From mud cracks to Optoelectronic devices- Our efforts in translating Invention to Technology

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On lien from
Jawaharlal Nehru Centre for Advanced Scientific Research

http://www.cens.res.in/Faculty/Details/Kulkarni
www.jncasr.ac.in/kulkarni

IAS, 04 Nov 2017

New generation transparent conductors

<u>OUTLINE</u>

- **Large area TCEs: Challenges**
- **Our efforts using Crackle lithography**
- **ITO-free applications**
- **New applications**
- **Summary**

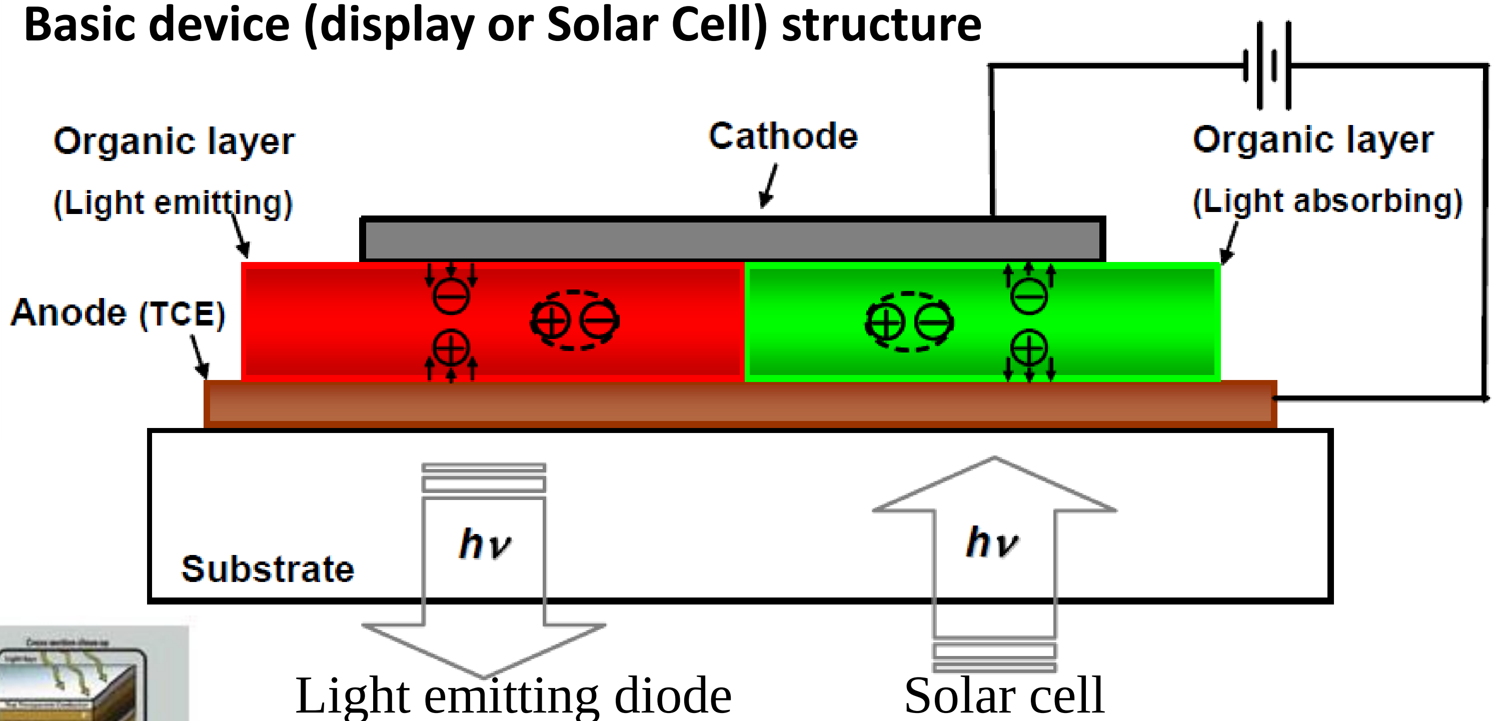
Transparent Conducting Electrodes (TCEs)

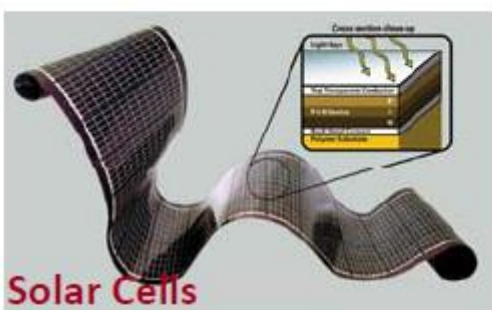
....a material that is transparent to visible light and yet electrically conducting.

TCE is a key component in any optoelectronic device!

Not a trivial solution....

Basic device (display or Solar Cell) structure





M. G. Kang dissertation 2009, University of Michigan

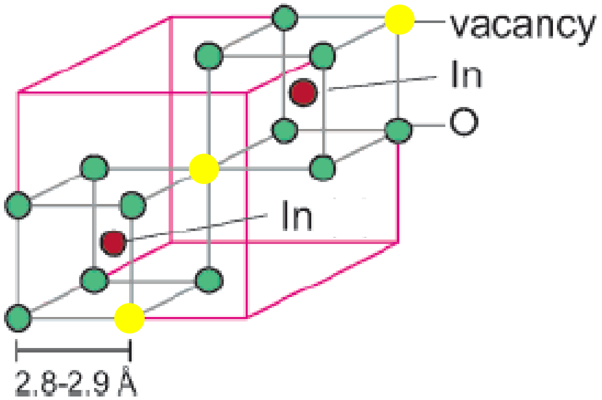
Currently used material: Indium tin oxide (ITO)

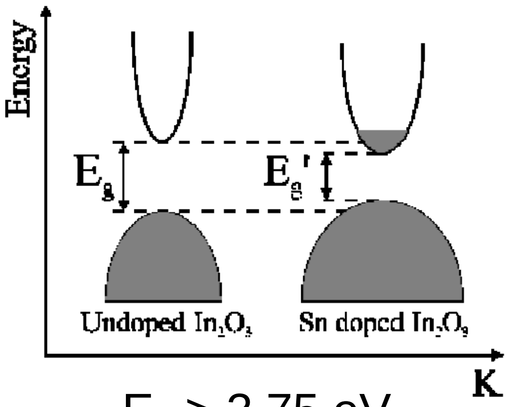
Excellent optoelectronic performance

T ~ 90% and R_s ~ 10 Ω per square

Sn acts as cationic dopant and substitutes Indium resulting in $Sn:In_2O_3$

J. Phys. Chem. B **2006, 110, 4793**





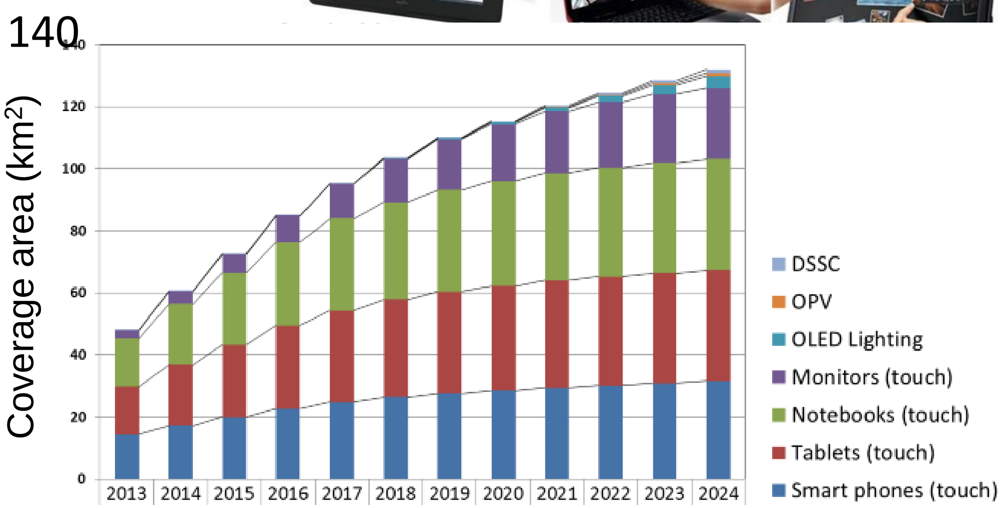
E_g > 3.75 eV

Addition of Sn dopants results in the formation of donor states just below the conduction band.

ITO: Limitations

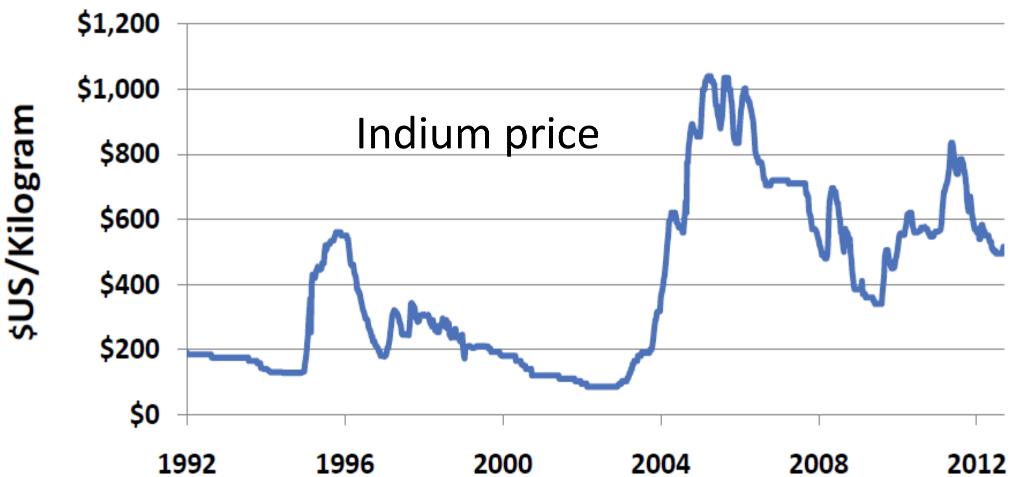
- Poor transmitter in UV and IR wavelengths
- Requires high temperature processing (> 600 °C).
- Electrical properties are very sensitive to film preparation conditions.
- Poor mechanical properties (cracks when bent) – not good for flexible electronics.

Applications are becoming larger



Source: IDTechEx

In ten years, ITO usage in displays will increase by 2-3 times.



Indium price is increasing and uncertain due to scarcity.

Source: www.IDTechEx.com

Transparent Conducting Electrodes (TCEs)

Electrochromic window panels: Active light control…

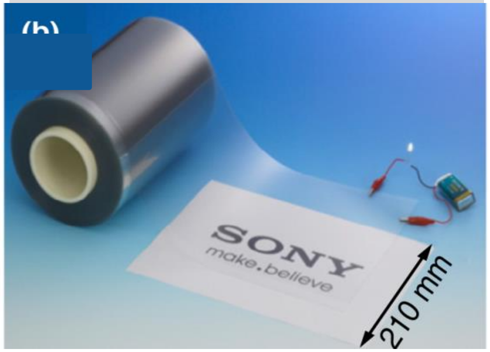
Large area TCEs in large numbers are required….

Alternative Transparent Conductors

Ultra-thin conducting electrodes

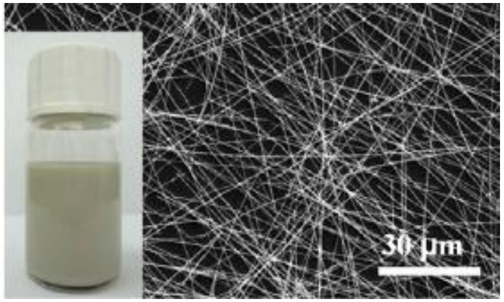
- **Graphene**
  - igh transmittance (97%)
  - igh sheet resistance (kΩ)
  - igh processing cost
- **Conducting polymers**
  - 80% Transmittance & 50 Ω/sq sheet resistance
  - Low processing cost
  - High material cost
- **Conducting networks of metal nanowires and CNTs**
  - High transmittance and average sheet resistance of Ag NWs
  - ontact resistance between the NWs
  - edundant wires
  - igh surface roughness
  - ercolation limited

Graphene coated PET roll



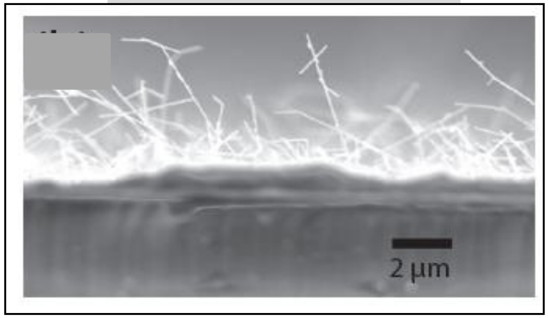
Appl. Phys. Lett. 2013, **102**:023112

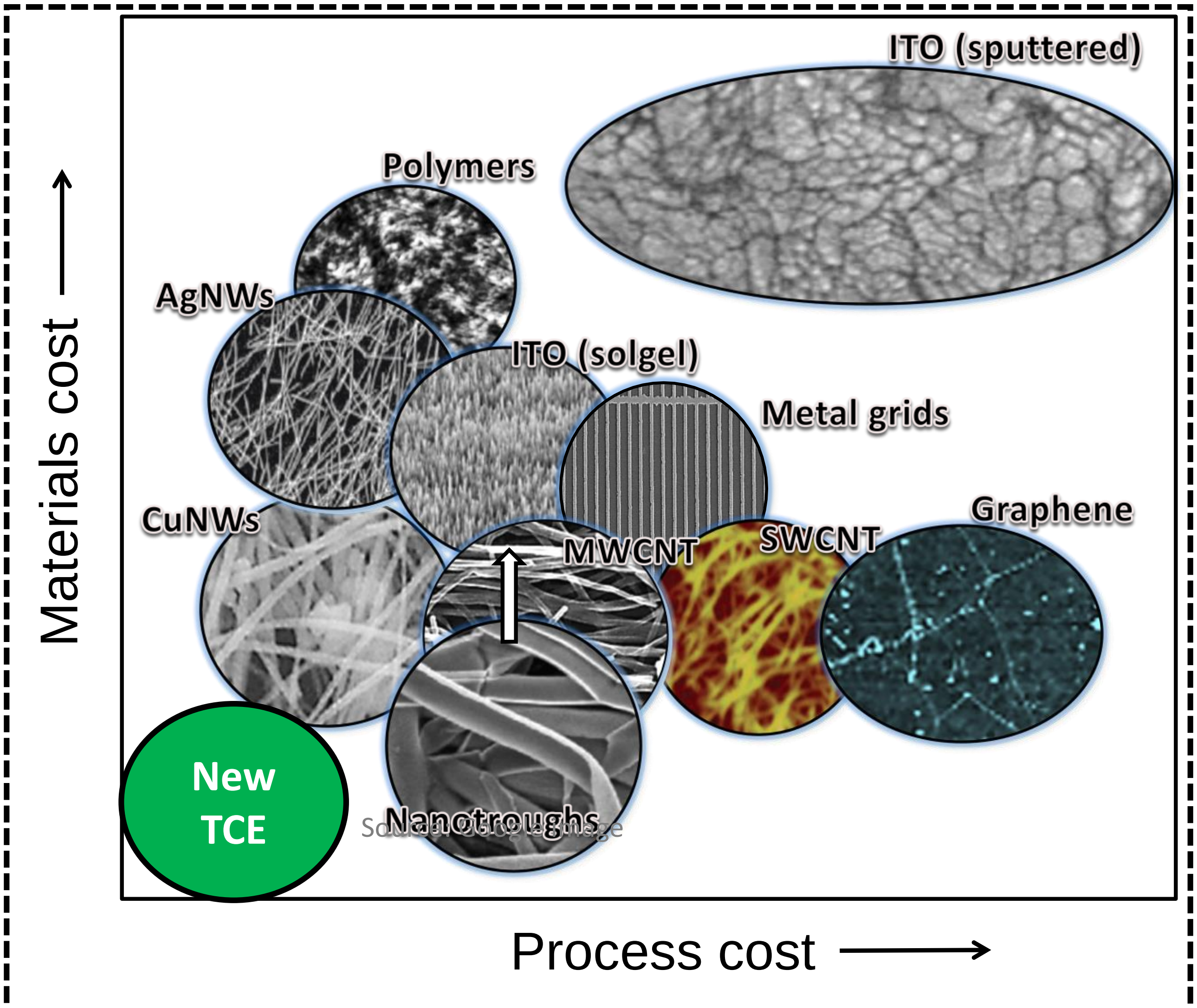
Ag nanowire network



Nanotechnology 2013, **24**:335202

Cross-section view





G. U. Kulkarni, S. Kiruthika *et al* Curr. Opin. Chem. Eng. **2015**, 8:60-68

Cracks tend to form spontaneously in a colloidal layer, upon drying, which can act as sacrificial template for deposition.

This is a network template in a plane.

Using Crack template

Mud cracks

Crack network as a template- requirements

Highly interconnected, low fill factor, large area-scalable, uniformity in fill factor, crack down to substrate, variable crack width, poor adhesion with substrate, affordable,…

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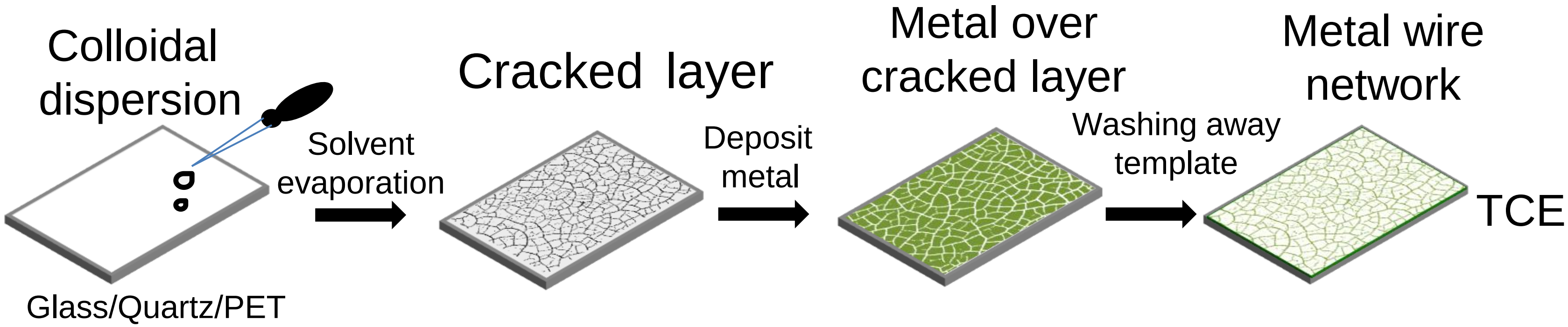
Using Crack template

Network in a plane



Using TiO_2 dispersion: Han et al., Adv. Mater. 2014; Kulkarni et al., Mater. Res. Exp., 2014

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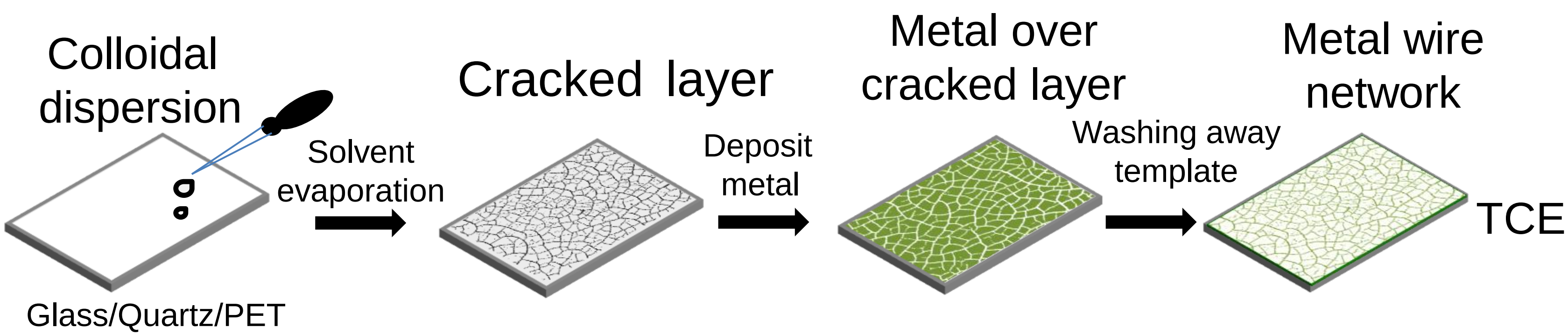
Network in a plane



Using TiO_2 dispersion: Han et al., Adv. Mater. 2014; Kulkarni et al., Mater. Res. Exp., 2014

Crack network as a template- requirements

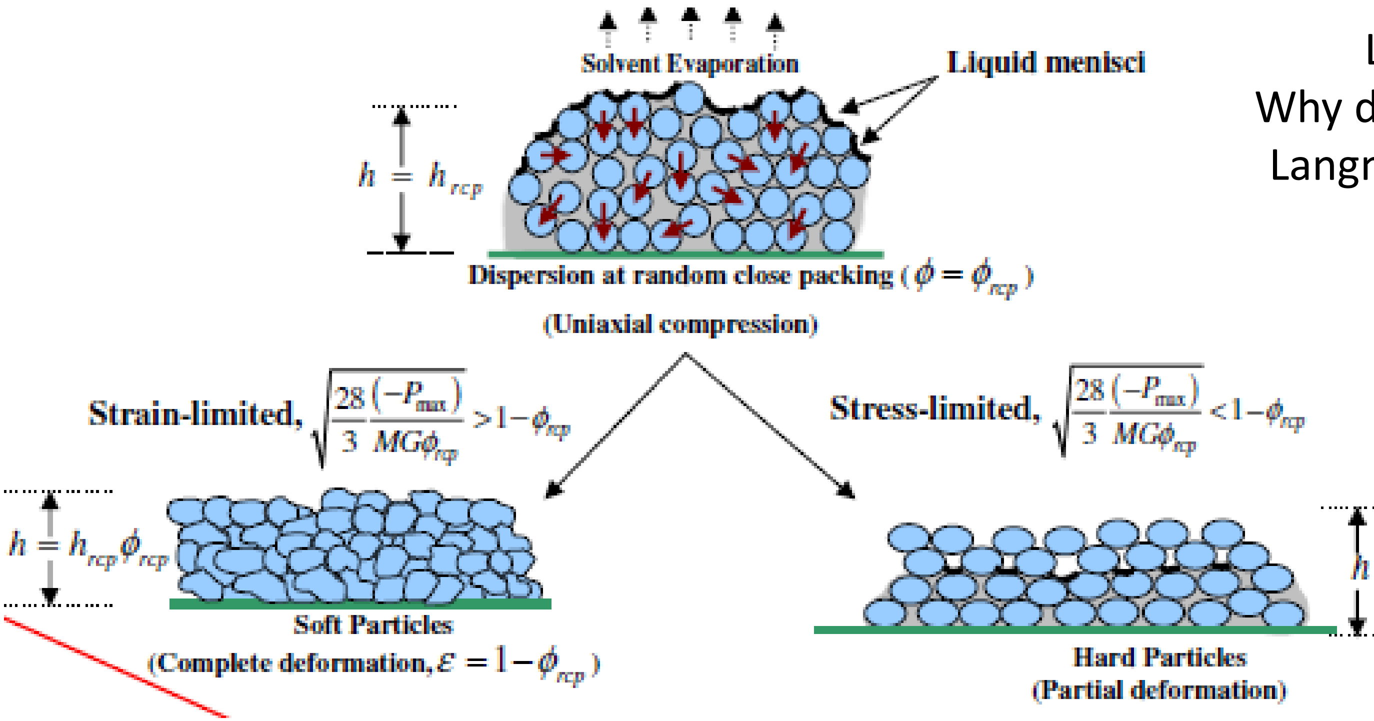
How to improve…?

Highly interconnected, low fill factor, large area-scalable, uniformity in fill factor, crack down to substrate, variable crack width, poor adhesion with substrate, affordable,…

Optimisation

Cracking in Drying Colloidal Films

Particulate films exhibit cracks above a critical thickness, due to the stress induced by solvent evaporation, which is widely seen in nature such as in mud cracking.



Lee and Routh,
Why do drying films crack?
Langmuir 2004, 20 9885.

If the particles are soft, they deform to close the pores created due to solvent evaporation, but in the case of hard particles the film cracks to release the stress.

Phys. Rev. Lett. **2007**, 98, 218302.

Films made of soft particles produce cracks with narrower widths.

Crack network as a template- requirements

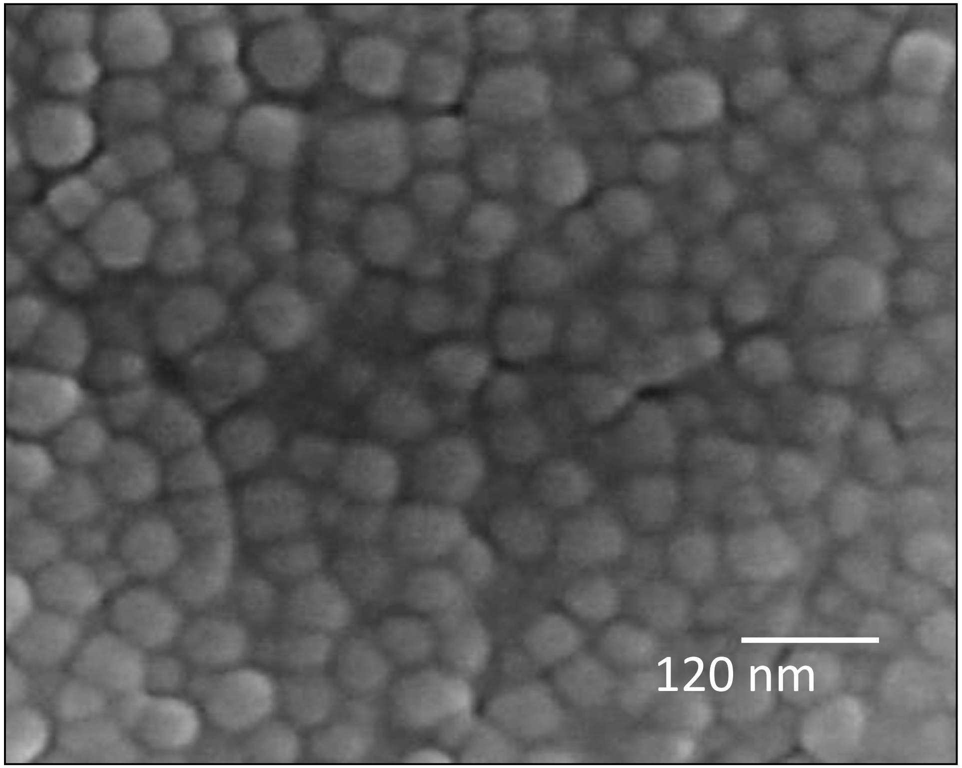
Highly interconnected, low fill factor, large area-scalable, uniformity in fill factor, crack down to substrate, variable crack width, poor adhesion with substrate, affordable,…

‘Search for Colloidal dispersion’

Crack network as a template- requirements

Highly interconnected, low fill factor, large area-scalable, uniformity in fill factor, crack down to substrate, variable crack width, poor adhesion with substrate, affordable,…

Acrylic resin dispersion



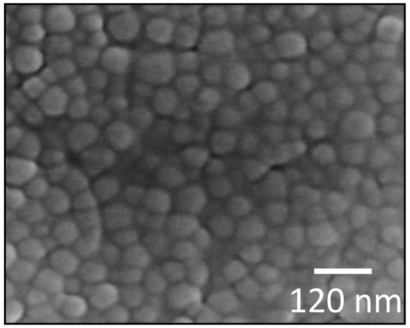
As the film dries, soft nanoparticles deform and pack tightly.

Cracking tendency of the film is thus reduced. When cracks do form, they will be much narrower.

Crack network as a template- requirements

Highly interconnected, low fill factor, large area-scalable, uniformity in fill factor, crack down to substrate, variable crack width, poor adhesion with substrate, affordable,…

Acrylic resin dispersion



Crack network as a template- requirements

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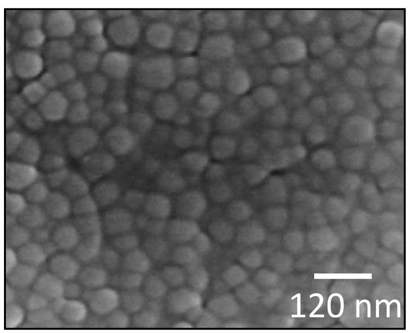
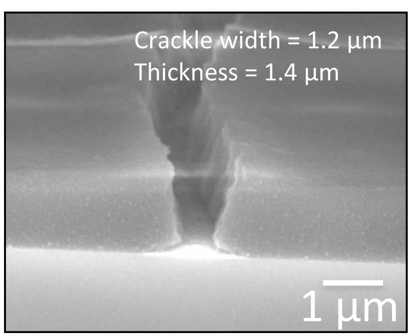
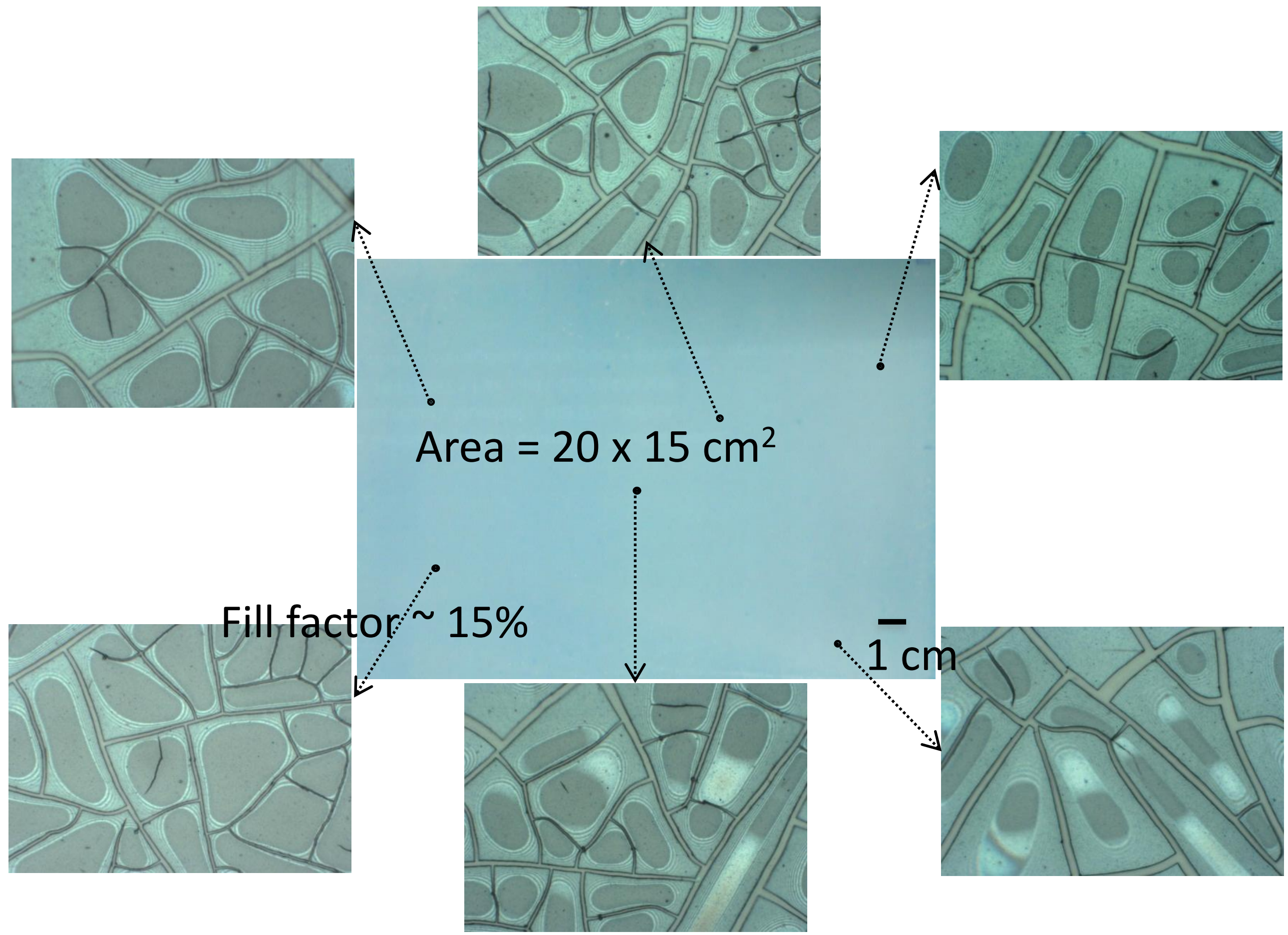
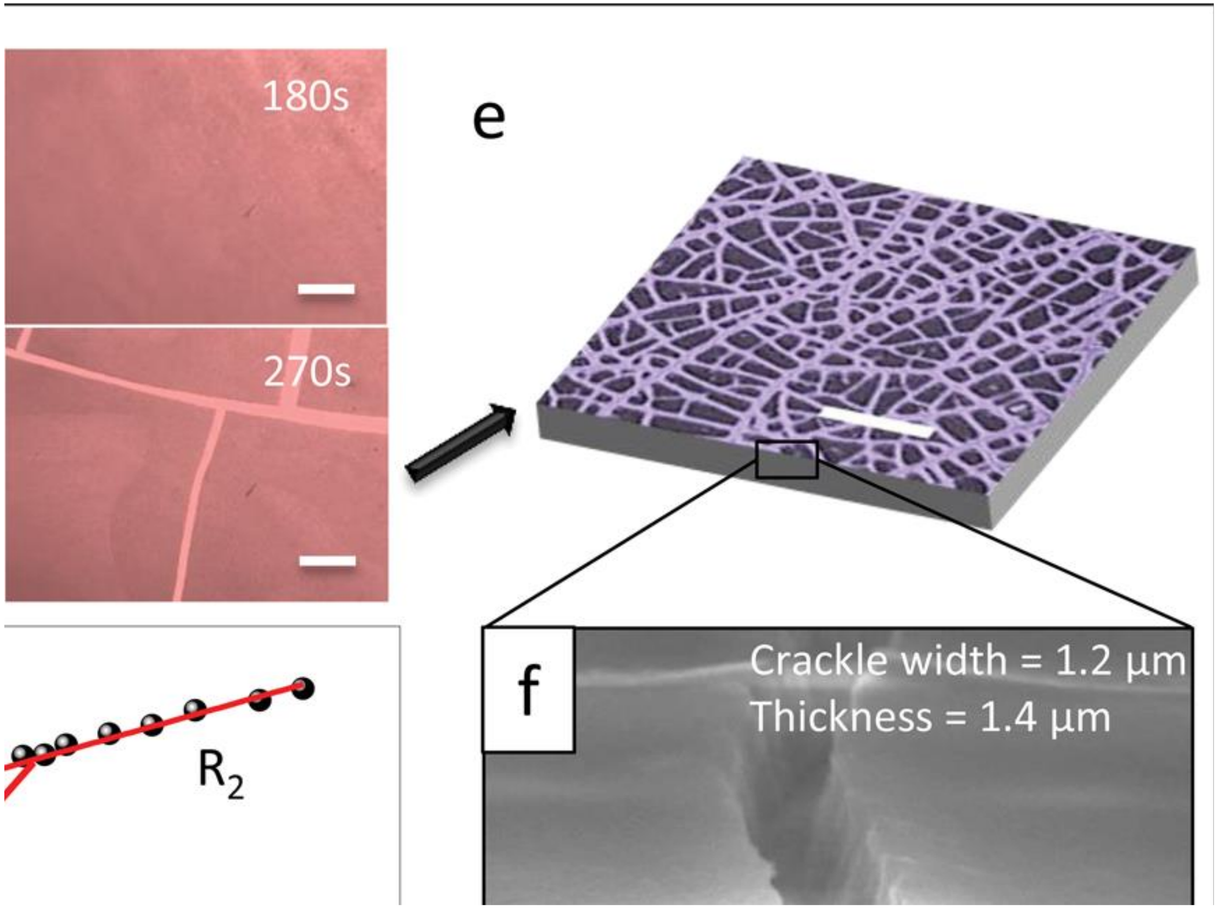






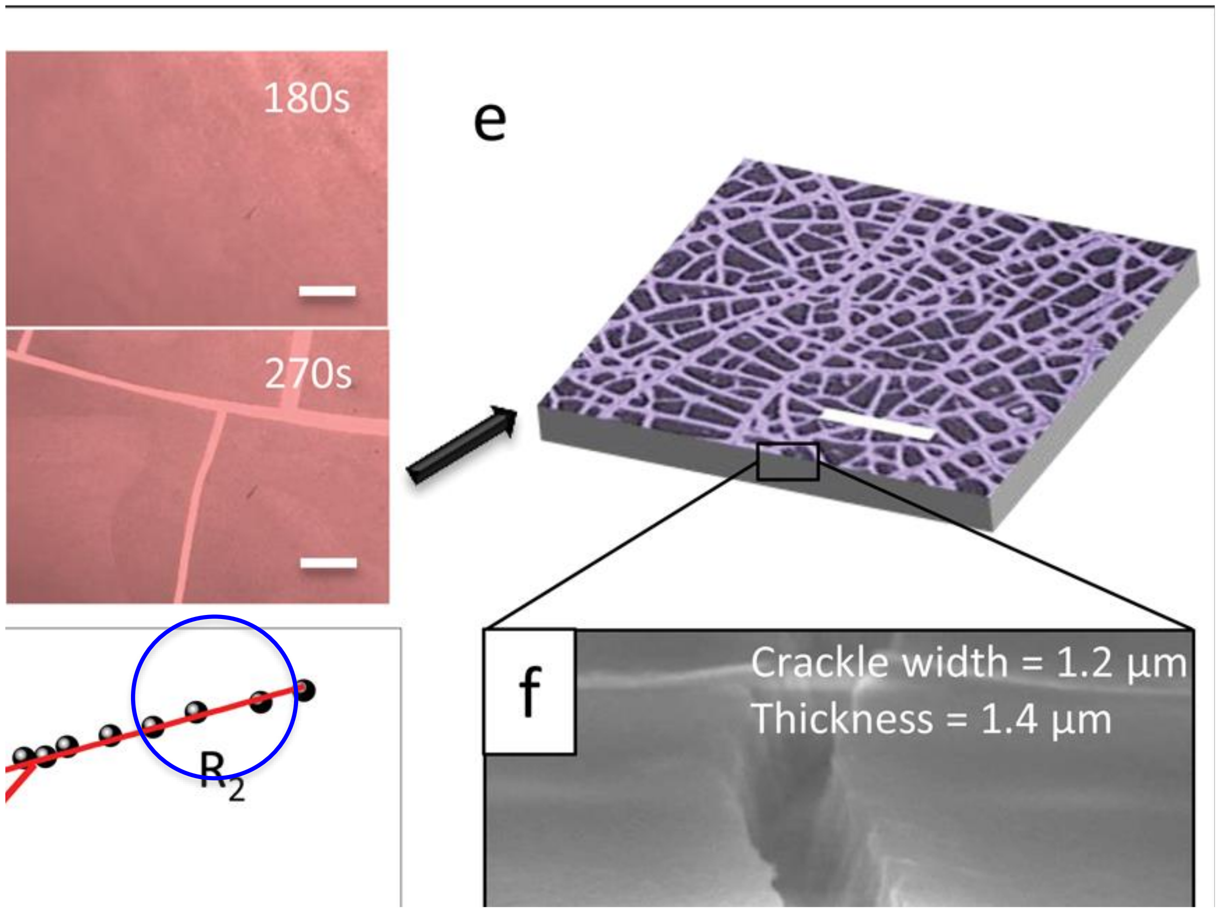
Kiruthika, Ritu, Mallik and Kulkarni, *J. Mater. Chem. C*, 2014

Variations with film thickness



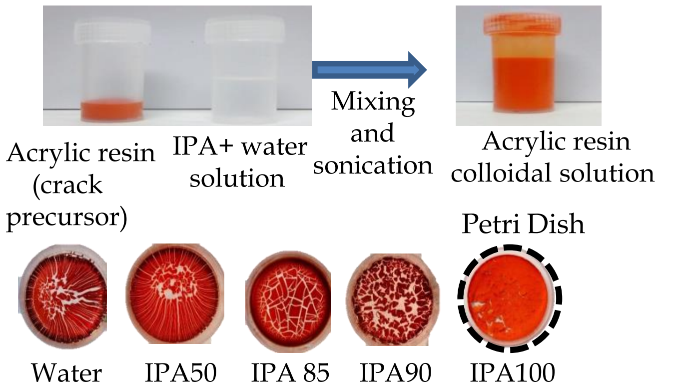
Above critical thickness, the crack width and polygonal cell size vary linearly.

Variations with film thickness



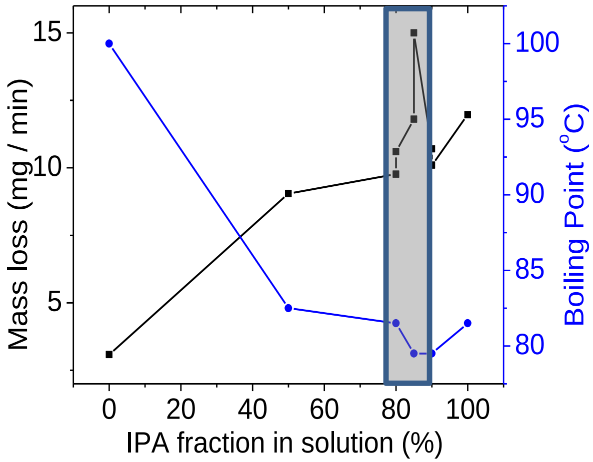
Above critical thickness, the crack width and polygonal cell size vary linearly.

Importance of the Solvent media in Crack formation

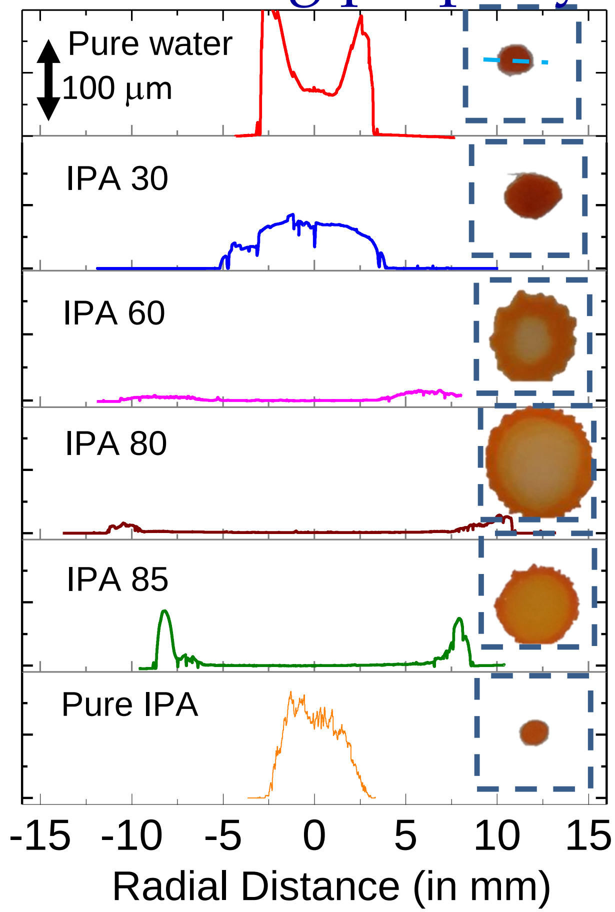


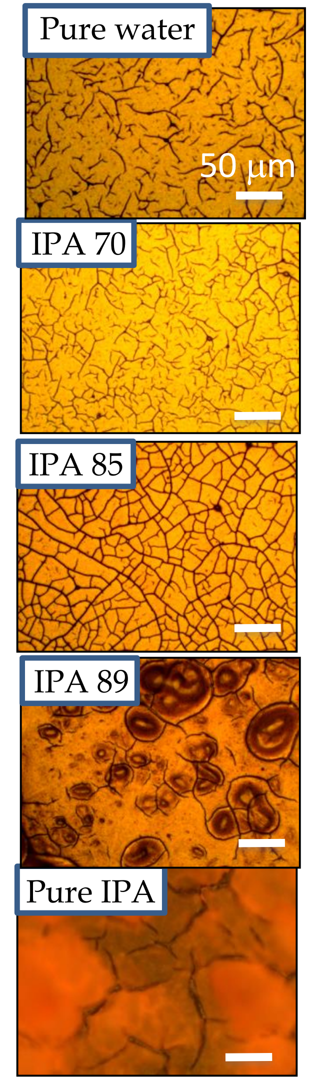
85% IPA show better cracking. But why ?

Evaporation studies



Wetting property

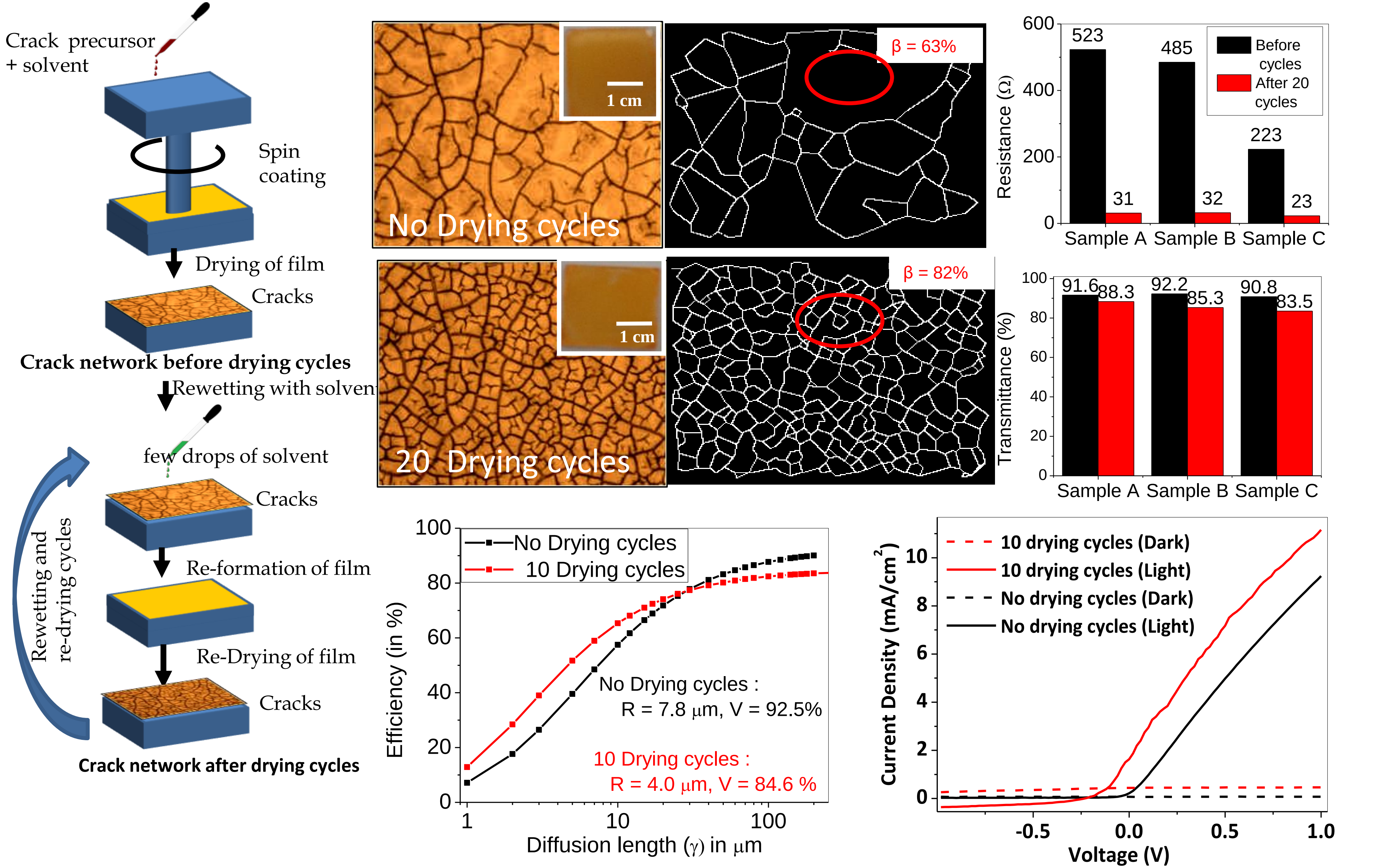




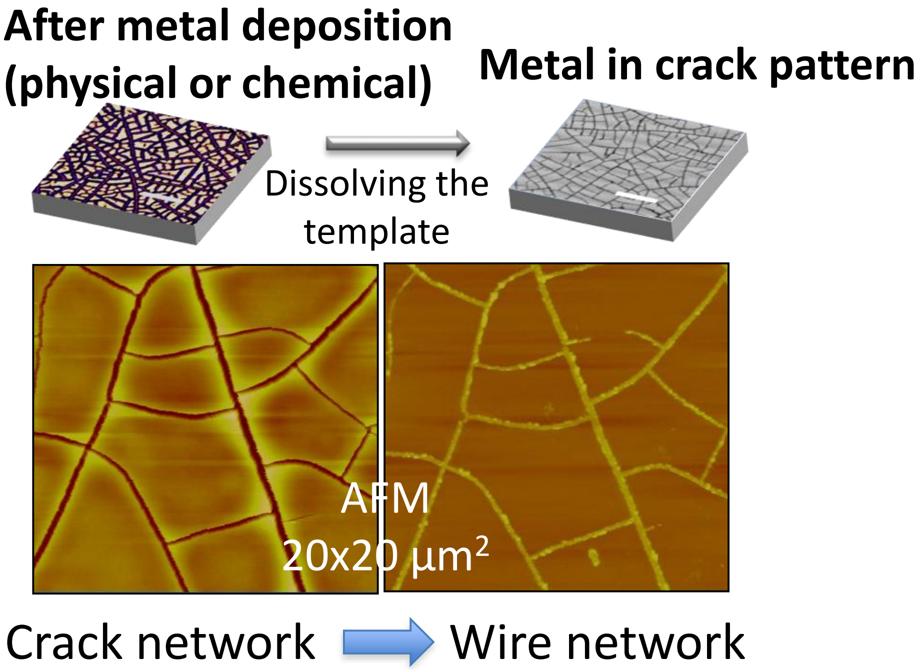
The study shows the better cracking of 85% IPA is due to its higher evaporation rate (low adhesion) and exceptional wetting nature, required for the cracking process. With spin coating solvent offered crack width < 500 nm which was utilized for making nano-meshes and hybrids.

A. Kumar , R. Pujar, K. D. M. Rao , S. Tarafdar, G. U. Kulkarni (*under preparation*)

Stress Modulation in Desiccating Crack Networks for Producing Effective Templates



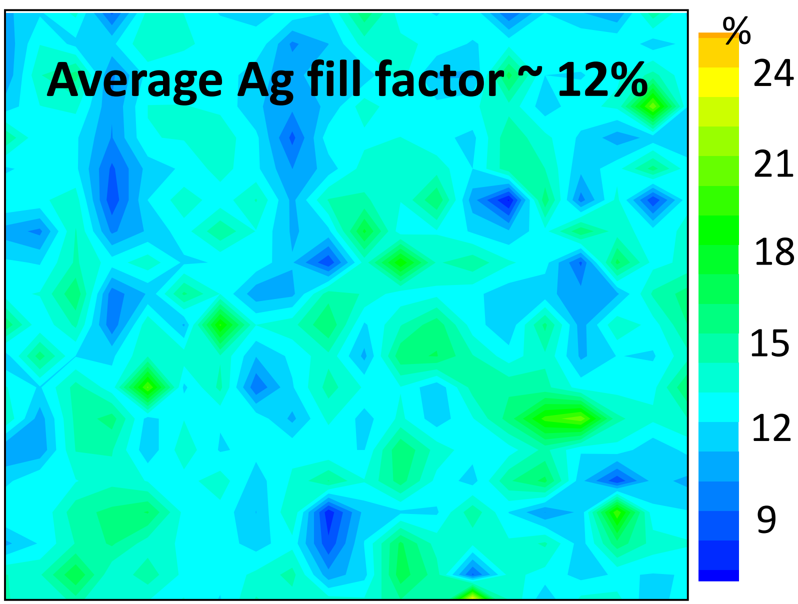
A. Kumar , R. Pujar, N. Gupta, S. Tarafdar, G. U. Kulkarni. *Appl. Phys. Lett.* **2017**, *111*, 013502



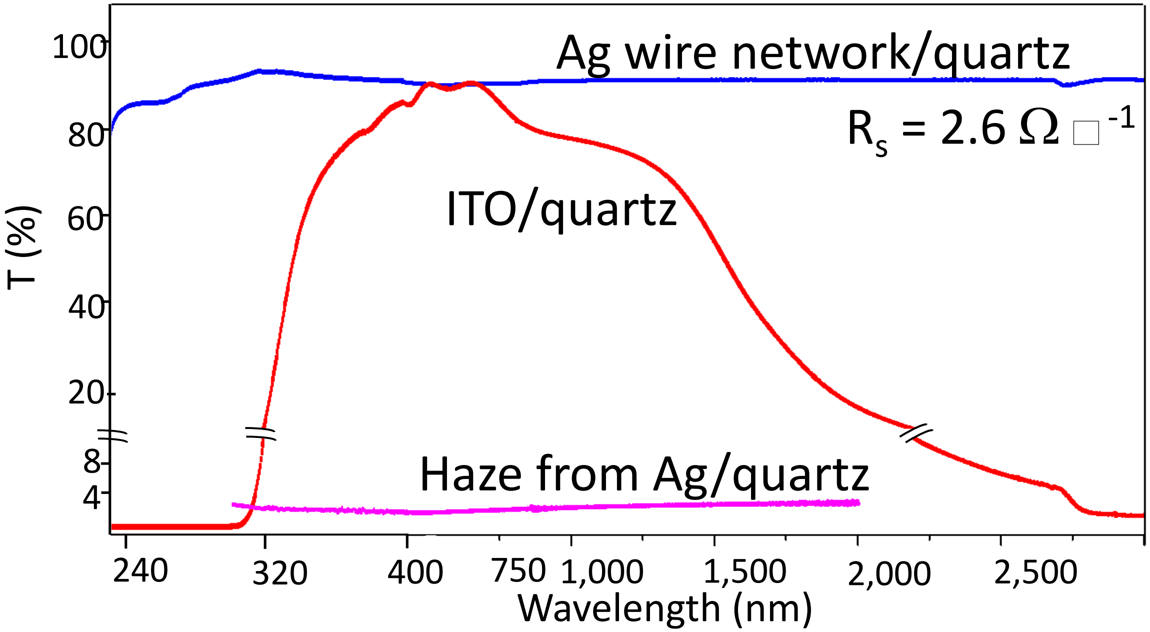
Profilometry image (1 x 1 mm^2)

Highly interconnected over virtually unlimited area

Metal (Ag) fill factor



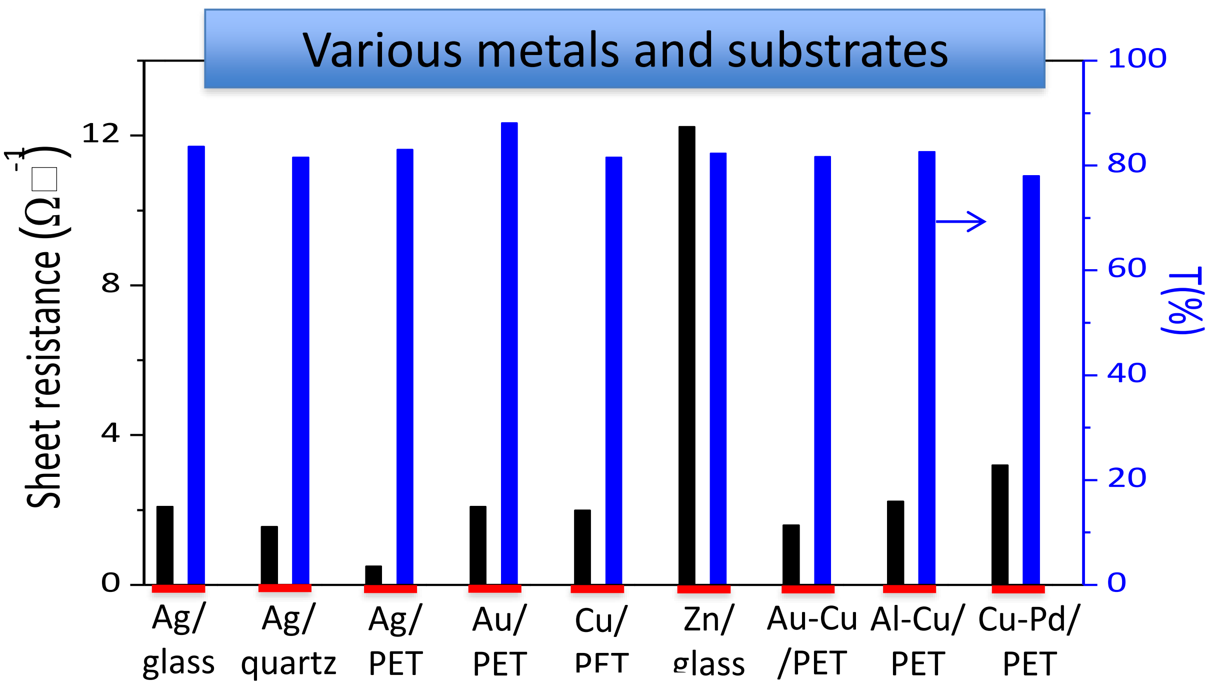
Mallik, Ritu and Kulkarni, *Adv. Mater. Inter*. 2014.



FoM ~ 2400

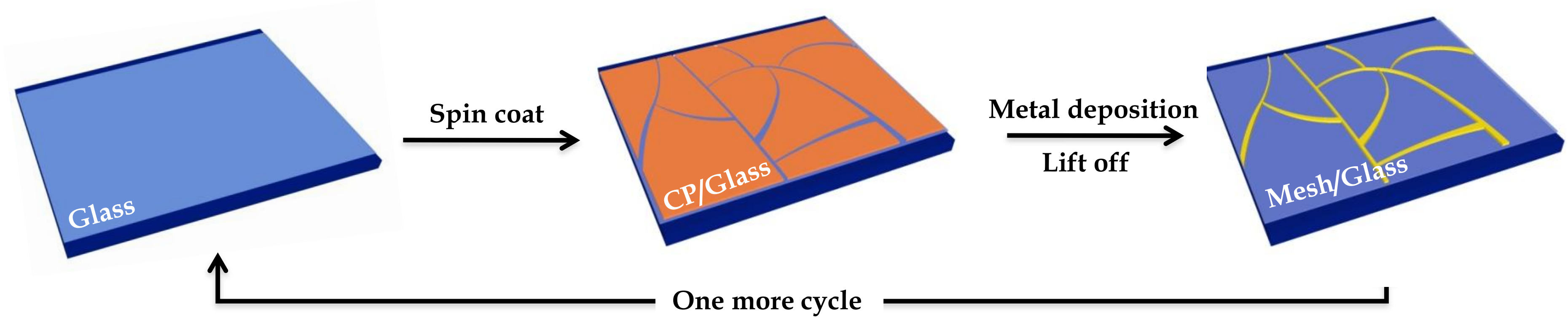
Wide spectral range TCE

Low haze

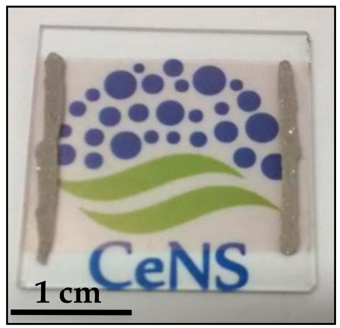


Ag wire network/PET

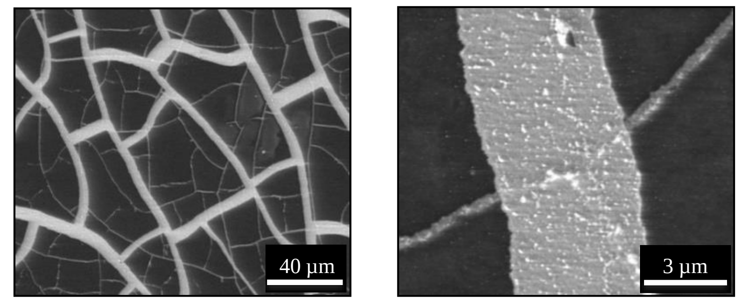
Mesh-over-mesh Transparent Electrodes

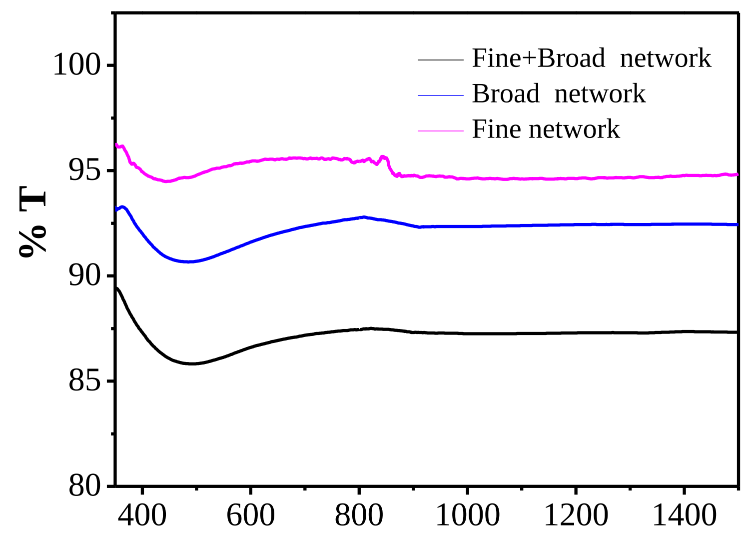


Fine metal network



Hybrid metal network



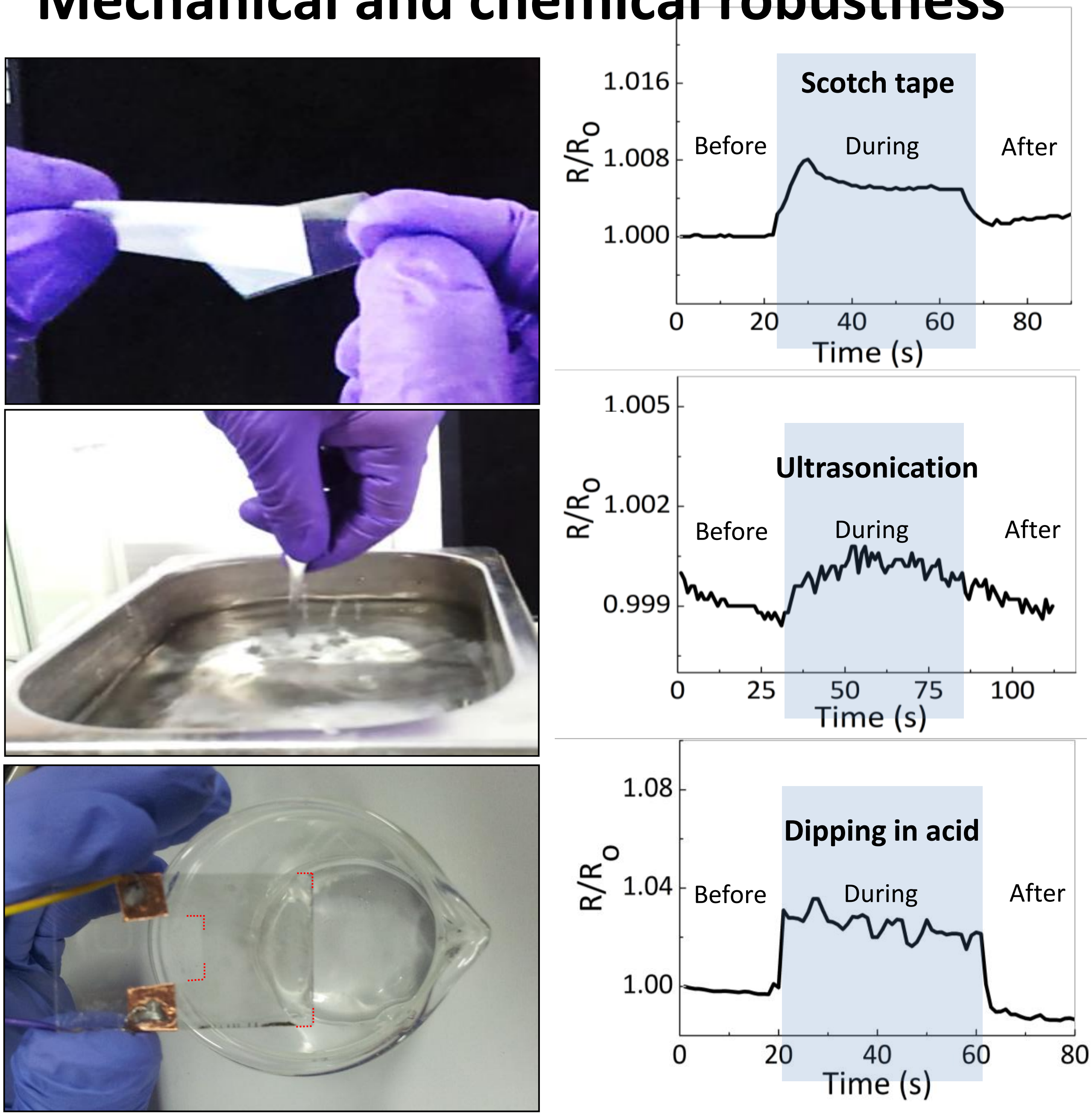


Merits:

1.Good transparency > 85%
2.Efficient charge collection due to fine metal network pattern
3.Low sheet resistance for hybrid TCE 20 Ω/☐

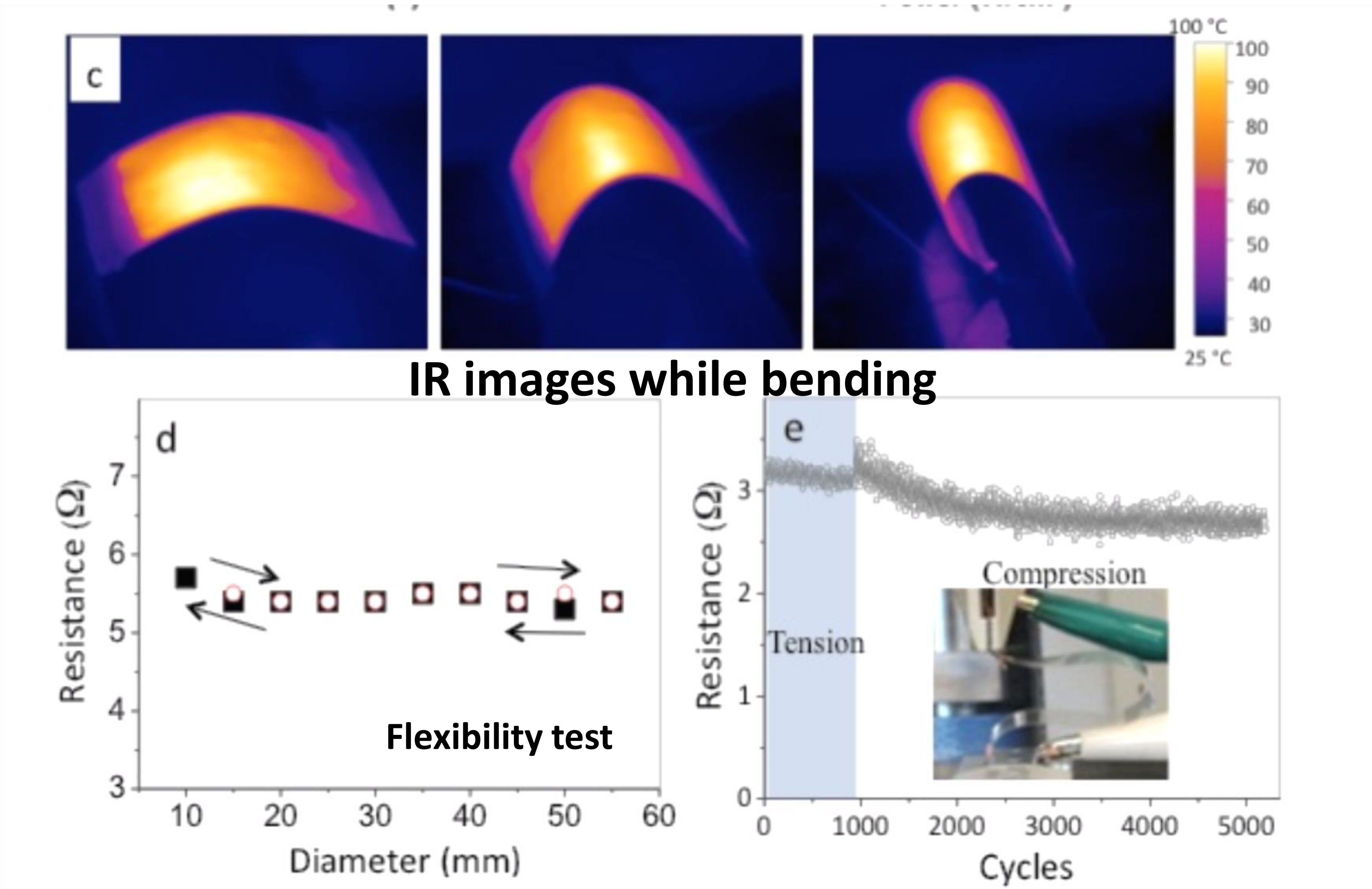
R. N. Pujar, A. Kumar, K. D. M. Rao and G. U. Kulkarni (Patent filed)

Mechanical and chemical robustness



Flexible Joule heaters

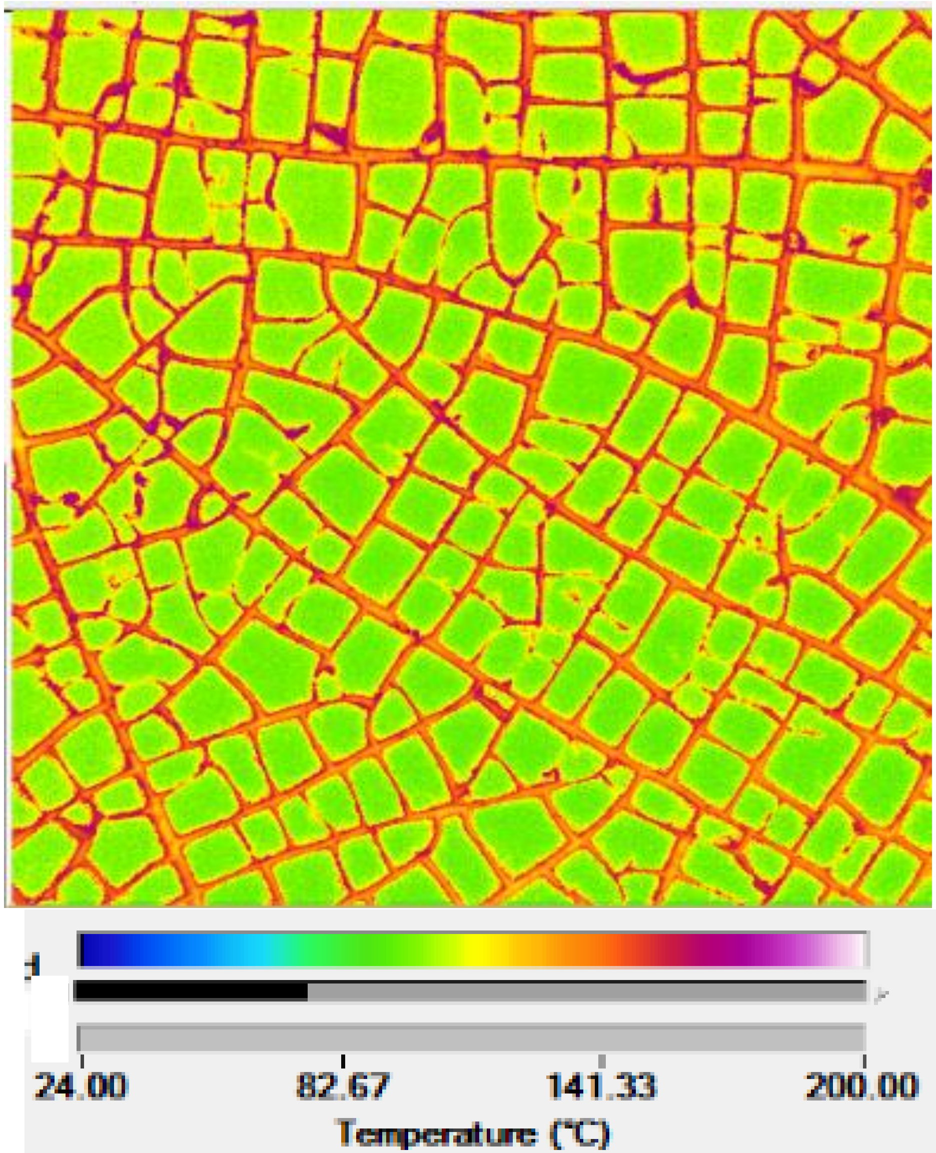
Applied voltage ~ 5 V

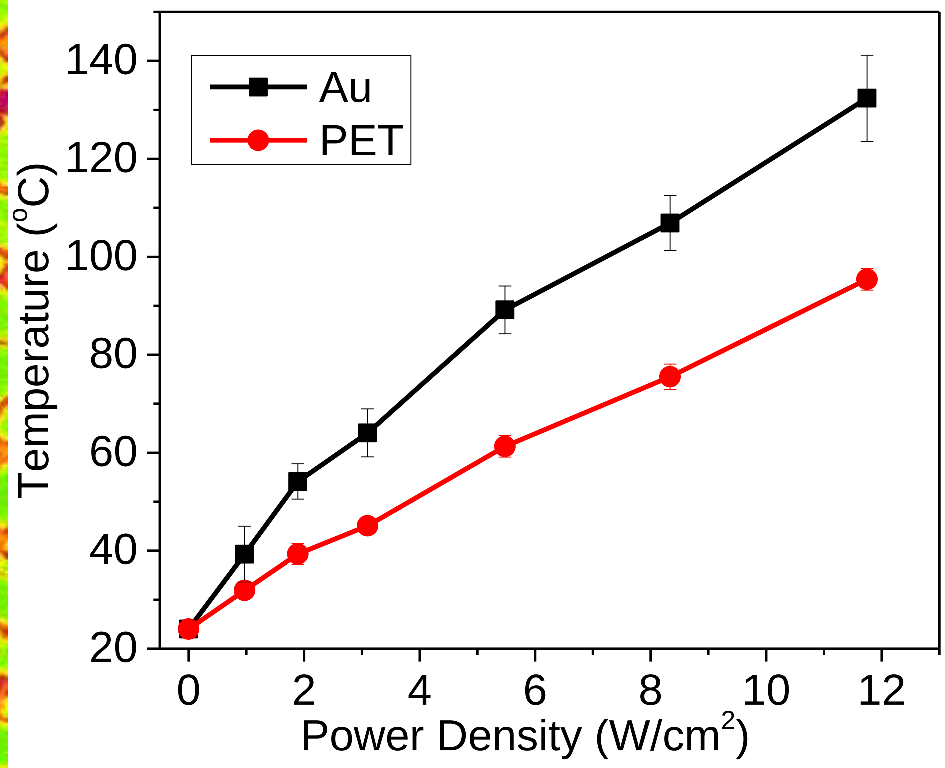


Mallik, Ritu and Kulkarni, *Adv. Mater. Inter*. 2014.

IR microscopy

Au wire network on PET, 6.9 Ω/□





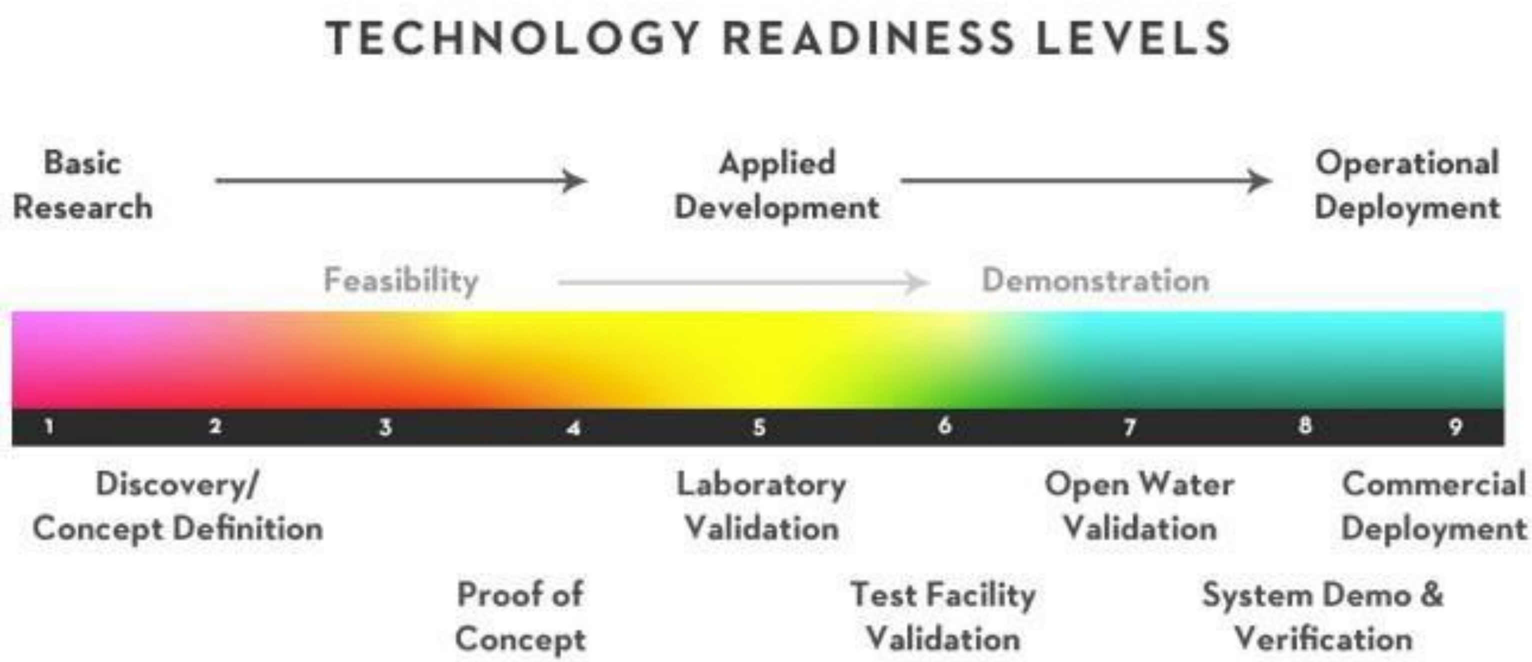
Joule heated with 1.8 V

Wire connectivity and thermal interface

R. Gupta, A. Kumar, S. Sadasivam, S. Walia, G.U. Kulkarni, T.S. Fisher, A. Marconnet, ACS AMI, 2017, 9, 13703

Translating Invention to Technology

Invention Ready



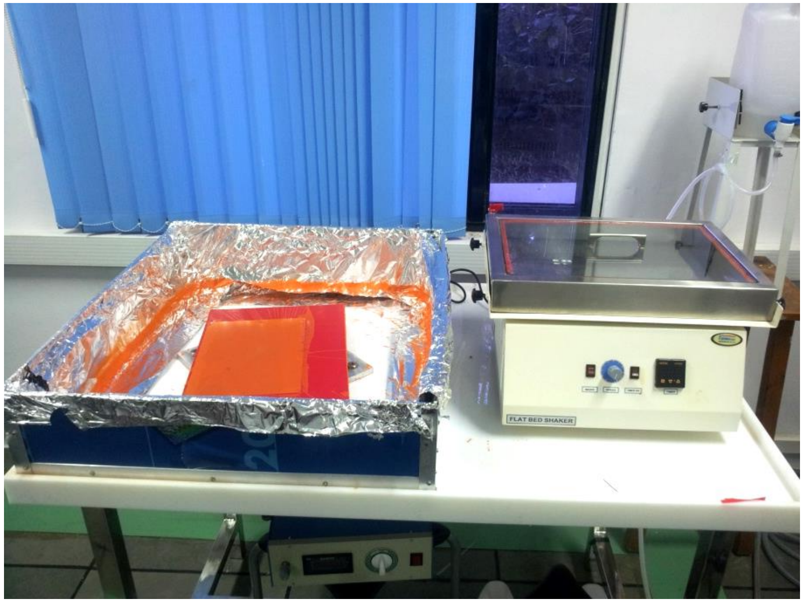
Market Ready

Universities, research organizations and innovators

Industry and companies

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

Large area metal mesh TCEs



Sn wire network on PET as transparent electrode

Touchscreen

Applications with metal wire mesh based TCEs

Defogger

Replace ITO electrodes

- Defrosting & Defogging panels
- Light control panels
- Transparent solar cells
- OLED
- Touchscreen
- Transparent EMI shields

New applications

- Transparent EMI shields
- Transparent heaters (high Temp)
- Flexible and curved touch screens
- Transparent capacitors
- Transparent Strain sensor
- Transparent Photodetector
- Transparent H_2 sensor
- Transparent supercapacitor

Applications in non-transparent domains!

S. Kiruthika, R. Gupta, K. D. M. Rao, S. Chakraborty, N. Padmavathy, G. U. Kulkarni, J. Mater. Chem. C 2014, 2, 2089.
K. D. M. Rao, G. U. Kulkarni, Nanoscale 2014, 6, 5645.
K. D. M. Rao, R. Gupta, G. U. Kulkarni, Adv. Mater. Interfaces 2014, 1400090.
S. Kiruthika, C. Sow, G. U. Kulkarni, Small, 2017, DOI: 10.1002/smll.201701906.
C. Hunger, K. D. M. Rao, R. Gupta, C. R. Singh, G. U. Kulkarni, M. Thelakkat, Ener. Tech., 2015, 6, 638.

Invisible Metal Mesh – i2M

Visibly transparent yet electrically conducting materials are rare. Tin doped indium oxide (ITO) is a conventionally used material in optoelectronics but is quite expensive. Transparent conductors made from the present invention, i2Ms, provide affordable solutions besides adding many novel features.

Based on a patented recipe, fine metal wire meshes are built onto common substrates (glass or PET) over large areas, maintaining high degree of uniformity. The resulting transparent conductors, i2Ms, show transmittance up to 90% and very low sheet resistance (~few ohm per square). A wide variety of metals including Sn, Cu, Ag and Au are possible, depending on the application.

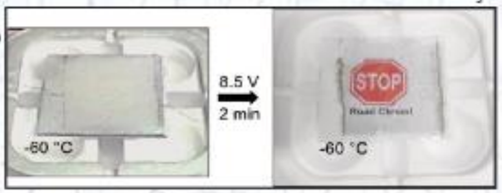
Touchscreen

A computer screen is made interactive by converting it into a touchscreen. A device with two i2Ms separated by a thin spacer serves as a resistive touchscreen in the example demonstrated. Such devices can be easily integrated into ATMs, floor map guides, game pads, mobile phones and even personal computers.

Defrosting or defogging panels

Metal wire networks with seamless junctions are ideal joule heaters for large area applications. With nominal power, i2Ms can defrost the host substrate effortlessly and enhance visibility, even while working at subzero polar temperatures! They are well suited for automobile wind shields, sign boards or for any outdoor application.

Defrosting

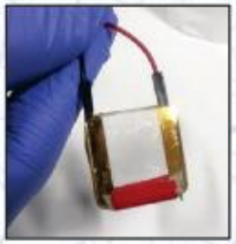


Defogging

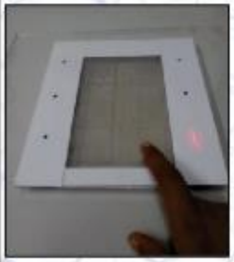
i2Ms can also defog a panel, from bathroom mirrors to industrial plants. On the left is shown a photograph of a circular transparent lid covering a steam zone. A part of the lid is joule heated using embedded i2M to realize defogging action.

Invisible Metal Mesh – i2M

Thin Film Heater (TFH)



i2Ms embedded between quartz plates serve as transparent heating platforms for a variety of applications. Quartz being transparent from UV to IR regions, such platforms are ideal in spectroscopy measurements. They can also be used as substrates for microscopy and diffraction.



Invisible Switches

A control panel with arrays of switches occupies physical as well as visual space, be it at industry, office or at home. Futuristic technology aims at smart windows and glass partitions integrating invisible switches. In the example shown, two patterned i2Ms separated by a thin spacer serve as an array of invisible switches. Such devices can be deployed at home along with lifestyle items and importantly, in industrial control rooms.

EMI shields and antennas

i2Ms can arrest unwanted electromagnetic radiation particularly in the microwave range. i2M panels can be used in anything - from transparent Faraday cages to microwave oven windows. Alternatively, they can serve as antenna, enhancing radio, wifi and bluetooth signals. As part of flip cover, a i2M layer is a true touch guard!

For Collaboration/Tech transfer, contact:

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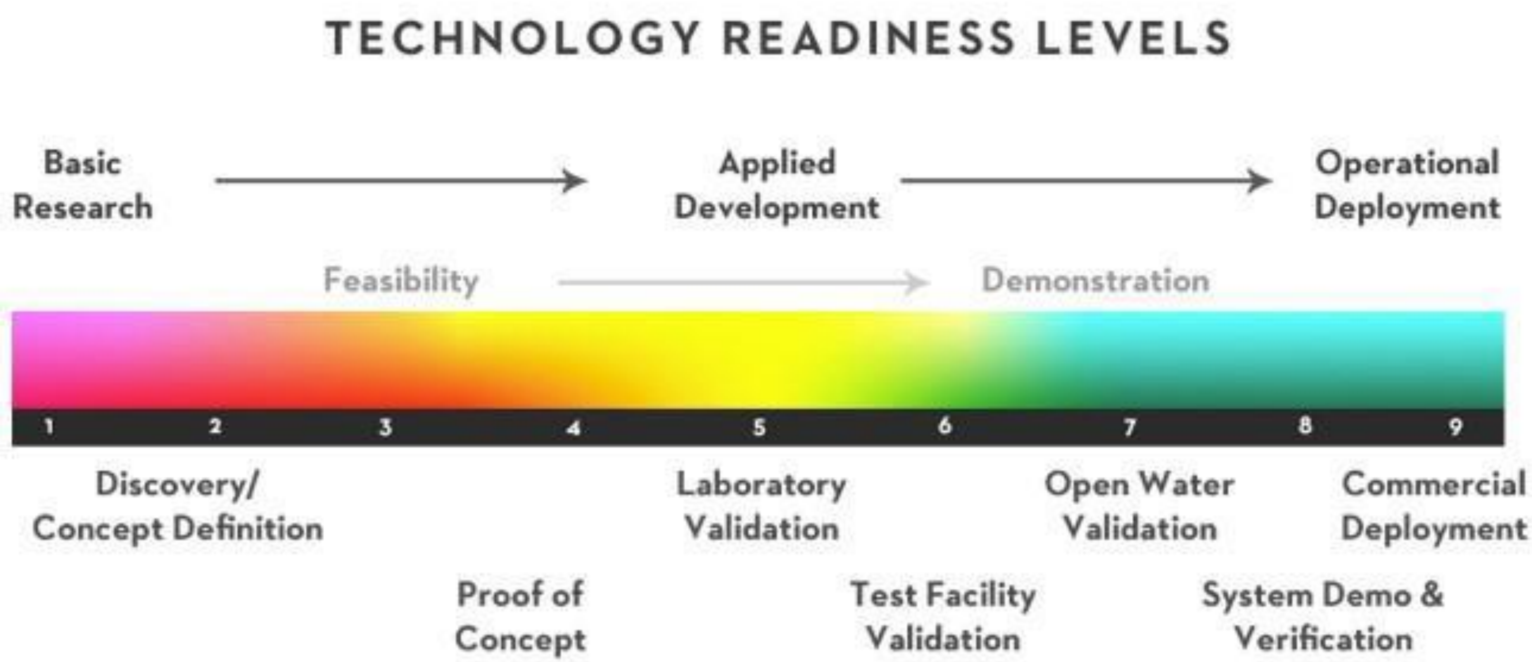
Visit our stalls at Technology expos

Translating Invention to Technology

…. Joint developmental projects with Industries!

Invention Ready



Market Ready

Universities, research organizations and innovators

Industry and companies

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

Coworkers

K.D.M. Rao
Ritu Gupta
S. Kiruthika
Ankush Kumar
Karthikeya
Sunil Walia
Indrajit Mondal
Ashutosh Singh

Solar cells
Prof. Mukundan T.
University of Bayreuth

Crack modeling
Prof. S. Tarafadar, Jadavpur University

Thermal transport
Prof. T.S. Fisher and Prof. A. Marconnet
Purdue University

OLED
Prof. P.K. Iyer, IIT Guwahati

Thanks to Nanomission and DST-EU project on Solar cells

Summary

- Transparent conducting electrodes have been realised using metal wire networks, produced using crack template and metal deposition.
- Entirely solution produced TCEs have been made. Roll-to-roll coating possible.
- Metal wire networks are highly interconnected with low and uniform fill factor.
- Wire junctions are seamless and of low resistance and lead to High thermal performance.
- Any metal and any substrate will do.
- A low cost method scalable to ultra-large area.

Transparent capacitor

Future work

- Different materials, heterostructures and plasmonics
- Percolation aspects

Patent information

1. Indian Patent Application No. 954/CHE/2013 filed on 5 March 2013.

2. International PCT Application No. PCT/IB2014/059411 filed on 4 March 2014.