Hybrid 2D black phosphorus/polymer materials: new platforms for device fabrication

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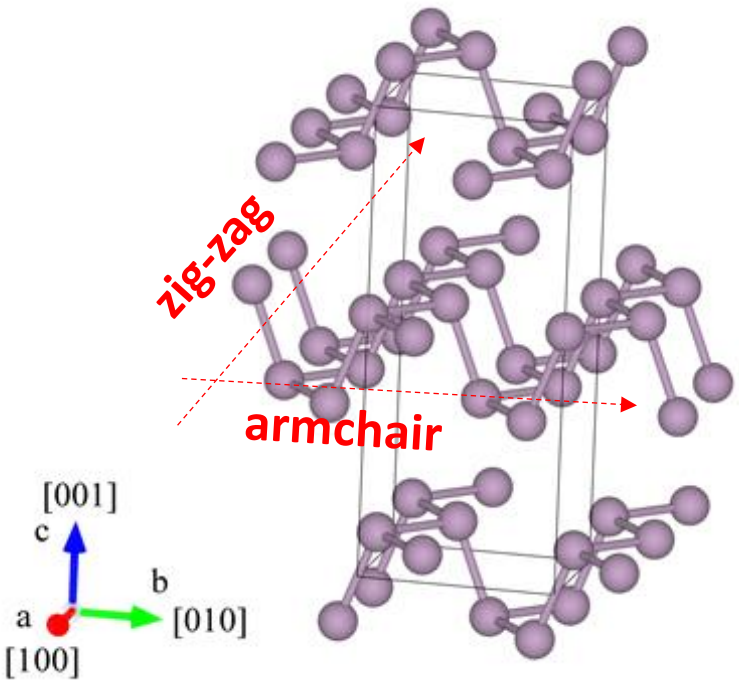
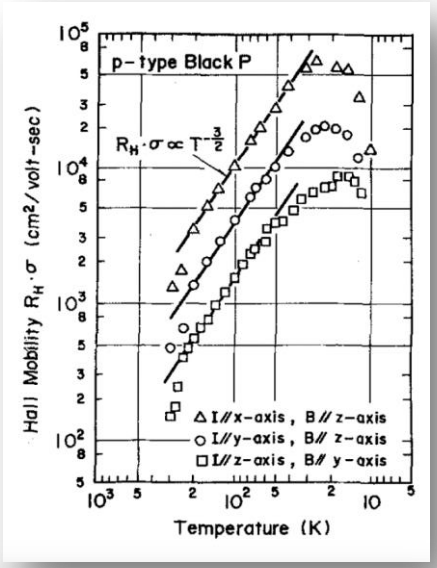
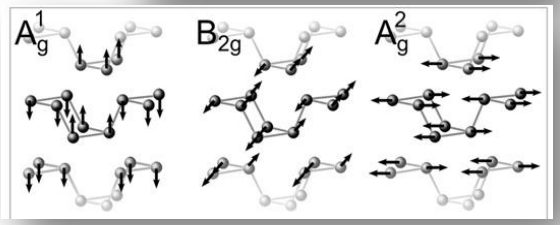
What is black phosphorus?

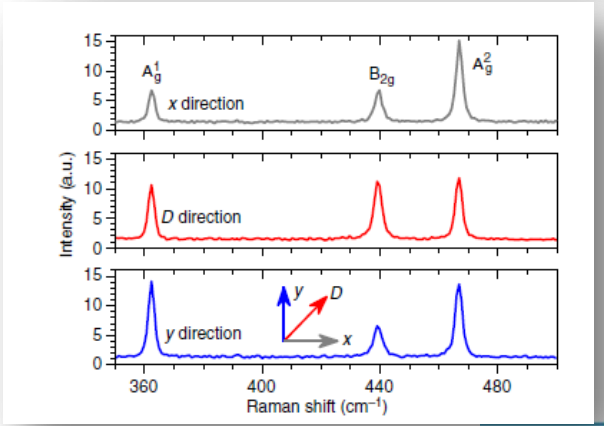


Cell parameters
a=3.13Å
b=10.47Å
c=4.37Å

- ✓In 1914 first successful synthesis (Bridgman) and in 2007 synthesis at room pressure (Lange, Nilges)
- ✓p-type semiconductor: 0.3eV direct band gap and high hole mobility (64,000 cm^2/Vs @ 20 K)
- ✓Vibrational modes of the crystal are Raman active

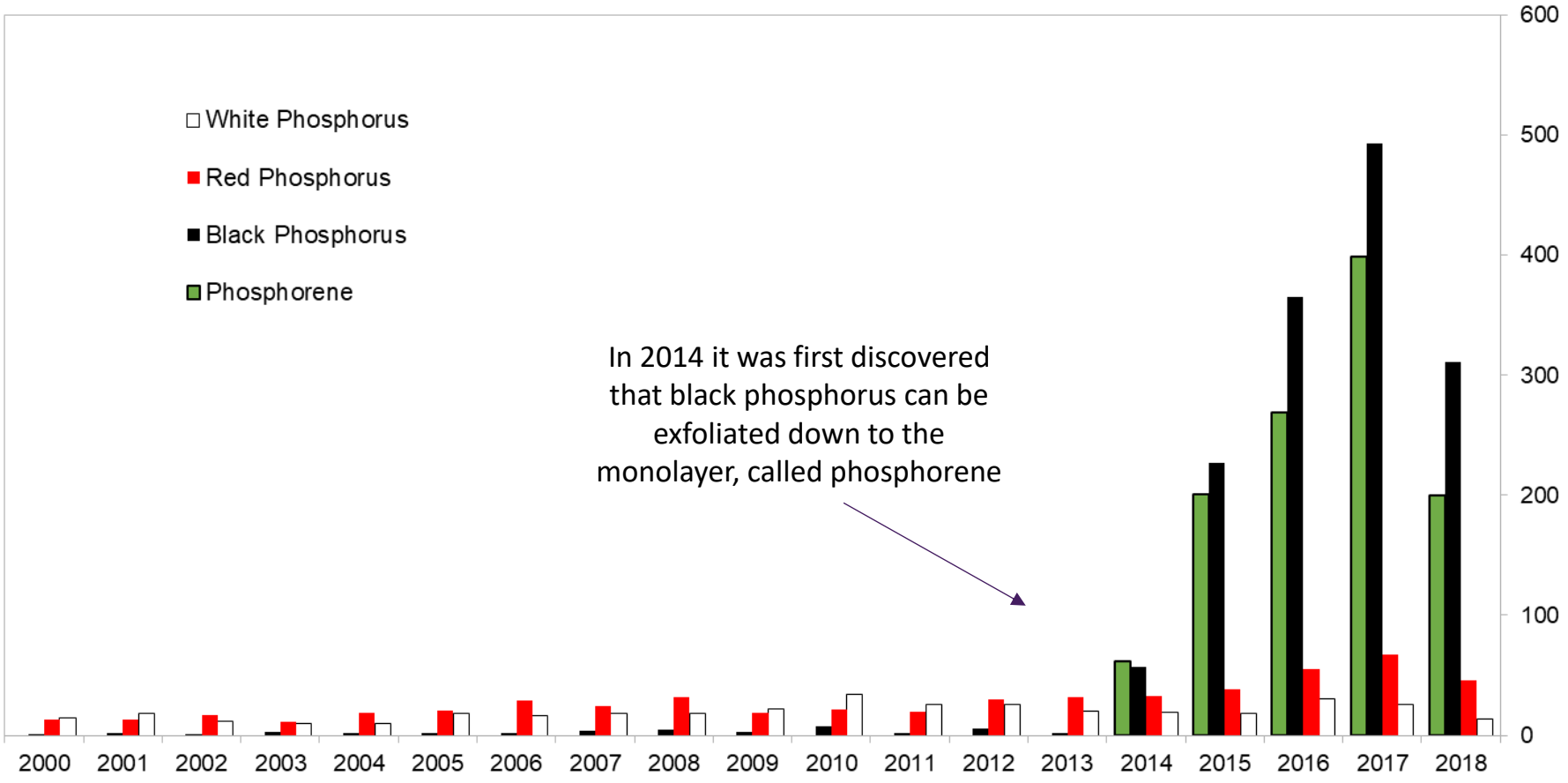






A. Morita, Appl. Phys. A 39 (1986), A. Castellanos-Gomez et al, 2D Mat. 1, (2014); F. Xia et al, Nat Comm 5, (2014)

The renaissance of black phosphorus



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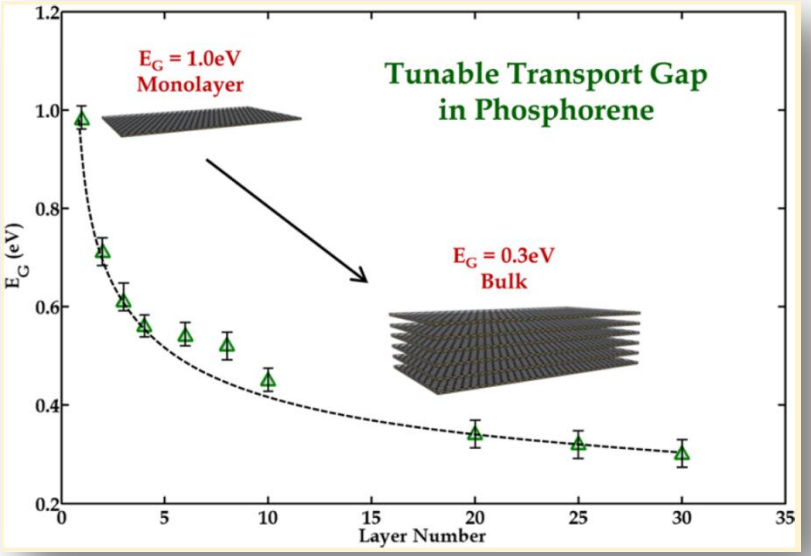
The renaissance of black phosphorus

- ✓Direct band-gap tunable with layer number



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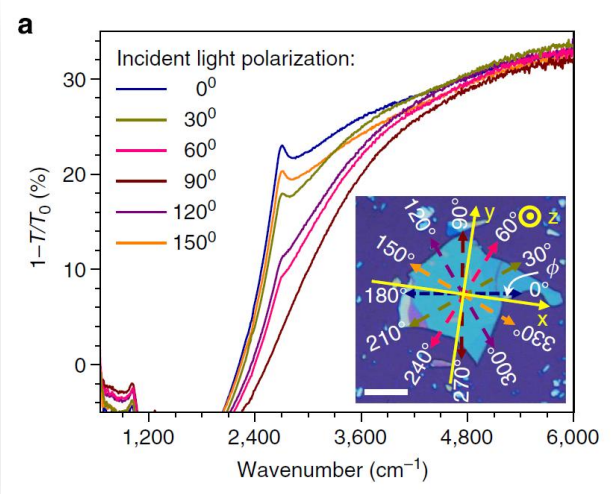
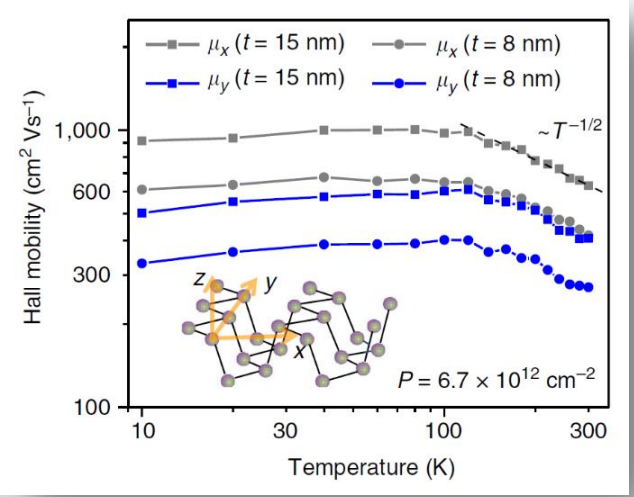
A. Castellanos-Gomez et al., 2D Mater. 1 (2014) 025001, S. Das et al., Nano Lett. 14 (2014) 5733, F. Xia et al., Nat. Comm. 5 (2014) 4458

The renaissance of black phosphorus

- ✓Direct band-gap tunable with layer number
- ✓In-plane anisotropy of optical and transport properties





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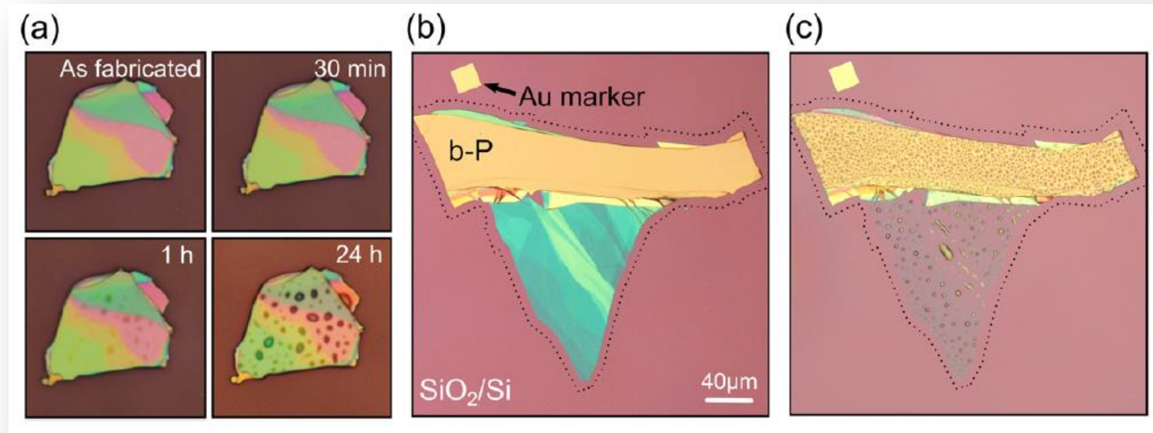
The renaissance of black phosphorus

✓ Direct band-gap tunable with layer number

✓ In-plane anisotropy of optical and transport properties

x ...but... It's highly reactive in air

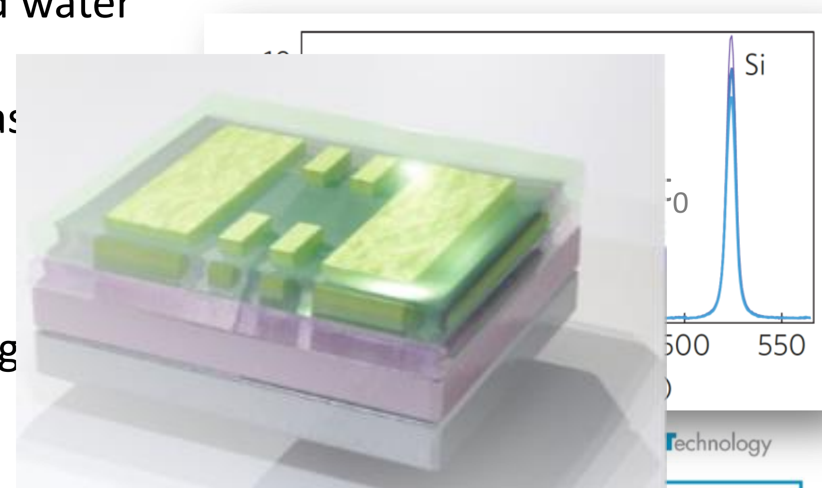


After 2 weeks in air

- Combined effect of light, oxygen and water
- Coating is needed to protect the bP devices

- Degradation is fas thinner flakes

- Raman signal suppression is a g indicator of bP oxidation

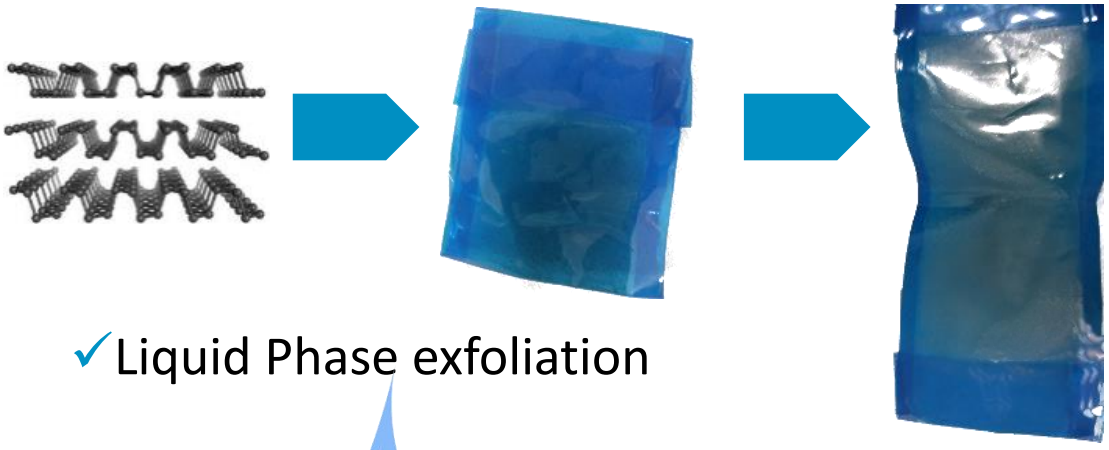


A. Castellanos-Gomez et al., 2D Mater. 1 (2014) 025001, S. Das et al., Nano Lett. 14 (2014) 5733, F. Xia et al., Nat. Comm. 5 (2014) 4458

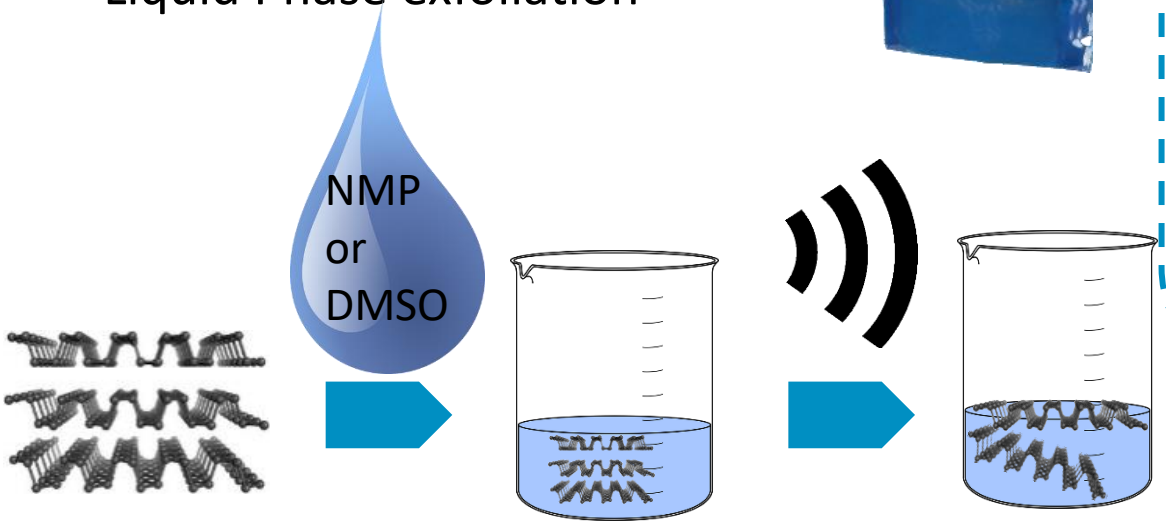
Few layer bP: production routes

x No few layer bP growth route up to now.

✓ Mechanical exfoliation with scotch tape method



✓Liquid Phase exfoliation



Need of a controlled environment!

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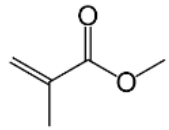
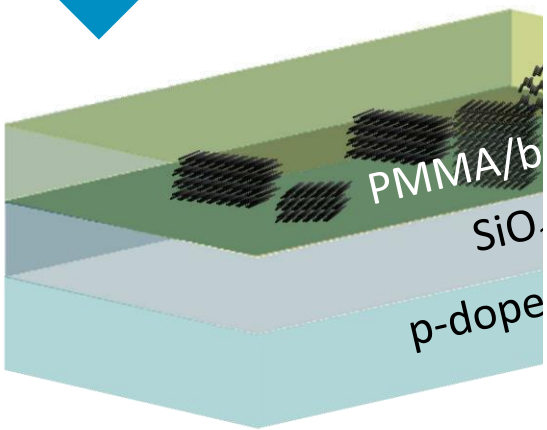
Our approach: nanocomposites preparation

bP bulk



Spin-



dissolution in solvent

MMA/bP
ocomposite

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Passaglia et al. Chem. Mat, 30 (2018); Telesio et al., Nanotechnology 29, (2018)

Why poly (methyl methacrylate)?

- PMMA is already used to coat mechanically exfoliated black phosphorus

→ Efficiently **protects** bP from degradation

- It's transparent in the visible region, allowing optical microscopy for bP flakes identification
- It's suitable for Raman spectroscopy
- It's thermally stable at room temperature, with a glass transition temperature around 150°C

→ Suitable to **check the bP** preservation in the process

- It's among the most common resists for electron beam lithography (EBL)

→ Suitable for **device fabrication**

Telesio et al., Nanotechnology 29, (2018)

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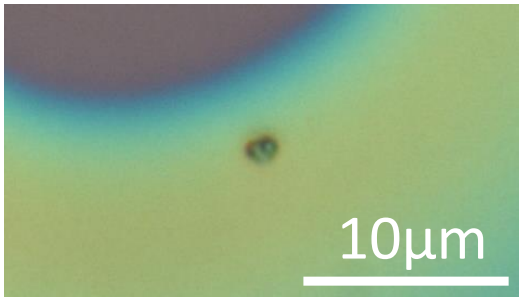
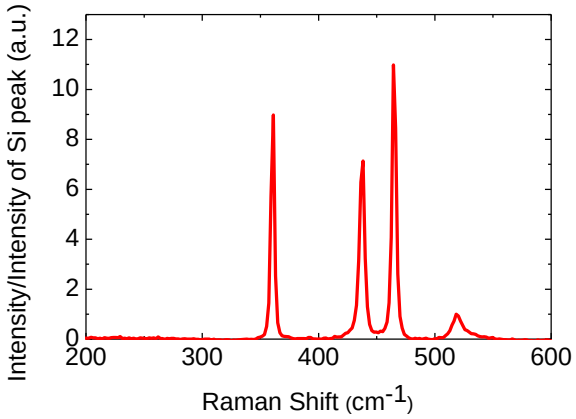
bP nanosheets identification and processing

Raman for identification

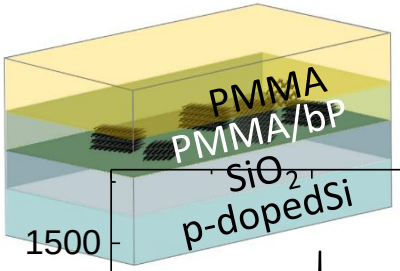




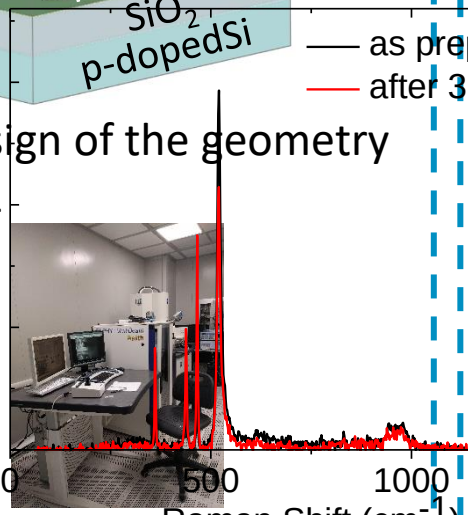
Suitable geometry
Raman activity

Device fabrication

- Spin-coating of a blank PMMA layer

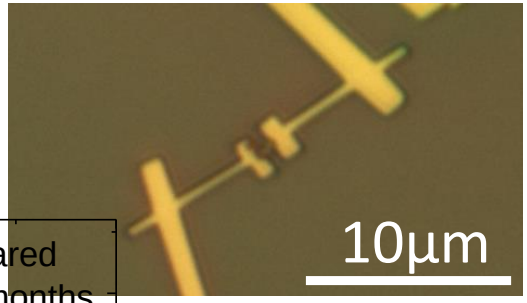


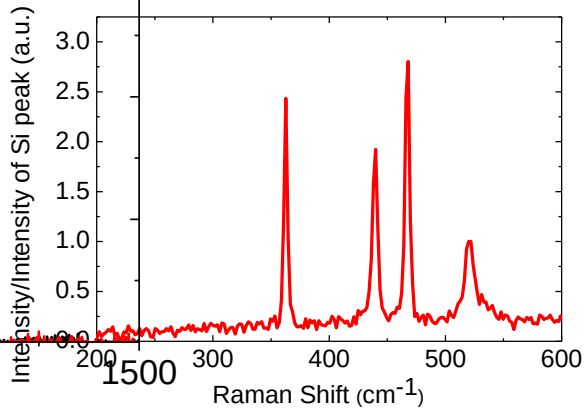
- Design of the geometry
- EBL



- Development
- Metal evaporation
- Lift-off
- Coating

Raman on the device

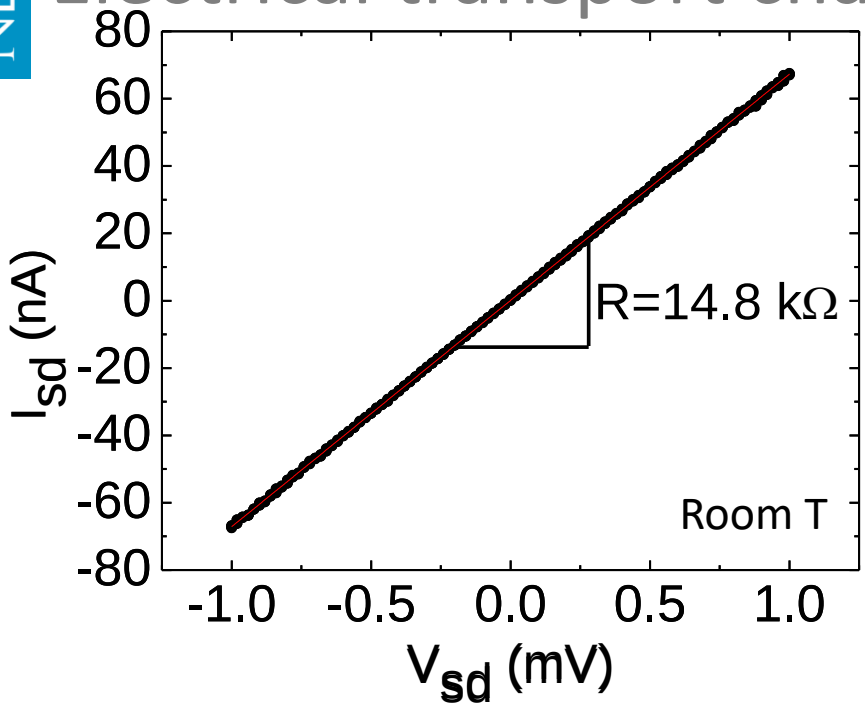


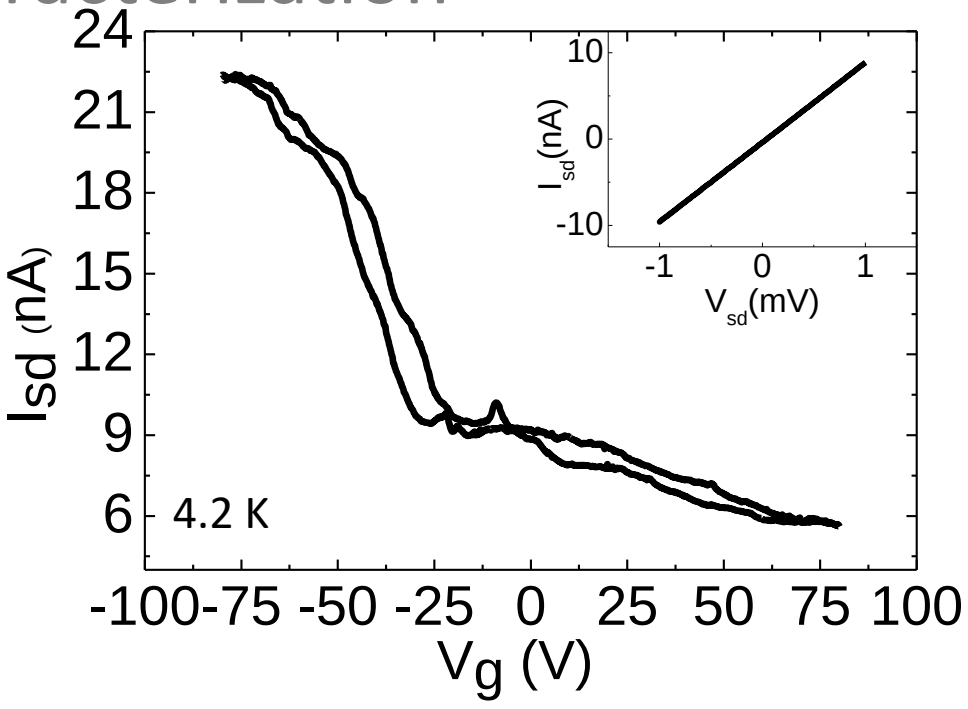


bP Raman signature is still observed

Telesio et al., Nanotechnology 29, (2018)

Electrical transport characterization



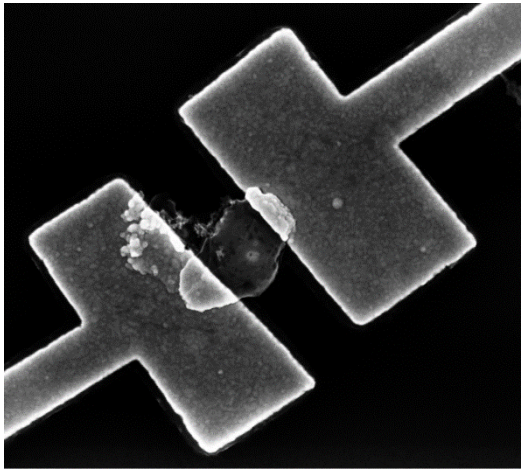


- **Ohmic** resistivity with values comparable with mechanically exfoliated material
- **p-type** behavior
- $\mu_{FE} = 35 \frac{cm^2}{Vs}$ **comparable with electronic grade LPE** material

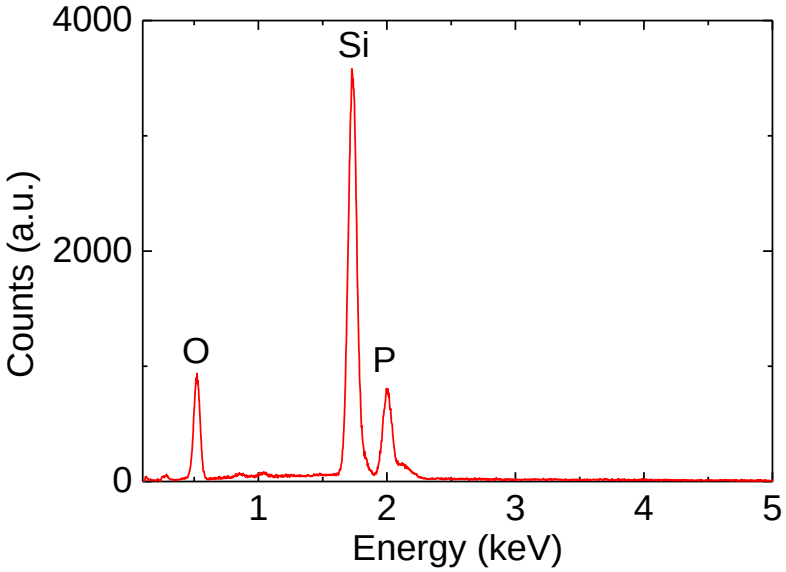
($\bar{\mu} = 25.9 \frac{cm^2}{Vs}$ in J. Kang et al. ACS Nano, 9, 3596, (2015))

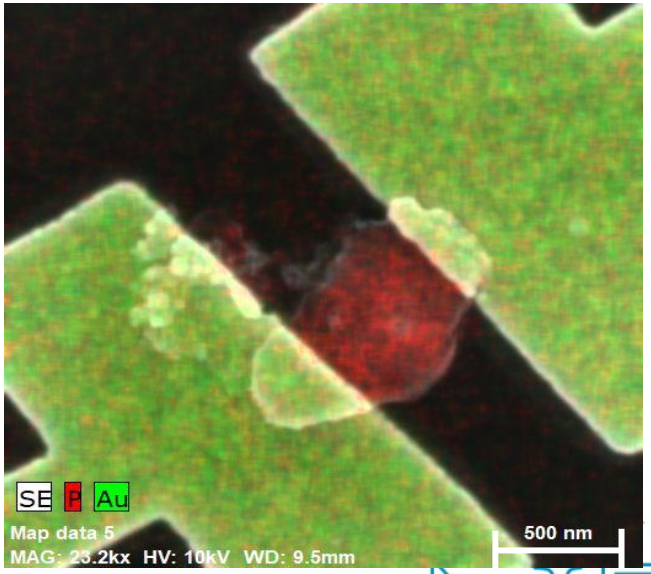
Telesio et al., Nanotechnology 29, (2018)

Scanning Electron Microscopy and Energy Dispersive X-Ray Analysis



- ✓ To check morphology and chemical composition of the device.
- ✓ Space-resolved chemical composition of the device





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Conclusions and outlooks

- ✓ We proved that sonication in **a vinyl monomer can efficiently exfoliate** bP and that its **polymerization process does not induce significant degradation**
- ✓ Even in very thin polymer films (approx. 50 nm) bP flakes are stable for over 3 months
- ✓ We realized devices using the nanocomposite, **without the need of a glove box** in any stage of the fabrication
- ✓ We obtained **resistances and mobilities comparable with electronic-grade liquid phase exfoliated bP**

- ❑ ...Use this framework as a platform to move towards applications

E. Passaglia et al, Chem. Mat, 30, 2036, (2018)
F. Telesio et al., Nanotechnology 29, 295601, (2018)

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*SEED Project : **Sur**face properties of black **Phos**phorus investigated by scanning tunneling microscopy*

Thank you for your attention!

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