Integration
- In-depth Analysis
- Suitablity to Sensing

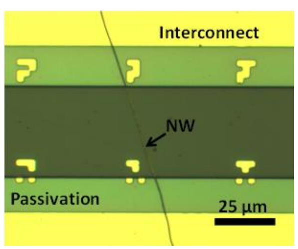
Generation 2

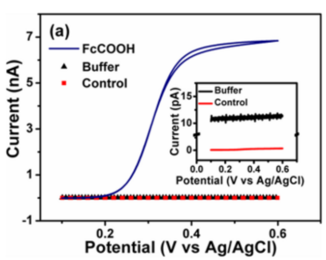
- Benchmark Gen 1
- Top Down Approach
- Reproducibility
- In-depth Analysis
- Glucose Detection

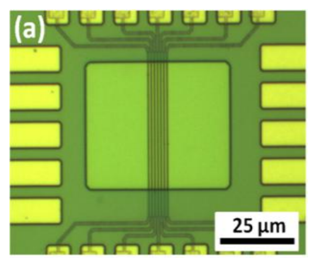
Generation 3

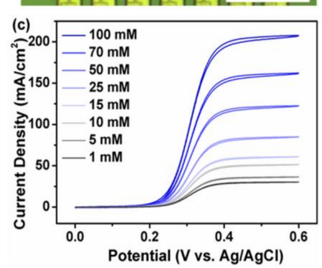
- Top Down Approach
- Platform Development
- Single NWs → Arrays
- Reduced packaging
- On-chip Counter Electrodes

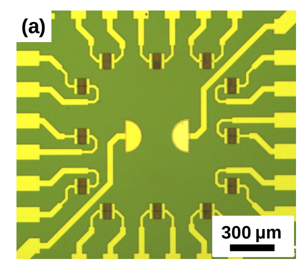
Development of Nanowire Electrochemical Devices

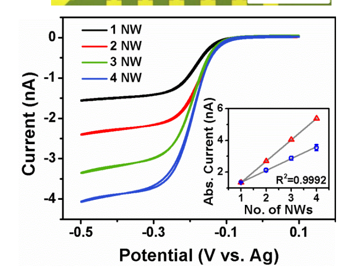












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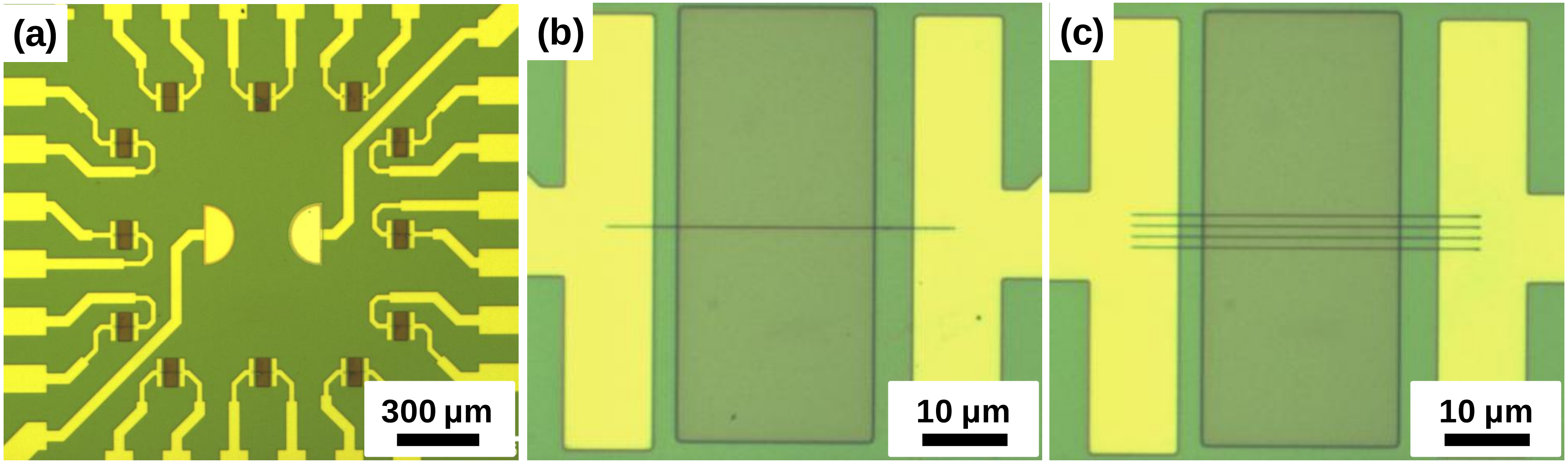
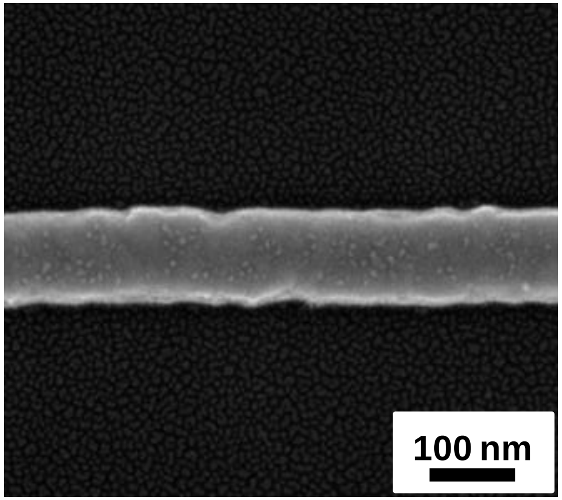
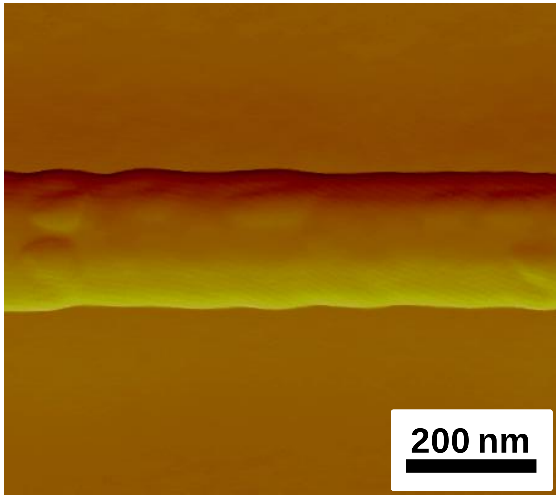
Nanowire Array Fabrication

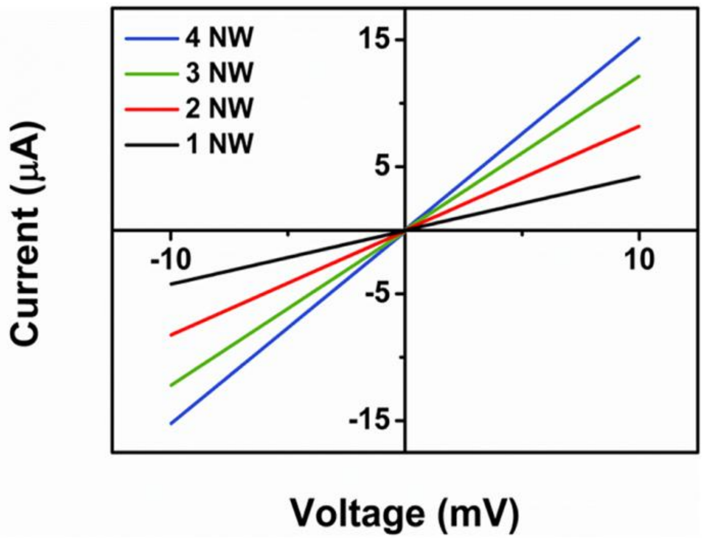


- Single nanowire electrodes and arrays of nanowire electrodes (2, 3 and 4 nanowires)
- Nanowire construction: 5 nm/50 nm Ti/Au
- Interelectrode distance in arrays ~ 2 μm
- On-chip Au counter electrodes located in the centre of device
- Silicon Nitride passivation layer ~ 500 nm thick

Gen 3: Structural and Electrical Characterisation







- Nanowire dimensions: width ~ 100 nm, height ~ 50 nm
- Nanowires and nanowire arrays displayed Ohmic electrical responses
- Increasing conductance was observed with increasing nanowires in array
- Average resistance for single nanowire was ~ 2050 ± 160 Ω
- Average resistance for array of 4 nanowires ~ 360 ± 160 Ω

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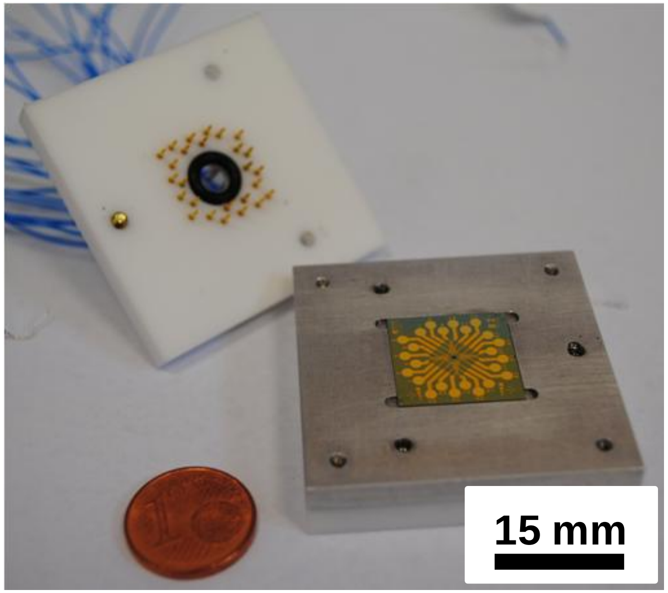
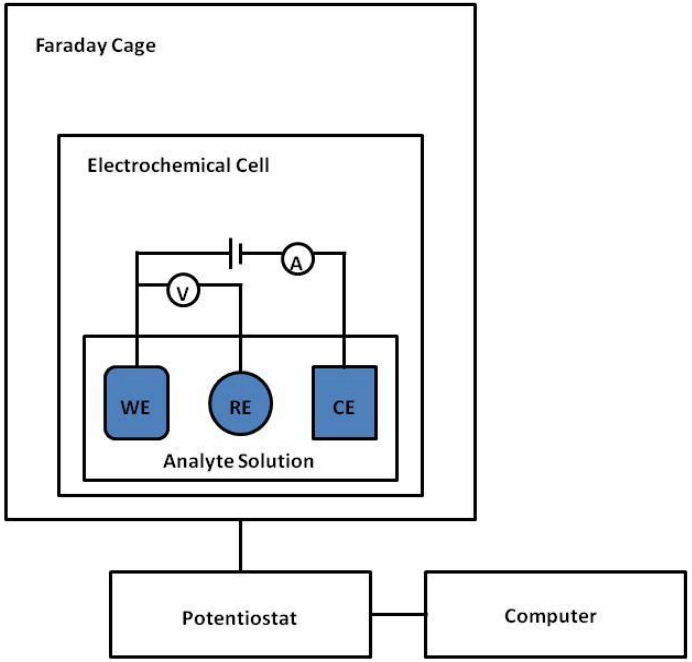
Characterisation of Nanowire Arrays



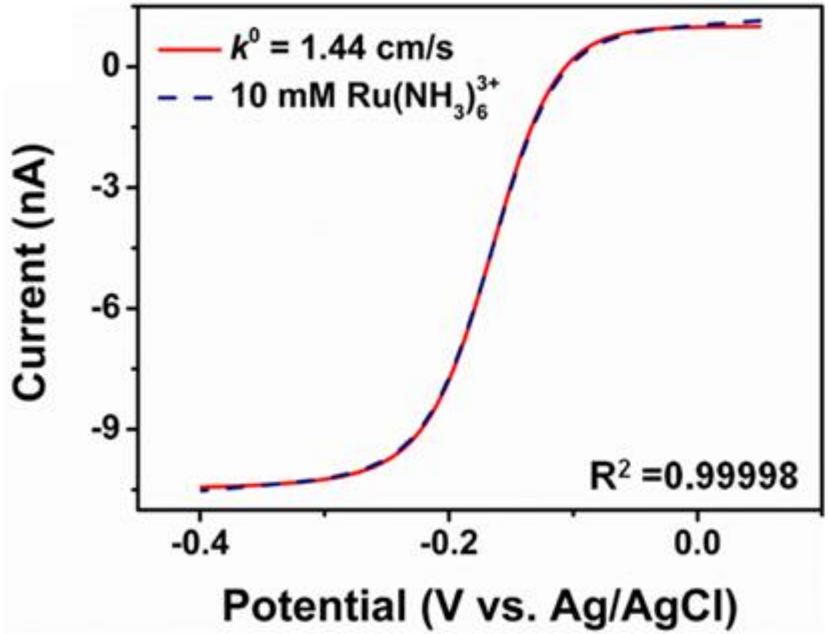


- Novel electrochemical cell removes packaging requirements
- Electrochemical cell volume ~ 150 µL
- Steady-state reductive voltammetric responses in 1 mM $Ru(NH_3)_6^{3+}$ in 10 mM PBS
- Average cathodic current at single nanowire: -1.355 ± 0.032 nA
- Low background current observed in buffer solutions only

Reduction Kinetic Studies

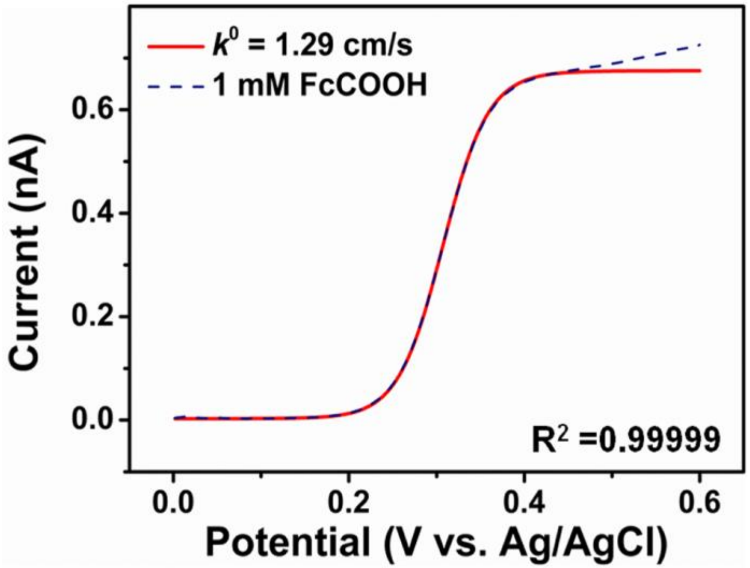
$$k_{red} = k^0 e^{-\alpha F(E-E^{0'})/RT}$$

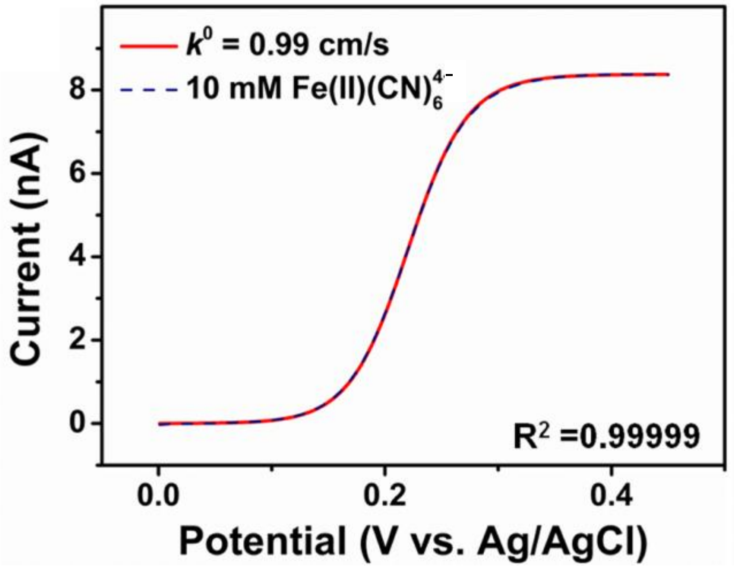
$$i_{bv} = \frac{i_{mt}}{1 + e\left[\frac{-F(E-E^{0\prime})}{RT}\right] + \frac{m}{k^0} e\left[\frac{\alpha F(E-E^{0\prime})}{RT}\right]}$$



- Reduction of $Ru(NH_3)_6^{3+}$ at nanowire electrodes was found to be excellently described by Butler-Volmer kinetics
- An average k^0 value of 1.2 cm/s was determined
- Values consistent with those reported

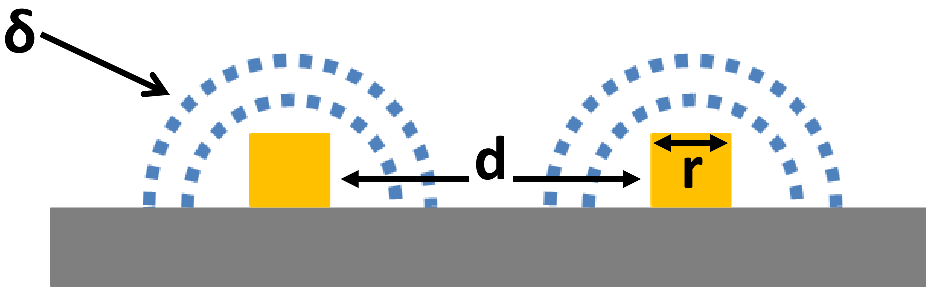
Oxidation Kinetic Studies

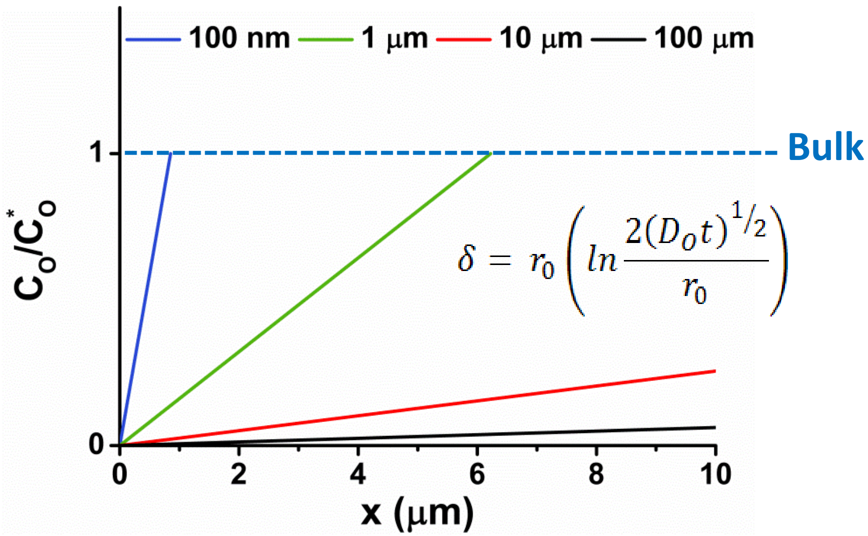




- Single electron oxidation reactions of FcCOOH and Fe(CN)$_6^{4-}$ excellently described by Butler-Volmer kinetics
- High k^0 values determined in both cases indicates rapid electron transfer to nanowires
- Values observed for FcCOOH consistent with values observed at nanoskived nanowires
- k^0 values for Fe(CN)$_6^{4-}$ consistent with that reported for nanodisk electrode of radius ~11 nm

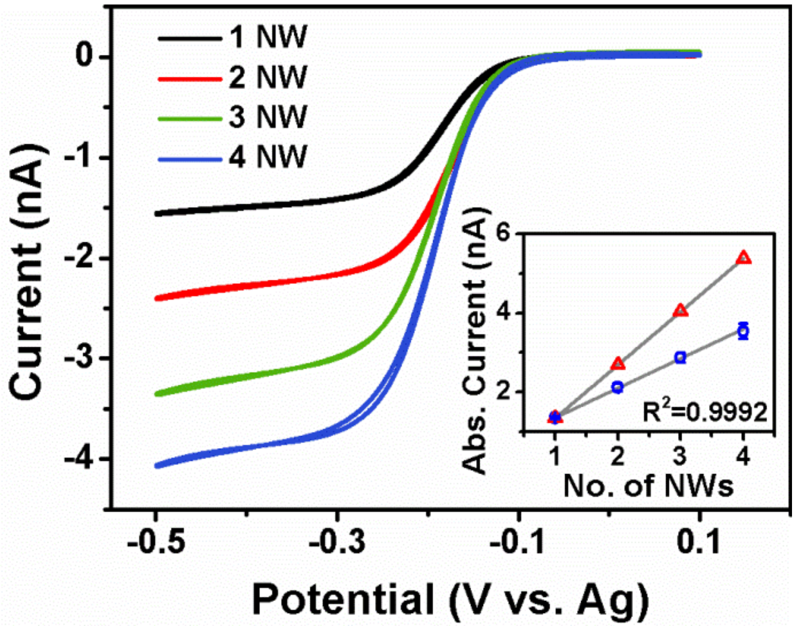
Diffusion to Nanoelectrode Arrays





- Nernst diffusion layer is distance to bulk concentration from electrode.
- In arrays neighbouring diffusion profiles should not overlap.
- Estimated thickness of diffusion layer for single nanowire was ~ 850 nm for r_0 = 100 nm
- Nanowire Arrays designed with 2 µm spacing → **d > 2δ**

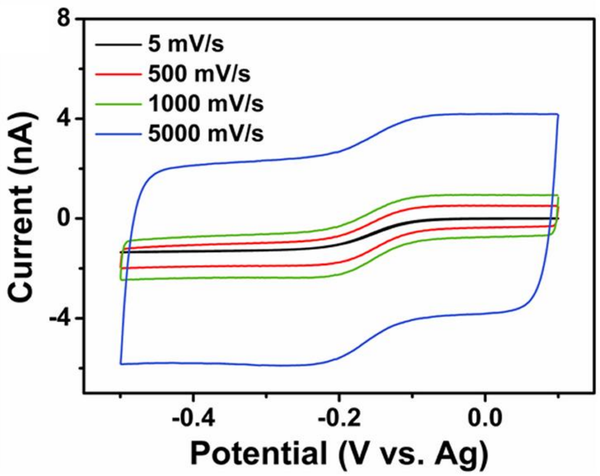
Cyclic Voltammetry at Nanowire Arrays

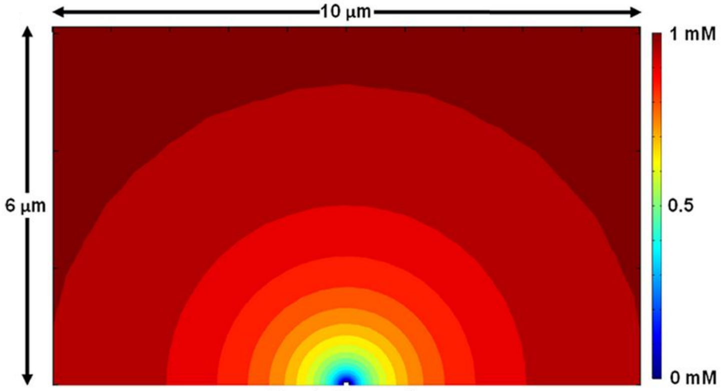


- Steady-state current was observed at all arrays.
- Increased current was measured with increasing nanowires in array.
- However measured current at 4 nanowires ≠ 4 x 1 nanowire.
- Indicates that interelectrode spacing of ~ 2 µm may not be sufficient to provide independent diffusion to each electrode in the array.

Analysis of Diffusion Processes

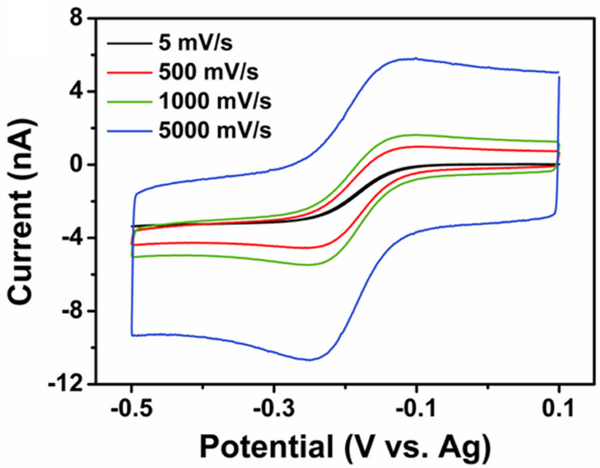
Single Nanowire Electrode

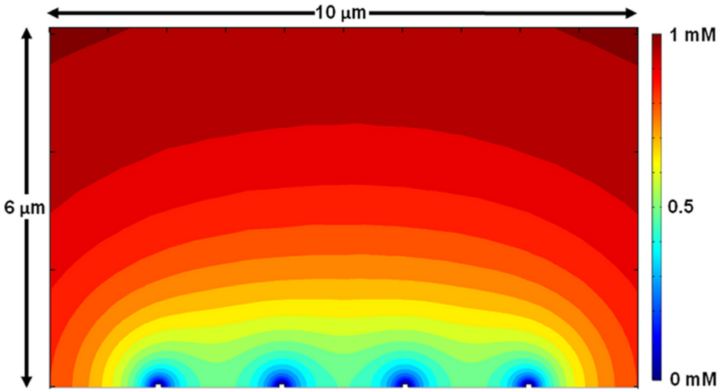




Single Nanowire:
w = 100 nm, *h* = 50 nm

4 Nanowire Electrode Array

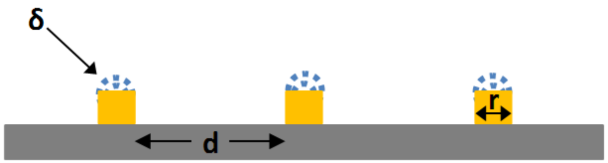




Four Nanowire Array:
w = 100 nm, *h* = 50 nm, *d* = 2000 nm

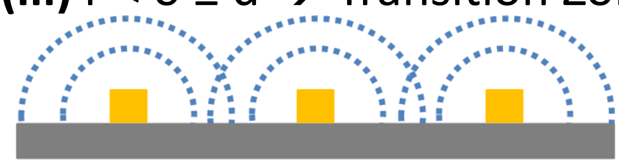
Diffusion Processes at Nanowire Arrays

(i) δ« r → Planar Diffusion

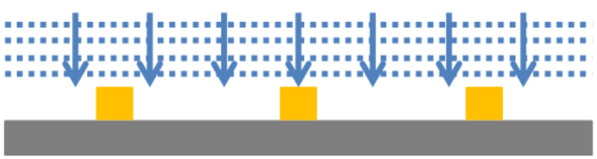


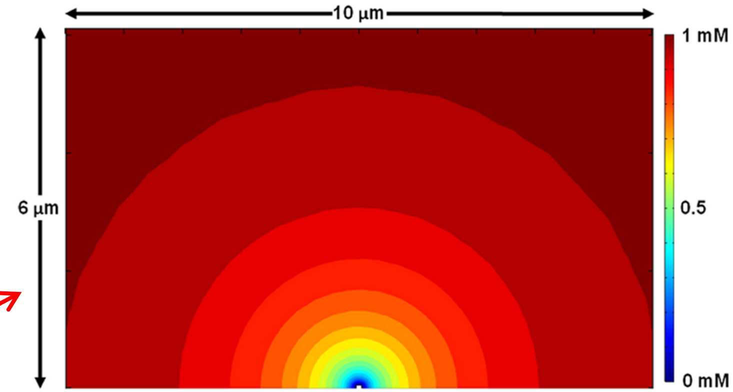
(ii) δ = r < d→ Radial Diffusion

(iii) r < δ ≤ d → Transition Zone



(iv) δ» d → Planar Diffusion



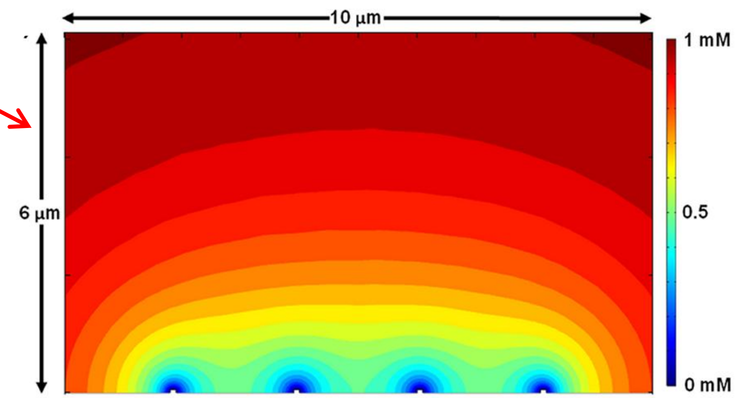


Single Nanowire:
w = 100 nm, *h* = 50 nm

δ = diffusion layer thickness

r = critical dimension

d = interelectrode distance

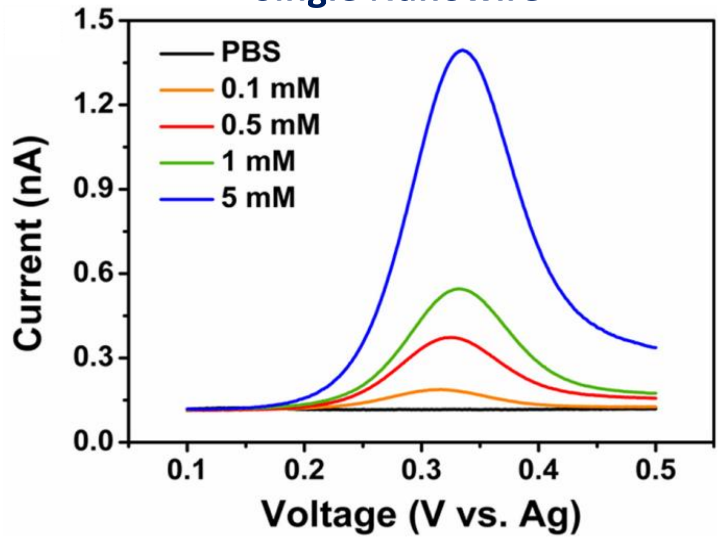


Four Nanowire Array:
w = 100 nm, *h* = 50 nm, *d* = 2000 nm

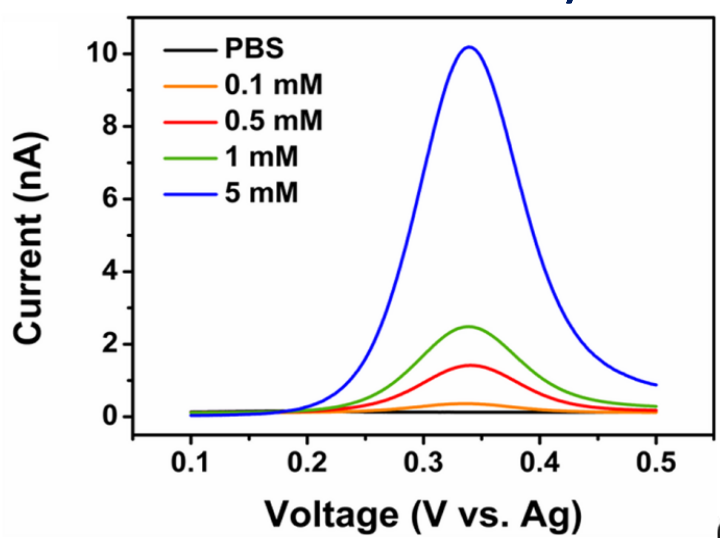
SWV at Single Nanowires and Arrays

- Square Wave Voltammetry is commonly used electroanalytical technique
  - Increased Faradic signal
  - Reduced Capacitive signal
  - Higher S/N
  - Lower detection limits
- SWV in range of concentrations of FcCOOH in 10 mM PBS
- Peak current for **single nanowire in 5 mM ~ 1.4 nA**
- Peak current for **4 NW Array in 5 mM ~ 10.2 nA**
- Peak current at **4 NW Array > than 4 x 1 NW**
- Demonstrates suitablity of arrays towards sensing

Single Nanowire



4 Nanowire Array



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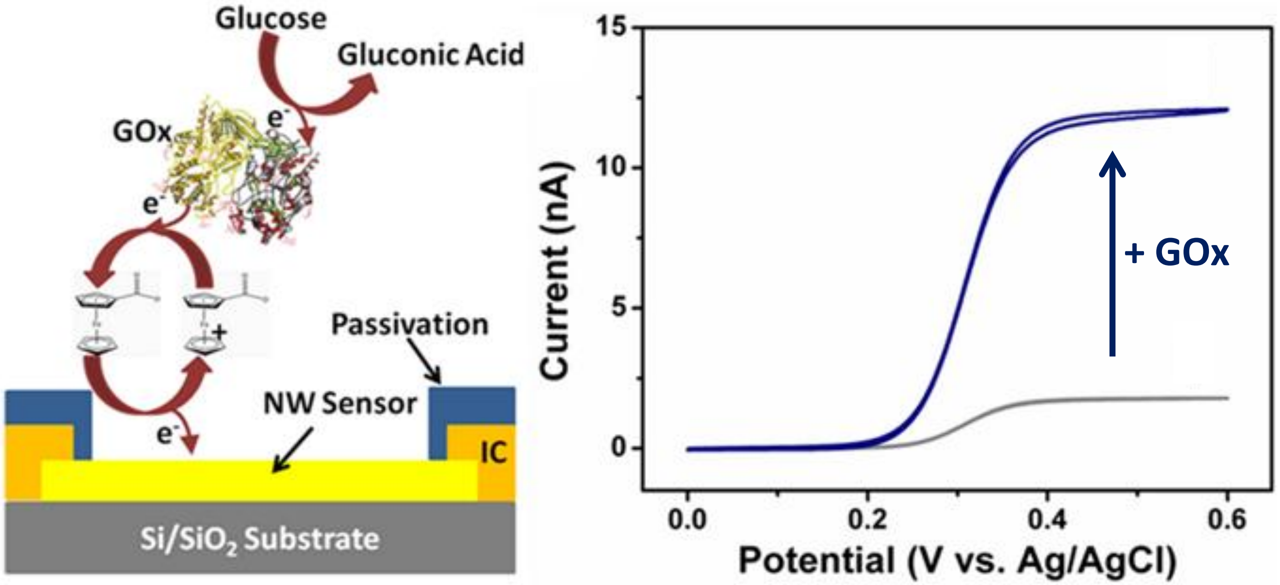
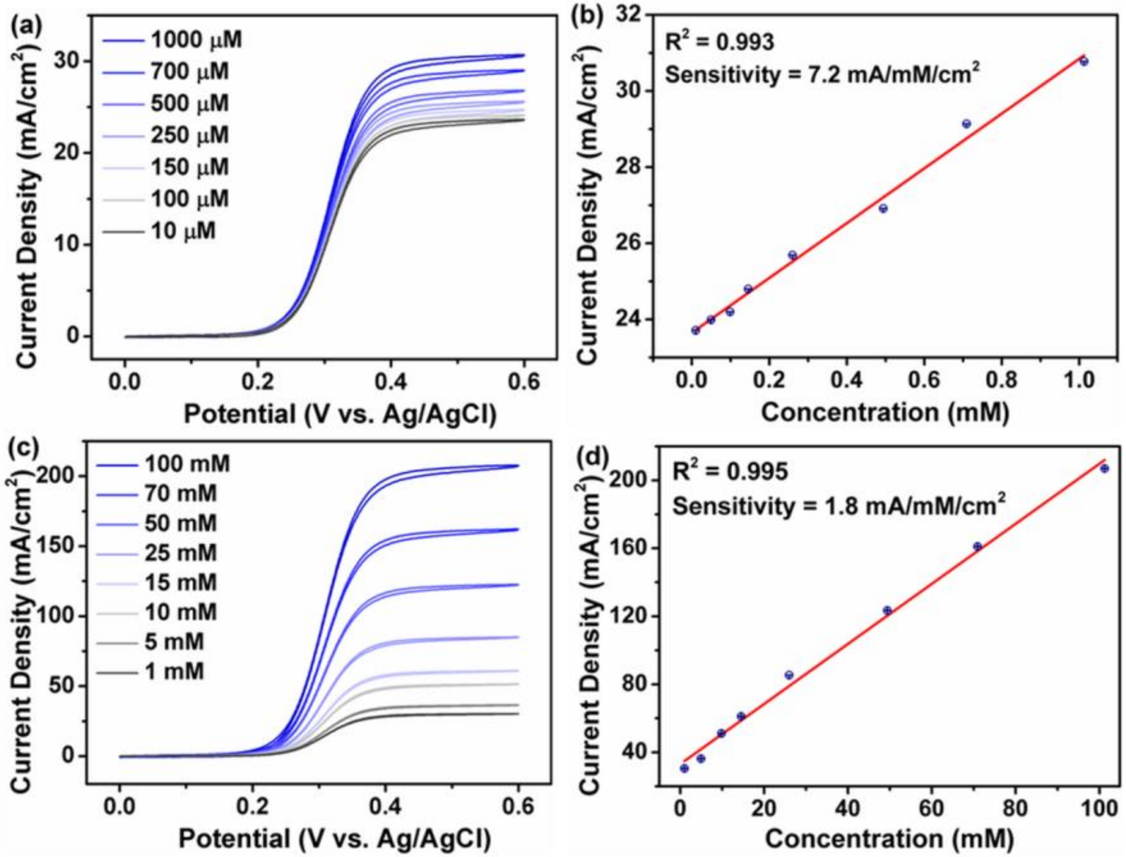
Mediated Glucose Detection



- Enzymatic detection of Glucose via Glucose Oxidase in the presence of a mediator, FcCOOH
- Redox Mediated detection:
  - Increases measureable signal
  - Reduces overpotentials required to oxidise Glucose
  - Reduces contributions from interfering species
- In absence of GOx, only FcCOOH signal measured in the presence of Glucose

Glucose Detection at Single Nanowires



- Measurement range : 10 µM – 100 mM Glucose

Lower linear range 10 µM–1 mM:

- LOD~ 3 µM
- High sensitivity ~ 7.2 mA/mM/cm^2

Upper linear range (1 mM–100 mM):

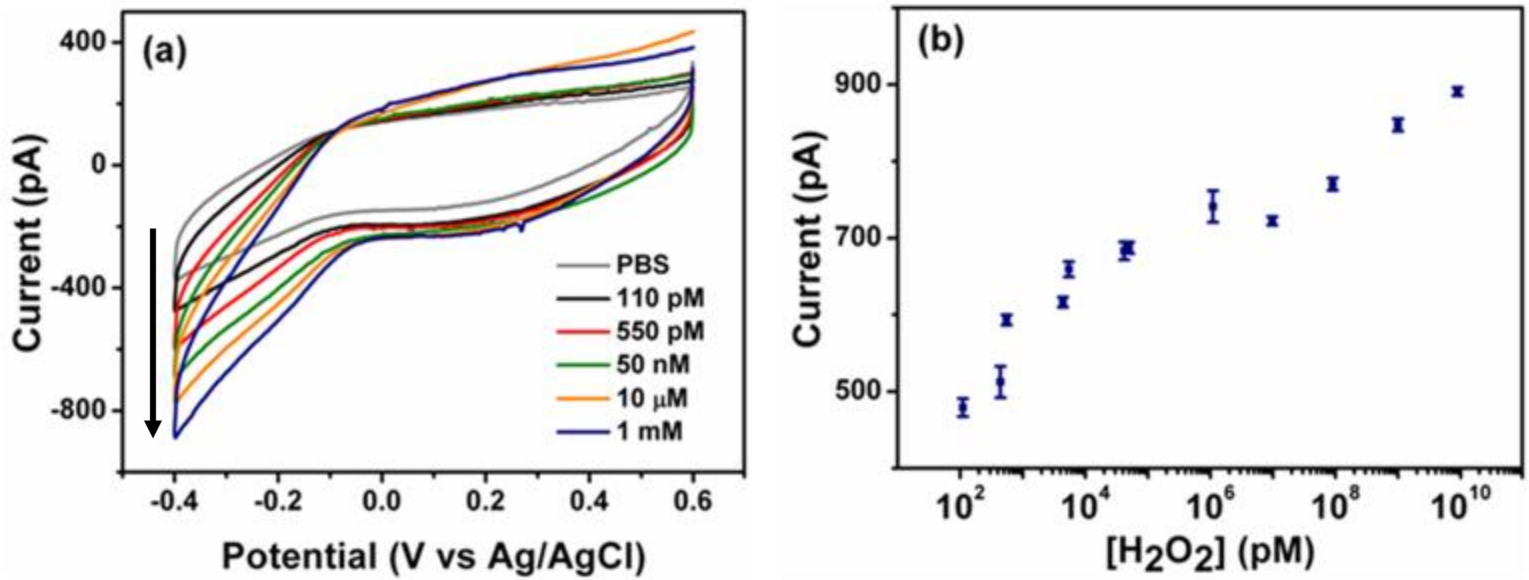
- LOD: ~17 µM
- Sensitivity ~ 1.8 mA/mM/cm^2

- Nano-SOA: ~0/005 mA/mM/cm^2

- Blood glucose required detection range: 0.5 mM – 15 mM
- Alternative media e.g. saliva or tears: ~100 µM – 500 µM

K. Dawson, et al, *Analyst,* **2011,** 136 (21), 4507-4513.

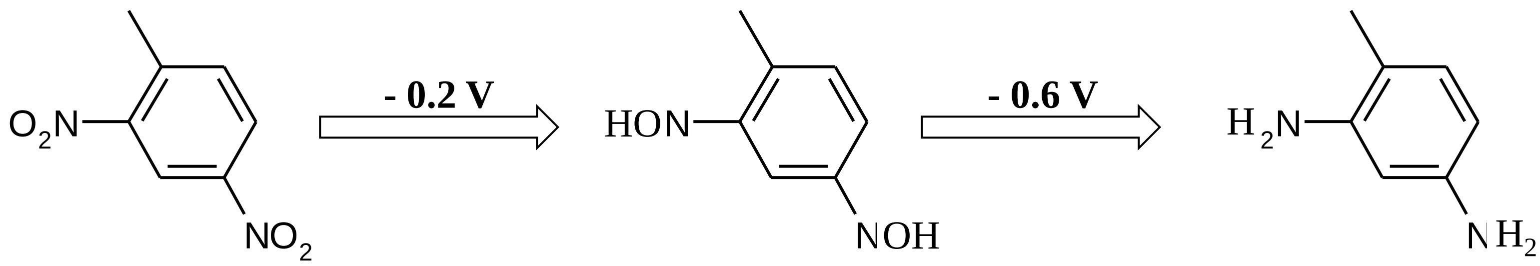
Hydrogen Peroxide Detection



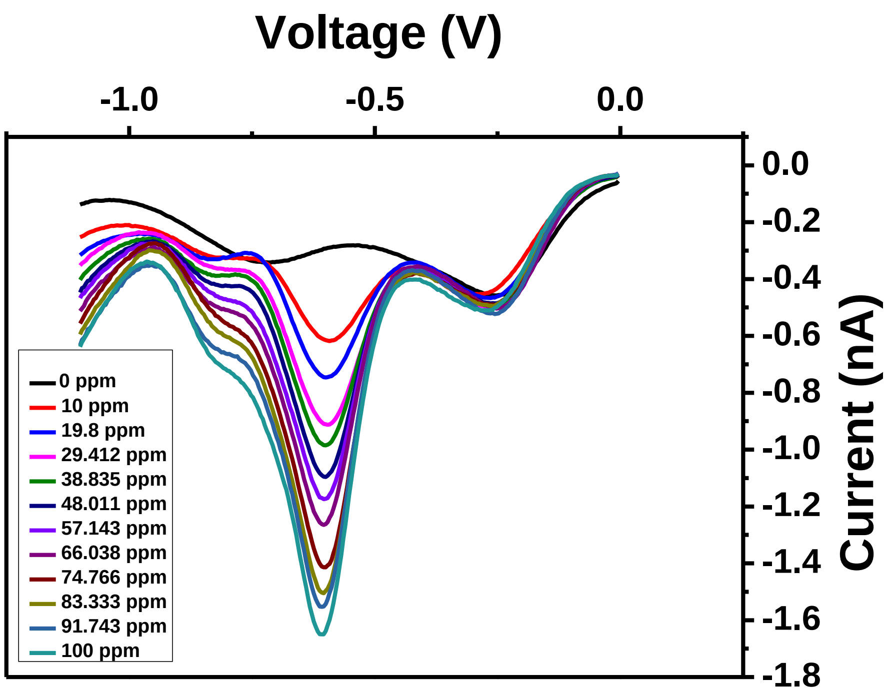
- H_2O_2 key target analyte: environmental analysis, food spoilage, biomedical applications & homeland security
- Requires low detection limits over wide concentration range
- CV of H_2O_2 exhibits a reductive peak at -0.4 V vs. Ag/AgCl in 100 mM PBS, pH 7.0
- Detection range 10^{-10} to 10^{-2} M, lowest concentration detected 110 pM
- Comparative to detection limits observed for modified electrodes (Prussian blue, HRP)

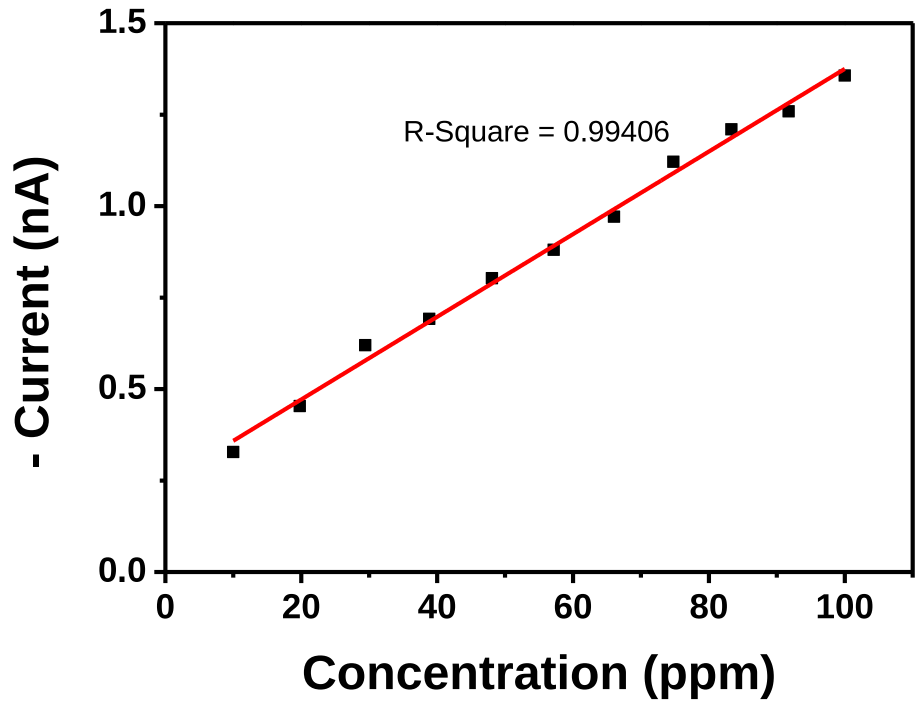
K. Dawson, et al *Anal. Chem., 2011, 83, 5535-5540.*

Electrochemical-based DNT detection in H_2O

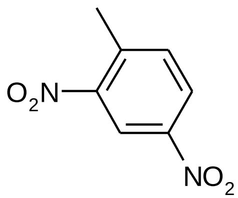
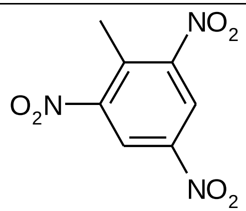
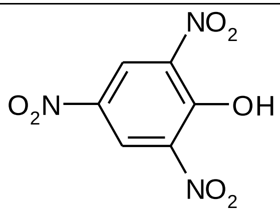
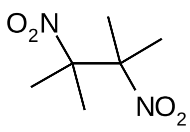
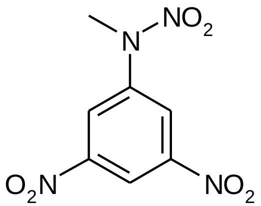
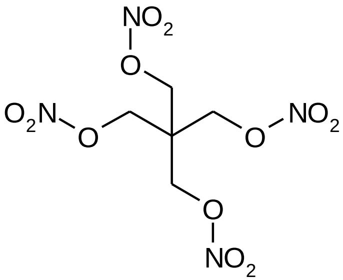
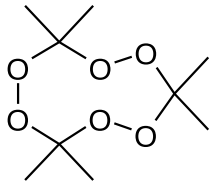
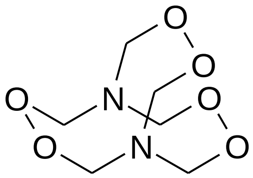


2,4-Dinitrotoluene (DNT)



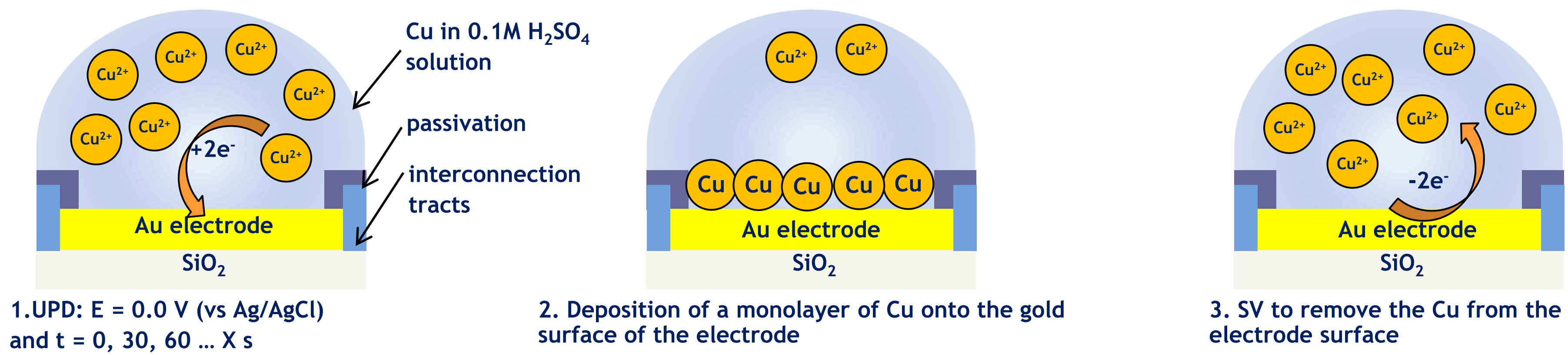


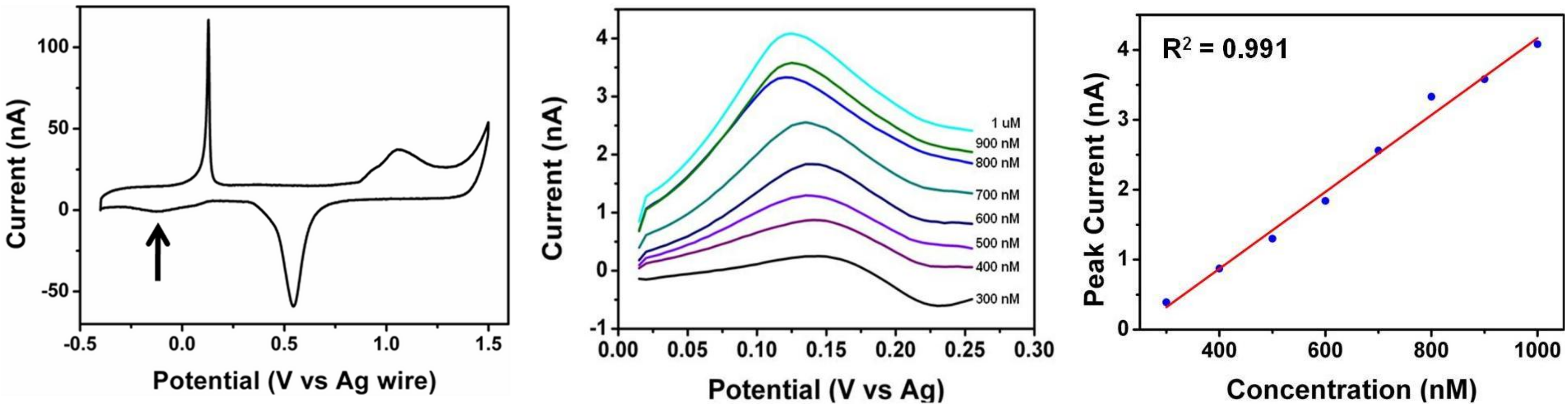
Explosive Compounds

 2,4-Dinitrotoluene (DNT)	 2,4,6-Trinitrotoluene (TNT)	 Picric acid (PA)
 2,3-Dimethyl-2,3-dinitrobutane (DMNB)	 Cyclotrimethylenetrinitramine (RDX)	 2,4,6-Trinitrophenyl-*N*-methylnitramine (Tetryl)
 Pentaerythritol tetranitrate (PETN)	 Triacetone triperoxide (TATP)	 Hexamethylene triperoxide diamine (HMTD)

Molecular structure of common explosive compounds

Trace Copper Analysis





–(a) Background subtracted stripping voltammograms of a series of Cu^{2+} solutions in 0.1M H_2SO_4 at a gold nanowire electrode for 60s. (b) Electrochemical current vs. concentration for a deposition time of 60s.

Conclusions

- Single nanowire electrodes exhibited steady state – behaviour, fast electron transfer kinetics and low capacitance.
- Increased detection limits for Hydrogen Peroxide at unmodified electrodes
- Enhanced sensitivity to Glucose detection at nanoelectrodes – detection in non-capillary media (pain free)
- Applied to the detection of cations and organic molecules
- Diffusion controlled – design for use

SEVENTH FRAMEWORK PROGRAMME

Phast-ID	**FP7-ICT-2009 (STREP)**
CommonSense	**FP7-SEC-2010-1 (STREP)**
E-Brains	**FP7-ICT-2009-5 (STREP)**
NanoFunction	**FP7-ICT-2009-5 (NOE)**

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SFI/ 09/RFP/CAP2455 (RFP)

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Tyndall National Institute
Institiúid Náisiúnta

Nanowire Sensor Development

Generation 1

- Single NW Electrode
- Bottom Up Approach
- Facile Integration
- In-depth Analysis
- Suitablity to Sensing

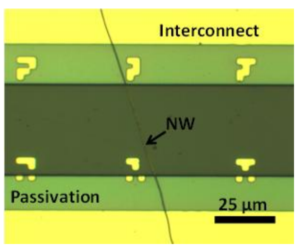
Generation 2

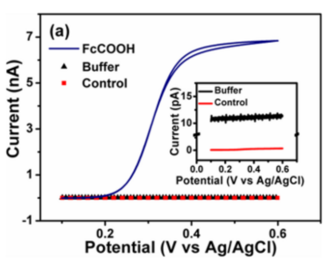
- Benchmark Gen 1
- Top Down Approach
- Reproducibility
- In-depth Analysis
- Glucose Detection

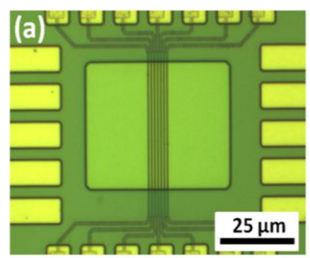
Generation 3

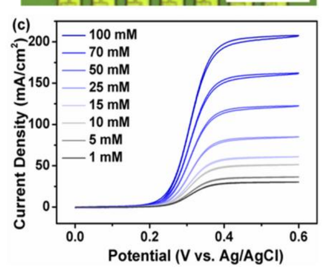
- Top Down Approach
- Platform Development
- Single NWs → Arrays
- Reduced packaging
- On-chip Counter Electrodes

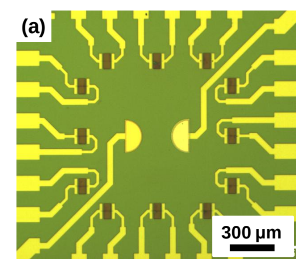
Development of Nanowire Electrochemical Devices

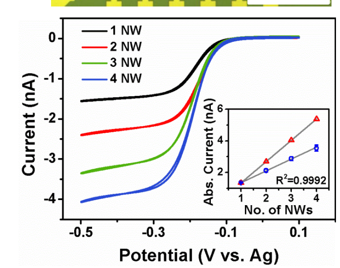












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