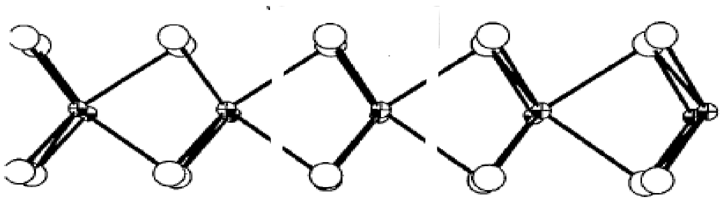
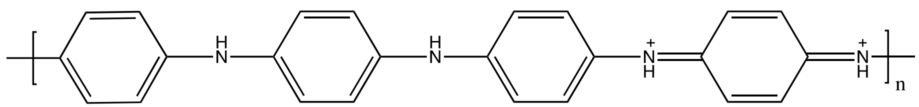
Structure and Properties of Exfoliated MoS_2-Polyaniline Nanocomposites





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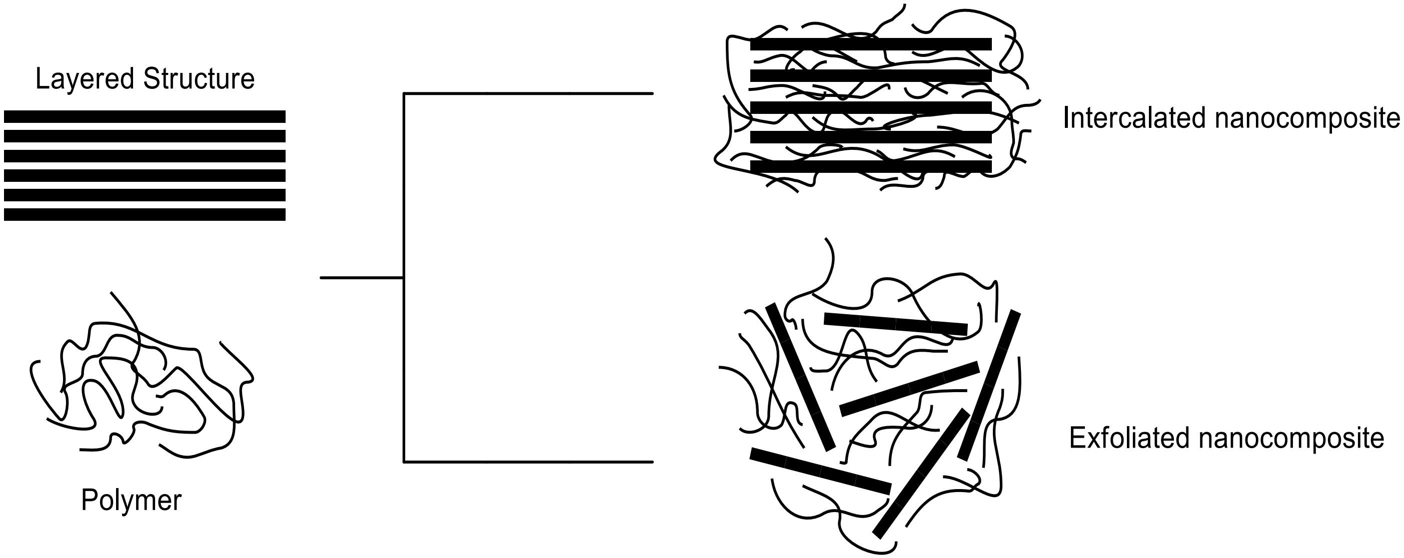
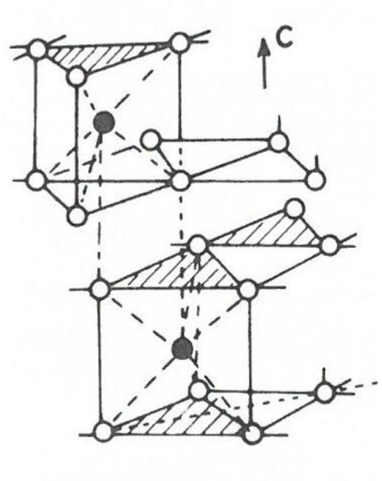
Nanocomposites

- Ongoing UPEI project investigating nanocomposites of layered materials and polymers

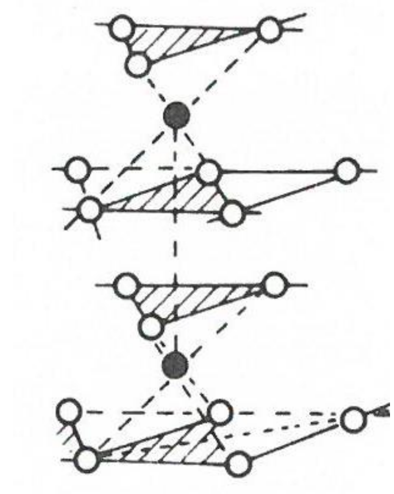


2H-MoS_2



- Normal bulk MoS_2.
- Semiconductor with 1.2 eV indirect gap

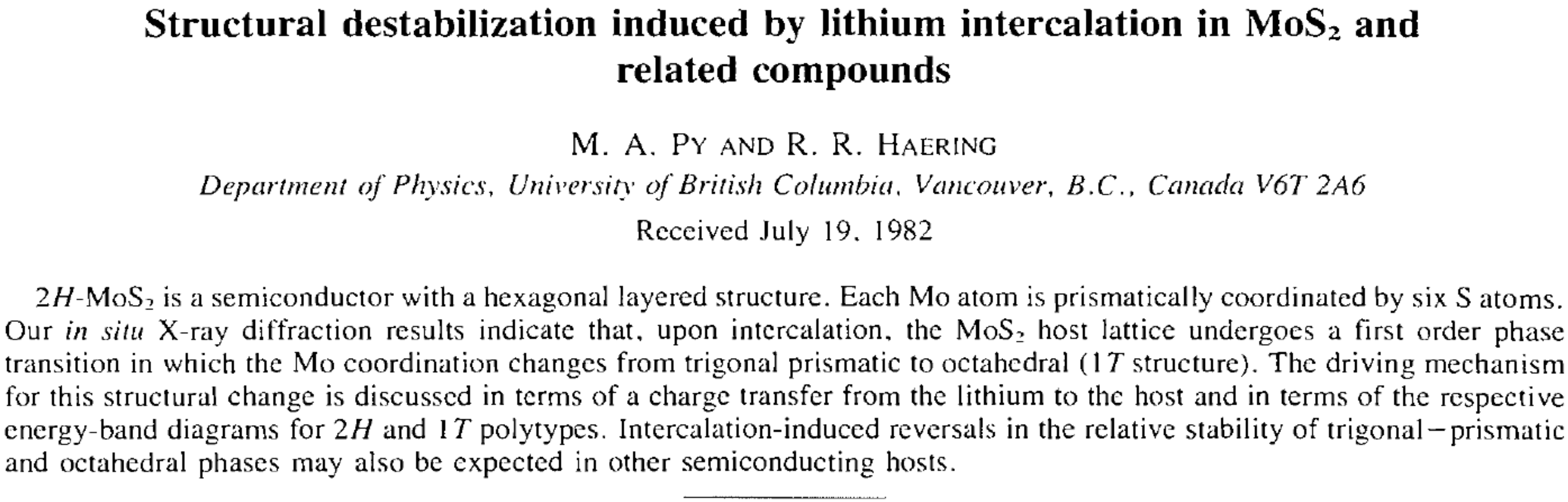
1T-MoS_2



- Equilibrium structure for bulk Li_xMoS_2
- 2H to 1T transition driven by electron transfer to MoS_2
- Metastable after Li removed
- **Metallic**

Discovery of 1T structure in Li_xMoS_2

Can. J. Phys. **61** (1983) 76



Structural destabilization induced by lithium intercalation in MoS_2 and related compounds

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Received July 19, 1982

2*H*-MoS_2 is a semiconductor with a hexagonal layered structure. Each Mo atom is prismatically coordinated by six S atoms. Our *in situ* X-ray diffraction results indicate that, upon intercalation, the MoS_2 host lattice undergoes a first order phase transition in which the Mo coordination changes from trigonal prismatic to octahedral (1*T* structure). The driving mechanism for this structural change is discussed in terms of a charge transfer from the lithium to the host and in terms of the respective energy-band diagrams for 2*H* and 1*T* polytypes. Intercalation-induced reversals in the relative stability of trigonal–prismatic and octahedral phases may also be expected in other semiconducting hosts.

“Graphene-analogous” single-layer MoS_2

- 2H-type single layer has 1.9 eV direct band gap
- Potential applications in electronics, optoelectronics, sensors, photoluminescence, catalysis, nanotubes, energy storage…

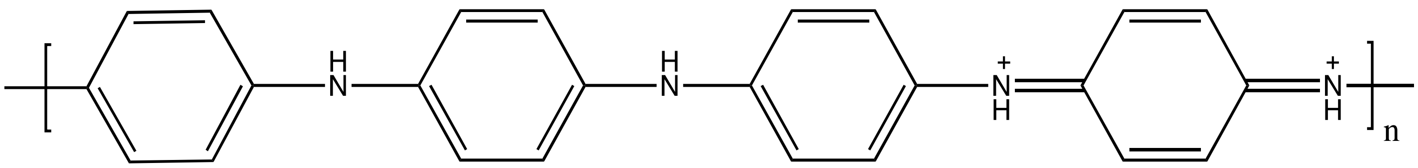
Produced by, for example:

- Mechanical exfoliation of bulk 2H-MoS_2
- Exfoliation by lithium intercalation - produces 1T phase[2]
- Reaction of molybdic acid and thiourea - produces 2H-MoS_2 in exfoliated state[1]

*[1] H.S.S Ramakrishna Matte et al. (2010) Angewandte Chemie **122**, 4153-4156.*
*[2] D. Yang et al. (1991) Phys. Rev. B **43**, 12053. (Bob Frindt group, SFU)*

Conducting polymer polyaniline (PANI)

- Various forms. Doping of the emeraldine salt form required to form mobile charged polarons and bipolarons.



Emeraldine Salt

- Electrical conductivity $\sigma \sim 10^{-1}$ to 10^{3} S/cm[1] (doping, disorder, chain length….)

1. Kaiser, Advanced Materials 13 (2001) 927

MoS_2-PANI Nanocomposites

Worldwide research activity on related materials and applications, e.g.:

- Supercapacitors (specific capacitance 400 - 600 F/g)[1]
- Li ion batteries
- Electrochemical sensors…

Most literature on layered NCs, 1T-MoS_2 -PANI, large MoS_2:PANI ratios, and few-layer 2H-MoS_2-PANI

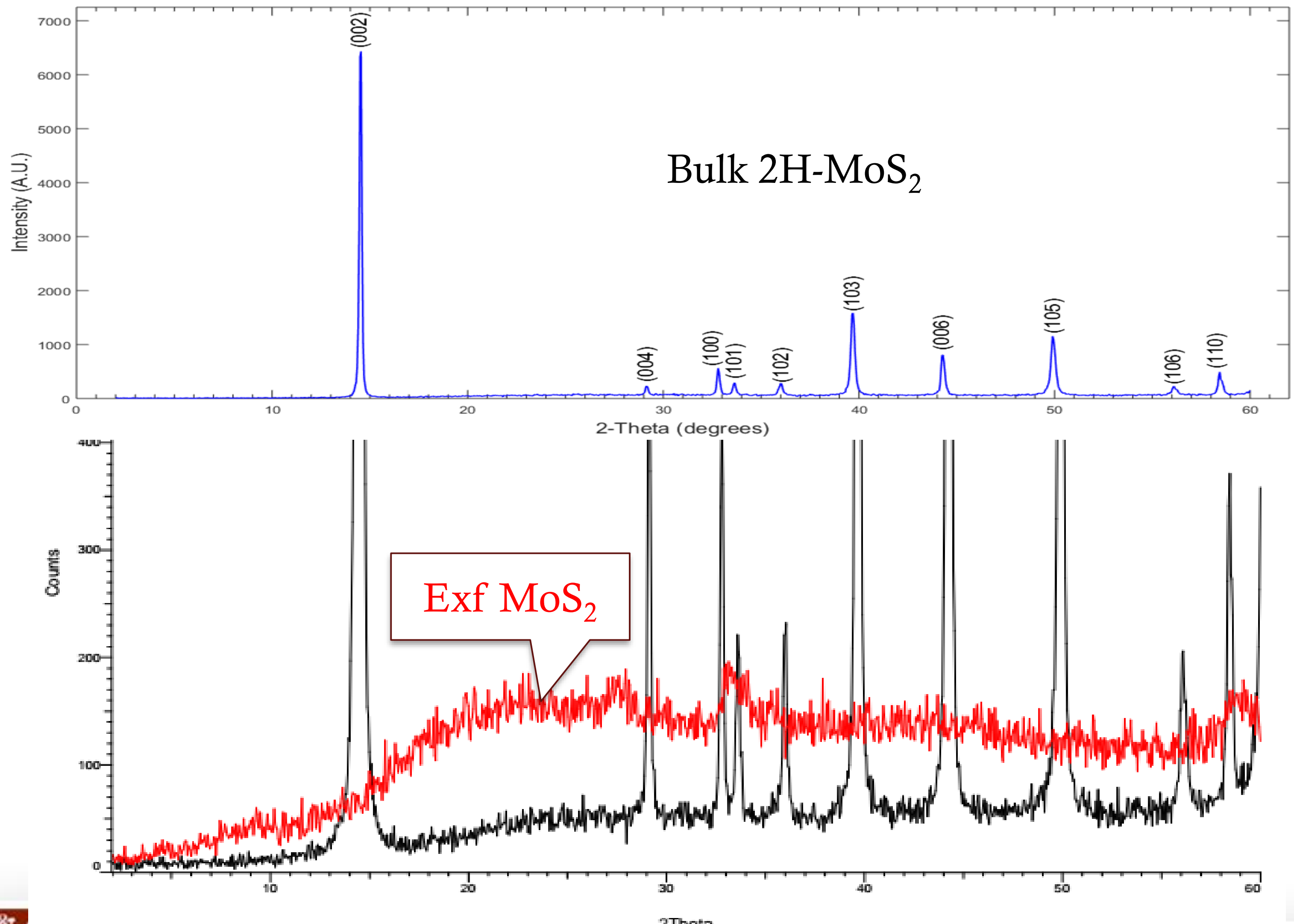
This work – Exfoliated single-layer 2H-MoS_2-PANI NC , small MoS_2:PANI ratios

1. *Ansari et al, J Colloid and Interface Science 504 (2017) 276; Gopalakrishnan et al, Nano Energy 12 (2015) 52; Zhao et al, Chemical Engineering Journal 330 (2017) 462*

Synthesis

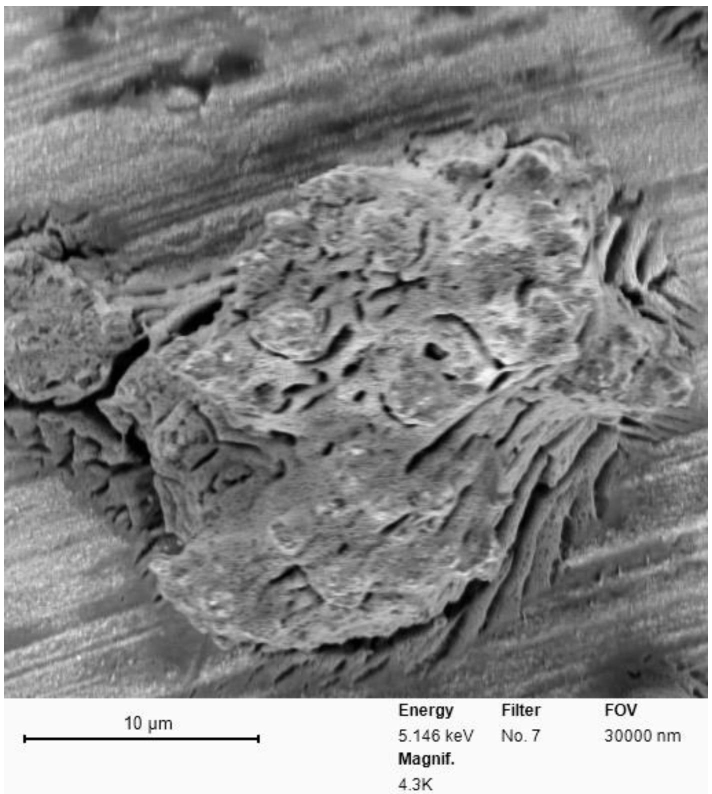
- 2H-type exfoliated MoS_2 was prepared directly by combining molybdic acid with an excess of thiourea. Mixture heated at 500˚C for 3 hours under nitrogen atmosphere.
- Nanocomposites synthesized using *in-situ* polymerization of the aniline monomer in the presence of exfoliated MoS_2. (MoS_2 added to a mixture of aniline and 1M HCl at 0^o C, followed by addition of ammonium persulfate, vacuum filtration and isolation of the product.)
- NCs containing 1% to 50% MoS_2 by weight of PANI
- Two syntheses ("trials") of each

Powder XRD of MoS_2

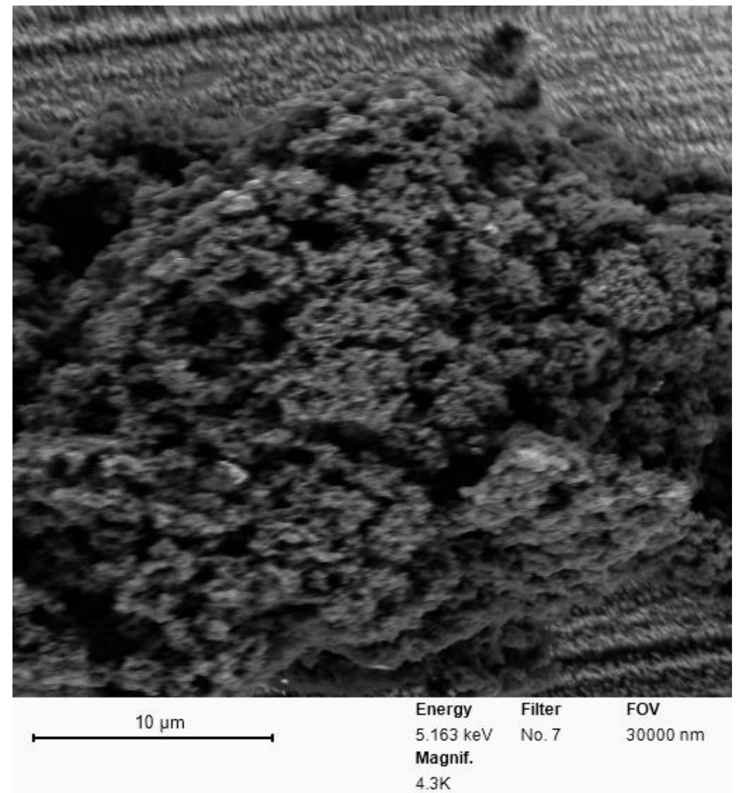


SEM

1% MoS_2-PANI trial 1



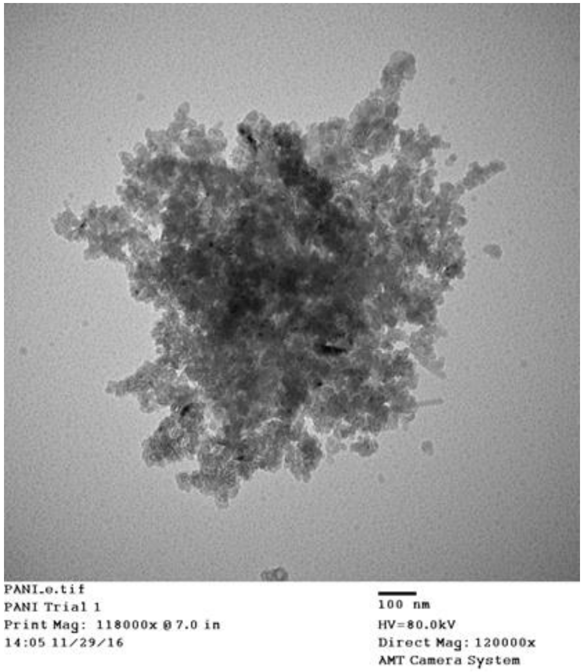
20% MoS_2-PANI trial 1



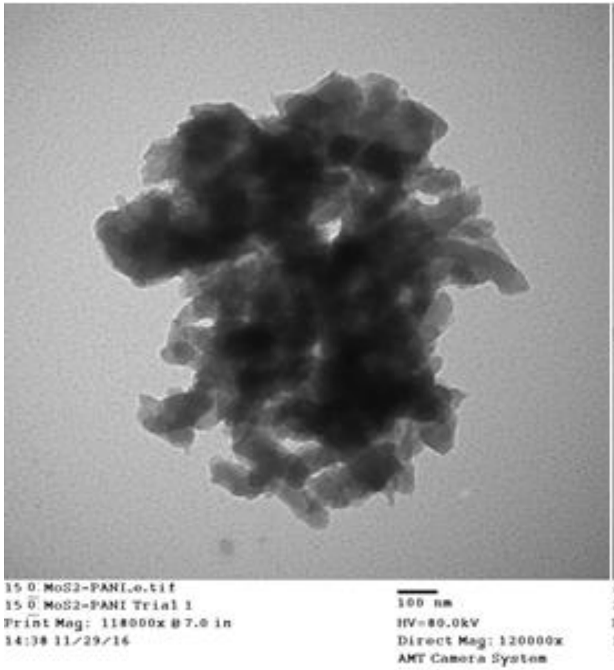
TEM

- No evidence of MoS_2 layers restacking - Exfoliated NC

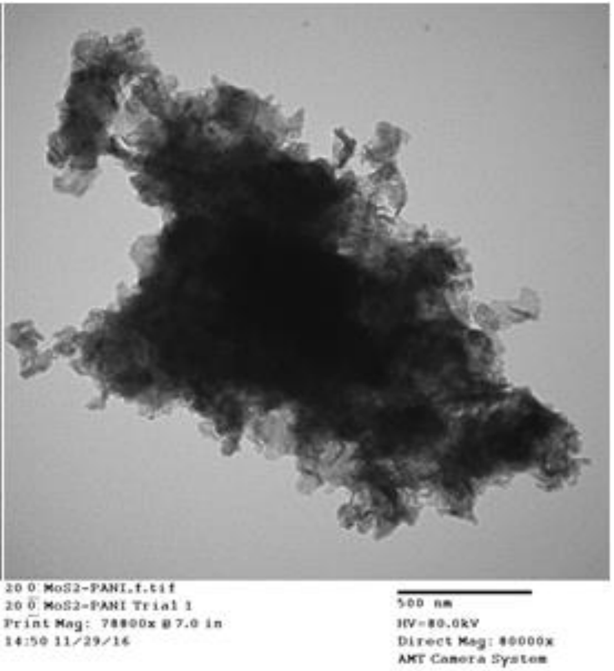
PANI



15% MoS_2-PANI

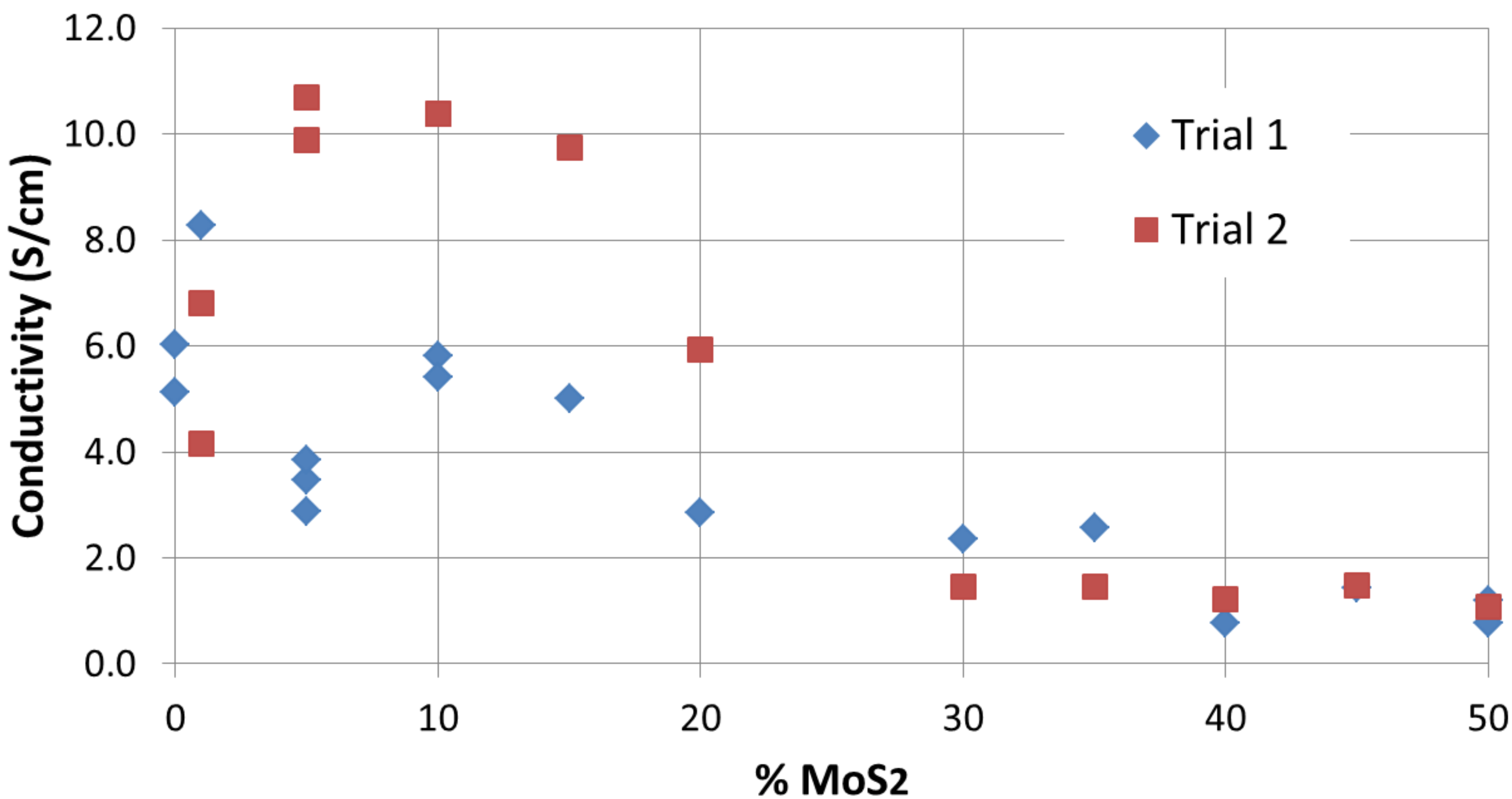


20% MoS_2-PANI



Room – Temperature Conductivity

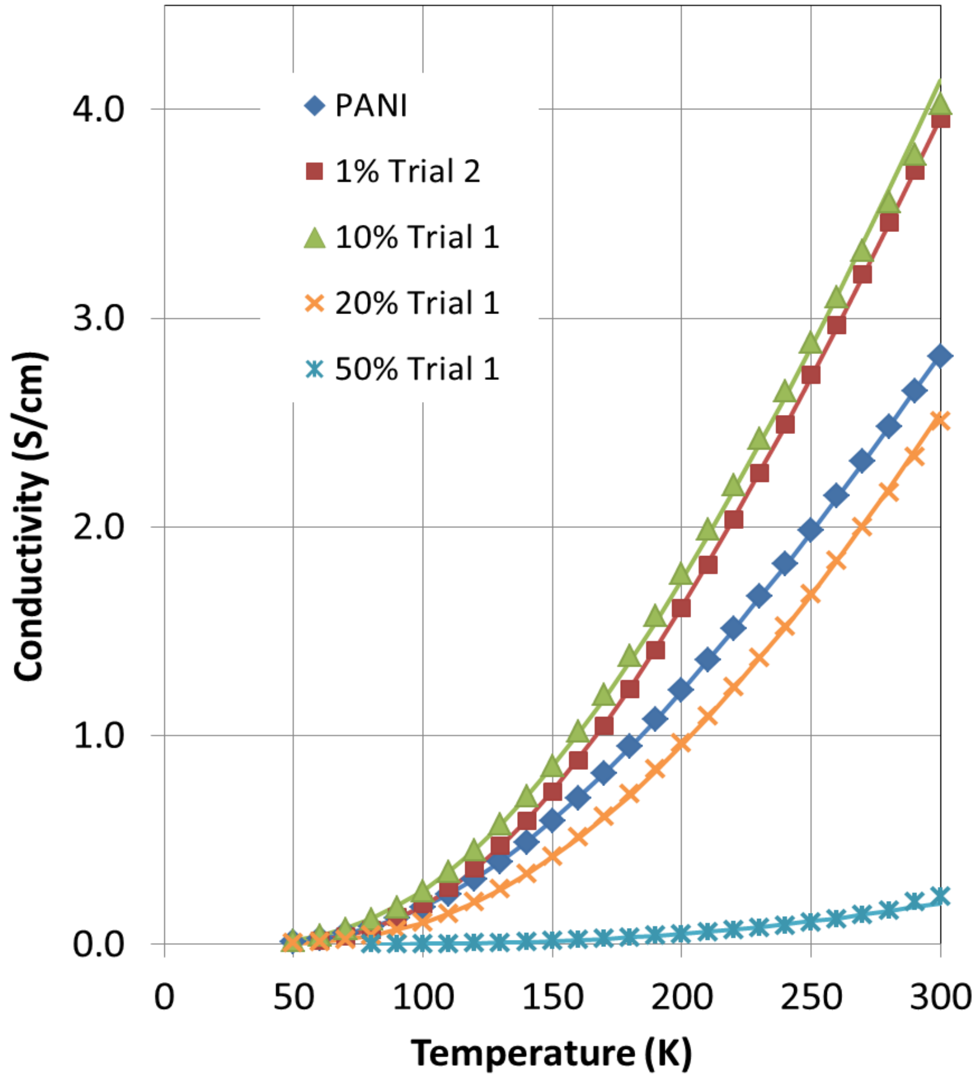
- van der Pauw method on pressed pellets in lab air
- Some samples attracted visible water droplets – these measured in dry air desiccator
- No detectable conductivity in exfoliated MoS_2



Variable-Temperature Conductivity

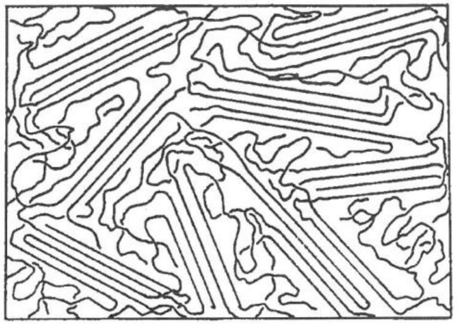
- In vacuum
- 50 – 300K

- Exposure to vacuum reduces room temperature conductivity. (Alters PANI doping?)
- Lines are fits: next slide…



Fits to Heterogeneous Conduction Model

- For lower-conductivity polymers, conductivity σ often well-described by[1]



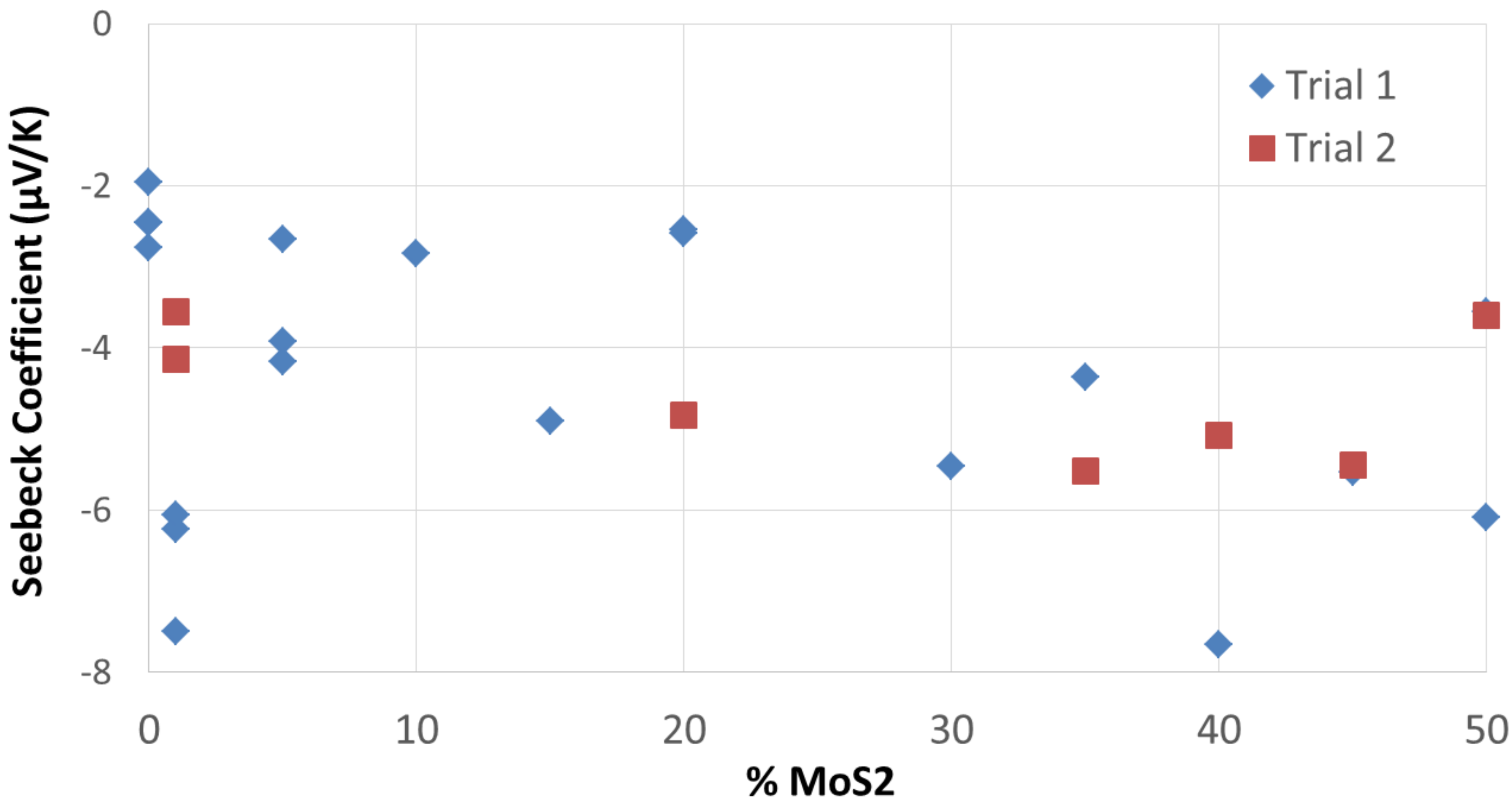
$$\rho = \sigma^{-1} = f_c \rho_m \exp\left(-\frac{T_m}{T}\right) + f_n \rho_0 \exp\left[\left(\frac{T_0}{T}\right)^{\gamma}\right]$$

- First term: Good conduction in ordered regions (quasi-one-dimensional metal). Resistance often small. Not needed to fit our data.
- Second term: Hopping-type conduction through disordered regions.
- γ = 0.25 : Mott's variable-range hopping (VRH) model in 3D.
- γ = 0.5 : quasi-1D VRH *(or 3D hopping with significant e-e interaction, or tunneling with charging effects…)*
- γ ≈ 0.5 determined from our fits to PANI and NC (0.4 to 0.6).

1. Kaiser, Advanced Materials 13 (2001) 927 and references therein

Seebeck coefficient

- Room temp, pellet between polished Cu electrodes, one heated
- Pellets attracting water or corroding Cu not included
- PANI usually positive in literature, but sometimes negative



Discussion

- Nanocomposites with 1 to 15 % MoS_2 **sometimes** have greater conductivity than PANI, much greater than 2H-MoS_2
- A possible explanation: MoS_2 in some nanocomposites is in 1T form (metallic).
- Alternatively, presence of MoS_2 during polymerization could influence order or doping level of PANI, improving its conductivity.
- Seebeck: n-type metallic behaviour, same conduction mechanism for PANI and NC
- Variable-T: consistent with an inhomogeneous conduction model

Future work

- Attempt to determine1T or 2H structure in the nanocomposite – Raman spectroscopy?
- Explore how PANI and NC properties depend on synthesis conditions
- Related NCs
- Applications?

QUESTIONS?