Hybrid metrology approach for simultaneous characterisation of multiple properties at the nanoscale

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Agenda

- Challenges of metrology for nanomaterials
- Multiparameter metrology for nanotechnology
- Final comments

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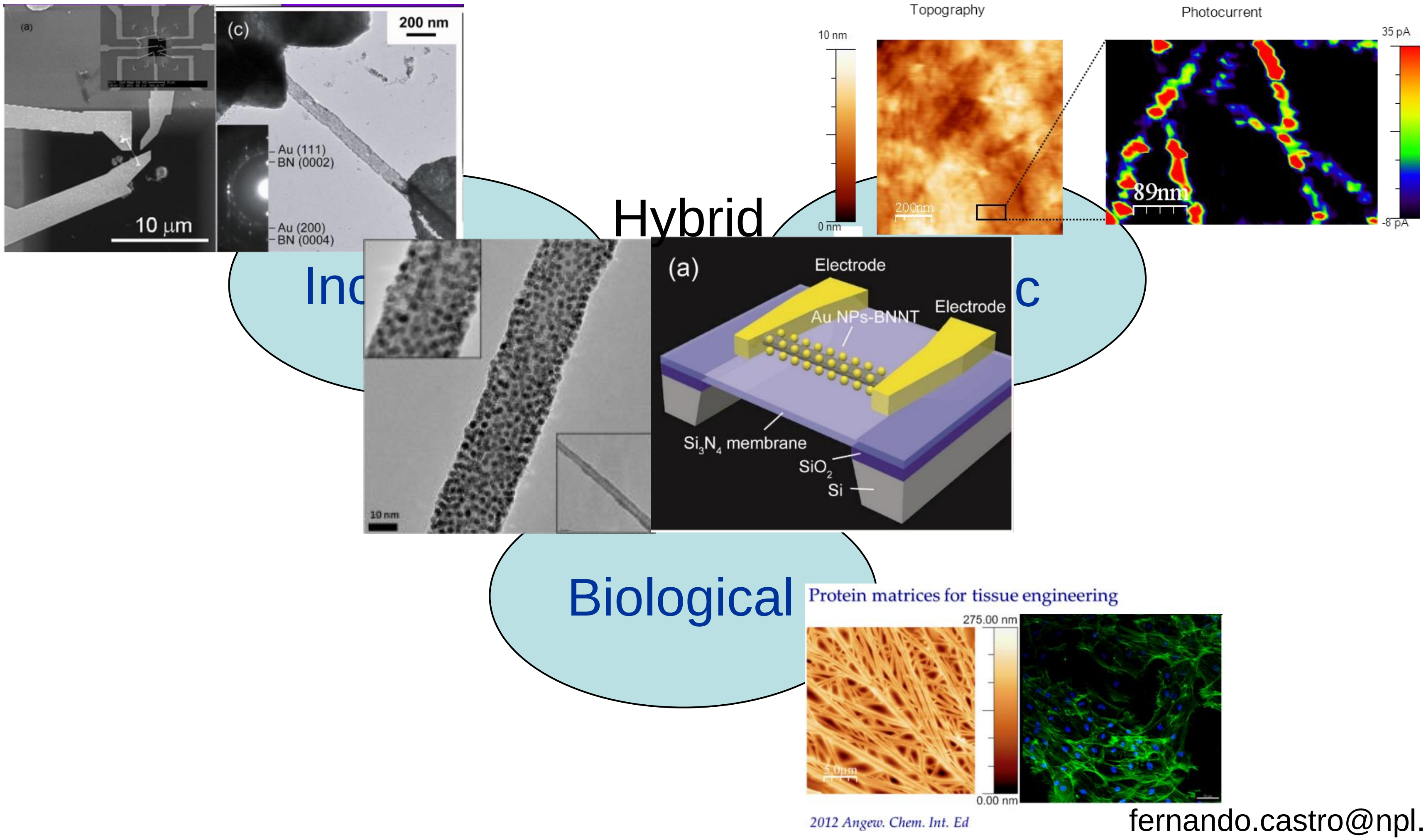
Nanomaterials - materials composed of one or more engineered components with at least one dimension between 1 nm and 100 nm.



Hybrid

Inc

c

Biological

Protein matrices for tissue engineering

2012 Angew. Chem. Int. Ed

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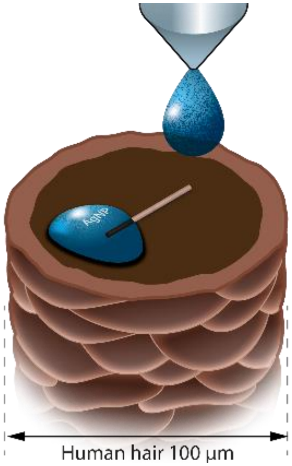
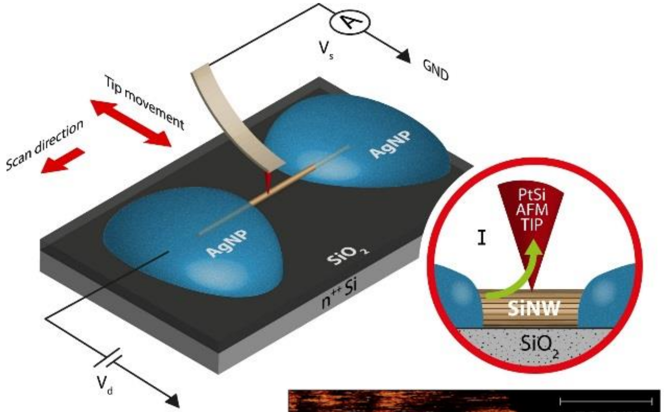
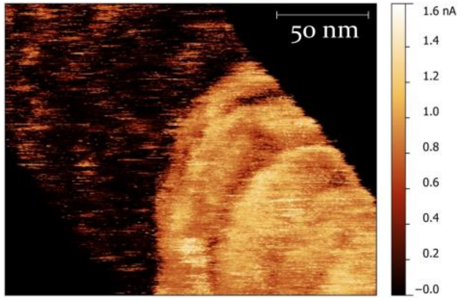
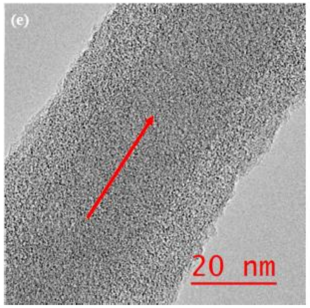
Complex nanomaterial applications require multiple characterisation methods

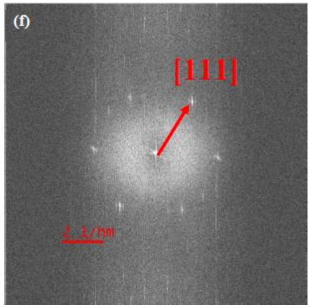
Ink-jet printed nanowire transistors

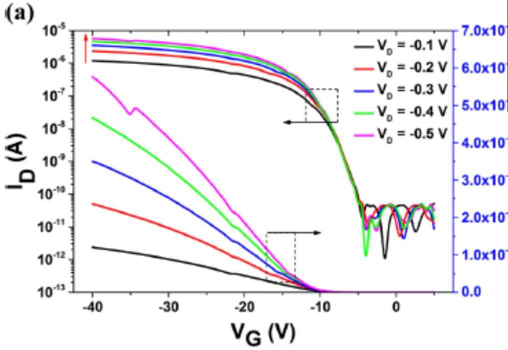


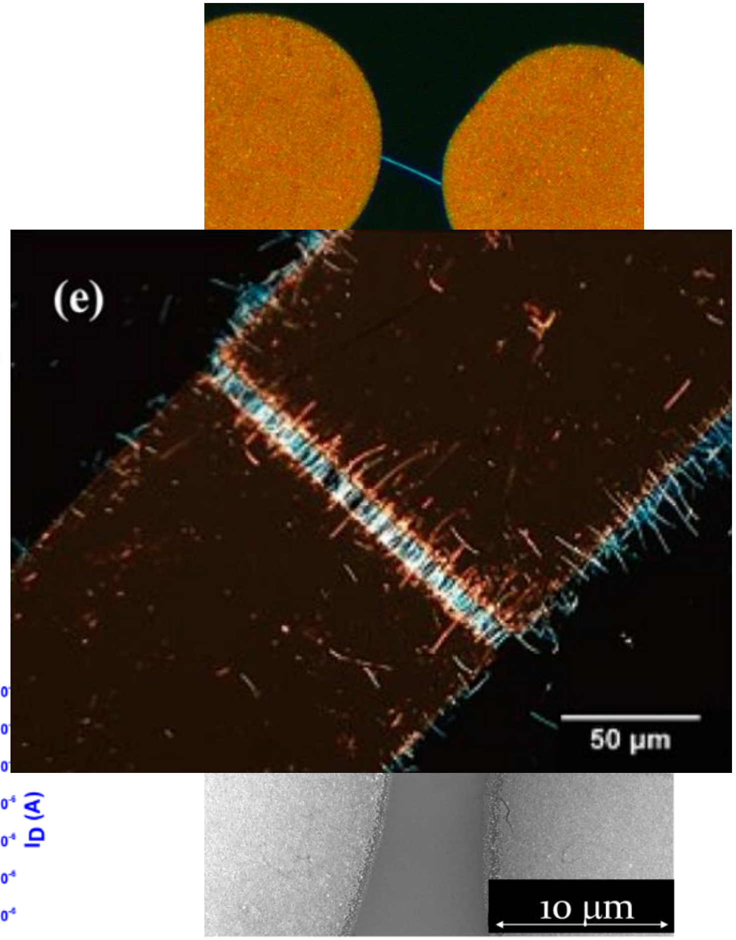












Rigas et al. submitted 2016

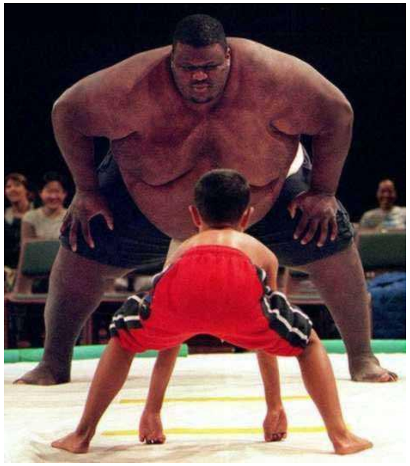
Structure-property relationship

Complex materials require multiple characterisation methods

Challenges of sequential nanoscale metrology

- Can I find the same exact position?
- Is my sample contaminated?

Powerful probes can damage/change delicate specimens



- Did I change my sample properties?
- Has my sample degraded?

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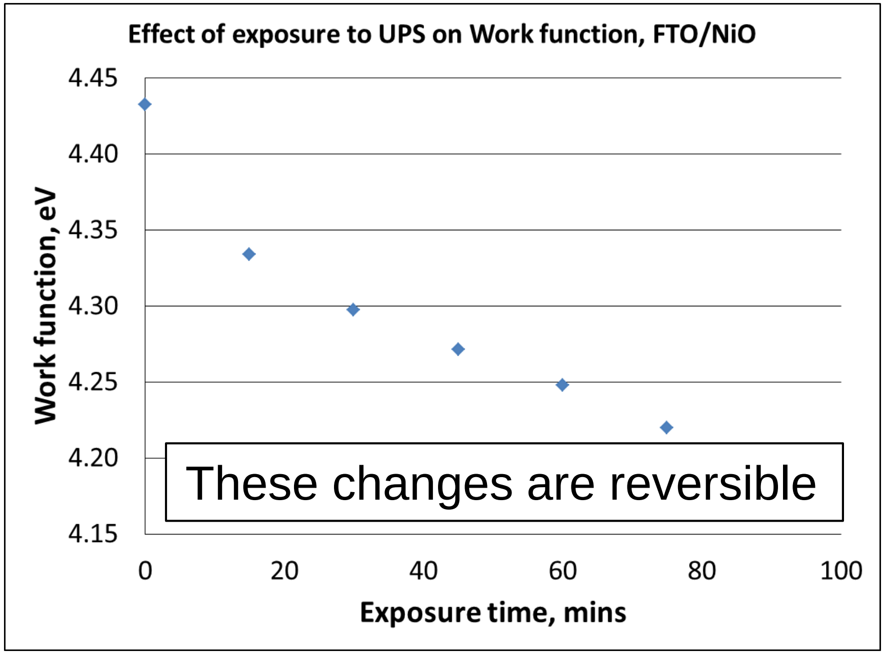
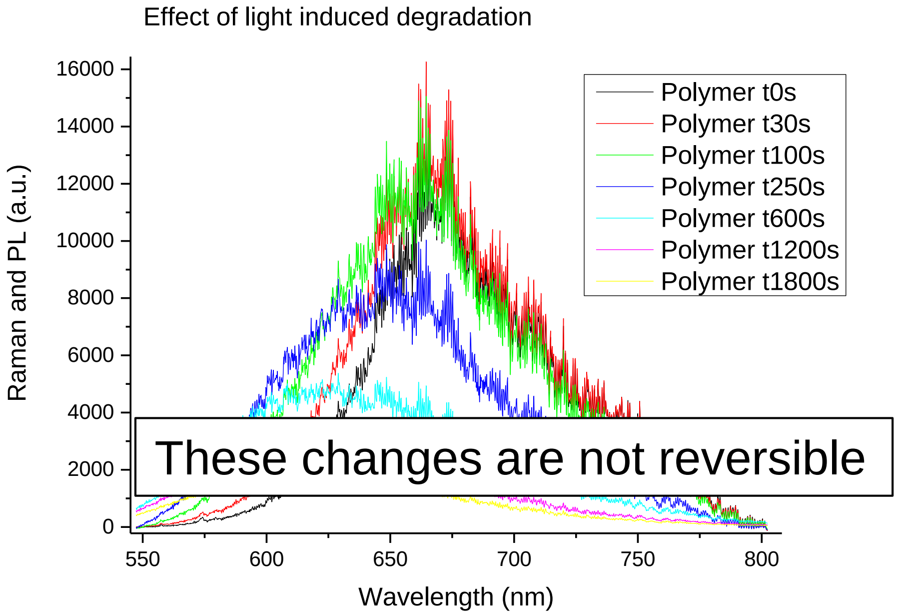
Accurate measurement vs useful measurement

Ultraviolet Photoelectron Spectroscopy
on Oxide thin film



These changes are reversible

Photoluminescence on nanostructured
polymer blend



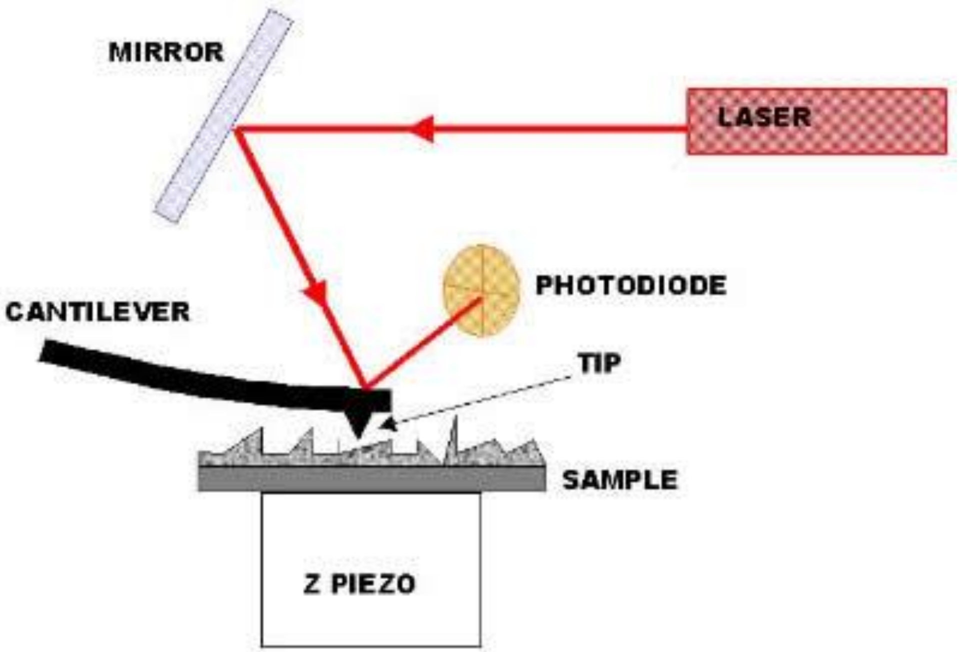
These changes are not reversible

Significant property changes during measurement

Even a fully calibrated, low uncertainty measurement does not guarantee dataset is useful for the sample manufacturer.

Can we develop methods that allow measurements of multiple properties simultaneously?

Scanning probe microscopy already does that



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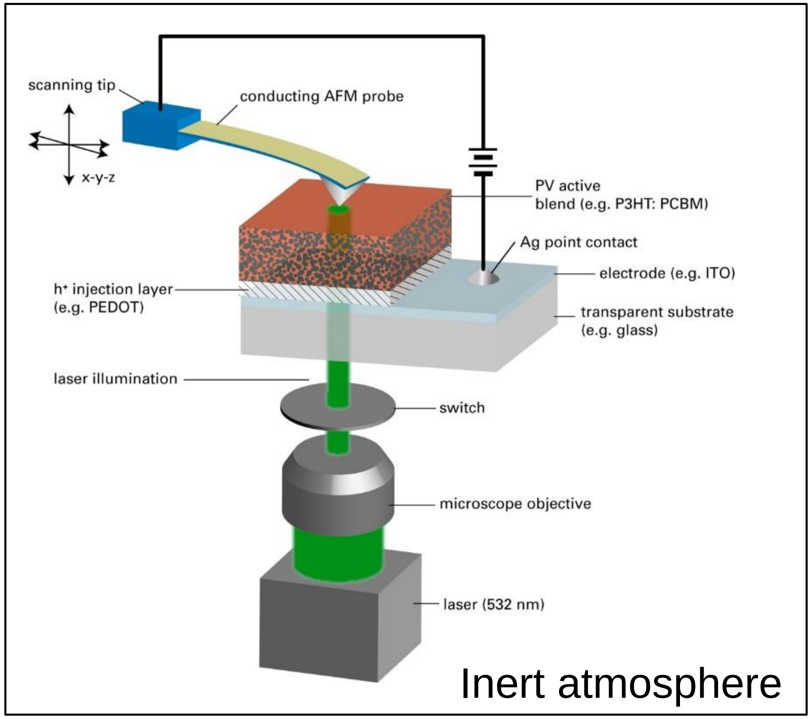
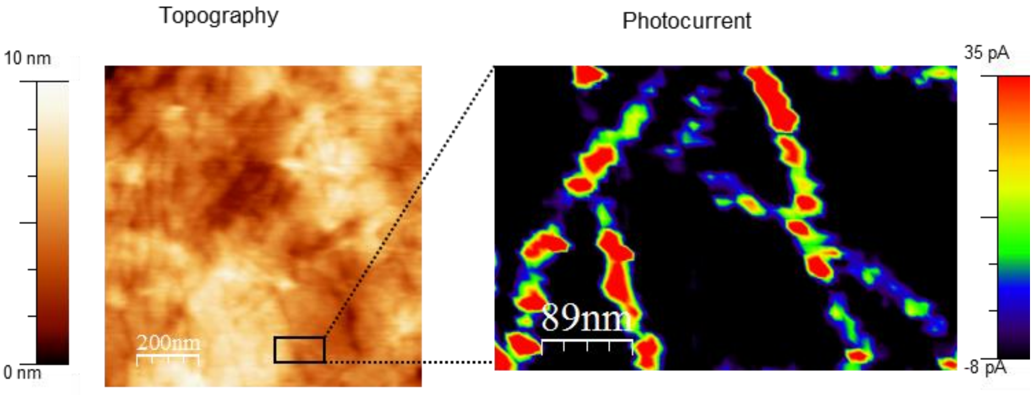
Photoconductive Atomic Force Microscopy



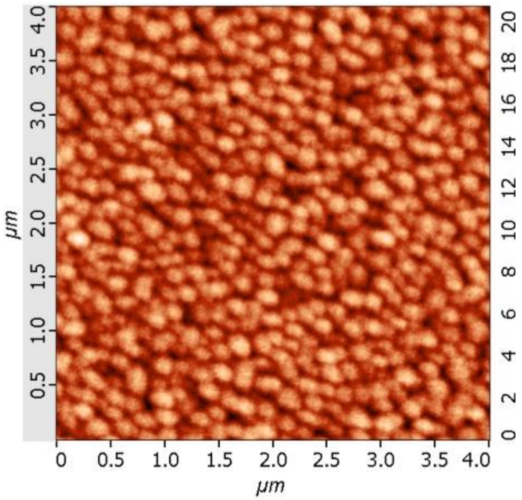
Inert atmosphere



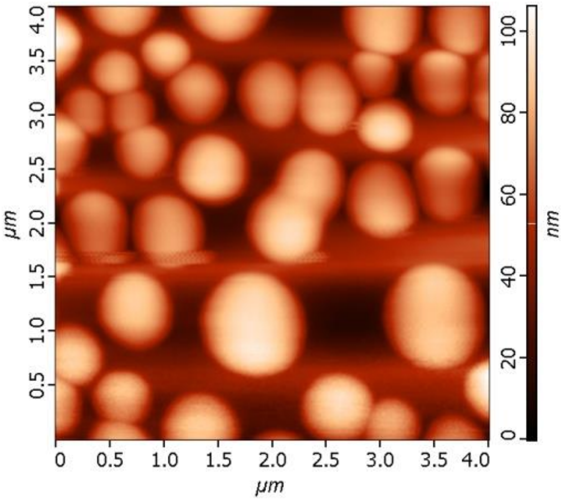
Does not provide chemical information

Nicholson and Castro, **Nanotechnology** 21 (2010) 492001 (review)
Tsoi et al. **Energy Environ. Sci.**, 4 (2011) 3646
Kim et al. **J. Mater. Chem.** C 3 (2015) 9224-9232

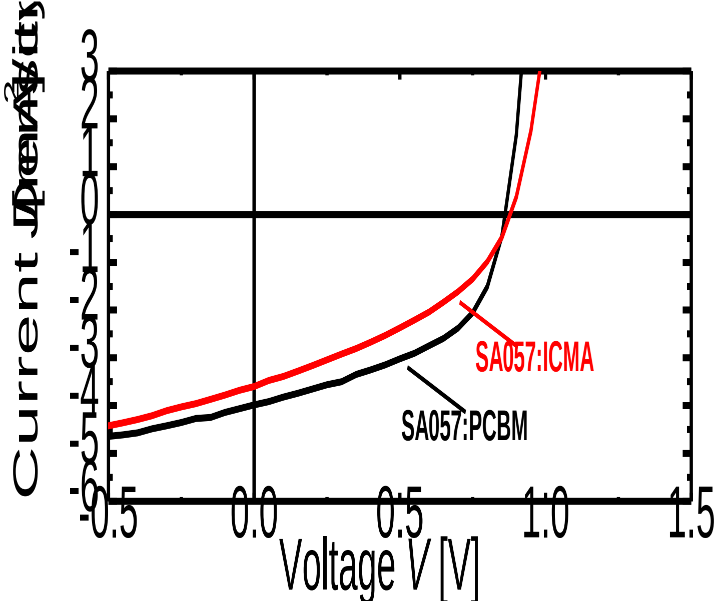
Can we identify the local composition?

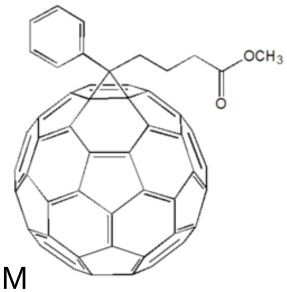


Si TPT-BT:PCBM

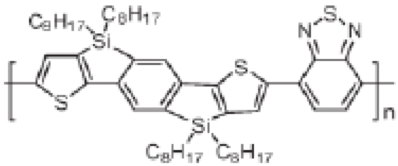


Si TPT-BT:ICMA

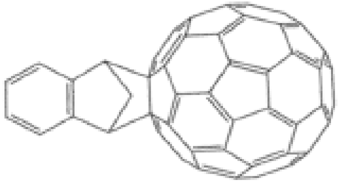




PCBM



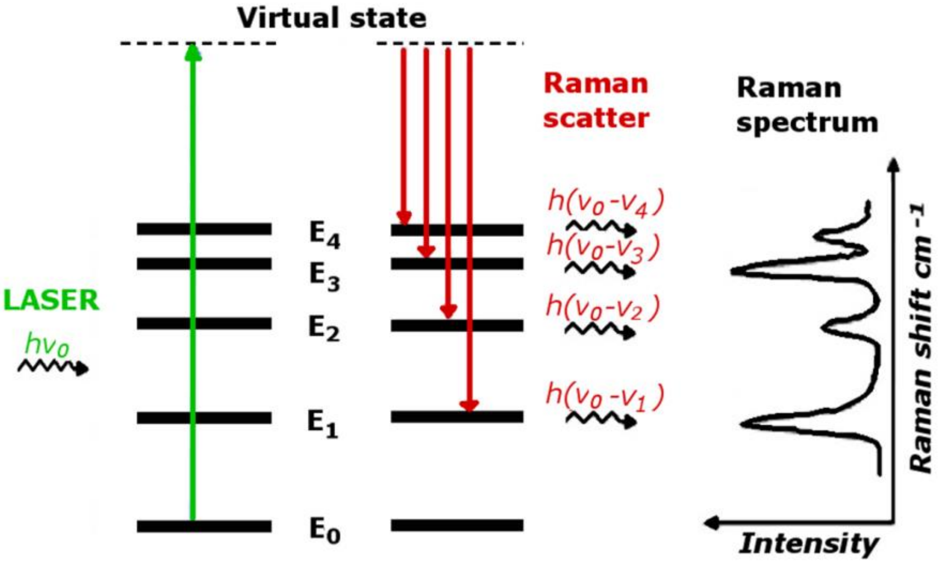
Si TPT-BT

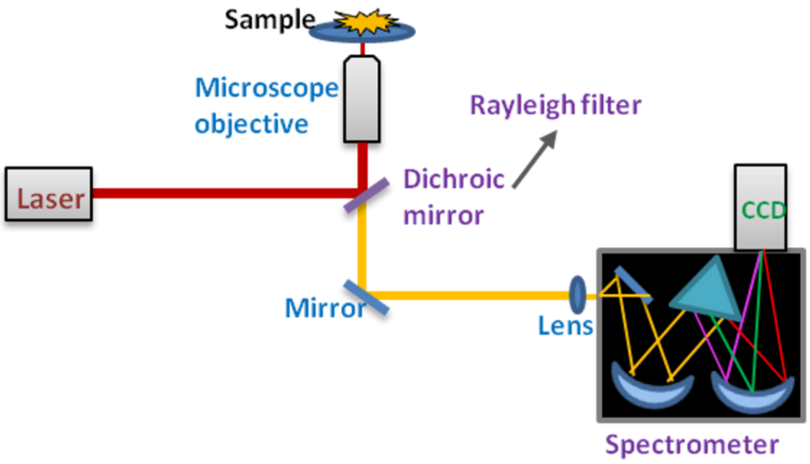


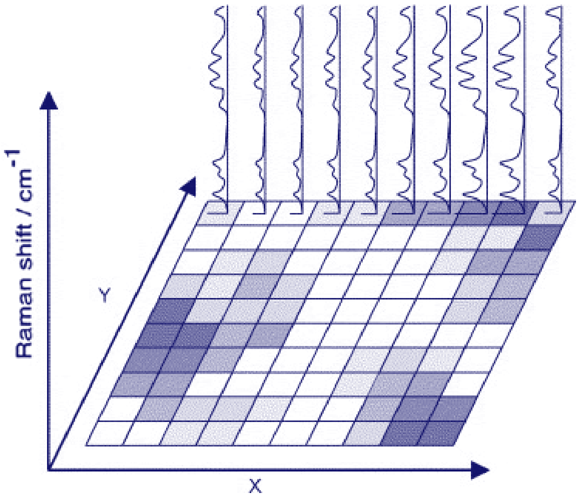
ICMA

Kumar et al. under review 2016

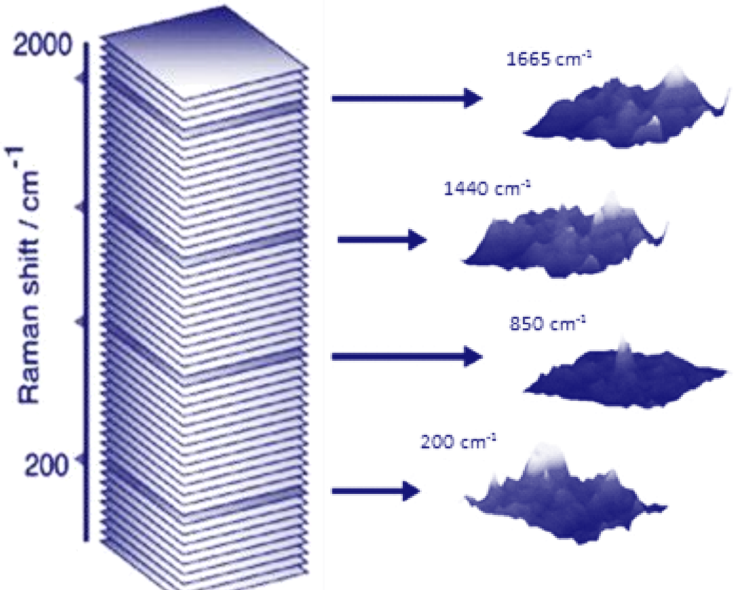
Raman Spectroscopy





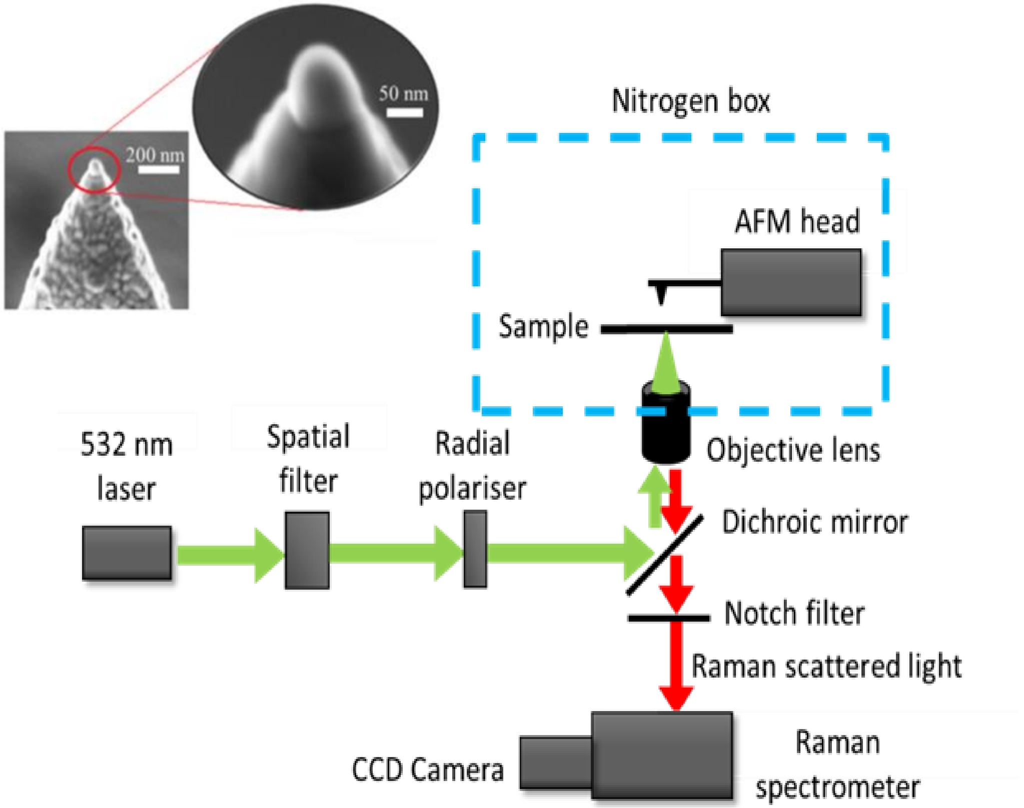


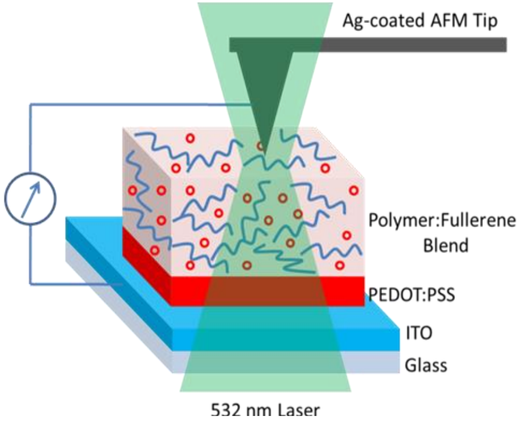
Raman spectral data-cube →

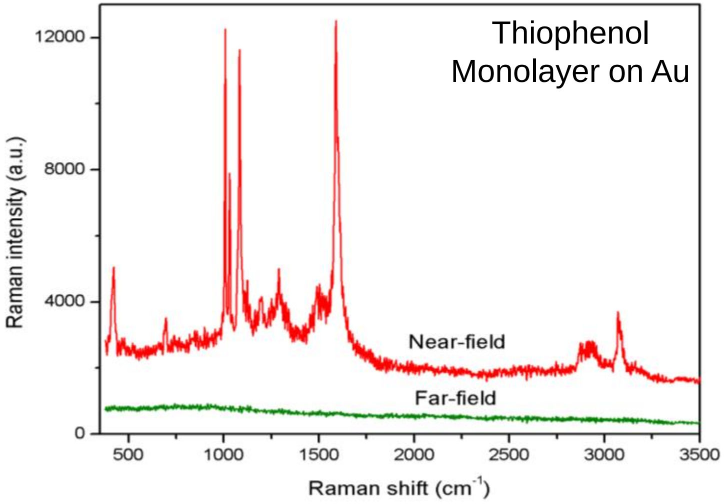


Tip-enhanced optical spectroscopy (Nanoscale Raman/Photoluminescence)

NPL National Physical Laboratory





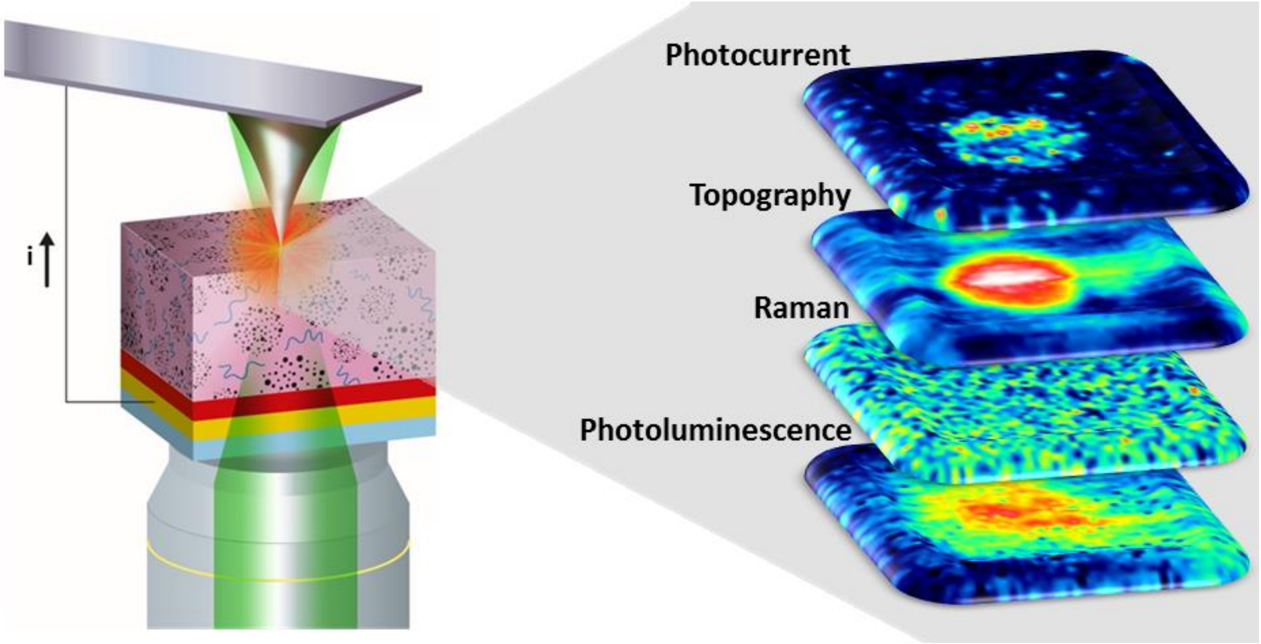


- Laser excites plasmon resonance
- Enhanced electromagnetic field close to the AFM tip

$$EF = \frac{(I_{Tip\text{-}in} - I_{Tip\text{-}out})/A_{NF}}{I_{Tip\text{-}out}/A_{FF}}$$

Nicholson and Castro, Nanotechnology **21** (2010) 492001 (review)
Kumar et al. under review 2016

Can we measure electrical performance, chemical and topographical information at the same time?



Naresh et al, submitted (2016)

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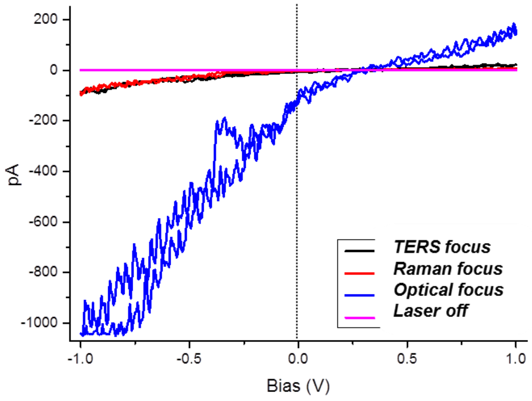
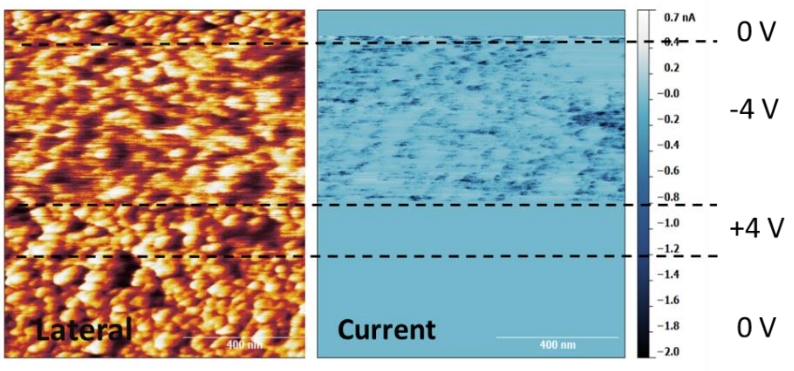
Possible issues that may affect reliability of data

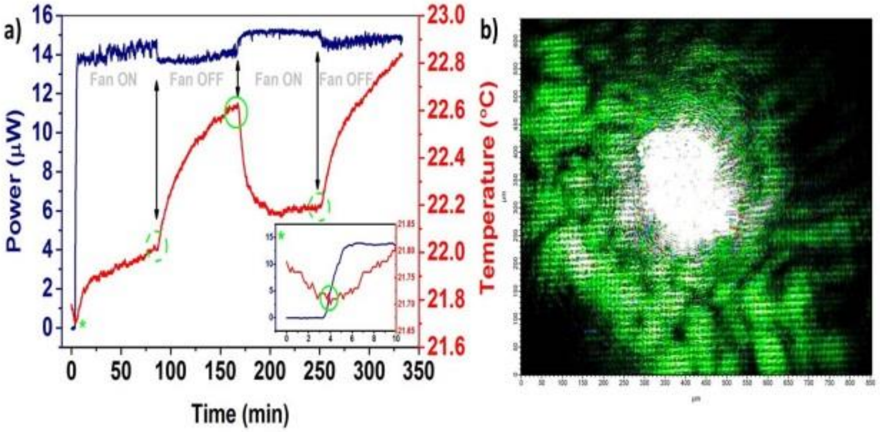
Optimisation of focusing position



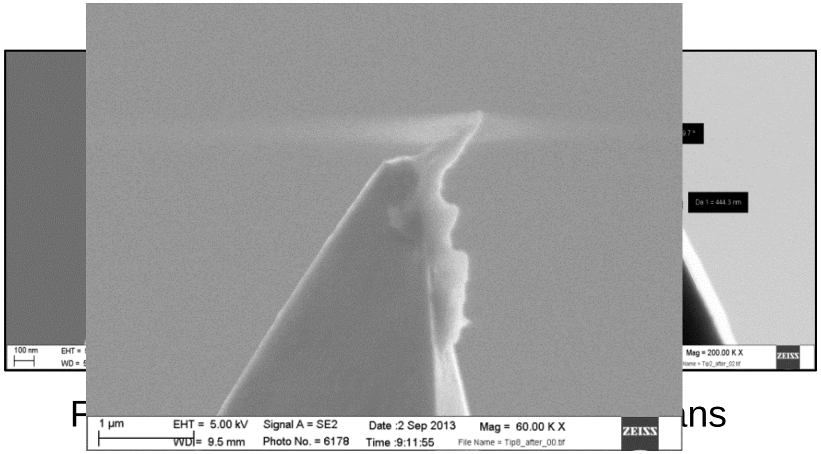
Avoid/minimise crosstalk



Excitation stability and spatial homogeneity



Tip degradation



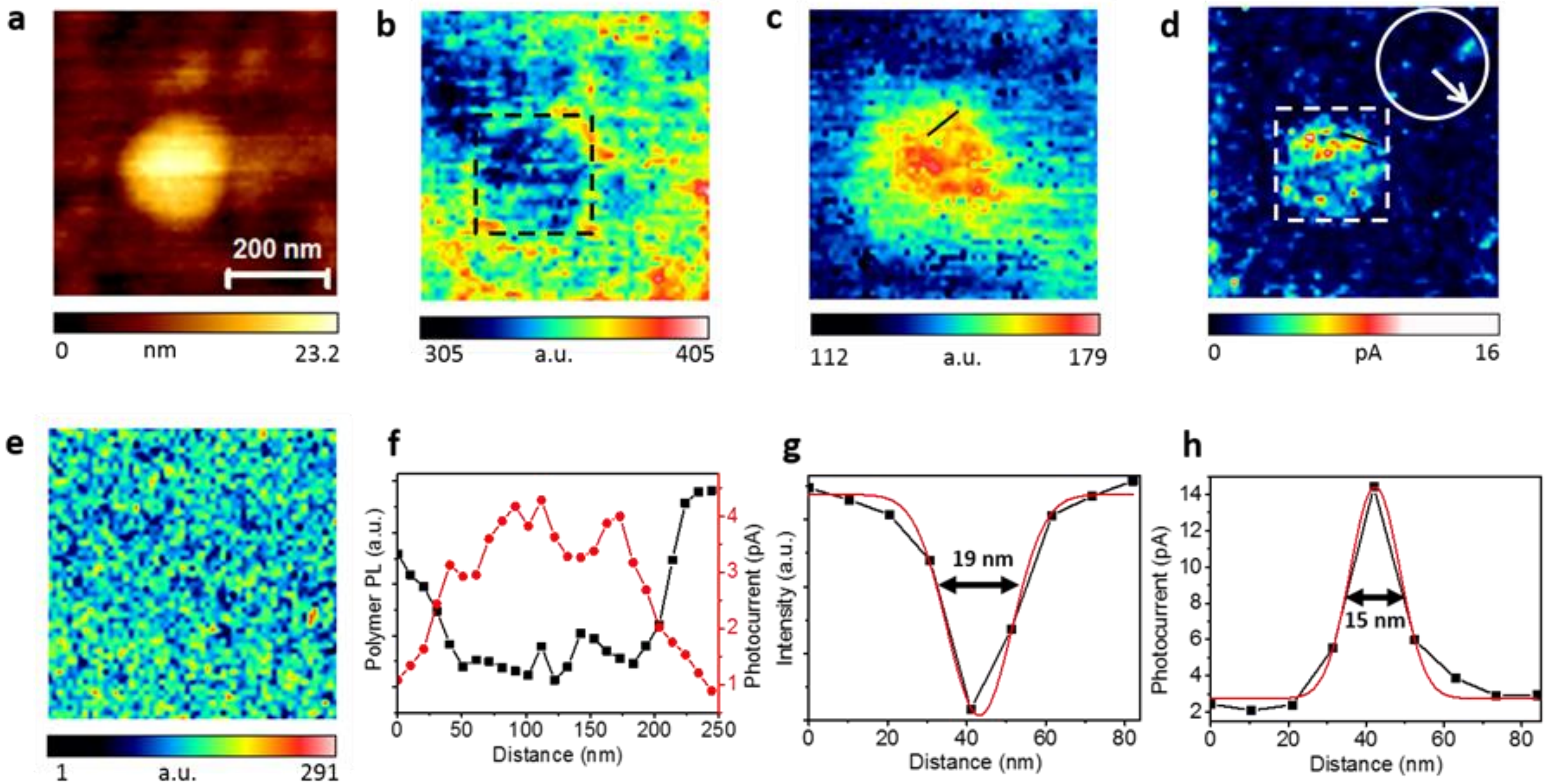
Simultaneous Topography, Electrical, Optical Microscopy (STEOM)

Topography

Polymer Photoluminescence

Fullerene Photoluminescence

Photocurrent



Polymer Raman

Indication of measurement resolution

Naresh et al, under review (2016)

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Are probe depths similar?

The probe depths are determined by their dependence on the electric near-field intensity (E).

- Intensity of Raman signal is $\propto E^4$,
- Intensity of PL signal is $\propto E^2\eta$, where η is the PL quantum yield in the near-field

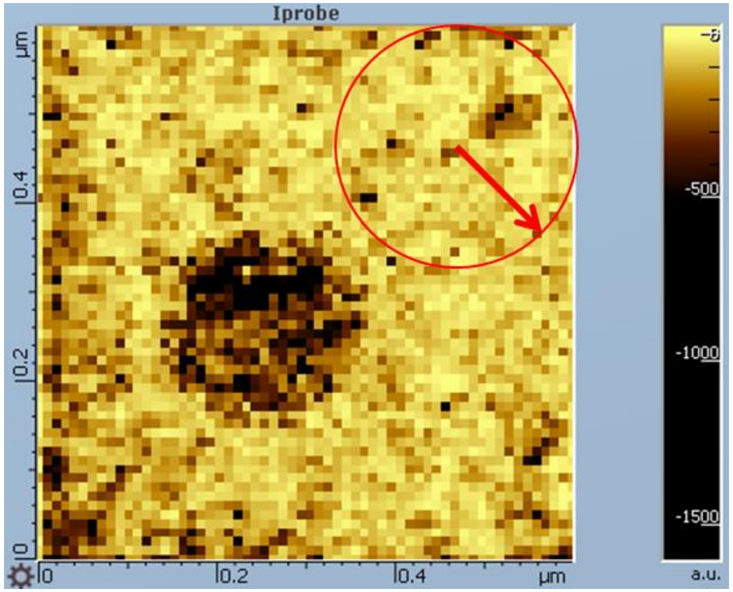
For small plasmonic enhancement of η, PL signal $\propto E^2$

Implication:

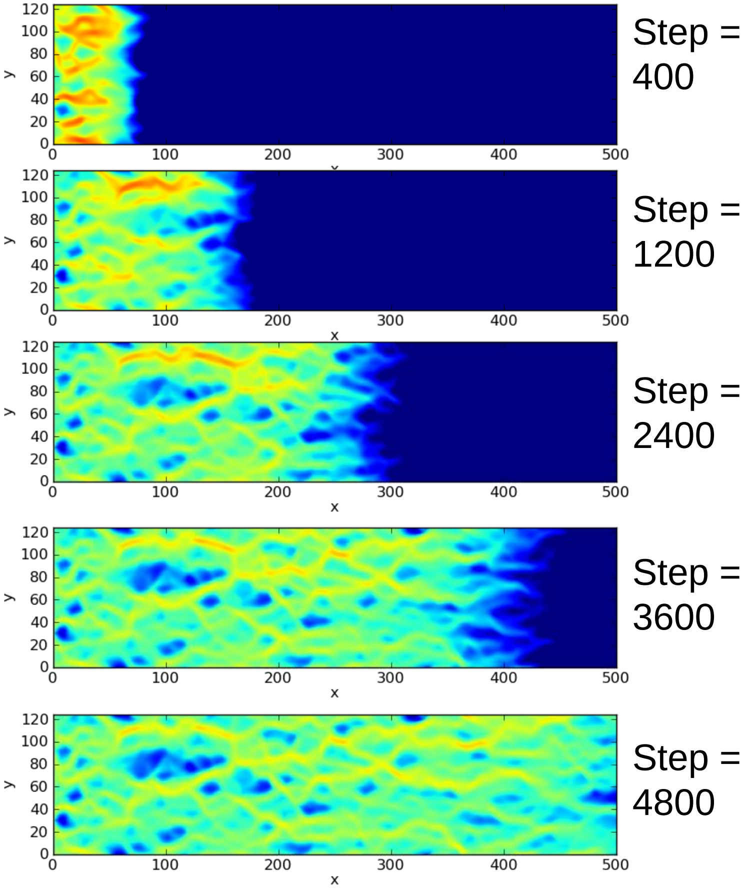
- Raman probes the top surface
- PL probes surface and subsurface

Nanoscale Photocurrent mapping

(Photoconductive atomic force microscopy)



Simulated time evolution of photocurrent density in a homogeneous OPV film

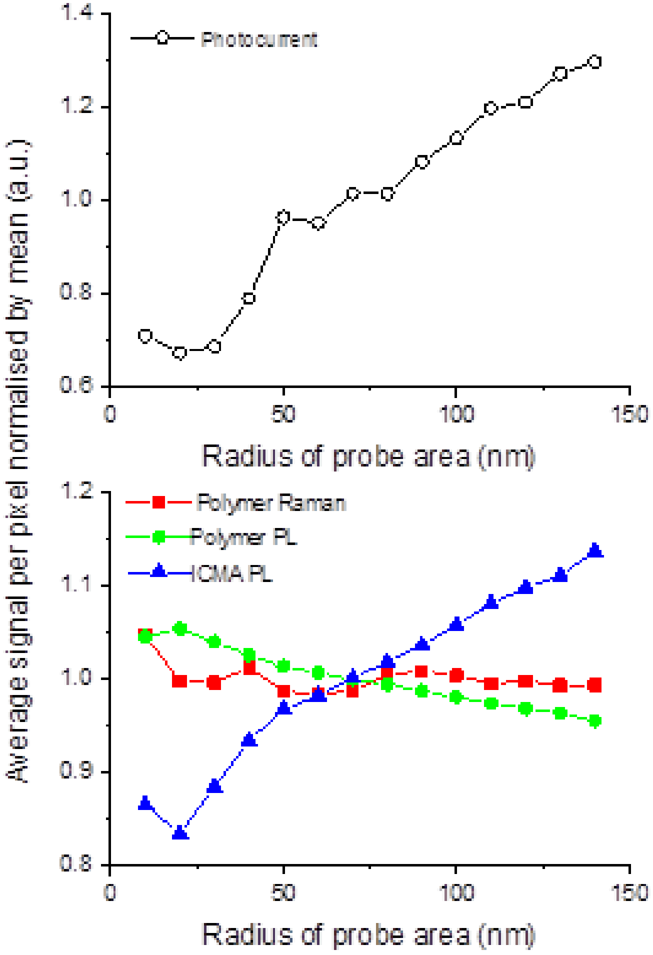


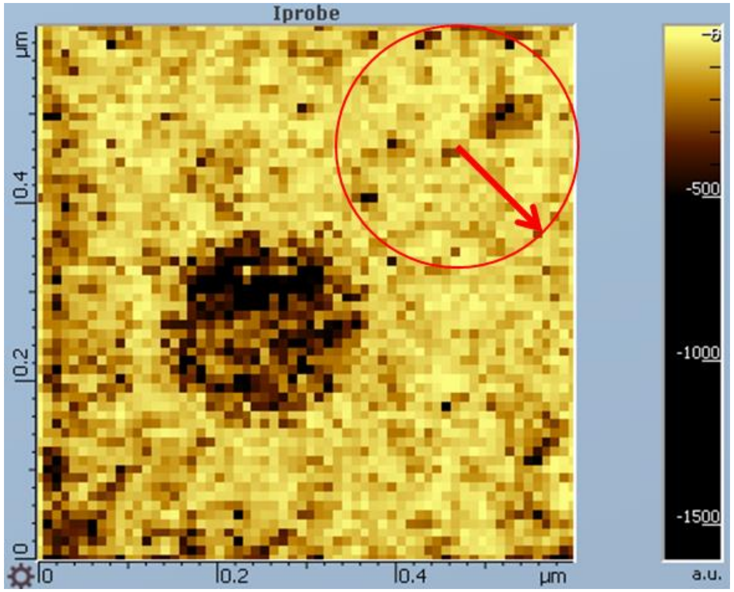
Why do we see small areas with high photocurrent?
Possible reasons

- Random currently fluctuations
- Measurement artefact (e.g. variation in contact resistance)
- Local compositional variation

Blakesley and Castro, Phys Rev B 2015
Kumar et al. 2016, submitted.

Potential for performance improvement

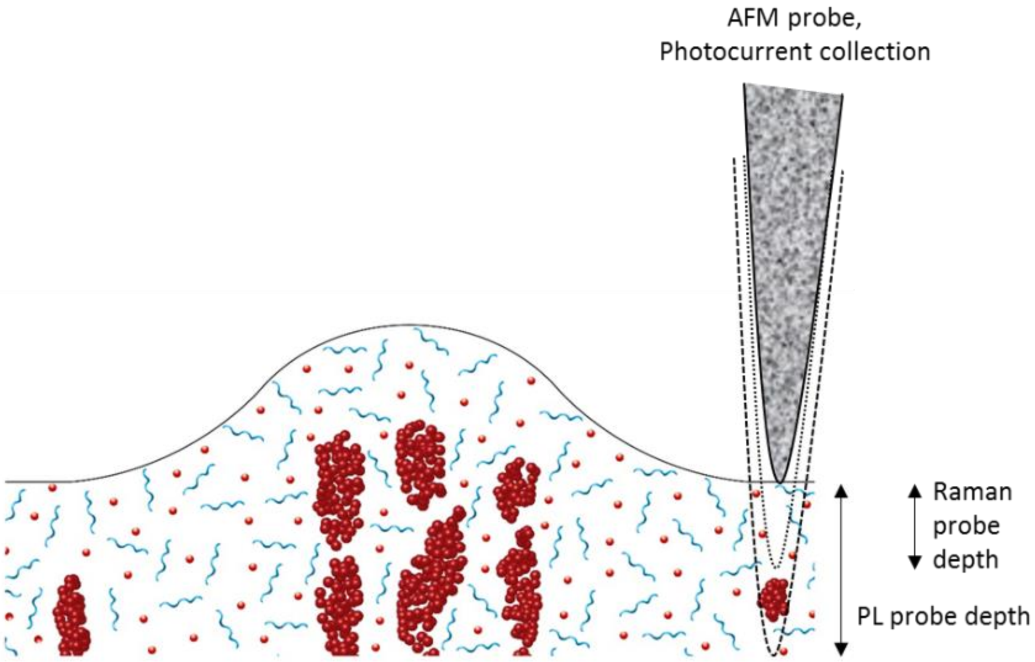




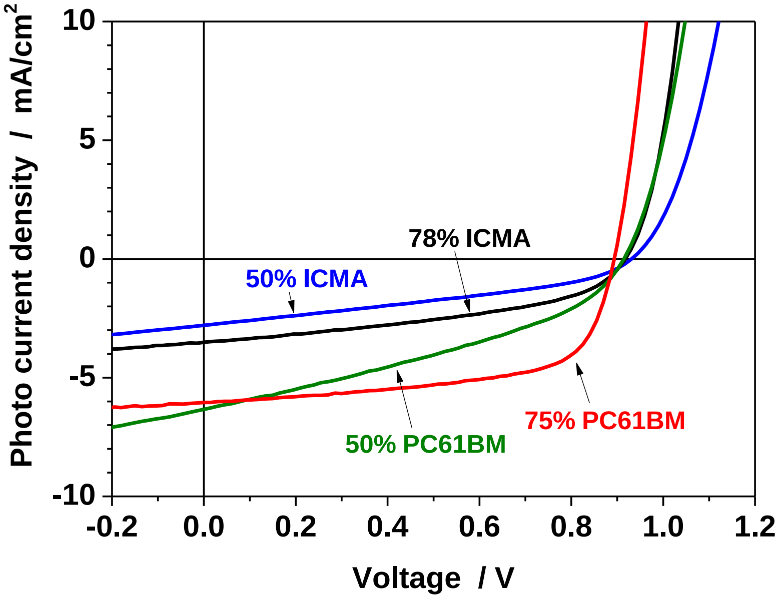
Photocurrent

PV efficiency could be at least doubled if optimised donor-acceptor composition could be achieved

Inferred nanostructure of solar cell polymer-fullerene blend

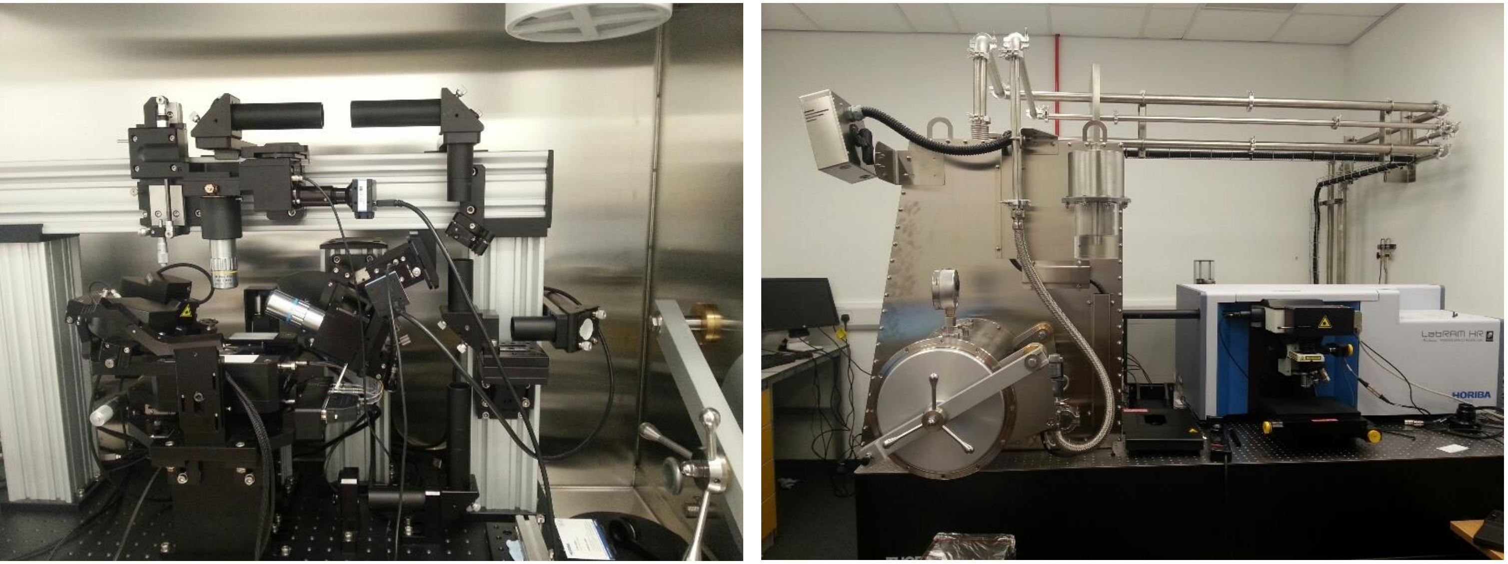


Change in manufacturing procedure by increasing fullerene content lead to increase in device performance by a factor of 2.



Final remarks

- Complex nanomaterials/devices require complementary characterisation methods
- Demonstration of simultaneous topography, electrical and optical microscopy (STEOM): allows direct correlation between chemical composition-topography-electrical performance
- New characterisation possibilities for organic, 2D and nanoelectronics



Unique capability
Atmospheric control
3 optical axes

Acknowledgements

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National Physical Laboratory

NPL

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University of Surrey (UK)

Dr Maxim Shkunov

Gregorios Rigas

Scallops Project
Technology Strategy Board
Driving Innovation

Department for
Business, Energy
& Industrial Strategy

ThinErgy

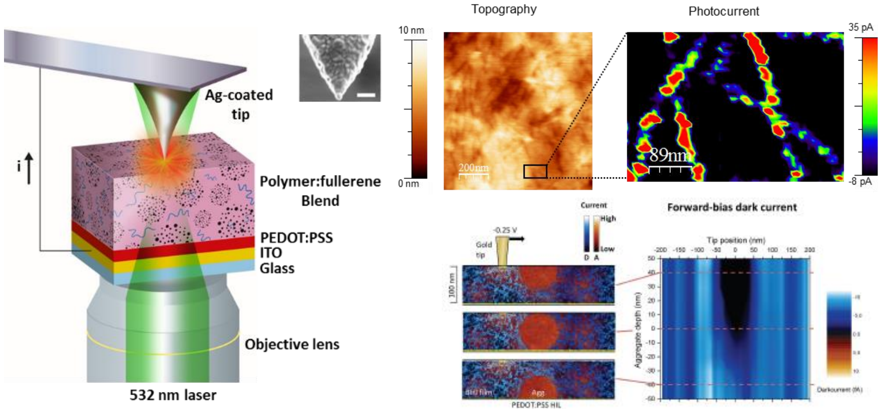
EMRP
European Metrology Research Programme
Programme of EURAMET
The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

Advanced Electronic Materials

NPL National Physical Laboratory

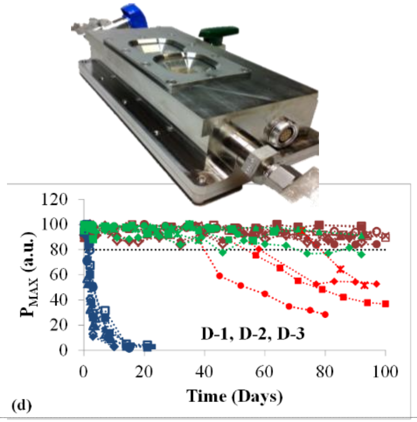
Nanoscale functional characterisation

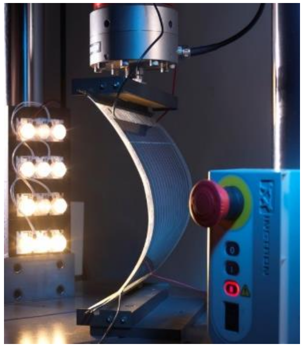
Novel mapping methods & innovative modelling



Stability (in-situ characterisation)

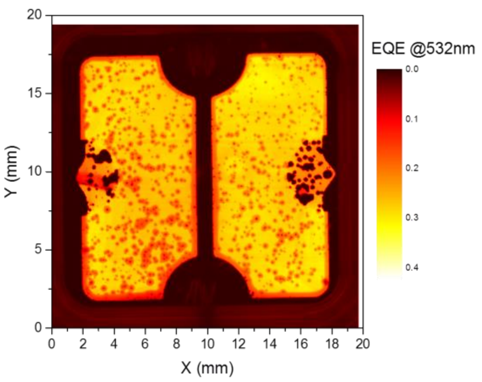
Novel in-situ characterisation & accelerated tests

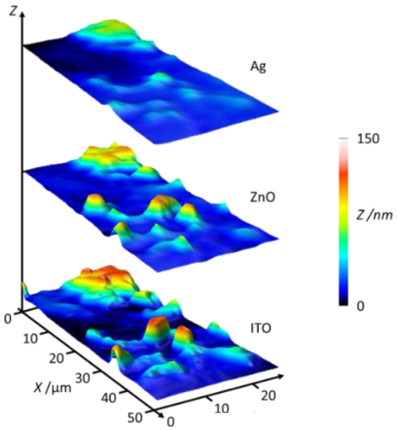




Quality control

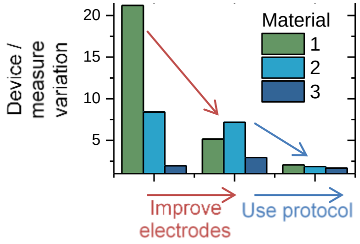
Advanced defect characterisation

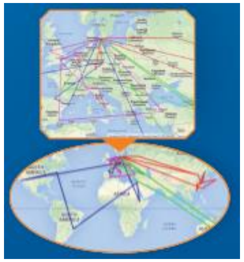




Standardisation

Measurement protocols International Round Robins





Collaborations in 2015

Stakeholder groups oe-a Organic Electronics Association, VAMAS, EERA European Energy Research Alliance, StableNextSol COST MP1307, bsi., IEC

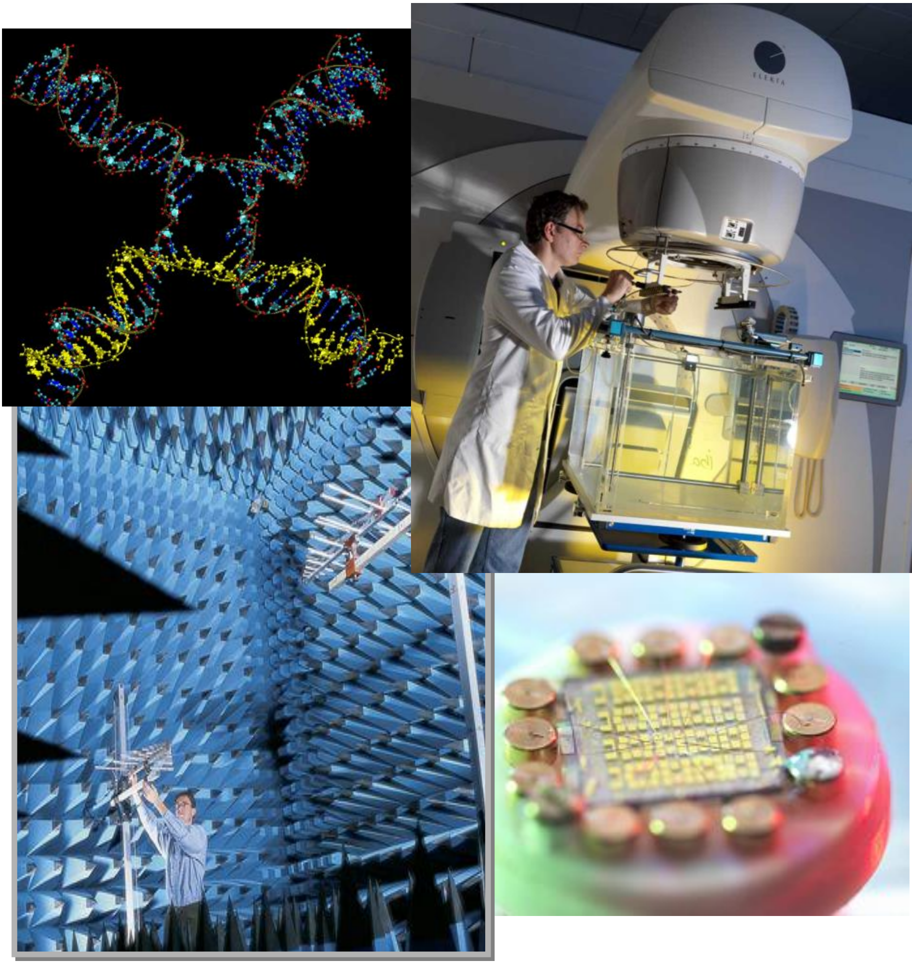
Companies MERCK, Eight19, CANATU, TÜVRheinland, SEFAR, FOM TECHNOLOGIES

R&D/NMIs EMPA, specific, imec, ECN, cea, leti, JRC EUROPEAN COMMISSION, VSL, INMETRO, PTB, Fraunhofer, CMI

Universities Imperial College London, University of Surrey, Loughborough University, DTU Technical University of Denmark, Universitat de València

National Physical Laboratory

- Founded in 1900
- World-leading National Measurement Institute (Top 3 among ~100)
- 650 staff, 450 Graduate/PhD scientists - multidisciplinary



36,000 m^2 national laboratory

Develop & disseminate UK's measurement standards, ensure they are internationally accepted

Multidisciplinary R&D and technical services for public and private sector

Knowledge transfer, and advice between industry government and academia

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- Even the best calibrated instruementation, the lowest measurement uncertainty, when applied to a material that changes properties during the measurement, will give you the wrong result.

The measurement is correct but the result is meaningless!

Traditional metrology is expert in the measurement

End-user/customer is expert in the materials

There is a need for expertise bridging the gap between both worlds. That is Materials Metrology!

Include examples (photocurrent map or linearity of DSSCs, XPS/UPS of TCOs, others). Some changes in sample may be obvious (example of a film with a burned hole due to high power laser). Others are not easy to identify (xps example where the change is immediate during the measurement but fades away later on (transient effects).

Materials Metrology understands the interaction between sample and experiments in detail to ensure accurate and reliable methods provide customers with meaningful results.