Zinc oxide nanorod p-n junction piezoelectric energy harvesters: mechanism, developments and applications

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Outline

- Background principles
- Synthesis Method
- ZnO nanorod morphology
- Screening, p-n junctions and passivation
- Proper characterisation
- Wireless sensor nodes
- Recent developments

Piezoelectric effect

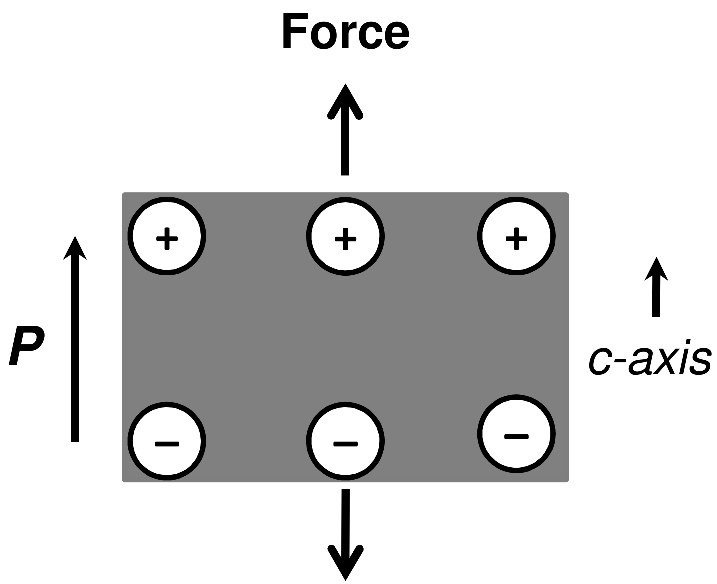
Stress

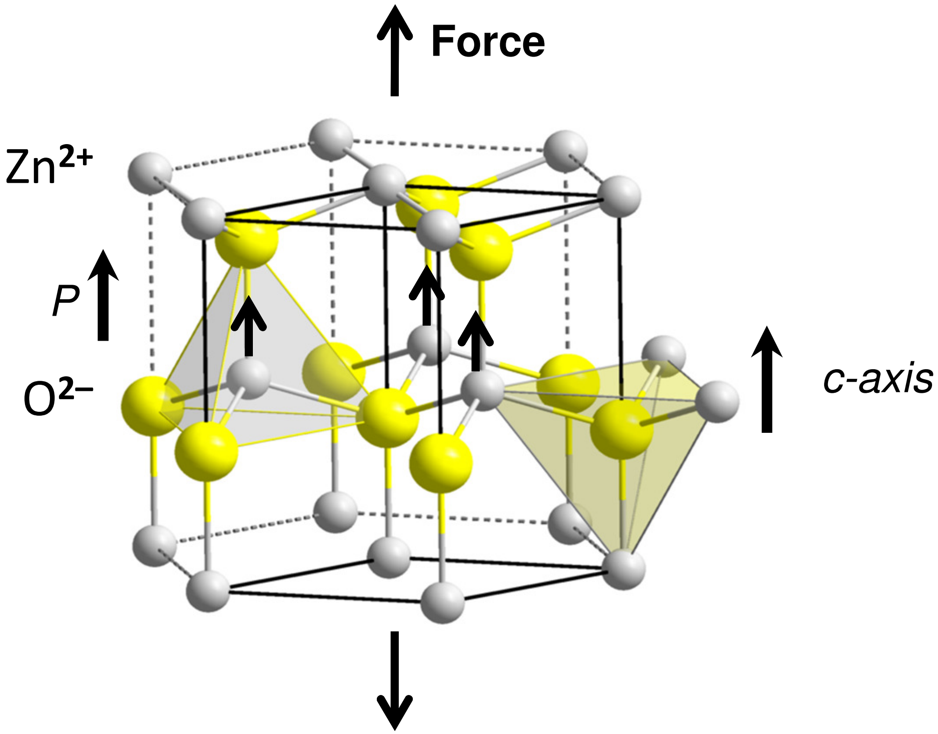
↓

Offset of charged ions

↓

Polarisation



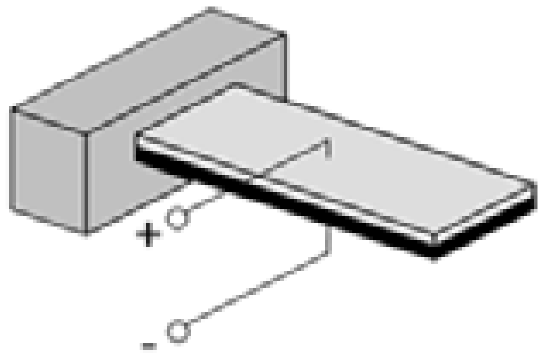


- Polarisation → potential difference if unscreened

Piezoelectric energy harvesting

- Basic design developed from piezoelectric sensors: cantilever vibrates and alternating charge harvested in external circuit

- Lead zirconate titanate (PZT) most common material used for energy harvestors



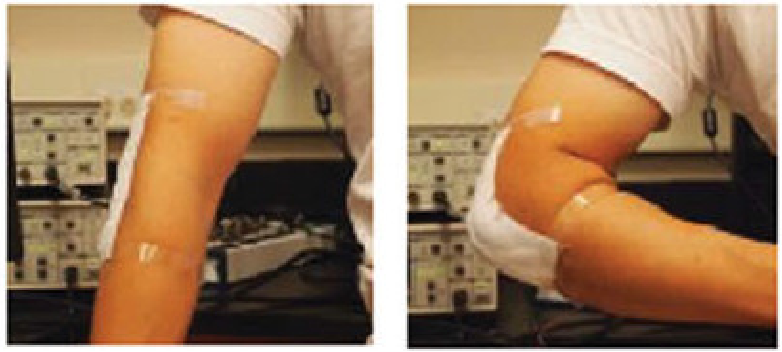
Anton and Sodano
Smart Materials and Structures
16, R1–R21 (2007).

Cook-Chennault, Thambi, and Sastry
Smart Materials and Structures
17, 43001 (2008).

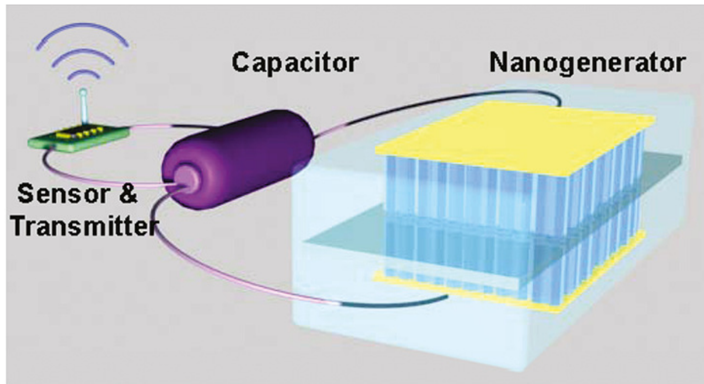
Beeby, Tudor, and White
Measurement Science and Technology
17, R175 (2006).

Piezoelectric energy harvesting

- Power microdevices or charge batteries
- On clothing, in remote locations, etc.
- Potential for self-powered systems



Lee *et al. Adv. Mater.* **24**, 1759–1764 (2012)

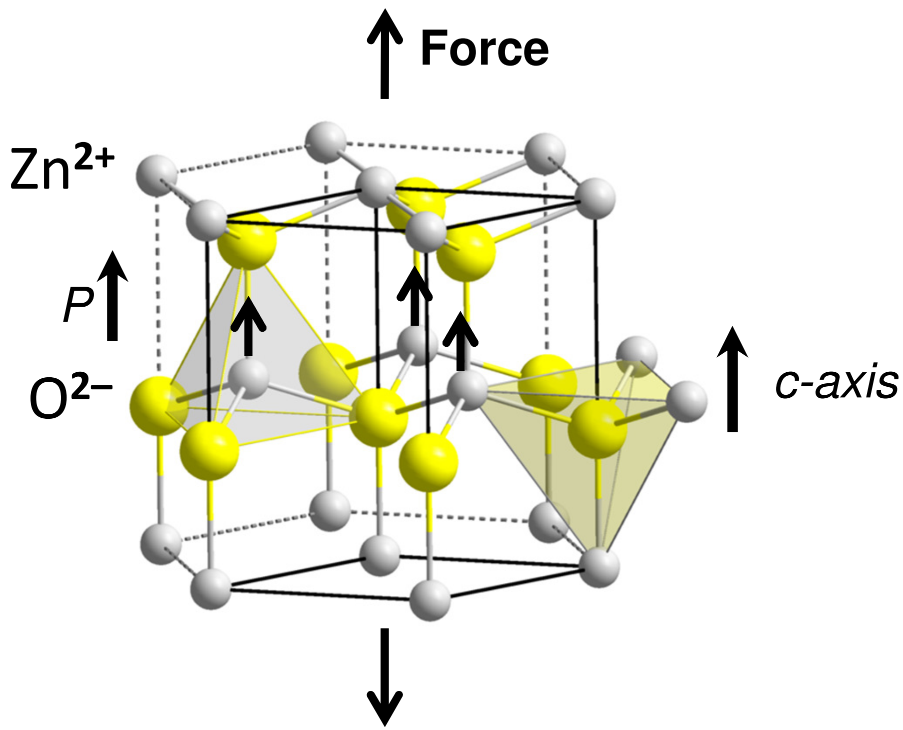


Hu *et al.* Nano Lett. 11, 2572–2577 (2011)

Why ZnO nanorods?

- Lower d_{33} than many other piezoelectrics ZnO: 5-12 pC/N,[1] PZT: 100-400 pC/N.[2]
- Easily produced nanostructures – solution synthesis
- Can coat almost any surface

Wurtzite structure



[1] Tokarev *et al. Sov. Phys. Solid State* **17** 629 (1975).

[2] Ledermann *et al. Sens. Act. A* **105**, 162 (2003).

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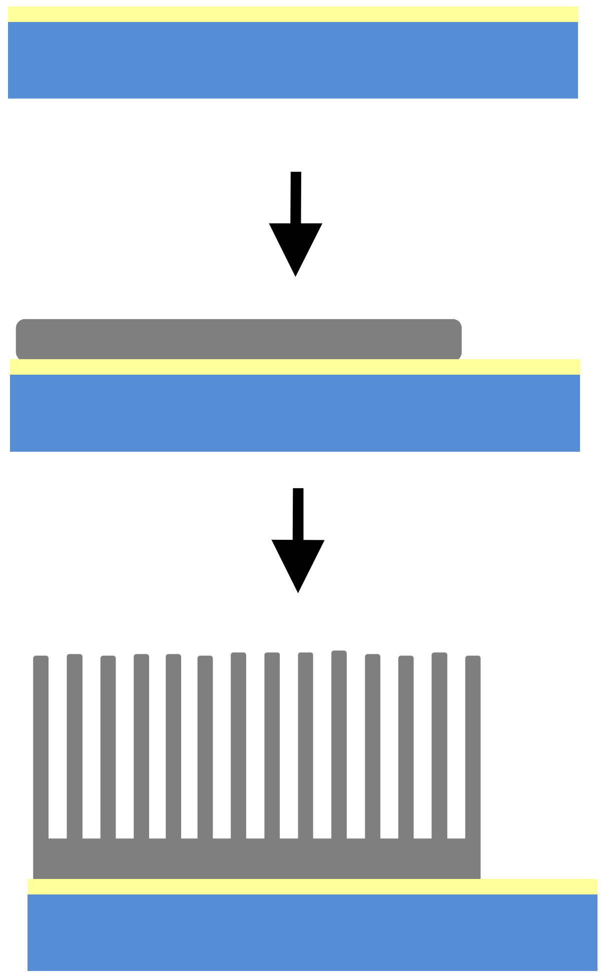
ZnO nanorod synthesis

- Conductive substrates: polyethylene terephthalate (PET) coated with indium-tin oxide (ITO)
- Sputtered ZnO seed layer
- ZnO nanorods grown in aqueous chemical bath at 90 °C using zinc nitrate and hexamethylenetetramine (HMT)



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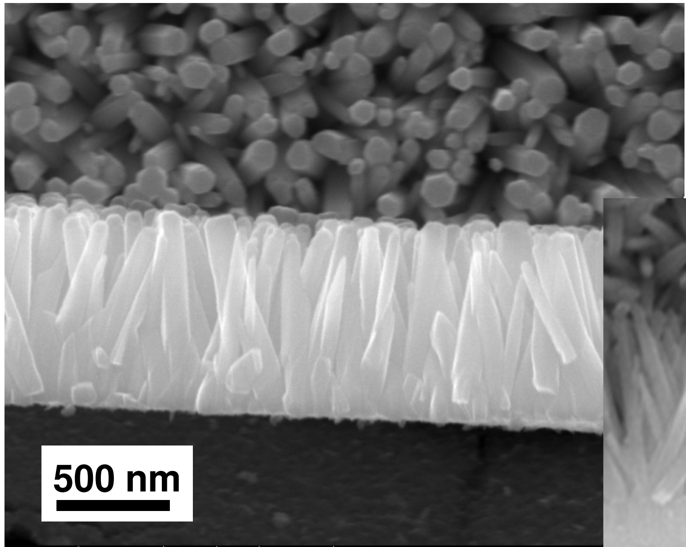
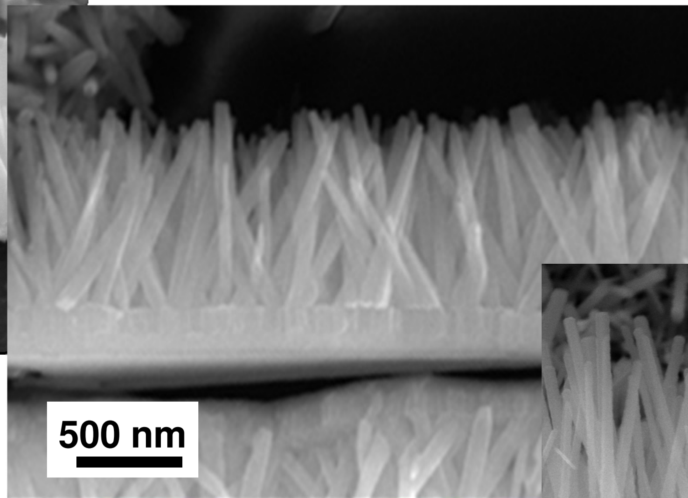
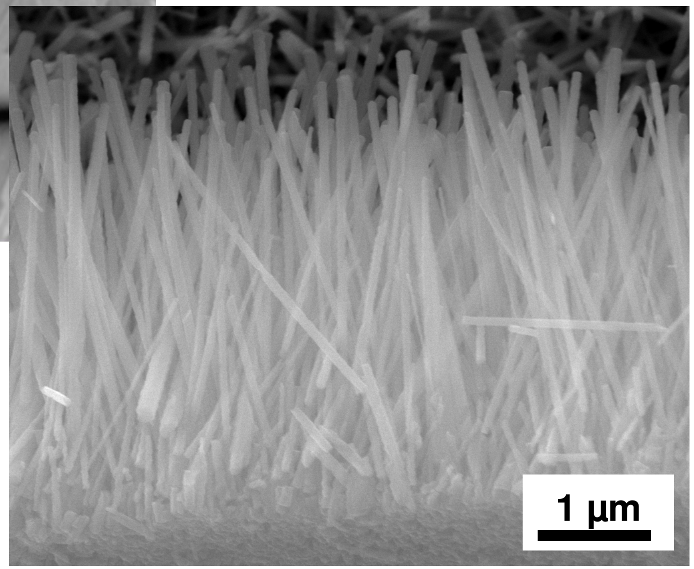
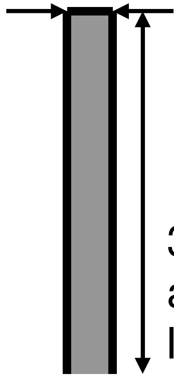
ZnO nanorods



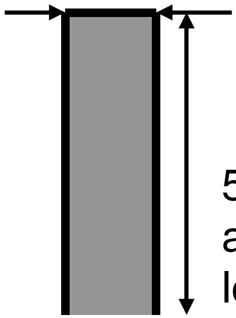






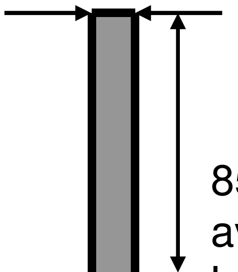
80 nm average diameter

3 µm average length



200 nm average diameter

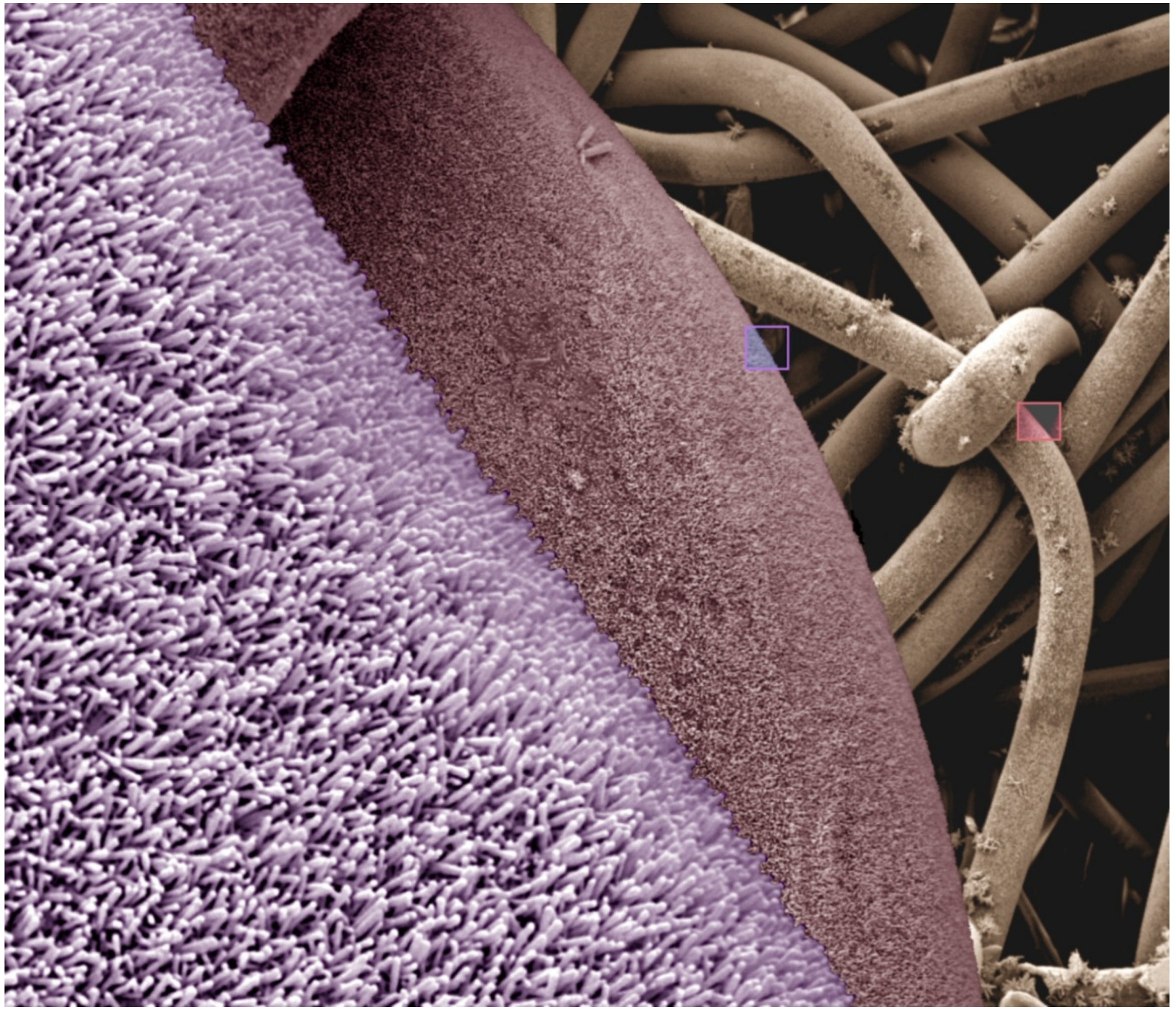
500 nm average length



60 nm average diameter

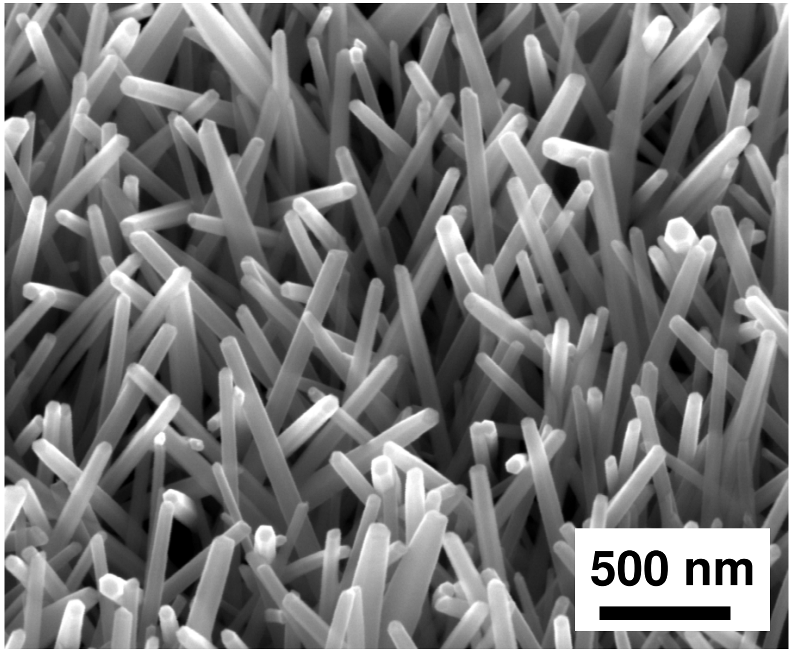
850 nm average length

ZnO nanorods

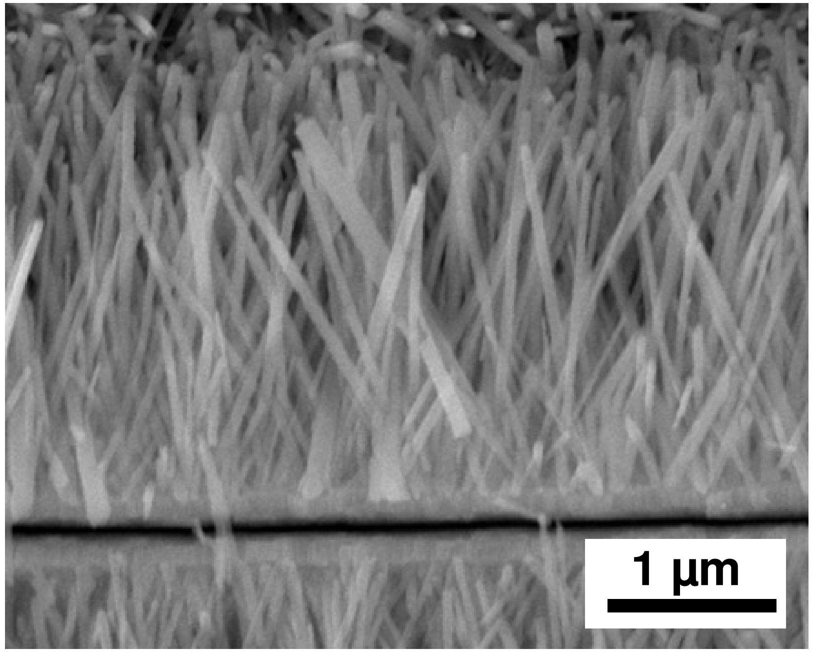


ZnO nanorods: energy harvestors

30° tilt



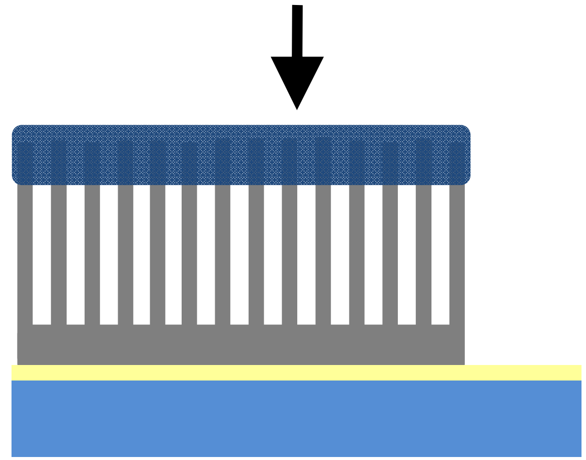
Cross-section



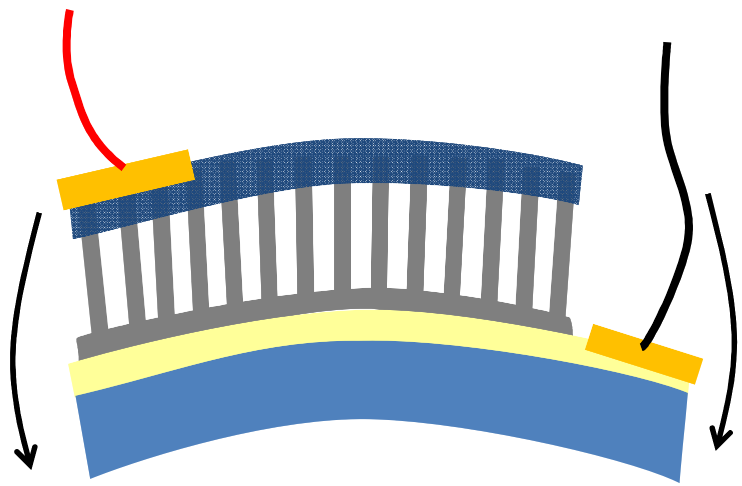
- Average diameter 75 nm
- Average length 2 µm
- Aspect ratio ~25:1

Device fabrication

- P-type layer added → diode
  - PEDOT:PSS spray-coated from aqueous suspension

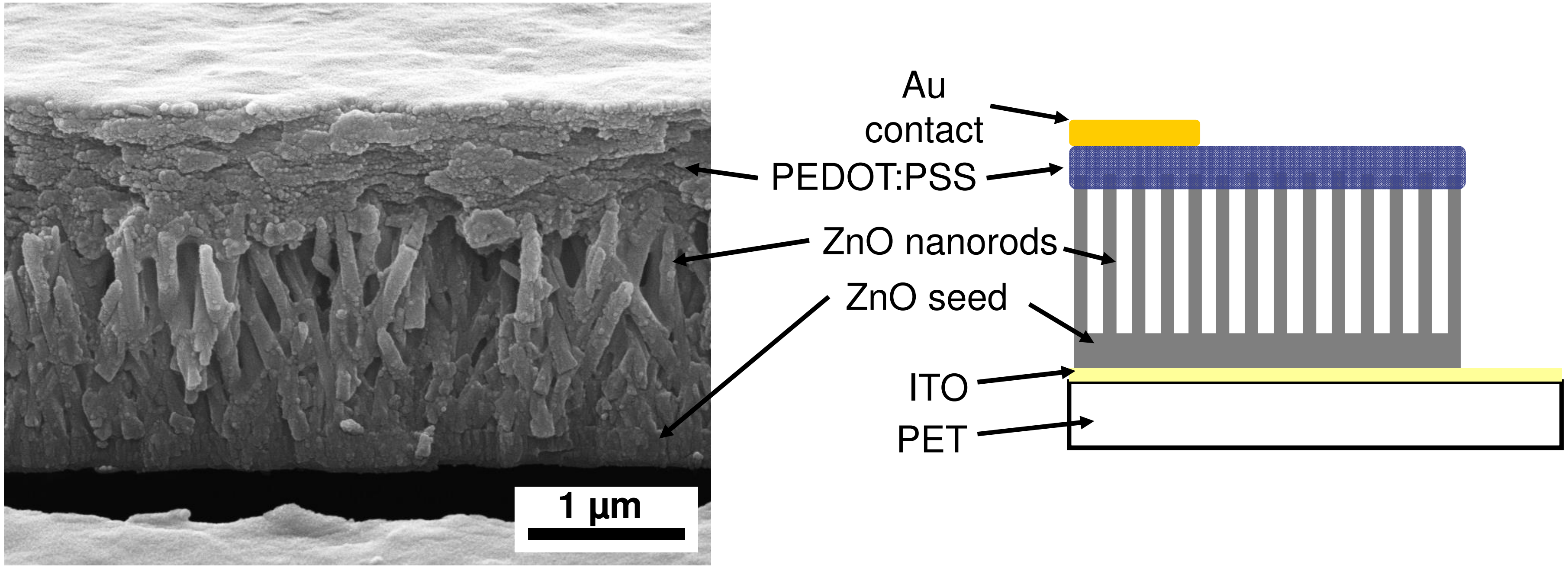


- Electrodes added → flexible energy harvesting device

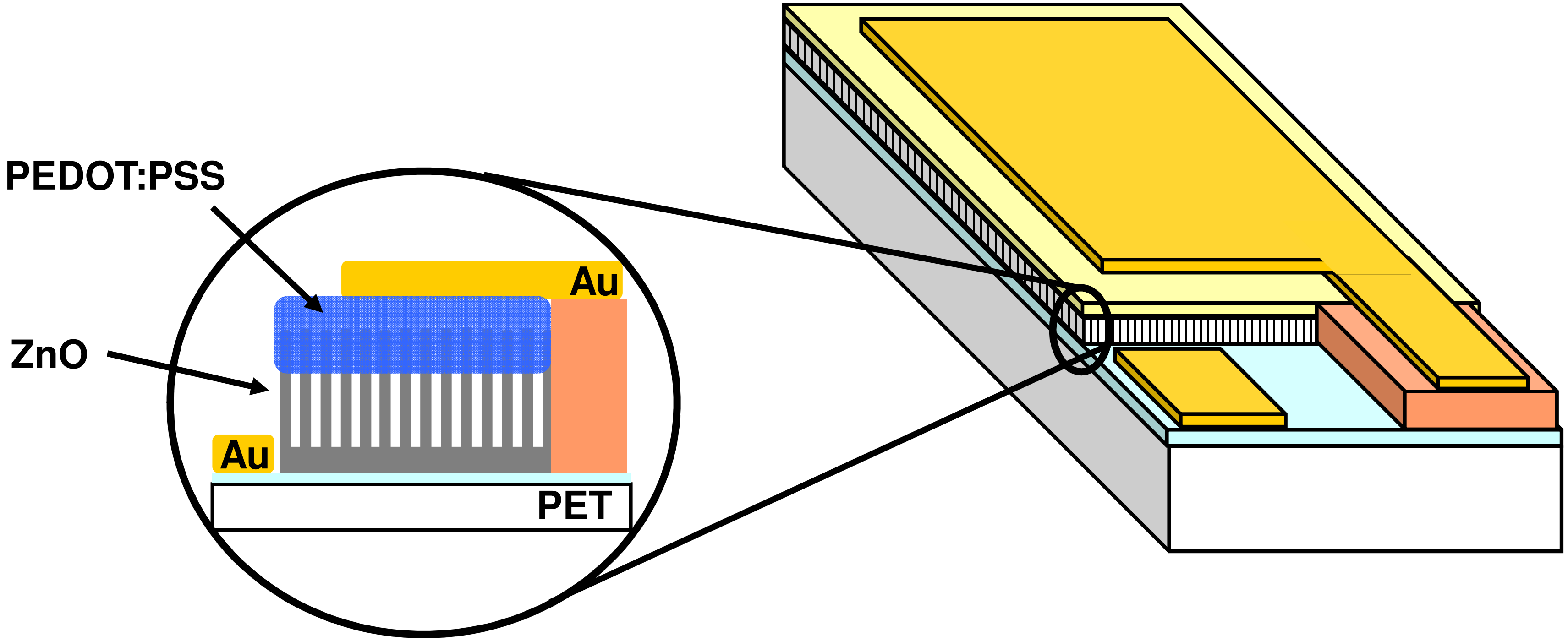


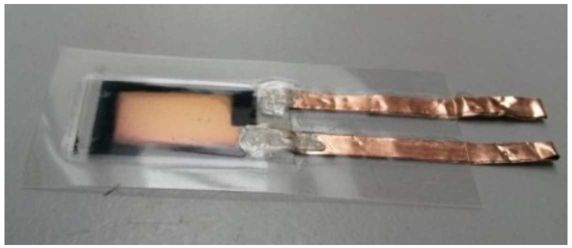
Device fabrication

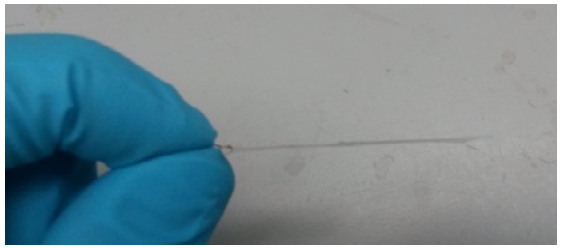
- PEDOT:PSS spin-coated → p-n junction



Device structure

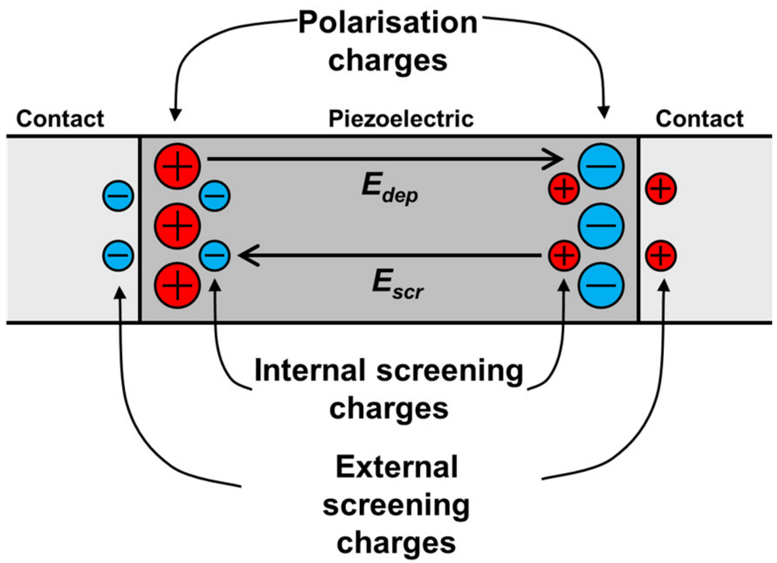






PEDOT:PSS and screening

- Screening reduces measured potential difference
- Metal contacts and internal carriers screen rapidly
- Built-in bias at p-n junction reduces screening rate
- Slower screening from p-type → voltage measured



E_{dep} – depolarisation field

E_{scr} – screening field

$$V_{out} \propto E_{dep} - E_{scr}$$

Briscoe et al., *Adv. Energy Mater.* **2**, 1261–1268. (2012).
doi: 10.1002/aenm.201200205

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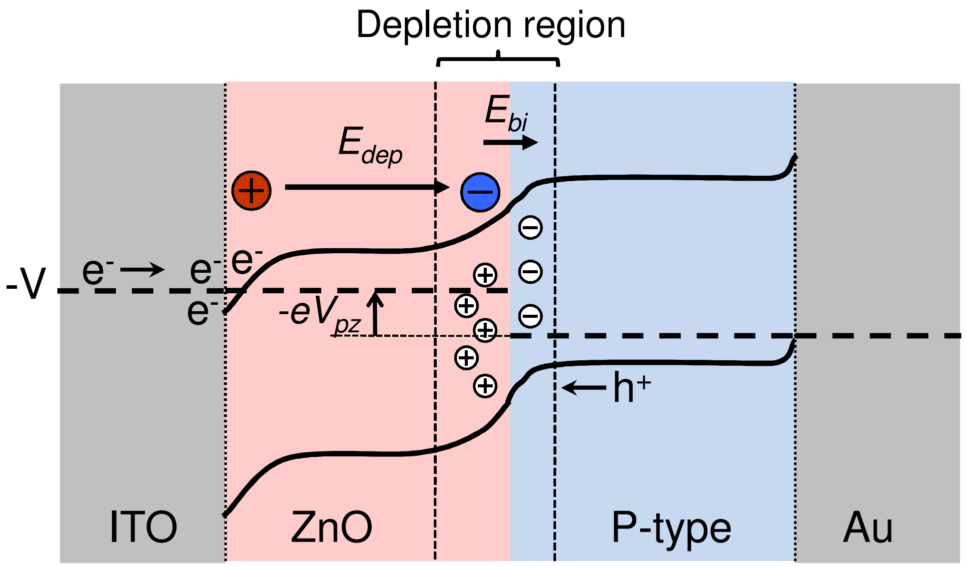

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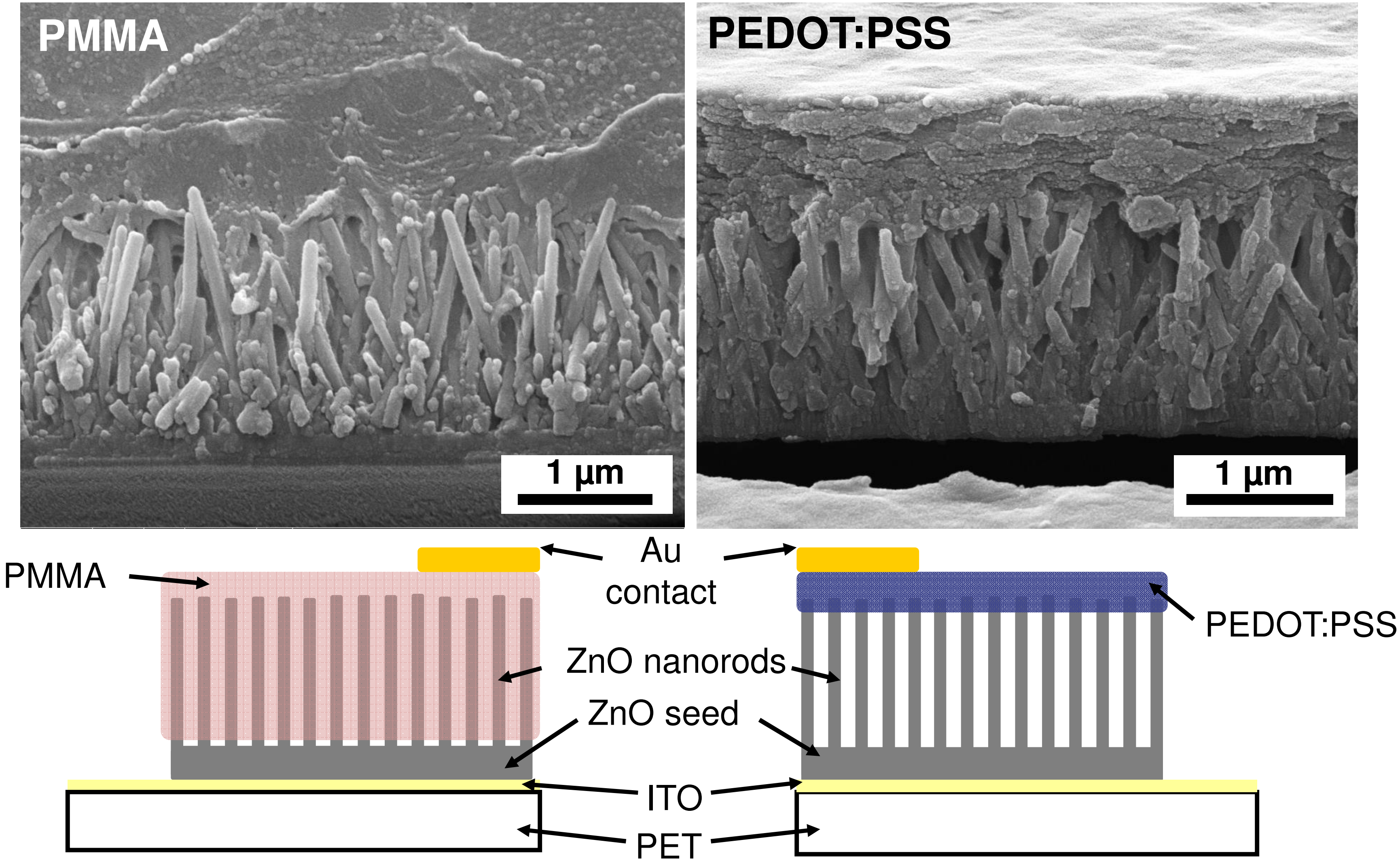
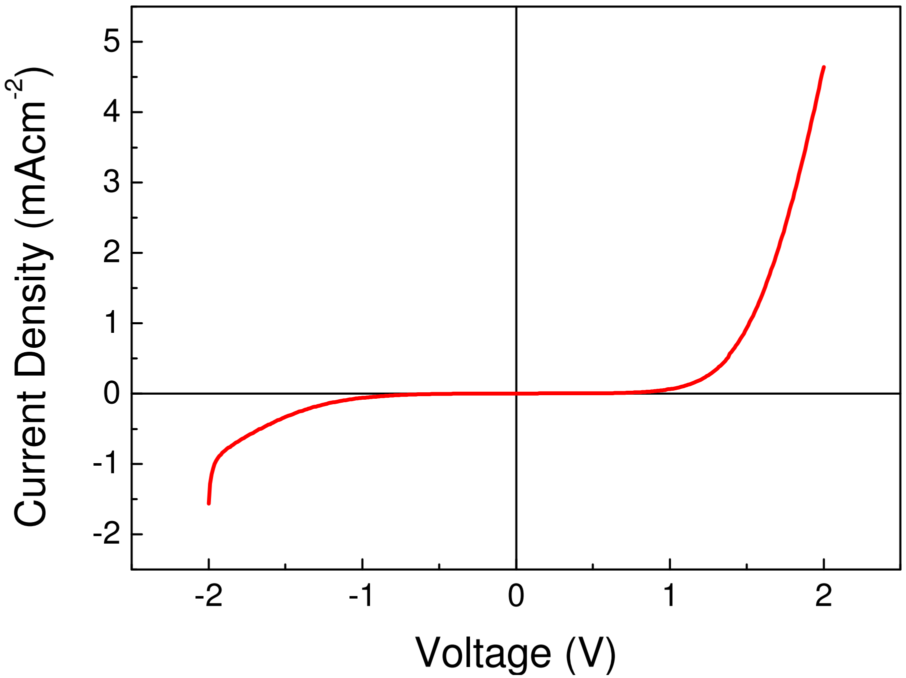
Device comparison

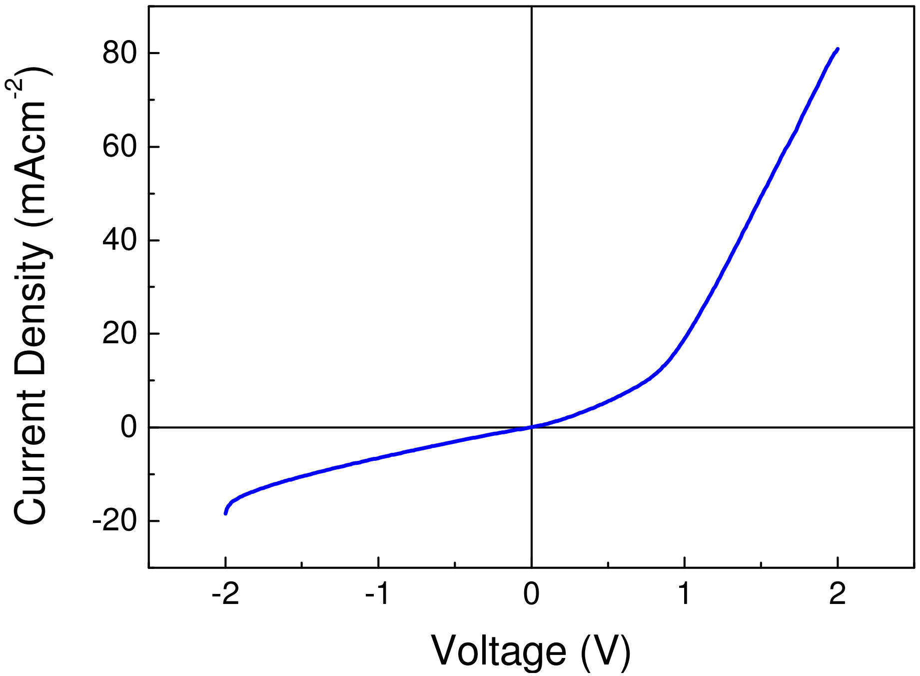


Current-voltage

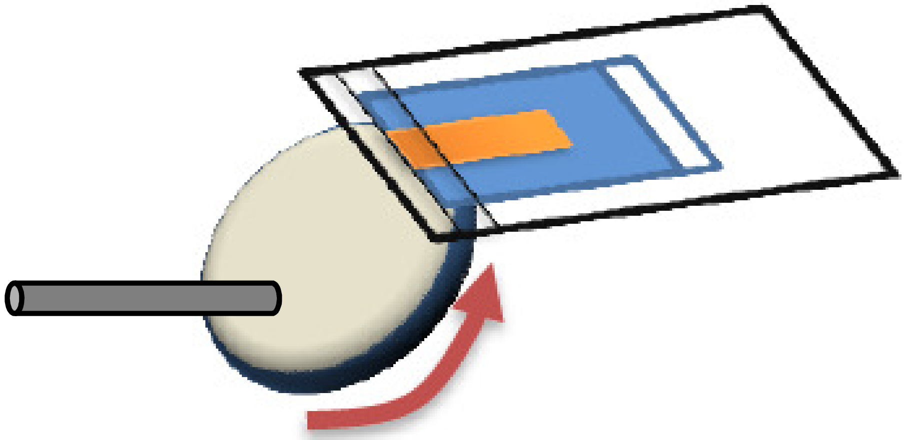
- ZnO/PMMA
- High resistance with almost symmetrical breakdown

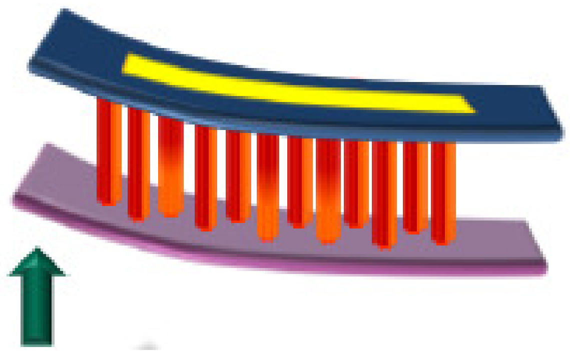


- PEDOT:PSS
- Diode characteristics with high leakage



Controlled bending

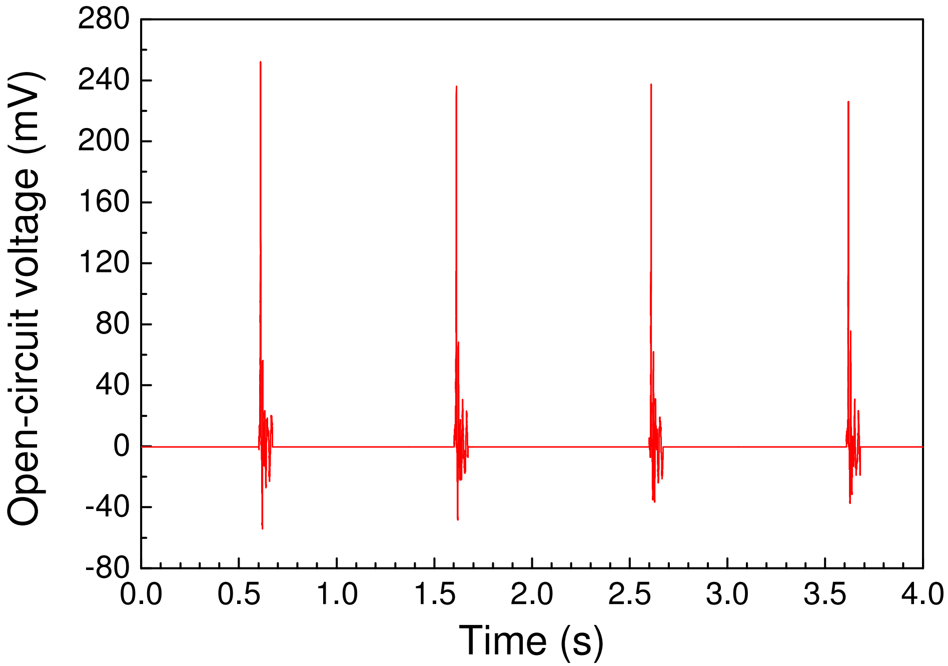




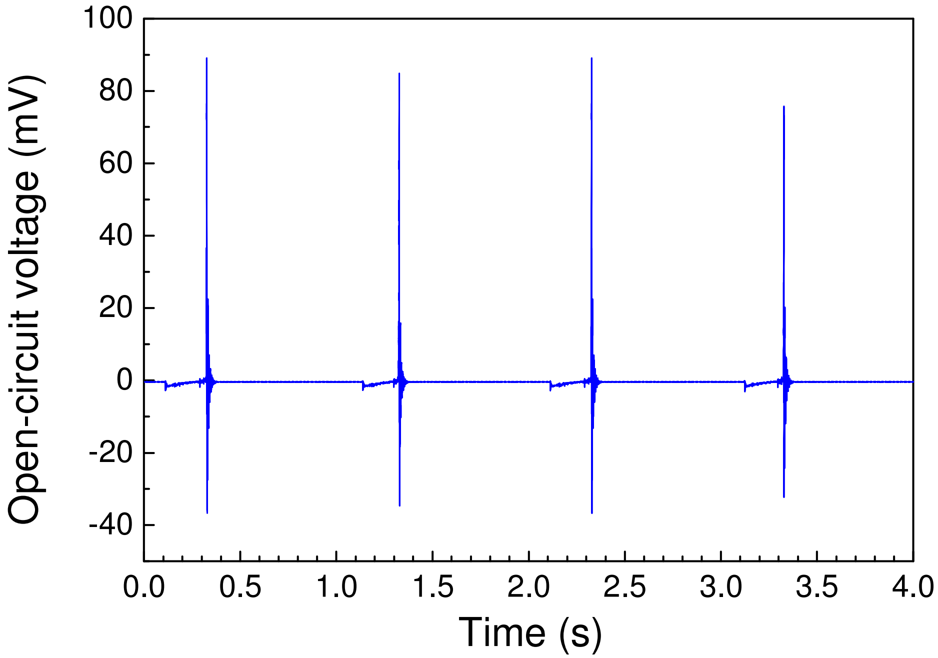
- Cam used to produce controllable deflection of flexible substrate
- Voltage or current peak measured as substrate drops from cam
- Avoids resonance effects of substrate

Controlled bending

PMMA



PEDOT:PSS

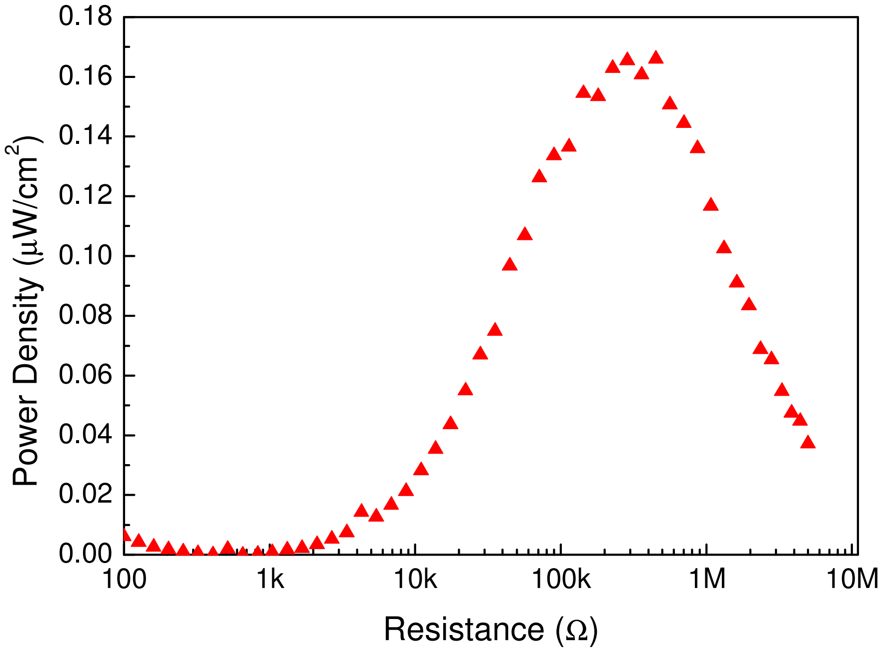


- Peak open-circuit voltage highest for PMMA device

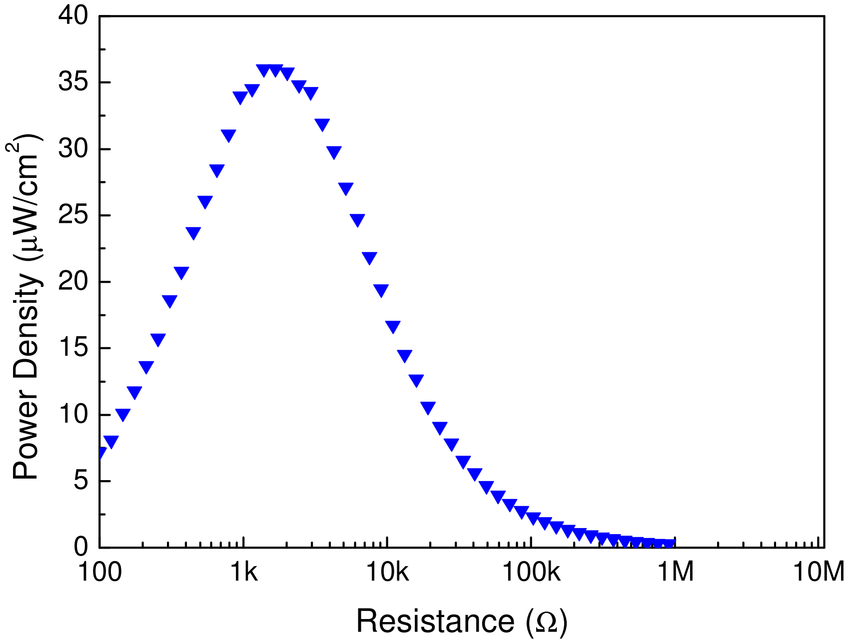
J. Briscoe *et al.* (2013) *Energy Environ. Sci.* **6**: 3035–3045. doi: 10.1039/C3EE41889H

Controlled bending - Load matching

PMMA



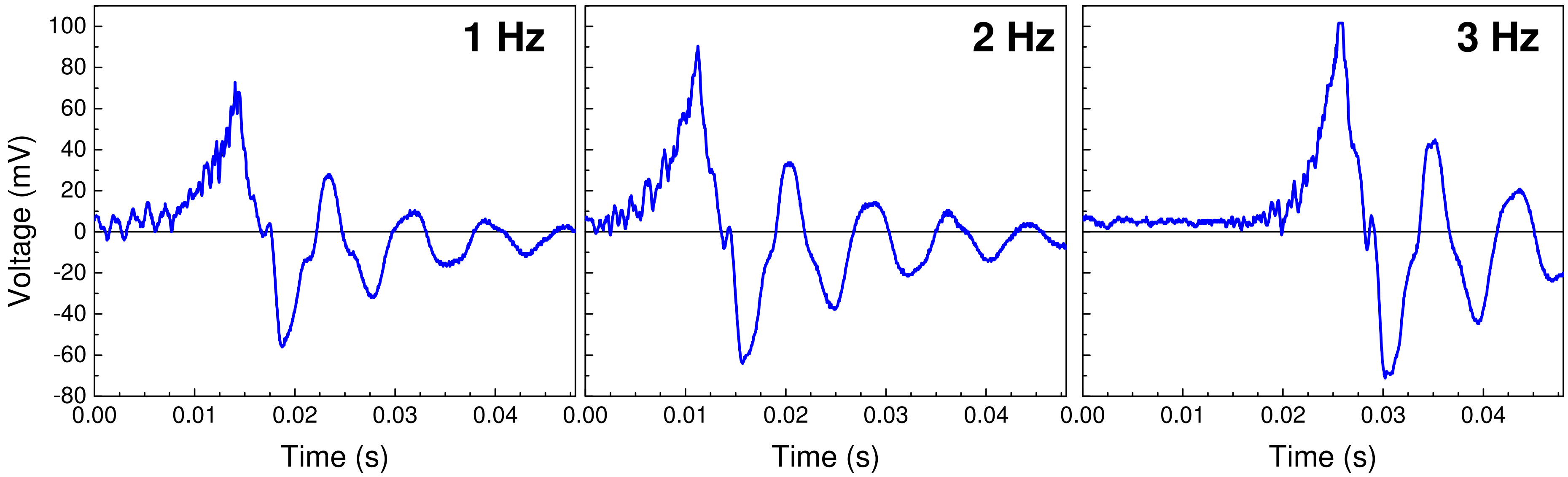
PEDOT:PSS



	ZnO/PMMA	ZnO/PEDOT:PSS
V_{oc} (mV)	252	90
Load R (kΩ)	286	1.68
Area power density (μWcm^{-2})	0.165	36
Volume power density (mWcm^{-3})	0.30	144

- Power from V_{oc} x J_{sc} overestimates by 4x

Controlled bending - Rate dependence



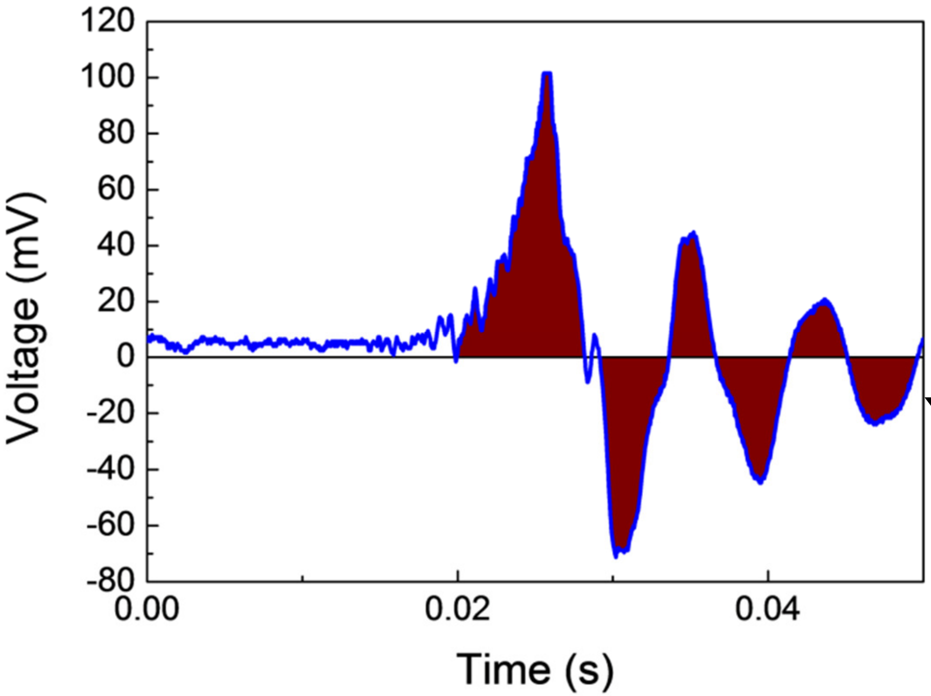
V_{peak} ~ 75 mV

V_{peak} ~ 90 mV

V_{peak} ~ 100 mV

- Peak open-circuit voltage increases with bending rate (1 Hz leads to measured peak velocity of 0.8 m/s)

Controlled bending - Rate dependence



- Faster strain → higher peak voltage but with shorter duration.
- Total energy given by integrating over time:

$$E = \int_{t_1}^{t_2} \frac{V(t)^2}{R_{load}} dt$$

	ZnO/PMMA	ZnO/PEDOT:PSS
V_{oc} (mV)	252	90
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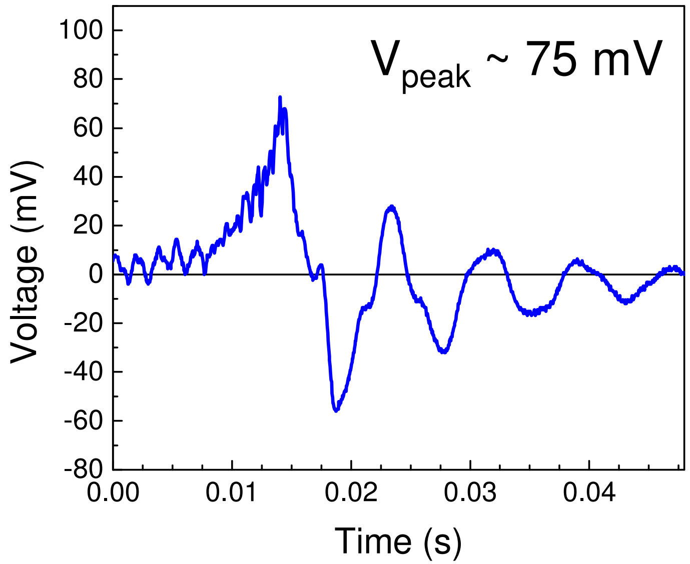
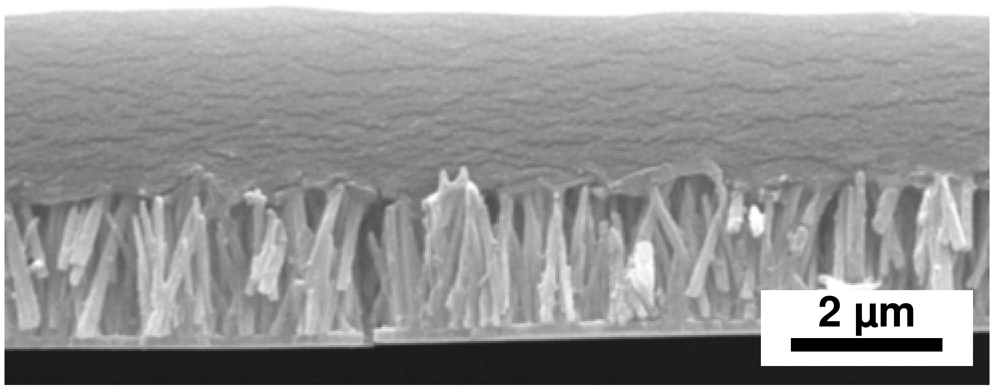
Area power density (μWcm^{-2})	0.165	36
Volume power density (mWcm^{-3})	0.30	144
Energy output (nJcm^{-2}/cycle)	0.17	38.6

Device output

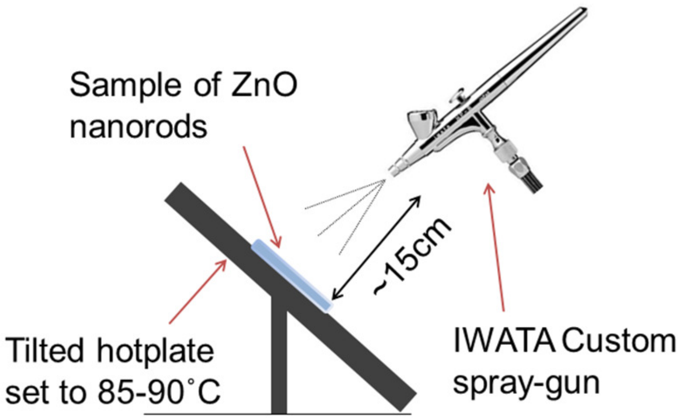
- Device output is still quite low
- Peak voltage is too low to be useful
- Need other ways to improve devices
- Is screening still an issue?
- What about the ZnO surface?





Surface passivation

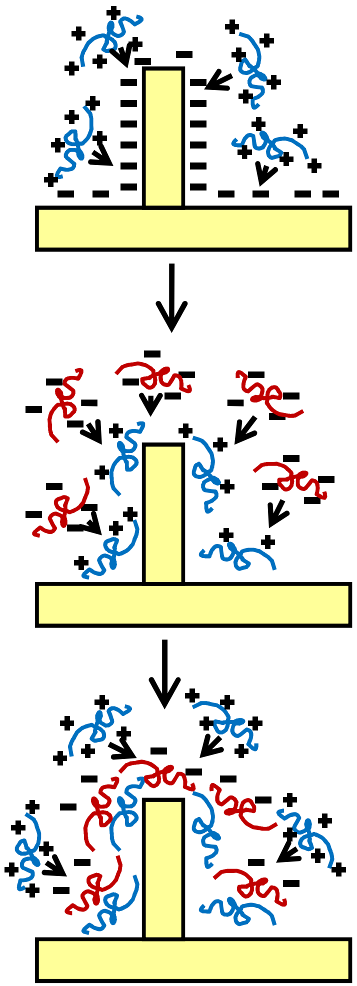
CuSCN spray deposition



- 0.15 M CuSCN solution in propyl sulphide spray-coated onto nanorods at ~80 °C
- 10 or 20 layers coated (5 or 10 ml)

Hatch, S., et al. (2013). *Thin Solid Films* 531: 404-407
DOI: 10.1016/j.tsf.2012.12.114

Layer-by-layer polyelectrolytes



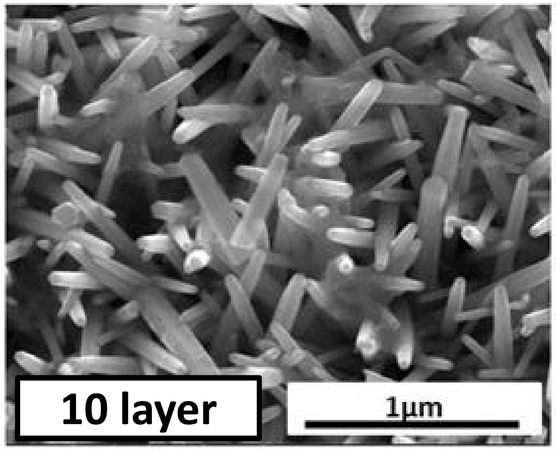
- Dipped into 10 wt%, aqueous solution of PDADMAC and rinsed with DI water
- Dipped into 10 wt% aqueous solution of PSS → 1 bilayer
- Repeated to form 2 or 4 bi-layers of polyelectrolytes

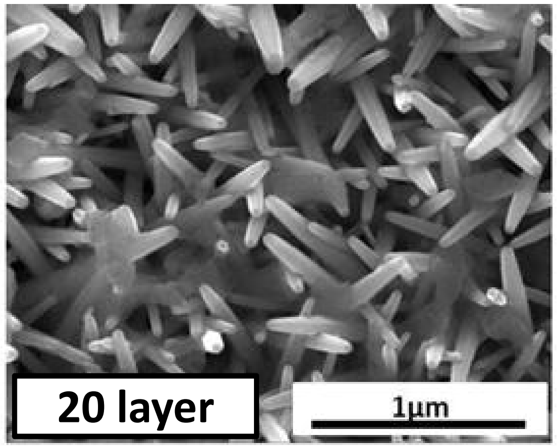
PDADMAC = Poly(diallyldimethylammonium) chloride

PSS = Polystyrene sulfonate

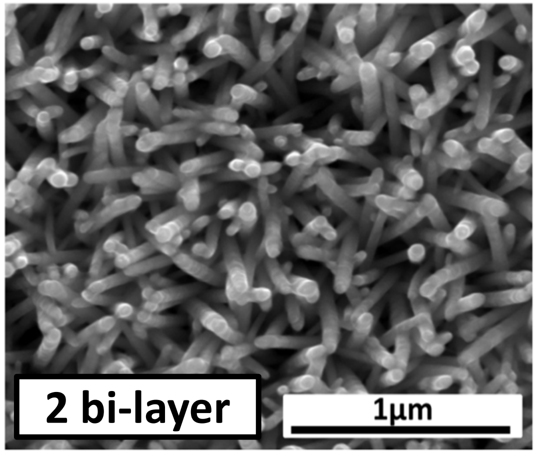
ZnO nanorods: surface passivation

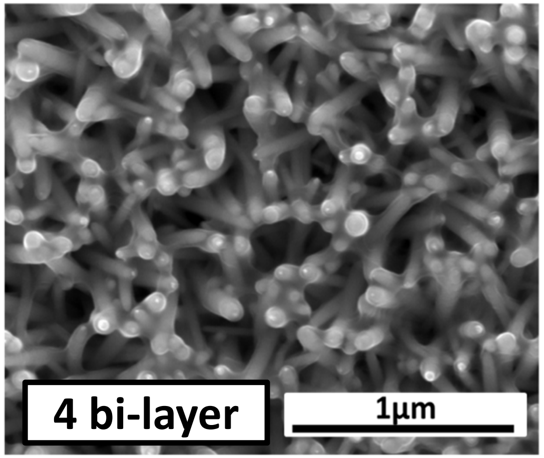
CuSCN spray deposition





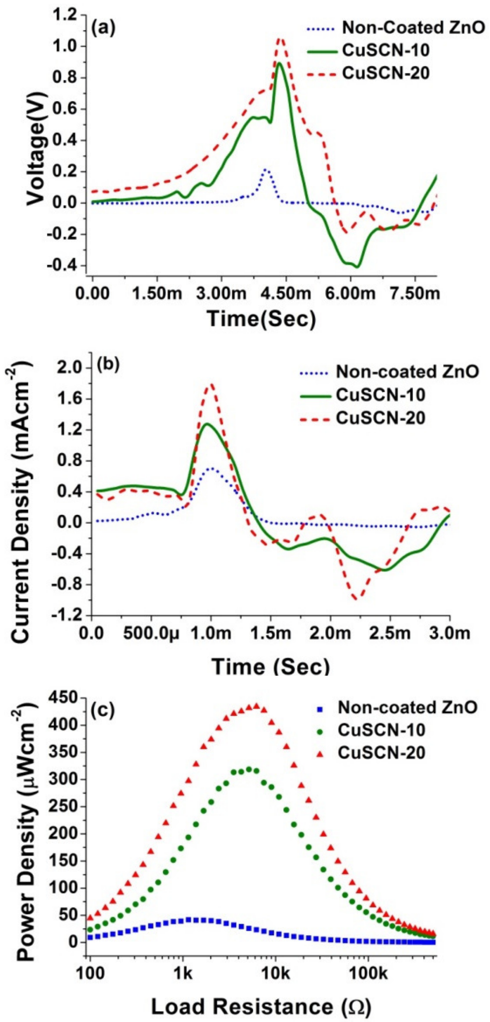
Layer-by-layer polyelectrolytes



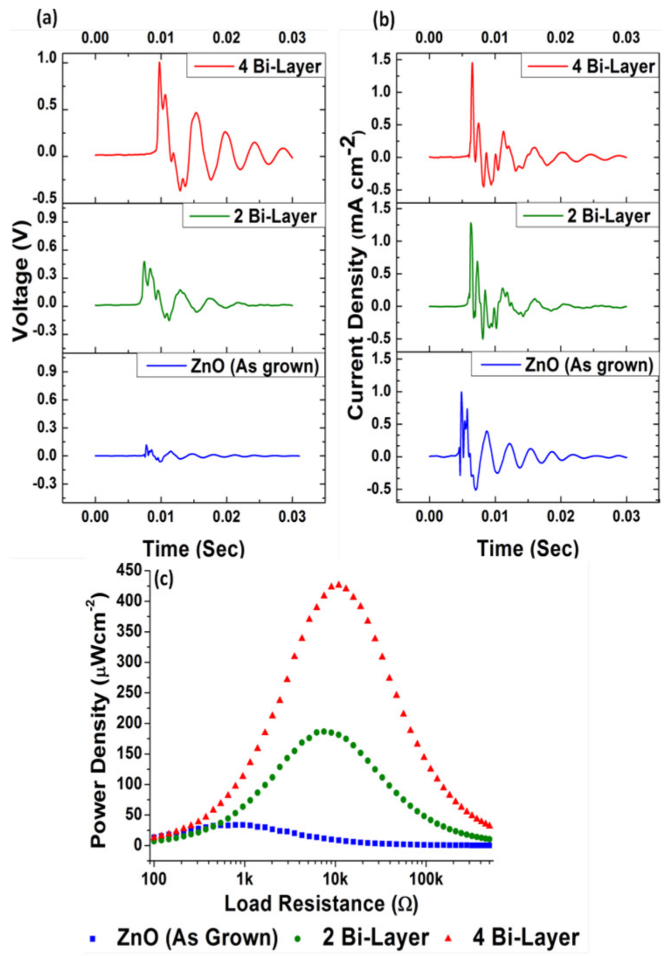


Power output

CuSCN



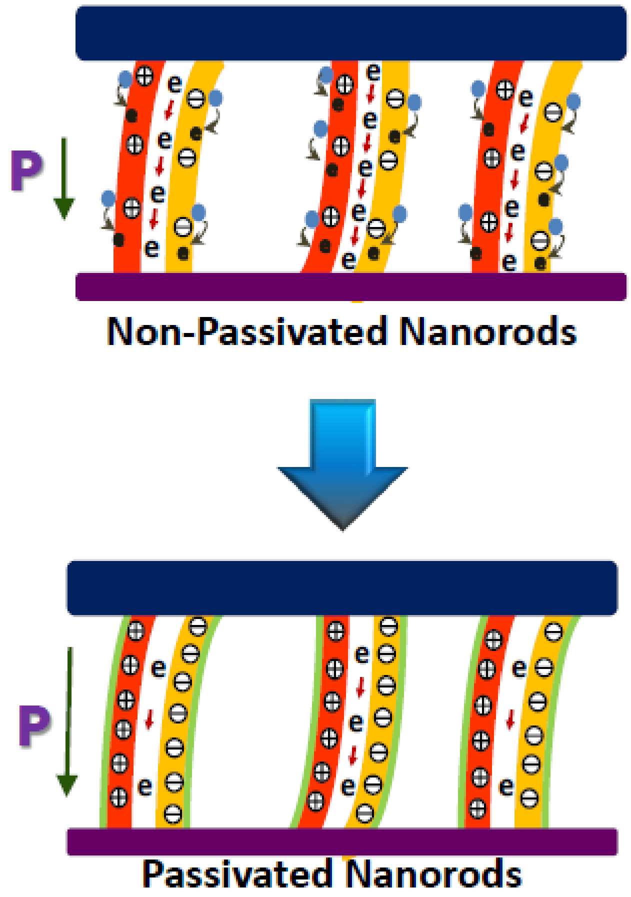
Polyelectrolytes



Mechanism

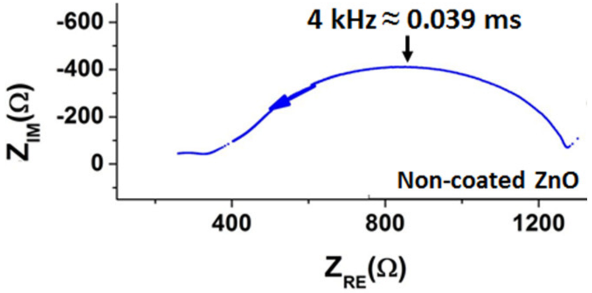
- Free carriers in ZnO screen polarisation internally by re-distributing in response to the polarisation

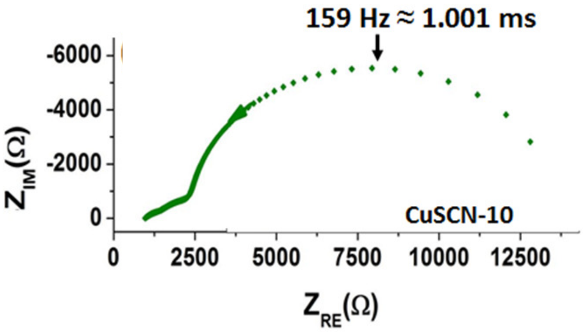
- Passivation of surface reduces carrier concentration, reducing the internal screening

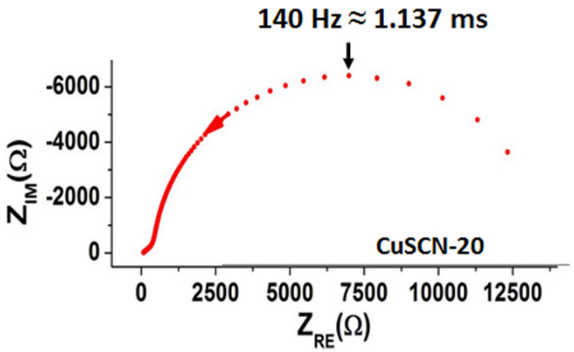


Electrical Impedance

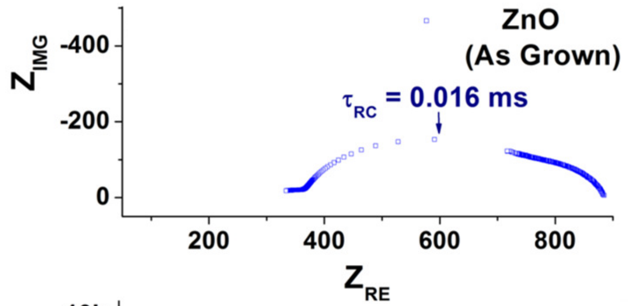
CuSCN

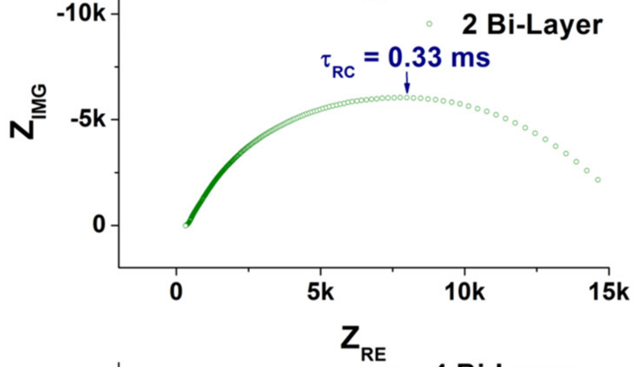


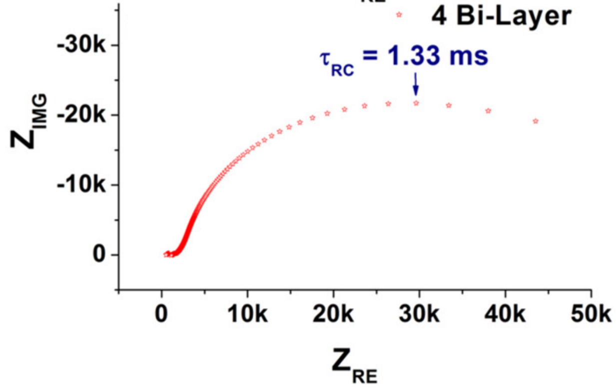




Polyelectrolytes







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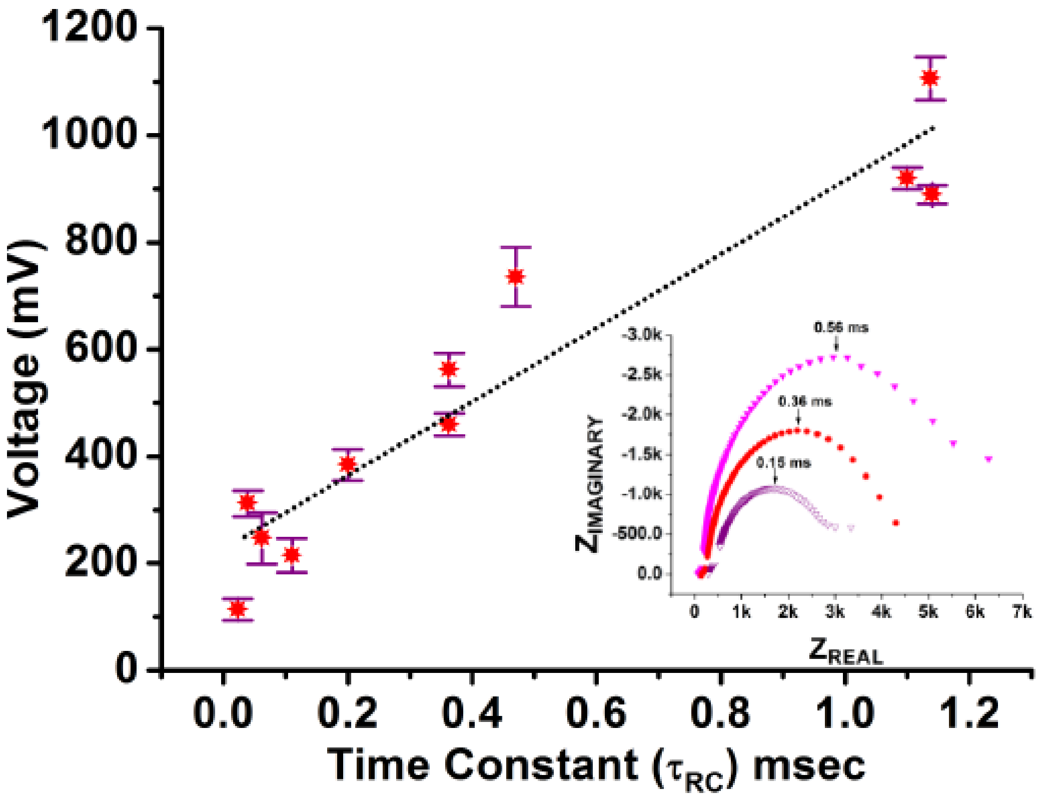


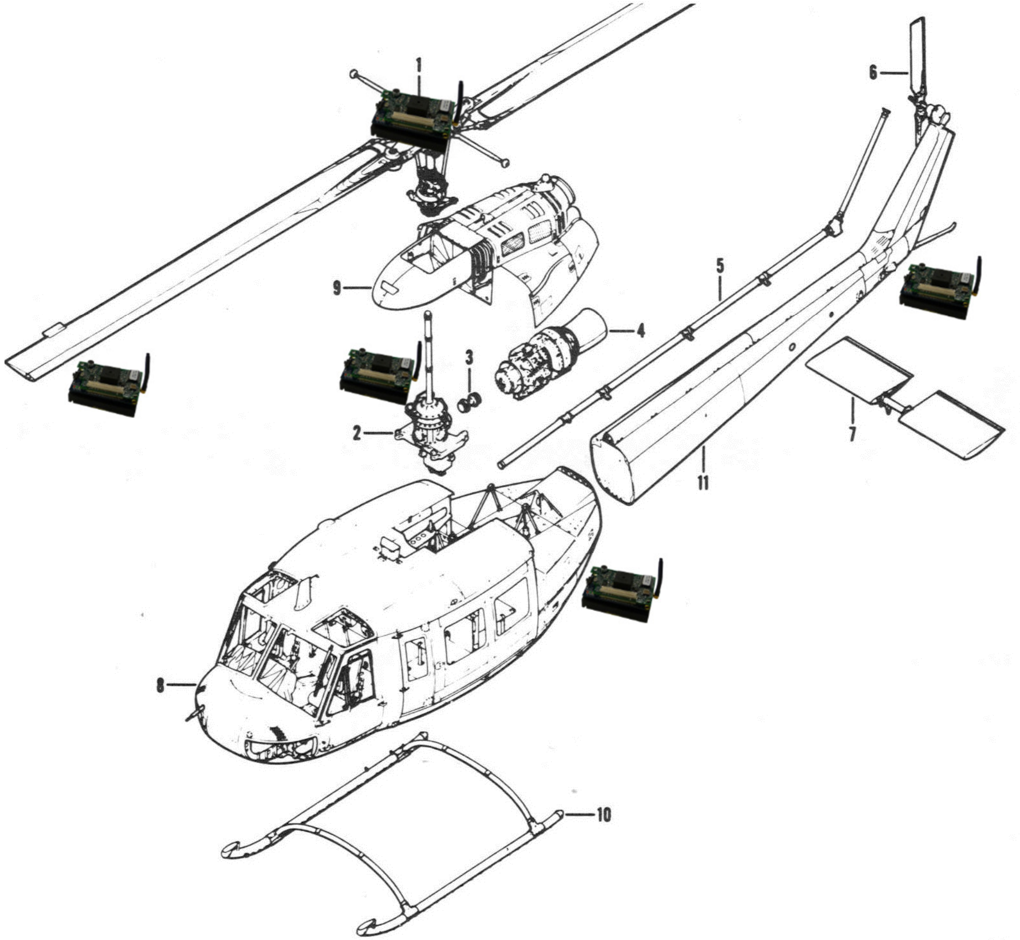
- Time constant of system shows good correlation with peak voltage

Wireless sensor nodes

- HUMS key to ensuring helicopter safety
- Components distributed through aircraft
- Vibration provides key indicator of component health
- Also provides excellent source of energy!

Wireless sensor nodes

- IVHM – ‘integrated vehicle health management’ - sensors distributed through aircraft
- Wiring in difficult and expensive
- Wireless nodes easy to install
- Ideally ‘fit and forget’
- Batteries require replacement
- Energy harvesting desirable



Summary

- ZnO nanorods produced by chemical methods on flexible, polymer substrates
- P-n junctions made with polymer p-type material to reduce rate of screening of polarisation
- Compared to ZnO/insulator structure, p-n junction delivers 200x more power on load despite 3x lower V_{oc}
- Nanorod surface passivated using either inorganic CuSCN, or a polymer layer, increasing power output due to reduced screening
- Devices investigated for helicoptor sensor nodes
- Power output must be increased to give good duty cycle
- Recent investigations to vary seed layer, and top contact

Thank You

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University of West Bohemia, Czech Republic
Petr Novák
SPECIFIC, Swansea University, UK
Simone Meroni, Peter Greenwood, Joel Troughton, Trystan Watson,

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Further information

Screening: J. Briscoe *et al.* (2012) *Adv. Energy Mater.* **2**, 1261–1268. doi: 10.1002/aenm.201200205

Measurement: J. Briscoe *et al.* (2013) *Energy Environ. Sci.* **6**: 3035–3045. doi: 10.1039/C3EE41889H

CuSCN passivation: N. Jalali *et al.* (2014) *J Mater Chem A* **2**:10945. doi: 10.1039/c4ta01714e

PDDA/PSS : N. Jalali *et al.* (2015) *J Sol-Gel Sci Technol* **73**:544–549. doi: 10.1007/s10971-014-3512-4

Efficiency measurements: J. Briscoe *et al.* (2012) *Appl. Phys. Lett.* **101**, 093902. doi: 10.1063/1.4749279

Review paper: J. Briscoe and S. Dunn (2015) *Nano Energy* **14**: 15–29 doi: 10.1016/j.nanoen.2014.11.059