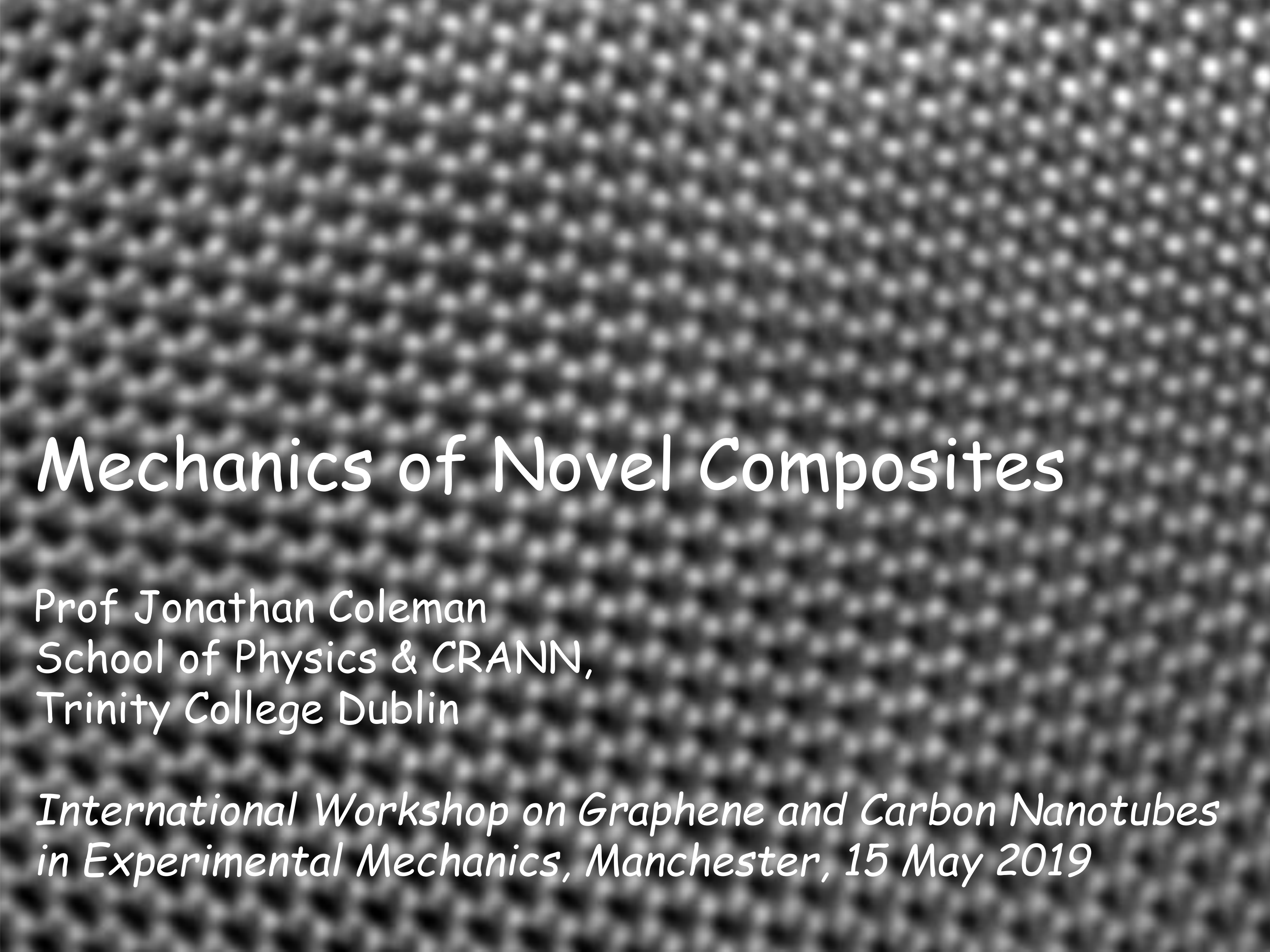
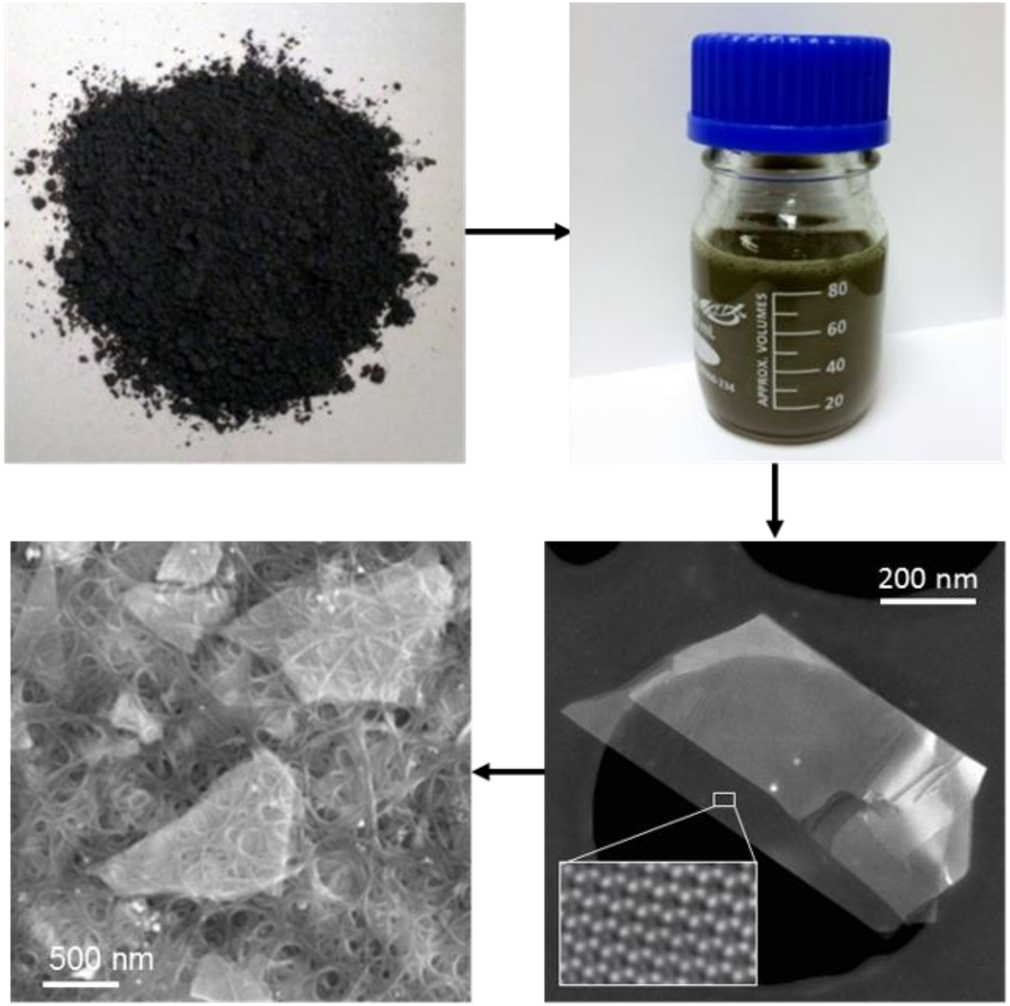


Mechanics of Novel Composites

Prof Jonathan Coleman
School of Physics & CRANN,
Trinity College Dublin

International Workshop on Graphene and Carbon Nanotubes in Experimental Mechanics, Manchester, 15 May 2019

Coleman Group: Making things from nano materials



Dispersion

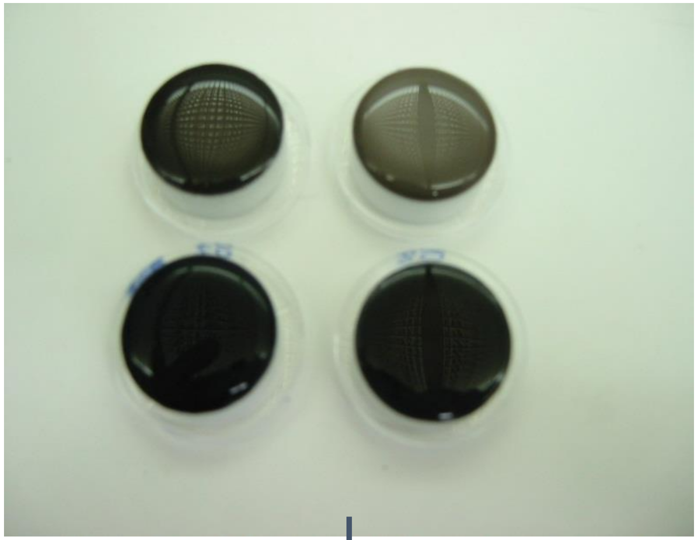
Exfoliation

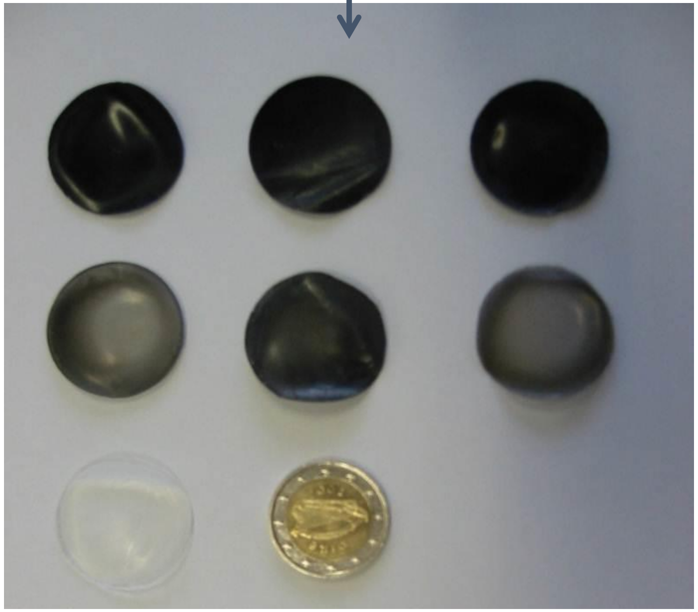
Processing

Functional Materials

Including composites

Historically: Mixing *Graphene* into plastics

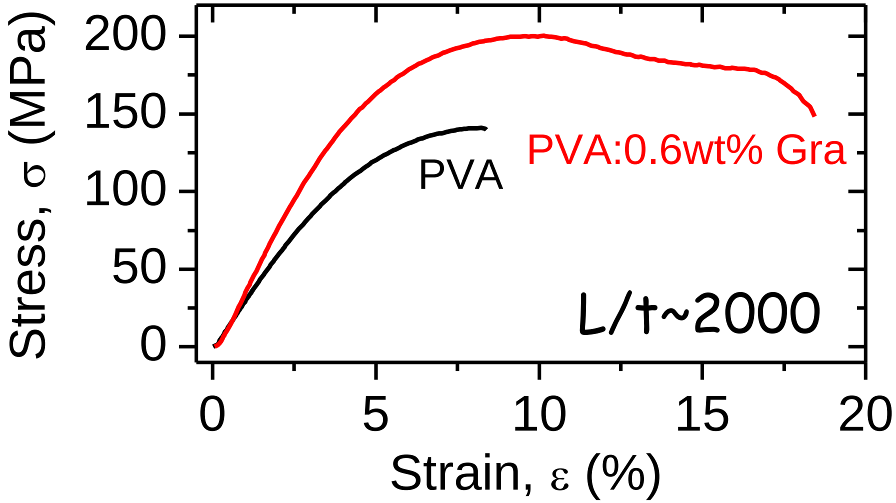


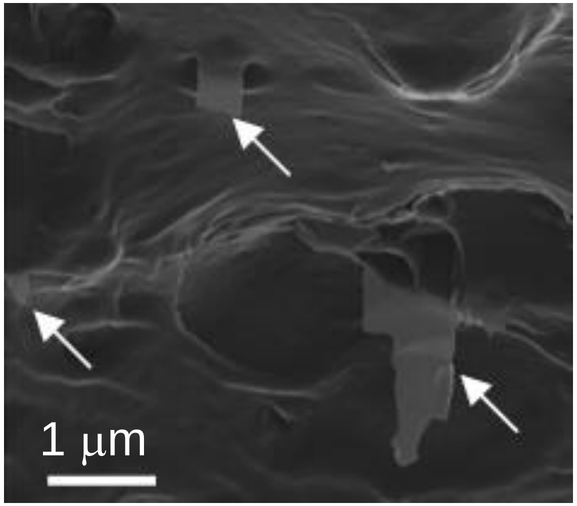


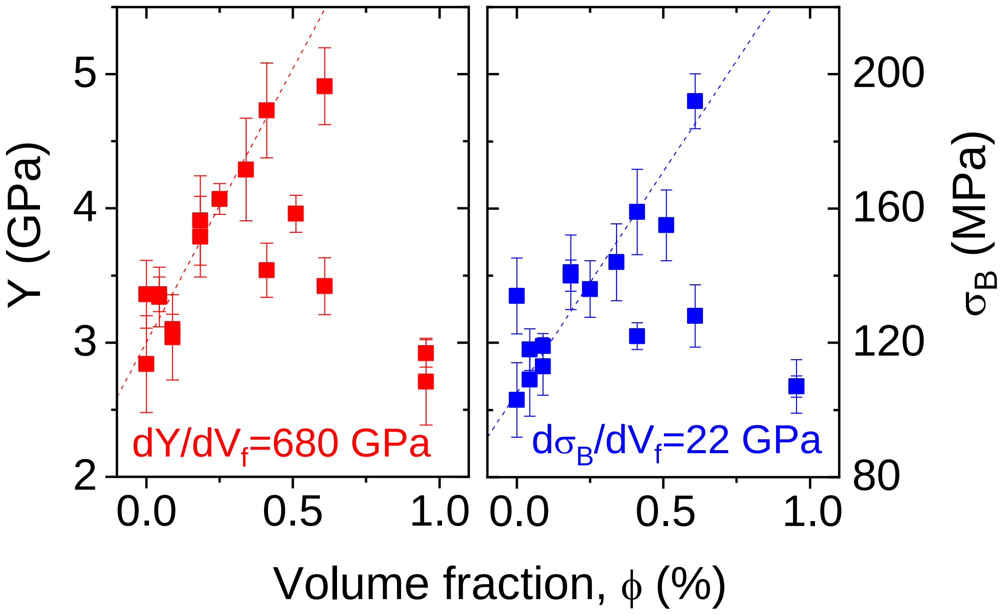
To improve properties

J Mater Chem 22, 1278

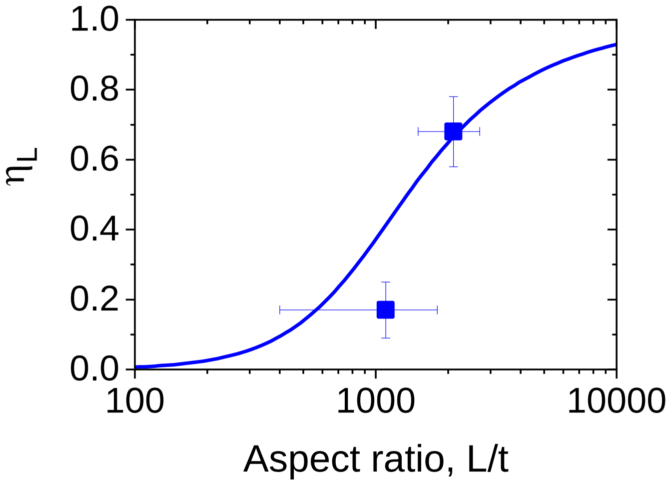
Reinforcement with large flakes?





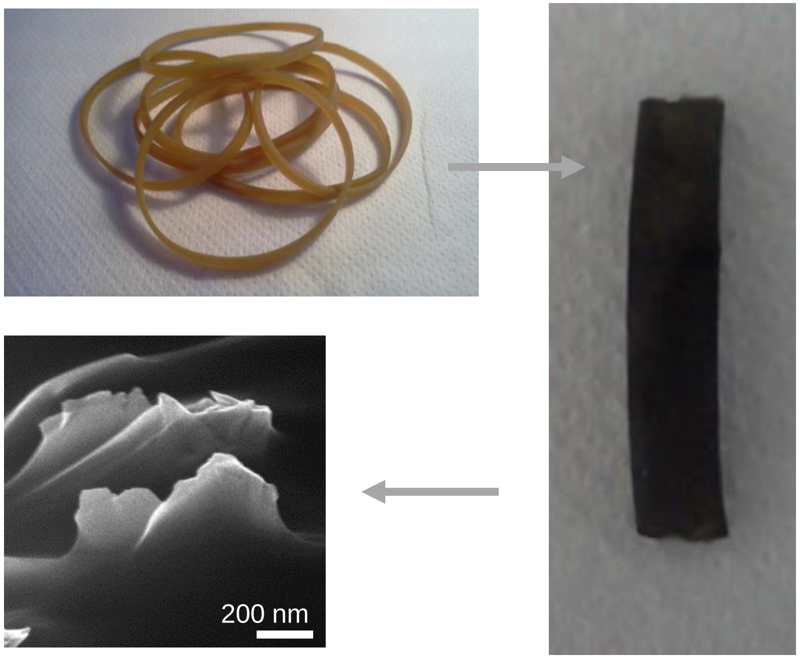


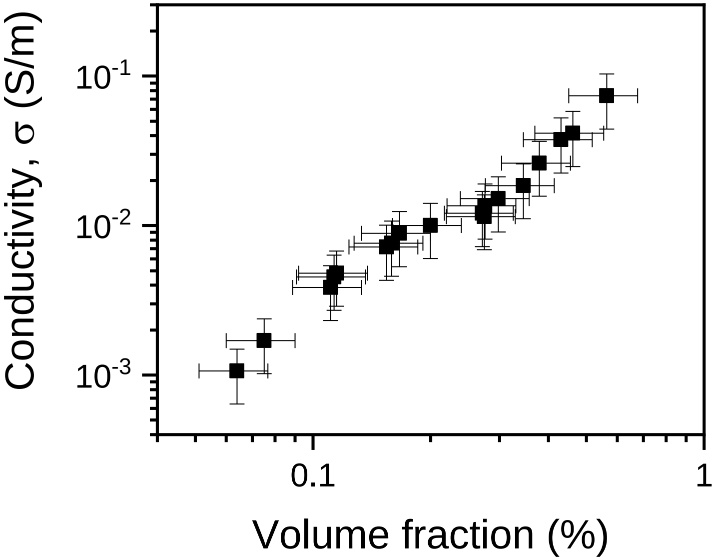
$$Y = \eta_L \eta_o Y_F \phi + Y_P (1-\phi)$$

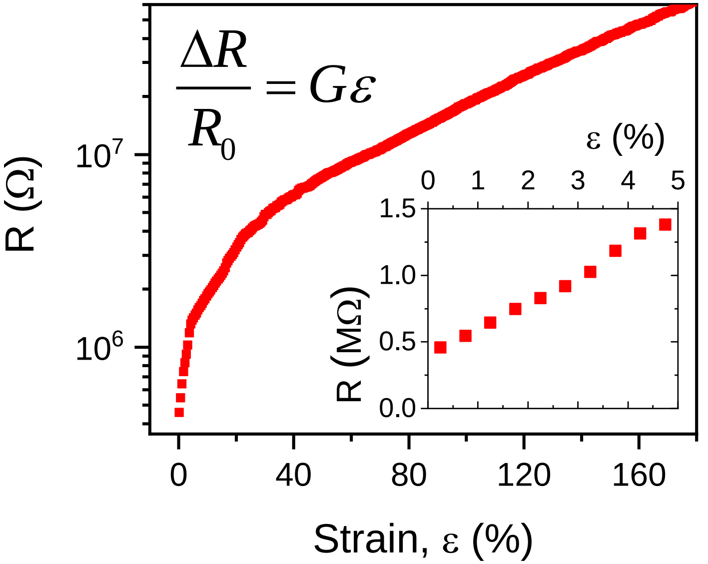


Follows shear lag theory

More recently: electromechanical properties
Graphene-rubber composite Strain-Sensors







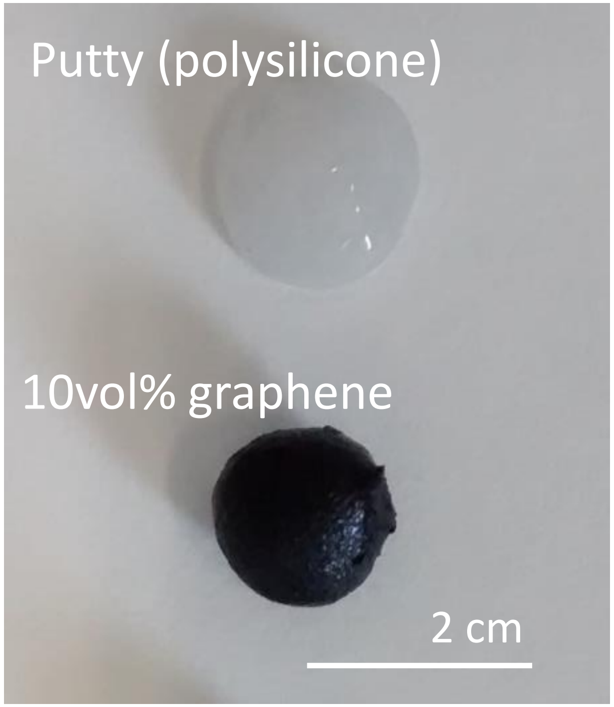
$R \sim e^{a\varepsilon}$: tunnelling

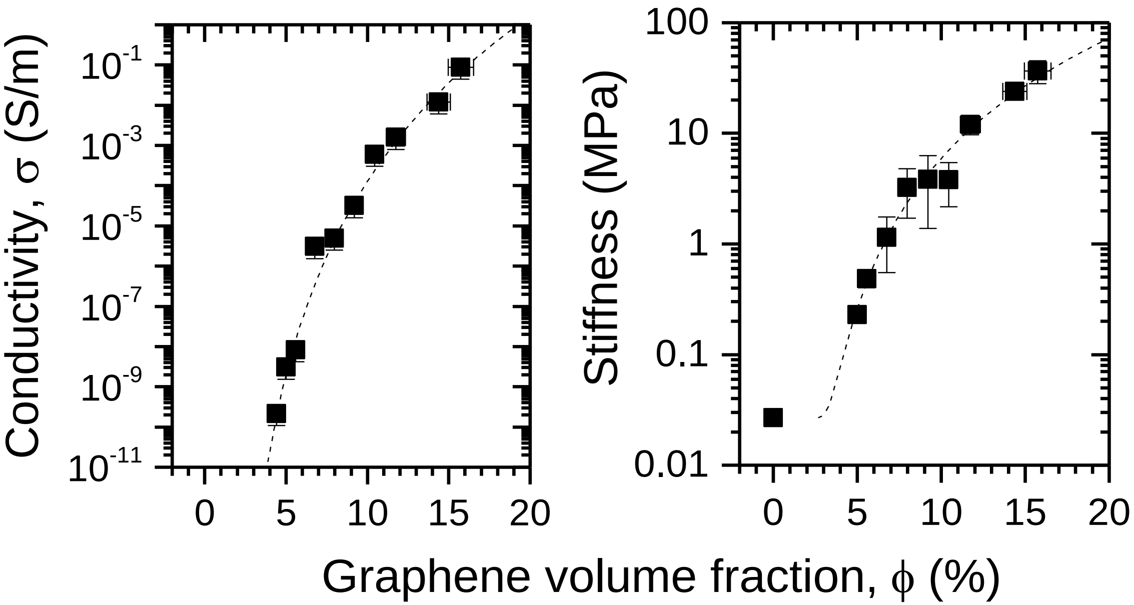
G~35

ACS Nano, 8, 8819

Application III; Composite Strain-Sensors

Add graphene to silly putty

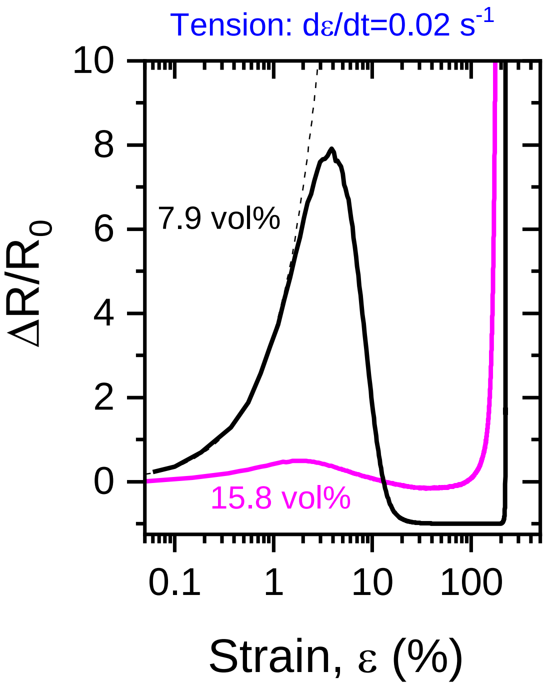


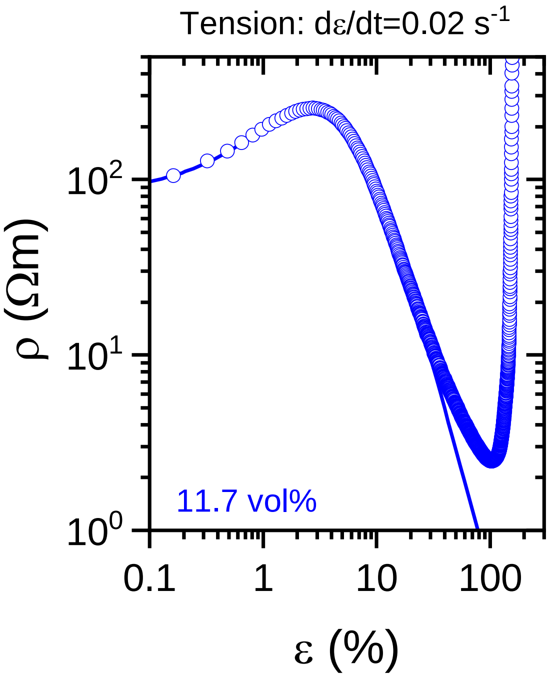


Electrical and mechanical properties both linked to nanosheet network

Science, 354, 1257

Unusual electro-mechanical behaviour (Payne effect)





Model based on:

ε-induced junction breaking+
Diffusion-driven reconnection+
Percolation

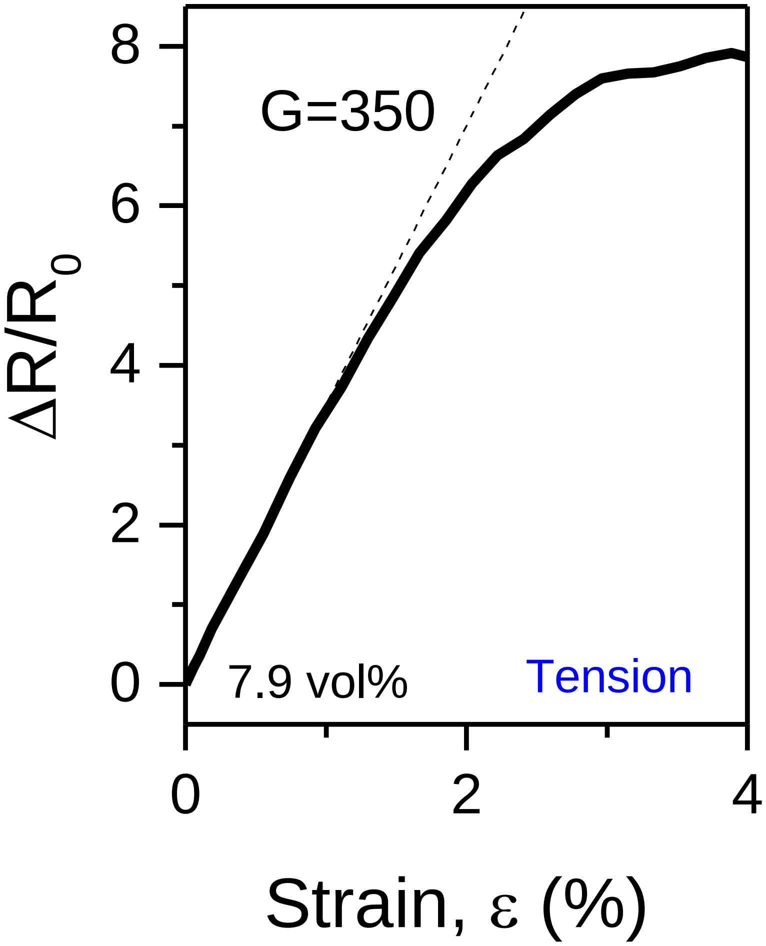
$$\frac{\rho}{\rho_0} = \left[\left(1 + \left(\frac{\varepsilon}{\varepsilon_c} \right)^{2m} \right)^{-1} + \frac{\varepsilon}{\varepsilon_t} \right]^{-n_\varepsilon}$$

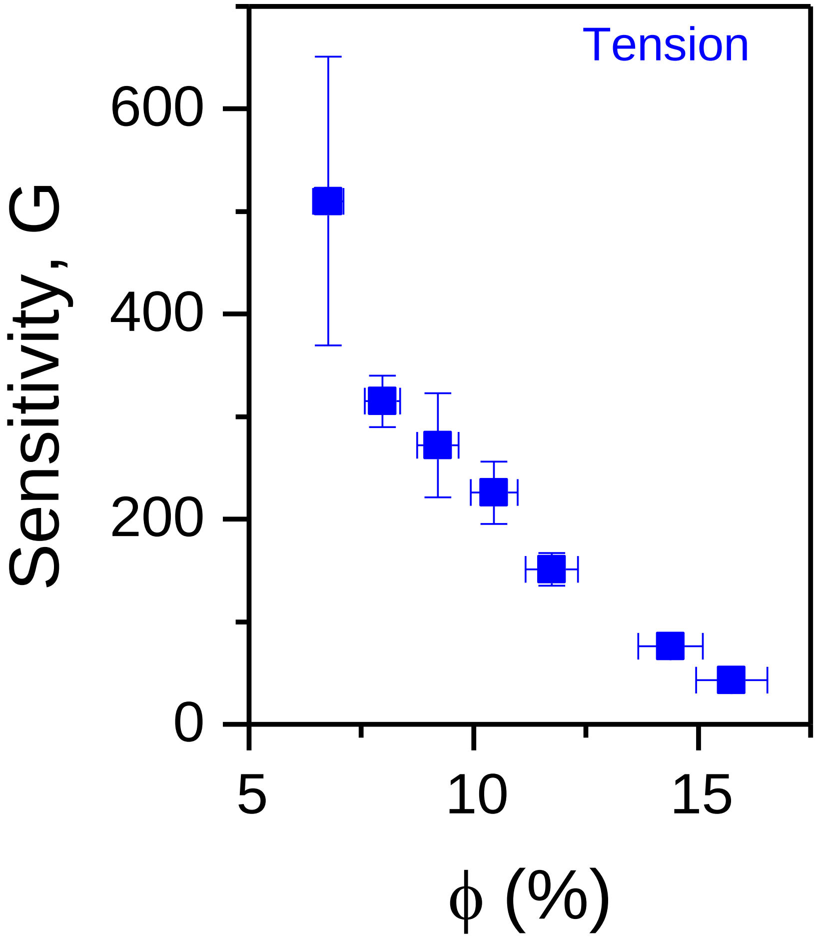
Implies extreme softness of polymer is important (low η, high D)

With Prof Bob Young (Manchester)

Works as a very good low-strain strain sensor with very high sensitivity

$$\frac{\Delta R}{R_0} = G\varepsilon$$



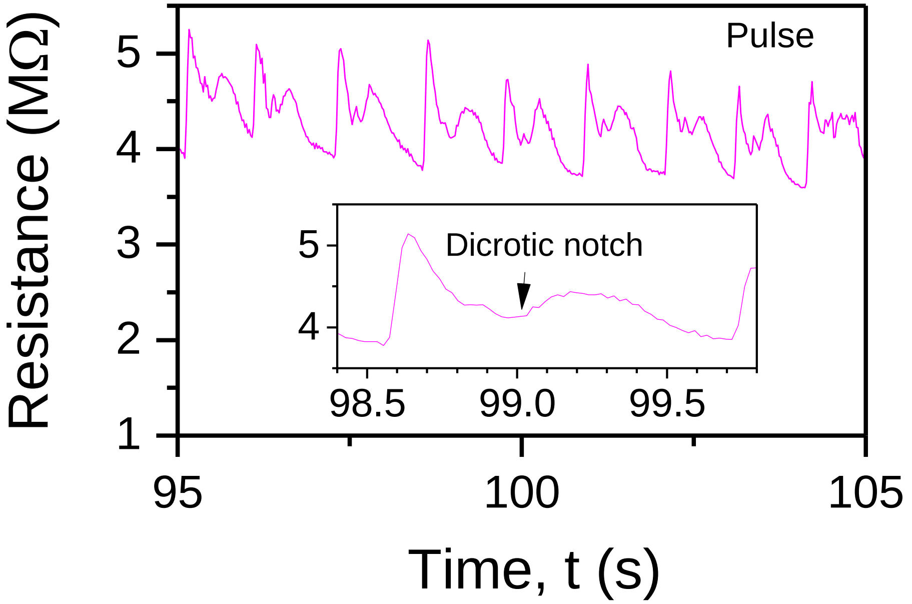


Science, 354, 1257

Use as a sensor to measure vitals!

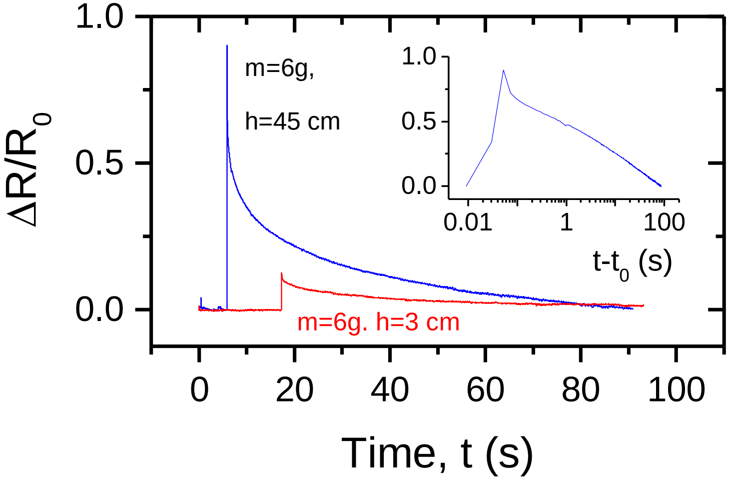
Science, 354, 1257

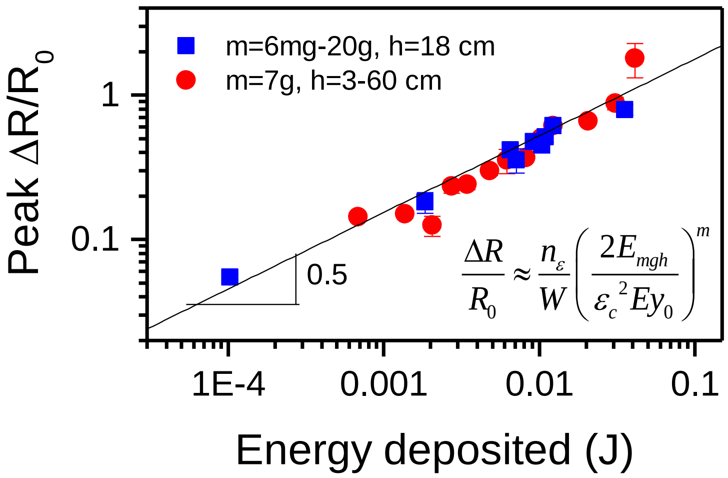
Unique precision



Amplitude gives blood pressure

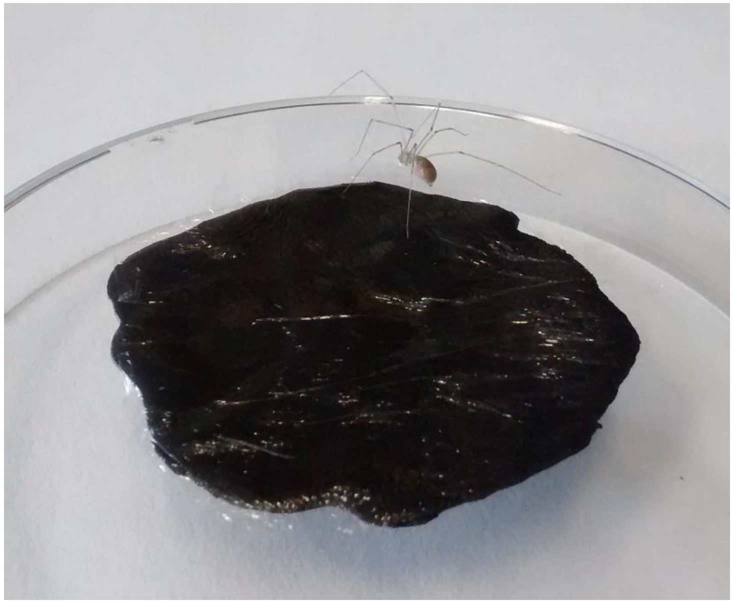
.....but its also an impact sensor – falling balls

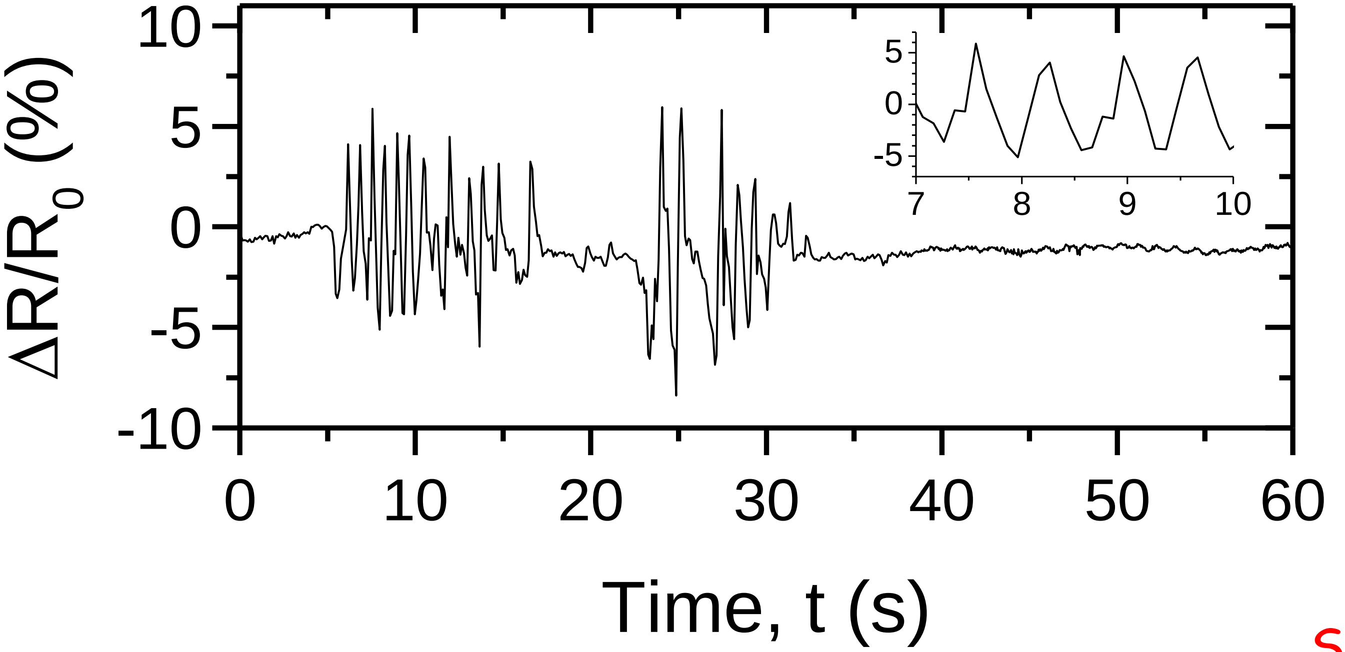




Science, 354, 1257

Adventures in biology.....

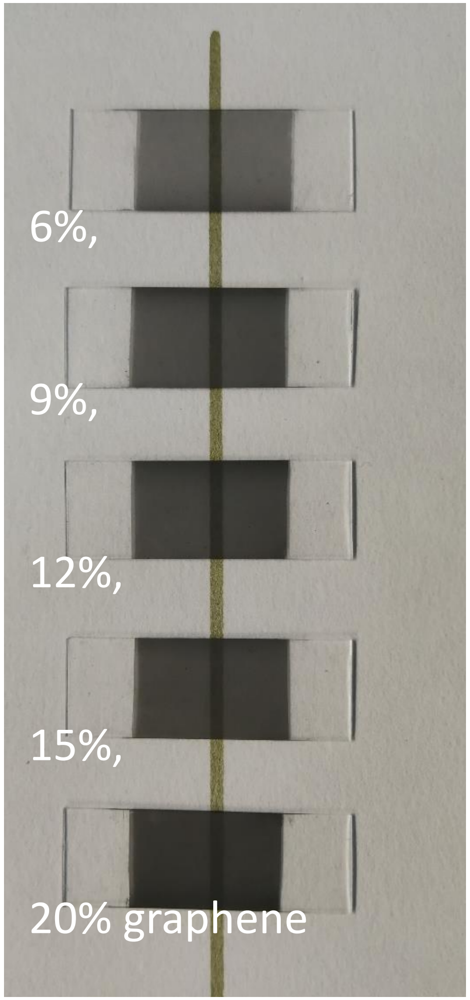




Individual spider footsteps

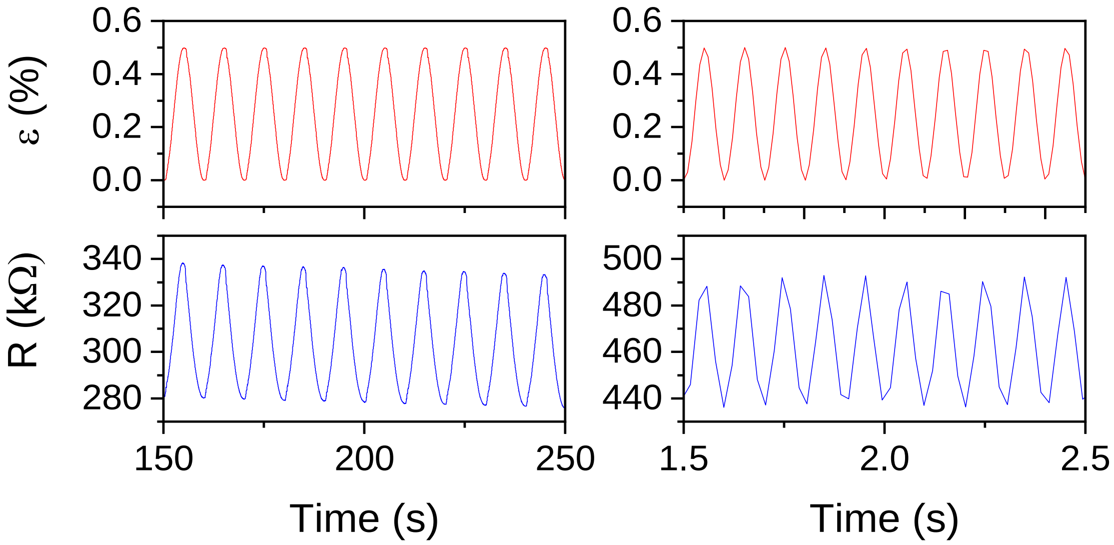
Science, 354, 1257

Into the future…
….turning G-putty into a practical sensor



Developed G-putty based inks which can be sprayed into thin films

-> sensitive sensors



0.1 Hz

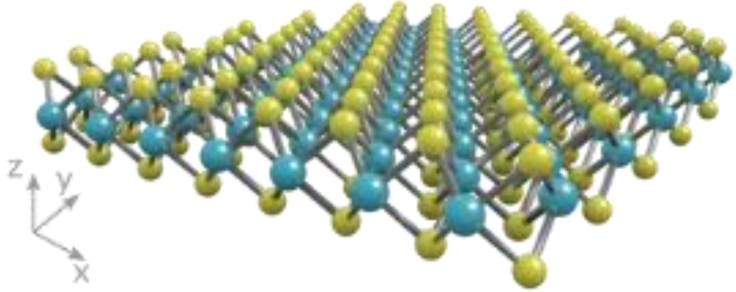
10 Hz

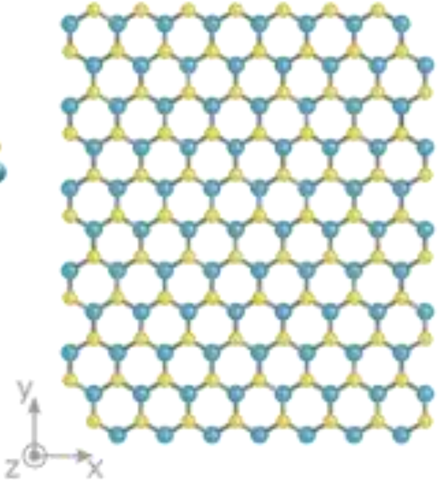
Sensing action based on tunnelling and junction breaking/reforming

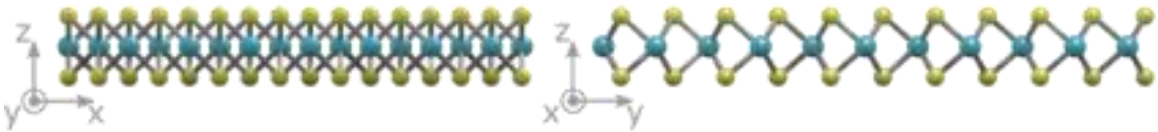
What about electro-mechanics of nanosheets themselves?

Some nanosheets have $E_g=f(\varepsilon) \rightarrow \rho=f(\varepsilon)$

MoS$_2$







$$\frac{\Delta R}{R_0} = G\varepsilon$$

Negative G:

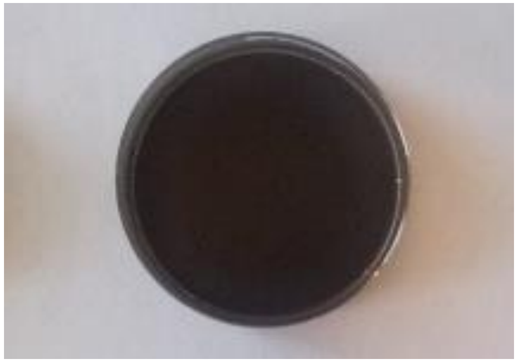
G~-50

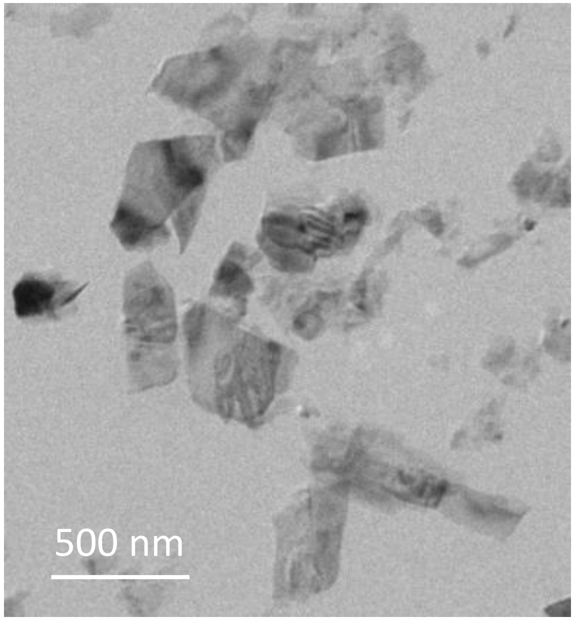
(multilayer)

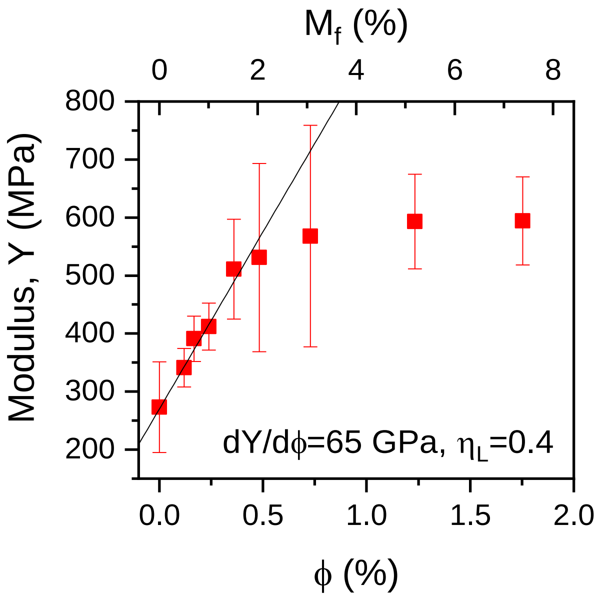
Produce MoS_2 nanosheets by liquid phase exfoliation

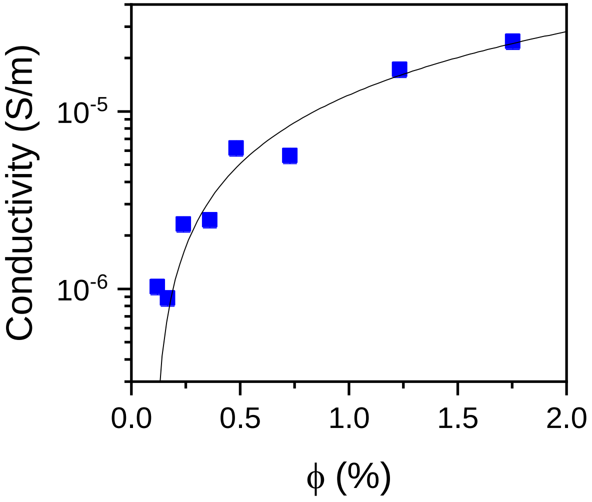
‹L/t›~50

MoS_2/PEO composites









Doping and crystal-isation (?)

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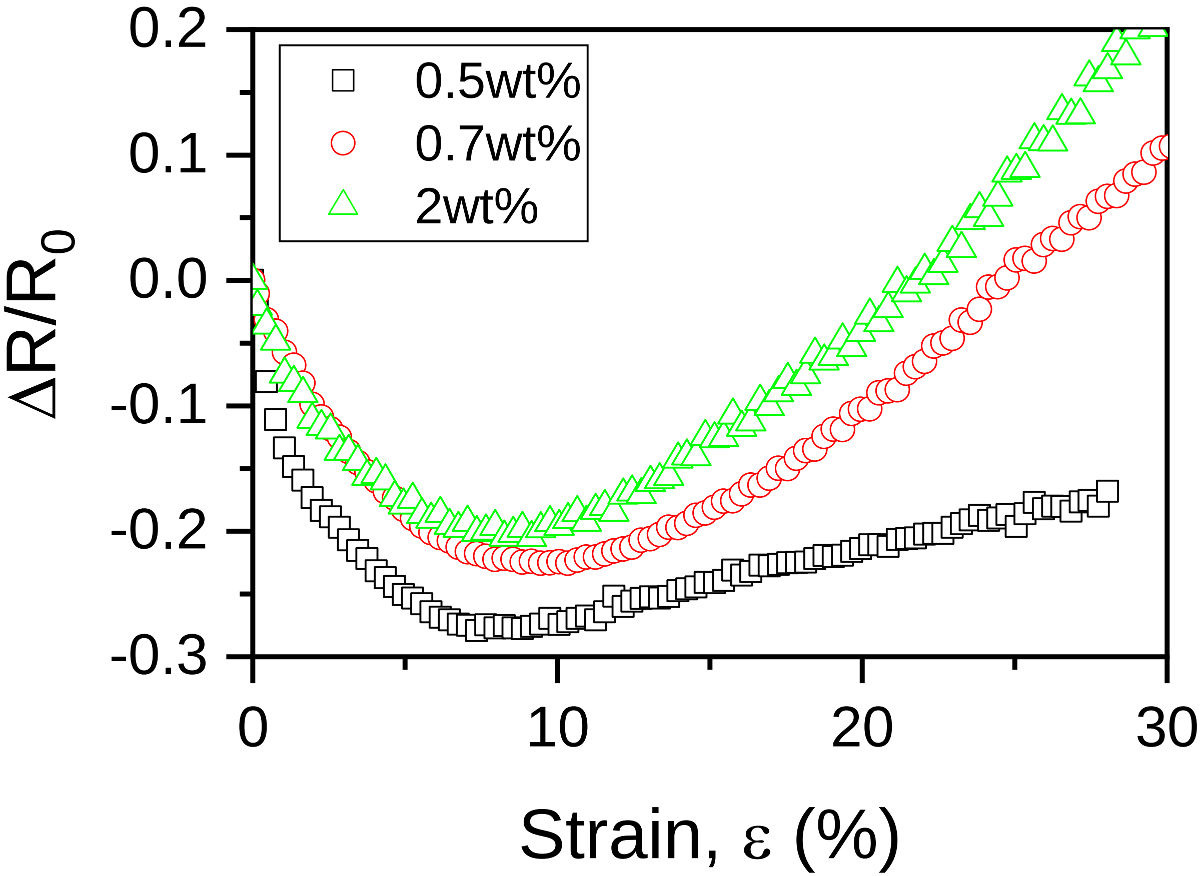
Measure electromechanical properties

1. Initial resistance decrease: Negative G

-25<G<-15

2. Later resistance Tunnelling?



(1) Assume: Applied strain stretching the nanosheets (at low ε)

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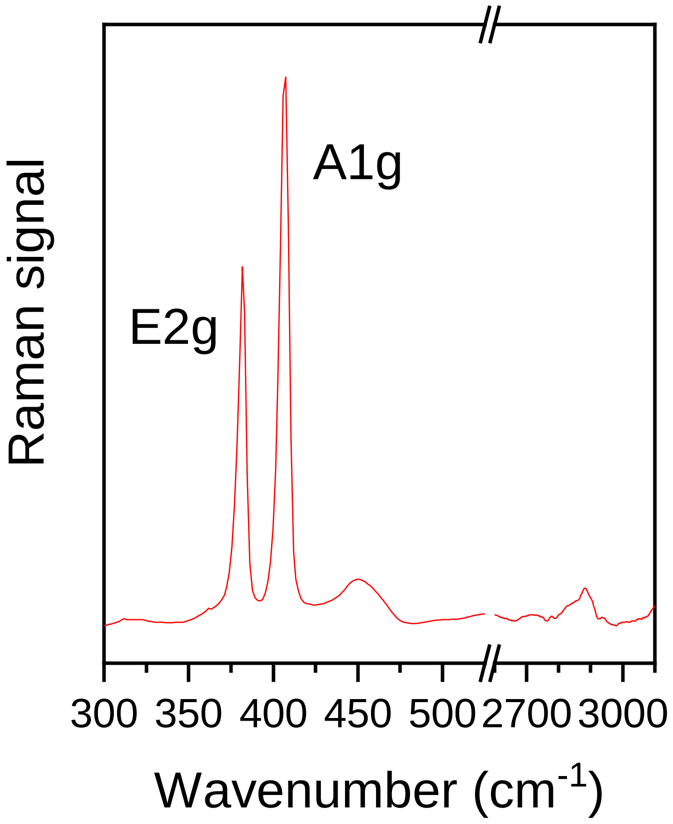
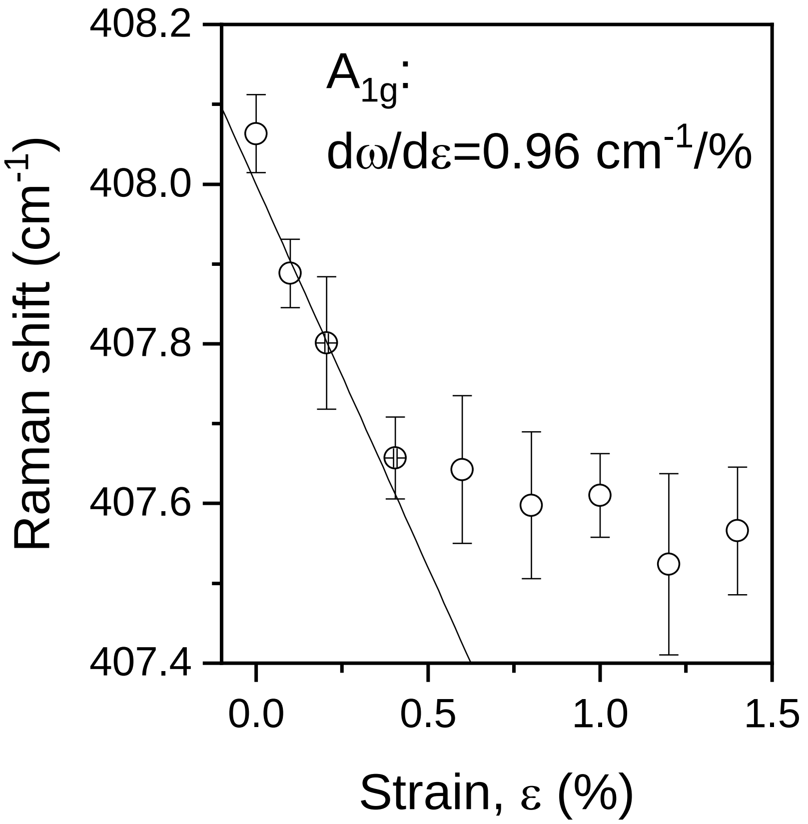
If strain transferred to nanosheets: Raman shift





See effective stress transfer

Prof Bob Young, Dr Zheling Li (Manchester)

Crude model for a nanosheet network

$$\frac{\Delta R}{R_0} = G\varepsilon$$

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$$\rho \propto \left(R_{NS} + R_J\right)$$ for a network

$$\frac{\Delta R}{R_0} = \left[\frac{1}{\rho_0}\frac{\mathrm{d}\rho}{\mathrm{d}\varepsilon} + 2\right]\varepsilon$$ for any material (at low strain)

Combining

$$\frac{\Delta R}{R_0} = \left[\frac{\mathrm{d}R_{NS}/\mathrm{d}\varepsilon + \mathrm{d}R_J/\mathrm{d}\varepsilon}{R_{NS,0} + R_{J,0}} + 2\right]\varepsilon$$

If nanosheets stretched

$$R_{NS}(\varepsilon) = R_{NS,0}G_{NS}\varepsilon + R_{NS,0}$$

Tunnelling

Combining

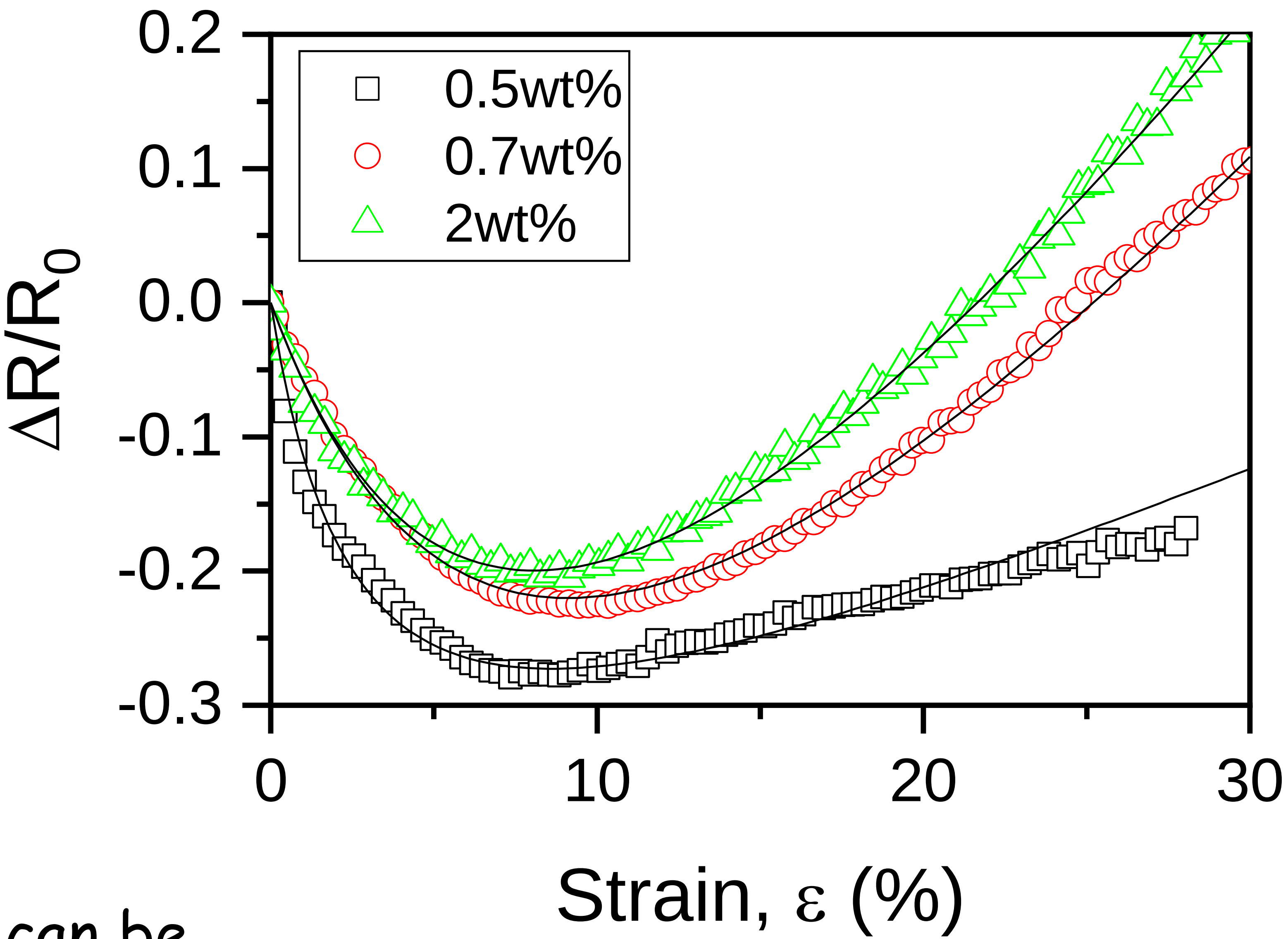
$$\frac{\Delta R}{R_0} = \left[\frac{G_{NS} + (\mathrm{d}R_J/\mathrm{d}\varepsilon)/R_{NS,0}}{1 + R_{J,0}/R_{NS,0}} + 2\right]\varepsilon$$

NS stretching

Measure PEO/graphene composite to find

$$\frac{\mathrm{d}R_J}{\mathrm{d}\varepsilon} \sim \frac{k\varepsilon}{\varepsilon_1 + \varepsilon}$$

Fits



Data can be described by a combo of G_{NS} and tunnelling

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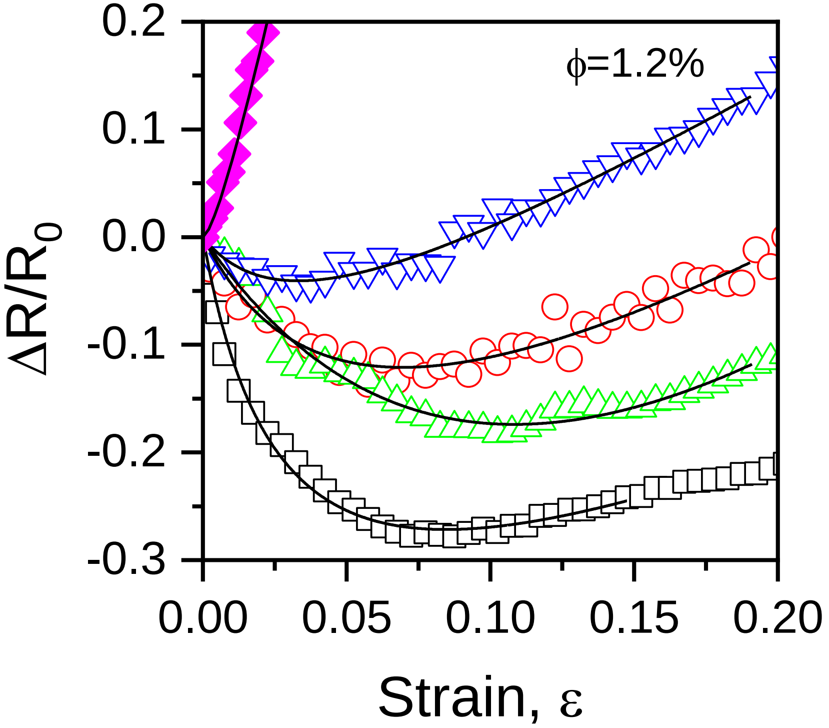
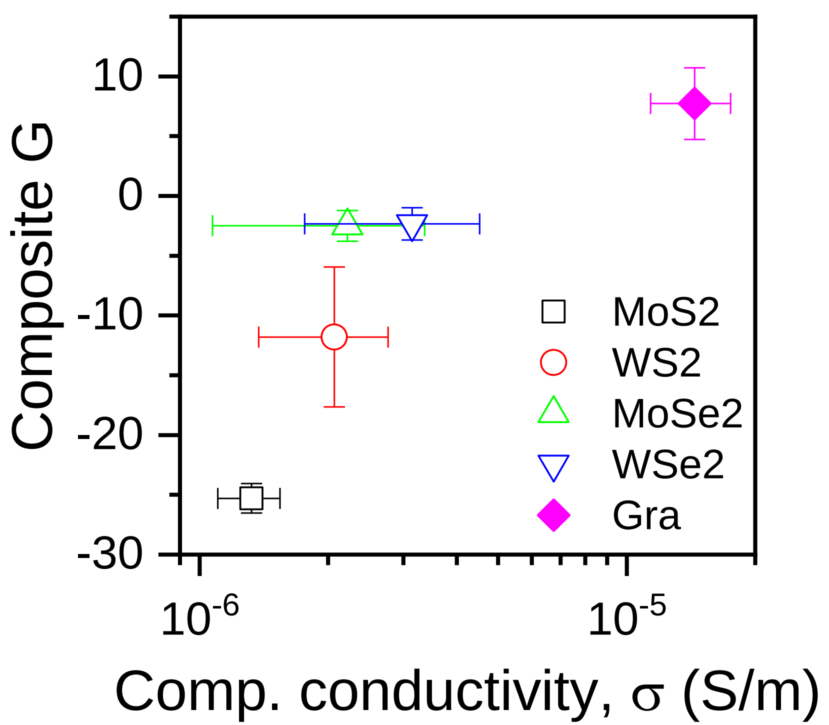
Other materials

$$\frac{\Delta R}{R_0} = \left[\frac{G_{NS} + (\mathrm{d}R_J / \mathrm{d}\varepsilon) \boxed{/ R_{NS,0}}}{1 + R_{J,0} / R_{NS,0}} + 2 \right] \varepsilon$$

Higher nanosheet conductivity shift mechanism away from nanosheets toward junctions:

Negative piezoresistance ↓ as nanosheet conductivity ↑





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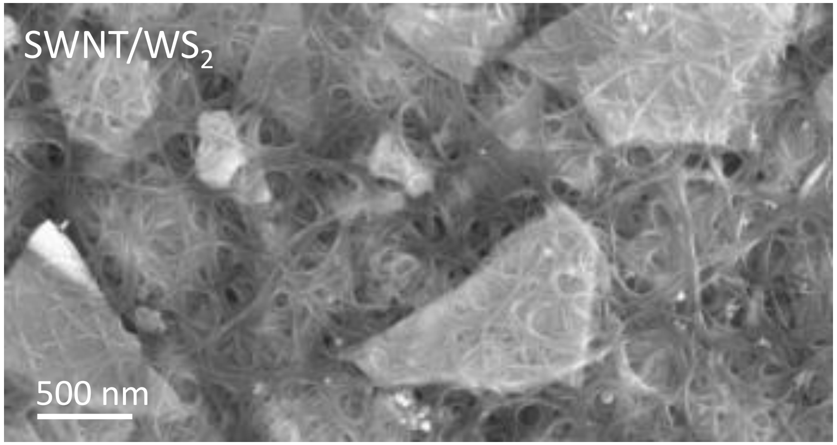
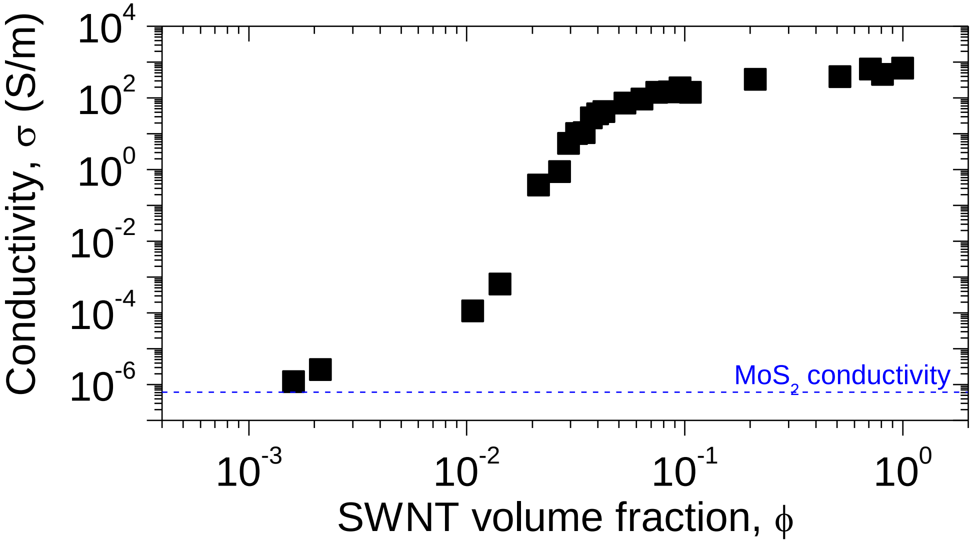
Those example used nanosheets as filler
Can nanosheets be the matrix?

Can have nano:nano composites
e.g. SWNT:NS
(1D:2D)



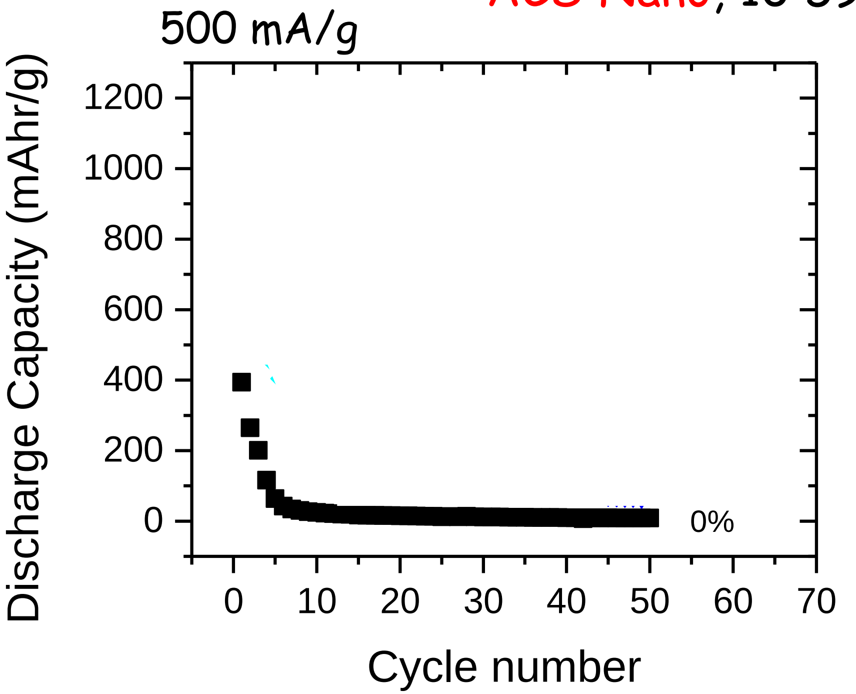
Increase conductivity dramatically

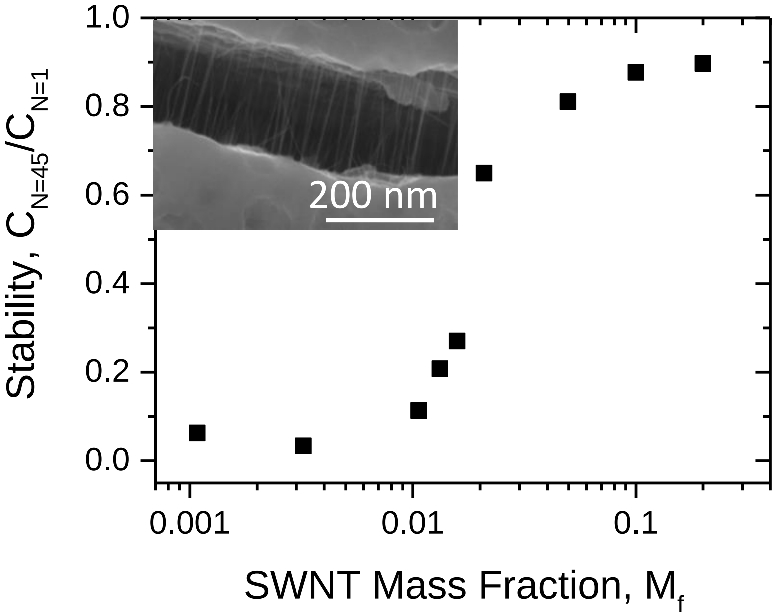


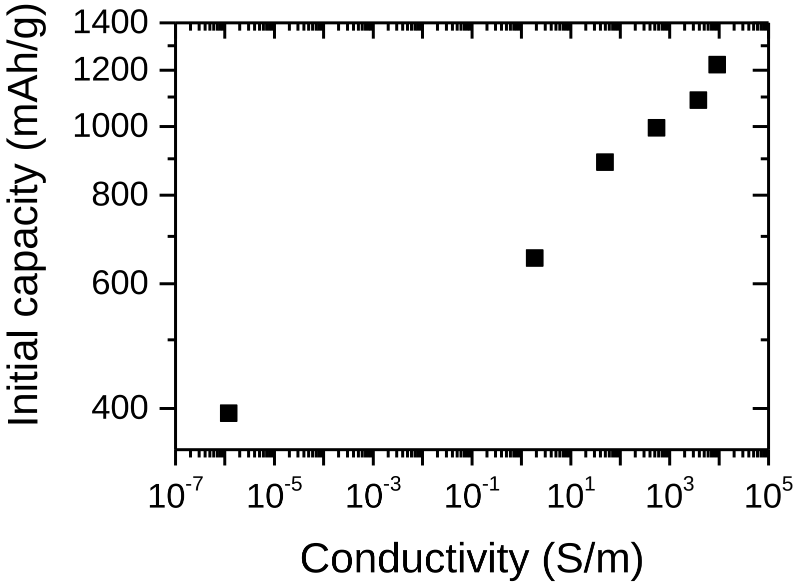
Using nano:nano comps as Li ion battery anodes

ACS Nano, 10 5980

MoS_2 can store Li but Capacity limited by conductivity and mechanical robustness



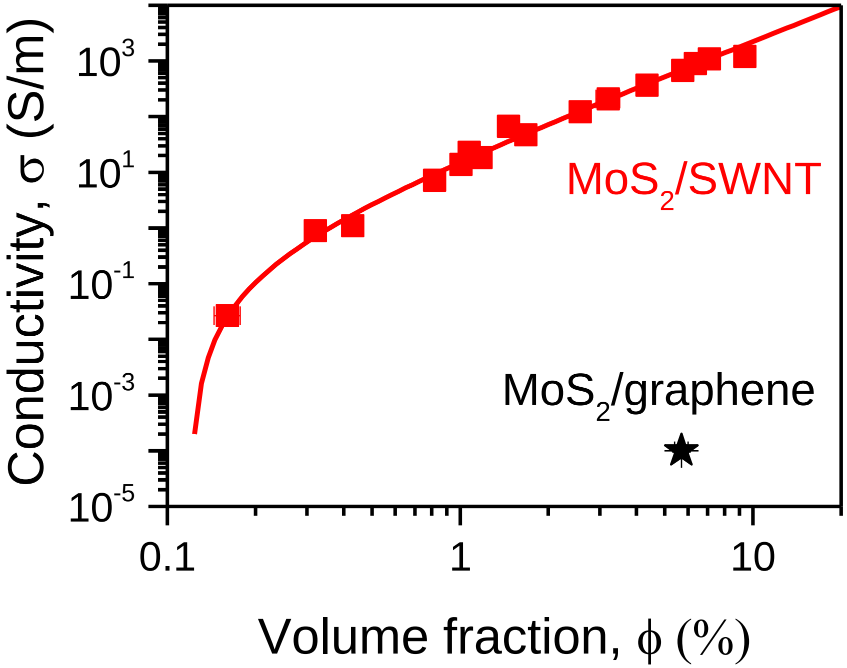


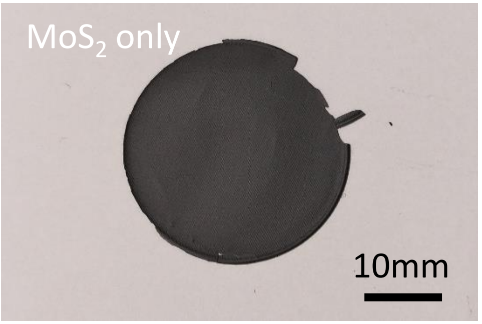


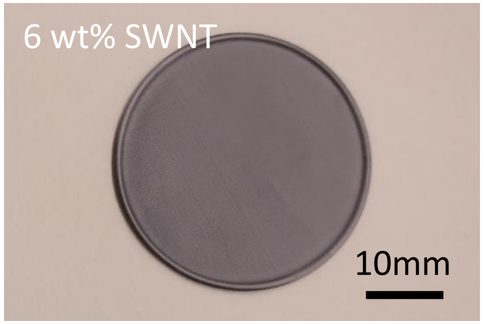
Composites of 1D:2D = nano:nano composites

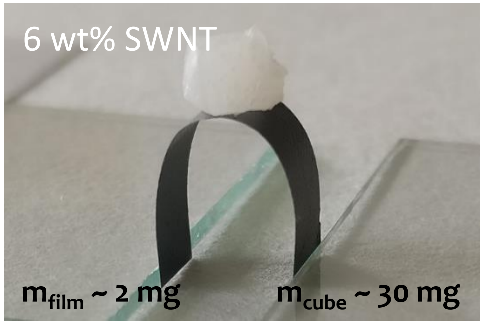
Chem Mater, 30, 5245

Conductivity increases, otherwise hardly studied









Mechanics are crucial – and unknown

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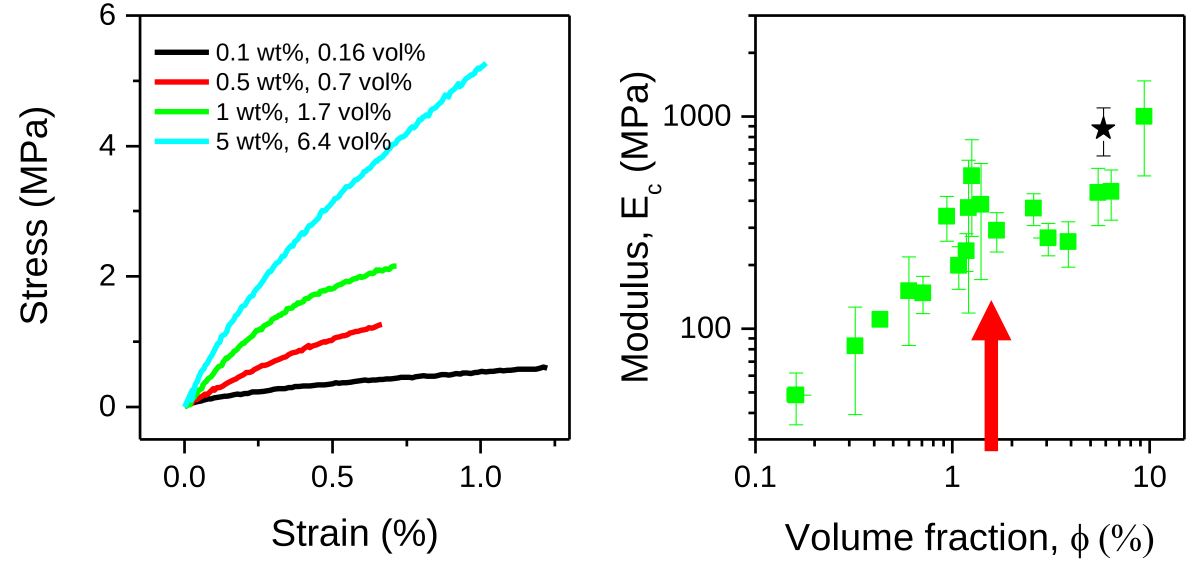
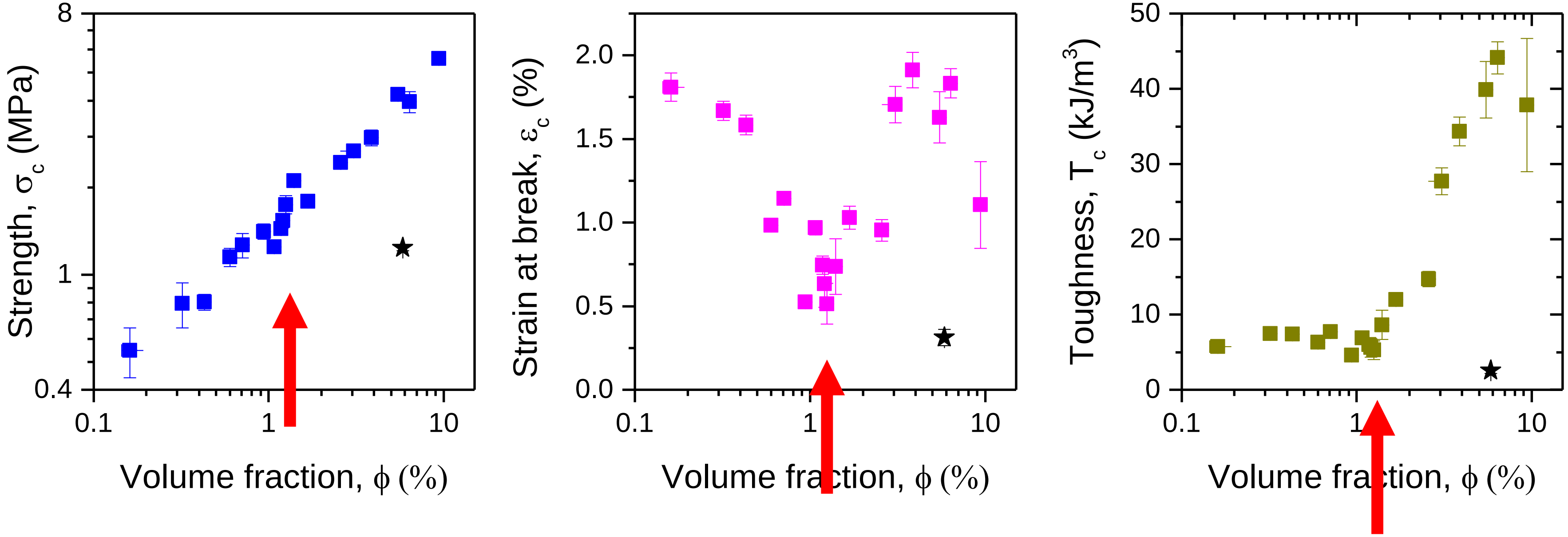
Comprehensive mechanical study

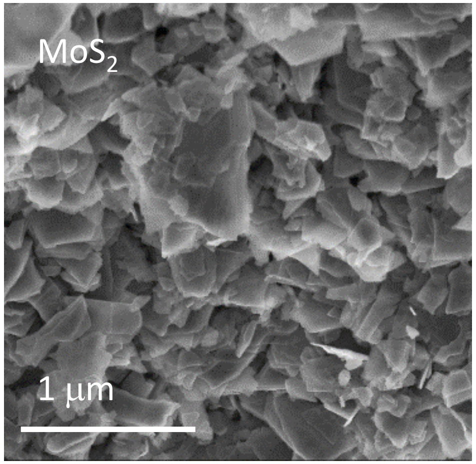


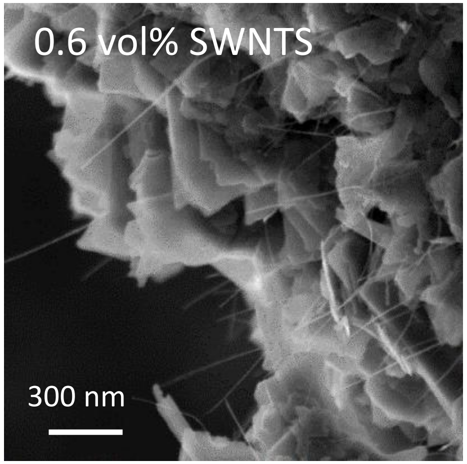


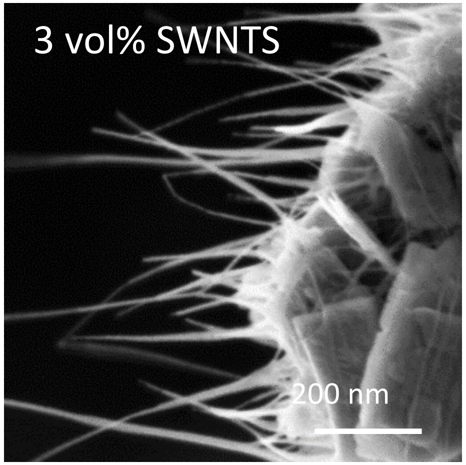
★ Graphene-MoS_2 composite

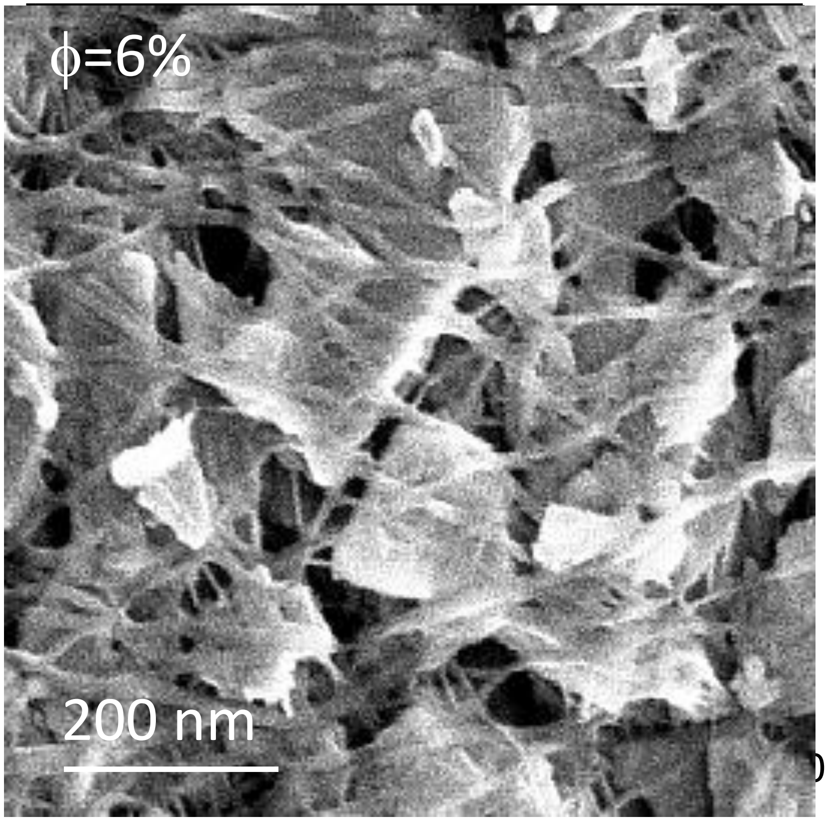
Something happens at 1%

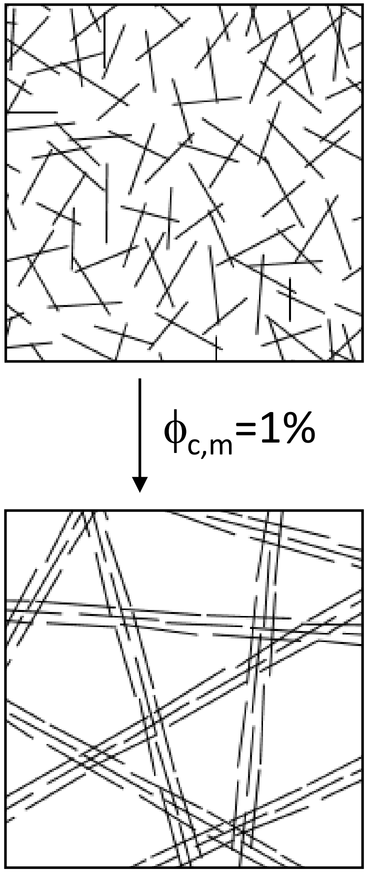
What happens at 1%?











Formation of continuous network

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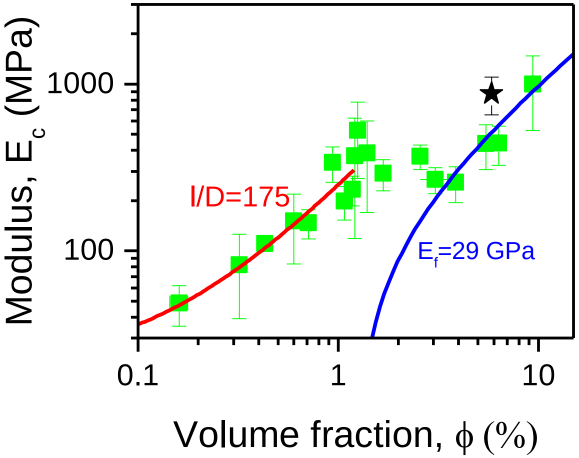
Mechanics modelling

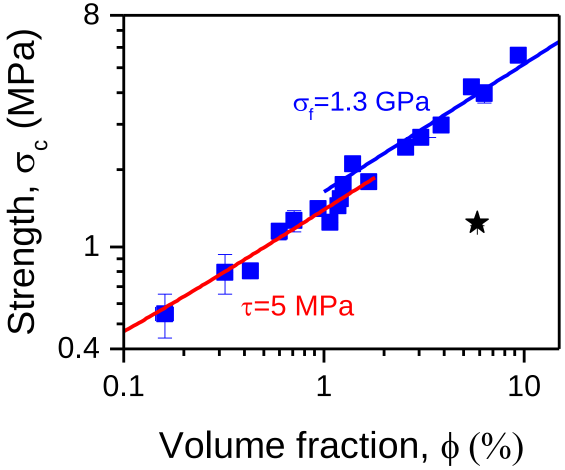
Red: composite, ϕ<1vol%
Blue: network, ϕ>1vol%

$$E_c = E_m\left(1-\phi+\frac{2l^2}{3D^2}\frac{\eta_0}{(1+\nu_m)}\frac{\phi}{\ln(1/\phi)}\right)$$

$$E_c = \eta_0 E_f(\phi-\phi_{c,m})$$

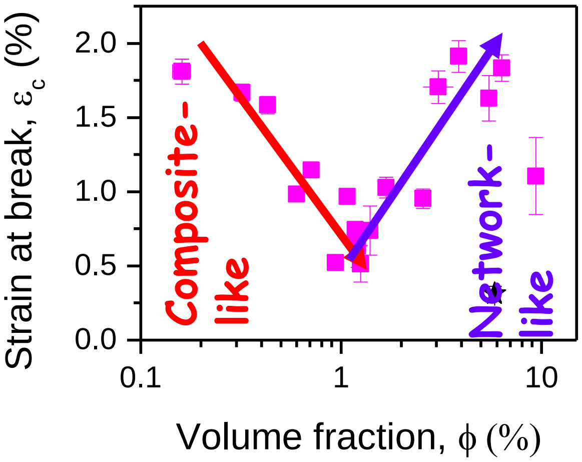
$$\sigma_c(l<l_c)=\frac{4}{\pi}\left[\sigma_m\tau_{fm}\frac{l}{D}\phi+\sigma_m^2(1-\phi)\right]^{1/2}$$

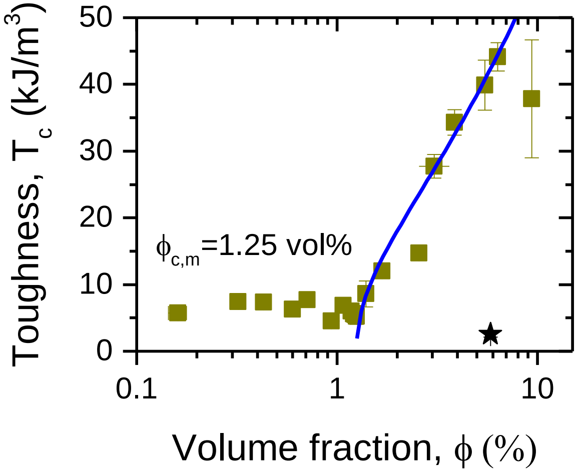




$$\sigma_c(l>l_c)=\frac{4}{\pi}\left[\sigma_m\sigma_f\phi+\sigma_m^2(1-\phi)\right]^{1/2}$$

Prof Bob Young
(Manchester)





$$T\propto\left(\frac{\phi-\phi_{c,m}}{1-\phi_{c,m}}\right)^k\frac{L_{NT}^2\tau_{NT}}{12D_{NT}}$$

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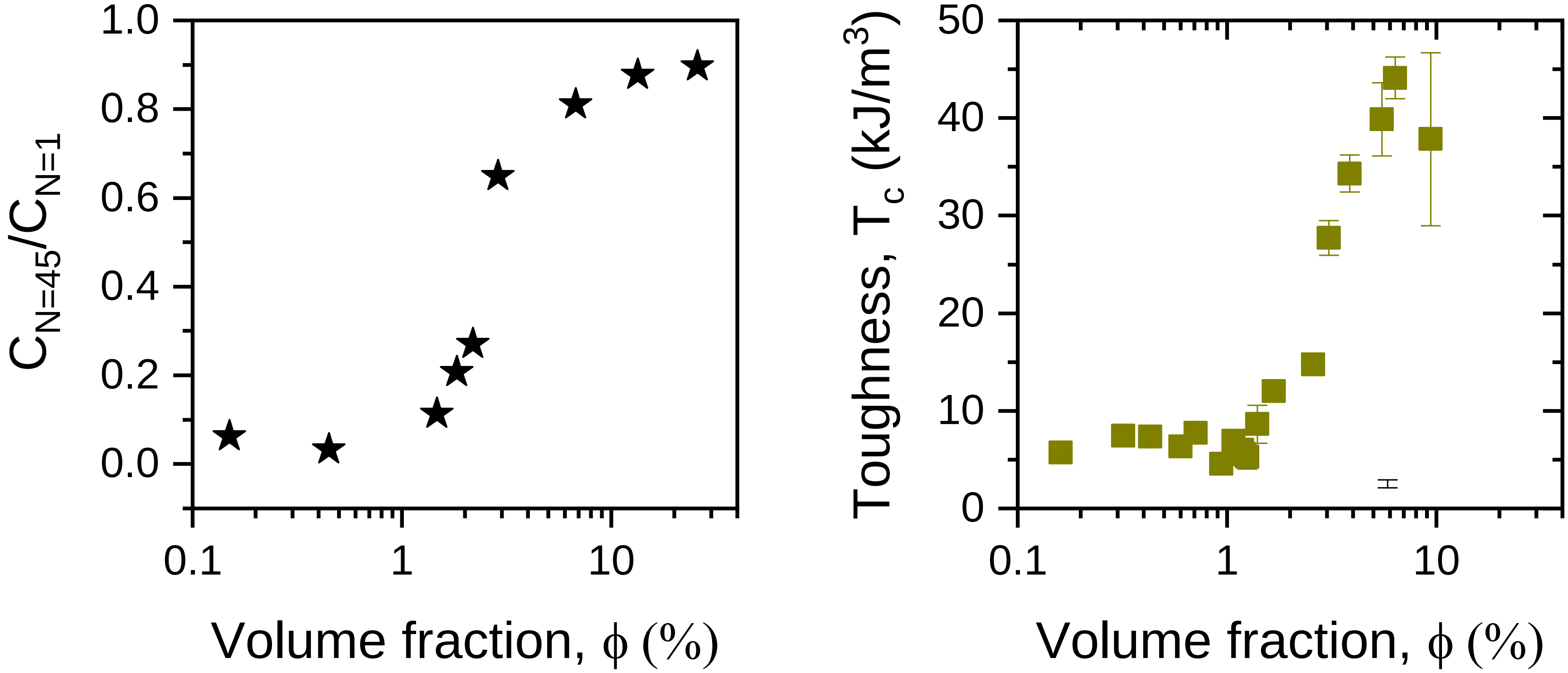
30, 5245

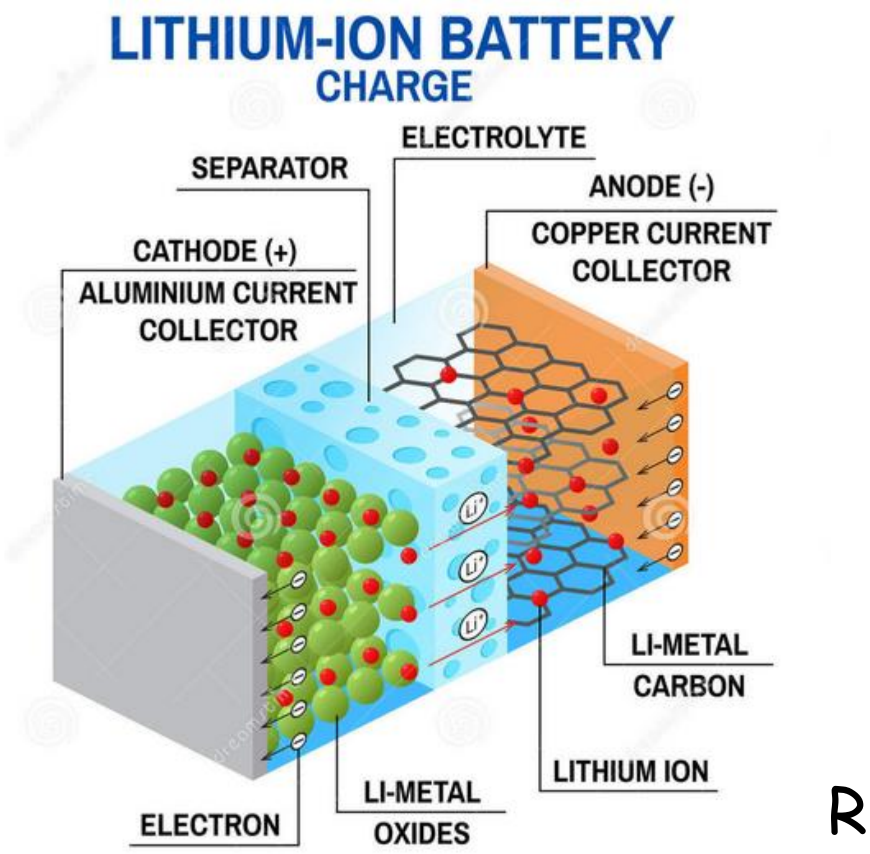
Stability and tensile toughness look similar

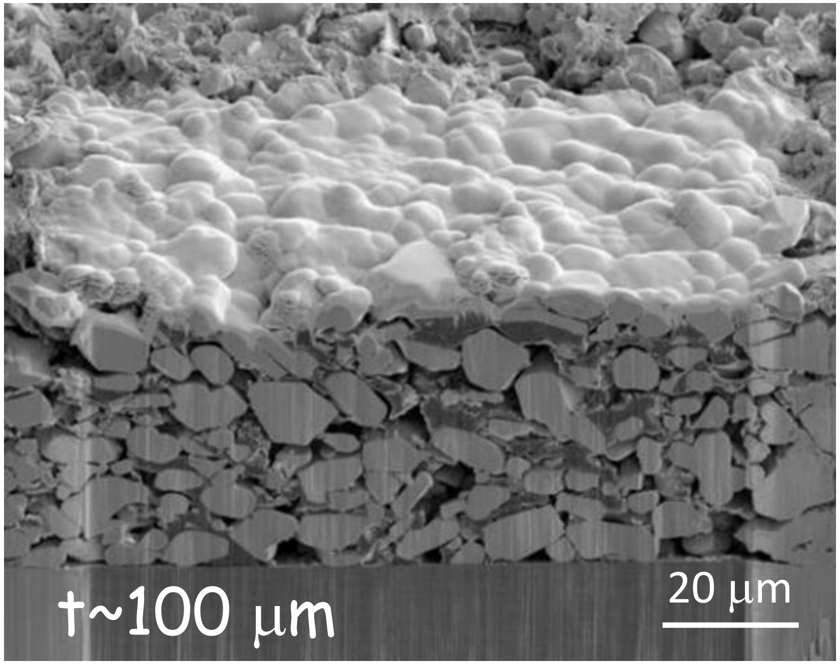
Continuous NT network mechanically stabilises film



Use this in real batteries?

Where to use nanotubes in batteries?





Replace the polymer binder and conductive additive

Aim:

1. Increase charge delivery
2. Improve mechanical properties of electrodes

Why improve mechanical properties of electrodes?

1. Stability (reduce chance of failure on cycling)
2. *Stop cracking during fabrication*

Cracking is very common in liquid-deposited particulate films: mud cracking

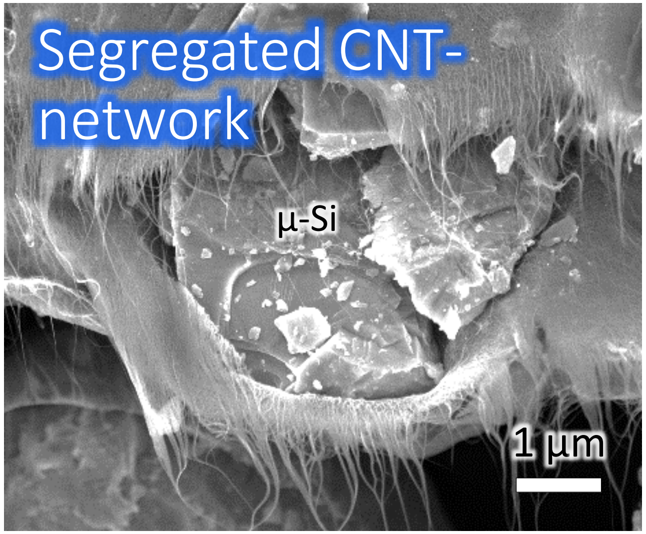
The critical crack thickness scales with the mechanical properties of the material

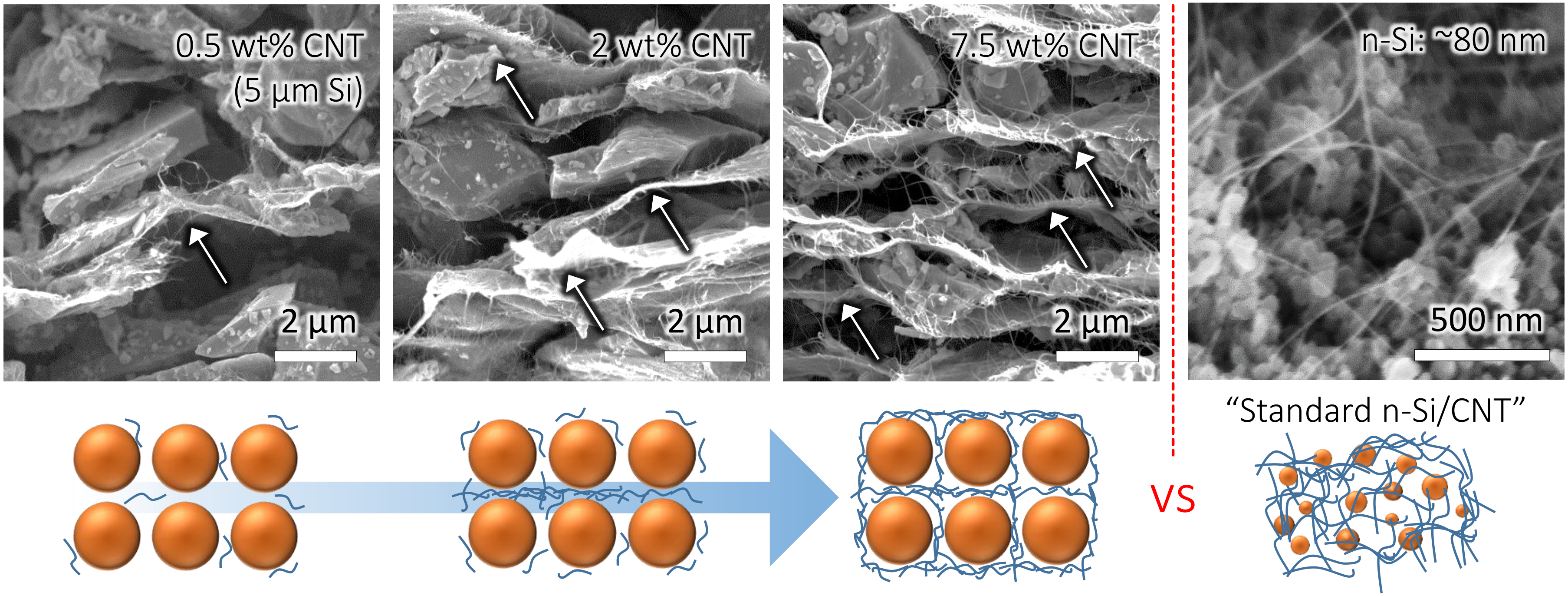
With Prof Nicolosi (TCD)

Nature Energy, in press

Can NTs reinforce real battery material and increase CCT?

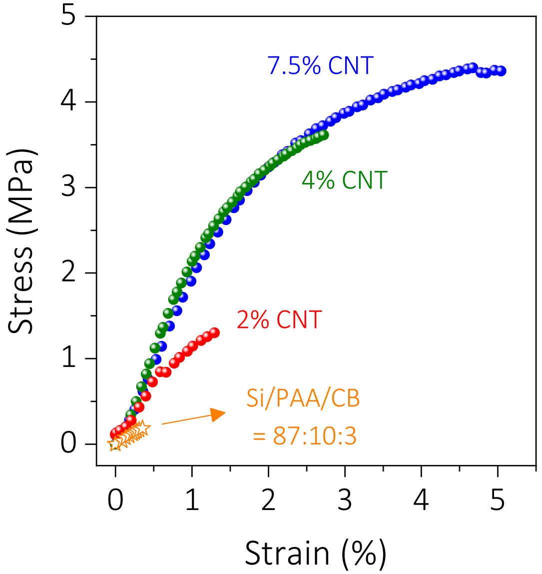
N.B battery particles usually > nanotube length

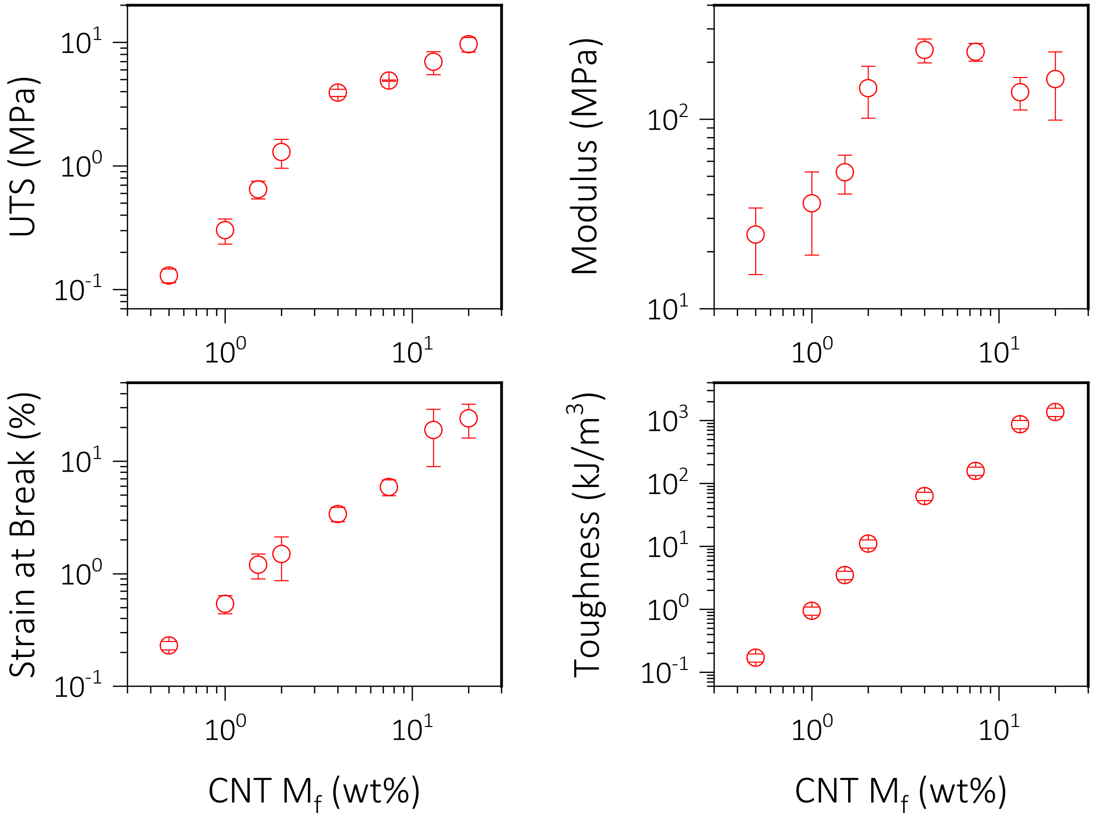


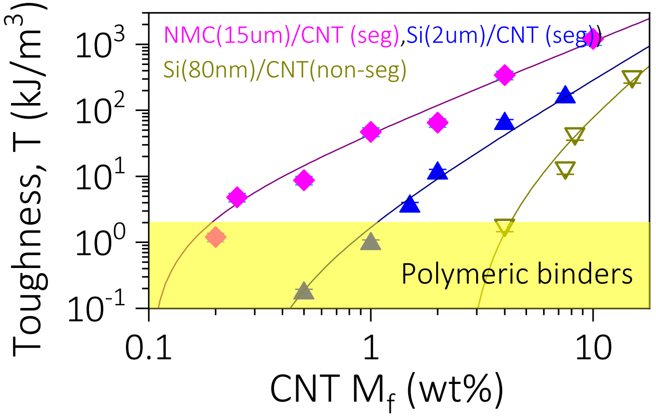


Nature Energy, in press

Significant increases in tensile properties



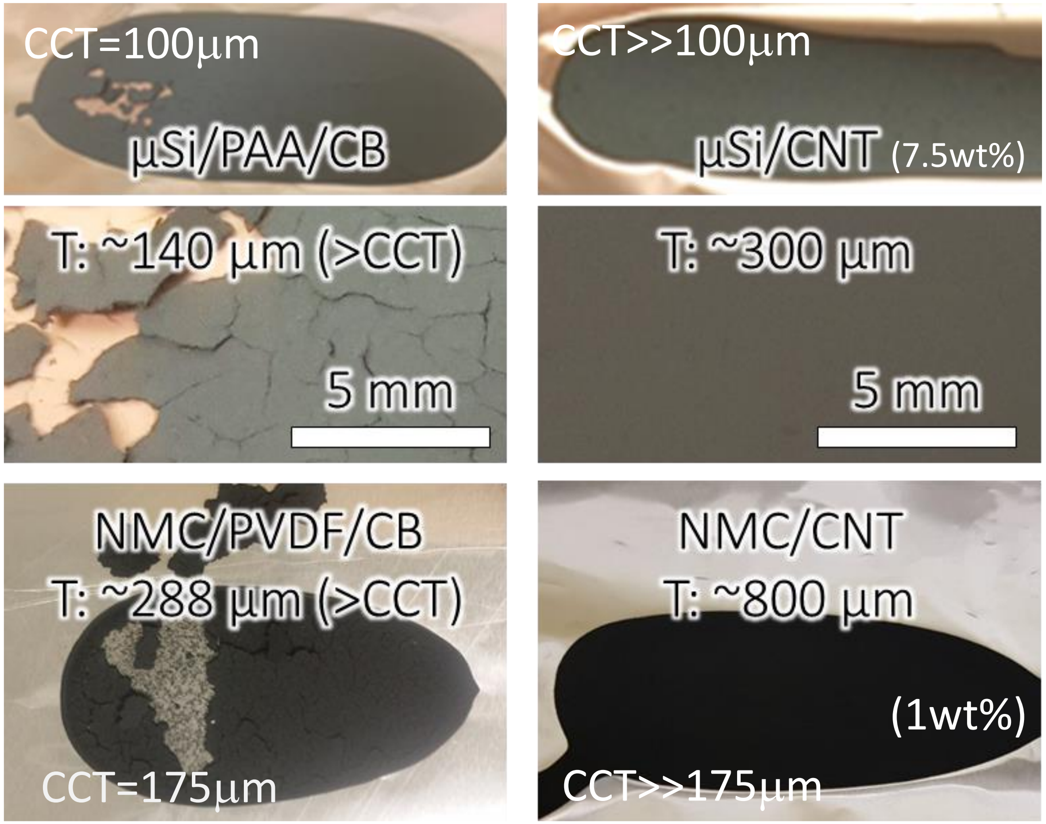


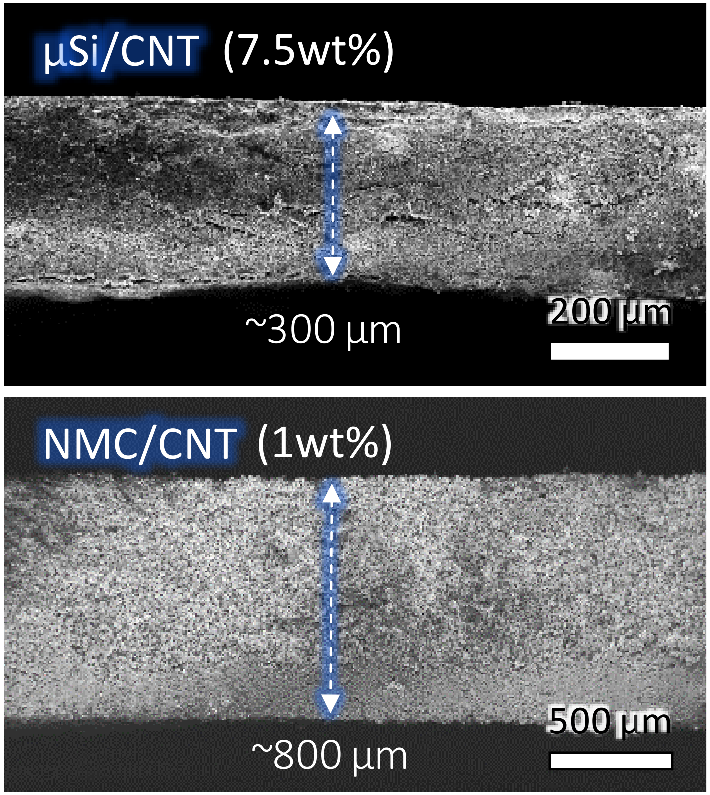


For all electrode materials tested (graphite, LTO, NMC, Si (various sizes)

Mechanical enhancement allows increase in CCT: Make thick electrodes

Nature Energy, in press



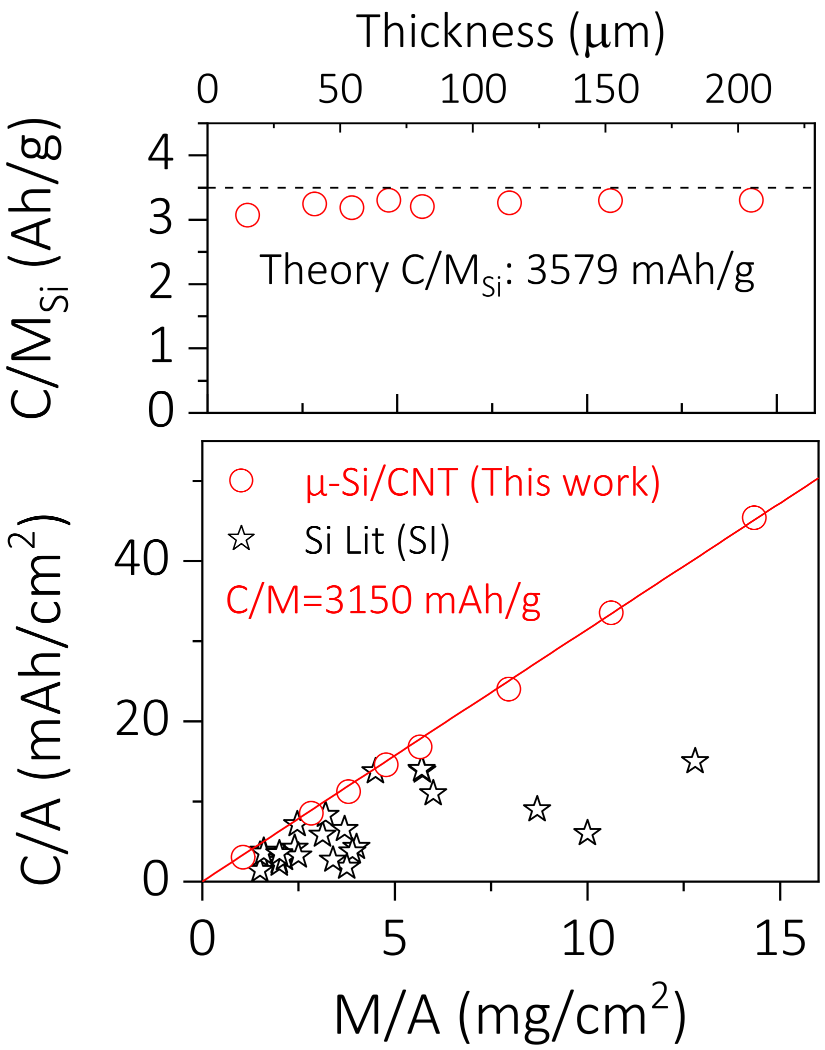


Record thickness

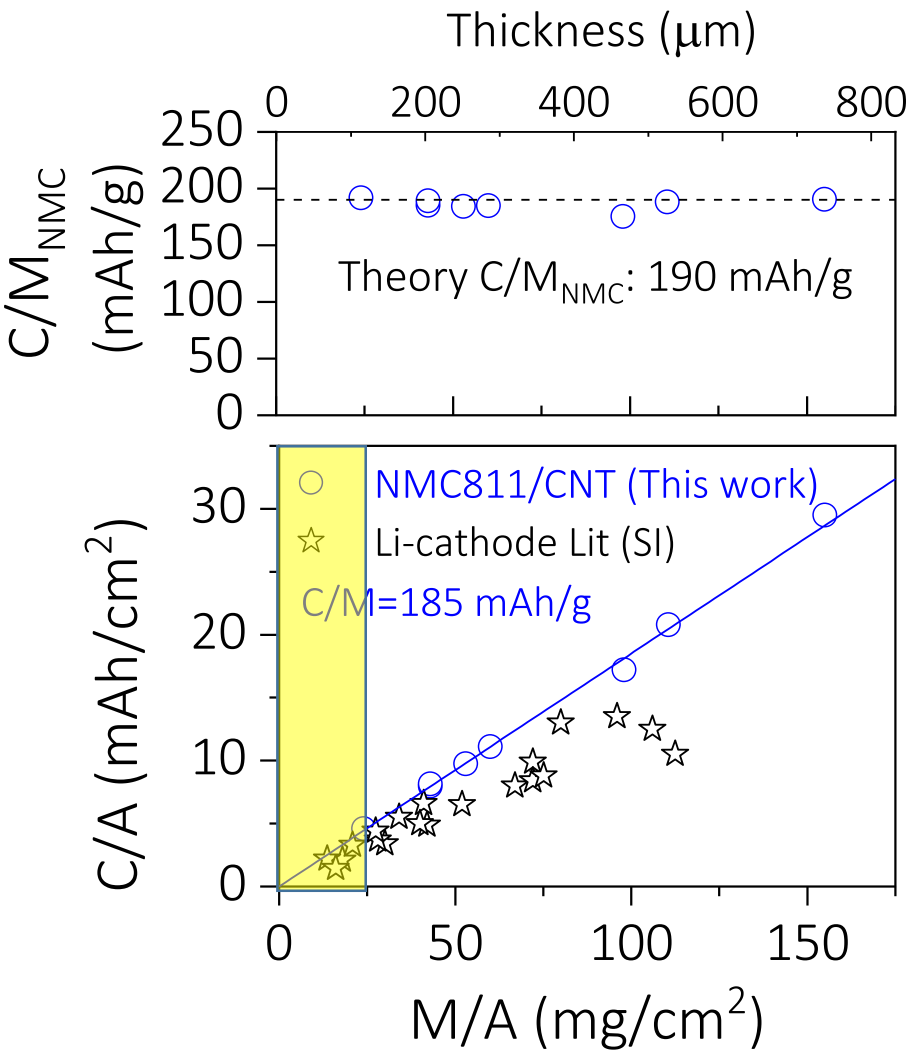
SoA Li storage capacity

Nature Energy, in press

Anode (Si/CNT)

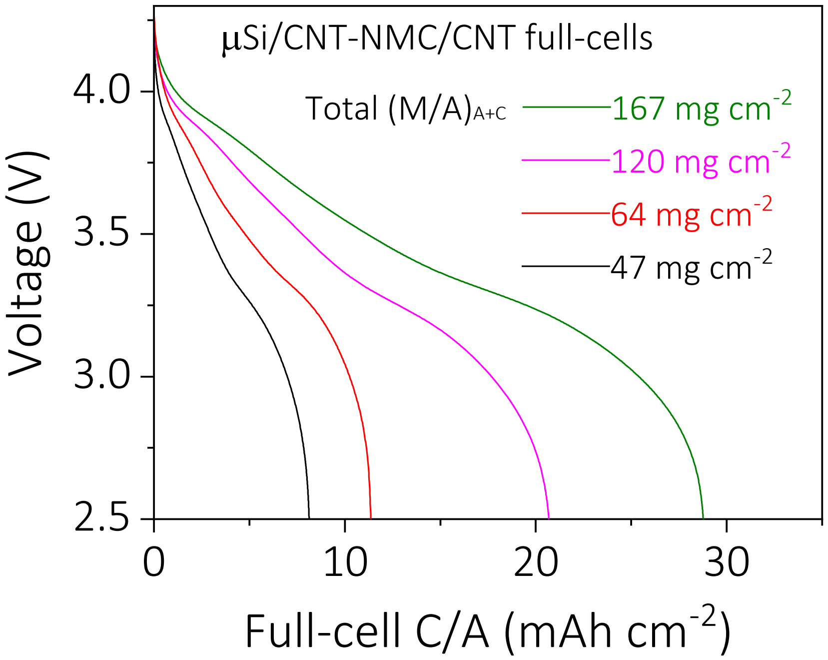


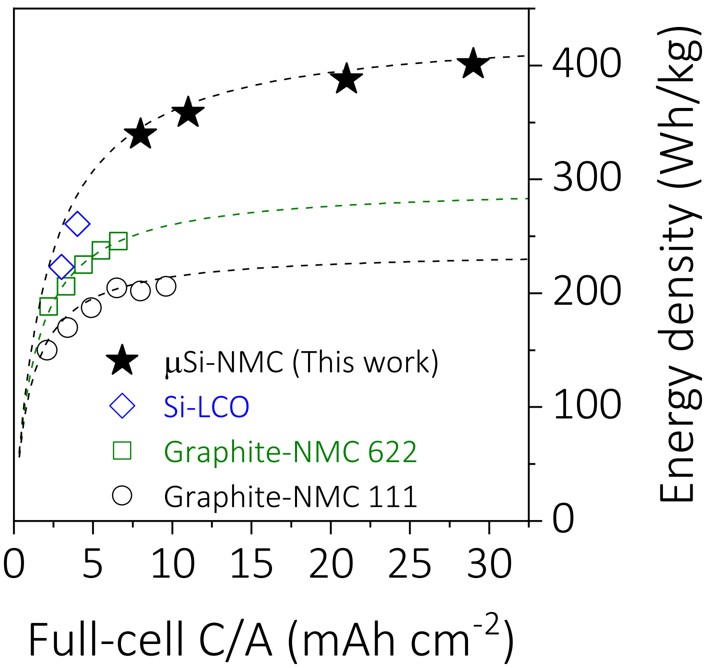
Cathode NMC/CNT)



SoA full cell capacity

Nature Energy, in press





Thick electrodes yields high capacity electrodes and so cells

High areal capacity leads to high energy density

Thanks to: Coleman Group

Nicolosi Group
Lyons Group
Moebius Group

<u>Backes group Heidelberg</u>

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