Optimization of Photodetection Analysis for MXene Thin Films

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MS Thesis Defense
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Committee Members: Prof. Yury Gogotsi | Prof. Steven May

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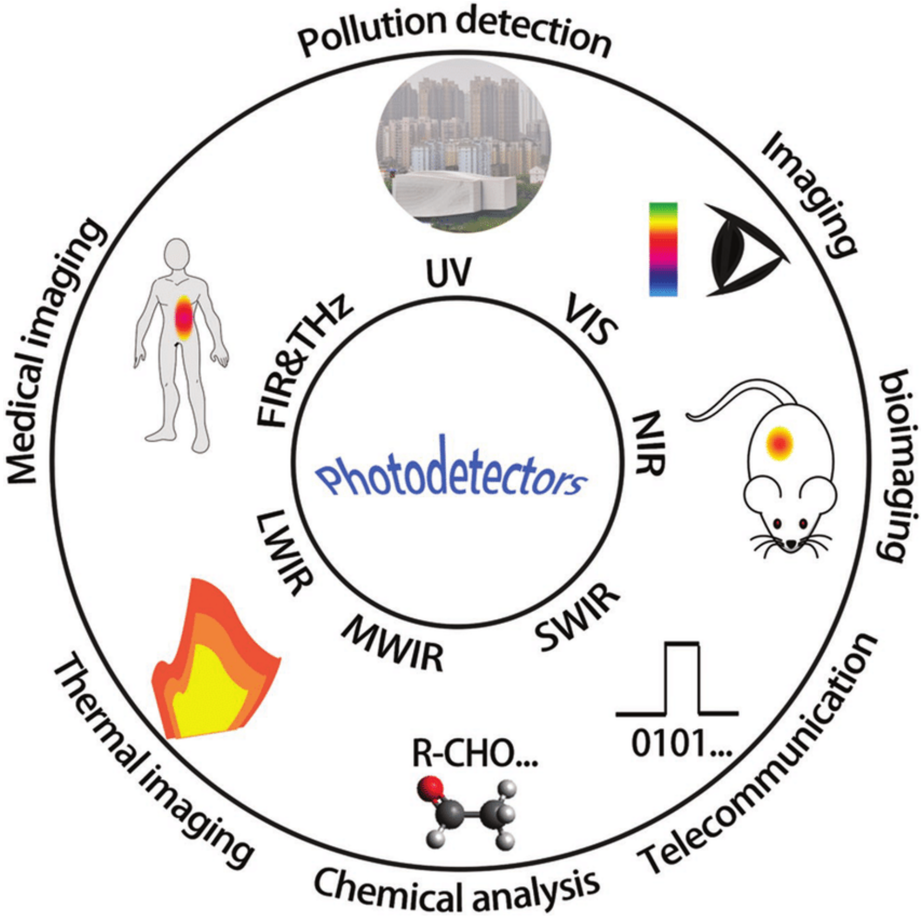
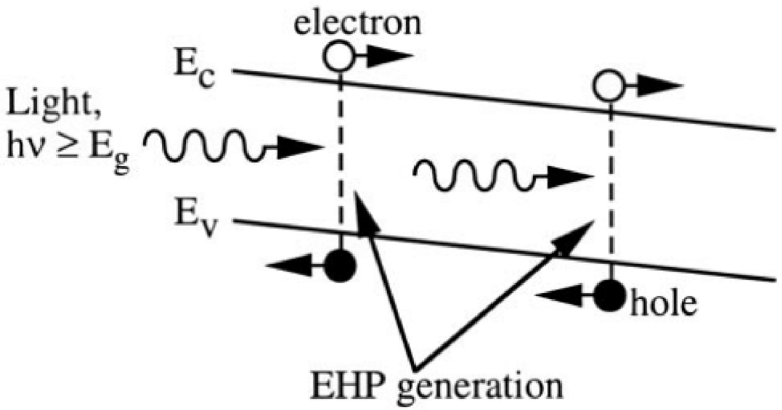
Photodetectors



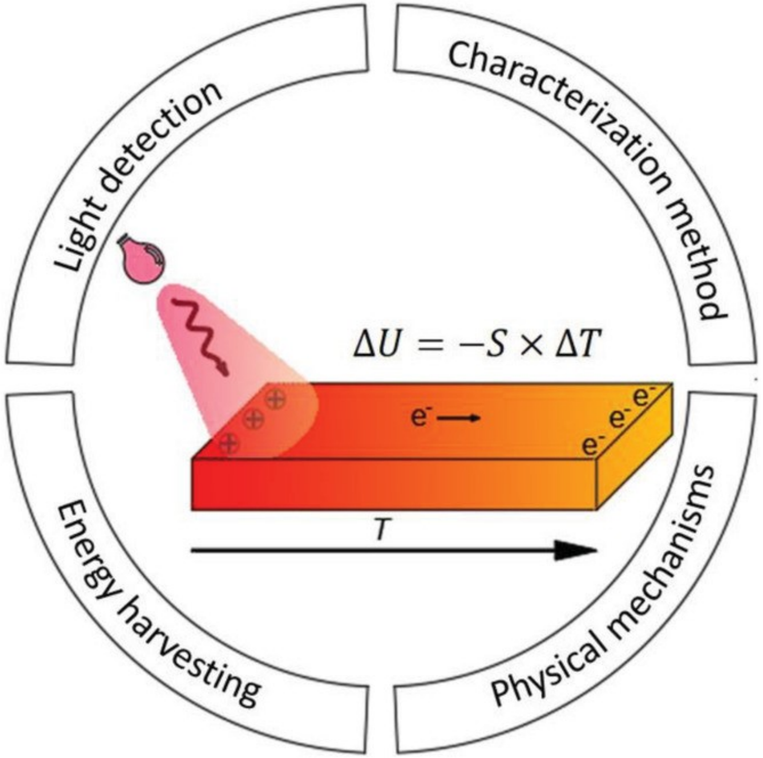
Zhuge, F. *et al. Advanced Materials Technologies* (2017) doi:10.1002/admt.201700005

Mechanisms for Photodetection

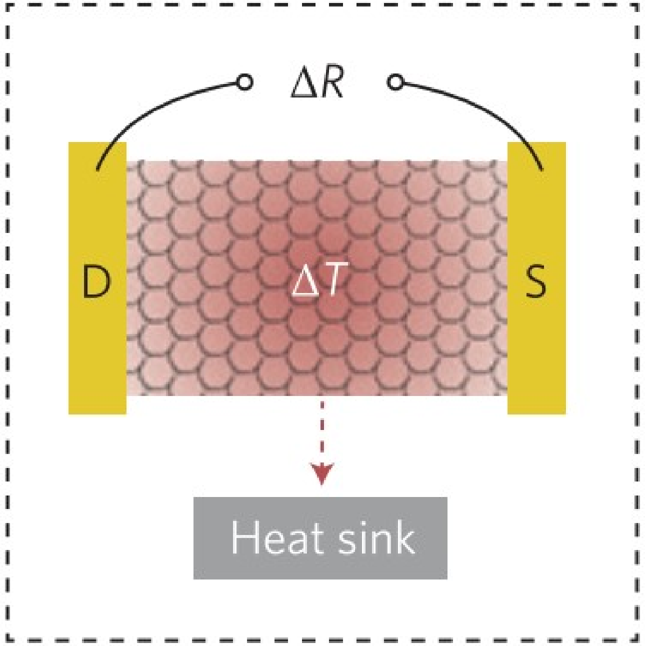
Photovoltaic Effect
or
Photoconductive Effect



Photothermoelectric Effect



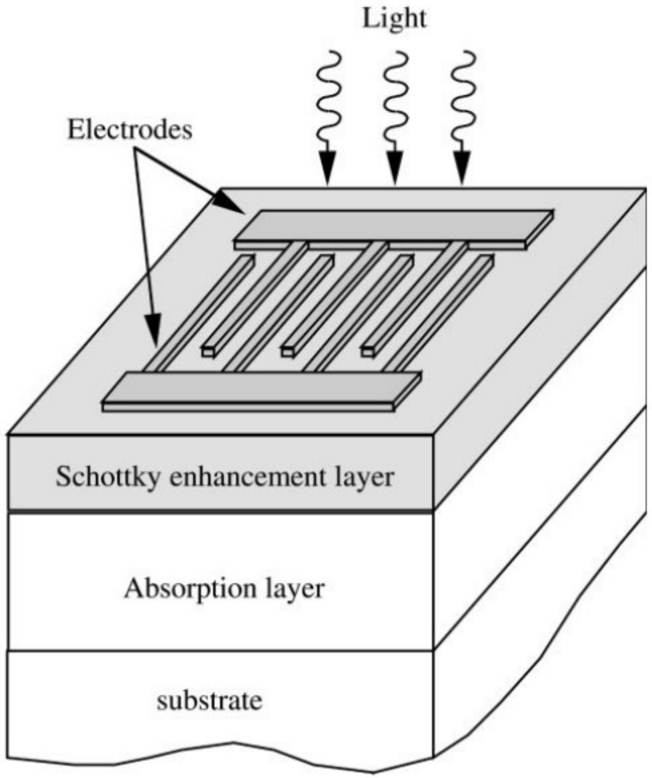
Bolometric Effect



Fay, P. *Encycl. Mater. Sci. Technol.* 6909–6923 (2001) doi:10.1016/B0-08-043152-6/01225-0.
Lu, X. *et al. Adv. Mater.* **31**, 1902044 (2019).
Koppens, F. H. L. *et al. Nat. Nanotechnol.* **9**, 780–793 (2014).

Photodetector Structures

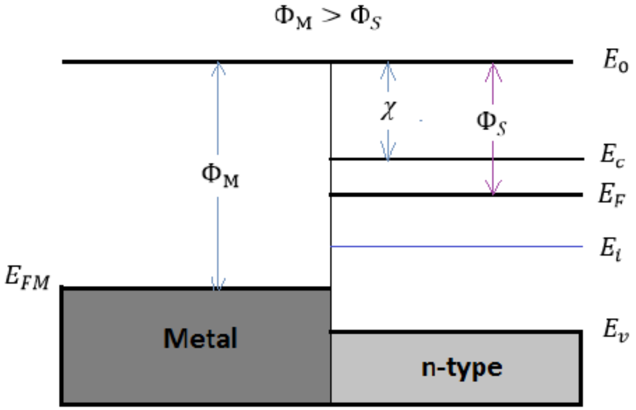
- Absorption layer
  - Typically made of semiconducting materials
  - Three main spectrum zones: ultraviolet (10 – 400 nm), visible (400 – 760 nm), and infrared (760 nm – 2.5 μm)
- Electrical contacts (electrodes)
  - Typically made of metallic materials
  - Can be transparent depending on the structure

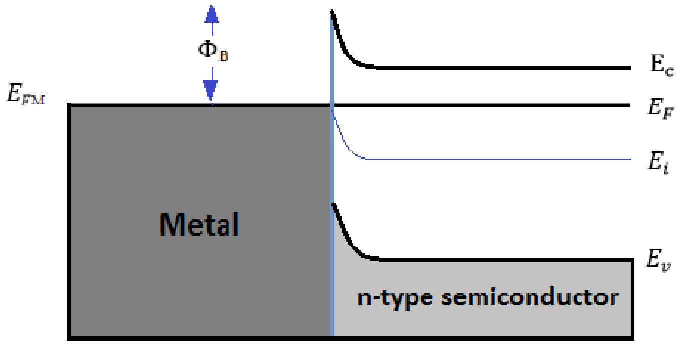


Fay, P. *Encycl. Mater. Sci. Technol.* 6909–6923 (2001) doi:10.1016/B0-08-043152-6/01225-0.

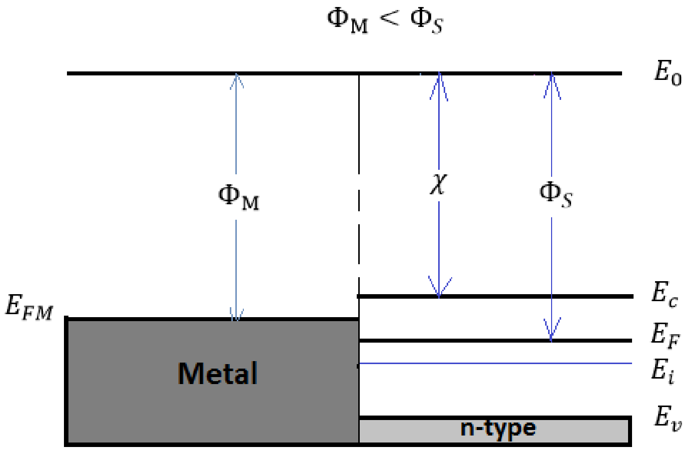
Contacts

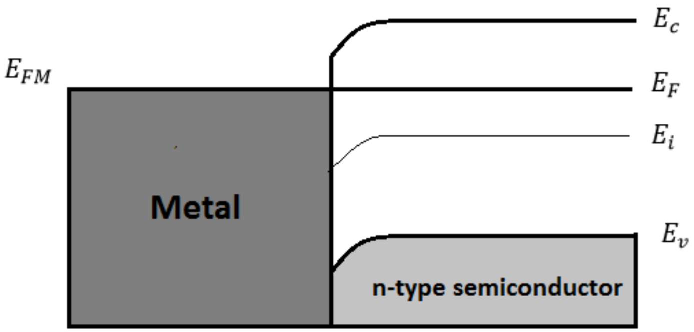
Schottky (Rectifying) Contact





Ohmic Contact

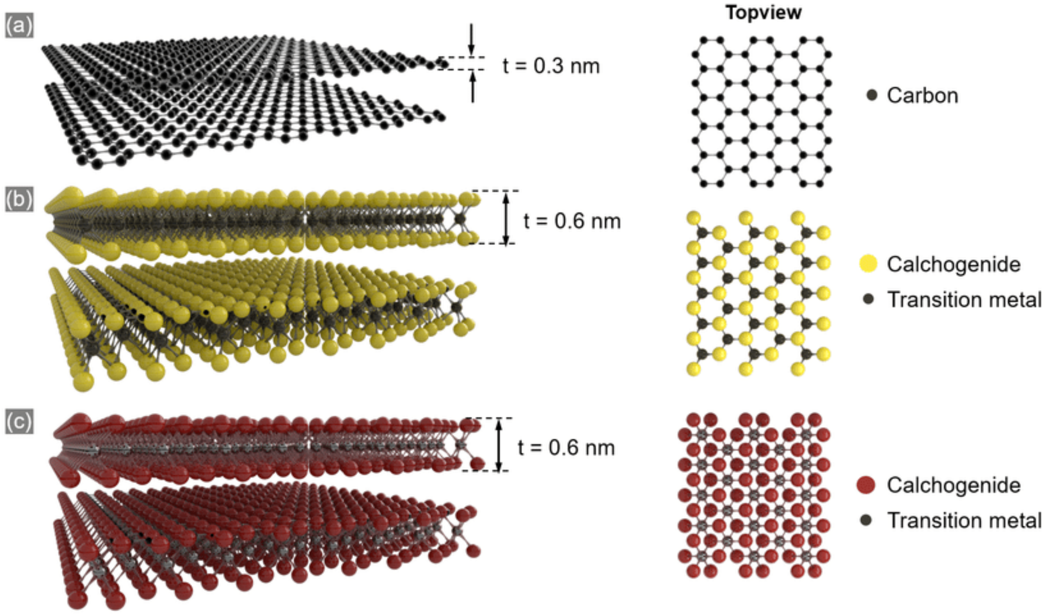




Pierret, R. F. *Semiconductor Device Fundamentals.* 478–481 (Addison-Wesley, 1995).

2D Materials for Photodetection

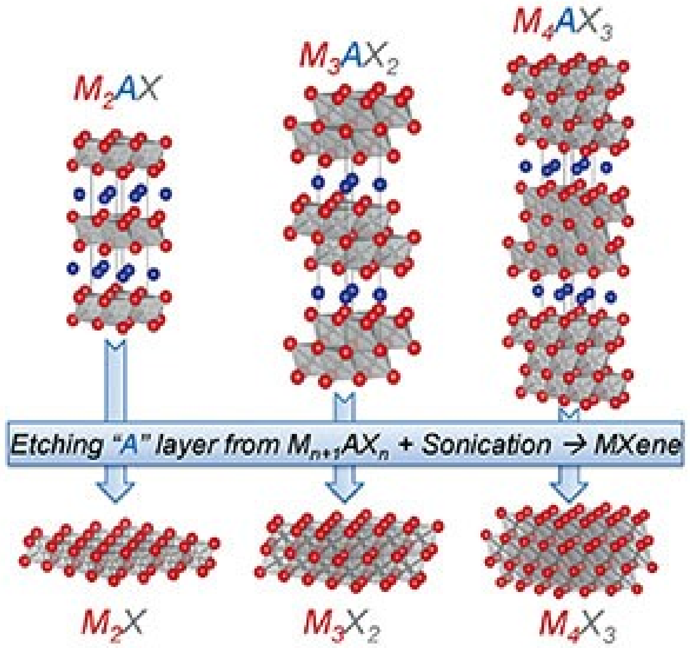
- Ease of processing and desirable optoelectronic properties
- Mechanical strength
- Thickness tunable band gap
- Examples:
  - Graphene
  - Transition metal dichalcogenides (TMDs) - MoS_2



Wagner, Stefan. (2018). doi: 10.18154/RWTH-2018-229791.

Introduction to MXenes

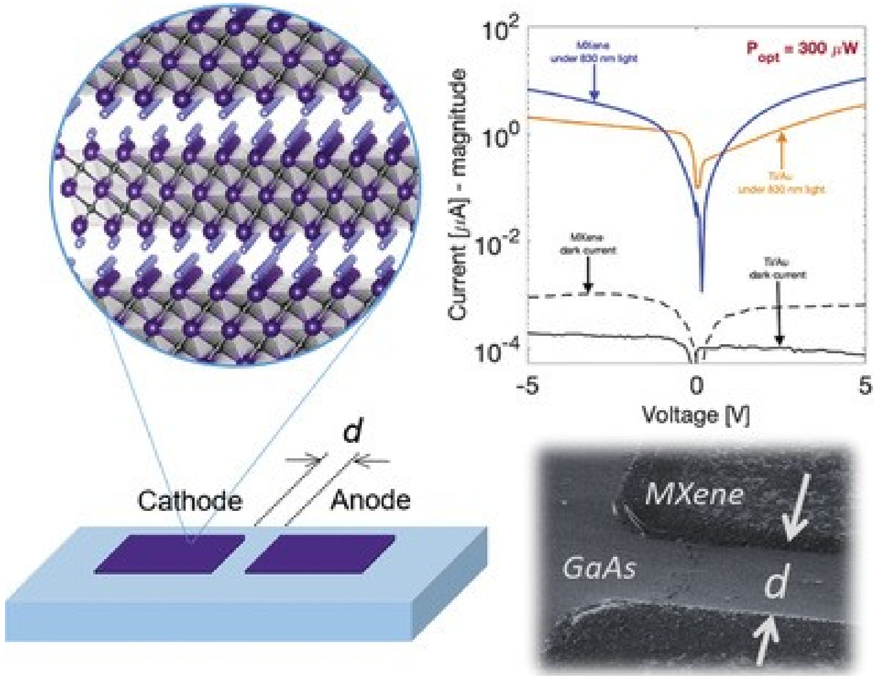
- Discovered at Drexel University in 2011
- Novel class of 2D materials
- General formula of $M_{n+1}X_nT_x$
    - M: early transition metal
    - X: either carbon or nitrogen
    - T: functional group
    - *n* is between 1 to 4
- Tunable properties based on a variety of surface terminations and chemical compositions



M. Naguib, *et al*. Advanced Materials, 26.7 (2014): 992-1005.

Why MXenes?

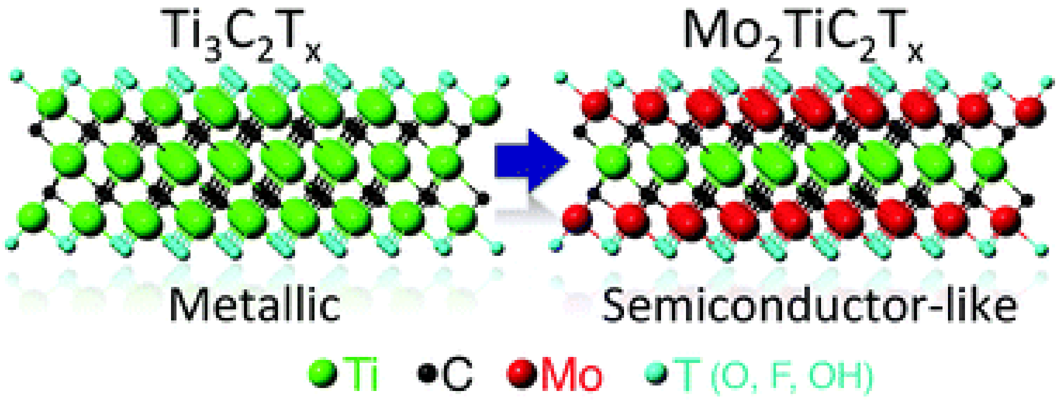
- High electronic conductivity
- Hydrophilic surface
- Low cost
- Facile synthesis methods
- Tunable properties
    - Work function
    - Band structure



Montazeri, K. *et al. Adv. Mater.* **31**, 1–9 (2019).

Why $Ti_3C_2T_x$ and $Mo_2TiC_2T_x$?

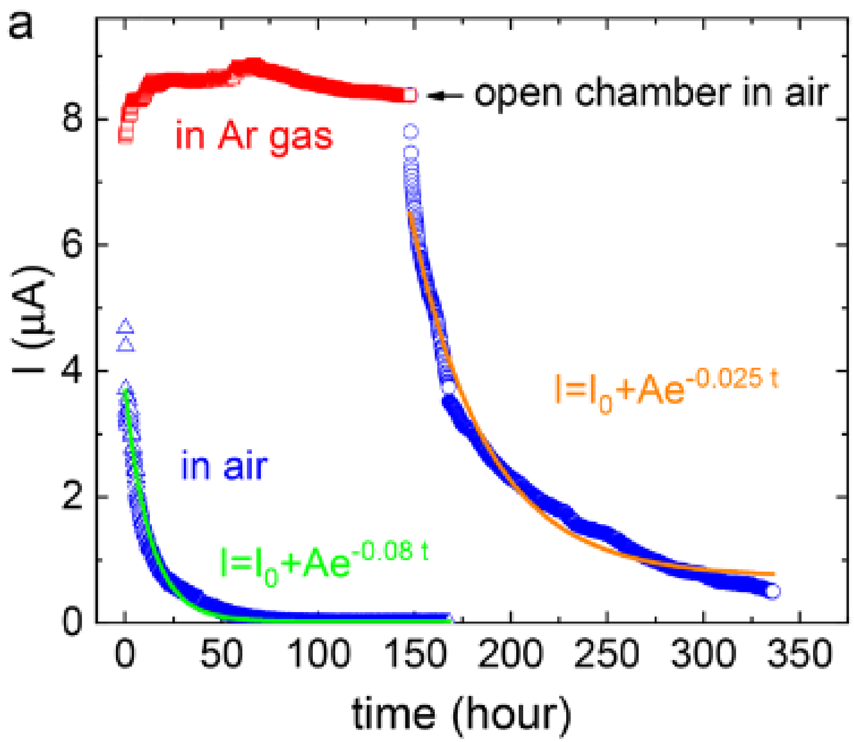
- $Ti_3C_2T_x$ is heavily studied, but $Mo_2TiC_2T_x$ is not
- Will the same testing method apply to both materials?
- $Mo_2TiC_2T_x$ is semiconductor-like, can this be verified using this test method?



B. Anasori. *et al*. *Nanoscale Horizons,* 1 (2016): 227-234

Photoresponse Influences

- Environment
- Ohmic vs. Schottky contacts
- Resistive-capacitive effects
- Electronic interactions
- Heating

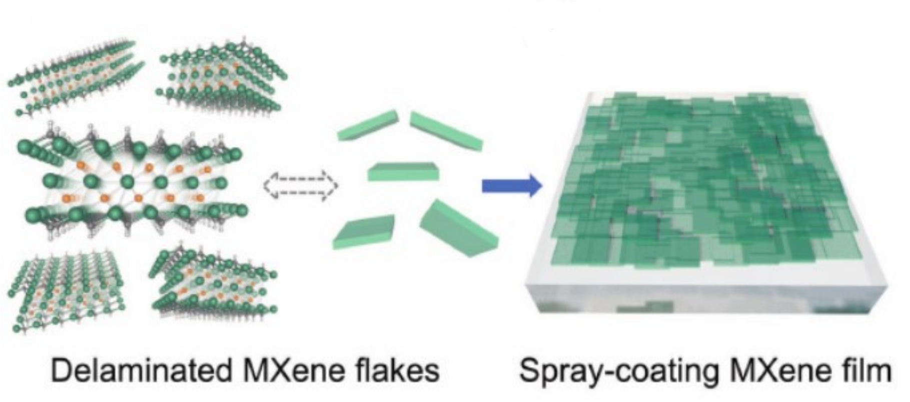


Chertopalov, S. & Mochalin, V. N. *ACS Nano* **12**, 6109–6116 (2018).

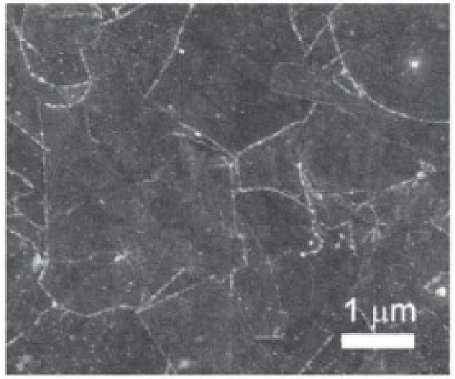
Interflake Interactions for 2D Materials

- Strong in-plane electronic interactions
- Weak out-of-plane van der Waals interactions
- Intercalants: molecules situated between two layers
  - Increase spacing between layers
  - Contribute to electronic properties

Schematic



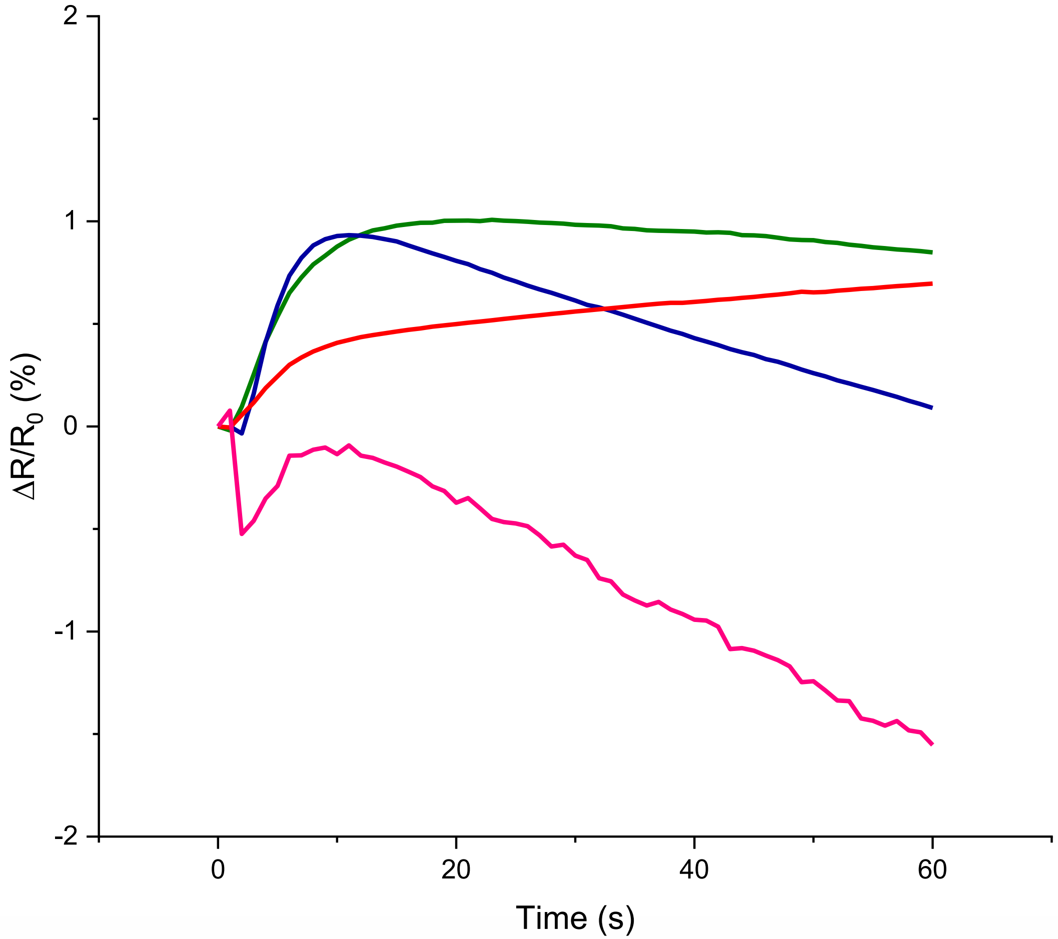
SEM



Wang, Z., Kim, H. & Alshareef, H. N. *Adv. Mater.* **30**, 1706656 (2018).

Photoresponse Characteristics

- Sign
- Shape
- Speed
- Strength

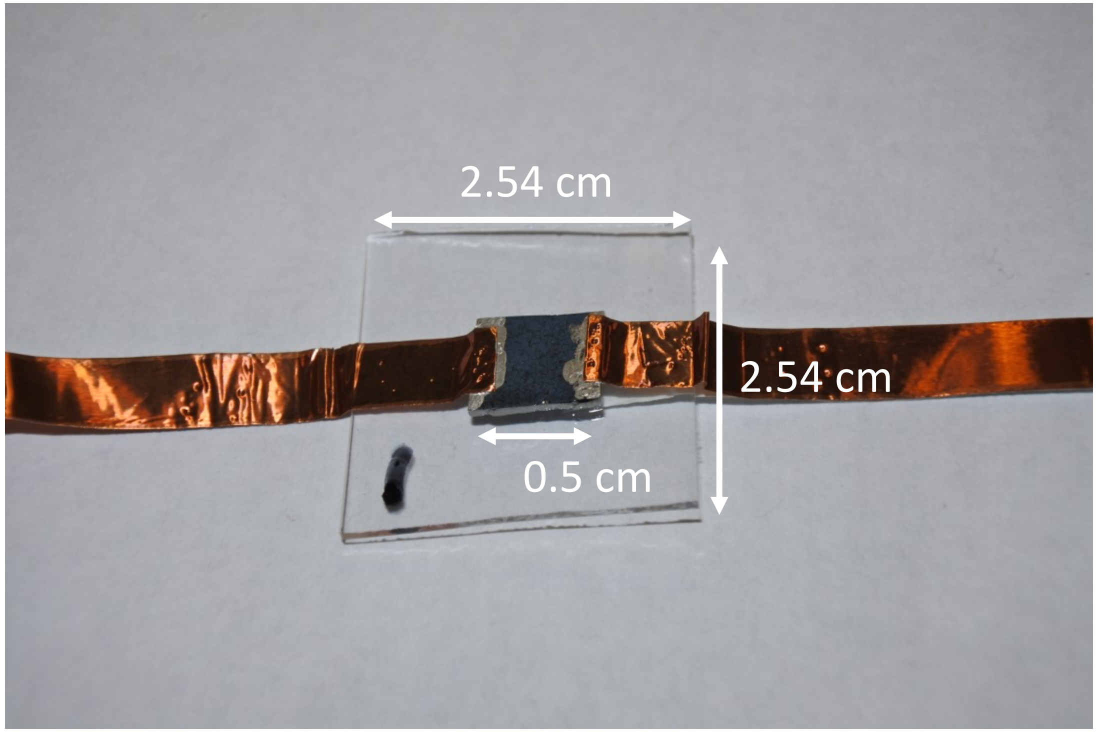


Objectives

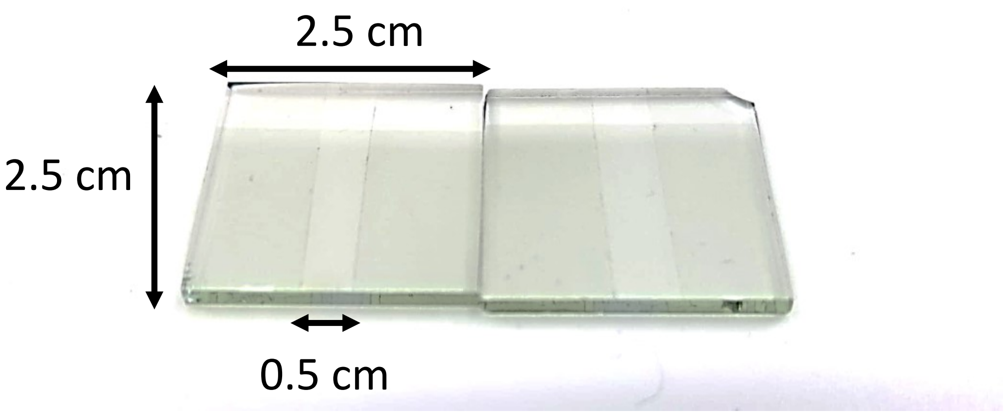
1. Determine best practices for optoelectronic characterization of MXenes
2. Probe effect of external stimuli on photoresponse of MXenes
3. Understand fundamental mechanisms of MXene optoelectronic behavior

Substrate Types

Pristine Glass Slide

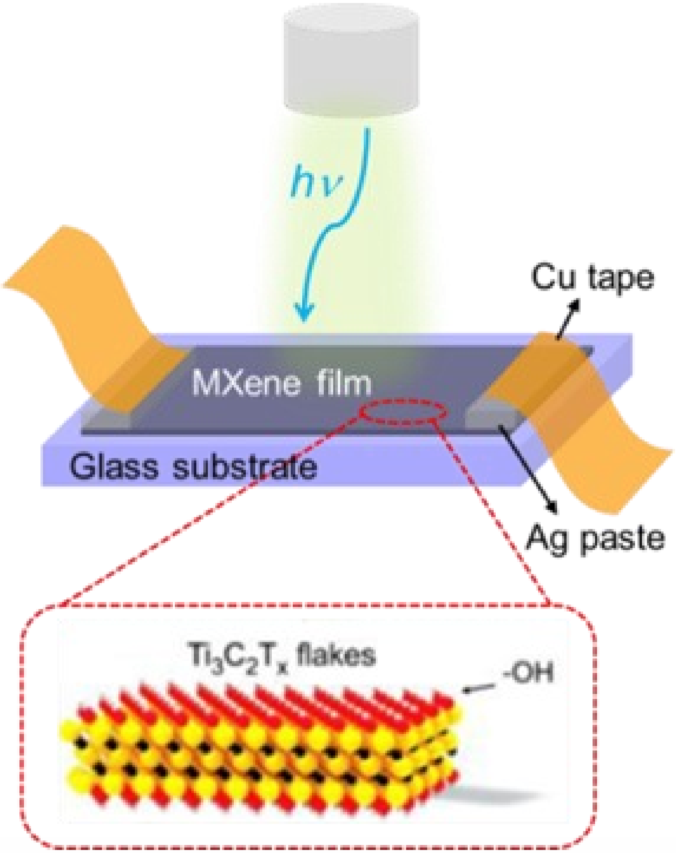


Patterned FTO

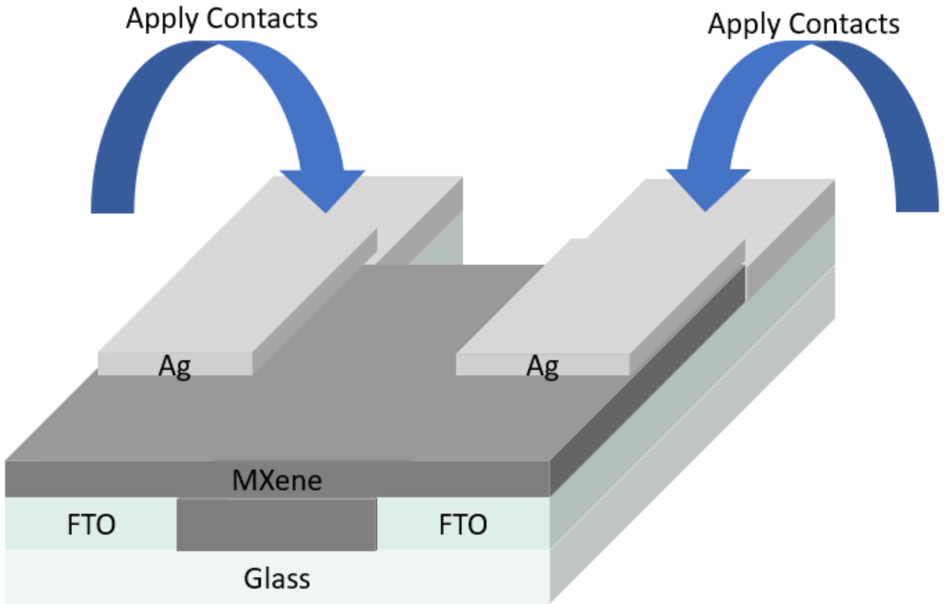


Contact Method

Ag Paint – Cu Tape



FTO or Ag Paint – FTO

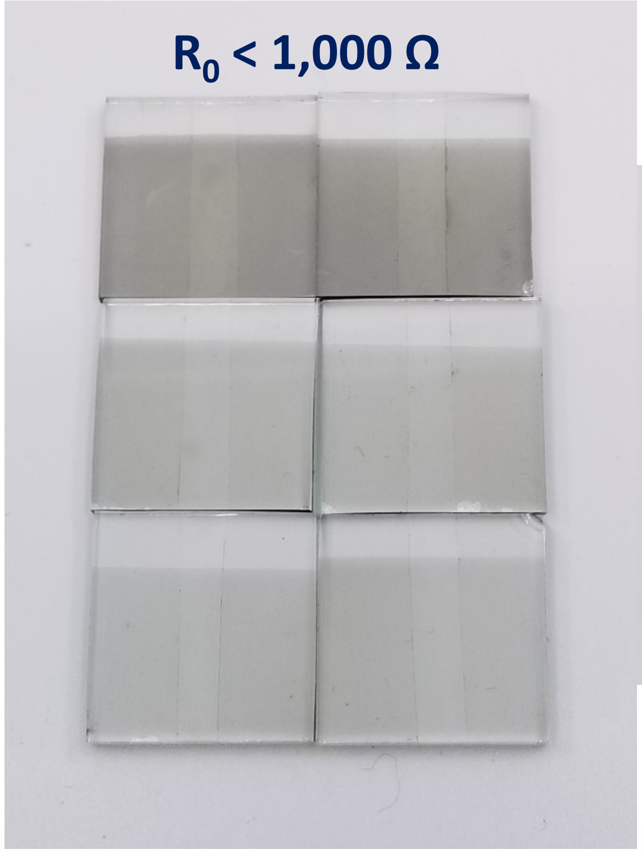


Thanks to Dr. Meiping Zhu for generating figure of $Ti_3C_2T_x$ contact method.

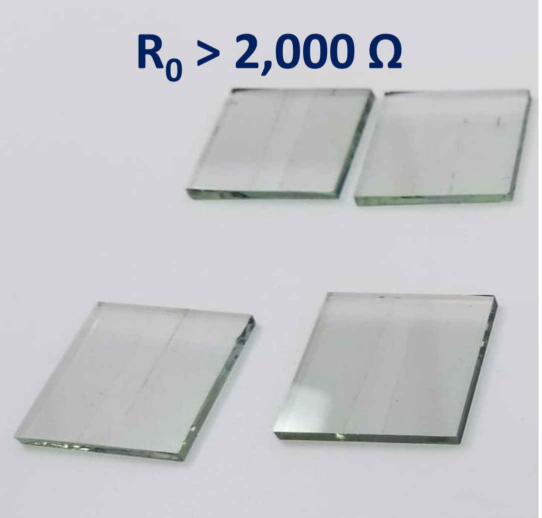
16 μm Free-standing Film of $Mo_2TiC_2T_x$

Spray Coating of $Ti_3C_2T_x$ and $Mo_2TiC_2T_x$

$Ti_3C_2T_x$

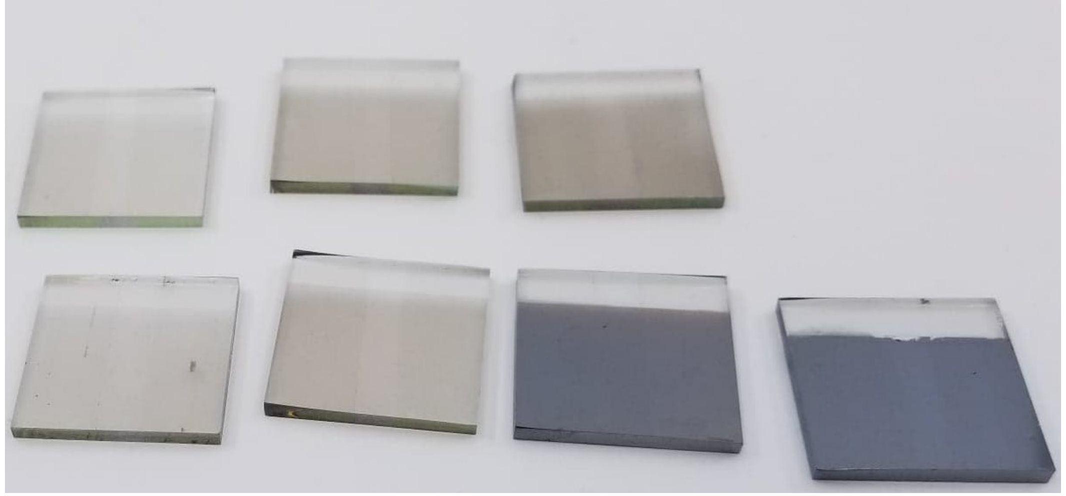


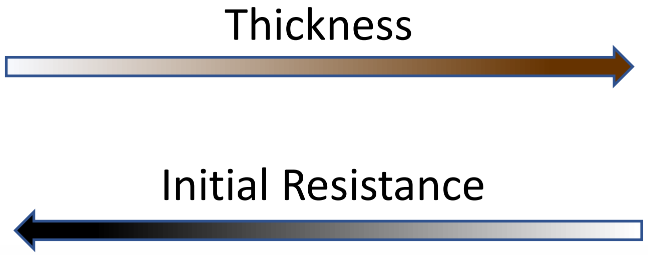
R_0 < 1,000 Ω



R_0 > 2,000 Ω

$Mo_2TiC_2T_x$



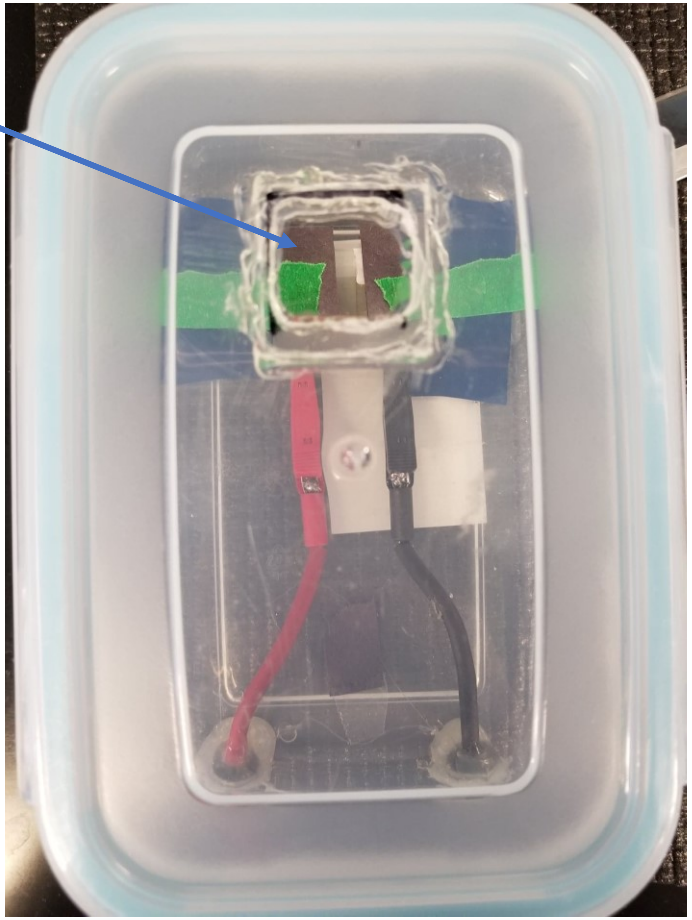


Thickness

Initial Resistance

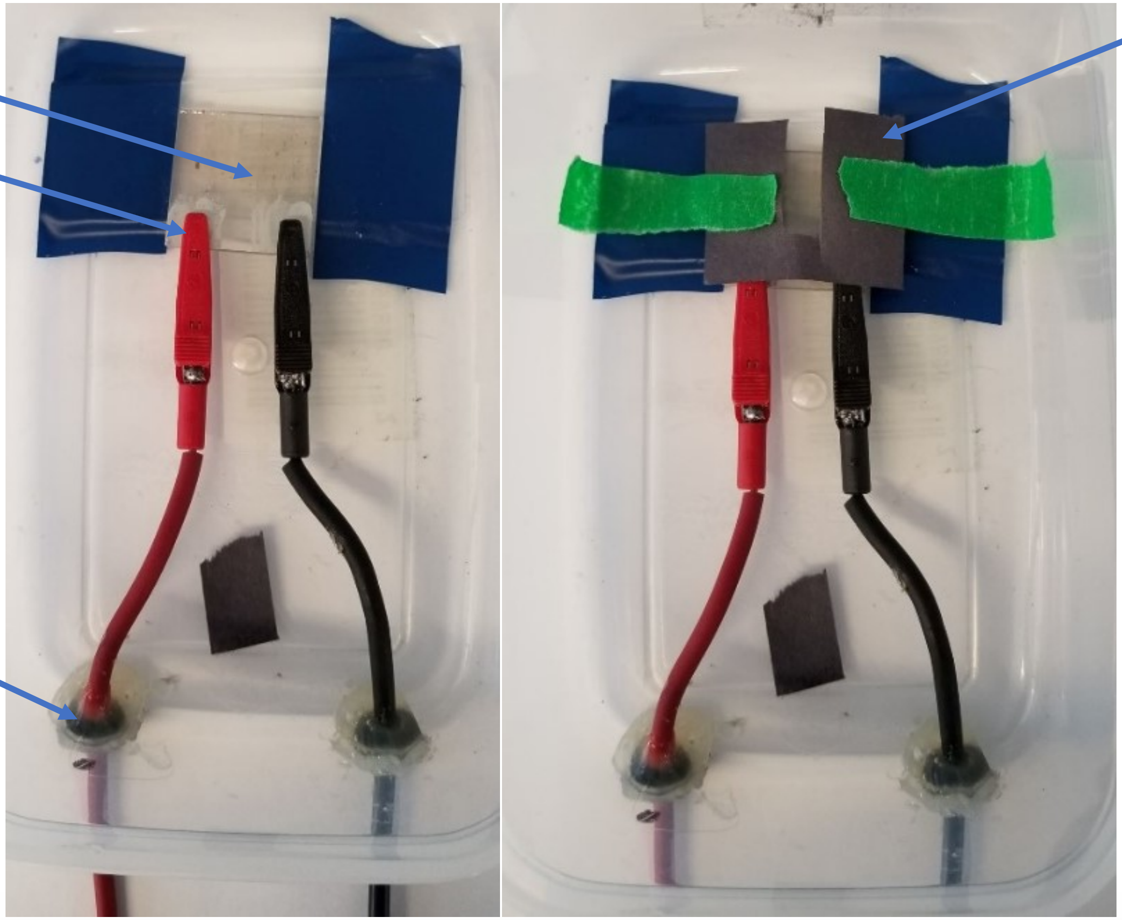
Test Environment with and without Mask

Containment Unit



Quartz Window

Removal and Application of Mask



Sample

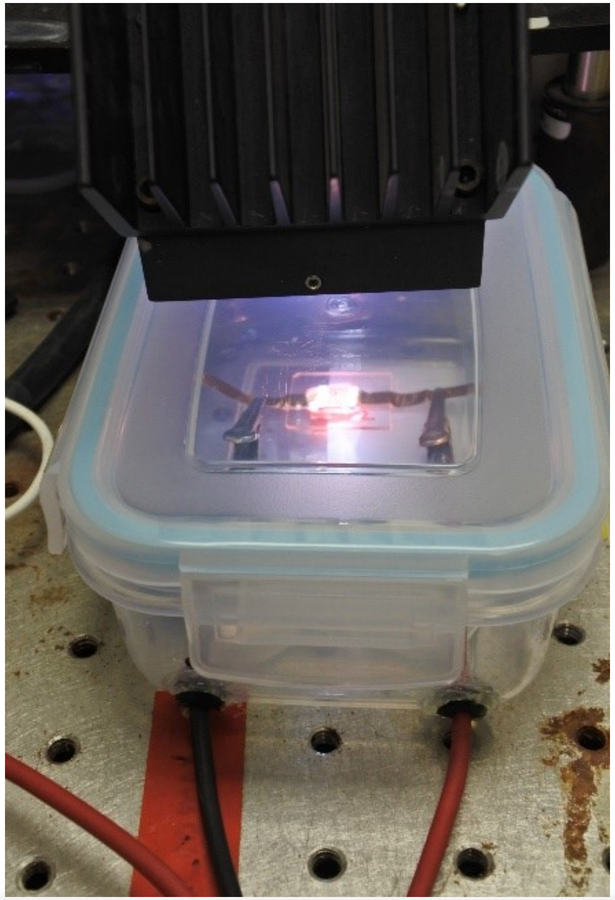
Electrode

Airtight Seal

Mask

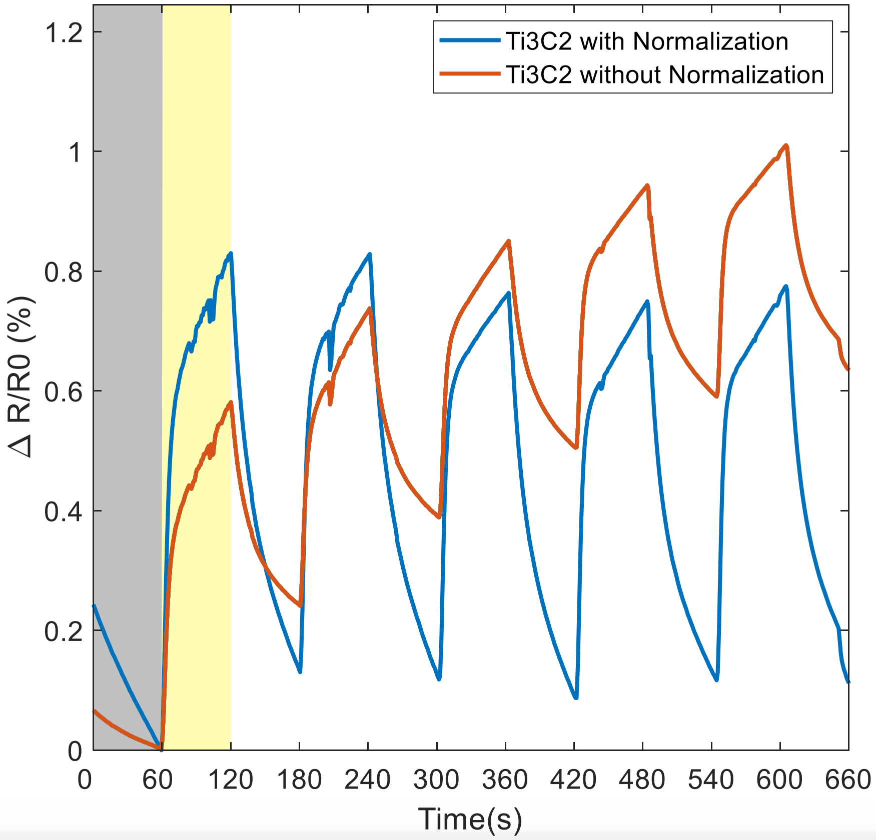
Optoelectronic Characterization

- White light
  - ~350 to 800 nm light
  - 0.85 sun intensity
- Apply constant current
  - Measure voltage
  - Calculate resistance
- Chopped illumination
  - 15 s cycles for pristine glass slides
  - 60 s cycles for FTO



Data Analysis and Manipulation

- Establish baseline using MATLAB
  - Reduces external influences
  - Reduces drift
- Normalize across all cycles
  - ΔR: difference between maxima and minima around change in cycle
  - R_0:initial resistance averaged for all cycles



Measuring the Photoresponse of $Ti_3C_2T_x$ and $Mo_2TiC_2T_x$

Controlled Variables

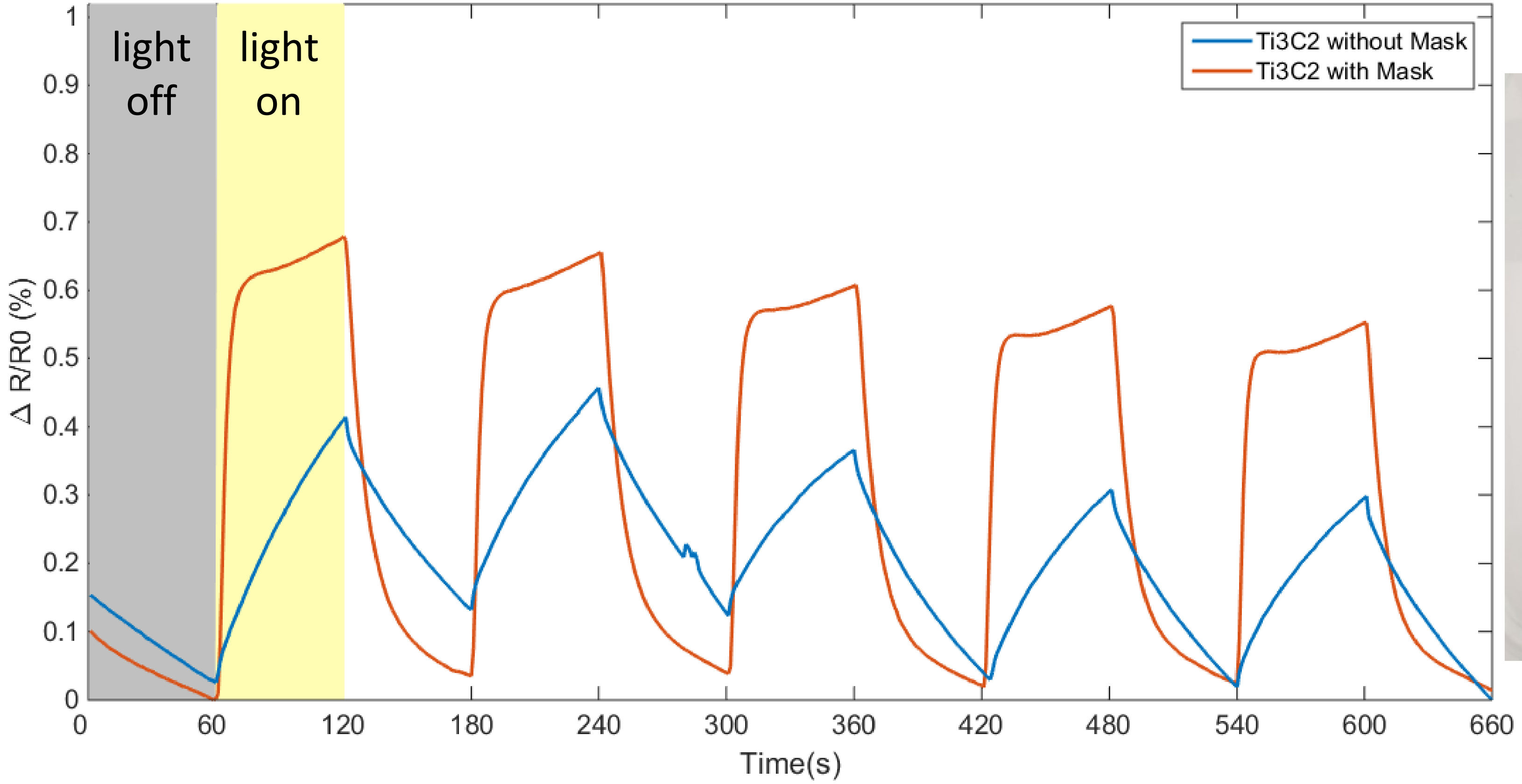
- Substrate preparation
- Light intensity
- Spectrum of light
- Inert environment

Manipulated Variables

- Contact method
- Film thickness
- Presence of Mask
- Atmosphere

Mask Improves Response of 300 Ω $Ti_3C_2T_x$ with Ag

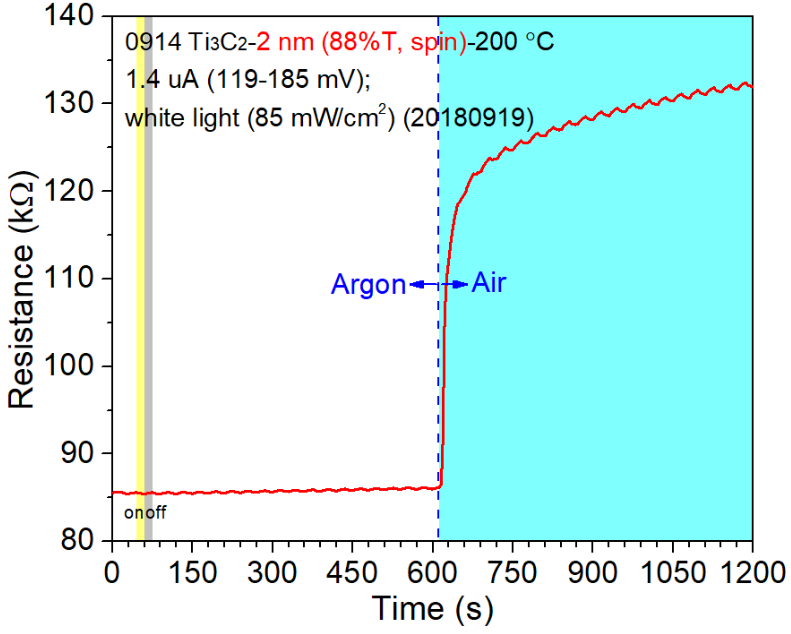
Without Mask



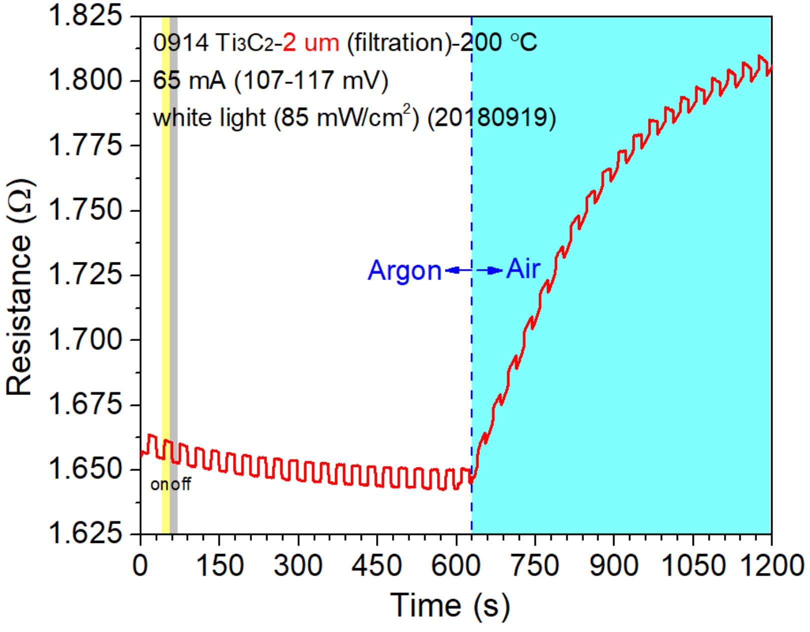
With Mask

Exposure to Air Increases Resistance of $Ti_3C_2T_x$

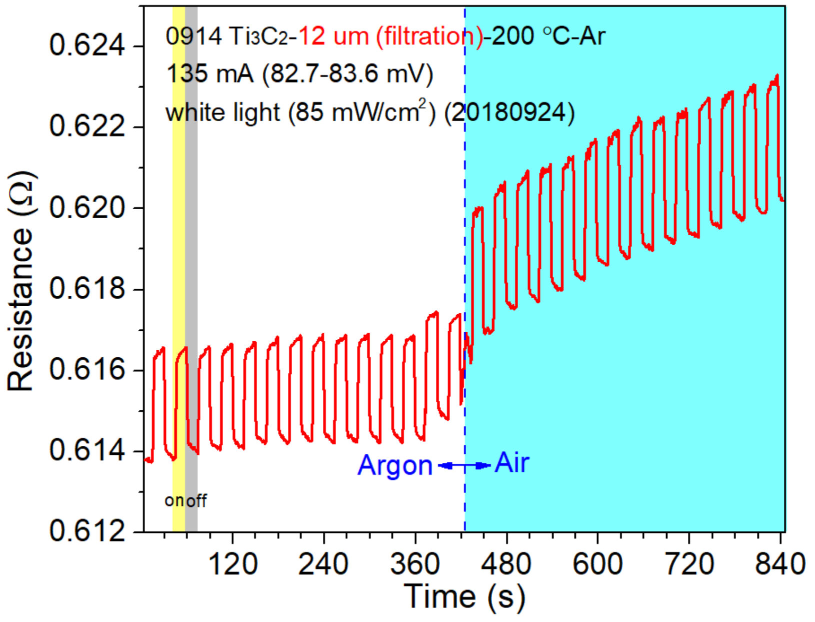
R_0 ~ 85 Ω



R_0 ~ 1.66 Ω

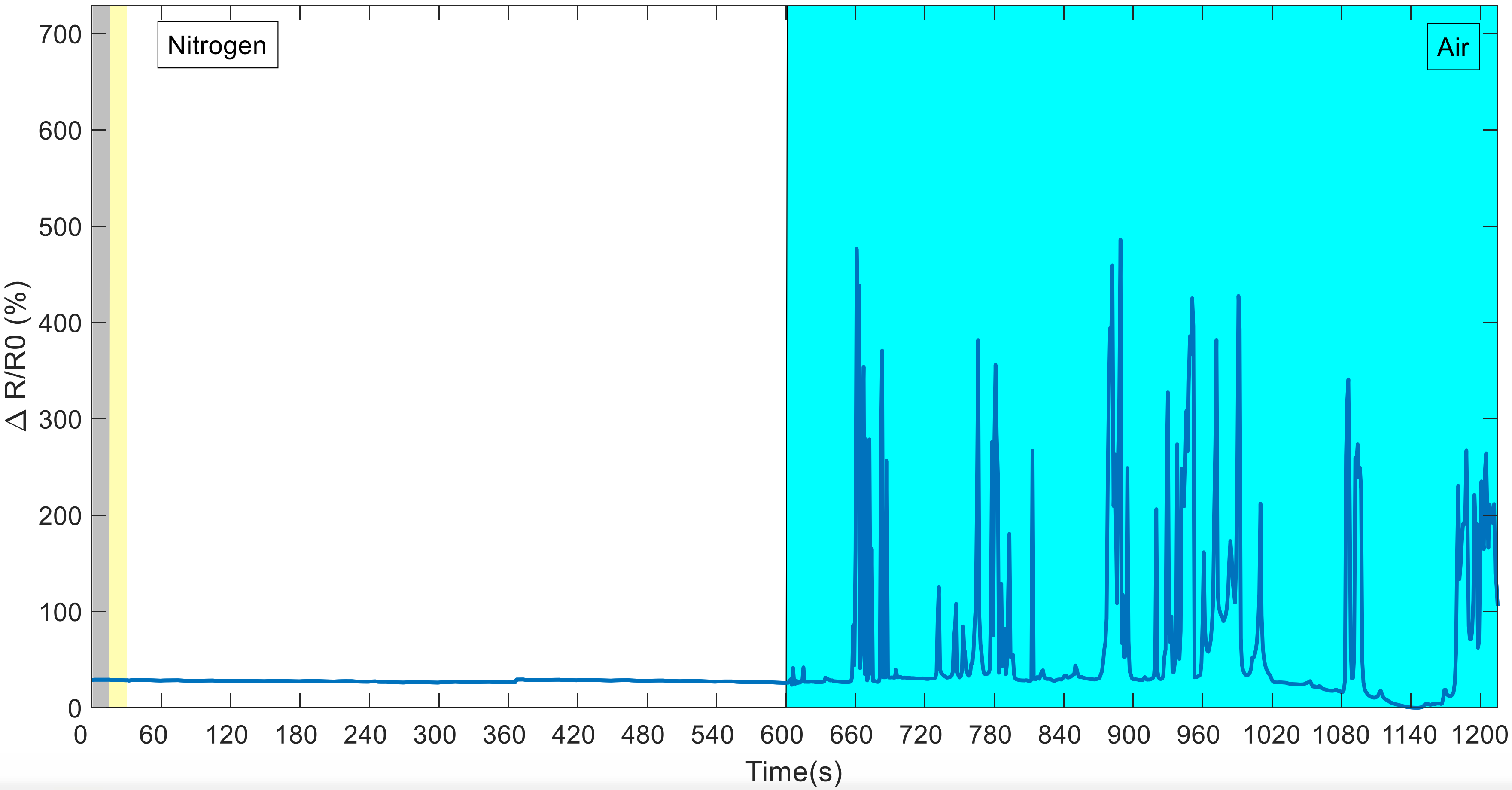


R_0 ~ 0.614 Ω



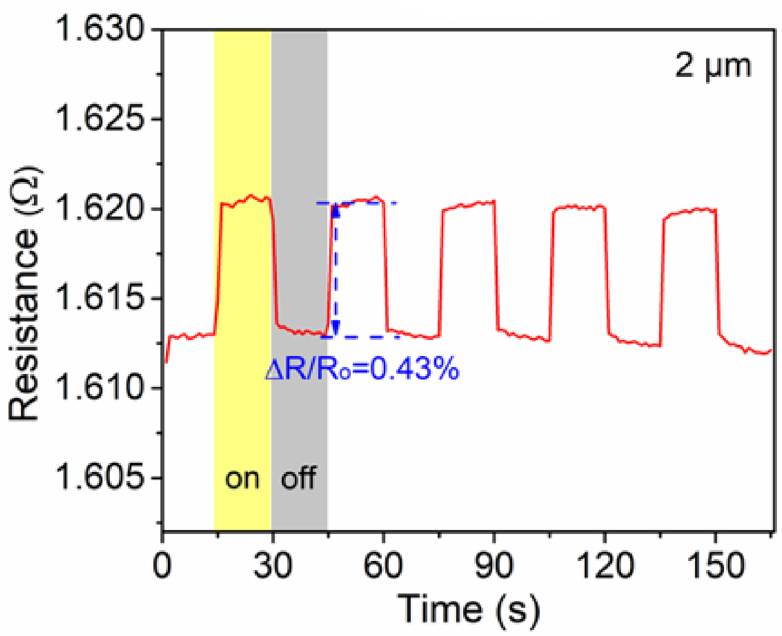
Thanks to Dr. Meiping Zhu for generating figures

Air also Destabilizes R_0 ~ 3,000 Ω $Mo_2TiC_2T_x$

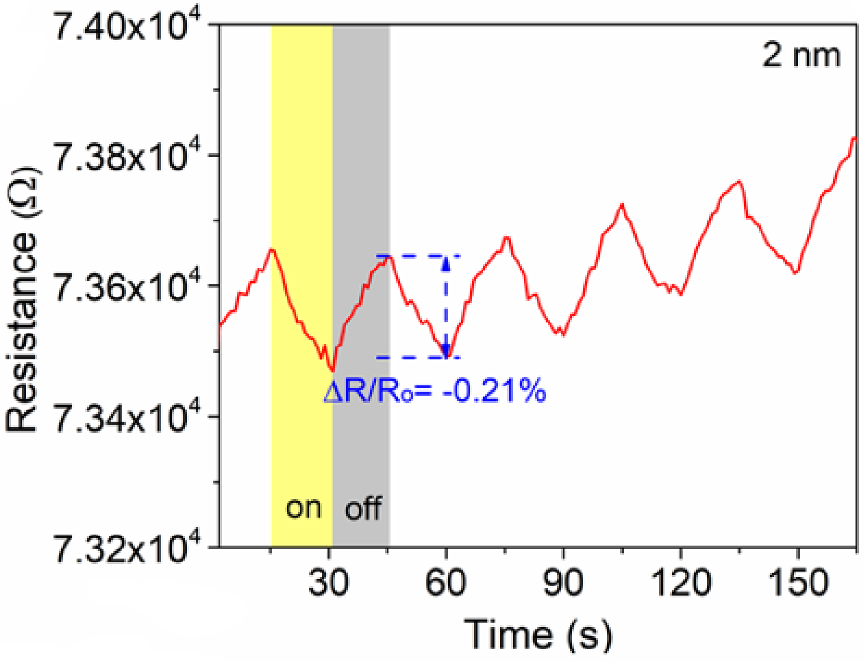


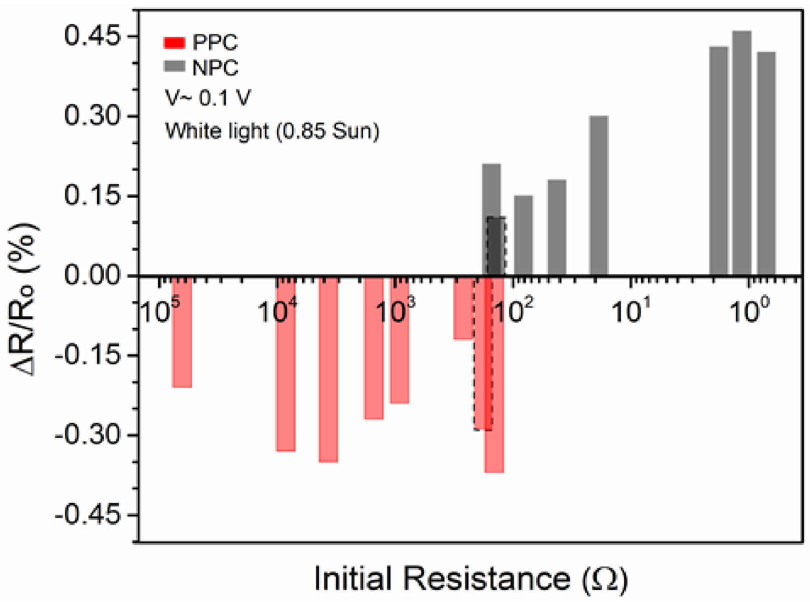
$Ti_3C_2T_x$ on Glass Slides with Ag-Cu Contact Experiences Switch in Photoconductivity

Negative Photoconductivity



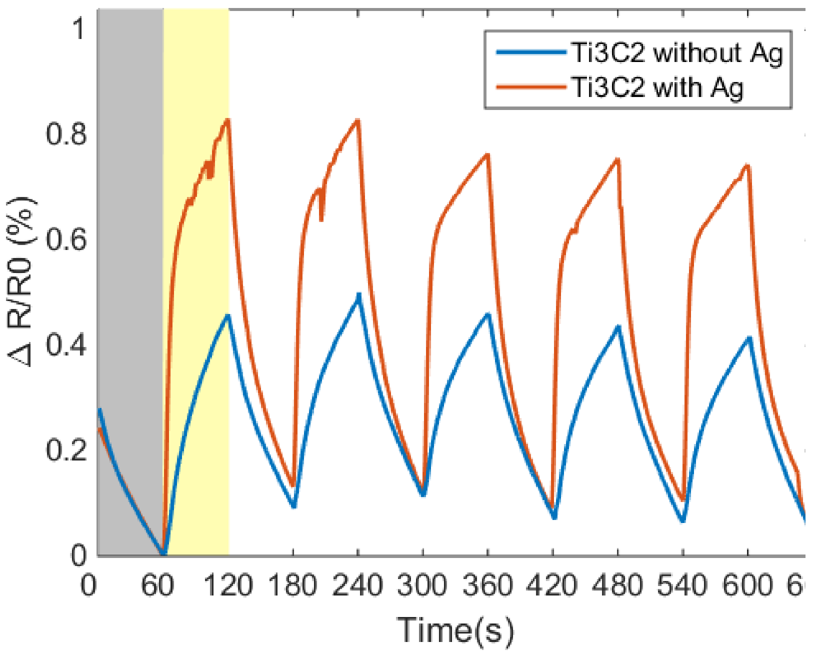
Positive Photoconductivity



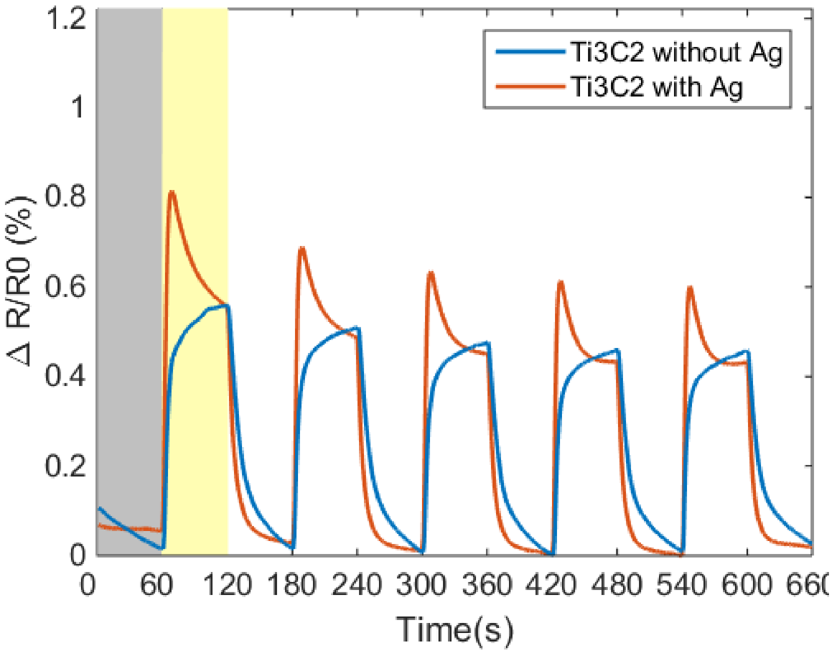


Thanks to Dr. Meiping Zhu for generating figures

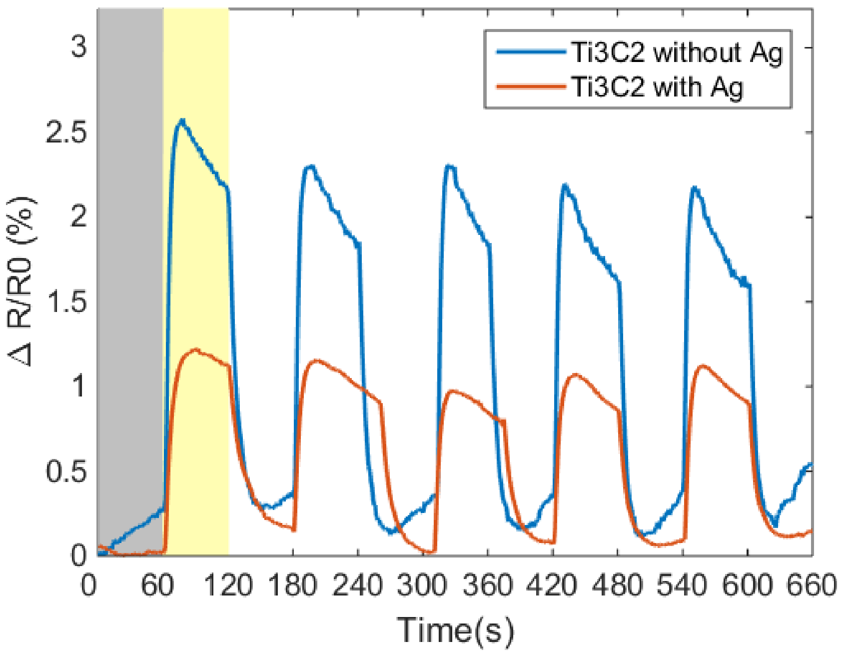
Ag-FTO Contact Influence on $Ti_3C_2T_x$ Lacks Consistency



R_0 ~ 260 – 300 Ω



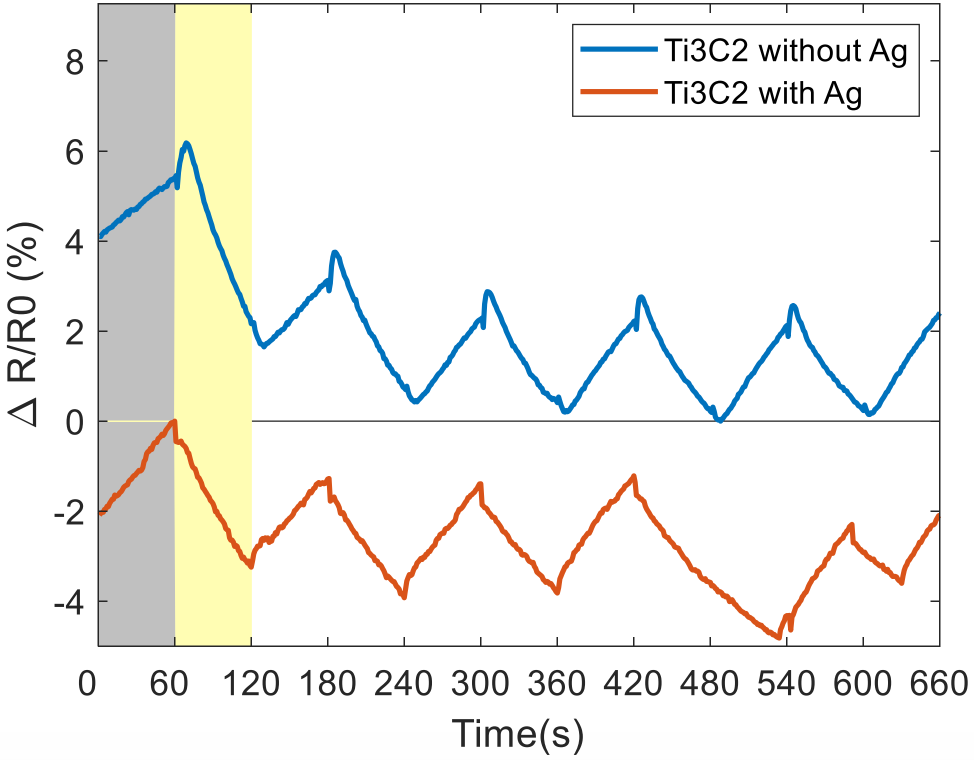
R_0 ~ 800 – 900 Ω



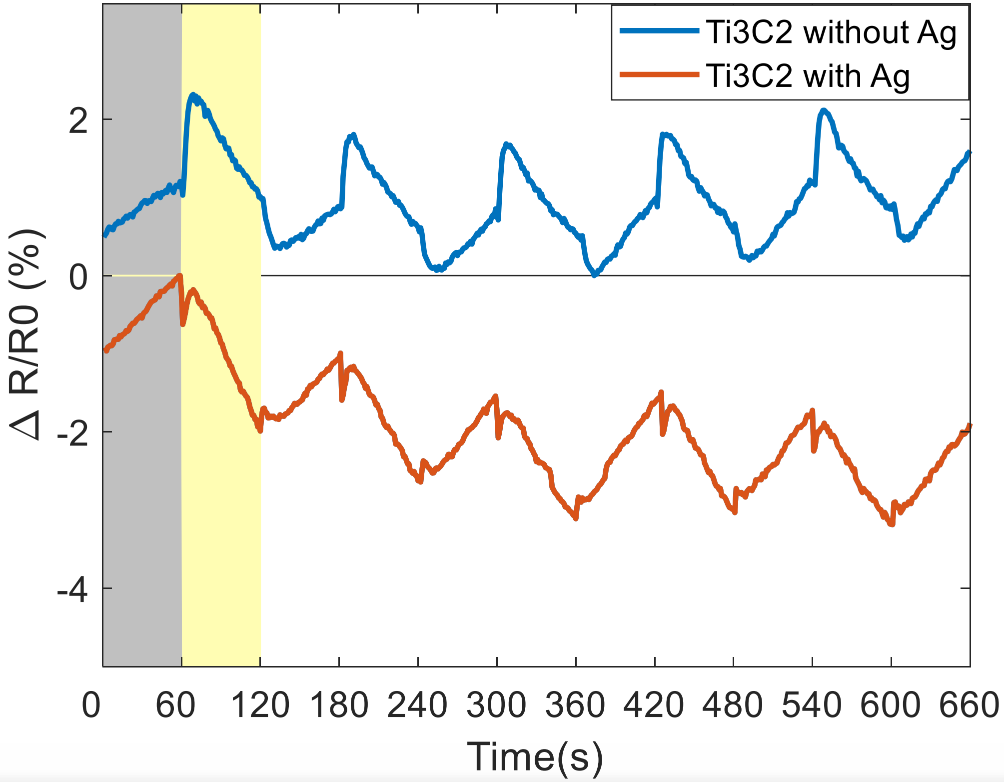
R_0 ~ 2,000 Ω

Ag-FTO Contact Switches Photoconductivity of $Ti_3C_2T_x$

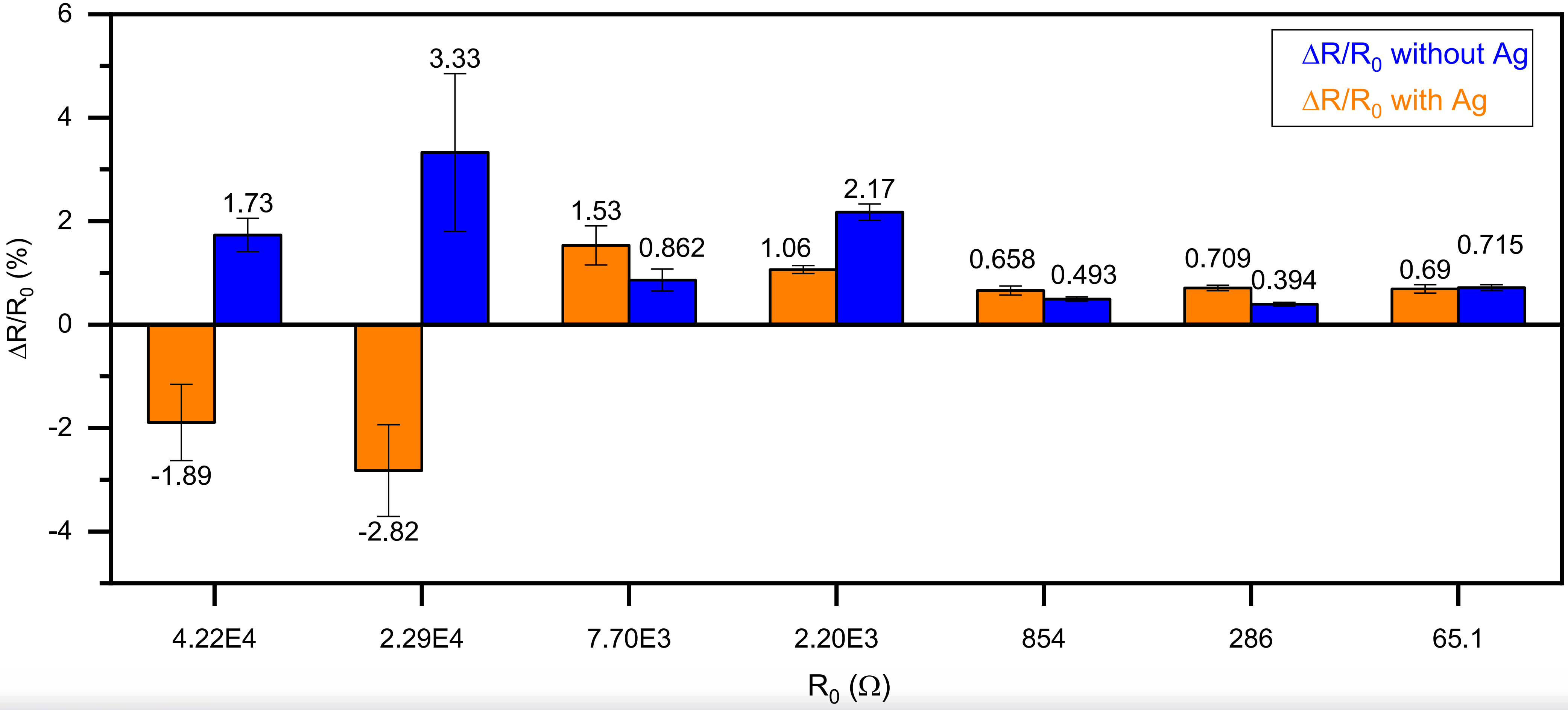
R_0 ~ 19,000 Ω



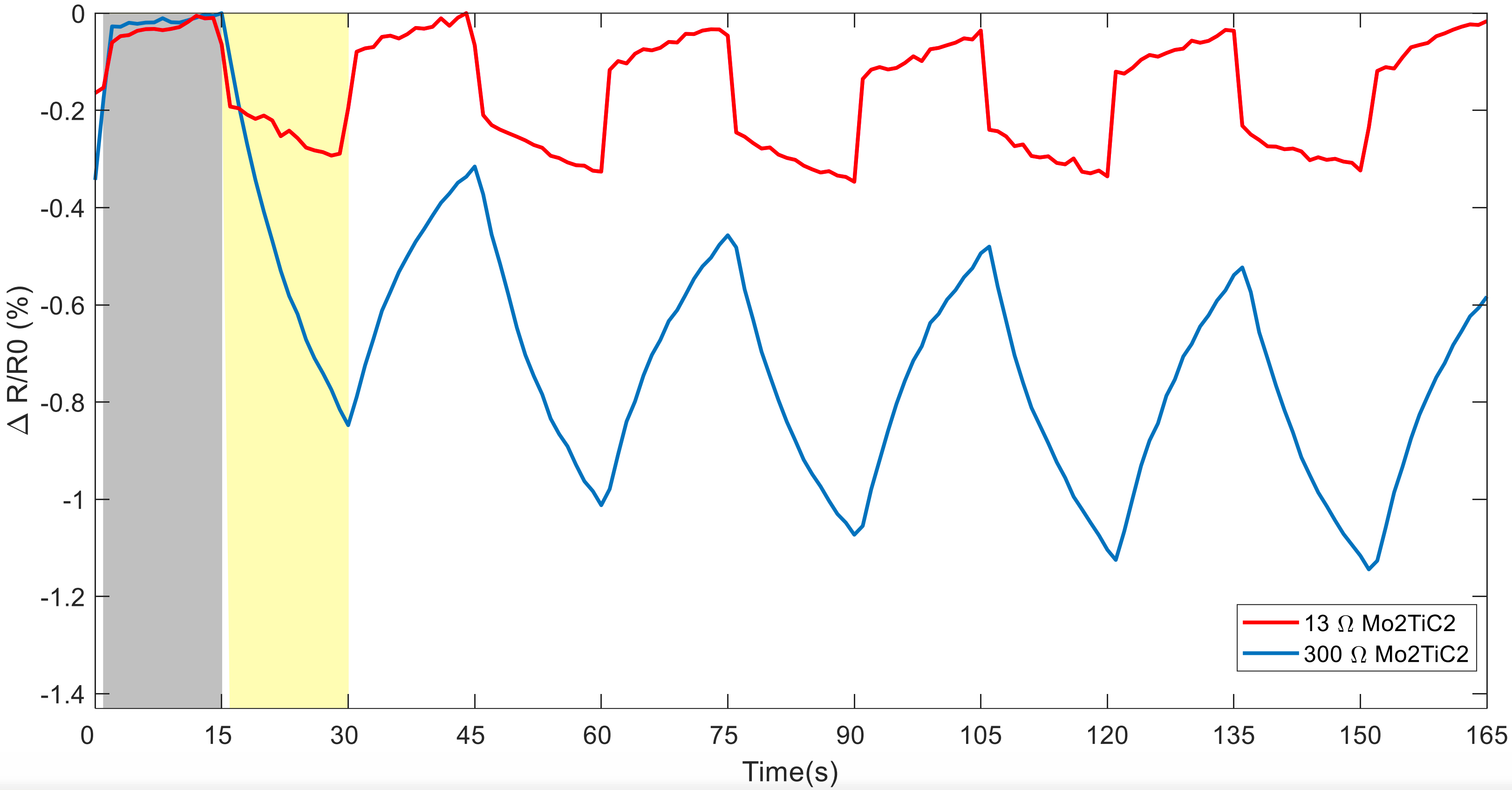
R_0 ~ 45,000 Ω



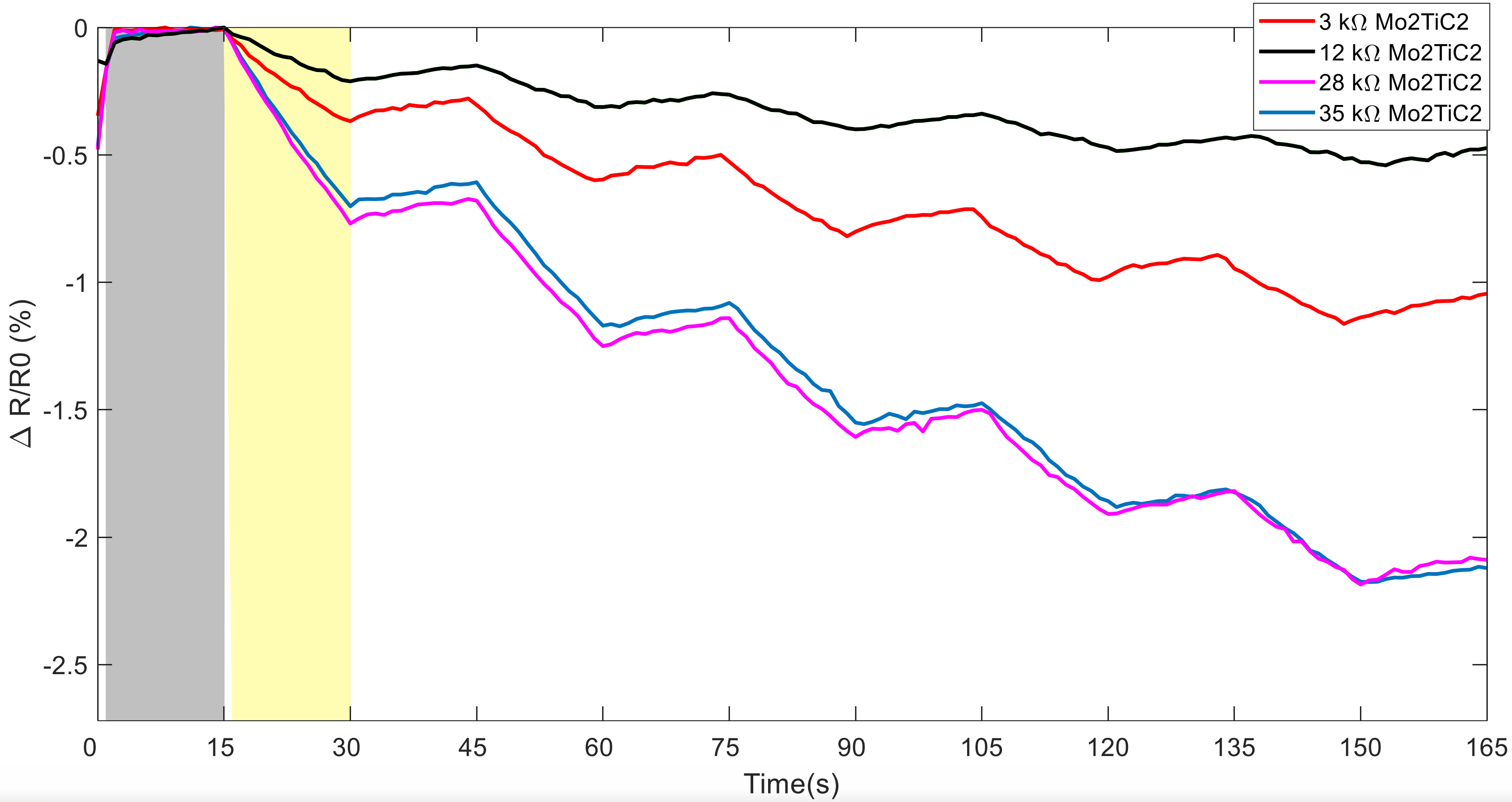
$Ti_3C_2T_x$ Experiences Switch in Photoconductivity upon Ag Contact Application



$Mo_2TiC_2T_x$ on Glass Slides with Ag-Cu Contact Exhibits Positive Photoconductivity



Thinner $Mo_2TiC_2T_x$ on Glass Slides Exhibit Gradual Positive Photoconductivity



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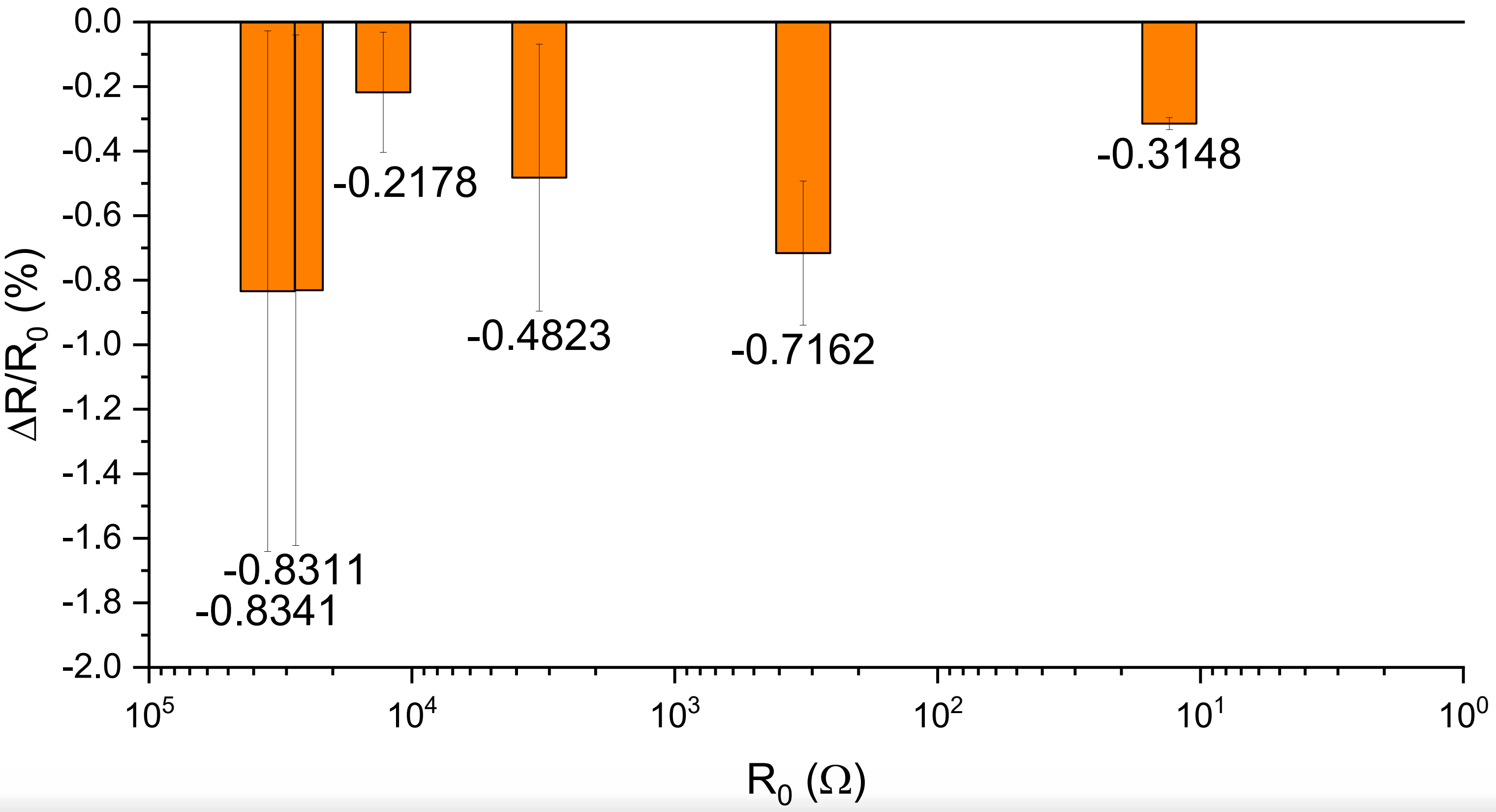
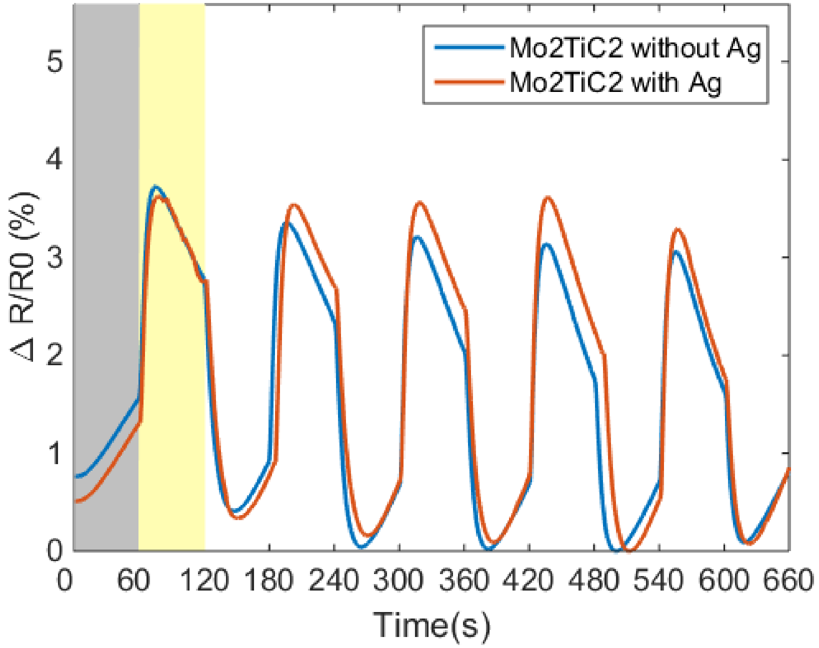
$Mo_2TiC_2T_x$ on Glass Slides Exhibit Consistent Positive Photoconductivity

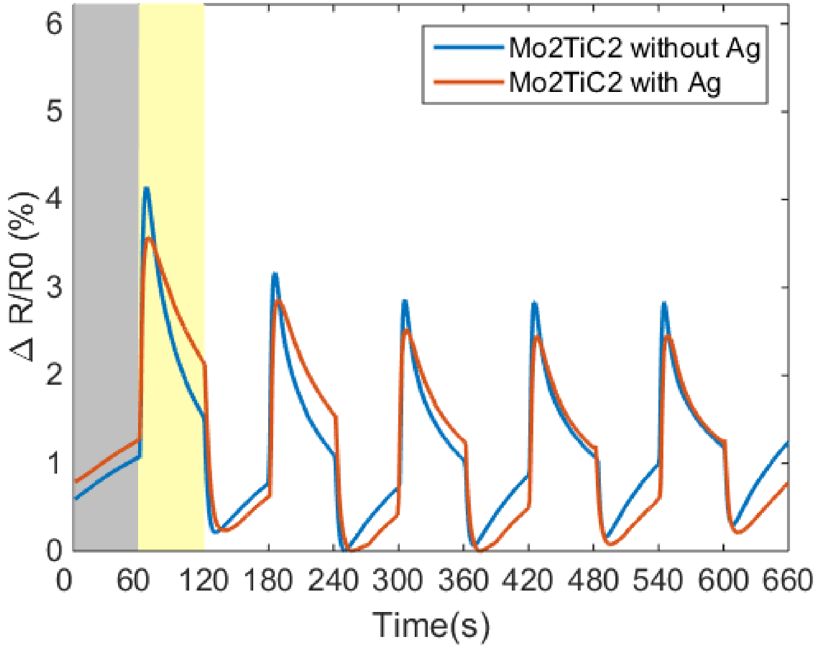


Ag Contact does not Significantly Influence Photoresponse of $Mo_2TiC_2T_x$ on FTO

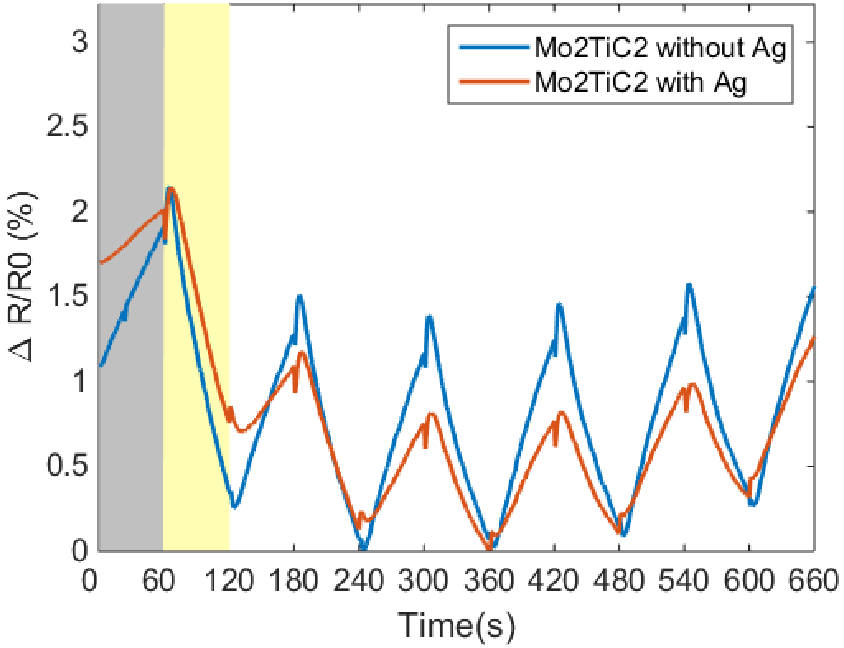
R_0 ~ 120 Ω



R_0 ~ 450 Ω

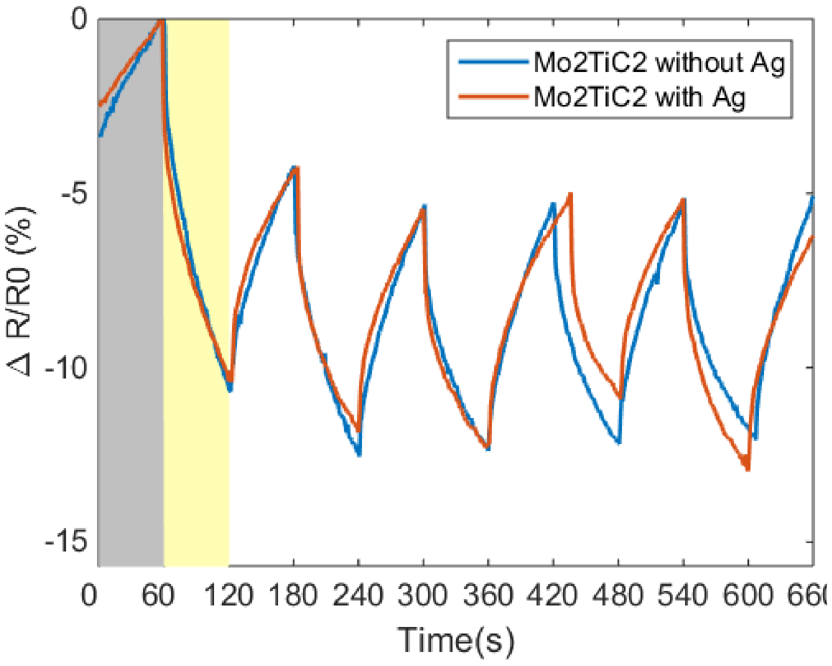


R_0 ~ 26,000 Ω

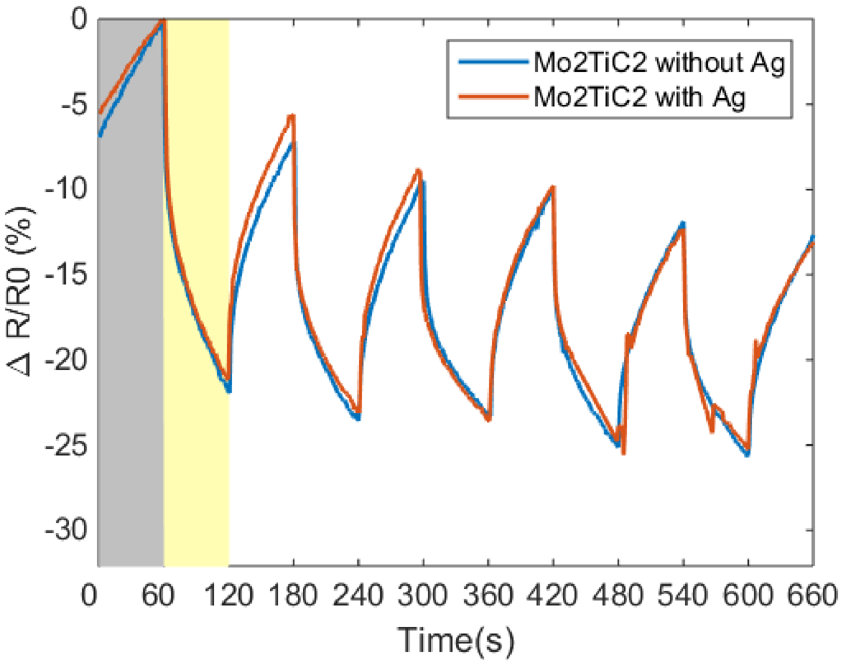


Thin $Mo_2TiC_2T_x$ Films on FTO Exhibit Consistent Positive Photoconductivity

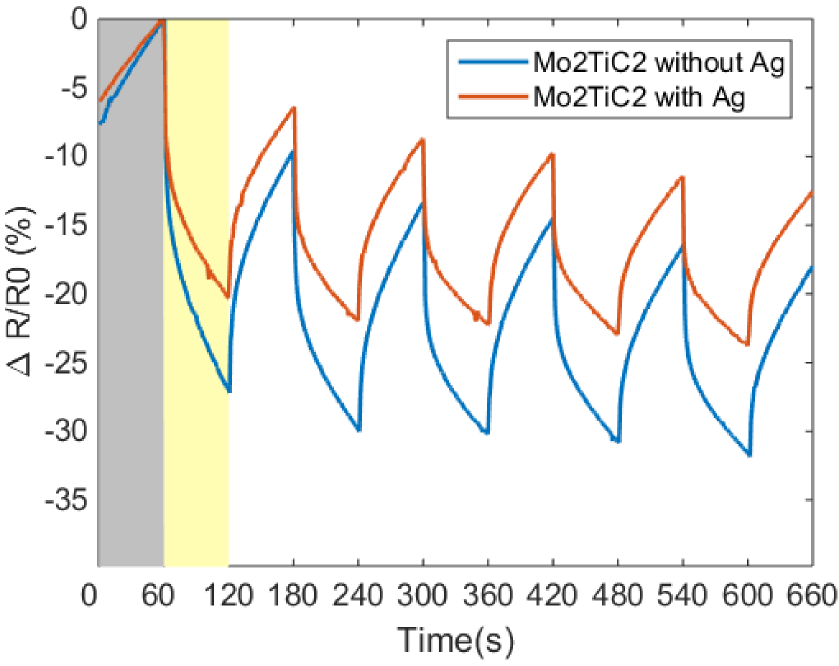
R_0 ~ 320,000 Ω



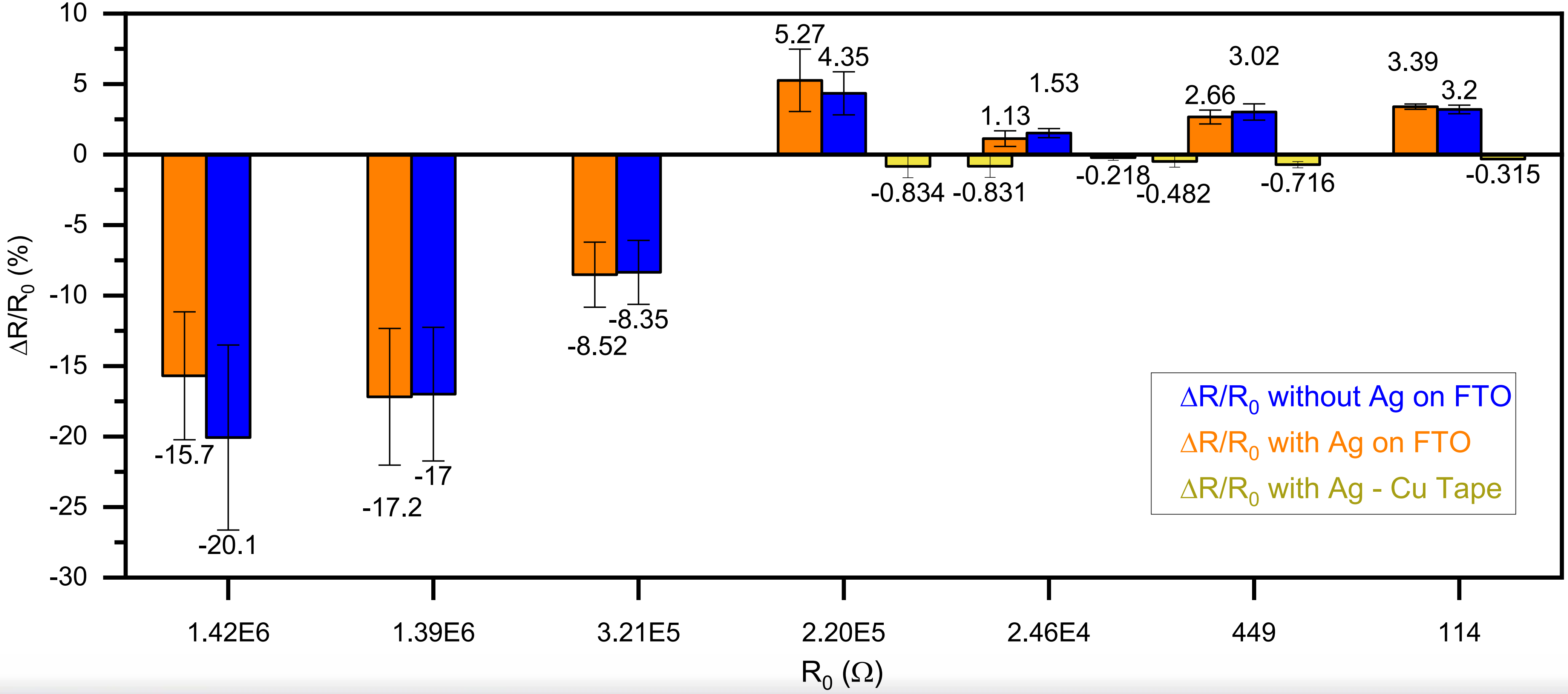
R_0 ~ 1,420,000 Ω



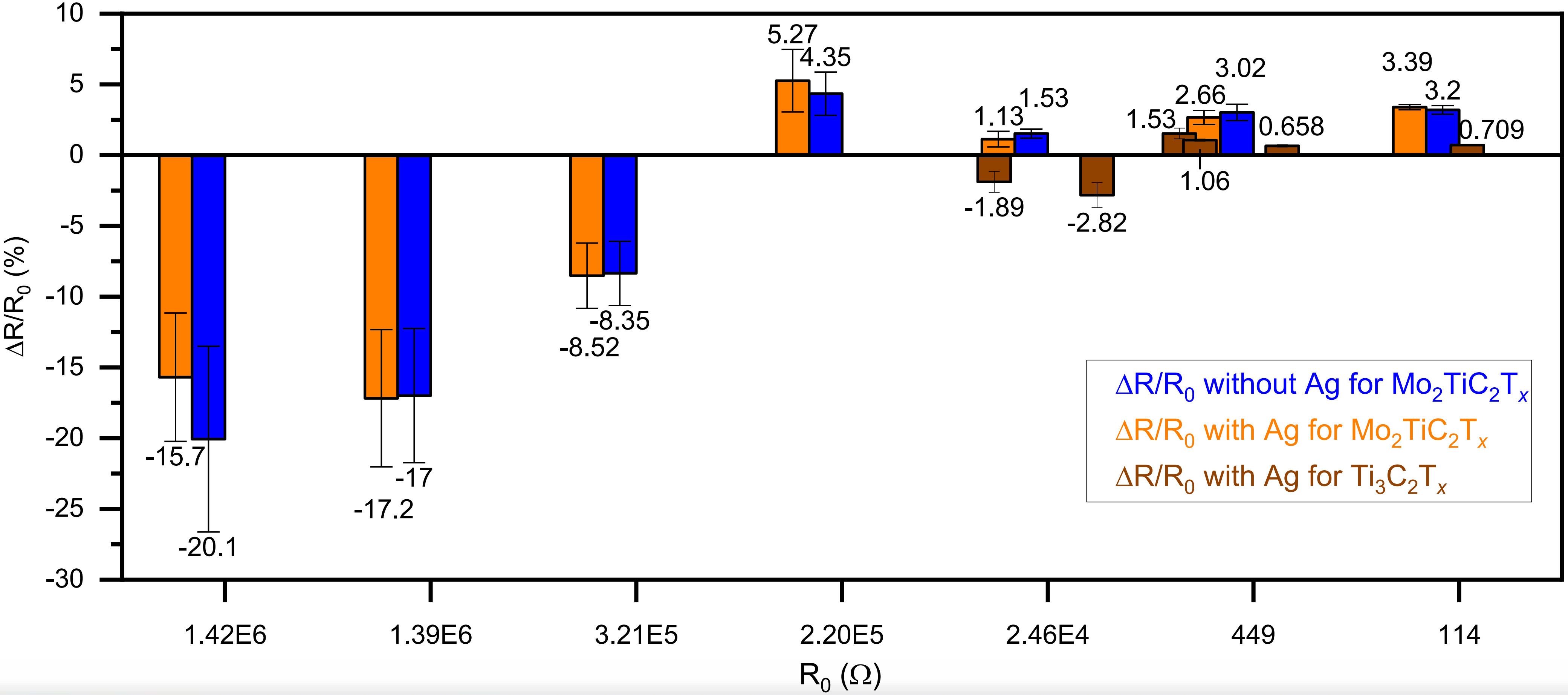
R_0 ~ 1,450,000 Ω



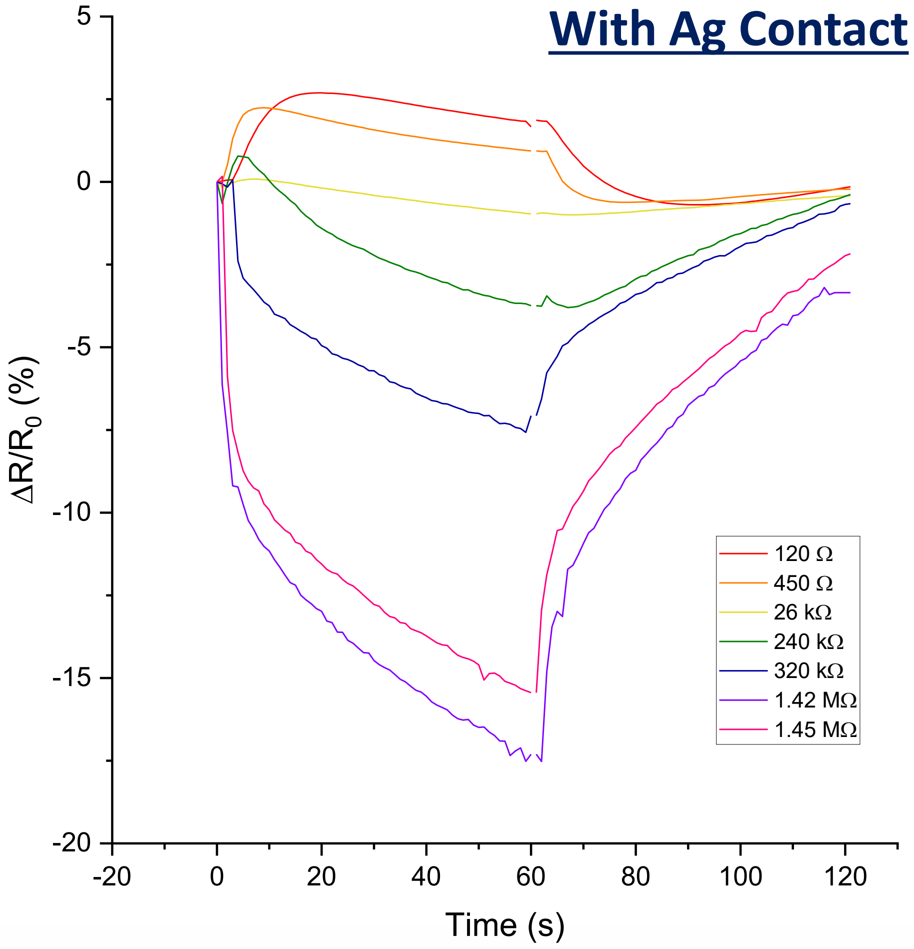
Contact Method Determines Measured Photoconductivity of $Mo_2TiC_2T_x$

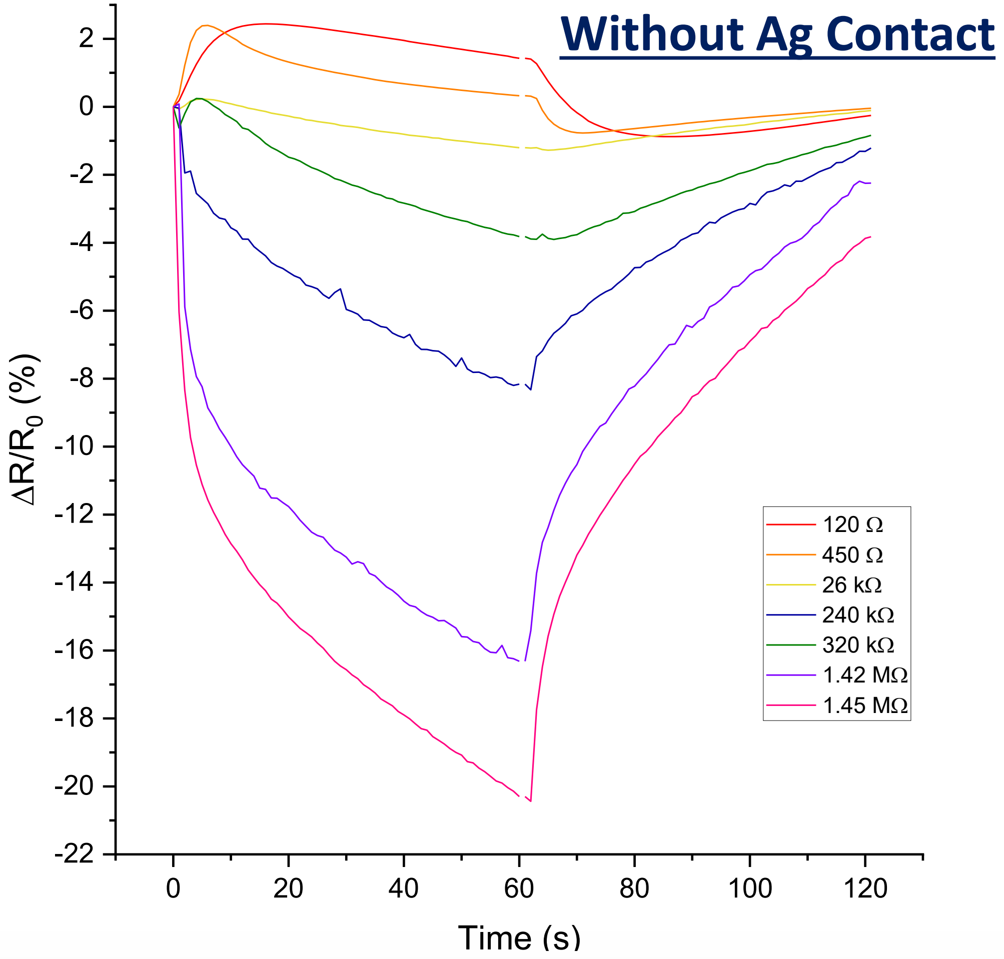


$Mo_2TiC_2T_x$ Experiences Larger Change in Resistance than $Ti_3C_2T_x$

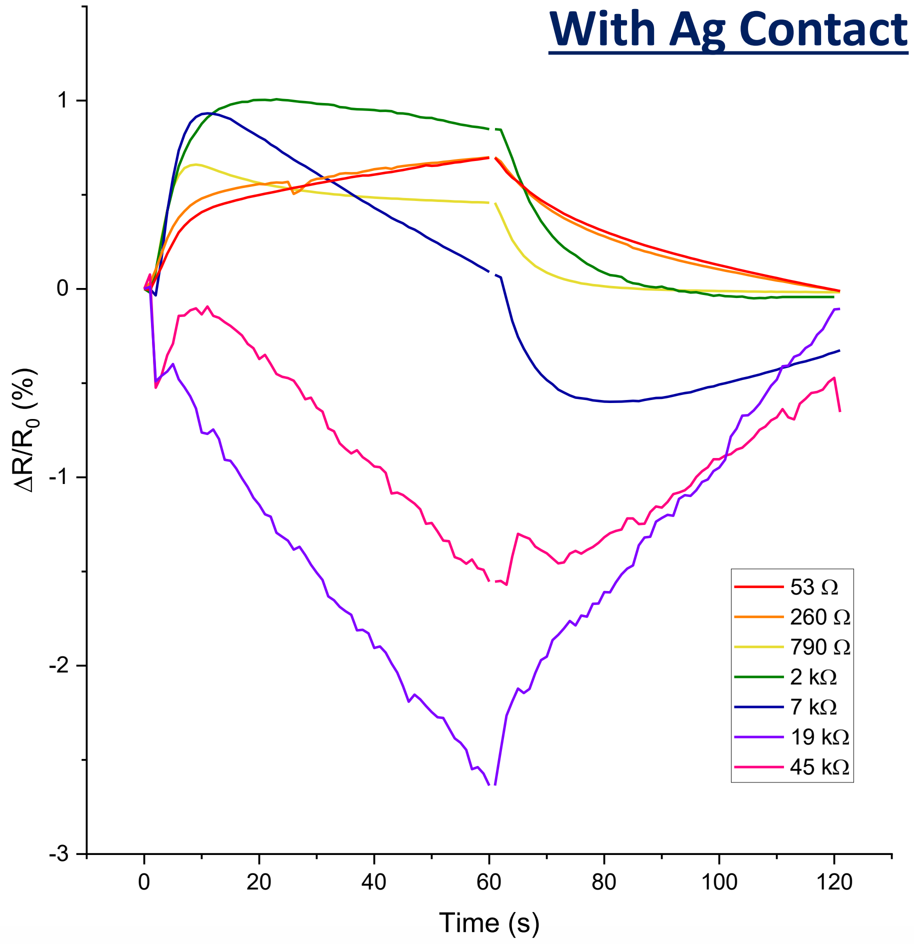


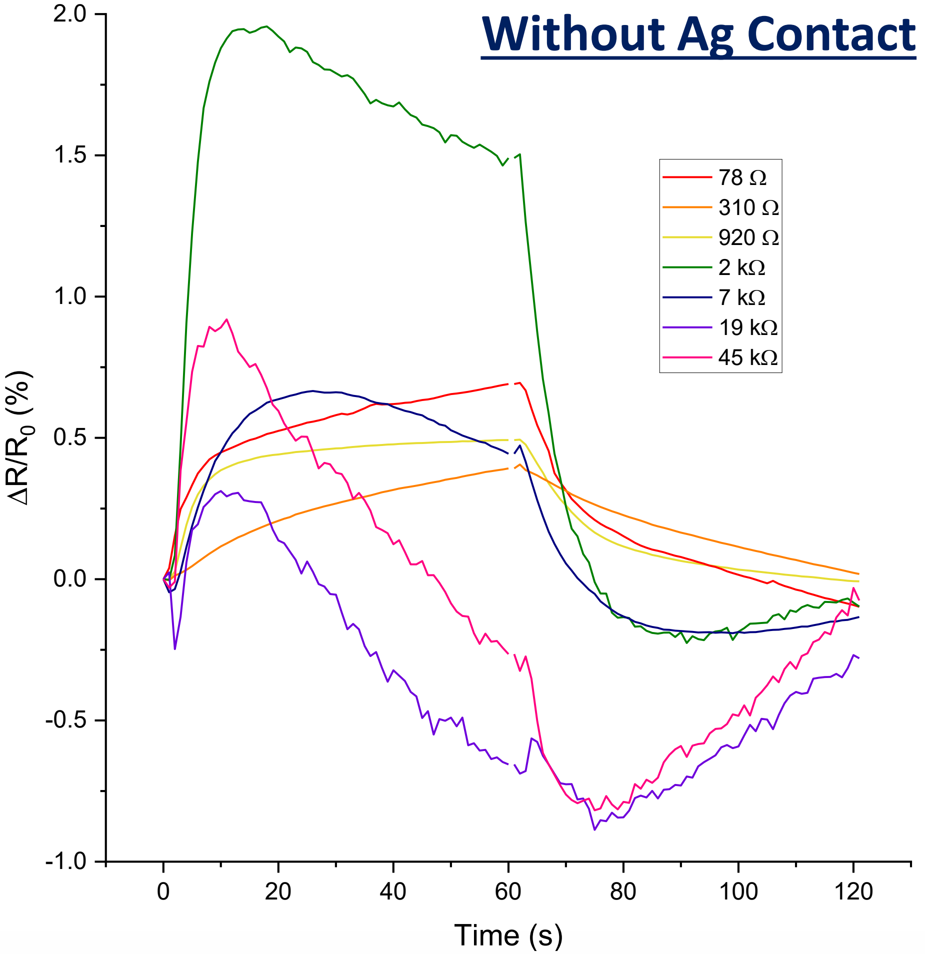
$Mo_2TiC_2T_x$ Shows Increase in Resistance Change with Decreasing Thickness





$Ti_3C_2T_x$ Photoresponse Lacks Trend with Decreasing Thickness





Conclusions

- Best practices:
  - Mask inactive area during optoelectronic characterization
  - Use patterned FTO or other transparent conducting oxide as contact method
  - Maintain inert environment

- Ti_3C_2 (without Ag contact): negative photoconductivity
- Mo_2TiC_2: switch from negative to positive photoconductivity

Future Work

- Probe intrinsic optoelectronic behavior of free-standing films
- Measure wavelength-dependent photoresponse of $Mo_2TiC_2T_x$ to verify positive photoconductivity
- Utilize terahertz spectroscopy to disentangle thermal and electronic influences
- Vary substrates to aid in heat transfer

Questions?

Thank you!