“Smart Functional Materials for energy: from laboratory to commercialization”

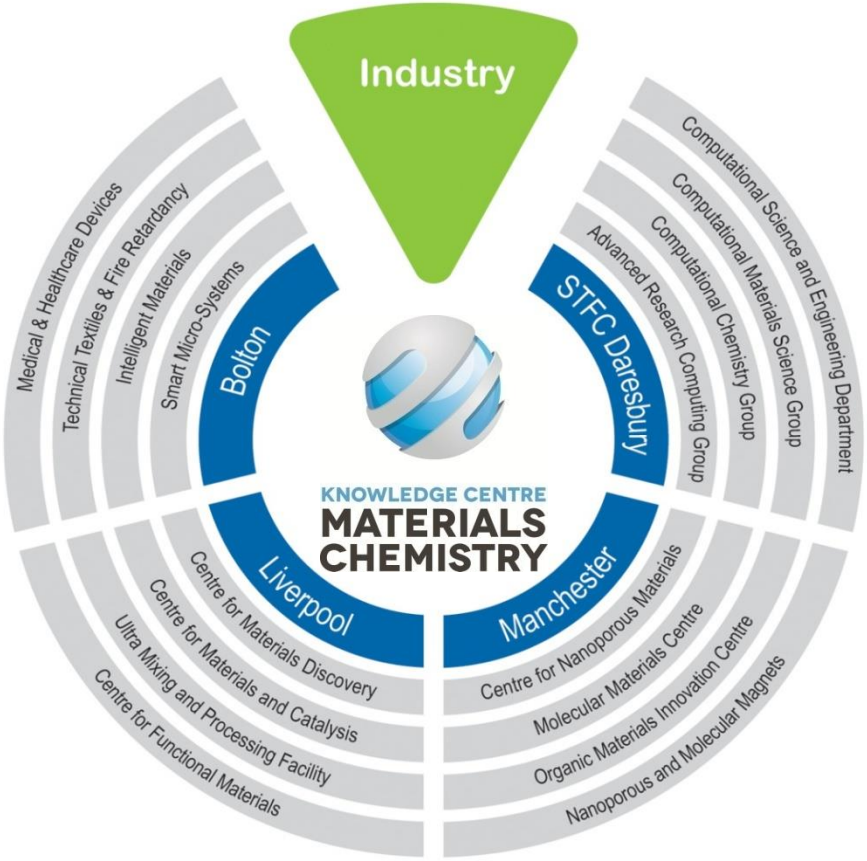
Prof. Elias Siores,

Provost, Research & Academic Development,

University of Bolton

Knowledge Centre for Materials Chemistry

- Virtual Centre for Collaborative R&D based in England's NW
- Single point of contact to four leading research institutions
- Pro-active help in formulating and delivering industry projects
- Dedicated project scientists in partner institutions for fast track project initiation
- Excellence in Knowledge Transfer



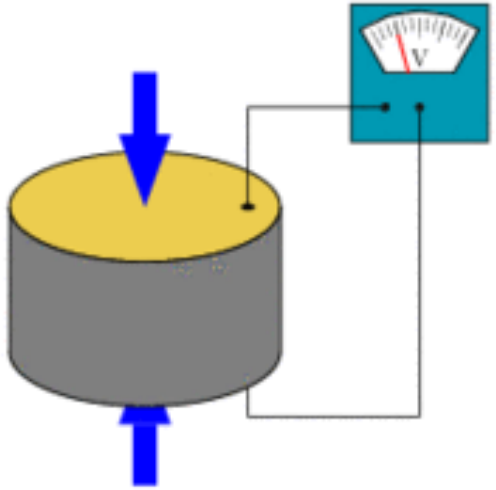
Piezoelectric effect

- Direct piezoelectric effect

-change in electric polarization with a change in applied stress.

- Converse piezoelectric effect

-change of strain or stress in a material due to an applied electric field.



Timeline

NOTION BY CHARLES COLOUMB, 1817

PIERRE & JACQUES CURIE, 1880

NAME GIVEN BY HANKEL, 1881

PIEZOELECTRICITY OF BaTiO3, 1946

LEAD ZIRCONATE TITANATE (PZT), 1952

PIEZOELECTRICTY OF POLYVINYLIDENE FLUORIDE (PVDF) BY KAWAI, 1969

Naturally occurring piezoelectric materials

- Bone
- Tendon
- Silk
- Wood
- Enamel
- Cane sugar
- Tourmaline
- Rochelle salt
- Berlinite
- Quartz etc.








Synthetic piezoelectric materials

Piezoelectric Ceramics

- Barium titanate ($BaTiO_3$)
- Lead titanate ($PbTiO_3$)
- ***Lead zirconate titanate (PZT)***

$Pb[Zr_xTi_{1-x}]O_3$ $0 \leq x \leq 1$

- Potassium niobate ($KNbO_3$)
- Lithium niobate ($LiNbO_3$)
- Lithium tantalate ($LiTaO_3$)
- Sodium tungstate (Na_2WO_3)

Piezoelectric Polymers

- Polyvinylfluoride (PVF)
- ***Polyvinylidene fluoride (PVDF)***
- Porous Polypropylene (PP)
- Fluoroethylenepropylene (FEP)
- Polytetrafluoroethylene (PTFE)
- Cellular cycloolefines (COC)
- Cellular polyethylene terephthalate (PETP)

Piezo Ceramics vs. Piezo Polymers ?

- Existing Ceramic based fibres are:
  - Lead zirconate titanate (Lead based)
  - Rigid, Brittle
  - Cannot be knitted/woven
  - Need to be embedded inside a further polymer matrix



- Polymer based fibres are:
  - Extremely flexible, high mechanical strength
  - Can be knitted/woven into complex 2-D and 3-D textile structures
  - High comfort level for wearable applications

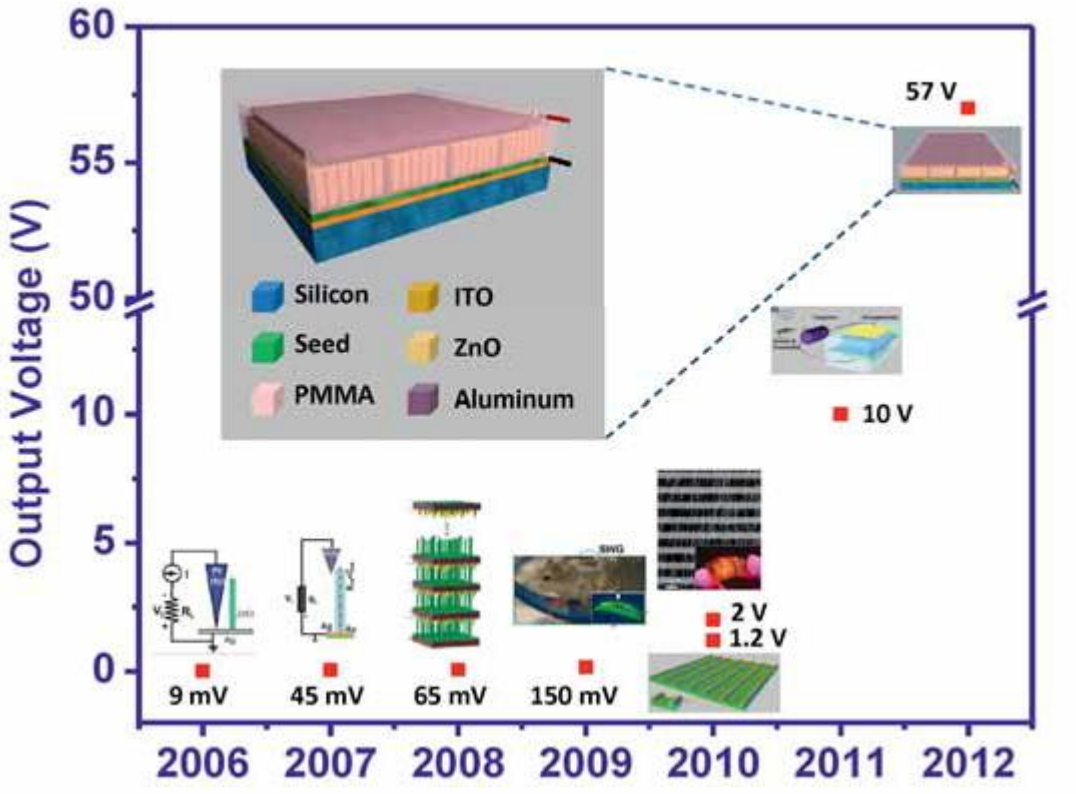


Piezo Ceramics vs. Piezo Polymers ?

Property	Units	PVDF Film	PZT	$BaTi0_3$
Density	10^3kg/m3	1.78	7.5	5.7
Relative Permittivity	ϵ/ϵ_0	12	1,200	1,700
d_{31} Constant	(10^{-12})C/N	23	110	78
g_{31} Constant	(10^{-3})Vm/N	216	10	5
k_{31} Constant	% at 1 KHz	12	30	21
Acoustic Impedance	(10^6)kg/m^2-sec.	2.7	30	30

Comparison of piezoelectric properties

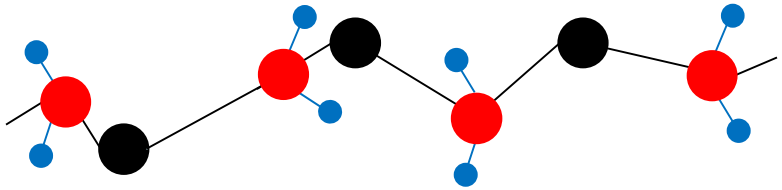
Current status of piezoelectric nanogenerators



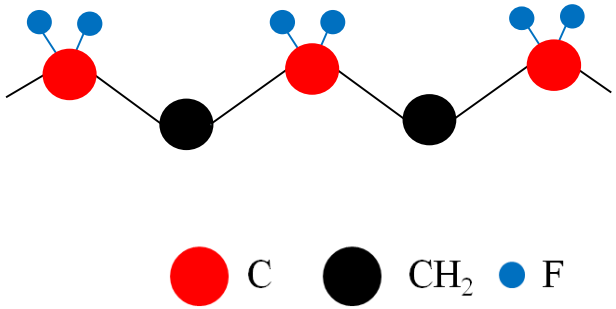
Z. L. Wang, Materials Today, 532 Dec. 2012 | Volume 15 | Number 12

Piezoelectric PVDF processing

- **Polyvinylidene fluoride (PVDF)** *: long chain semi-crystalline polymer*
- *Exists in multiple phases:* α, β, γ and δ phases out of which β , γ are piezoelectric
- **α phase** - Non-polar centrosymmetric



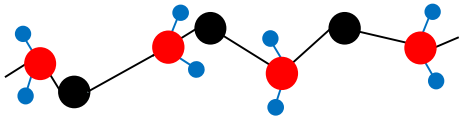
- **β phase** – Cells packed in parallel planes after stretching or extrusion



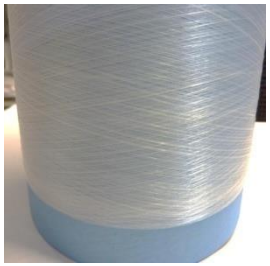
Piezoelectric PVDF processing



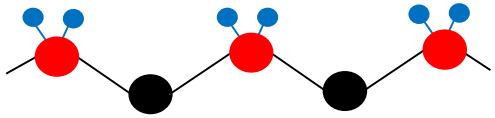
α-phase







β-phase

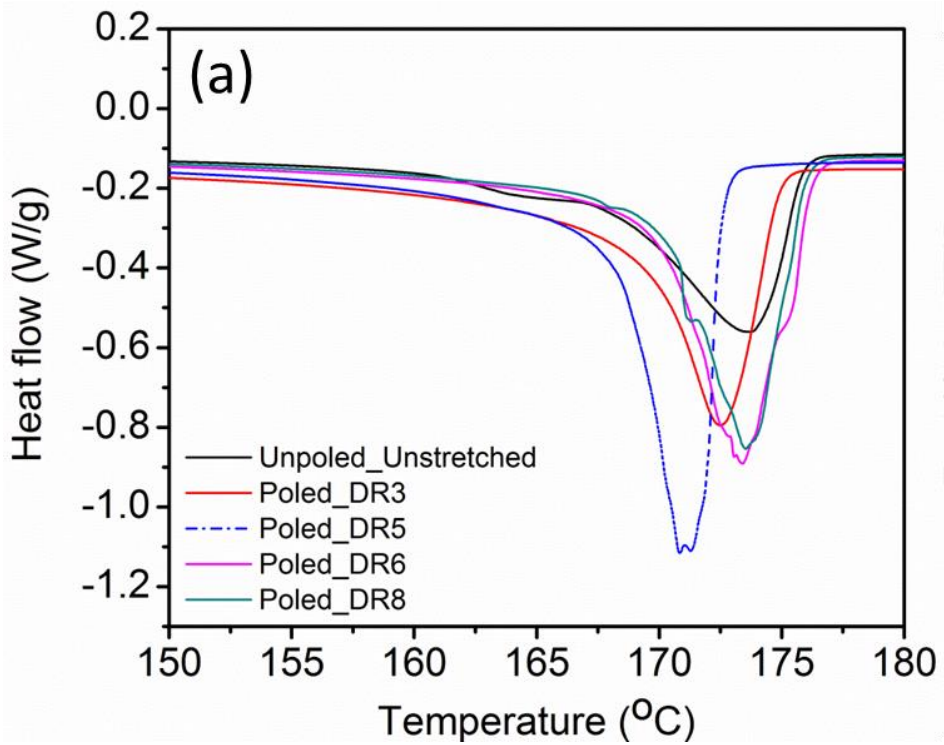


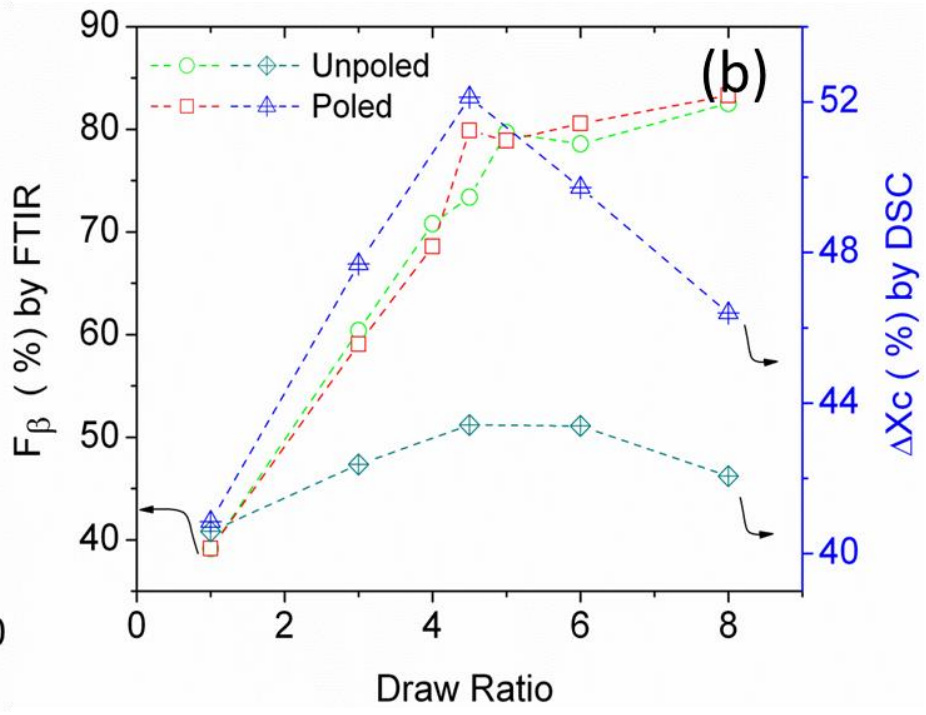


High stretching ratio + High voltage + Elevated temperature

On-line poling of piezoelectric PVDF filaments ***(Intl. Patent WO/2012/035350)***

Piezoelectric PVDF process optimisation

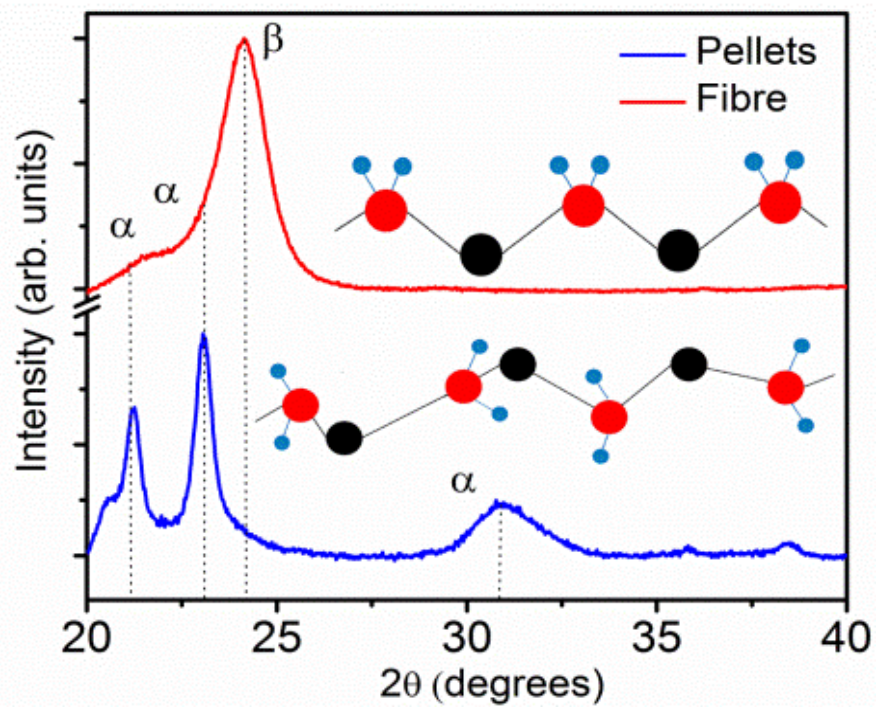


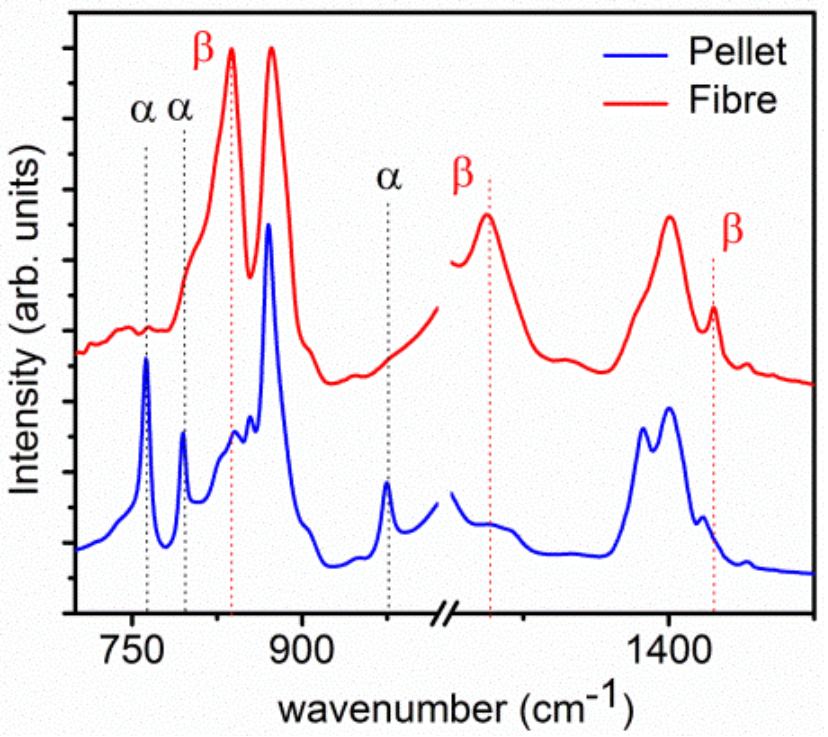


(a) DSC analysis of poled PVDF samples and (b) variation of β-phase content and ΔXc as a function of draw ratio and poling.

Piezoelectric PVDF processing

High β-phase monofilaments (85-90% by FTIR and XRD)





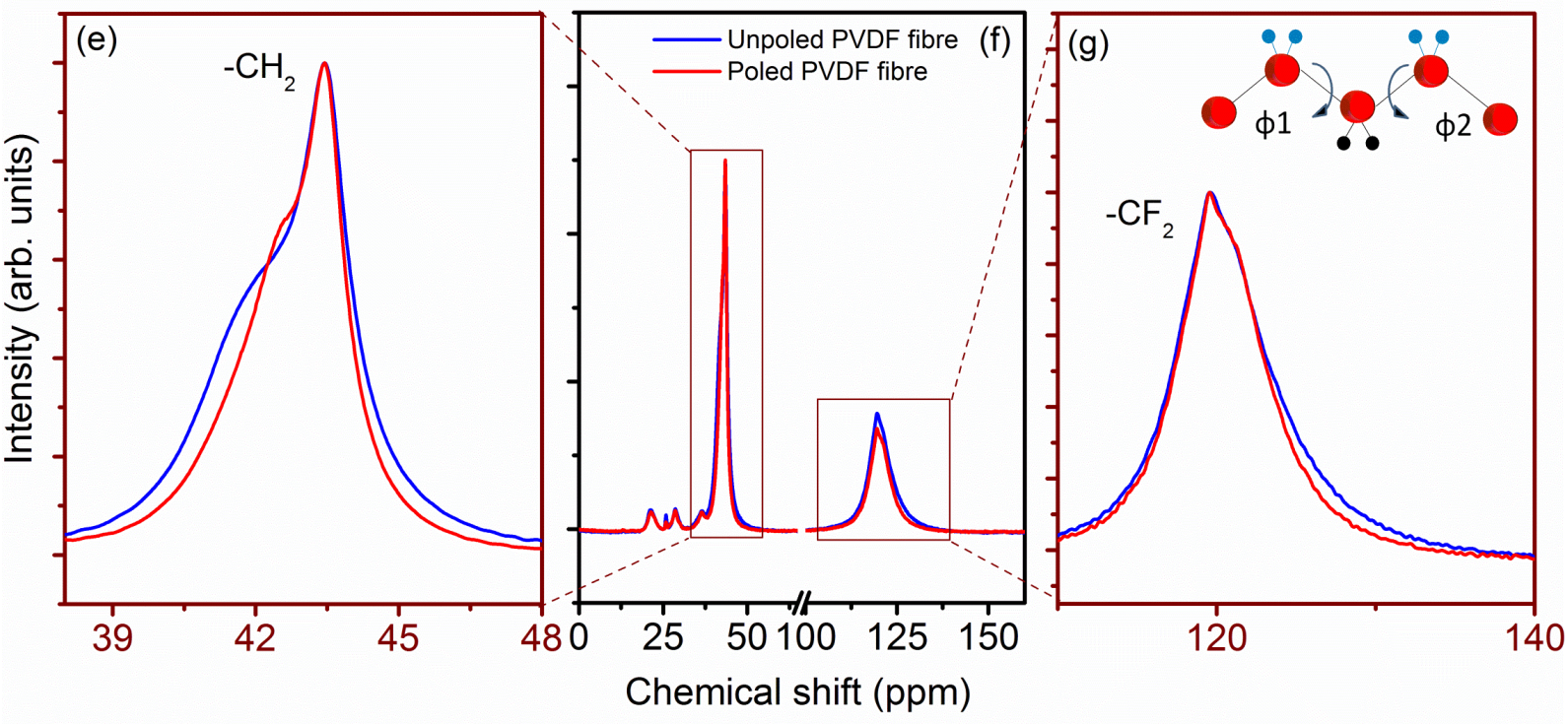
(a) XRD spectra of pellets and fibres showing the enhancement of the β phase, (b) enhancement of vibration associated with β phase measured with FTIR

Piezoelectric PVDF processing

FibrLec

University of Bolton

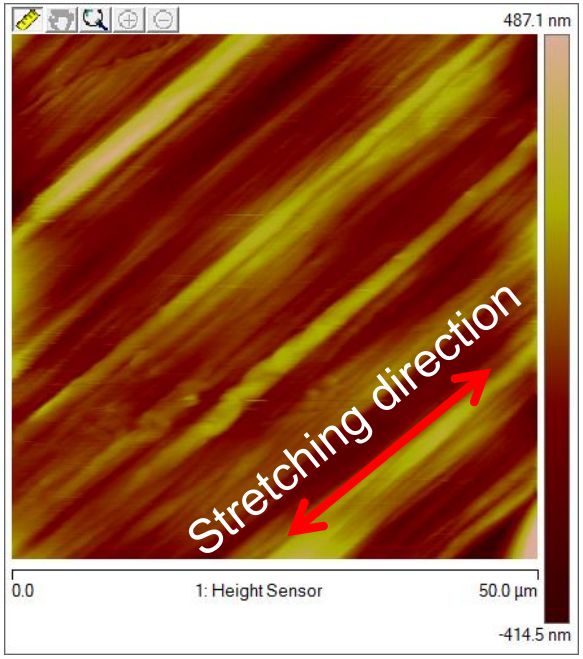
^{13}C NMR of poled and unpoled fibres

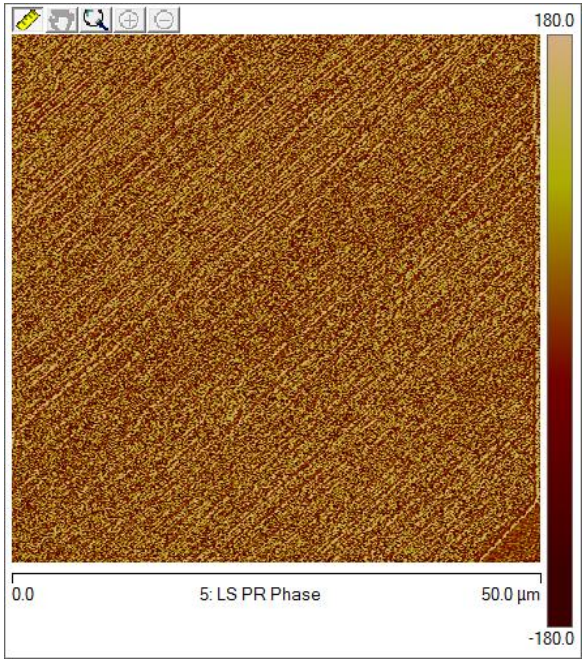


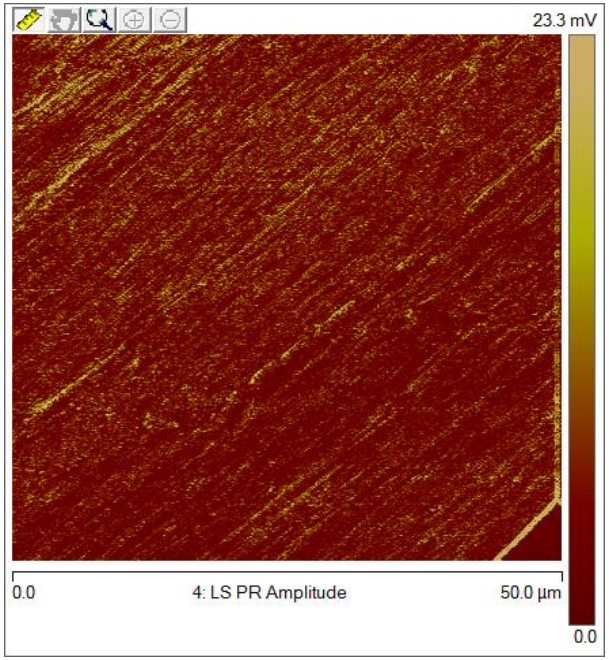
- $-CH_2$ at 44 ppm and $-CF_2$ at 122 ppm both show sharpening after poling
- Attributed to a change in the distribution of the backbone torsion angles (altered under applied electric field present during poling)

Piezoelectric PVDF processing

- *High β-phase monofilaments (85-90% by FTIR and XRD)*
- *d_{33} coeffecient of ~ 60 pm/V (by PFM)*

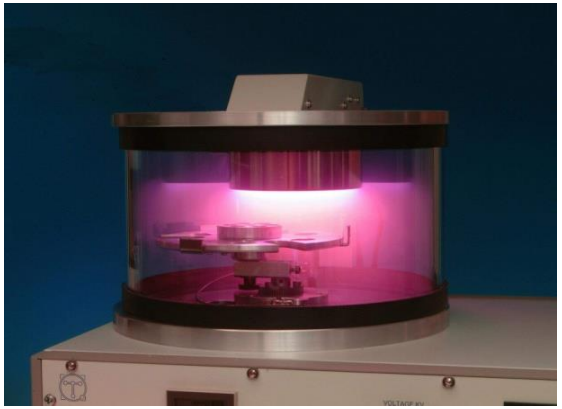


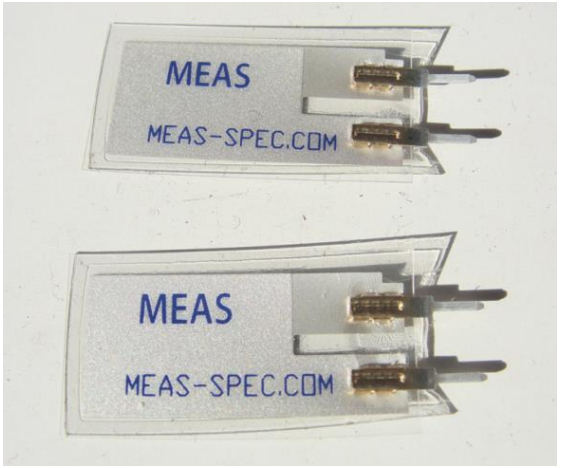




Problems with commercial piezo PVDF films

- Need to attach metal electrodes to commercial PVDF piezo thin films via sputtering (high cost)
- The poor fatigue resistance of the metal foil under repeated mechanical deformation
- Leads to failure of the piezoelectric sensor, making durability an issue





Overcoming metal foil fatigue & using PVDF fibres ?

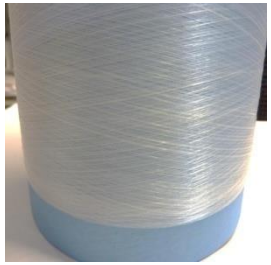
FibrLec

University of Bolton

✓Making one single coherent "3-D spacer" structure with integrated metallic electrodes enclosing the PVDF yarn → direct charge transfer

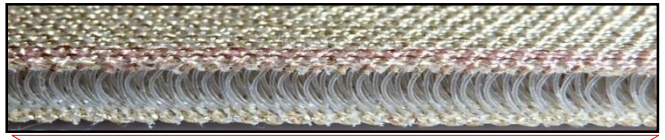


+





World's 1st all fibre piezoelectric fabric structure





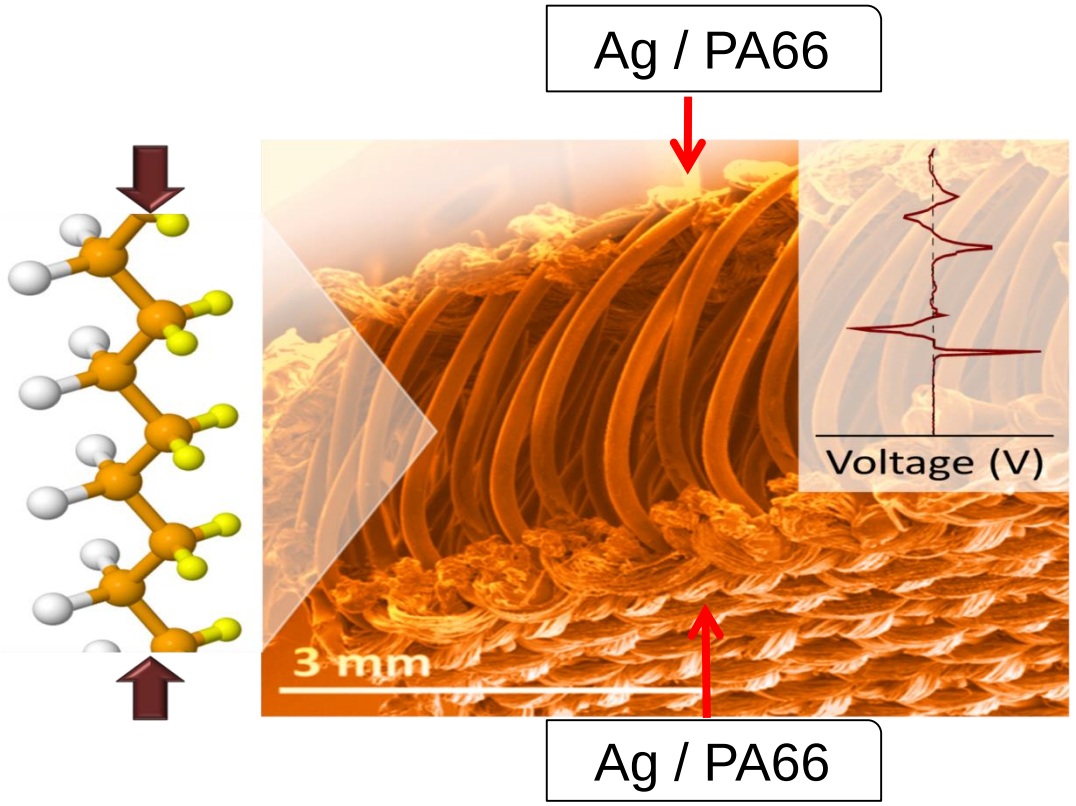
3-D spacer piezoelectric fabrics

Current production rates:

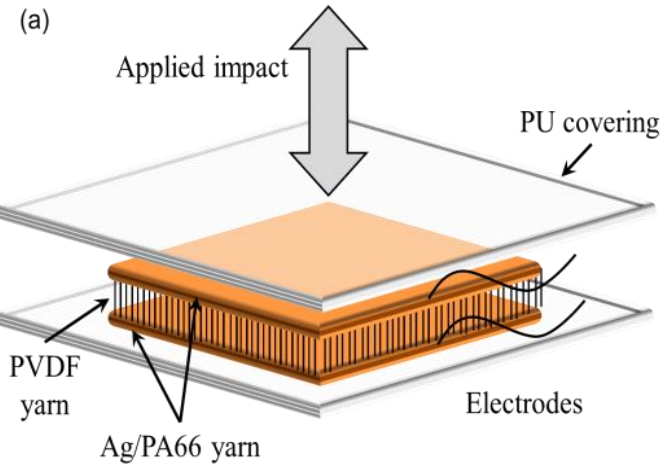
- *Piezo PVDF fibre: upto 500 m/min (up scaled from ~ 10-15 m/min)*
- 3D spacer fabric: upto 70 m^2/hr

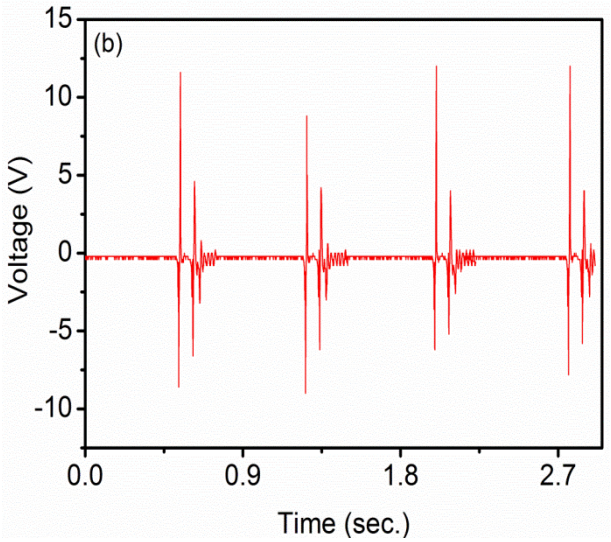
Advantages:

- *Excellent compression and resilience properties*
- *All fibre technology: lightweight & completely flexible*
- *Looks and feels no different to ordinary fabrics*



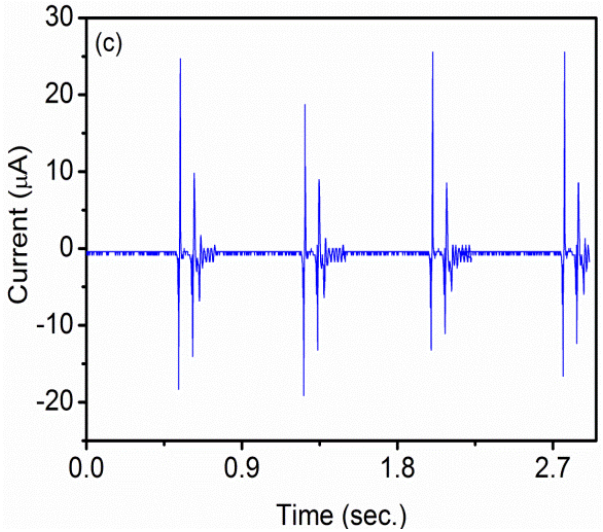
Energy harvesting using 3D piezo spacer fabrics

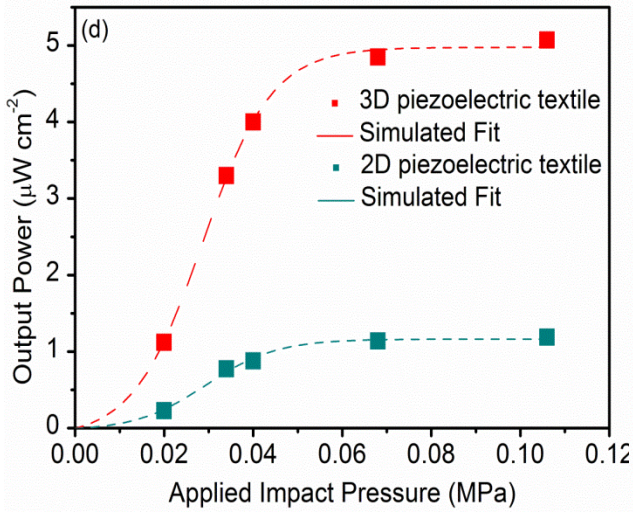


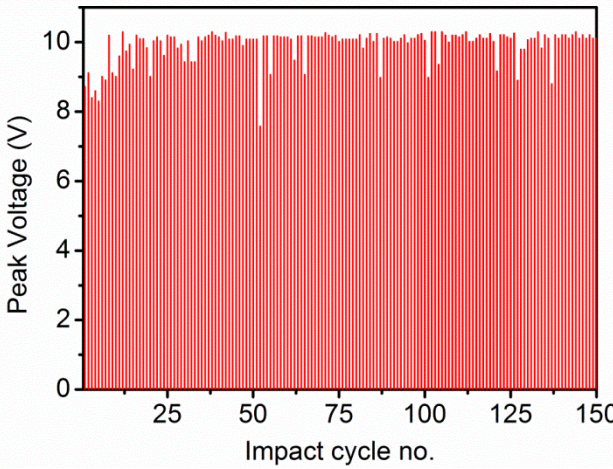


5 times higher power output vs. 2D piezoelectric textiles

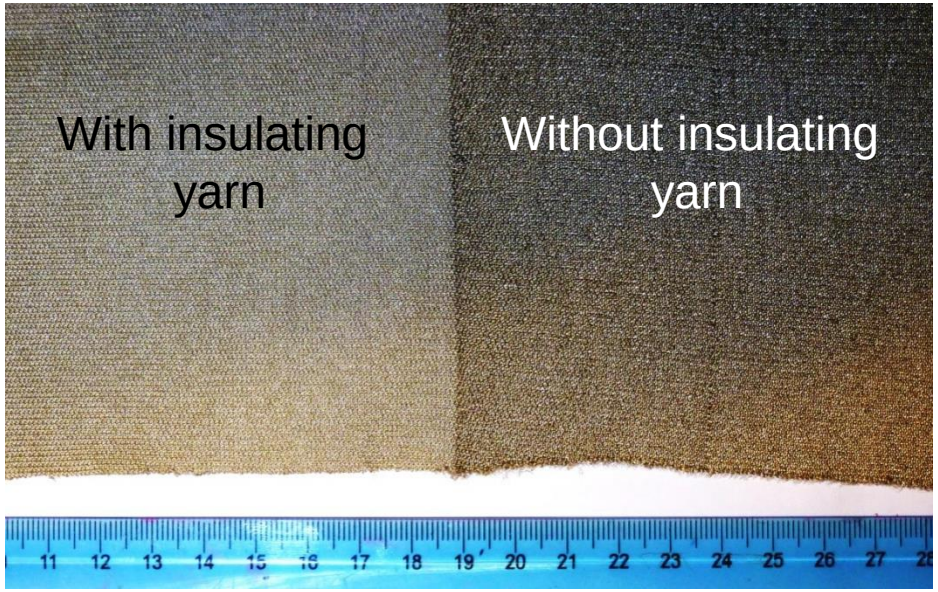
Highly stable output

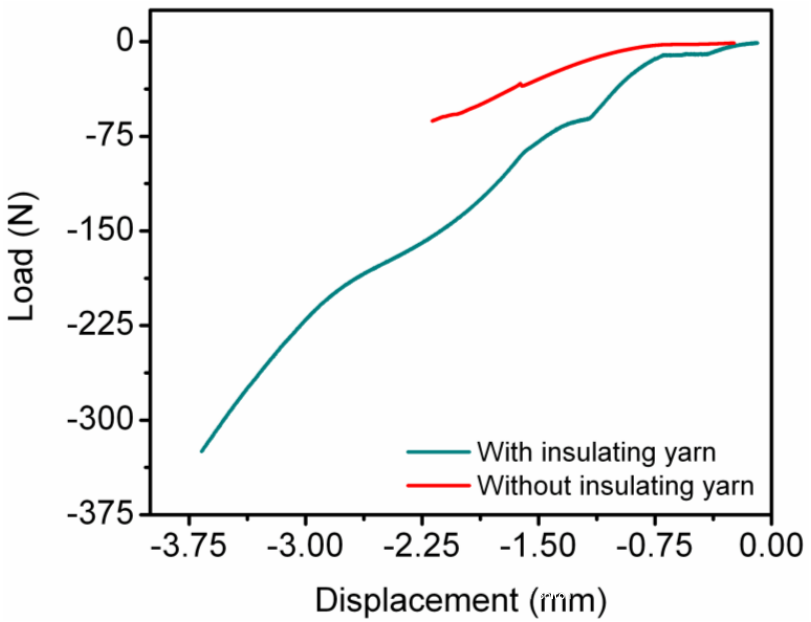




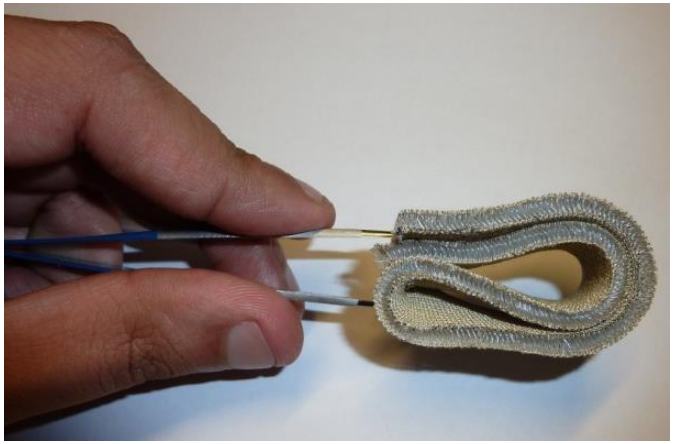


Energy harvesting using 3D piezo spacer fabrics

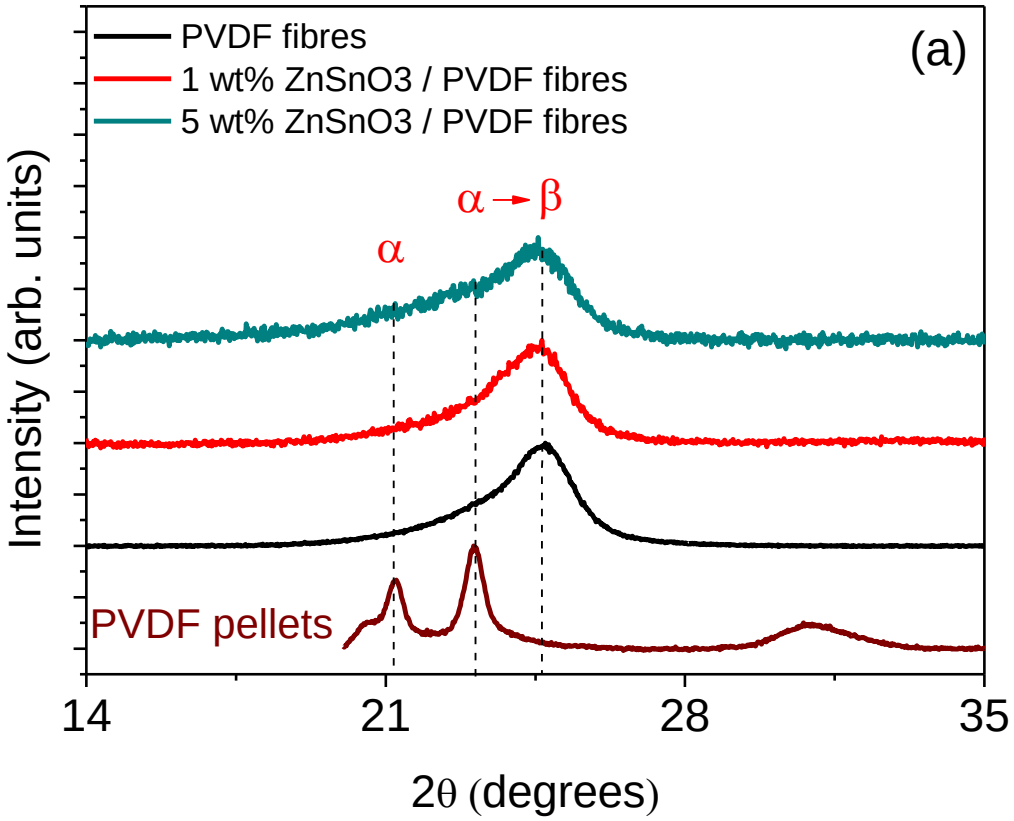


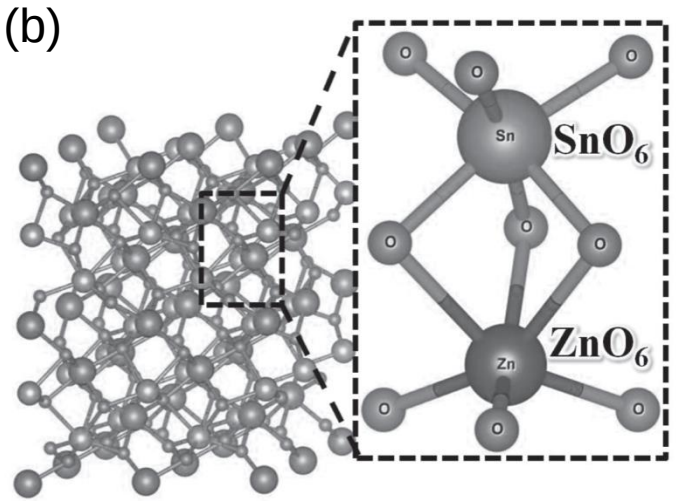


- *Tailored compressibility ranging from <0.02 Mpa to 0.13 Mpa (to match application)*
- *The flexural rigidity (11.25 g/cm) and bending modulus (3.14 kg/cm^2) tests, (using BSI 3356), show 3D PZ fabrics are comparable to conventional fabrics.*



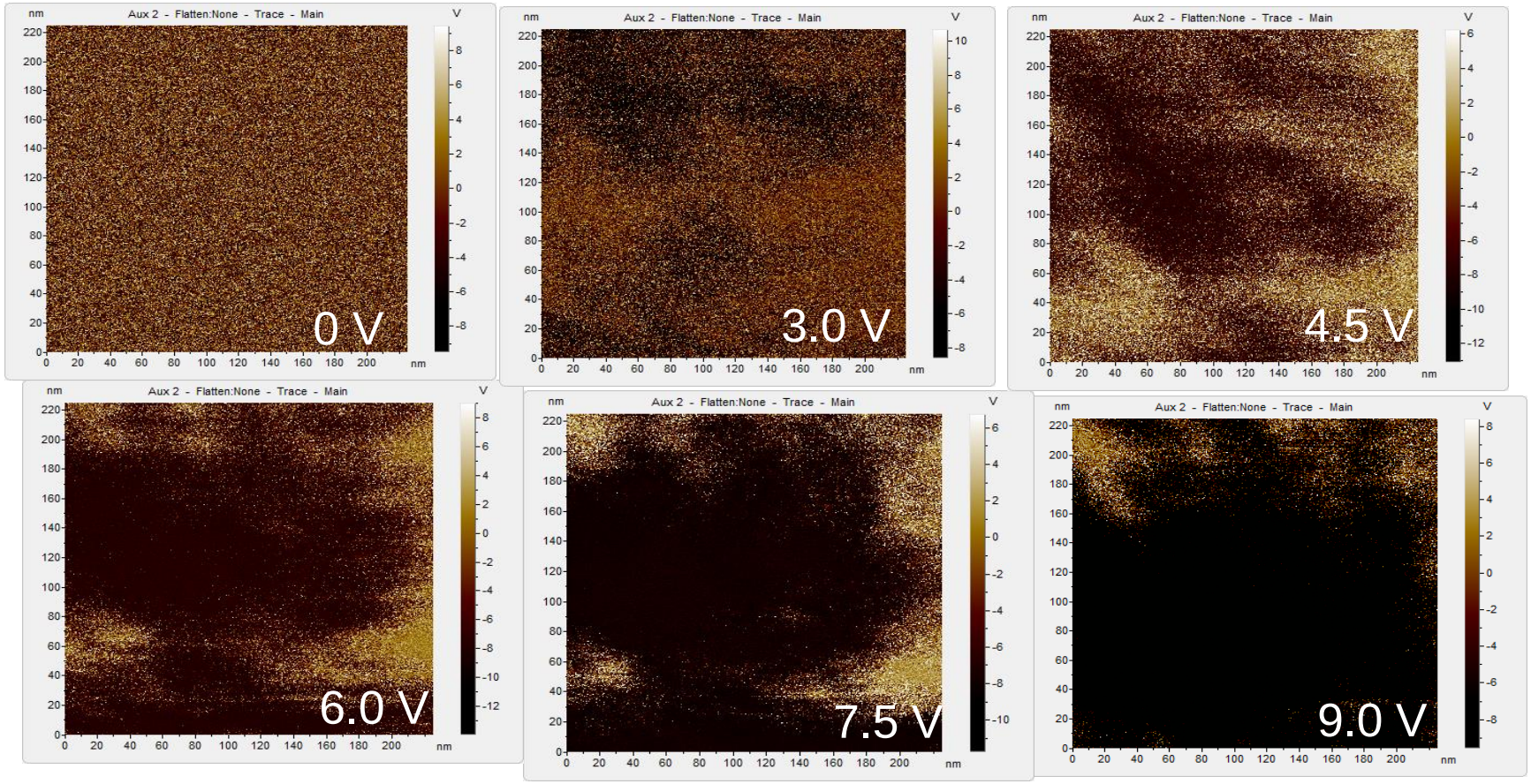
Enhancing the piezo properties of PZ yarns





(a) Change in the XRD spectra of $ZnSnO_3$/PVDF fibre samples, (b) crystallographic structure of $ZnSnO_3$, showing two octahedral frameworks of ZnO_6 and SnO_6

Enhancing the piezo properties of PZ yarns



- Change in phase of 4 wt% ZnSnO3 / PVDF fibres as a function of PFM applied bias
- d33 ~ 127 pm/V

Products

Based on patented technologies developed at the University of Bolton:

1. Continuous piezoelectric PVDF monofilaments, multi-filaments and tapes (Patent number WO/2012/035350)

   High β-phase (85-90%)

   High spinning rates (currently up to 500 metres/min)

2. 3-dimensional “spacer” technology based ***world’s first*** truly piezoelectric fabrics (*patent applied for*)

   Excellent compression and resilience properties

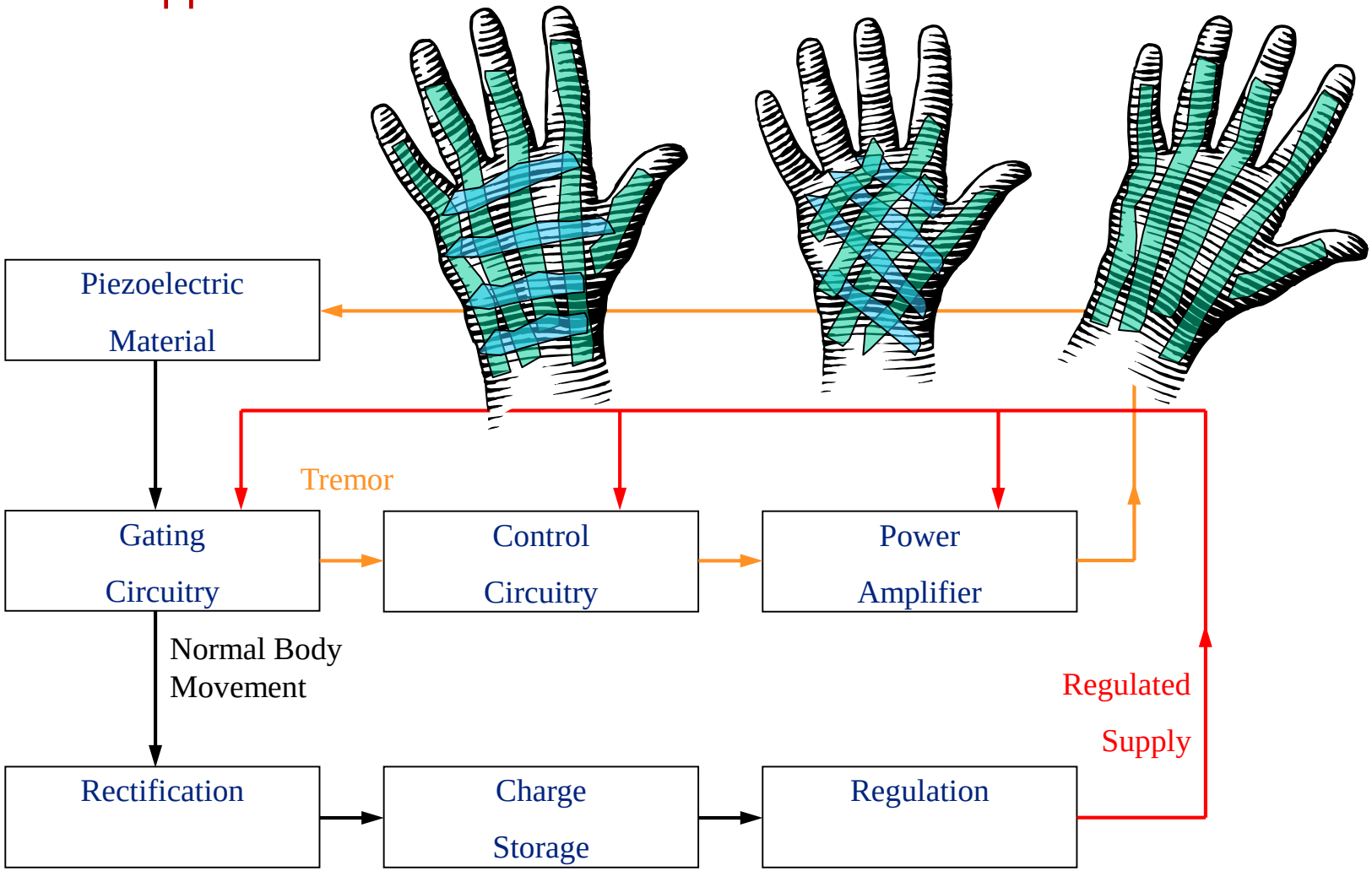
   All fibre technology: lightweight, highly flexible and highly comfortable

   Looks and feels no different to ordinary fabrics

   High production rates (currently up to 70 m^2/hour)

Applications

Tremor suppression



Applications of 3D piezo spacer fabrics

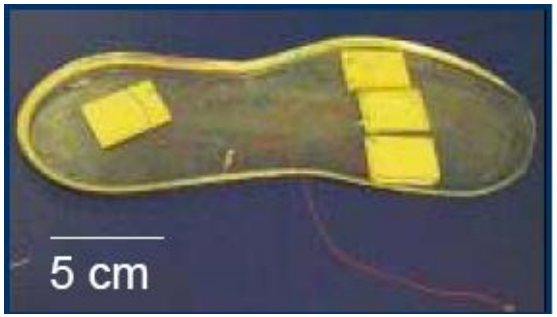


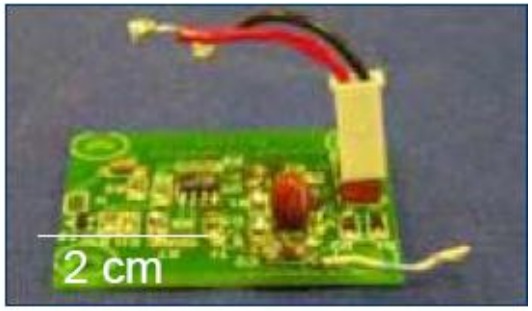
Applications of 3D piezo spacer fabrics



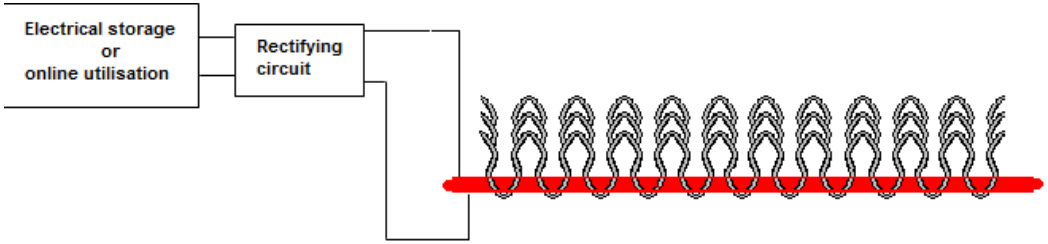
Applications

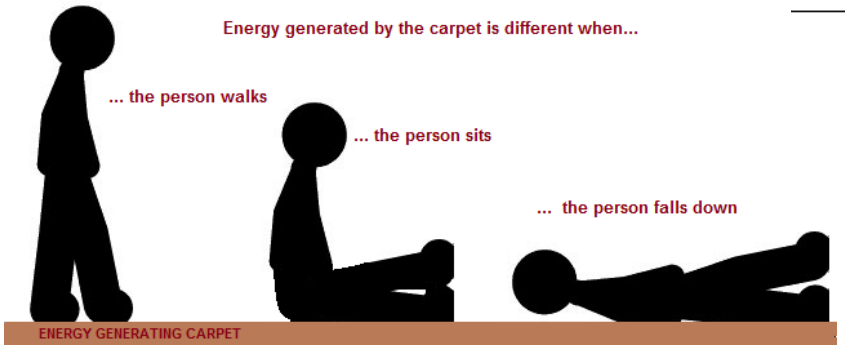
Mechanical/electrical energy harvesting











- Fall sensors for elderly
- Wearable energy harvesters

Applications of 3D piezo spacer fabrics

FibrLec

University of Bolton

FibrLec applications

Tyre applications

FibrLec material can be layered within the Tyre wall as part of the tyre infrastructure.

Four tyres layered with Fibrlec material will produce enough energy to power the batteries in all types of vehicles. This will create better MPG and power output charge.

The intelligent tyre

FibrLec material is also sensory in its attribute and allows data to be transferred to the driver, stating wear in areas of the tyre rather than just deflation sensors only.



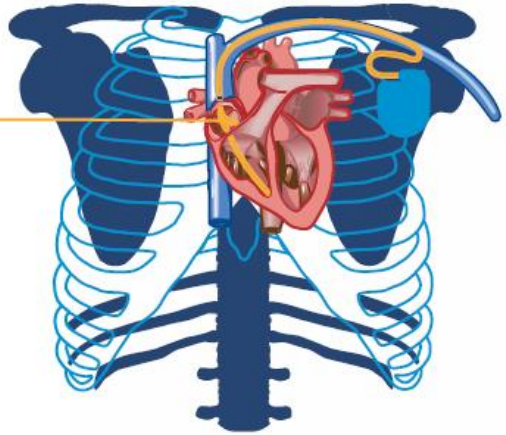
Applications

FibrLec

University of Bolton

Fibrlec material used in pacemaker equipment.

Fibrlec material placed into the exiting pacemaker will allow the patient to charge constantly with life time expectancy. This will mean that patients do not require any further surgery for battery replacement.



The sensory function of the material and its benefit of being woven and formatted into any shape can mean that the material can be woven into a shirt that allows medical staff to monitor the baby's heart beat at all times without ever losing the heart beat and the mothers simultaneously.



Hybrid Piezo Photovoltaic (HPP) Films and Fibres?

FibrLec

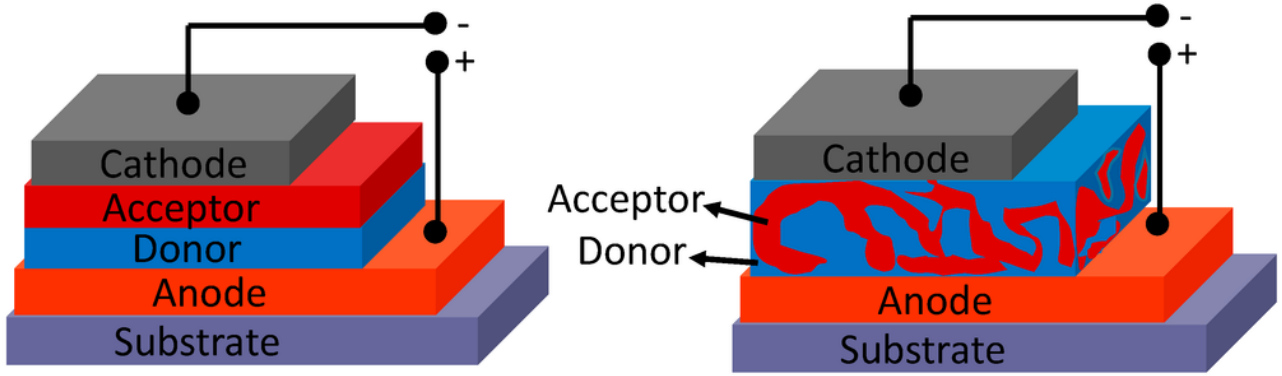
University of Bolton

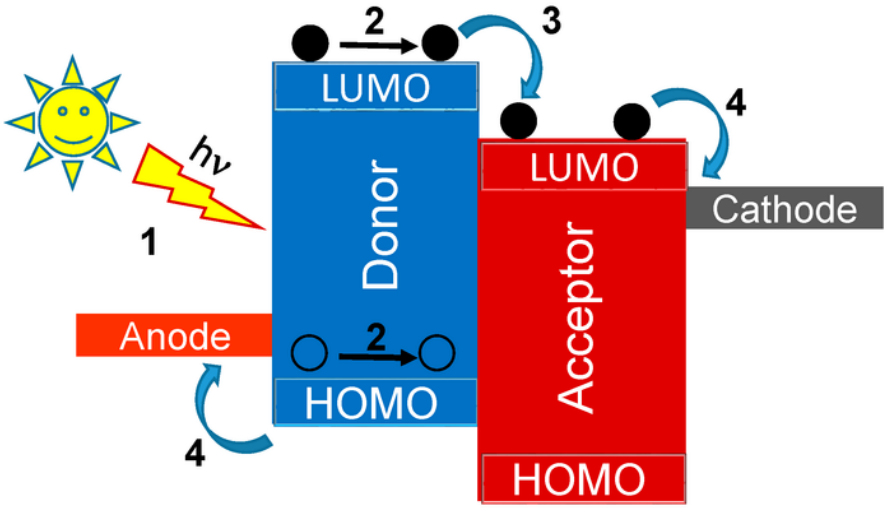
- Piezoelectric materials can convert mechanical energy to electrical energy, but if there is no mechanical stimuli…?

- Photovoltaic materials can convert sun light to electrical energy, but if there is no sun light...?

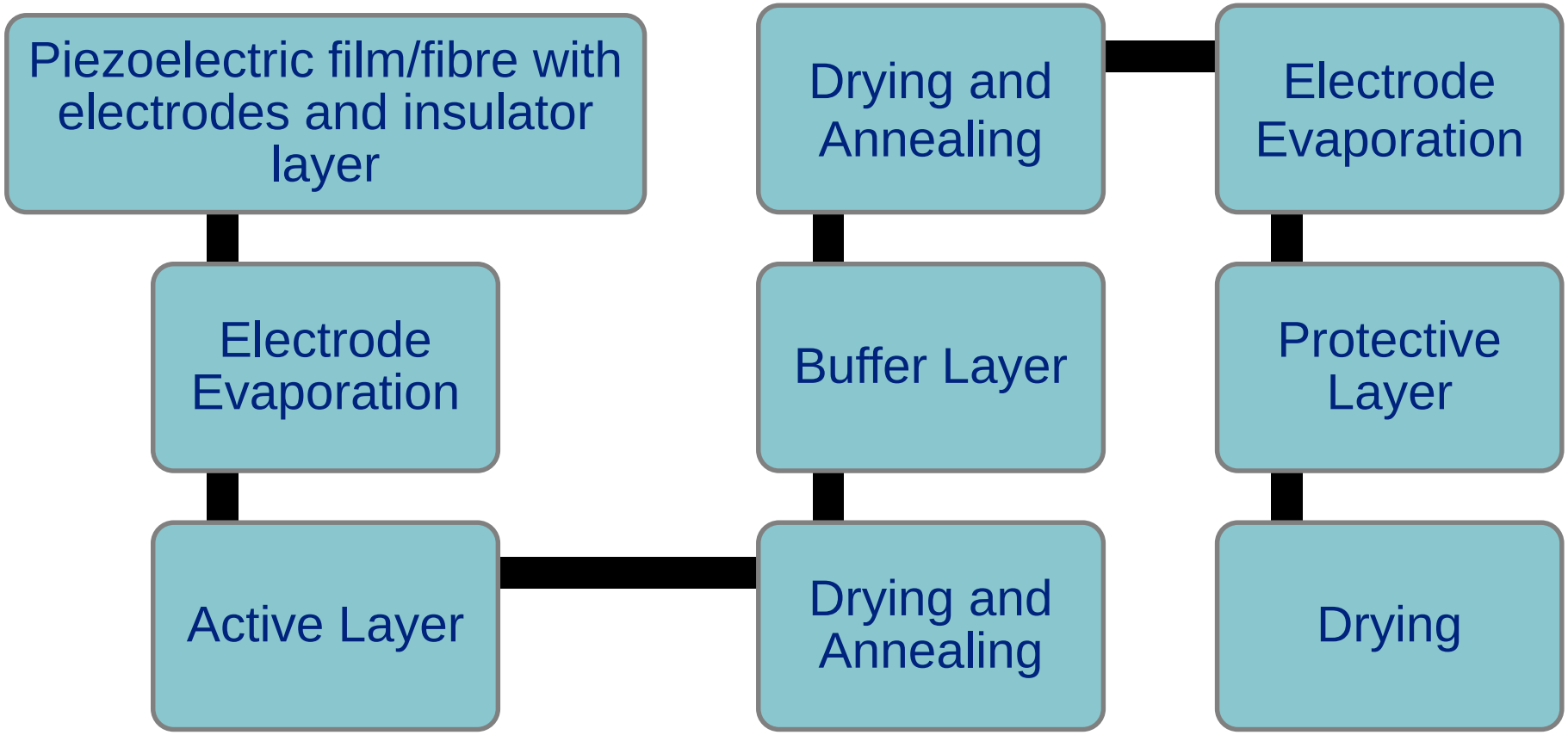
- HPP technology offers almost undisturbed energy generation by combining these two smart technologies into single fibre material.

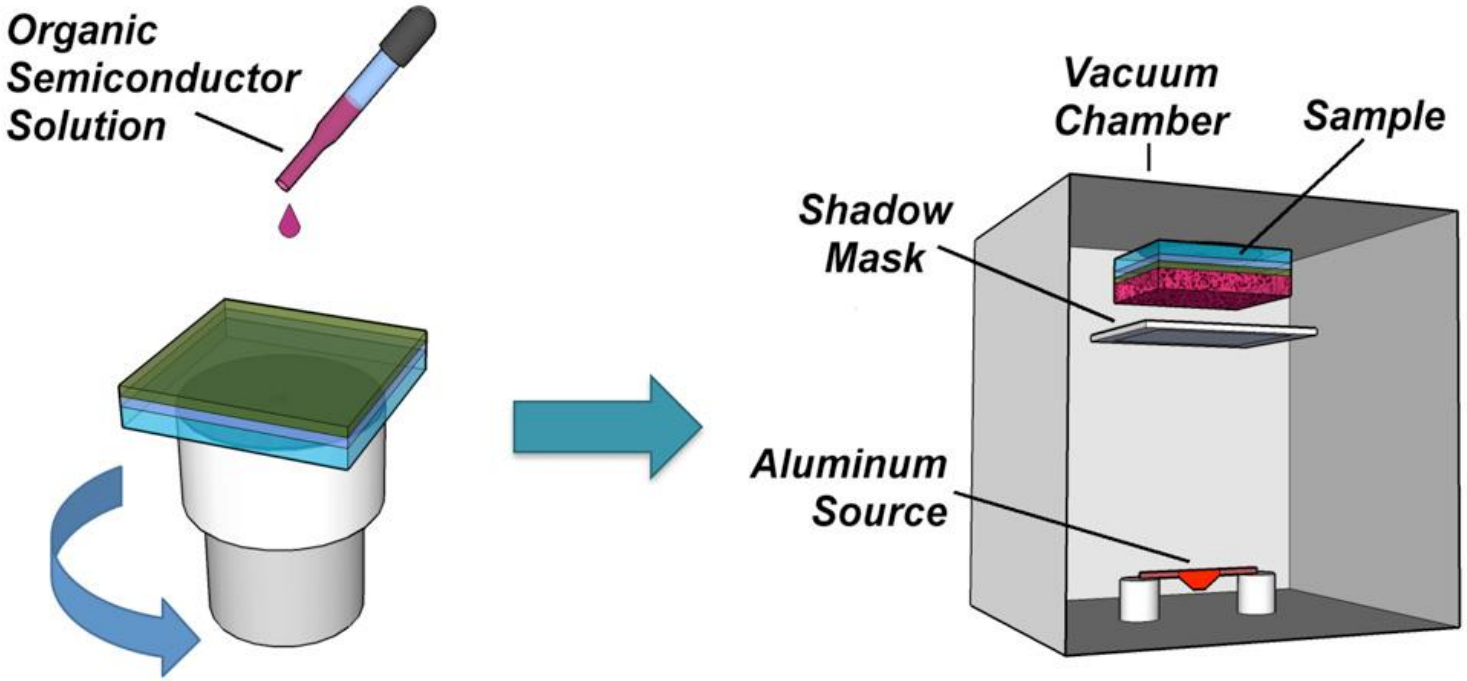
Organic Photovoltaic Cells



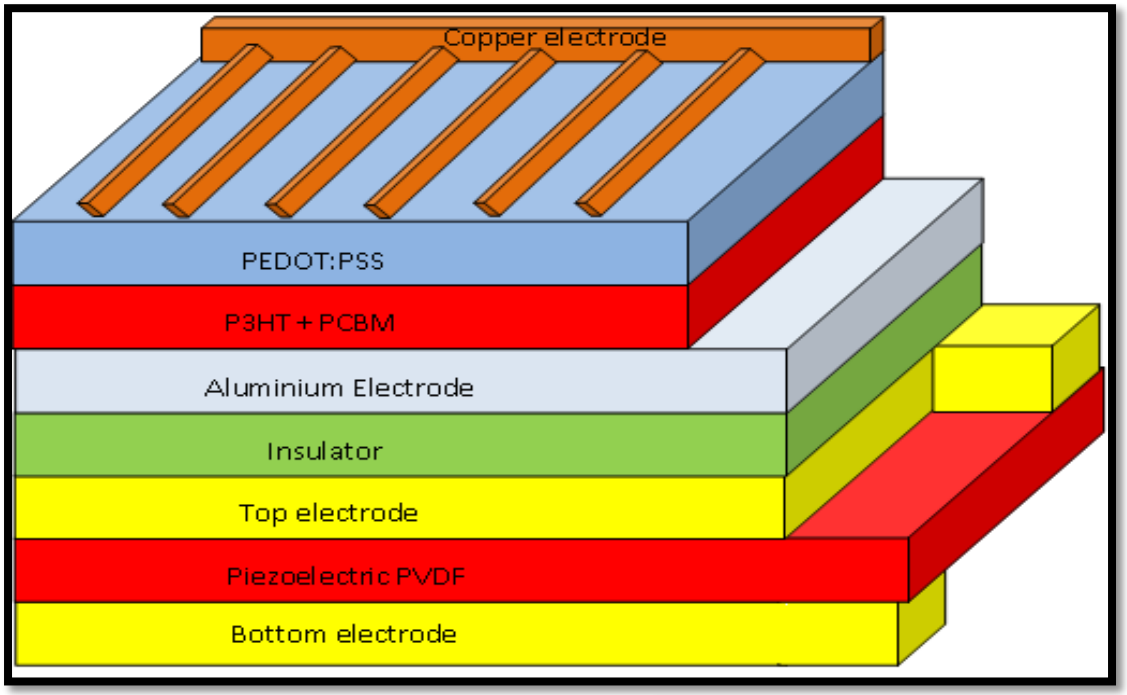


Production process of Hybrid Piezo Photovoltaic (HPP) Films and Fibres

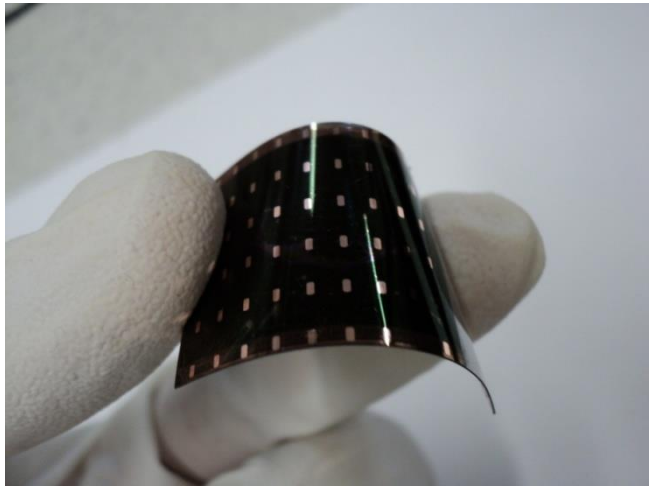



Organic
Semiconductor
Solution
Vacuum
Chamber
Sample
Shadow
Mask
Aluminum
Source

HPP materials produced at Uni. Of Bolton

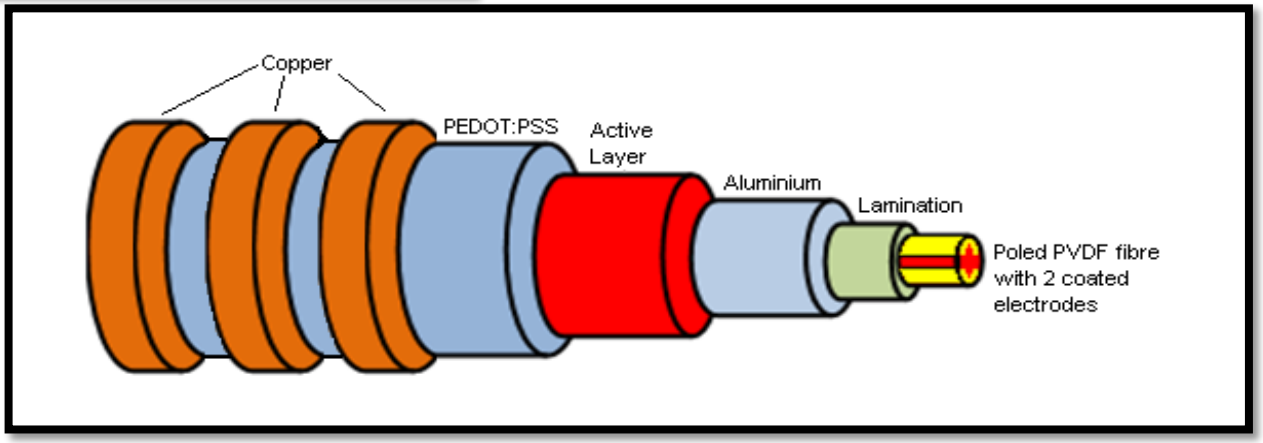


=

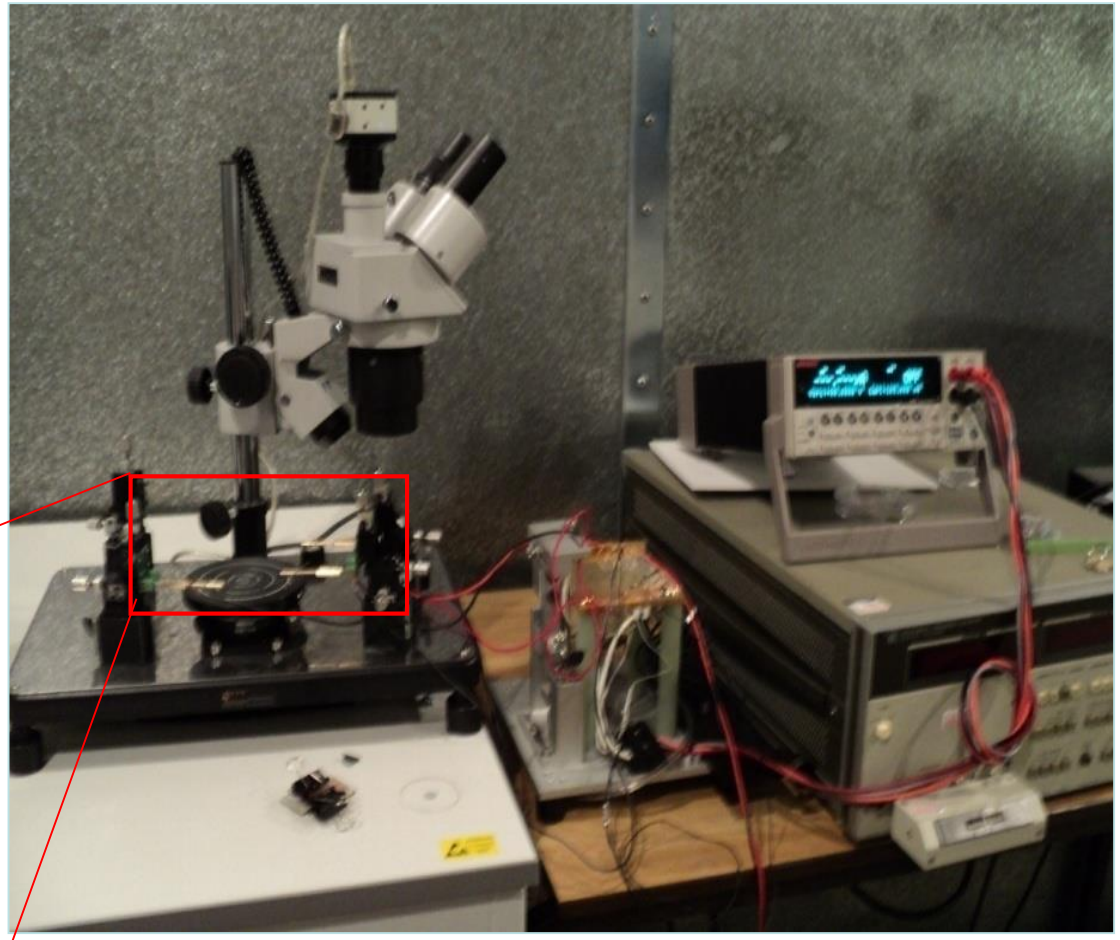


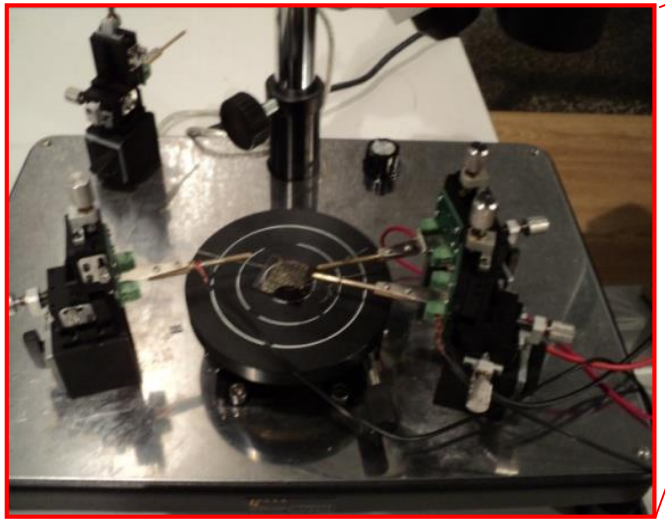


=

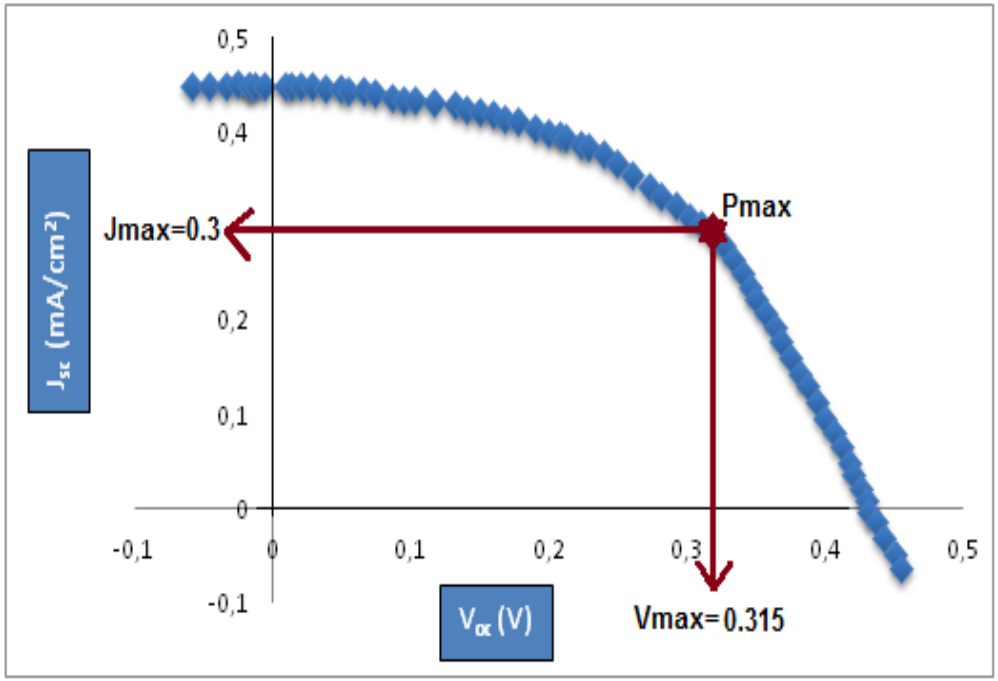


Power conversion efficiency measurement





Power conversion efficiency measurement



J_{max} V_{max} and P_{max} of produced hybrid device under standard (100mW/cm^2) light illumination

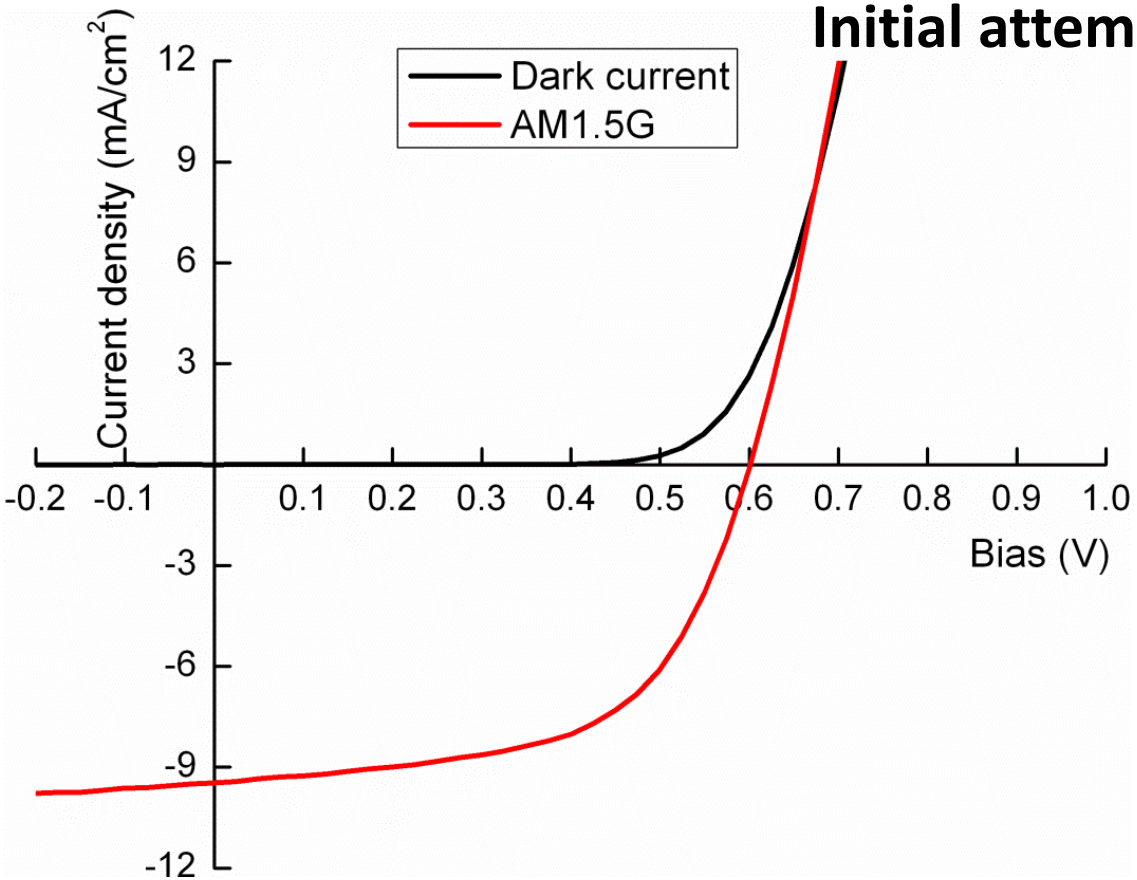
Enhancing the power conversion efficiency by using N-doped carbon nanotubes (CNTs)

FibrLec

University of Bolton

ITO / PEDOT:PSS / P3HT:PCBM:N-CNT / LiF / Al

Initial attempts



V_{OC} = 0.60 V

I_{SC} = –9.47 mA/cm²

FF = 60 %

PCE = 3.3 %

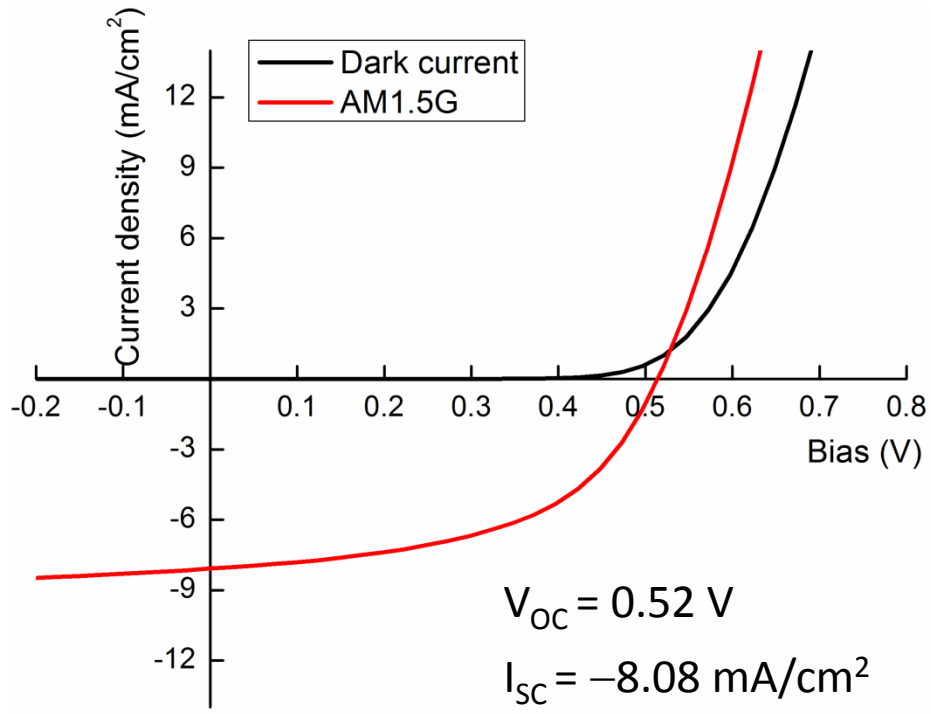
Area of the solar cell: 0.05 cm²

Enhancing the power conversion efficiency by using N-doped carbon nanotubes (CNTs)

FibrLec

University of Bolton

ITO / PEDOT:PSS / P3HT:PC[60]BM / LiF / Al



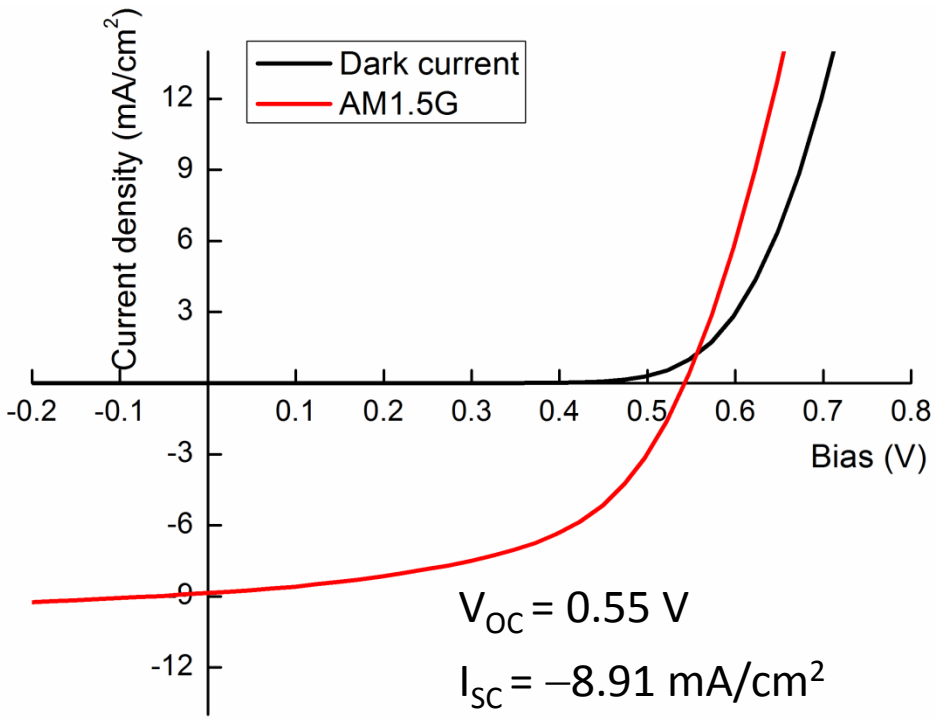
V_{OC} = 0.52 V

I_{SC} = –8.08 mA/cm^2

FF = 51 %

PCE = 2.15 %

ITO / PEDOT:PSS / P3HT:PC[60]BM:N-CNT (~ 1%) / LiF / Al



V_{OC} = 0.55 V

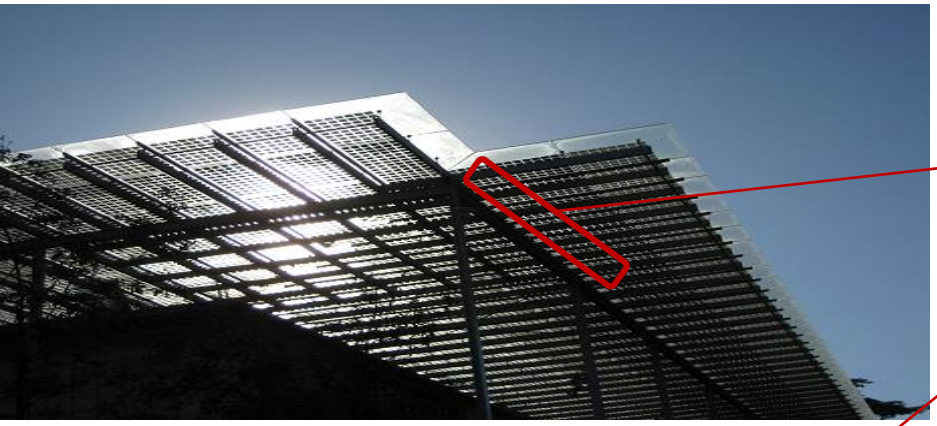
I_{SC} = –8.91 mA/cm^2

FF = 52 %

PCE = 2.53 %

With N-CNTs, PCE has a relative increase of ~18%, from 2.15% to 2.53%.

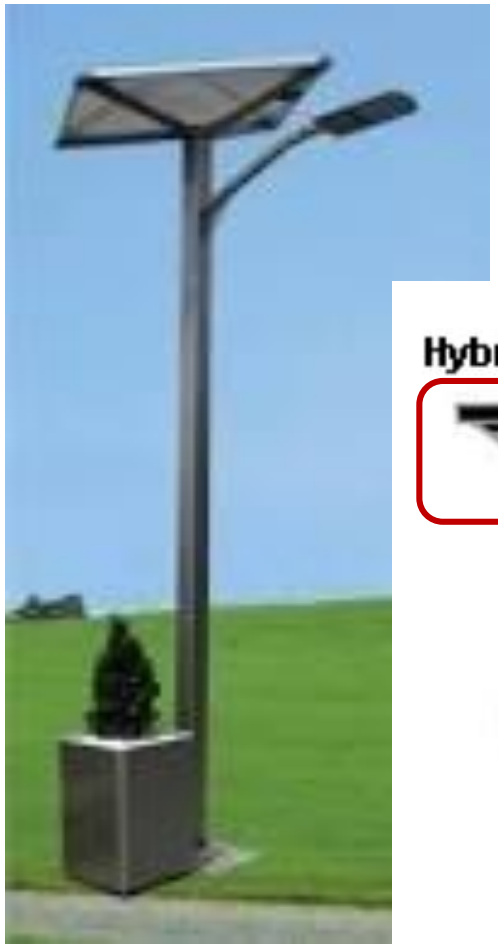
Applications



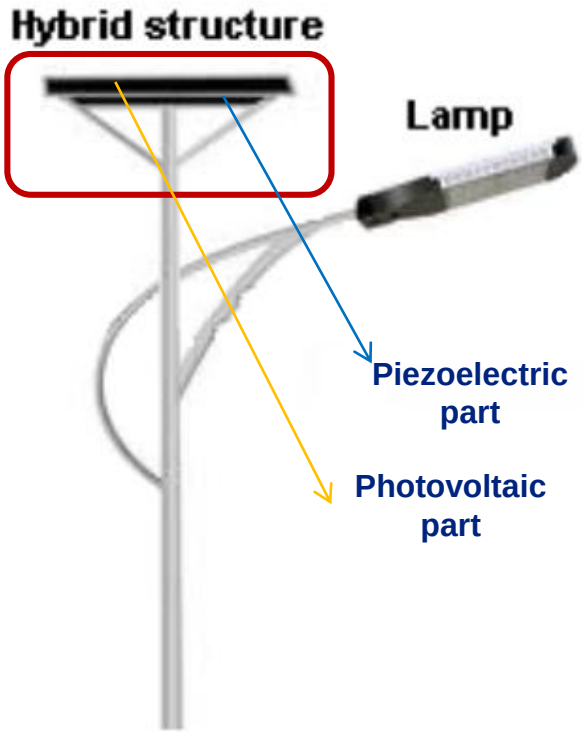


Piezoelectric-Photovoltaic hybrid structures can be used to produce roof top linings which can produce energy from sun, rain and wind depending on the design requirements.

Applications



Lamp posts, garden lights, traffic lights, bus stop shelters, train stations



Solar cells are extensively used to power decorative garden lights or even traffic lights.

If these are replaced with hybrid structures, harvested energy will be higher since the conversion will be from both mechanical to electrical energy as well as from solar to electrical.

Hybrid structures can be used in almost any areas that solar panels are used.

Applications

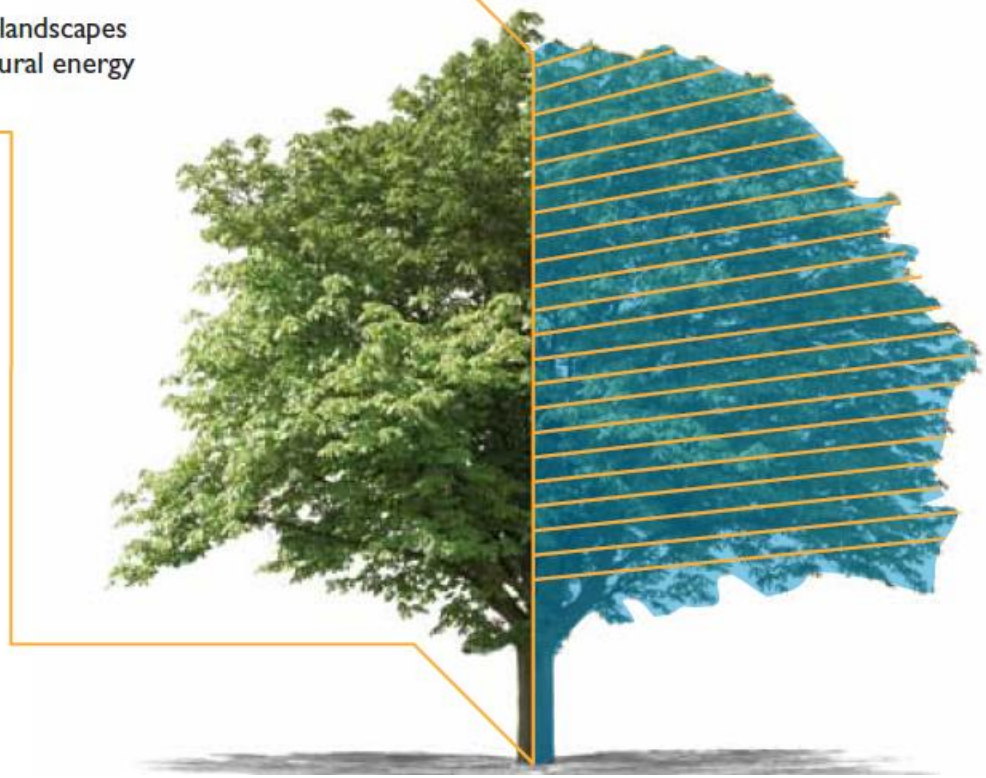
FibrLec

University of Bolton

Synthetic trees

Synthetic trees will allow the capture of all three natural resources, wind, Rain and sun. These trees can be placed in areas where solar panels are unacceptable.

Cosmetic benefits to already natural landscapes will be enhanced whilst capturing natural energy



Applications



Conclusions

- For the first time, continuous flexible piezoelectric filament (500 m/min) successfully produced by applying a high stretching ratio, heat and high voltage, simultaneously. (International Patent)
- Demonstration of 3D “spacer” based technology for truly piezoelectric fabrics (current production rate 75 m^2/hr)
- For the first time flexible hybrid piezoelectric-photovoltaic film and fibre have been successfully produced and tested. (International Patent)
- 5 International Awards have been obtained.
- **FibrLec company established in 2013 – from laboratory to commercialisation.**

Publications

1. Novel “3-D spacer” all fibre piezoelectric textiles for energy harvesting applications N Soin et al ***Energy Environ. Sci.***, 2014,**7**, 1670-1679
2. Continuous production of piezoelectric PVDF fibre for e-textile applications R L Hadimani *et al* ***Smart Mater. Struct.,*** 2013, **22**, 075017
3. An investigation of energy harvesting from renewable sources with PVDF and PZT D Vatansaver et al ***Smart Mater. Struct.,*** *2011,* **20(5),** 055019
4. Voltage response of piezoelectric PVDF films in vacuum and at elevated temperatures D Vatansaver et al ***Smart Mater. Struct.*** 2012, **21(8),** 085028.
5. Utilisation of smart polymers and ceramic based piezoelectric materials for scavenging wasted energy. I Patel et al. ***Sensors and Actuators A: Physical***, 2010, ***159*(2),** 213-218.
6. Hybrid Photovoltaic-Piezoelectric Flexible Device for Energy Harvesting from Nature, D. Vatansever et al. ***Adv. Sci. Technol.*** *2013,* **77**, 297-301.
7. Siores, E., & Hadimani, M. L. R. (2011). ***U.S. Patent Application*** *13/823,908*.
8. Hadimani, M. L. R., Siores, E., Vatansever, D., & Prekas, K. (2011). ***U.S. Patent Application*** *13/876,162*.

FibrLec

University of Bolton

“Smart Functional Materials for energy: from laboratory to commercialization”

University of Bolton