Electrochemical Intercalation in Layered Materials

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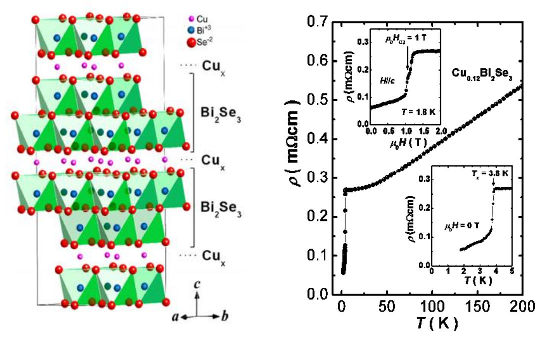
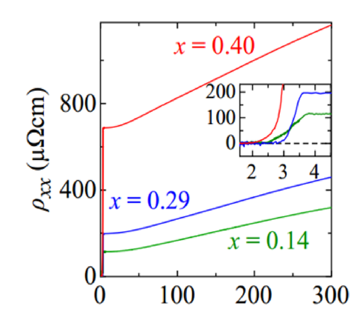
Introduction

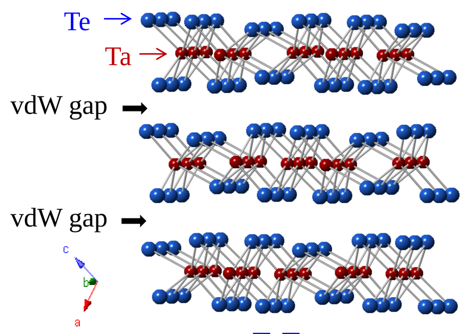
Intercalation of ions into the van der Waals gap of layered materials has been demonstrated as an effective approach to induce emergent quantum phenomena, as represented by the recent discovery of superconductivity at 4.4K in Cu-intercalated layered topological insulator Bi_2Se_3. Compared to the traditional technique in which the intercalation occurs during crystal growth and is driven by thermal energy, the electrochemical intercalation utilizes electrostatic force and thus much heavier ion doping can be realized. In $Cu_xBi_2Se_3$ prepared using the electrochemical method, enhanced superconductivity with higher transition temperature and sharper transition width has been observed. Motivated by previous success with electrochemical intercalation, we have extended our efforts to other interesting layered materials with van der Waals gaps, such as $TaTe_2$, $TaSe_2$ and black phosphorus. These materials display interesting properties as shown in the following graphs. The objective of this work is to look for novel exotic properties via electrochemical intercalation.



Superconductivity induced by Cu-intercalation in Bi_2Se_3 (PRL 104, 057001 (2010))

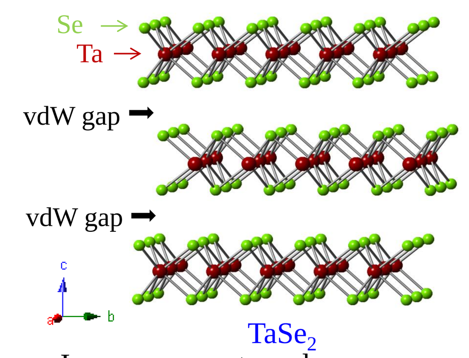


Heavy Cu doping by electrochemical intercalation in Bi_2Se_3 (PRB 84, 054513 (2011))



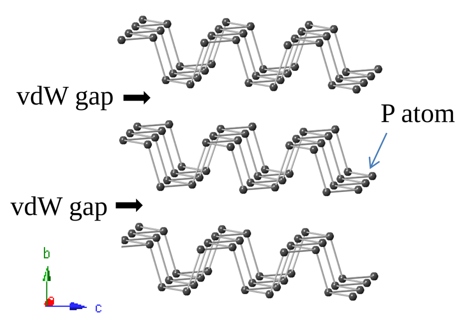
$TaTe_2$

- Structural transition at ~ 170K



$TaSe_2$

- Incommensurate and commensurate charge density wave (CDW) phase transitions at ~ 117K and 88K, respectively. Superconducting at ~0.2K



Black Phosphorus

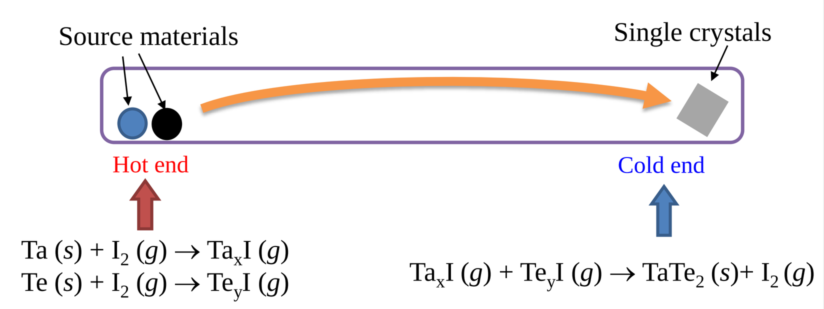
- Semiconducting with band gap ~ 0.19eV for bulk and 0.75eV for mono-layer.

[1] Du, et al, J. Appl. Phys. 107, 093718 (2010)
[2] Hor, et al, Phys. Rev. Lett. 104, 057001 (2010).
[3] Kumakura, et al, J. Phys. 46, 2611 (1996).
[4] Sasaki, et al, Phys. Rev. Lett. 107, 217001 (2011).
[5] Sorgel, et al, Mater. Res. Bull. 41, 987 (2006)

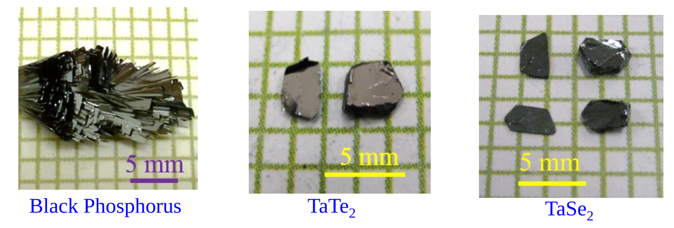
Method

Chemical Vapor Transport growth of single crystals

The stoichiometric ratio of starting materials (e.g. Ta and Te powder) were mixed, homogenized, and vacuum sealed into a quartz tube with iodine as the transport agent. The tube was then placed into a double heating zone furnace with the temperature of two heating zones fixed at 1000 C and 900 °C. Large high quality single crystals can be obtained after 2 week's vapor transport.



Ta (s) + I_2 (g) → Ta_xI (g)
Te (s) + I_2 (g) → Te_yI (g)
Ta_xI (g) + Te_yI (g) → $TaTe_2$ (s) + I_2 (g)

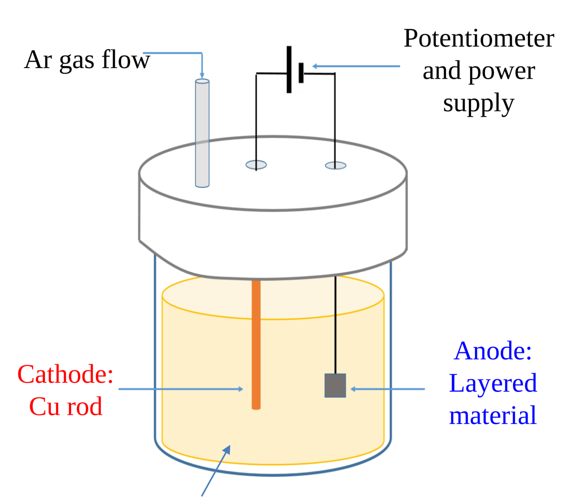


Black Phosphorus, $TaTe_2$, $TaSe_2$

Electrochemical Intercalation

During the intercalation, the saturate Iodide (CuI) - acetonitrile (CH3-CN) solution was used as electrolyte and supplied Cu ions. The layered host material ($TaTe_2$, $TaSe_2$, and black phosphorus) acted as the negative electrode, and a Cu rod was used as a positive counter electrode to resupply the Cu^+ ions that are lost from the solution. To prevent the oxidization of Cu^+ and air deterioration of sample, a continuous argon gas flow was maintained.

The constant current is generated by a electrochemical station using Chronopotentiometry mode. Various currents (15uA-75uA) and were attempted to control the amount of intercalated Cu.

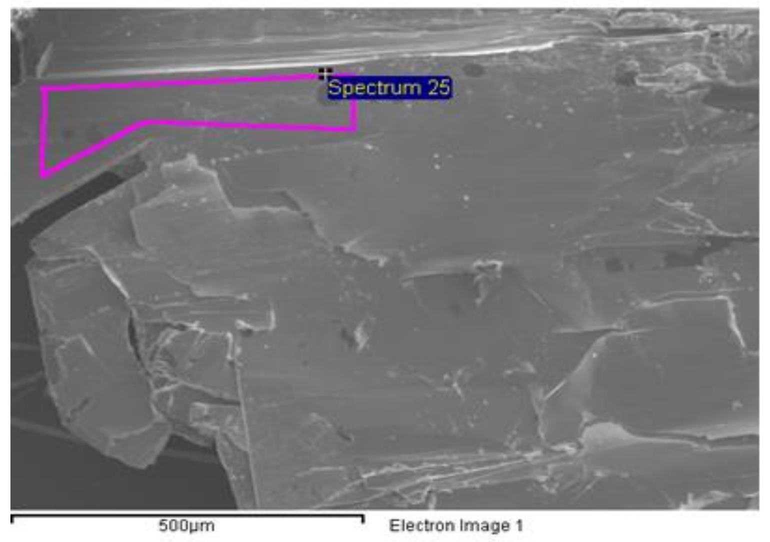


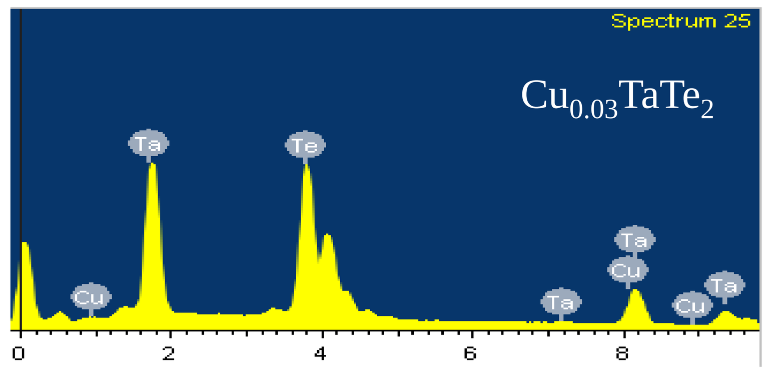
Electrolyte: Iodide (CuI) in acetonitrile (CH3-CN)

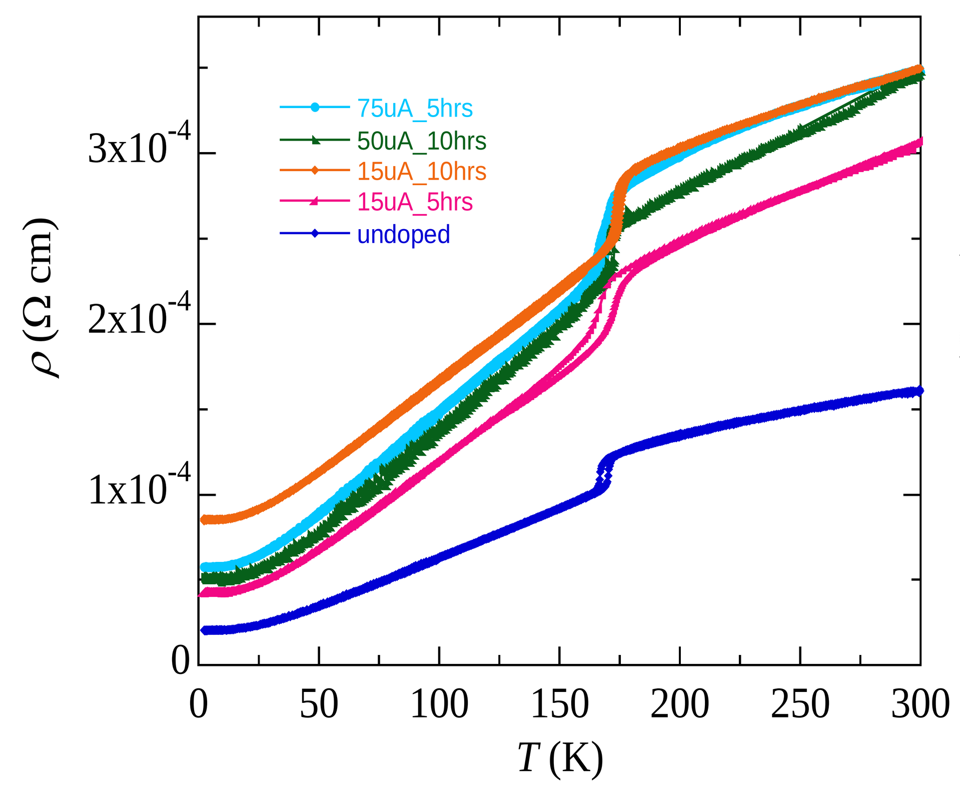
Cathode: Cu – e⁻ → Cu^+
Anode: $TaTe_2$ + Cu^+ → Cu_xTaTe_2

Results and Discussions

Cu_xTaTe_2

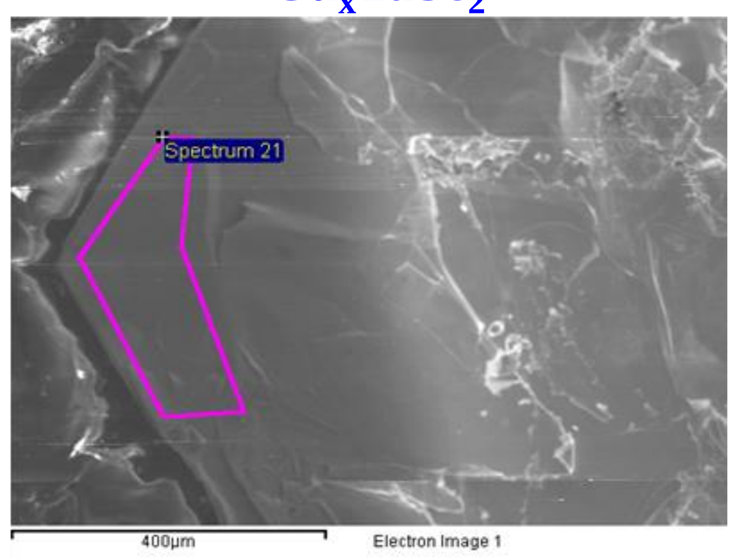


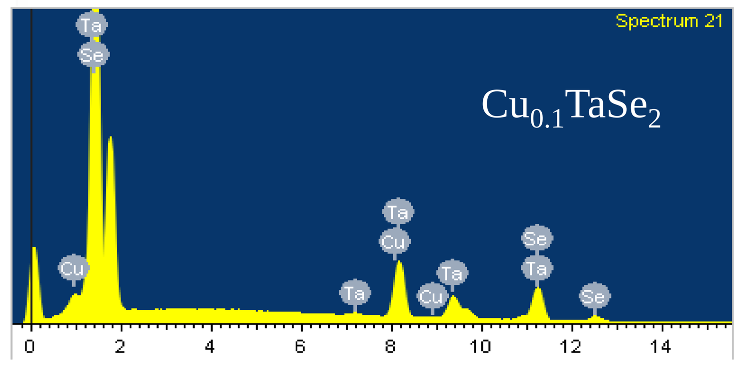


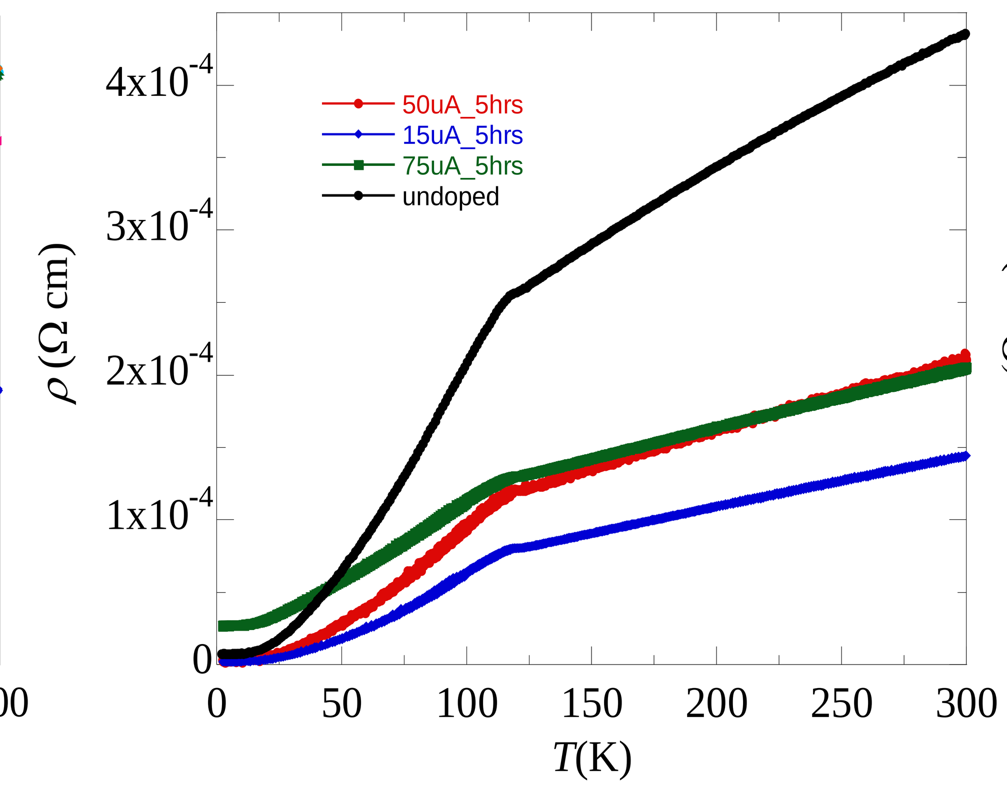


- Electrochemical intercalation was successful as evidenced by EDS analysis.
- Resistivity measurements revealed that Cu intercalation remarkably broadens the structural transition around 170K.

Cu_xTaSe_2

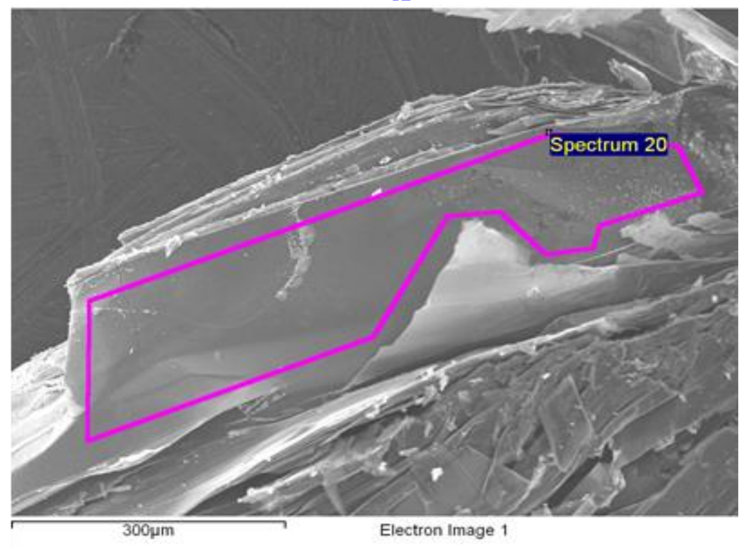


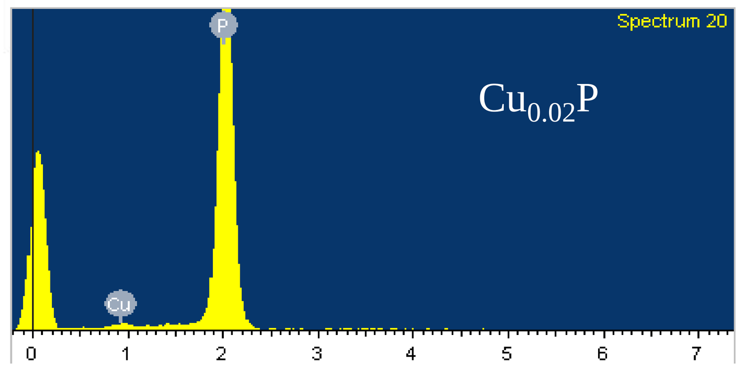


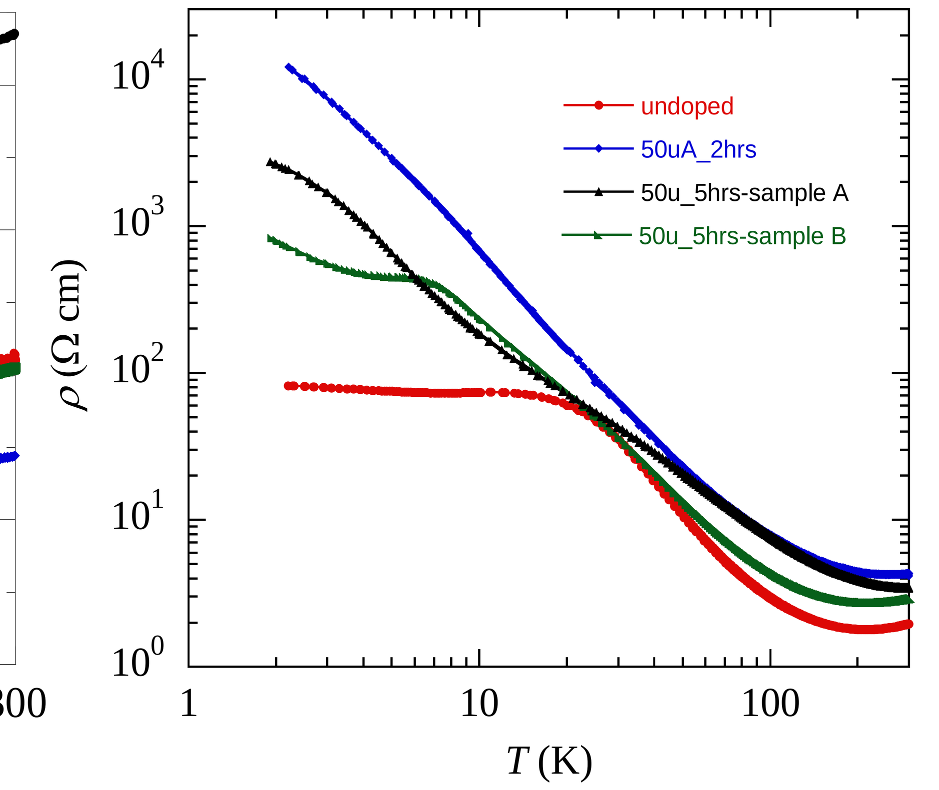


- Electrochemical intercalation was successful as evidenced by EDS analysis. Cu concentration as high as 10% was achieved.
- The resistivity of $TaSe_2$ was reduced by the Cu intercalation, while its CDW transition at 117K remains unchanged.

Cu_xP







- Electrochemical intercalation was successful as evidenced by EDS analysis.
- Resistivity measurements revealed suppression of the resistivity hump due to Cu intercalation around 20K.

Summary

- Electrochemical intercalation of Cu to $TaTe_2$, $TaSe_2$ and black phosphorus was successful as evidenced by EDS analyses.
- The Cu intercalation broadens the structural transition in $TaTe_2$, remarkably reduces the resistivity of $TaSe_2$ though it does not change its CDW transition, and significantly increases the resistivity of black phosphorus at low temperatures.
- New quantum phenomena (e.g. superconductivity) were not observed in these intercalated materials. Other element intercalation (e.g. Li) are still under investigation.

Acknowledgements

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