Cold Plasma Treatment of Metal Organic Frameworks for Carbon Capture Applications

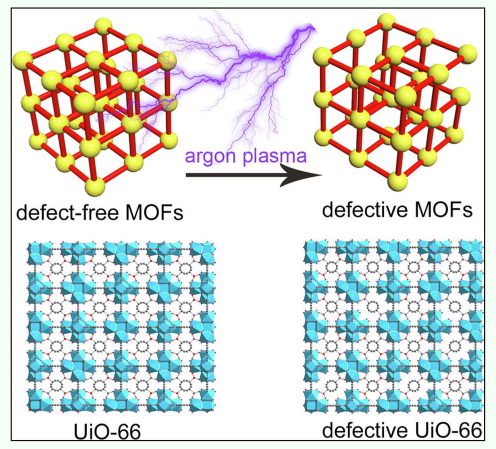
Olivia Walsh[1], Silvi Petrosyan[1], Austin Jones[1], Thi Nguyen[2], Nina Abramzon[1]
Physics and Astronomy[1], Chemical Engineering[2]
California State Polytechnic University, Pomona, Pomona, CA 91768

Abstract

Throughout recent centuries, technological advancement has led to an increasing issue in climate change, substantially due to carbon dioxide (CO2) emissions. It is imperative that CO2 emissions and atmospheric concentrations are reduced. Both Carbon Capture and Storage (CCS) and Direct Air Capture (DAC) have this potential, by capturing carbon at the emission source or directly removing it from the atmosphere. However, the widespread employment of these methods is limited by high costs and low efficiencies. Using materials with already high adsorption and separation ability could directly lower this cost. Metal-organic frameworks (MOFs) are crystalline compounds under exploration for use in CCS and DAC. These materials can be tuned for specific purposes; some research has shown that plasma treatment can be used to introduce a specific type of defect into the structure, increasing adsorption abilities without affecting the MOF's overall structure or stability. Here, we investigate the effects of atmospheric plasma surface treatment on the MOFs UiO-66 and UiO-67. The MOF is characterized before and after plasma treatment with various characterization techniques to observe changes in qualities such as wettability, stability, mass, color, surface area, and defects. In the project's second phase, the use of a lab-made atmospheric plasma reactor will be investigated as well. The experimental results will add to the communal understanding of the effects of cold plasma treatment on MOFs relating to carbon capture and, furthermore, may suggest a more cost effective and feasible method for MOF modification using the laboratory made plasma reactor.

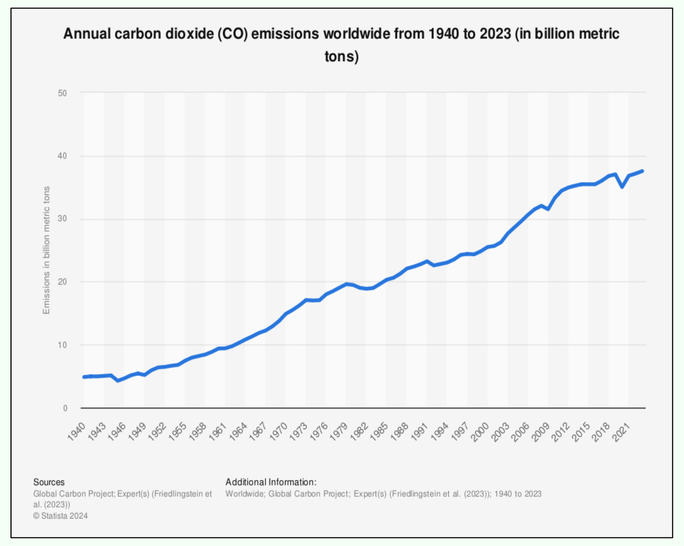
Background

MOFs
- Inorganic metal nodes connected with organic linkers
- Material with exceptionally high porosity & surface area
- May be chemically altered without changing the underlying topology, greater accuracy than other solids
- Increasing porosity and number of active sites may increase the carbon capturing
- Have specific surface area of just over 1000 m^2/g



PLASMA
- Fourth state of matter
- Gas energized until electrons freed from atoms or molecules
- Electrically conductive, internally interactive, and responsive to electromagnetic fields
- High concentrations of chemically active species at low temperatures
- Various applications, including surface cleaning, surface activation, and modification of materials

CARBON CAPTURE
- CCS: capturing CO_2 emissions at the source, such as at a power plant and transporting it underground for storage.
- DAC: the technique used to capture CO_2 in the atmosphere.
- To address global climate crisis, it is imperative to reduce CO_2 emissions
- CCS and DAC limited by costs of capture process



Methodology

PREPARATION
- MOF suspended in dimethylformamide (DMF) to known concentrations
- Solution deposited on mica, metal coupon, or glass slide. Hotplate used to dry deposited sample (60°C)

PLASMA TREATMENT
- Surfx Atmospheric Oxygen Argon Plasma System used to perform surface-treatment of samples

ATOMIC FORCE MICROSCOPY (AFM)
- Imaging method that can visualize the topographic properties of a surface at the nanoscale
- Tip scans across the surface, creates topographical map of surface
- Lose-range interactive forces between the tip and the surface
- Feedback loop utilized to maintain a constant interaction force as the surface is scanned

SURFACE ENERGY – WATER CONTACT ANGLE MEASUREMENT
- Goniometer used to measure contact angle of water droplets placed on double treatment versus single treatment metal coupon.
- Contact angles expected to decrease after plasma treatment

WATER DROPLET SURFACE AREA COVERAGE
- Image analysis (python), generates pixelated ratio of surface coverage and the metal coupon
- Expected surface coverage consistent with 100% absorption rate of deposited and double treated UiO-67 area on metal coupons

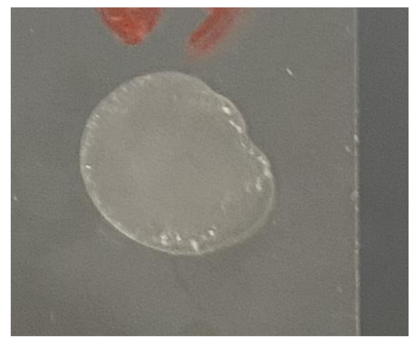
MASS & COLOR
- Mass expected to decrease, and color expected to change to a yellow after treatment

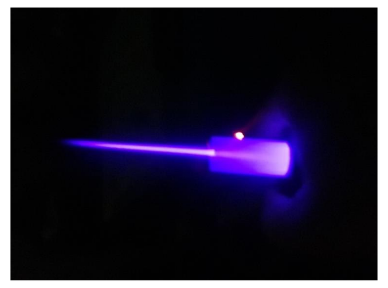
RAMEN SPECTRA
- Light beam dispersed off sample, creating unique "fingerprint" of reflected wavelengths
- Difference between incident and reflected angle of photon called Raman Shift
- Treated samples should be expected to see a larger Raman Shift

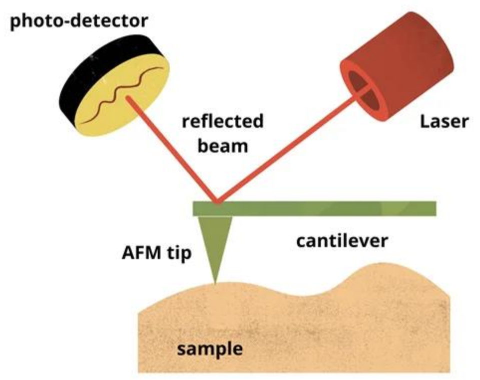
POWDER XRAY DIFFRACTION (PXRD)
- X-rays diffract off crystalline structures and specific angles that yield varying intensities
- Intensities vary depending on spacing within crystal lattice
- Non-uniform peaks in reflected intensity indicate defects within MOF after plasma treatment

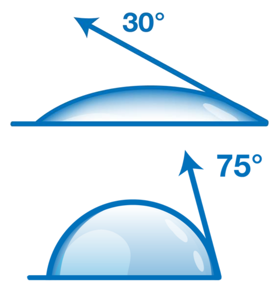
UV-VISABLE DIFFUSE REFLECTANCE SPECTRA (UV-DRS)
- Measures levels of reflected light at varying wavelengths from sample
- Lower levels of absorbance expected with plasma treated samples

BRUNAUER- EMMETT-TELLER (BET) ANALYSIS
- Measures how much of a gas goes through physisorption to determine surface area of sample
- Expect to see increased surface area expected after plasma treatment





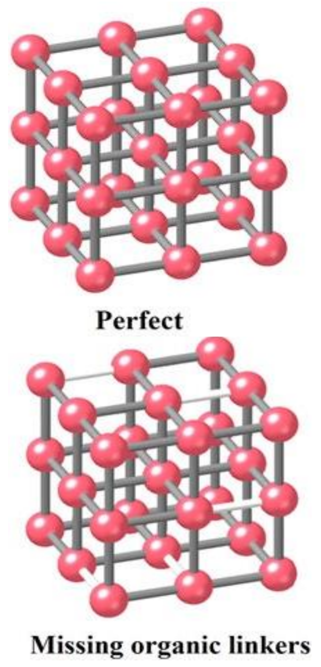




https://www.brighton-science.com/what-is-contact-angle

https://www.sciencedirect.com/science/article/abs/pii/S030626192031072

Expected Results



https://www.frontiersin.org/articles/10.3389/fchem.2021.673738/full

Missing Linker Defects:
- Presence of defects increase presence of coordinatively unsaturated metal sites (CUMs)
- Removal allows more molecule interaction with CUMs, which increase active sites for adsorption
- Argon plasma treatment shown to effectively create these defects
- Decreased mass, yellow color expected with defect formation
- Decreased water contact angle expected with defect formation
- AFM imaging to confirm integrity of structure remains after treatment as expected.

Results

AFM IMAGING

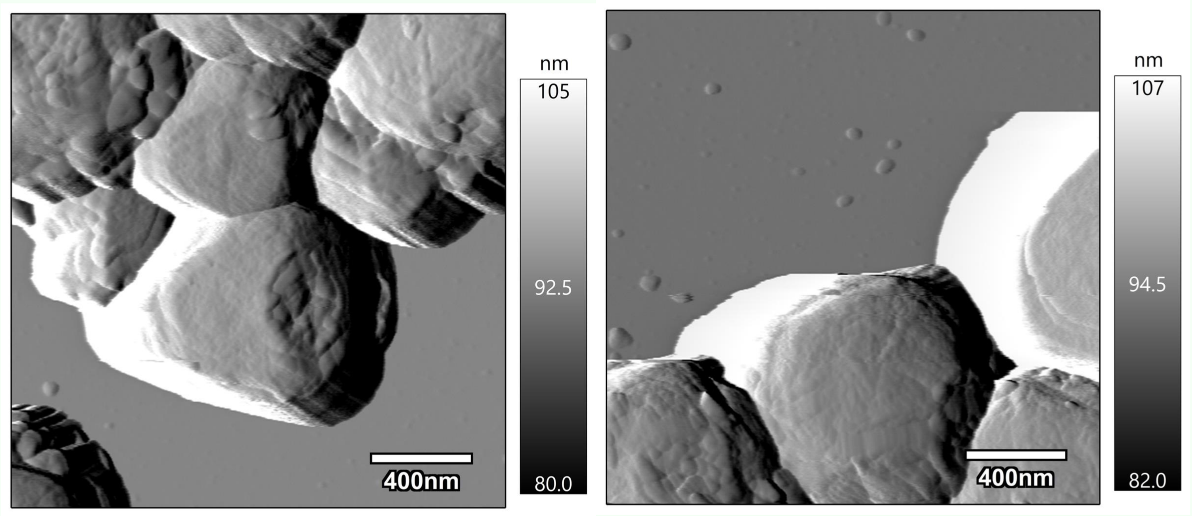


Fig. 1. AFM images of UiO-67. Taken in air using Asylum Instruments AFM in Tapping Mode.

DROPLET SURFACE AREA MEASUREMENTS

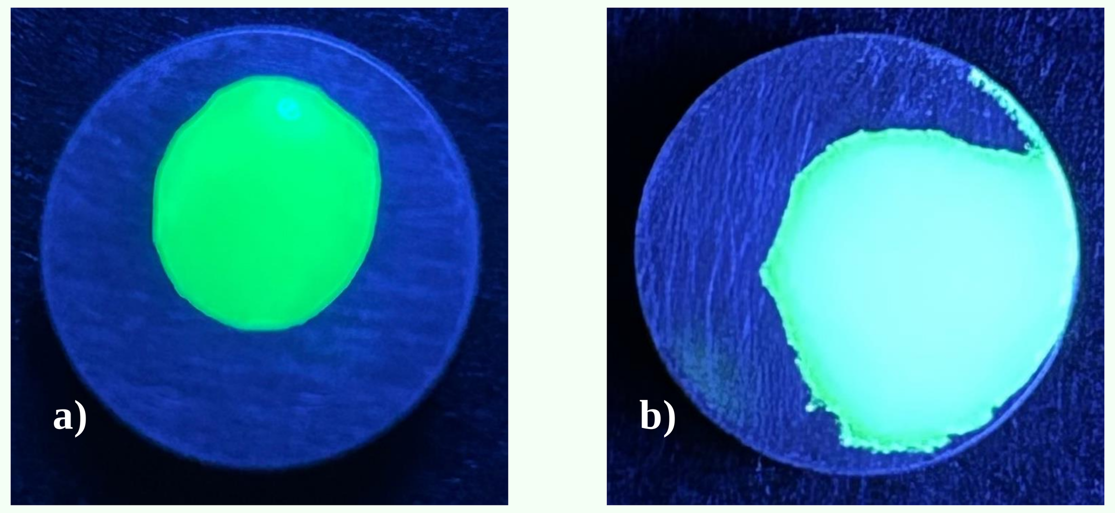


Fig. 2. Images of water droplets on metal coupons with UiO-67 deposited on surface. **a)** untreated UiO-67 **b)** plasma treated 2min UiO-67

Trials	Control (cm^2)	Treated (cm^2)
1	0.421	0.736
2	0.360	0.677
3	0.437	0.540
4	0.378	0.389
Average	0.399	0.359

Table 1: Surface area coverage after 2 minutes treatment

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