Fabrication of metal-organic framework thin films for luminescent sensing applications

NATIONAL ENERGY TECHNOLOGY LABORATORY

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Research & Innovation Center

Presented to the 2024 Central Regional Meeting of the American Chemical Society

November 7th, 2024

Disclaimer

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Authors and Contact Information

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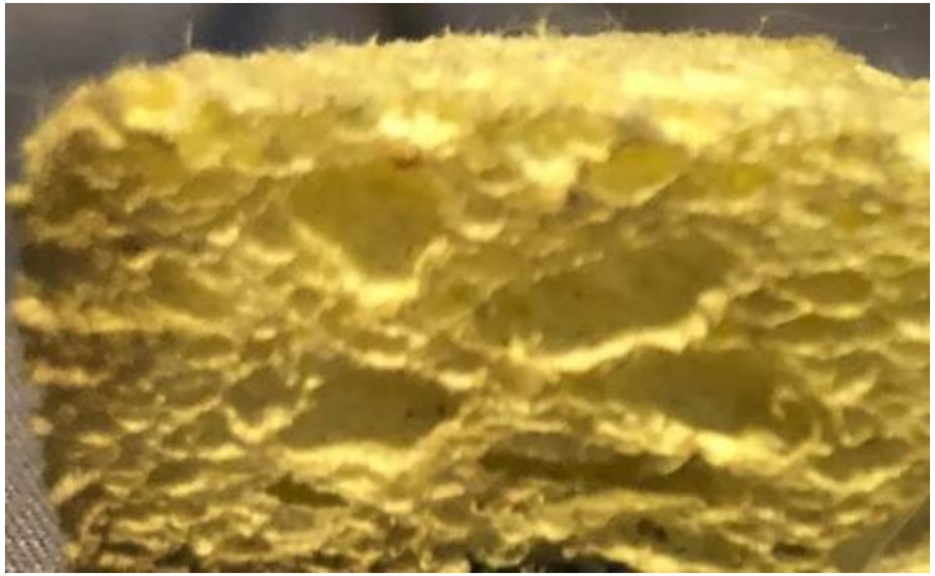
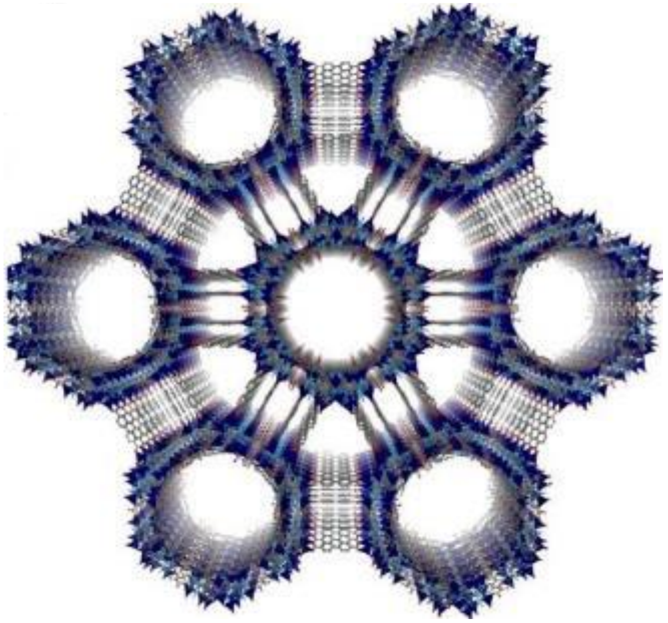
What is a MOF?

- Combination of **metal centers** connected by **organic linker**(s)
- Ordered structure, often **highly porous**
- Nearly a **limitless number** of variables to tune properties: metal centers, linkers, reaction conditions, etc.
- Applications in gas storage/separation, sensing, catalysis, drug delivery, emission displays, and many others

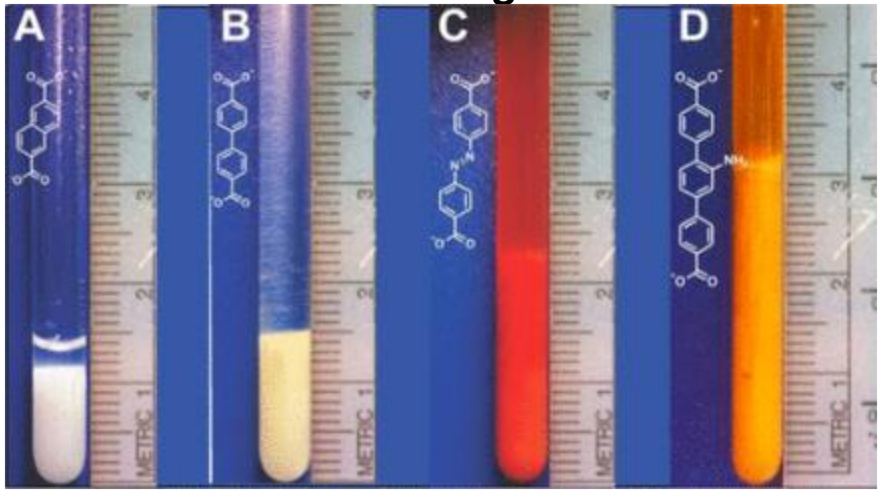




DOI: 10.1038/ncomms1618

Synthetic Methods for Tuning MOF Structure

Linker Exchange

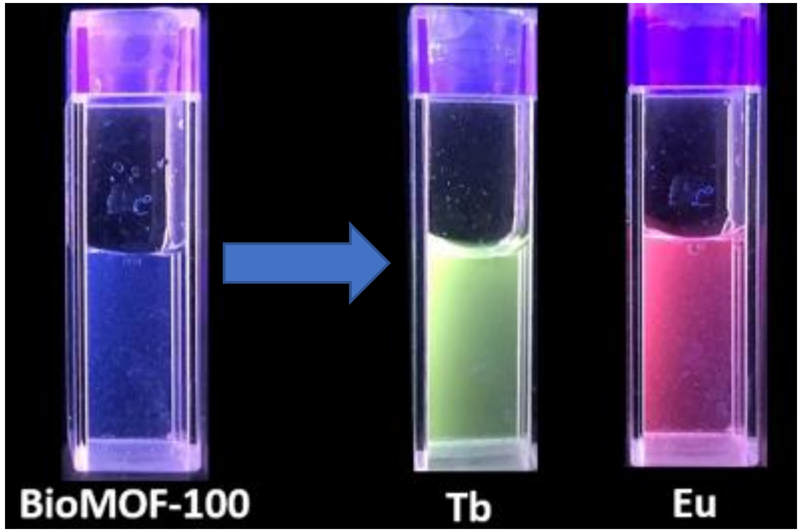


DOI: 10.1021/ja403810k

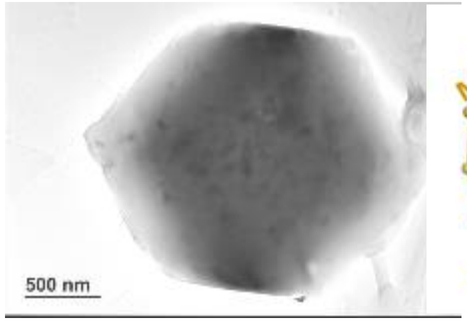
Cation Exchange

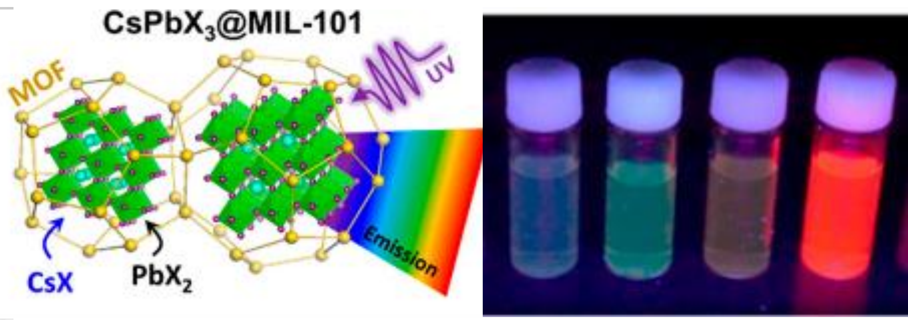
DOI: 10.1021/ja072871f

Host-Guest Interactions



Composite Materials



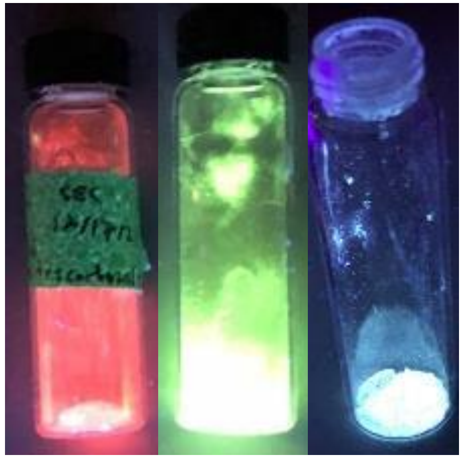


DOI: 10.1021/acs.chemmater.1c01386

DOI: 10.1021/acs.jpclett.9b00510

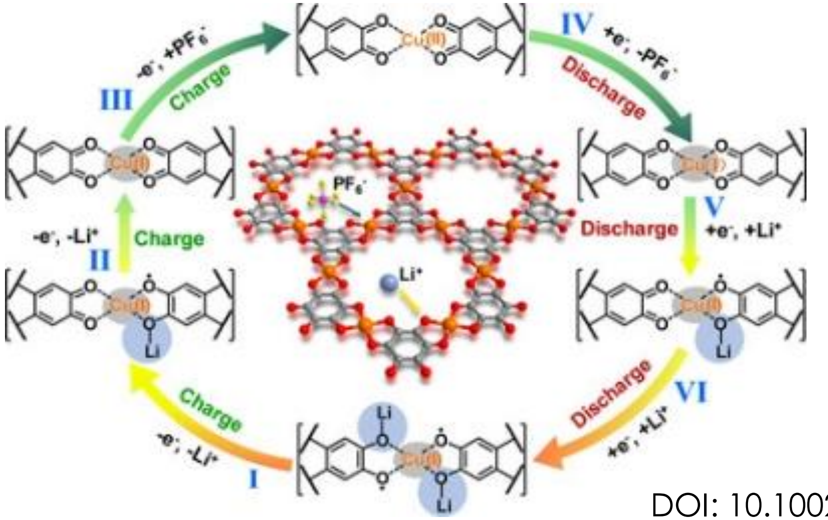
…Which Gives Rise to Exciting Properties

Luminescence



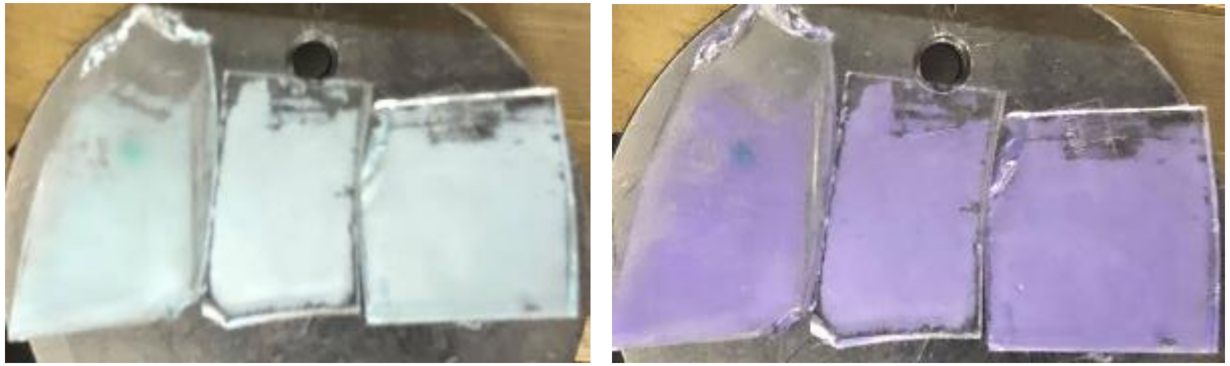
DOI: 10.1016/j.cej.2019.03.255

Redox Behavior



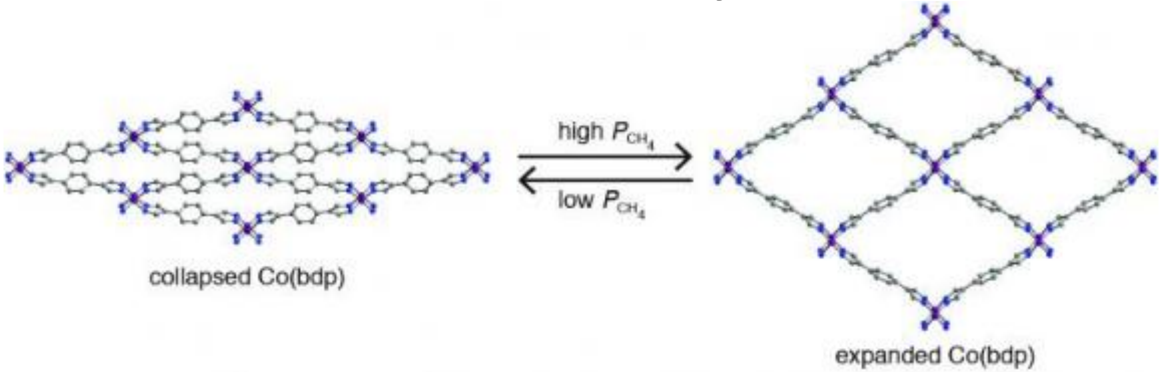
DOI: 10.1002/anie.201914395

Optical Transmission



Ambient Air ⟷ Under Vacuum

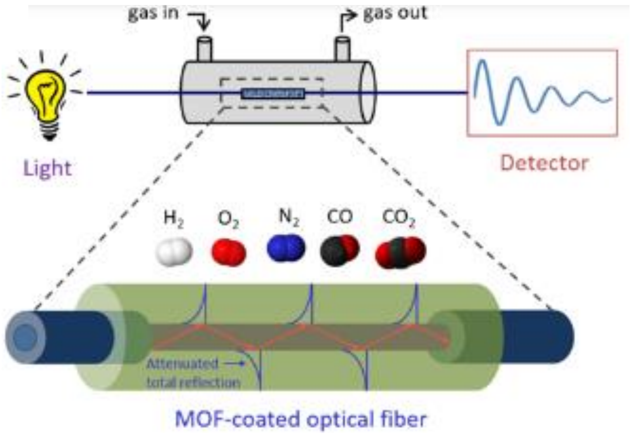
Structural Flexibility

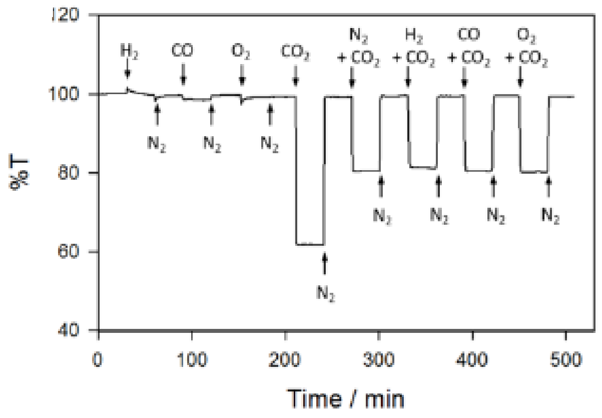


DOI: 10.1038/nature15732

…Enabling the Development of New Sensors

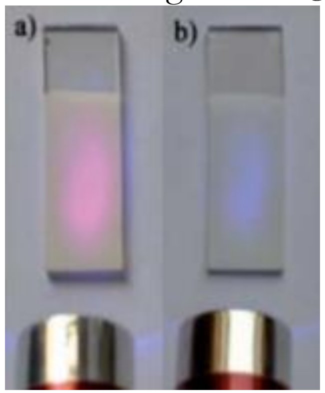
Refractive Index-Based

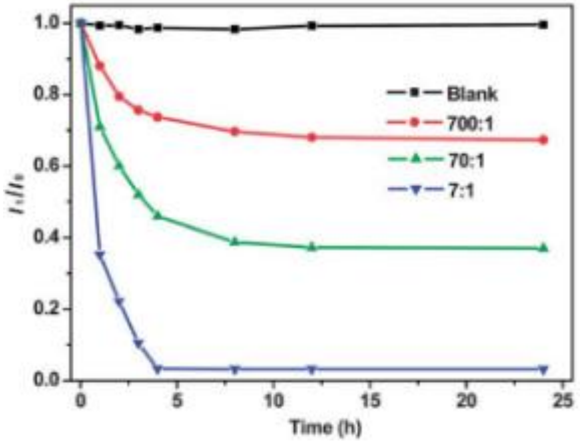




DOI: 10.1021/acssensors.7b00808

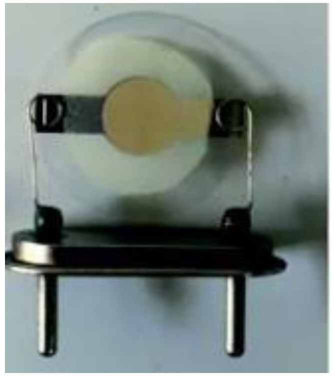
Luminescence-Based

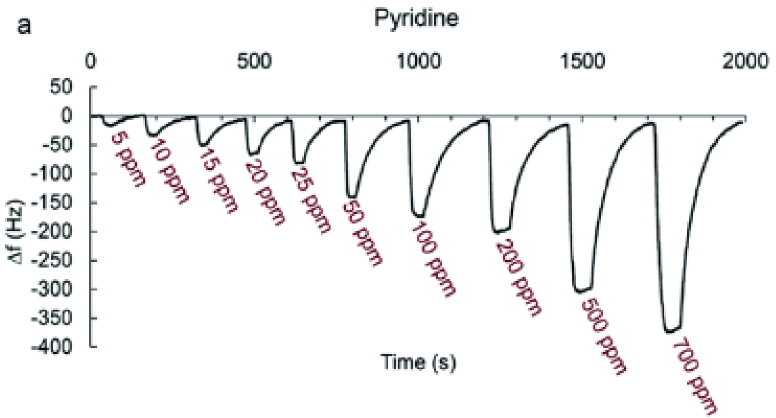




DOI: 10.1039/C9RA04152D

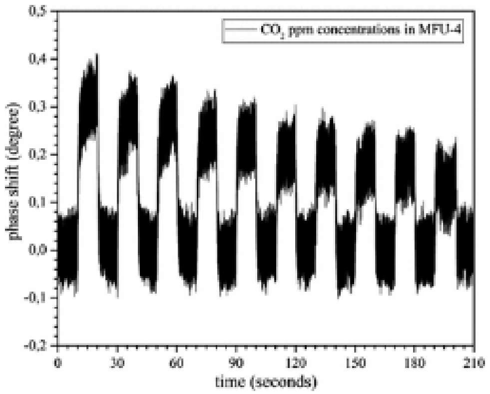
Quartz Crystal Microbalance

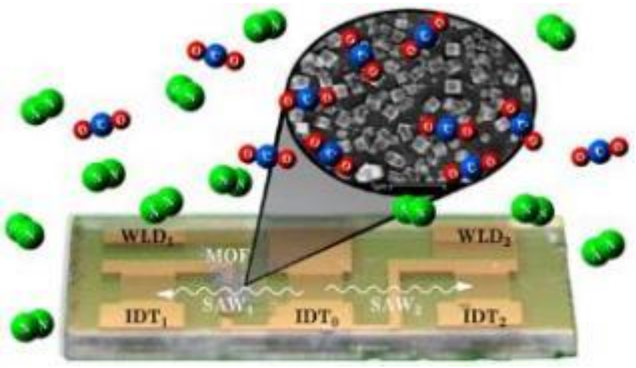




DOI: 10.1039/C9RA04152D

Surface Accoustic Wave Device





DOI: 10.1021/acssensors.7b00014

…Enabling the Development of New Sensors

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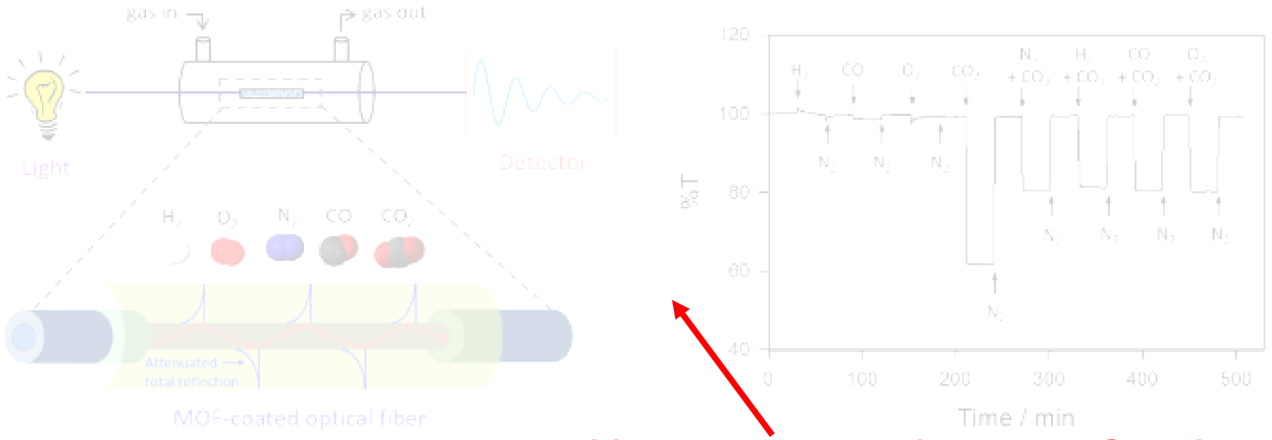
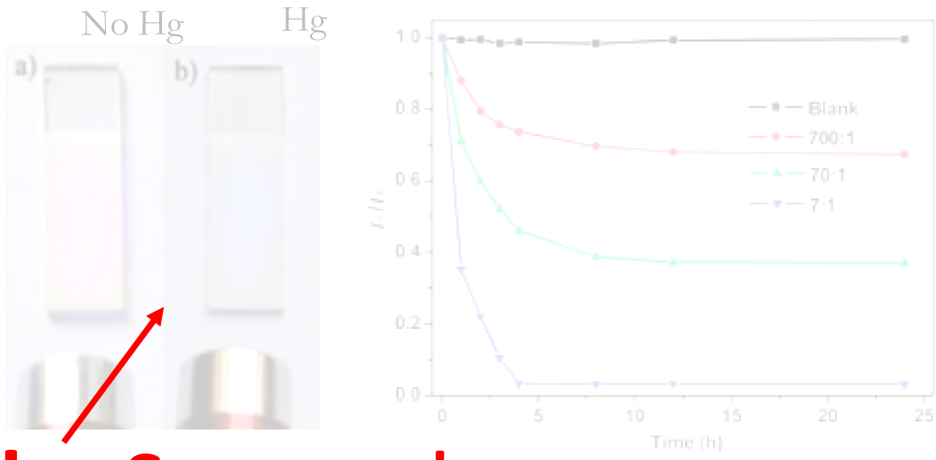
Refractive Index-Based



DOI: 10.1021/acssensors.7b00

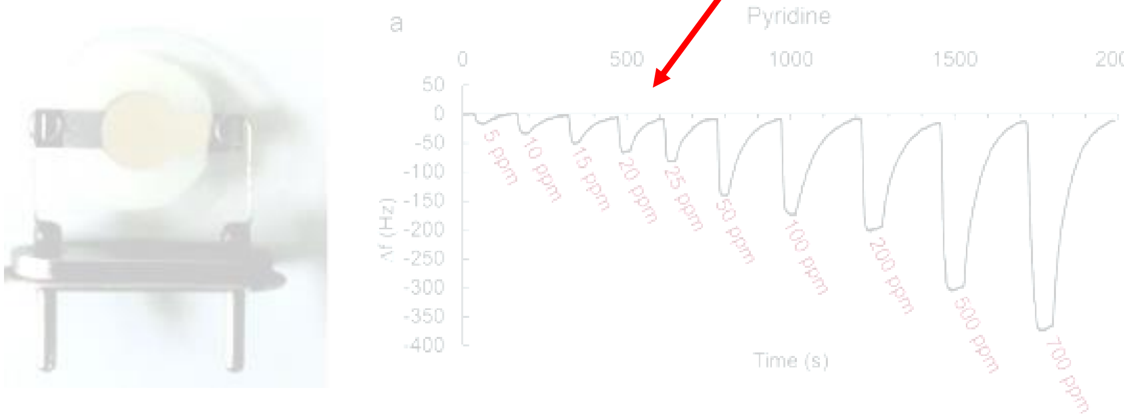
Luminescence-Based



DOI: 10.1039/C9RA04152D

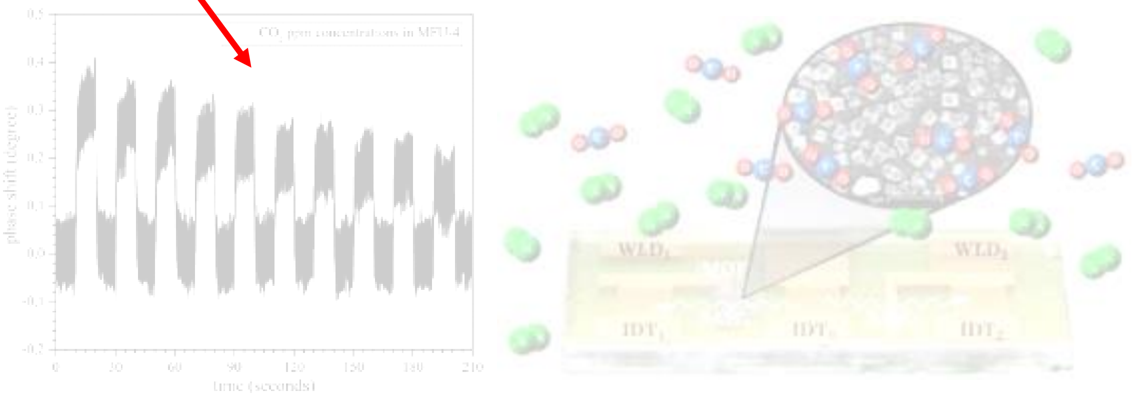
All Examples of <u>Thin Film</u> Sensors!

Quartz Crystal Microbalance



DOI: 10.1039/C9RA04152D

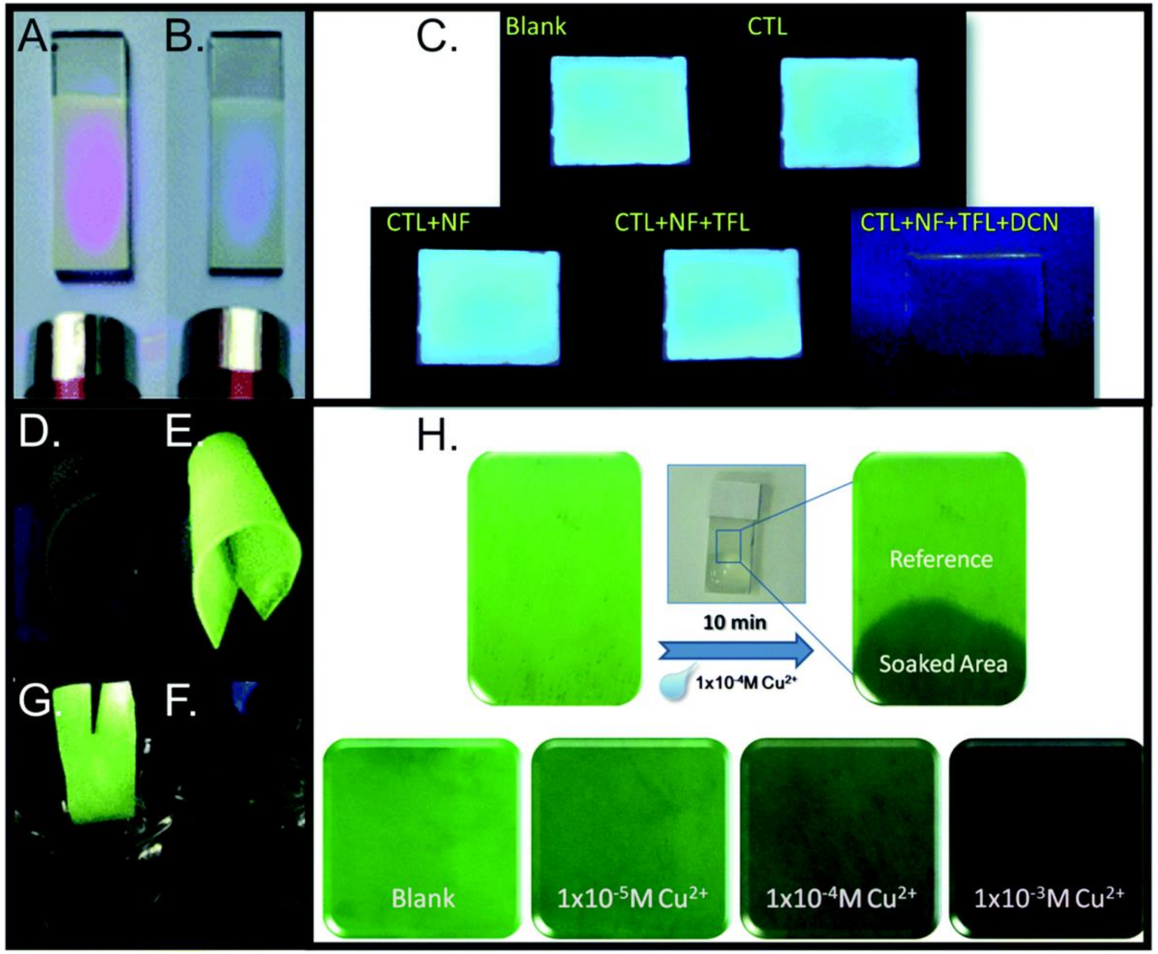
Surface Accoustic Wave Device



DOI: 10.1021/acssensors.7b00014

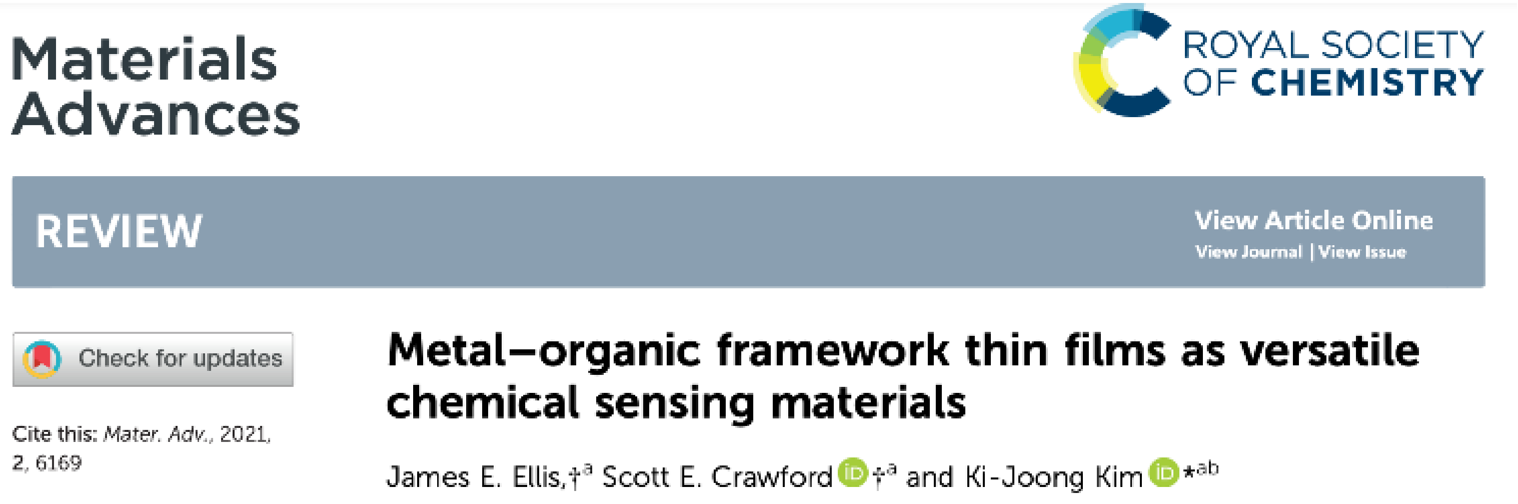
Benefits of Thin Films in Sensing Applications

- Improved sensitivity and/or response time
- Direct integration with sensor components (quartz crystal microbalances, optical fibers, etc.)
- Enhanced portability
- Ability to recycle/regenerate sensing material
- Scalability/mass production potential



A,B: 10.1039/C9RA04152D
C: 10.1039/C9RA08940C
D-F: 10.1016/j.snb.2015.05.129

For Further Information…


Materials Advances

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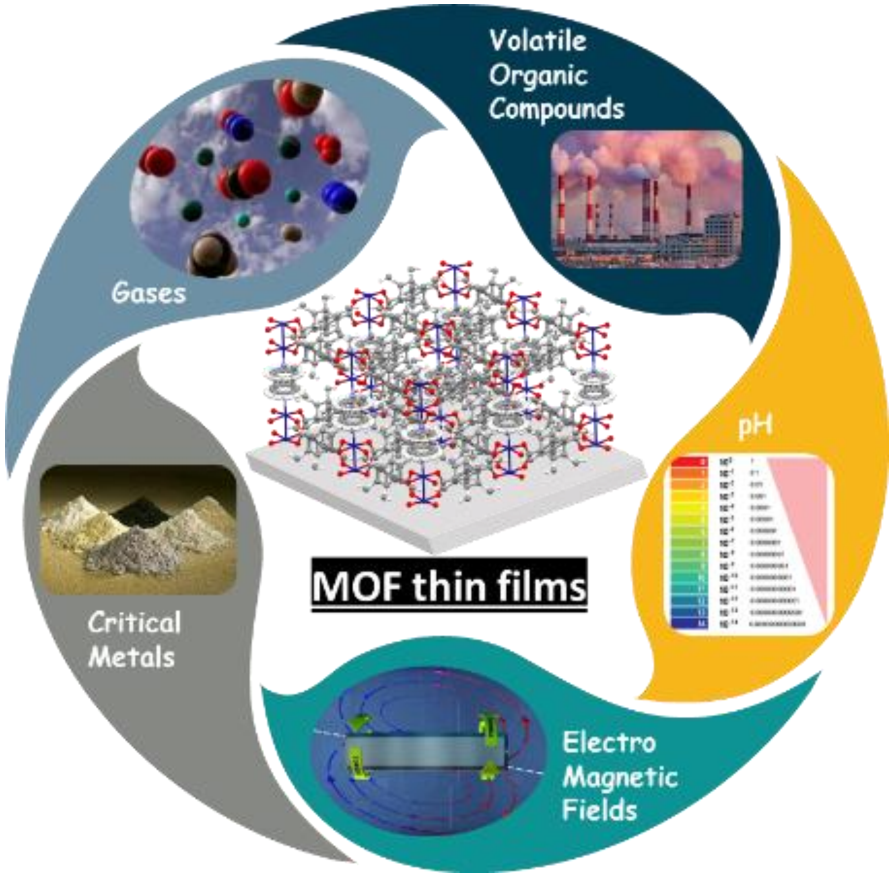
Cite this: *Mater. Adv.*, 2021, 2, 6169

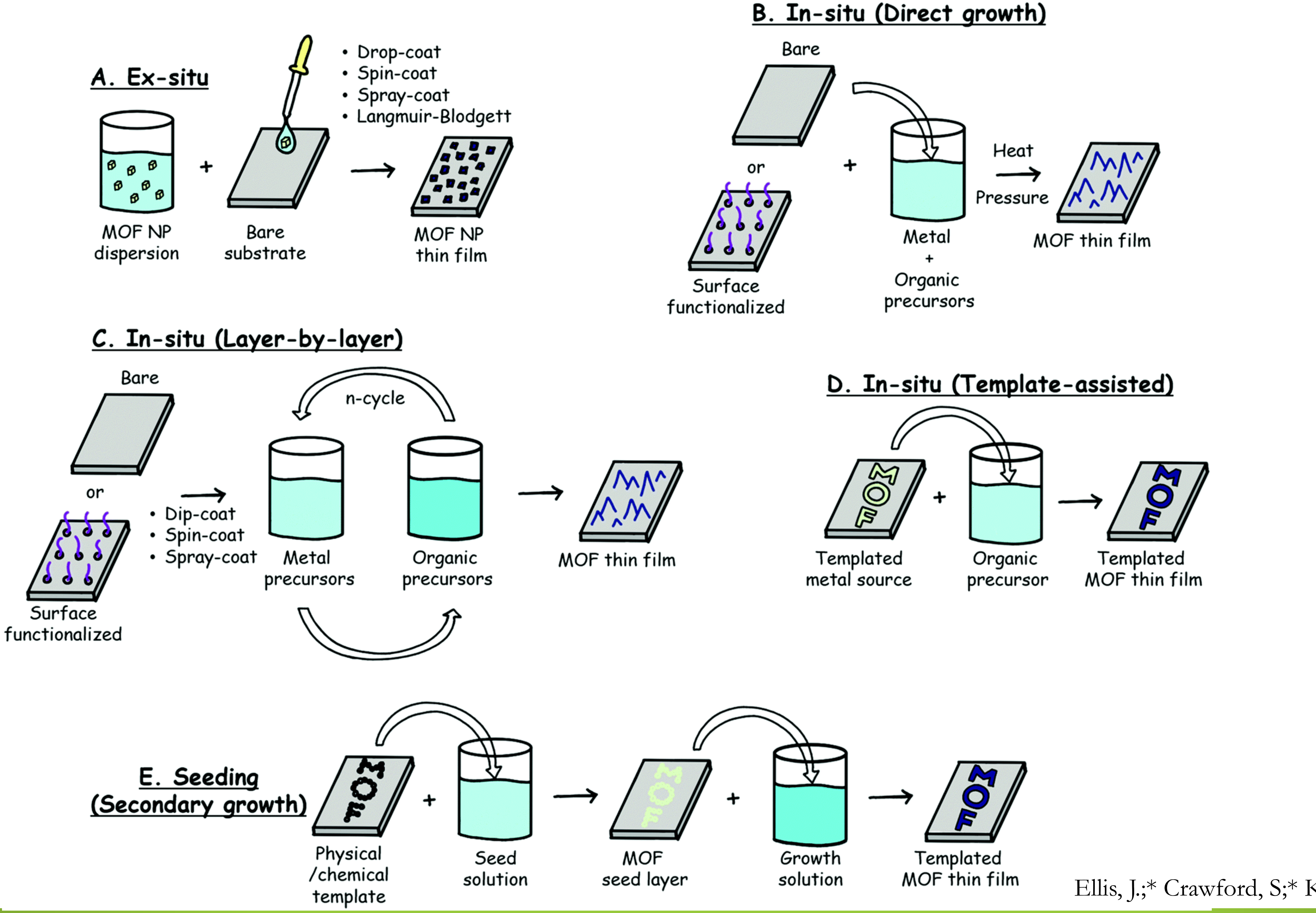
Metal–organic framework thin films as versatile chemical sensing materials

James E. Ellis,†[a] Scott E. Crawford †[a] and Ki-Joong Kim *[ab]



Ellis, J.;* Crawford, S;* Kim, K-J.; *Materials Advances* **2021**, *2*, 6169

Approaches for MOF Film Fabrication



Ellis, J.;* Crawford, S;* Kim, K-J.; *Materials Advances* **2021**, *2*, 6169

Many Approaches are Expensive/Tedious

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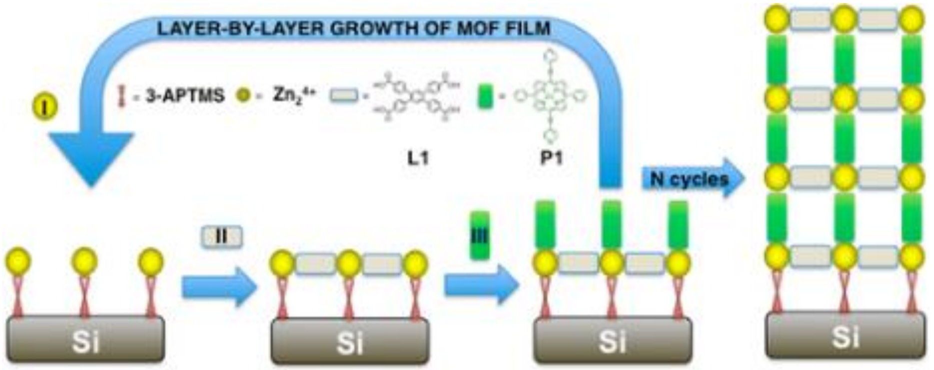
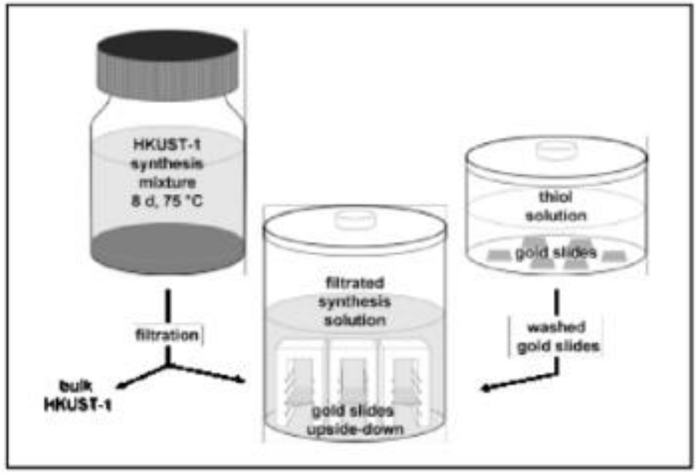
Layer-by-Layer



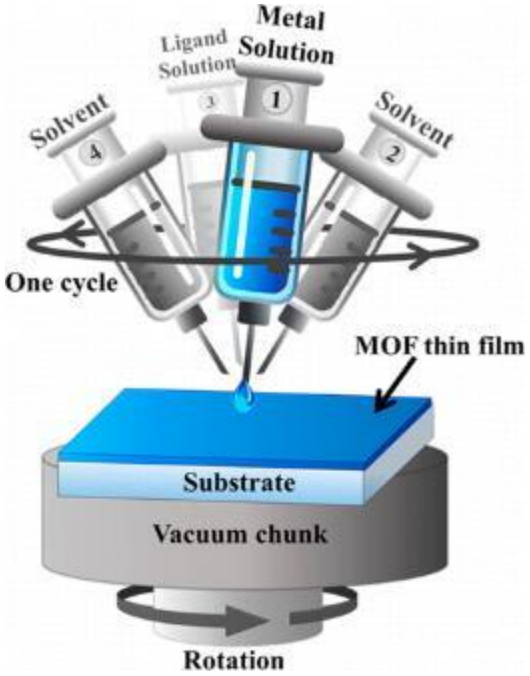
DOI: 10.1021/ja4078705

Solvothermal



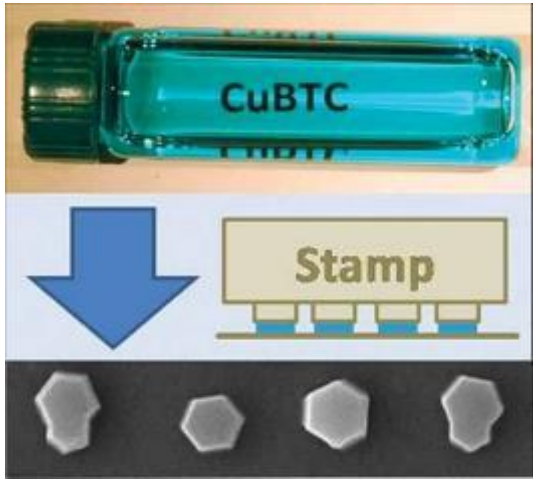
DOI: 10.1021/ja0701208

Spin Coating



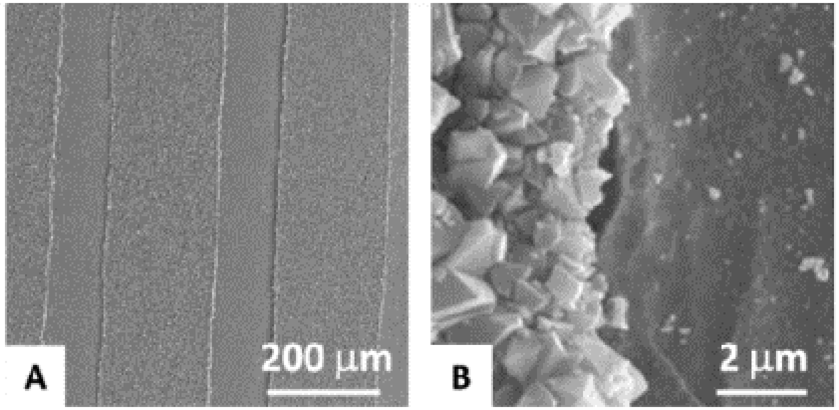
DOI: 10.1021/acsami.6b04701

Lithography/Patterning



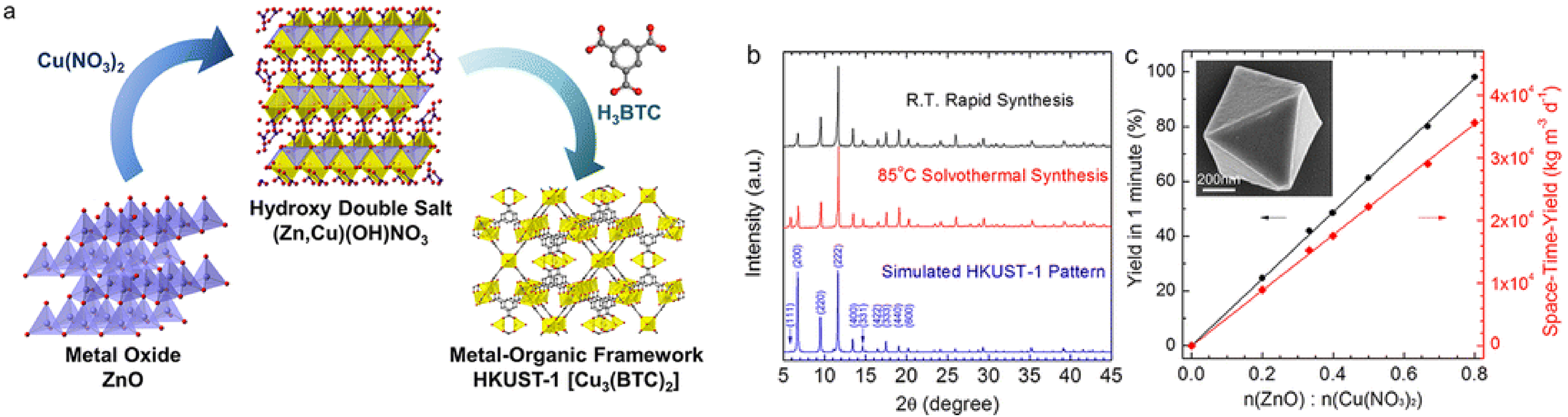
DOI: 10.1002/adma.200903867

Electrochemical



DOI: 10.1021/cm900069f

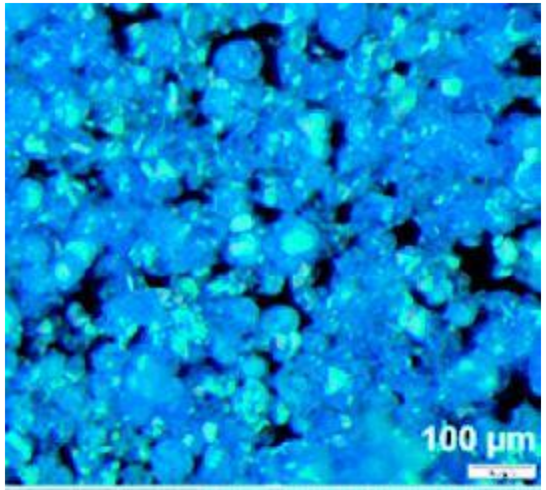
Alternative: Metal Oxide Templates



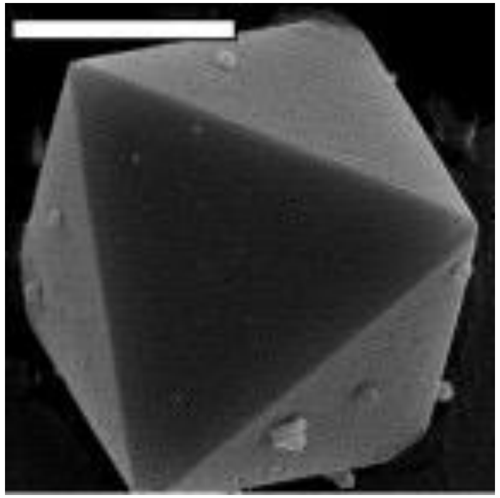
DOI: 10.1021/jacs.5b08752

Initial Target MOF: Cu-BTC

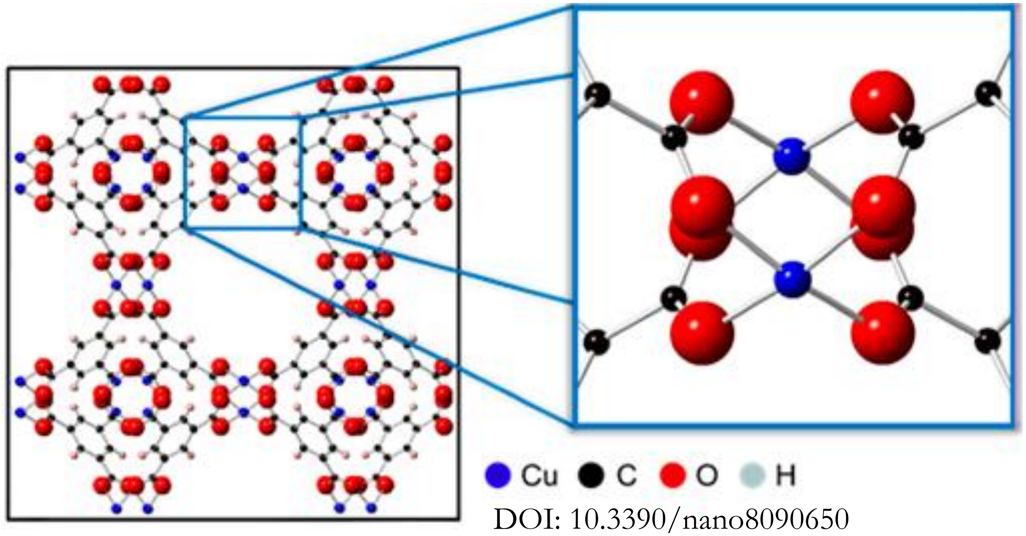
- MOF consisting of Cu^{2+} and benzene-1,3,5-tricarboxylate (BTC)
- <u>Well-studied</u> and <u>well-understood</u> synthesis and structural properties (both experimentally and computationally)
- Exhibits **high CO_2 storage capacity** (10.2 mol/kg at 15 bar, 25 °C)
- Exhibits **high CO_2 selectivity** (~20 CO_2:N_2 simulated under flue gas conditions)



10.1039/C8RA02439A



10.1016/j.micromeso.2008.06.040



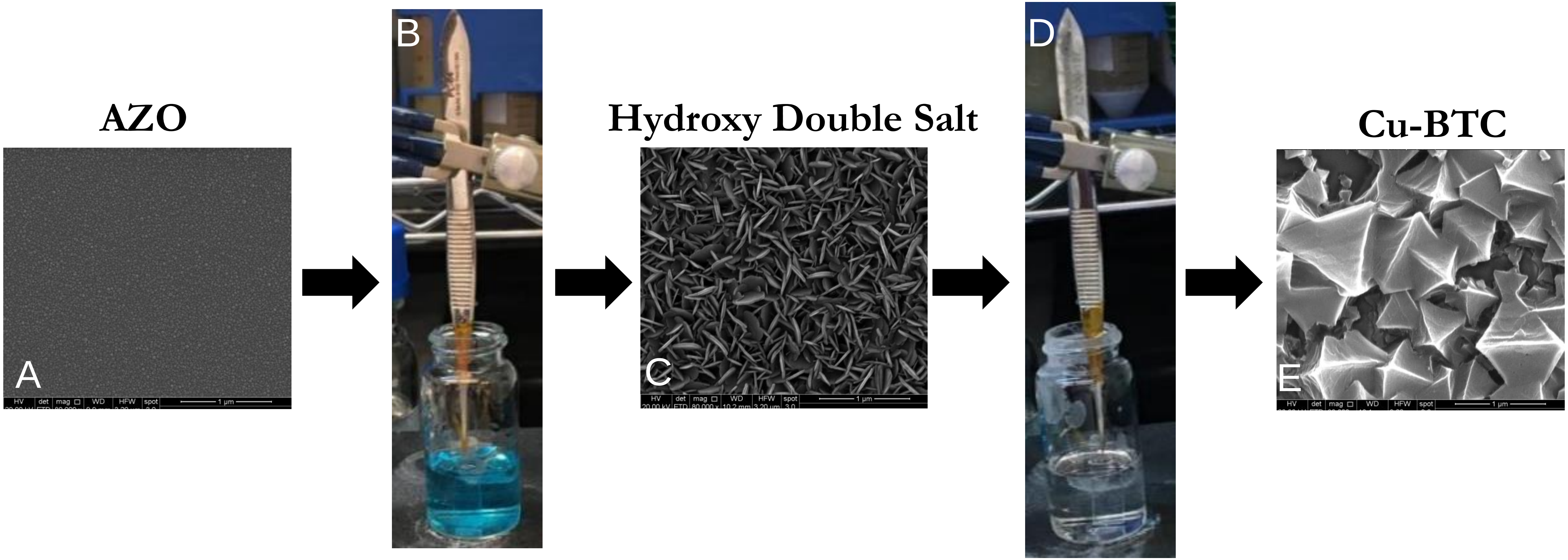
DOI: 10.3390/nano8090650

Chaffee, A.L., et al.; *Energy Fuels* **2009**, *23* (5), 2785
Yaghi, O.M., et al.; *J. Am. Chem. Soc.* **2005**, *127* (51), 17998
Chen, J-F., et al.; *AIChE J.* **2007**, *53* (11), 2832
Bordiga, S., et al.; *Phys. Chem. Chem. Phys.* **2007**, *9*, 2676
Bien, T., et al.; *Microporous Mesoporous Mater.* **2009**, *117* (1), 111

Our Approach: AZO Template

Cu Nitrate | **BTC in DMF:H_2O:EtOH**

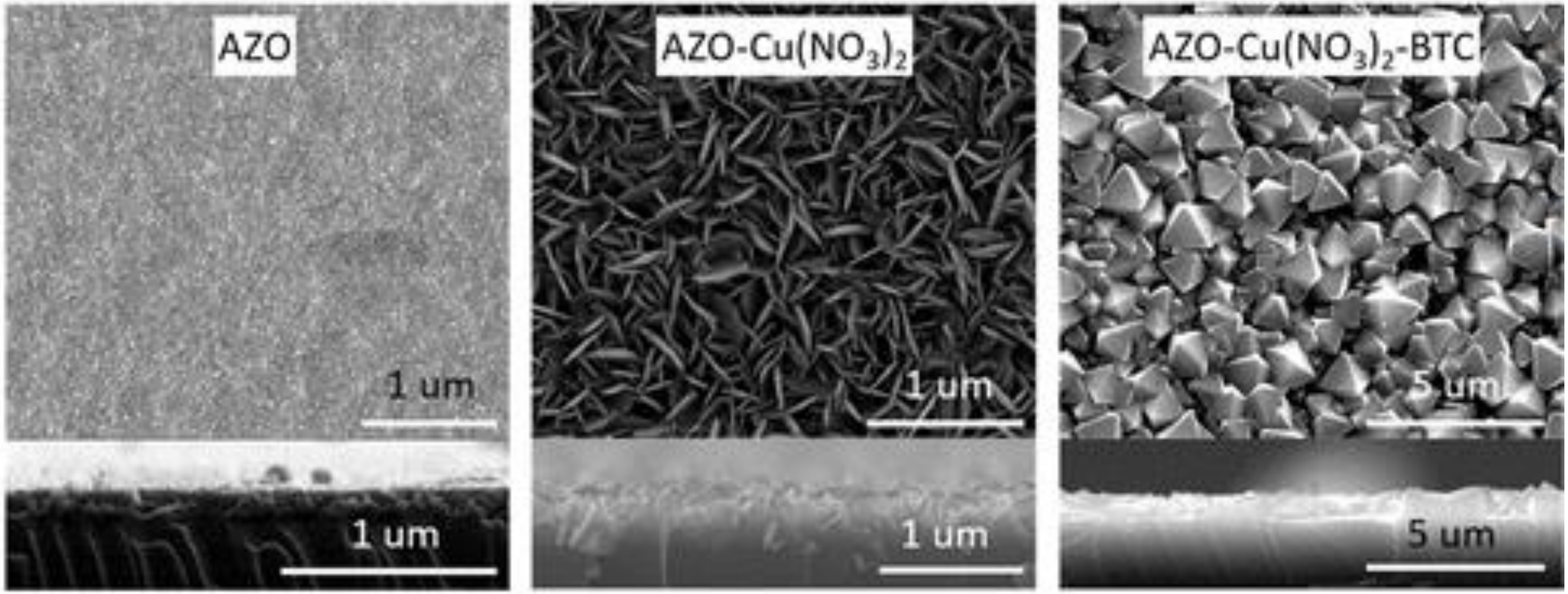
AZO → **Hydroxy Double Salt** → **Cu-BTC**



1 Minute | **15 Minutes**

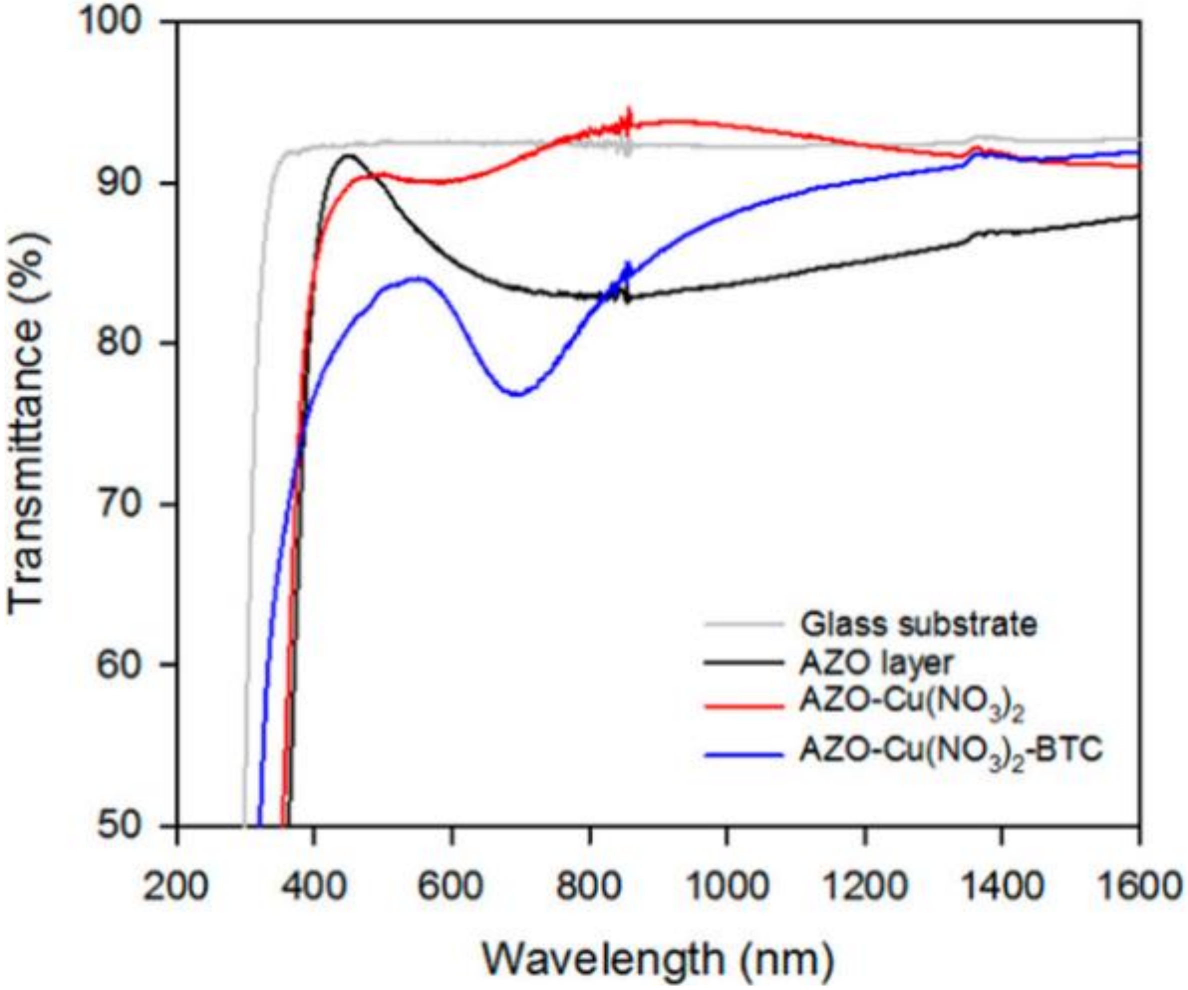
Crawford, S; Kim, K; Yu, Y; Ohodnicki, P. *Cryst. Growth Des.* **2018**, *18*, 2924

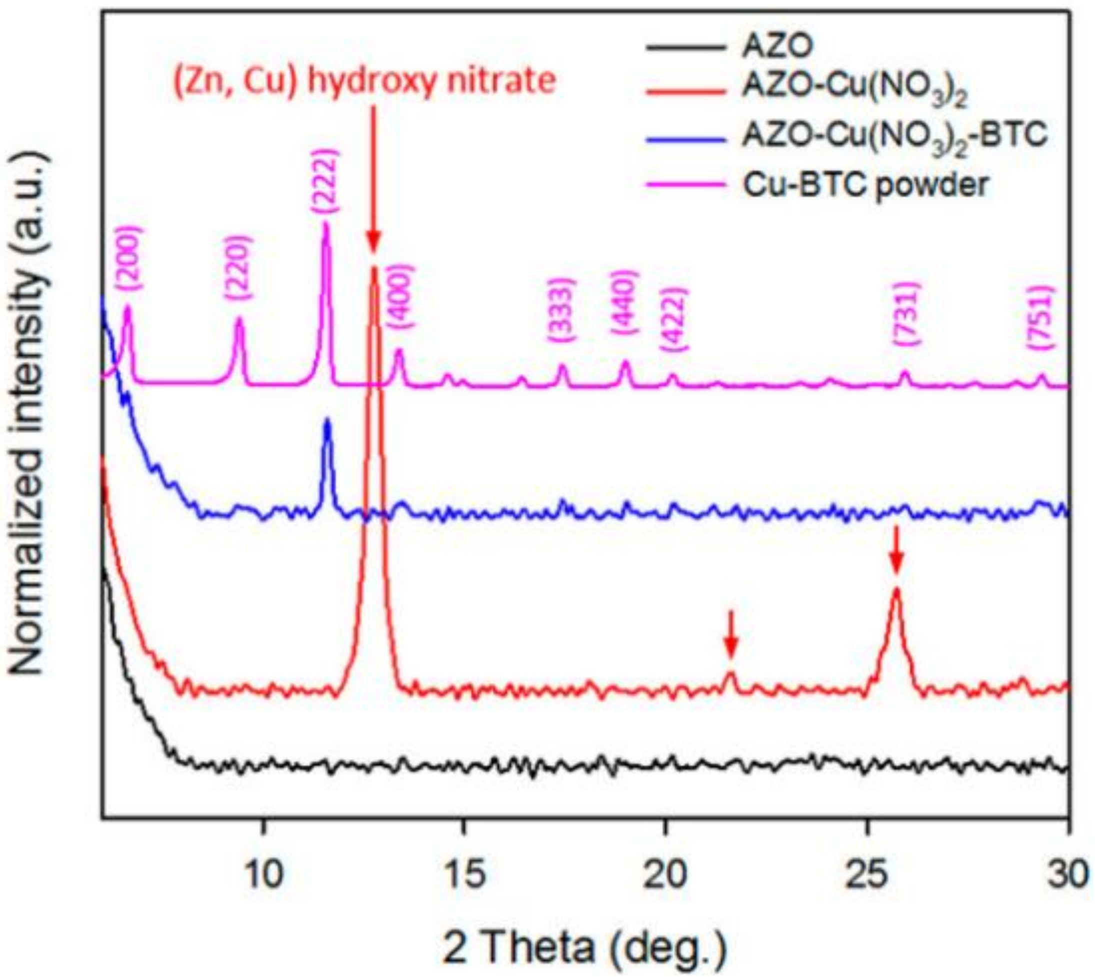
SEM Confirms Growth Mechanism



Crawford, S; Kim, K; Yu, Y; Ohodnicki, P. *Cryst. Growth Des.* **2018**, *18*, 2924

XRD and Optical Characterization

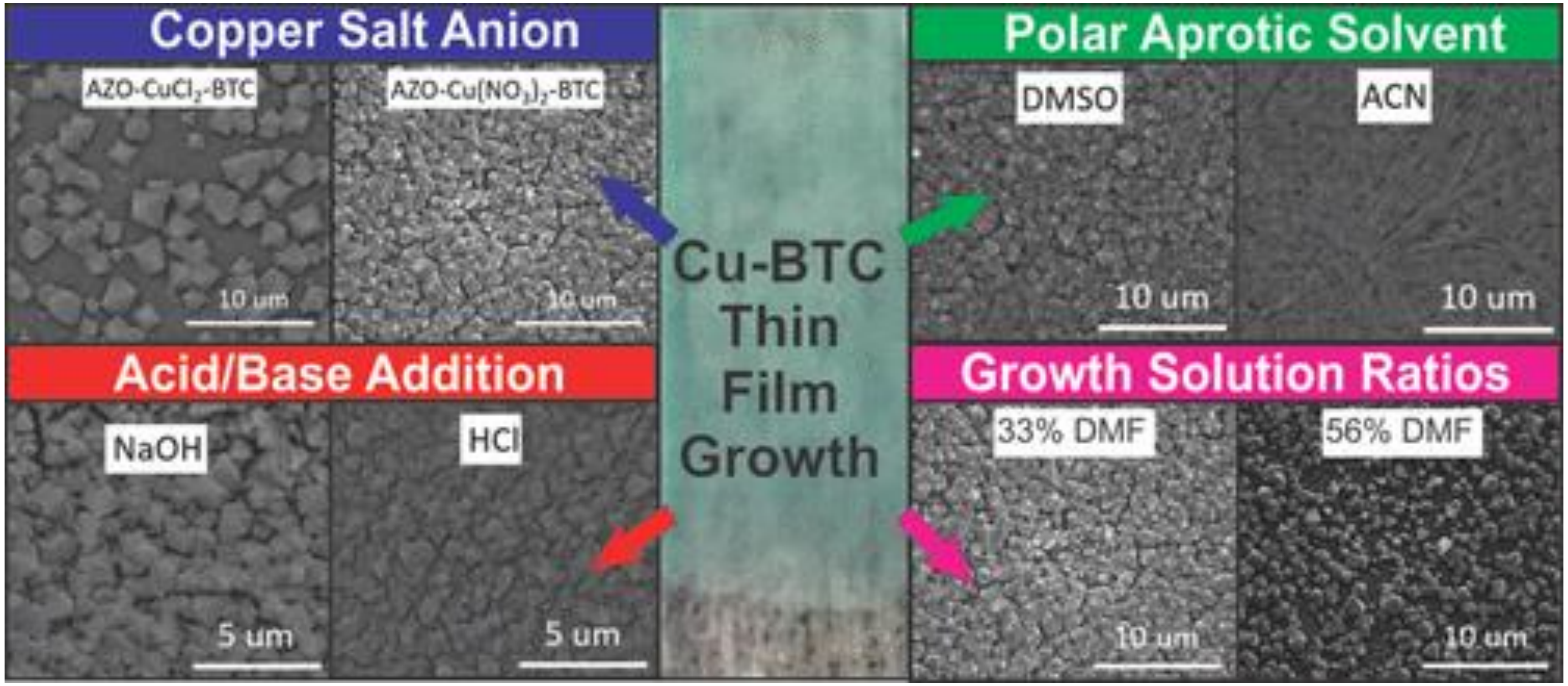




Crawford, S; Kim, K; Yu, Y; Ohodnicki, P. *Cryst. Growth Des.* **2018**, *18*, 2924

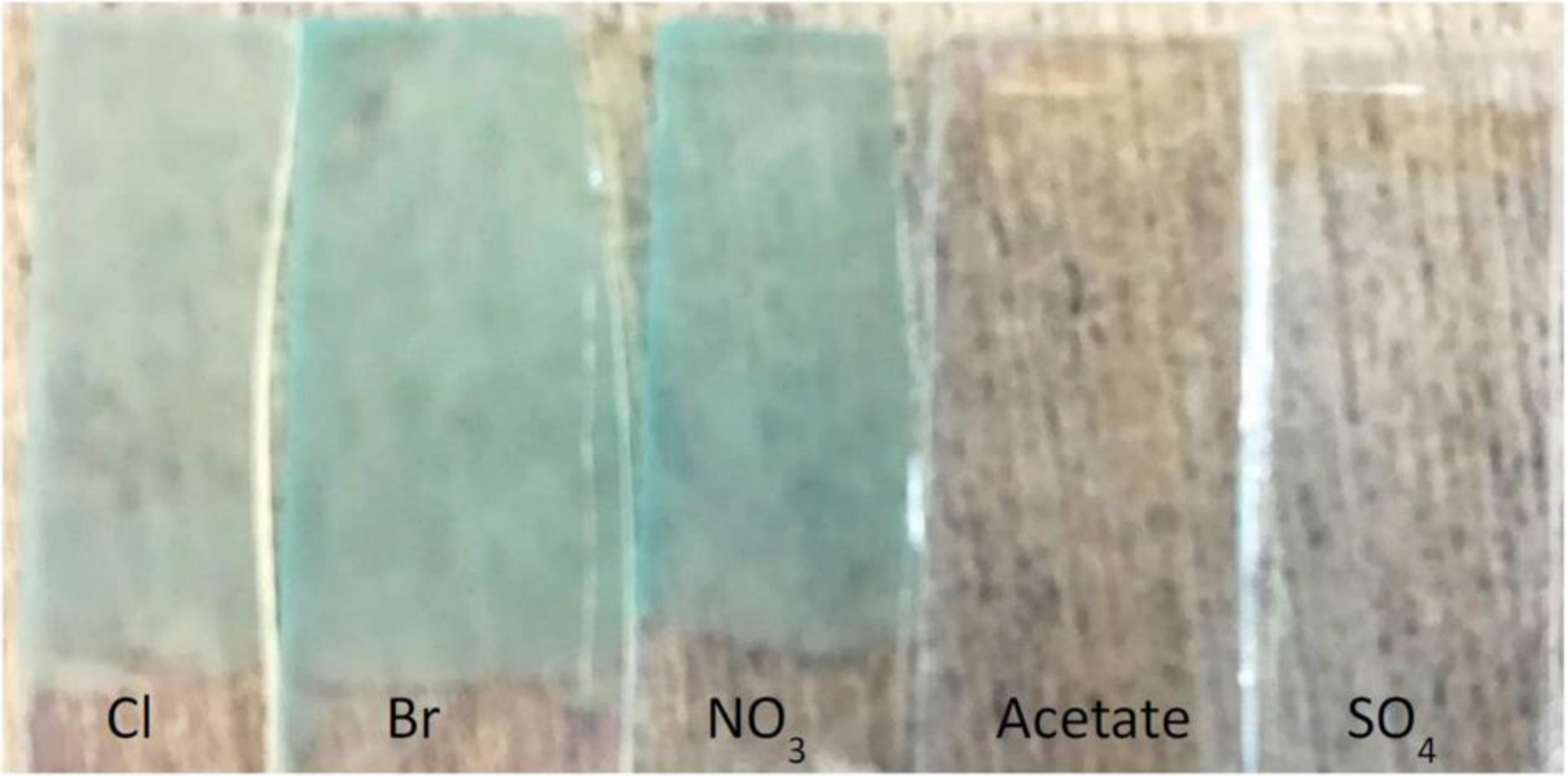
Optimization Strategies

- **Influence of:**
  - Copper Salt Anion
  - Solvent Conditions
  - Solvent Ratios
  - Acid/Base Additions

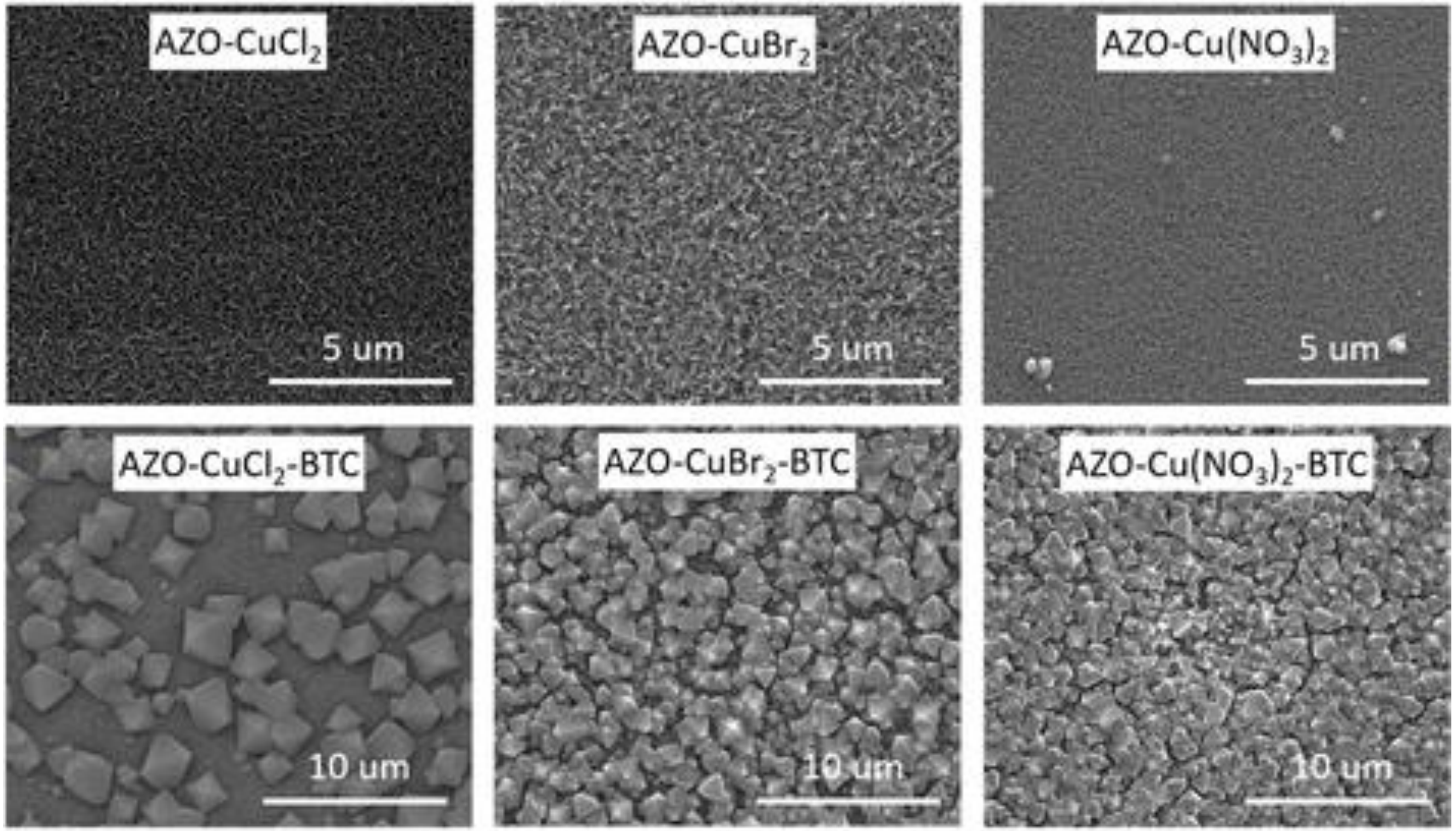


Crawford, S; Kim, K; Yu, Y; Ohodnicki, P. *Cryst. Growth Des.* **2018**, *18*, 2924

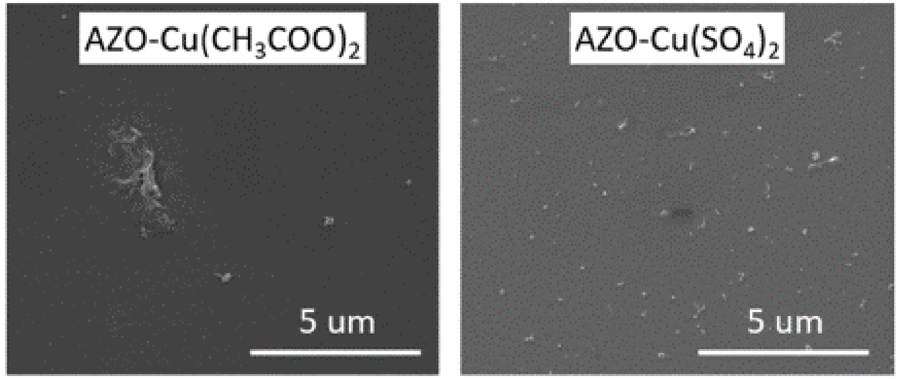
Copper Salt Anion



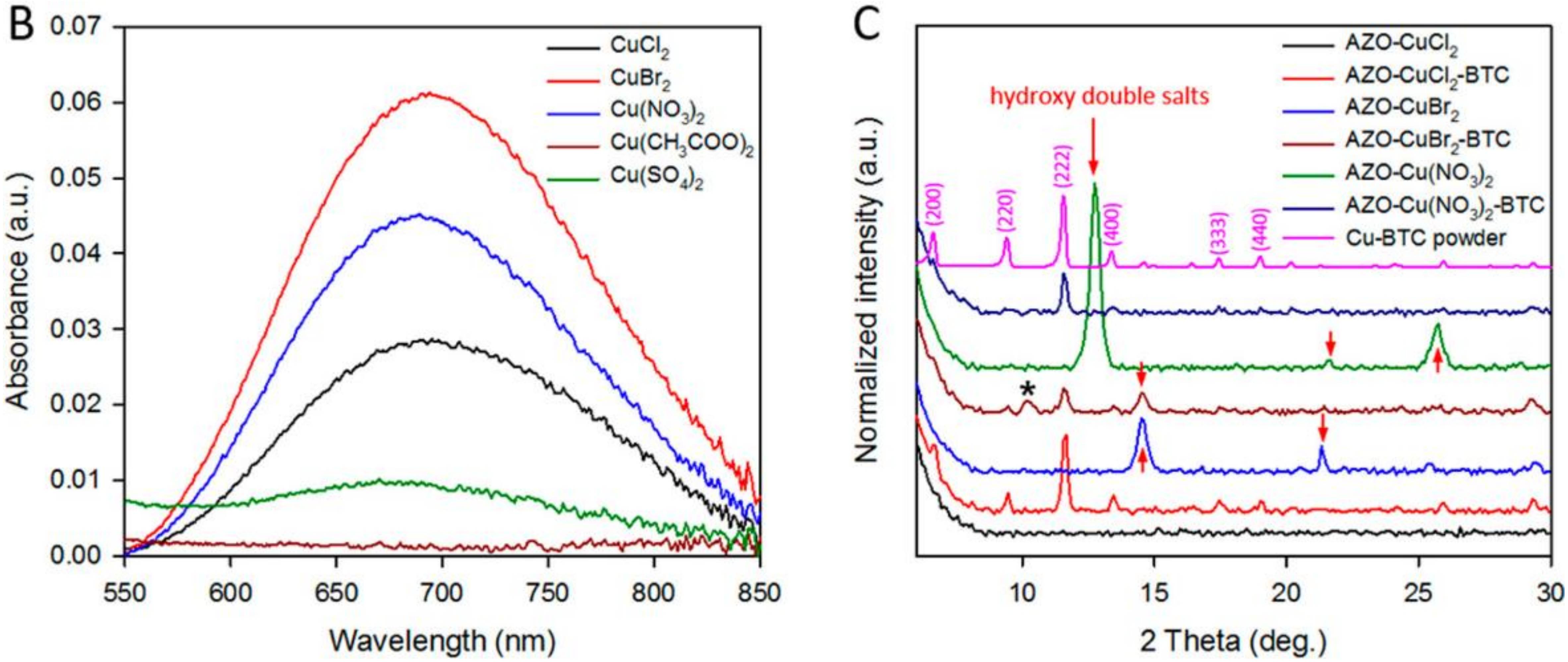
Anion Tunes MOF Morphology



*No HDS formation with sulfate, acetate

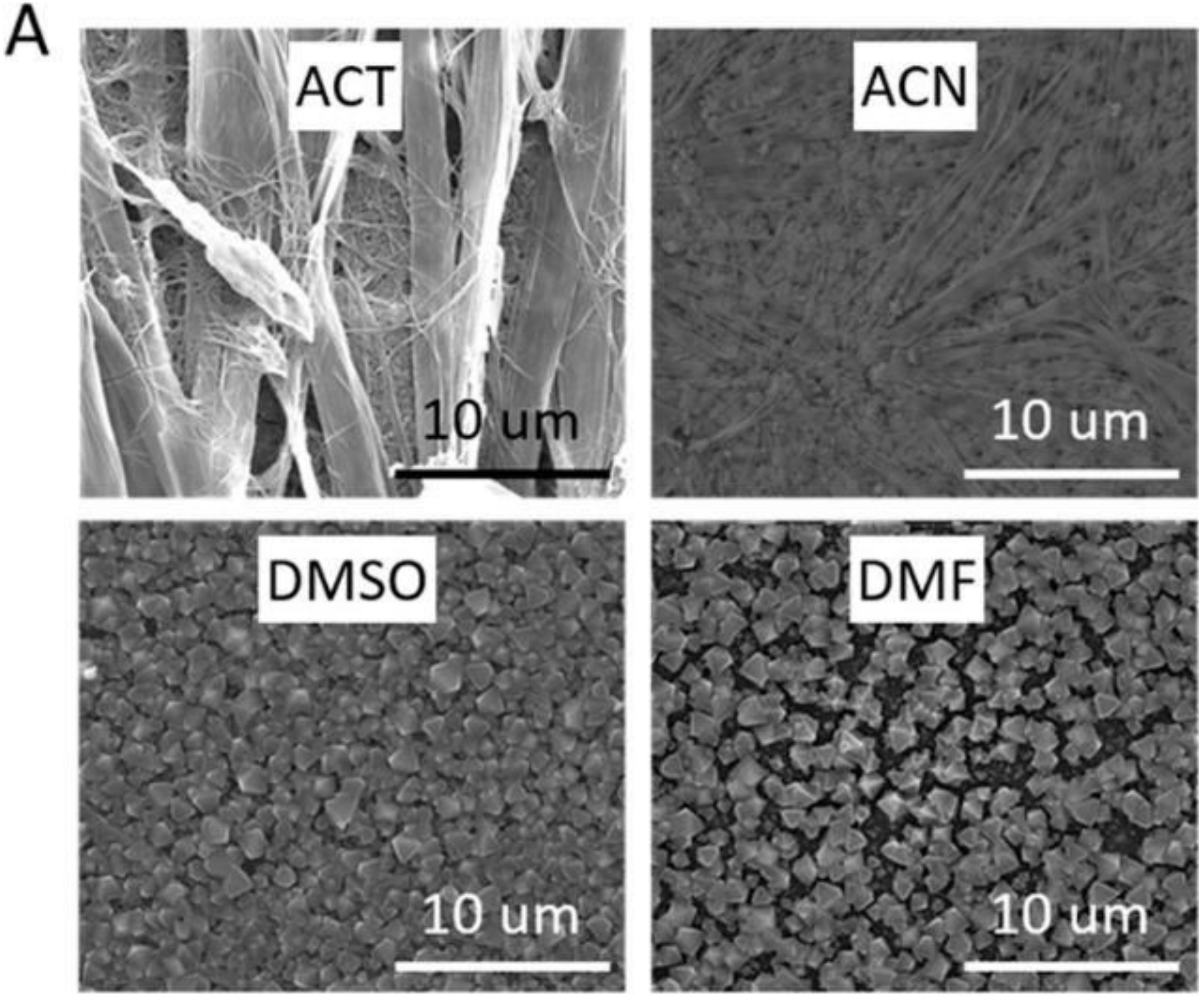


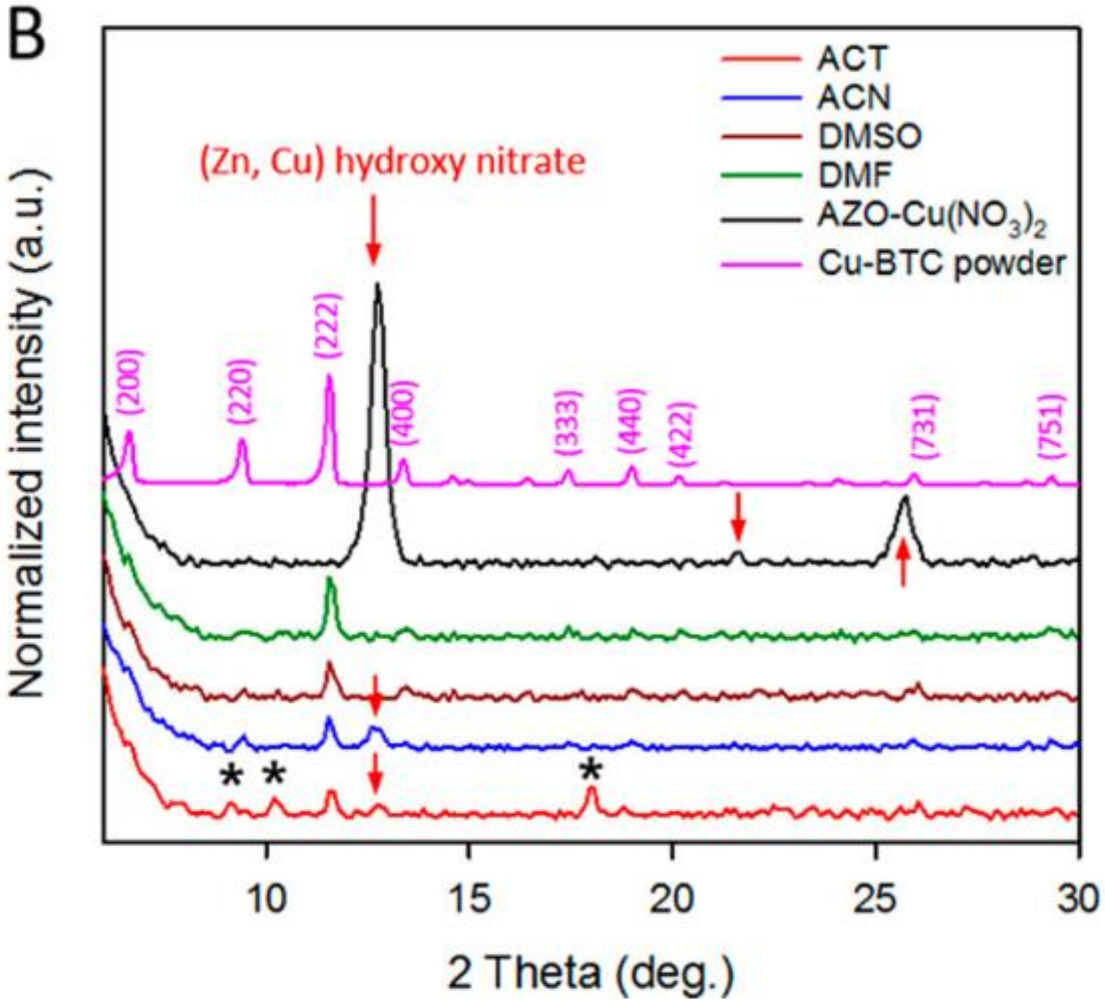
Optical and XRD Characterization



*- indicates $Cu_2OH(BTC)(H_2O)_n \cdot 2nH_2O$ phase

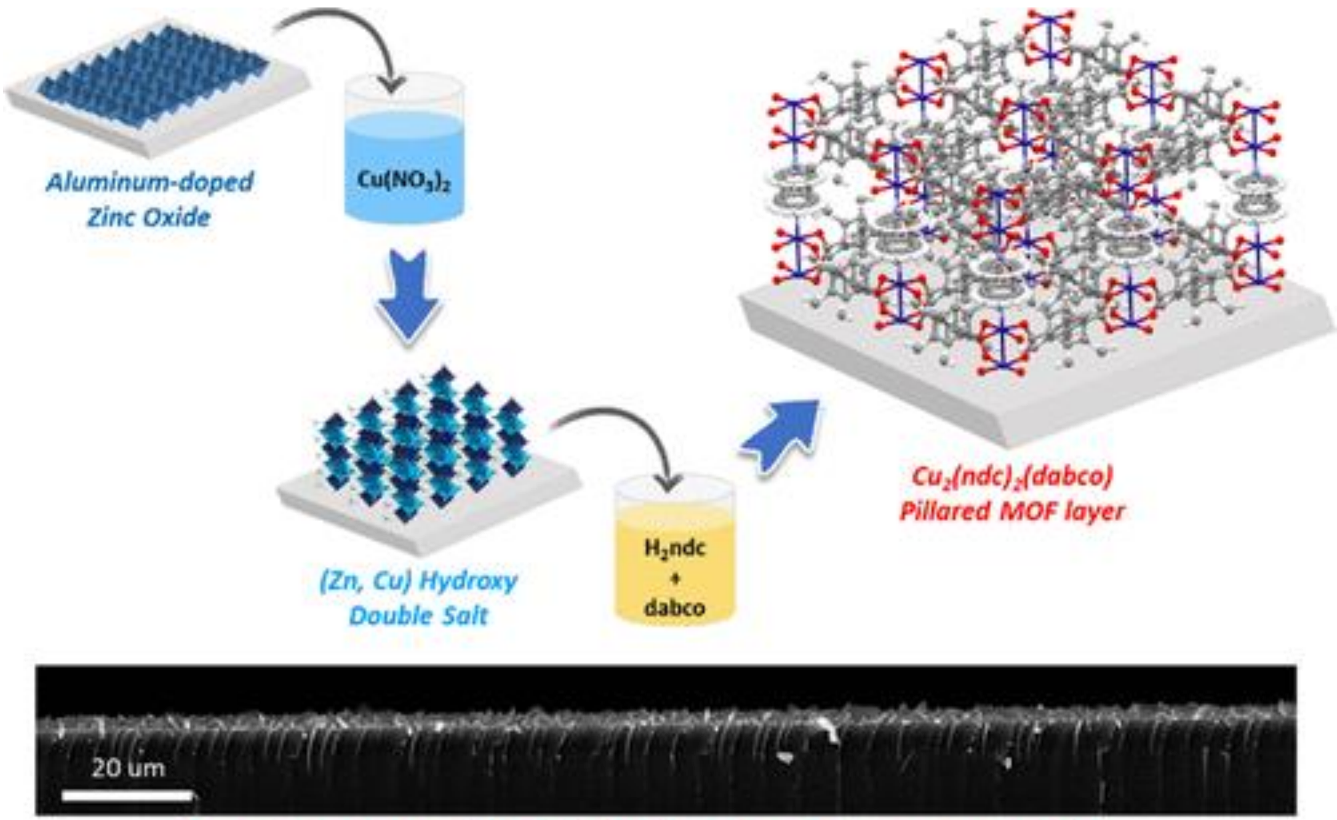
Influence of Polar Aprotic Solvent



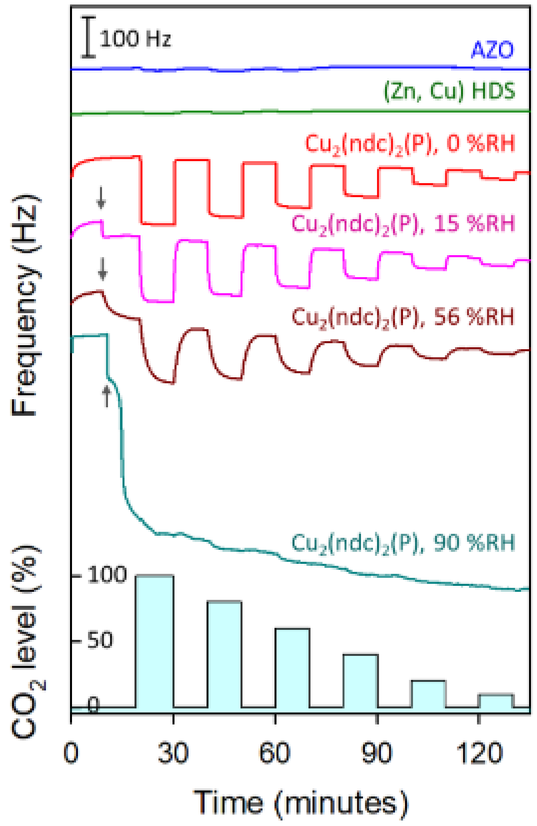


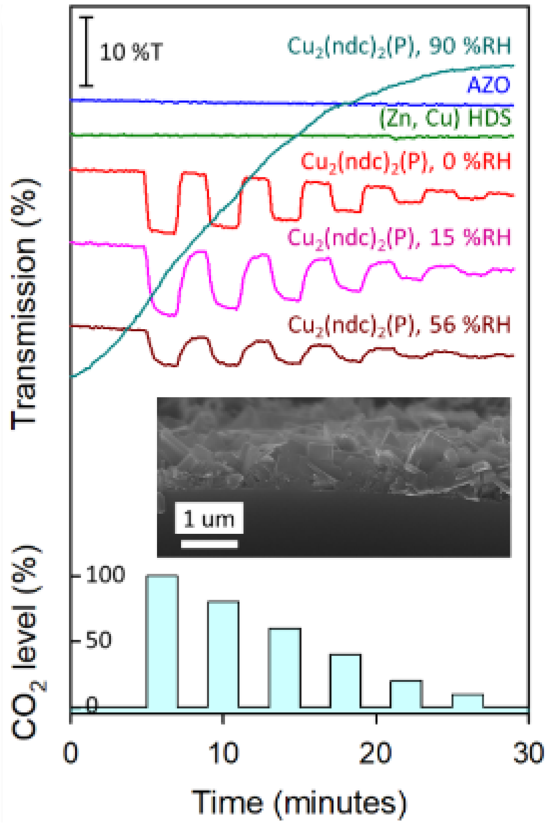
*- indicates $Cu_2OH(BTC)(H_2O)_n{\cdot}2nH_2O$ phase

Extension to Gas Sensing Applicatoins



Dense & Continuous Micro-Thick Pillared MOF Films on Large Scale

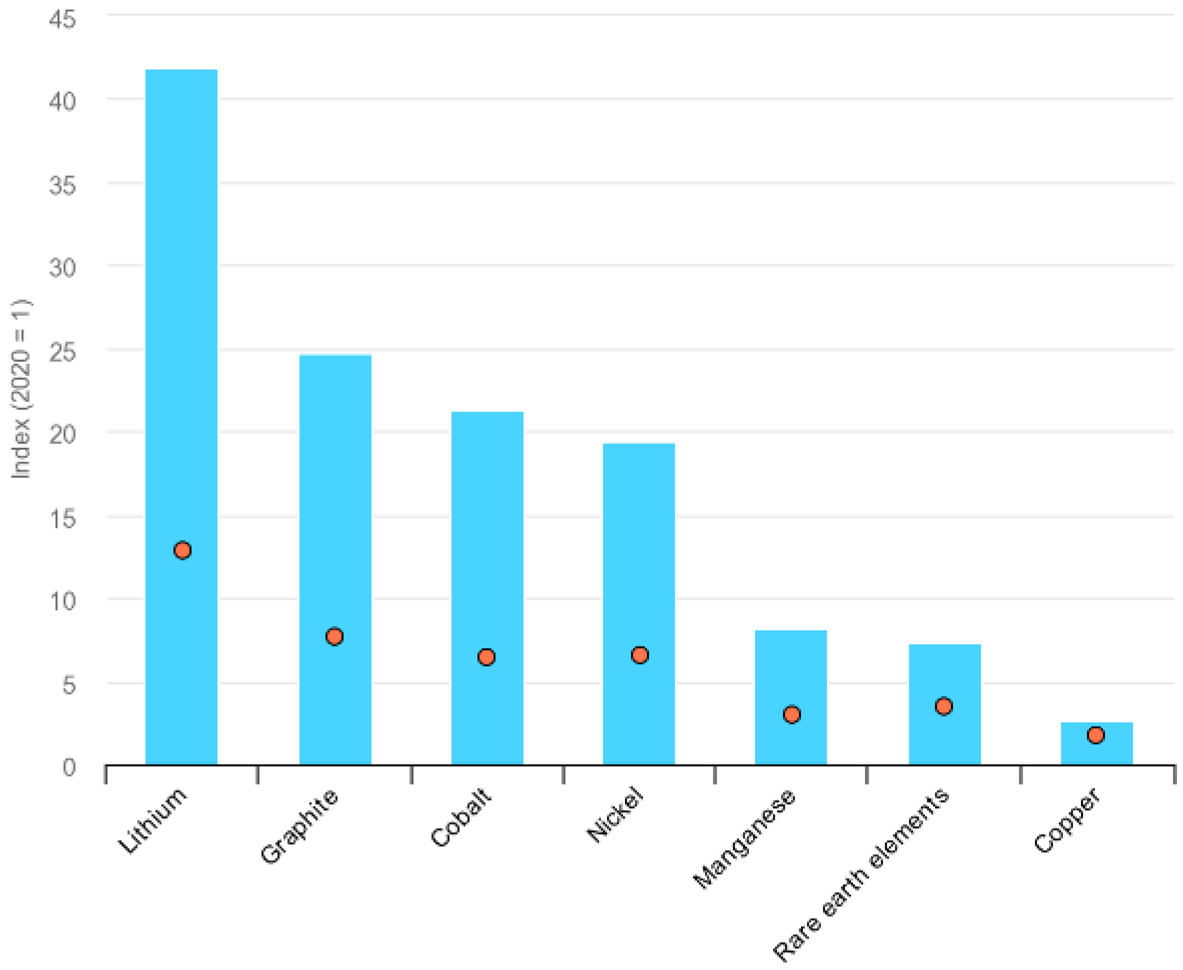




DOI: 10.1021/acsami.0c19621

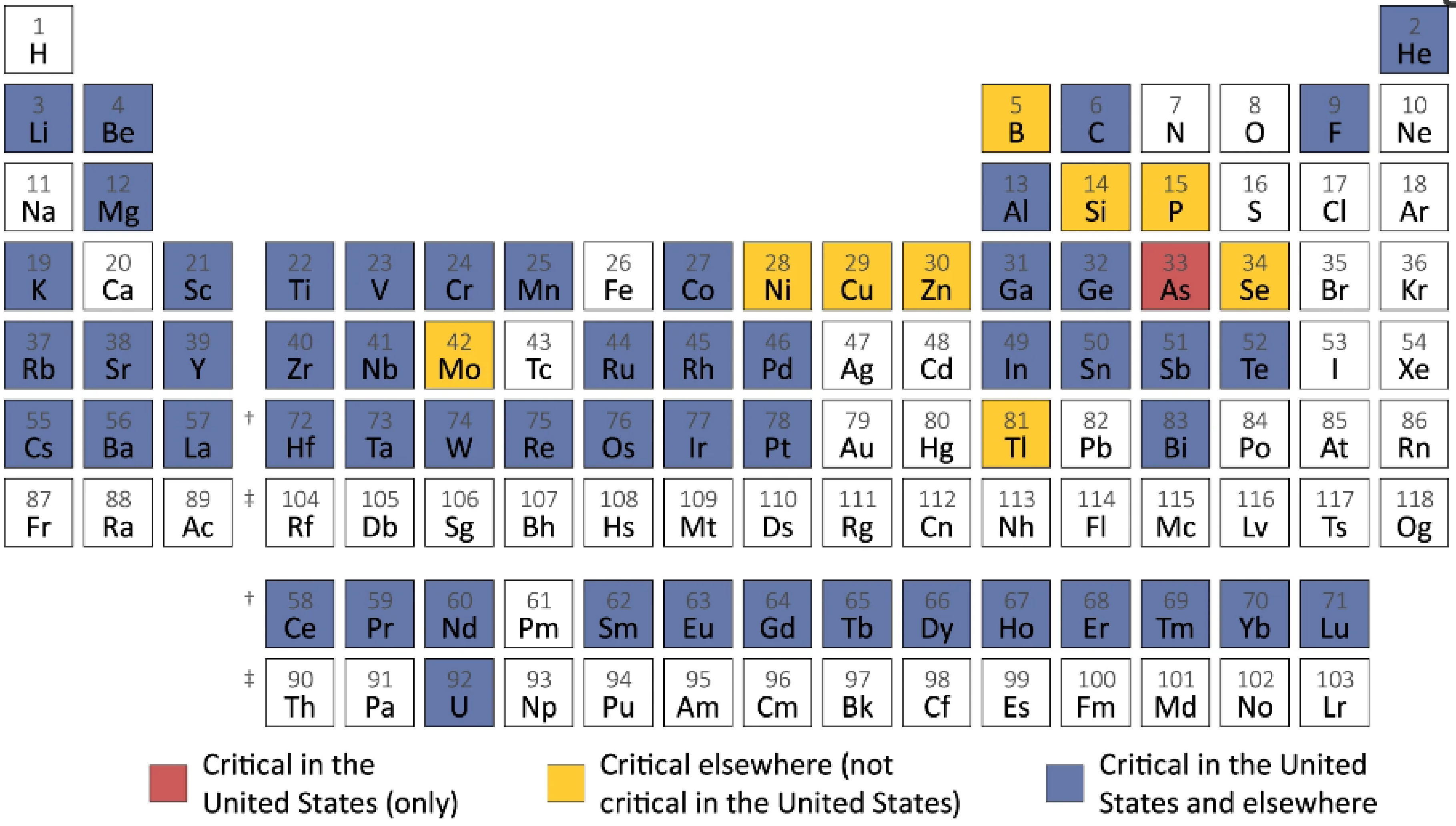
MOF Thin Films for Metal Ion Detection

- Increased global adoption of renewable energy sources will spur **increased demand** for mineral resources
- Global market for many metals is **highly monopolistic**
- Mining practices can be tedious, expensive, and **environmentally damaging**
- Alternative resources include coal-based products and electronic waste



International Energy Agency, "The role of critical minerals in clean energy transitions," 2021.

35 Critical Metals (USGS, 2018)



DOI: 10.1038/s41467-021-27829-w

Critical Metals from Alternative Sources

Coal

~70 to 140 ppm REE

DOI: 10.1016/j.coal.2016.04.005

Acid Mine Drainage
(0.07-7 ppm)

DOI: 10.1016/j.coal.2006.01.009

Coal Rock Refuse
(~250 ppm REE)

DOI: 10.1016/j.coal.2011.05.006

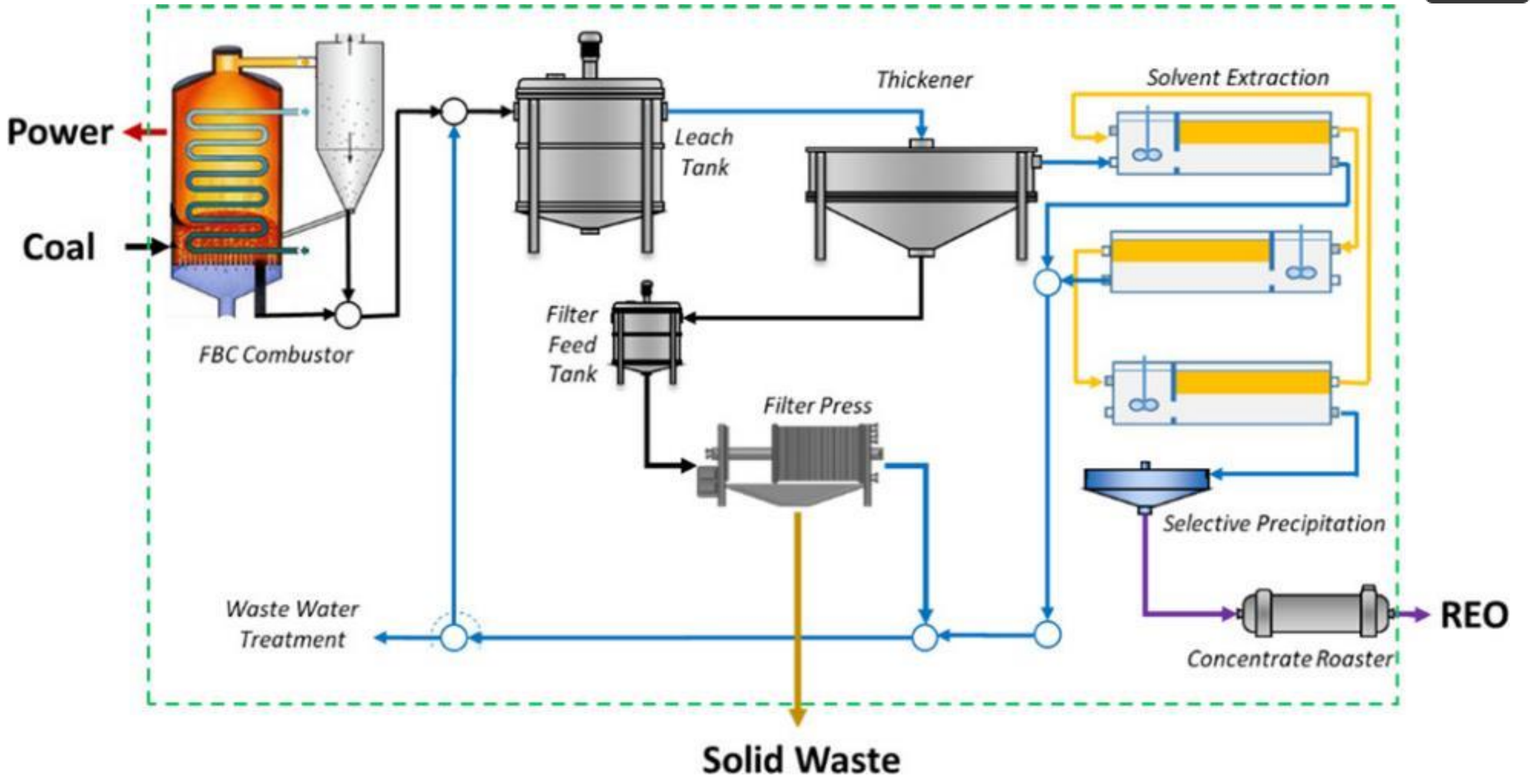
Coal Fly Ash
(~450 ppm REE)

DOI: 10.1007/s11356-015-4111-9

The Atlantic

- **Circuit Boards**
- **Phosphors**
- **Magnets**
- **Batteries**
- **Etc…**

Characterization Needs for Processing



DOI: 10.1021/acs.energyfuels.9b00295

Rapid Characterization Methods Needed

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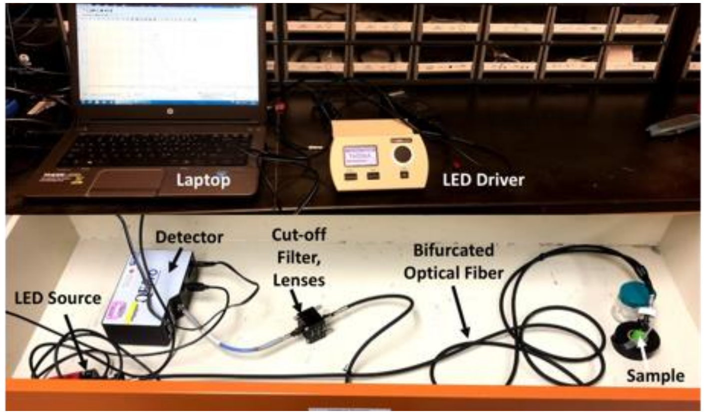
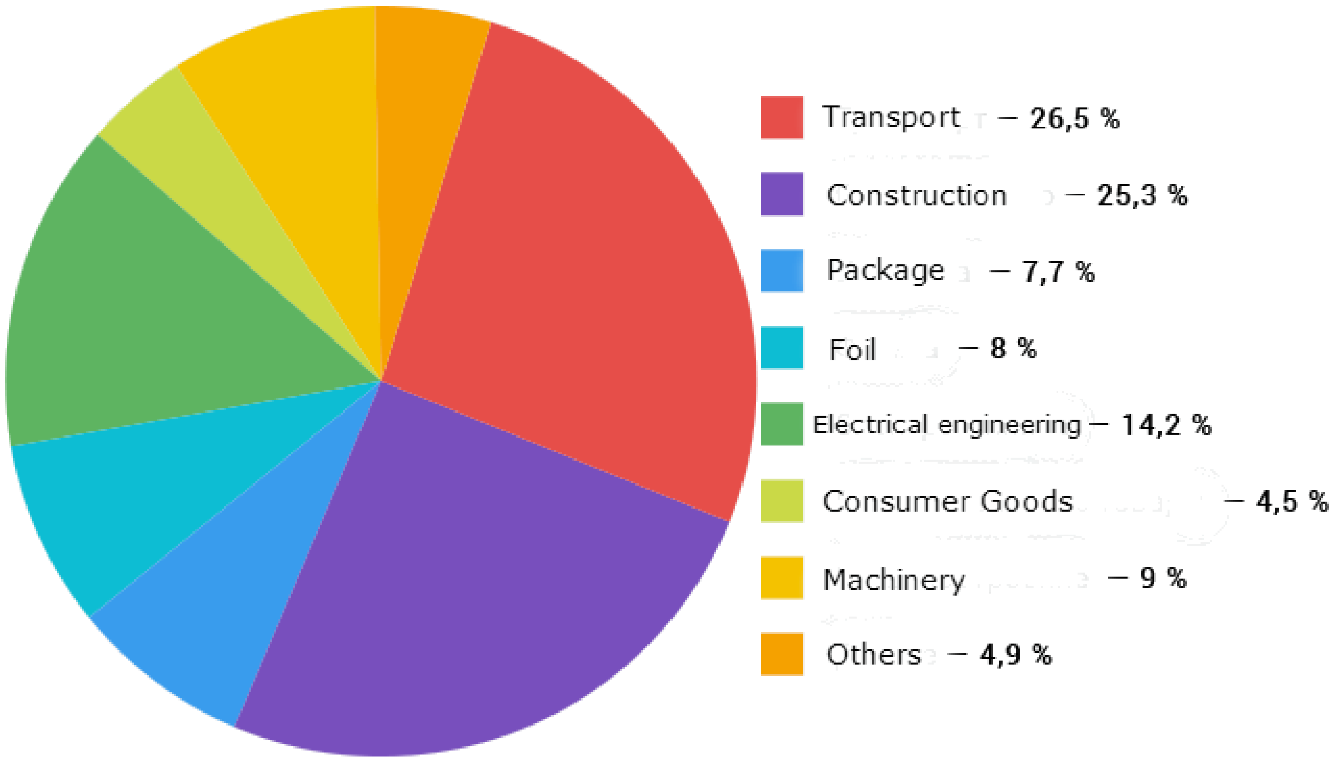
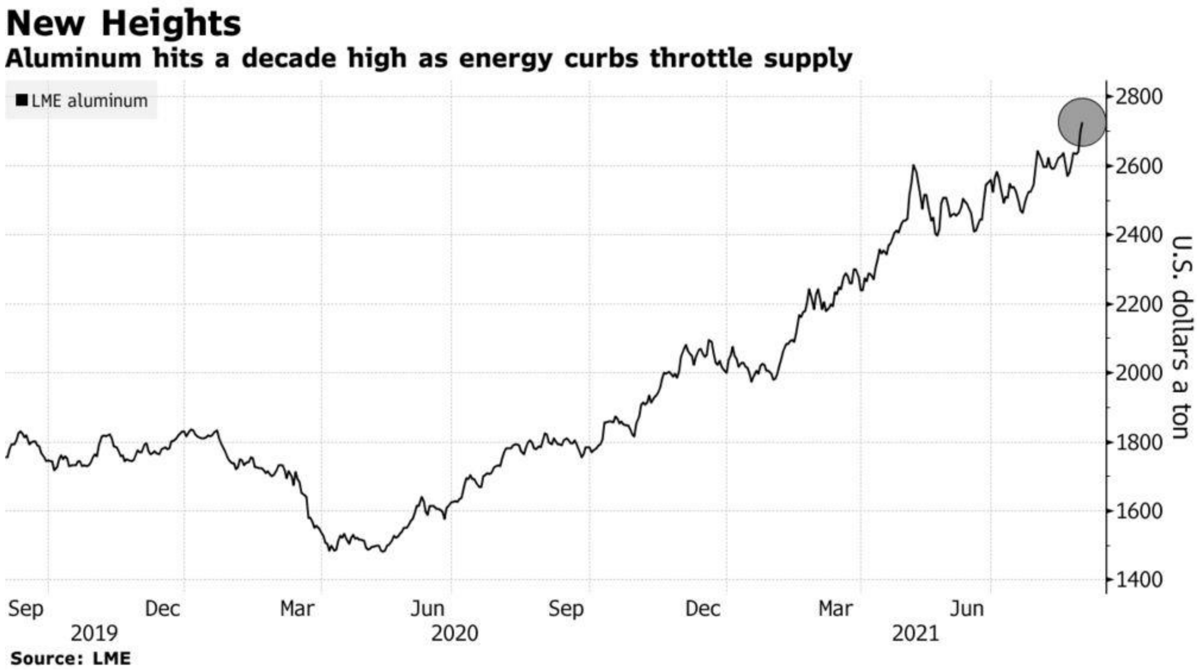


Technique	Instrument Cost	Detection Limit	Portable?
Inductively-Coupled Plasma Mass-Spectrometry	~$180k	Part-per-trillion	No
X-Ray Fluorescence Spectroscopy	~$13-17k	10s of part-per-million	Yes
Laser-Induced Breakdown Spectroscopy	~$30-50k	10s of part-per-million	Yes
Luminescence Spectroscopy	~$18-35k	10s of part-per-billion	Yes

Luminescent sensors can provide significantly higher sensitivity than portable XRF or LIBs techniques at a comparable cost, while providing significant cost and time savings over ICP-MS

Importance of Aluminum

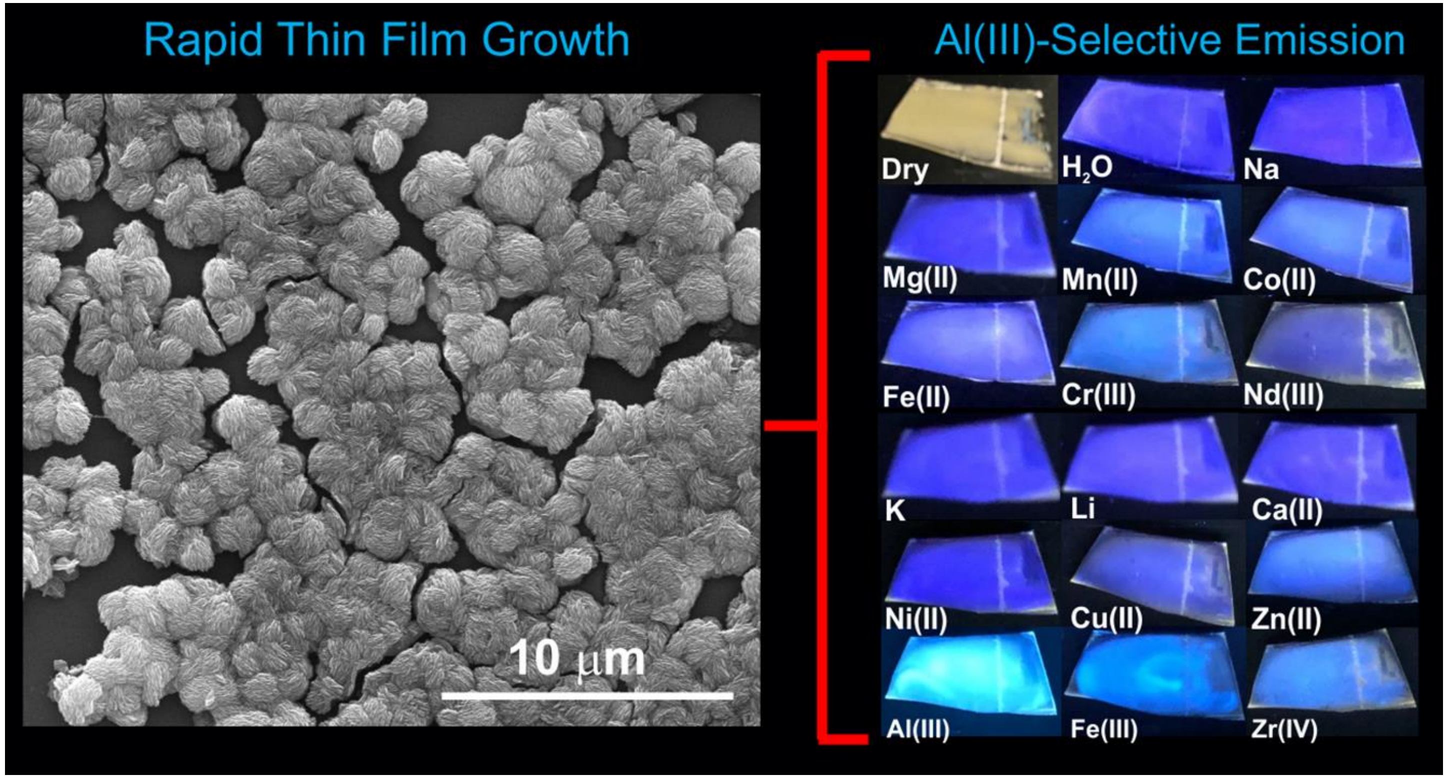




Source: CRU Group

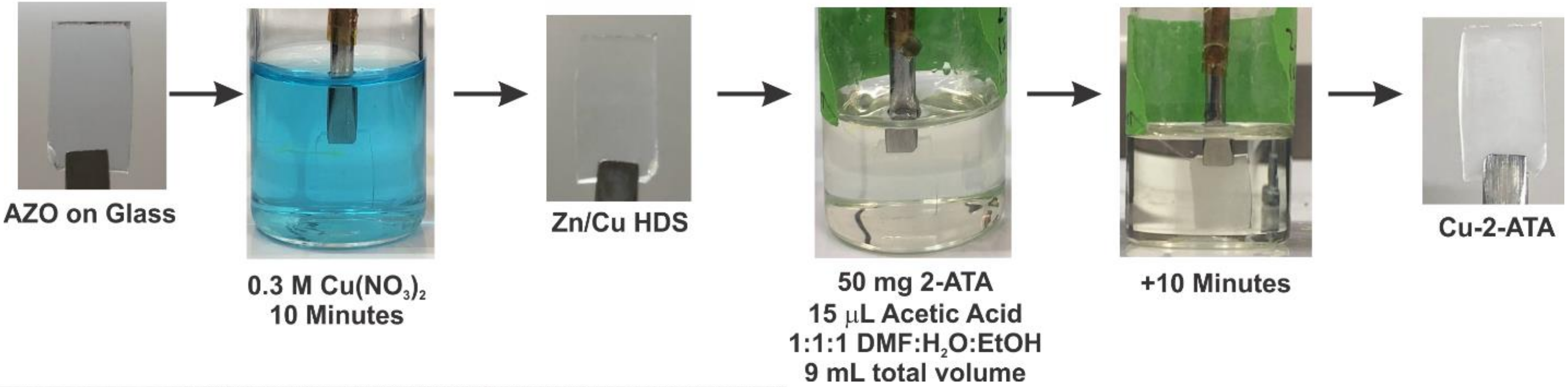
Detection of Aluminum

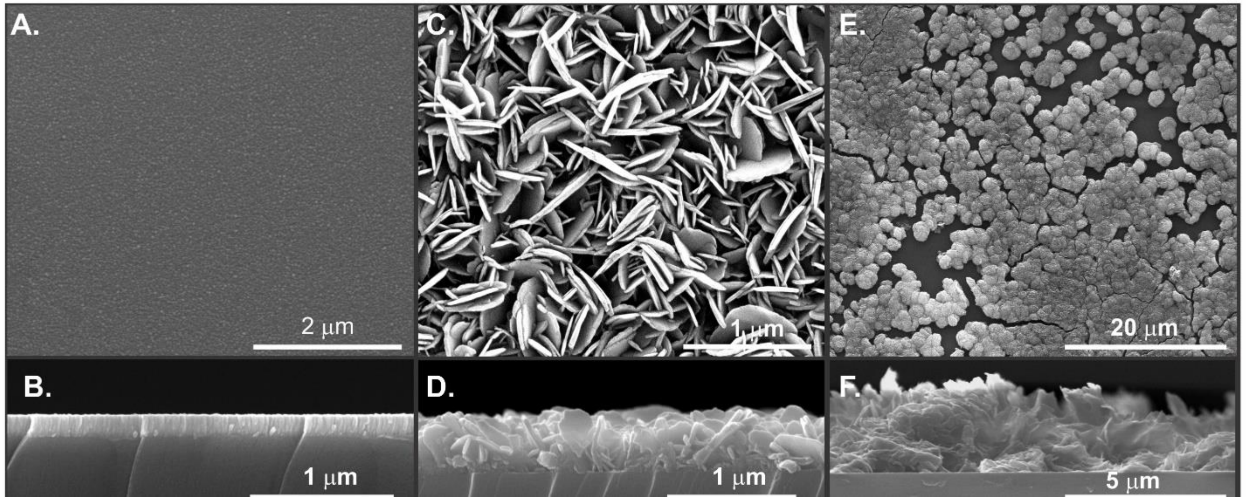
- Aluminum is one of **35 critical metals/minerals** (USGS 2018)
- Aluminum is **abundant in coal and its utilization byproducts**
- Aluminum is also **a common interferant** for extracting REEs and other high value metals

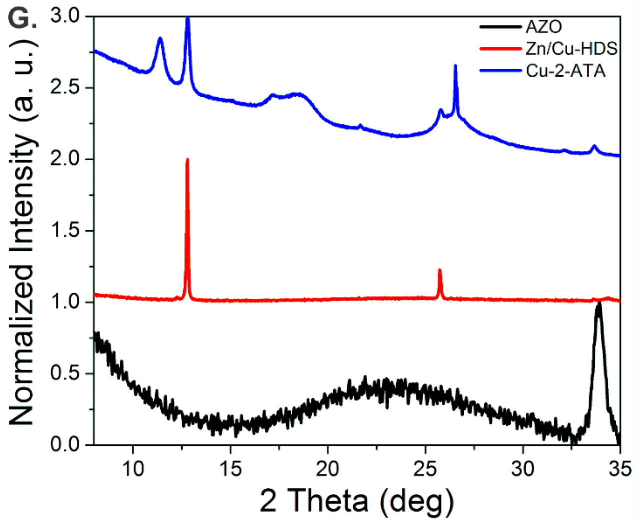


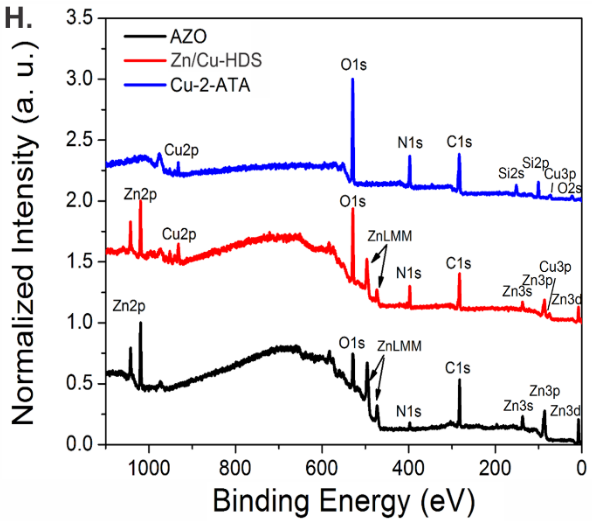
Crawford, S.E., Kim, K.J., Diemler, N, Baltrus, J.P, *ACS Appl. Opt. Mater.* **2023**, *1*(2), 587

Fabrication of a MOF Thin Film Al(III) Sensor



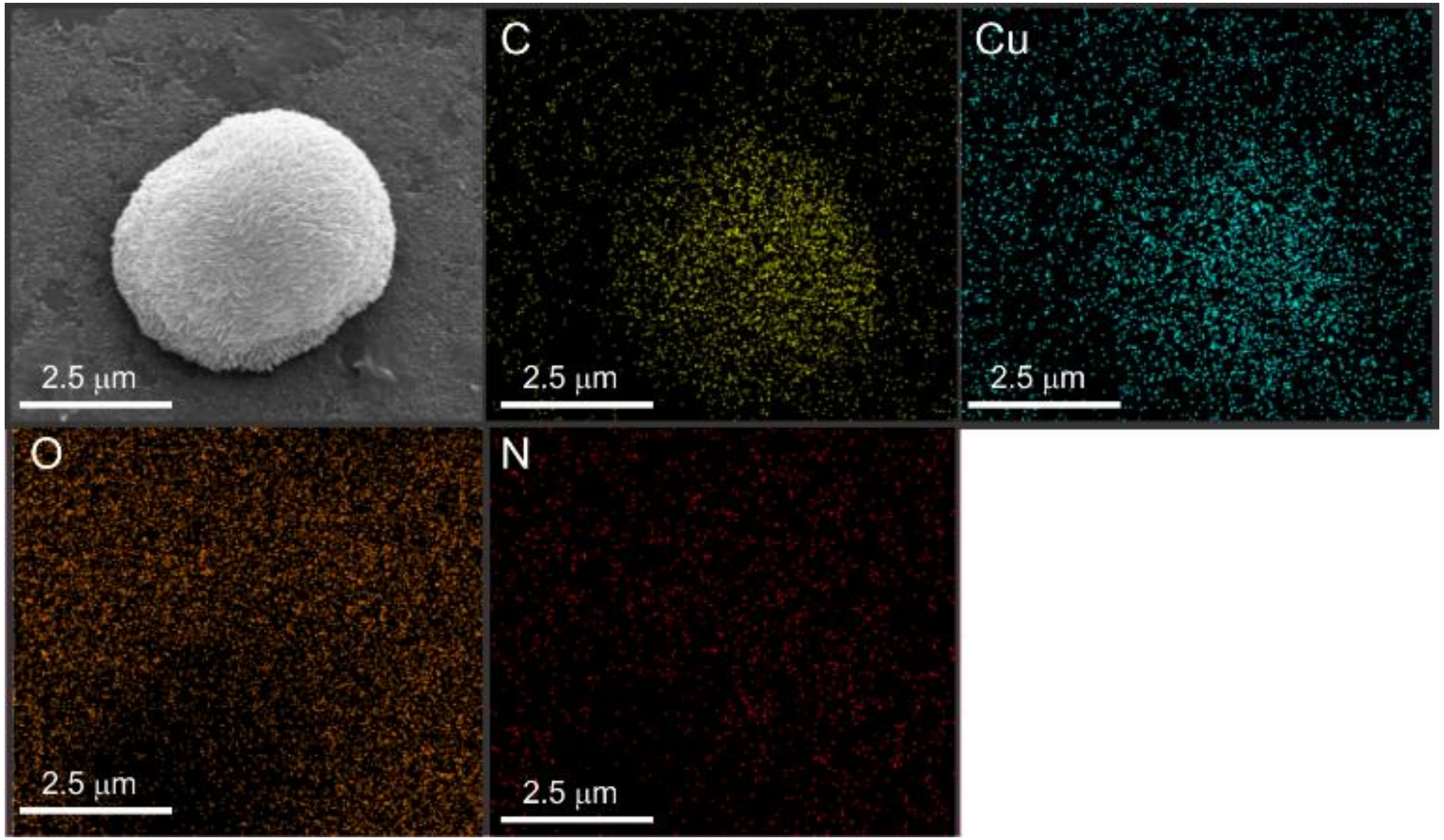


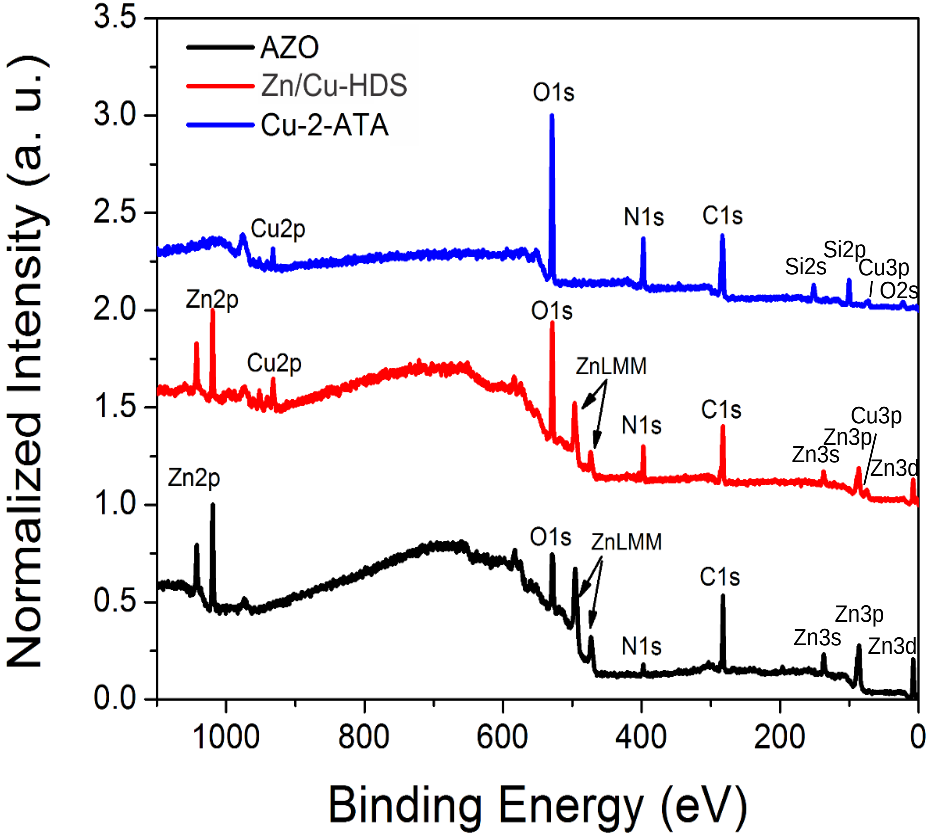




AZO: aluminum-doped Zinc Oxide; ***HDS***: Hydroxy Double Salt; ***2-ATA***: 2-aminoterephthalic acid

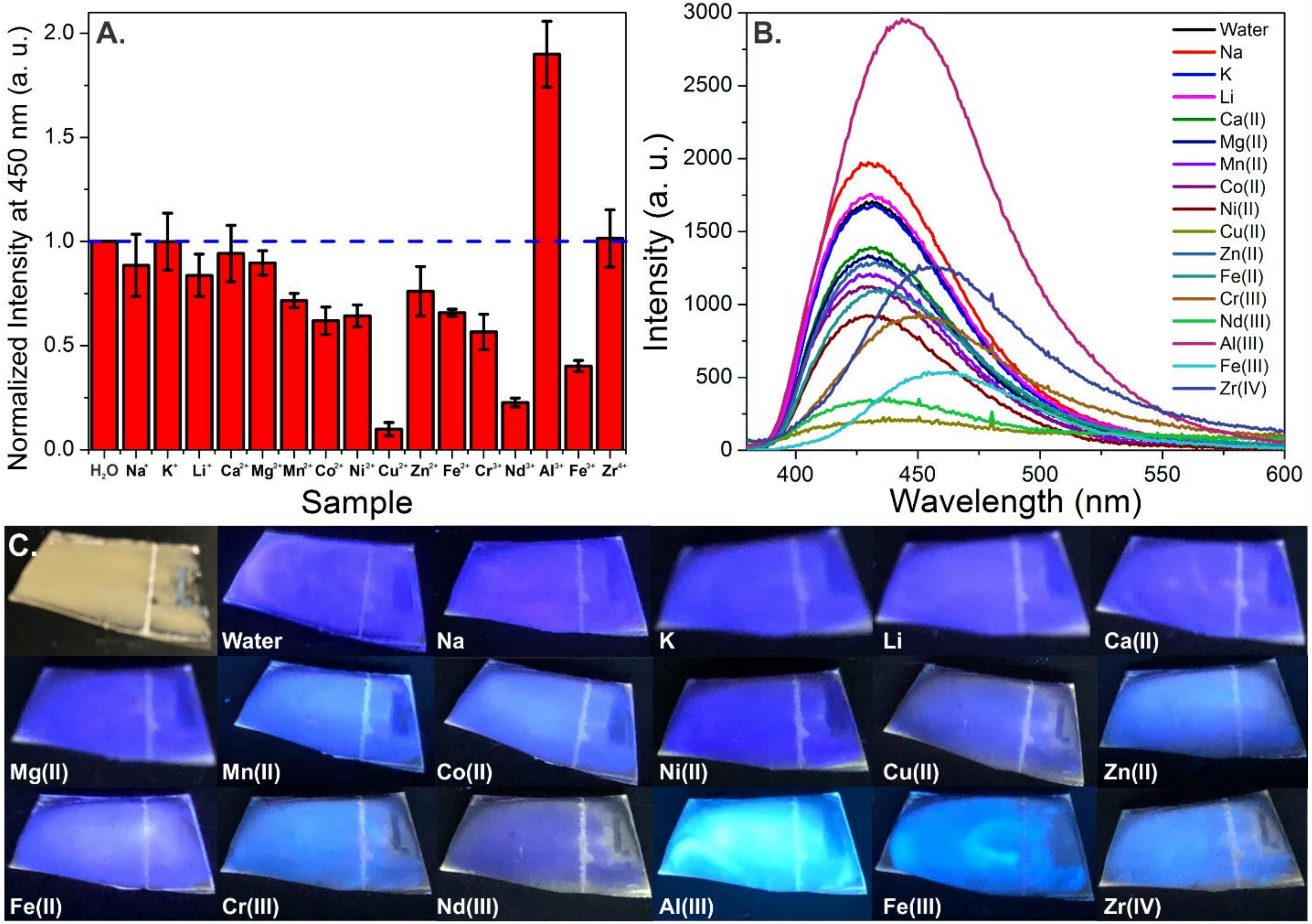
SEM Indicates Cu-rich Structures





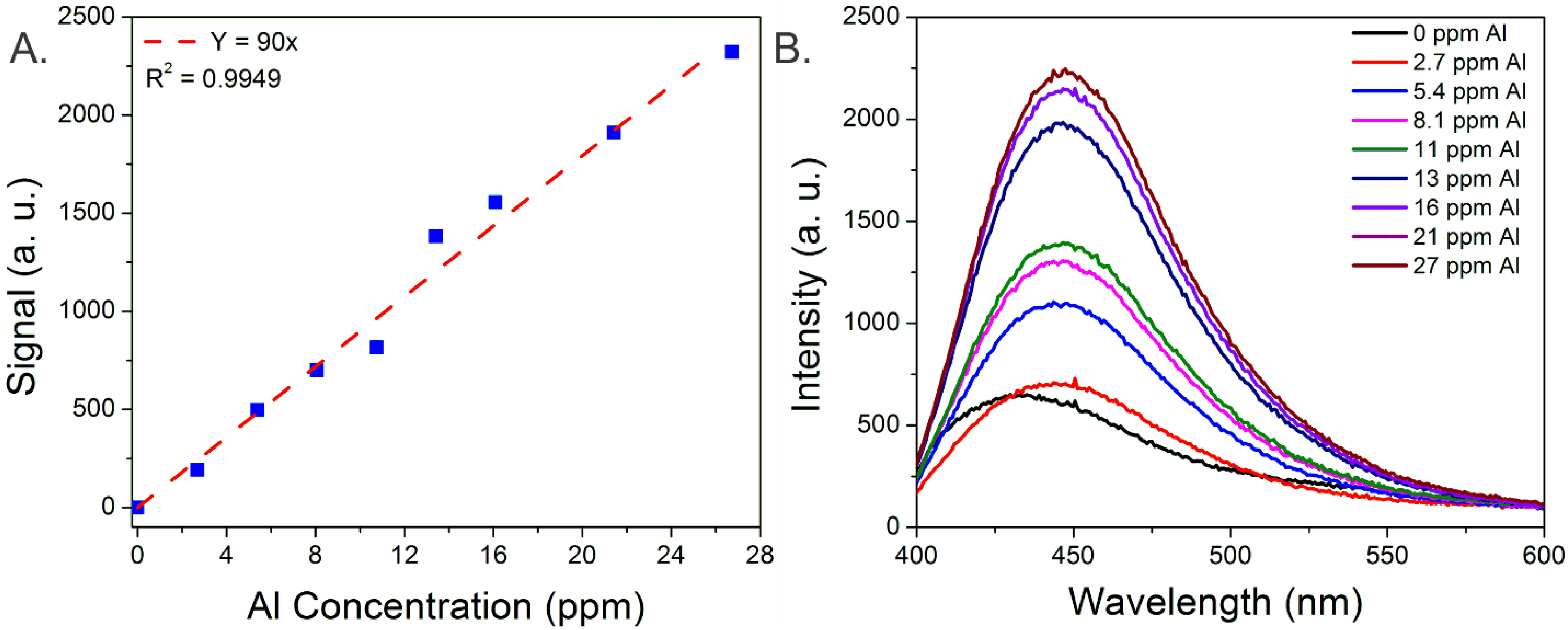
Luminescent Sensing of Aluminum

NATIONAL ENERGY TECHNOLOGY LABORATORY



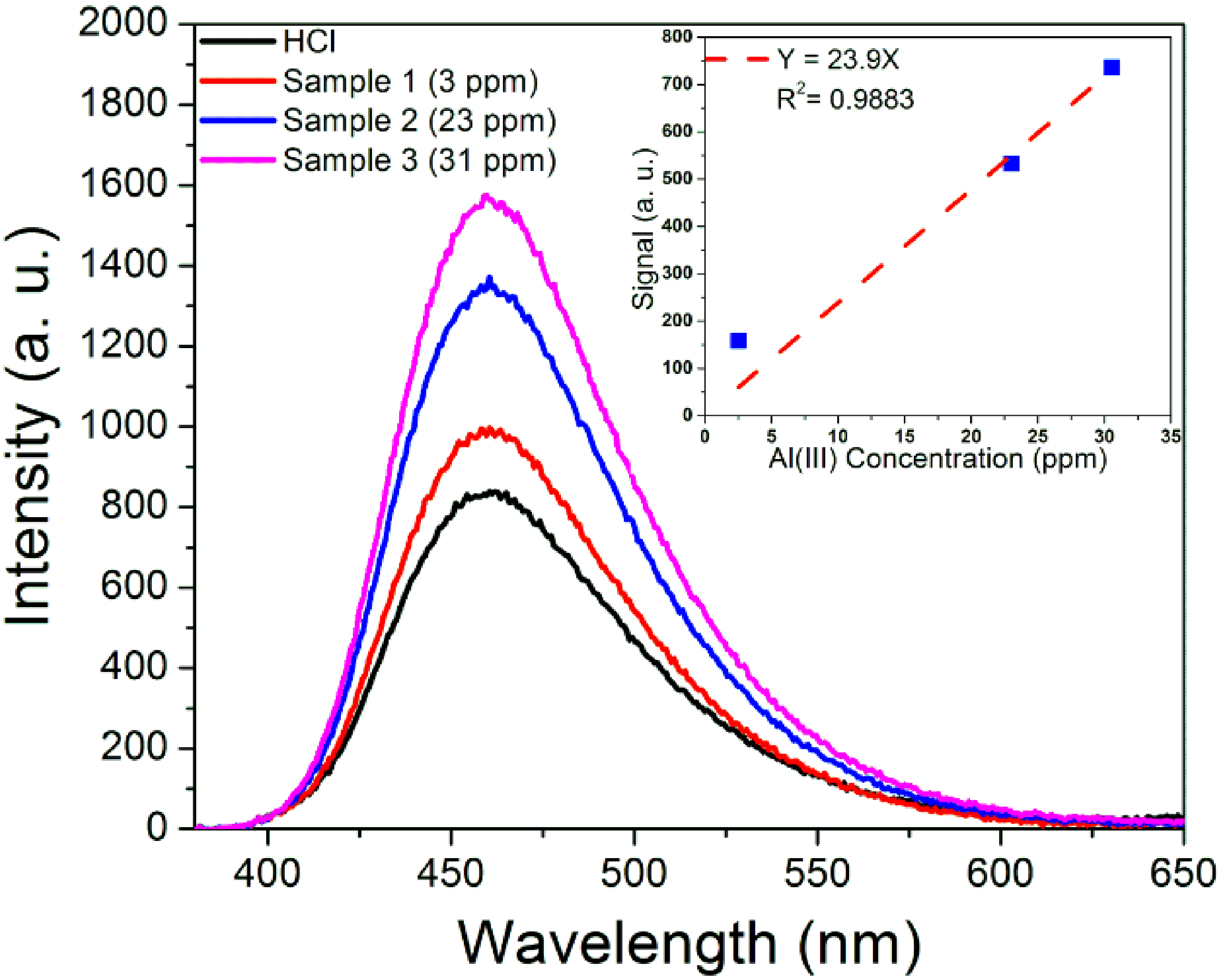
- Aluminum is an economically critical metal as defined by the USGS
- Aluminum is abundant in coal and its utilization byproducts
- Aluminum is also a common interferant for extracting REEs and other high value metals
- Sensing response is selective when tested against 16 different metals

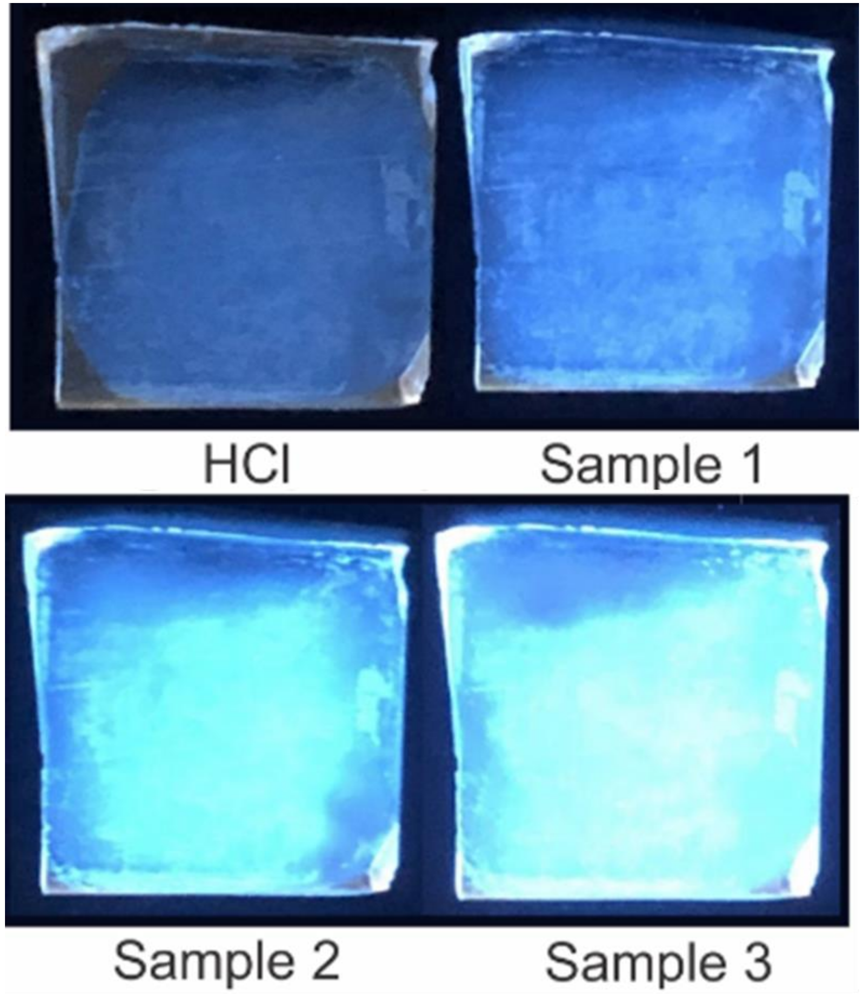
Part-Per-Billion Limits of Detection



Crawford, S.E., Kim, K.J., Diemler, N, Baltrus, J.P, *ACS Appl. Opt. Mater.* **2023**, *1*(2), 587

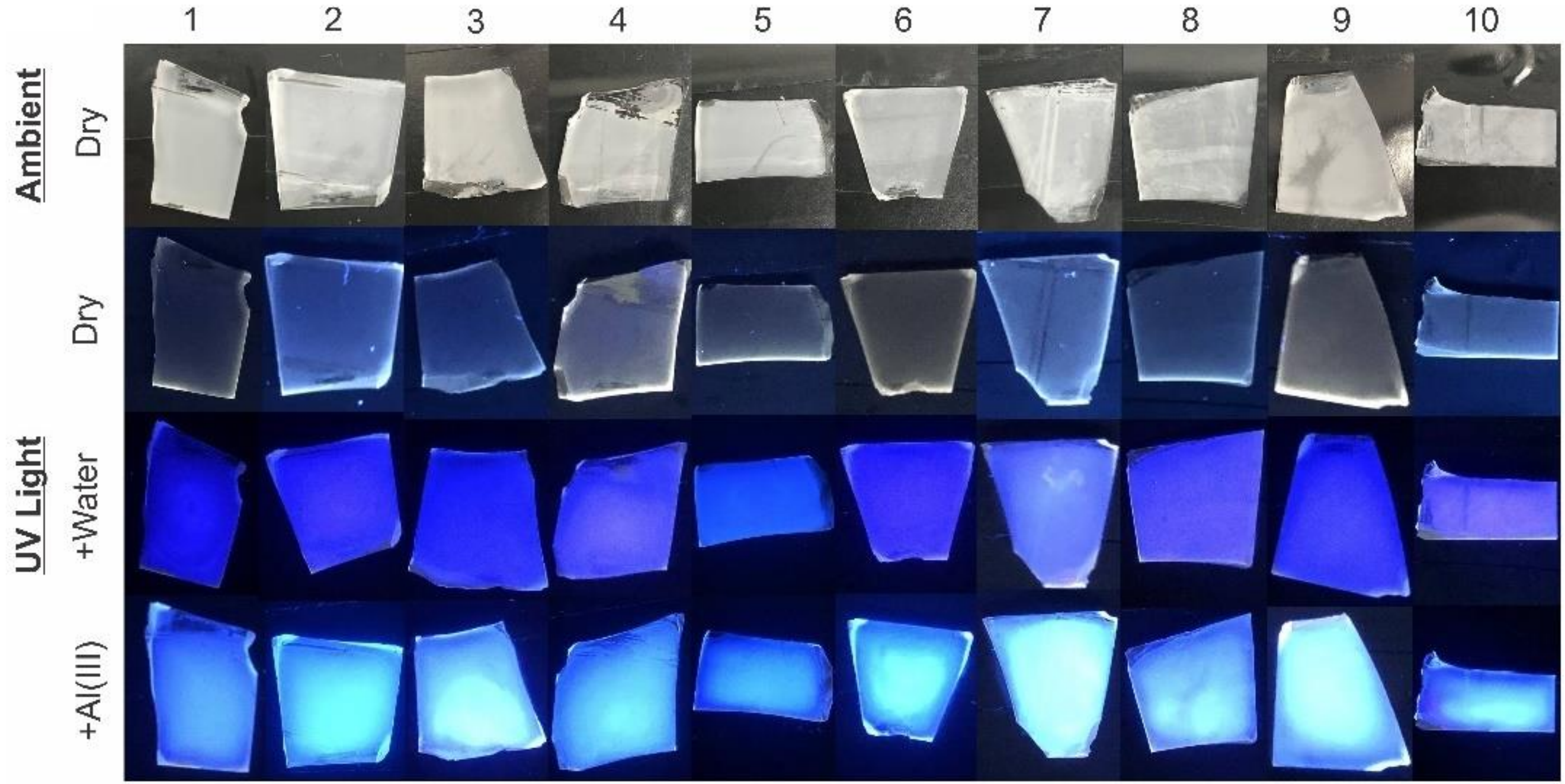
Deployment in Fly Ash Leachate Samples



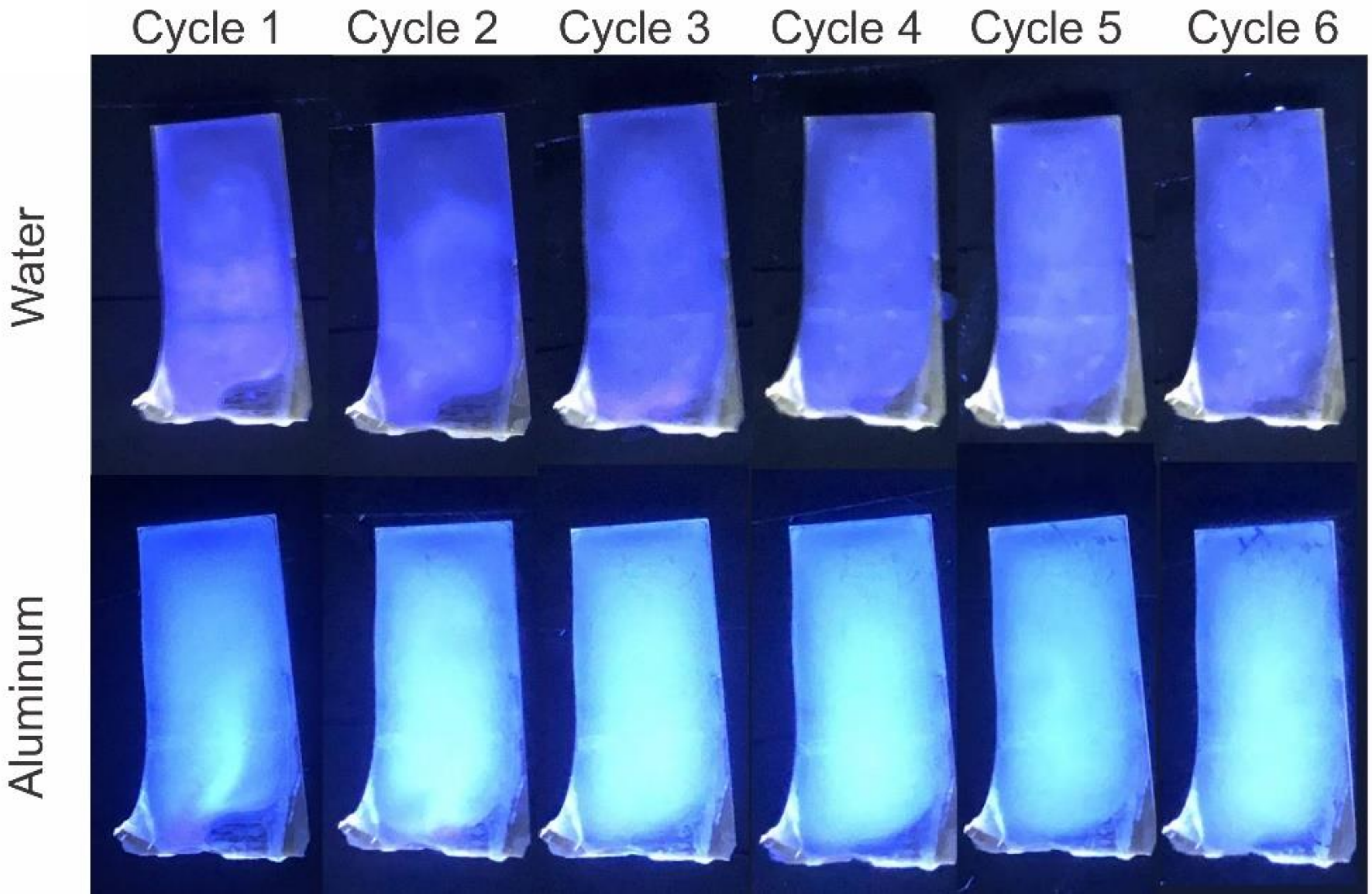


Crawford, S.E., Kim, K.J., Diemler, N, Baltrus, J.P, *ACS Appl. Opt. Mater.* **2023**, *1*(2), 587

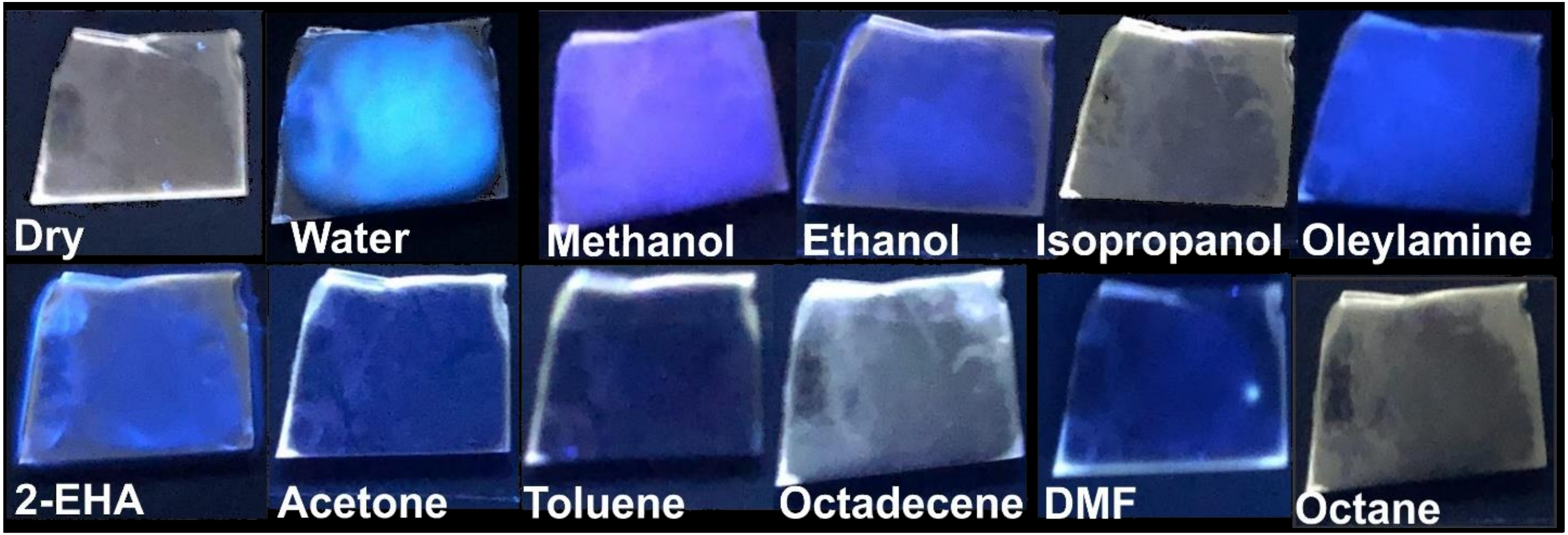
Reproducible Synthesis and Response



Stability Across Multiple Sensing Cycles



Solvent-Selective Luminescence



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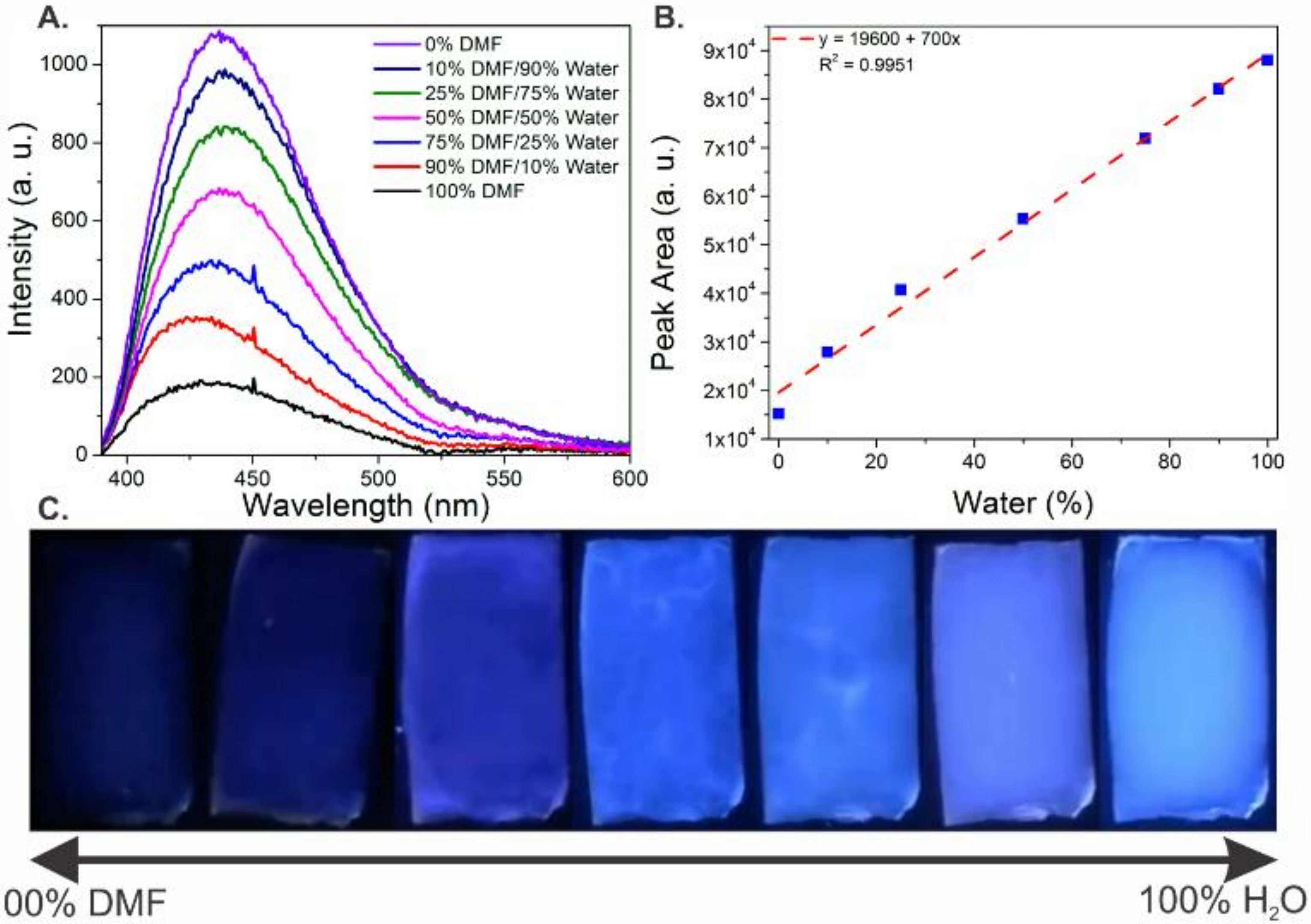
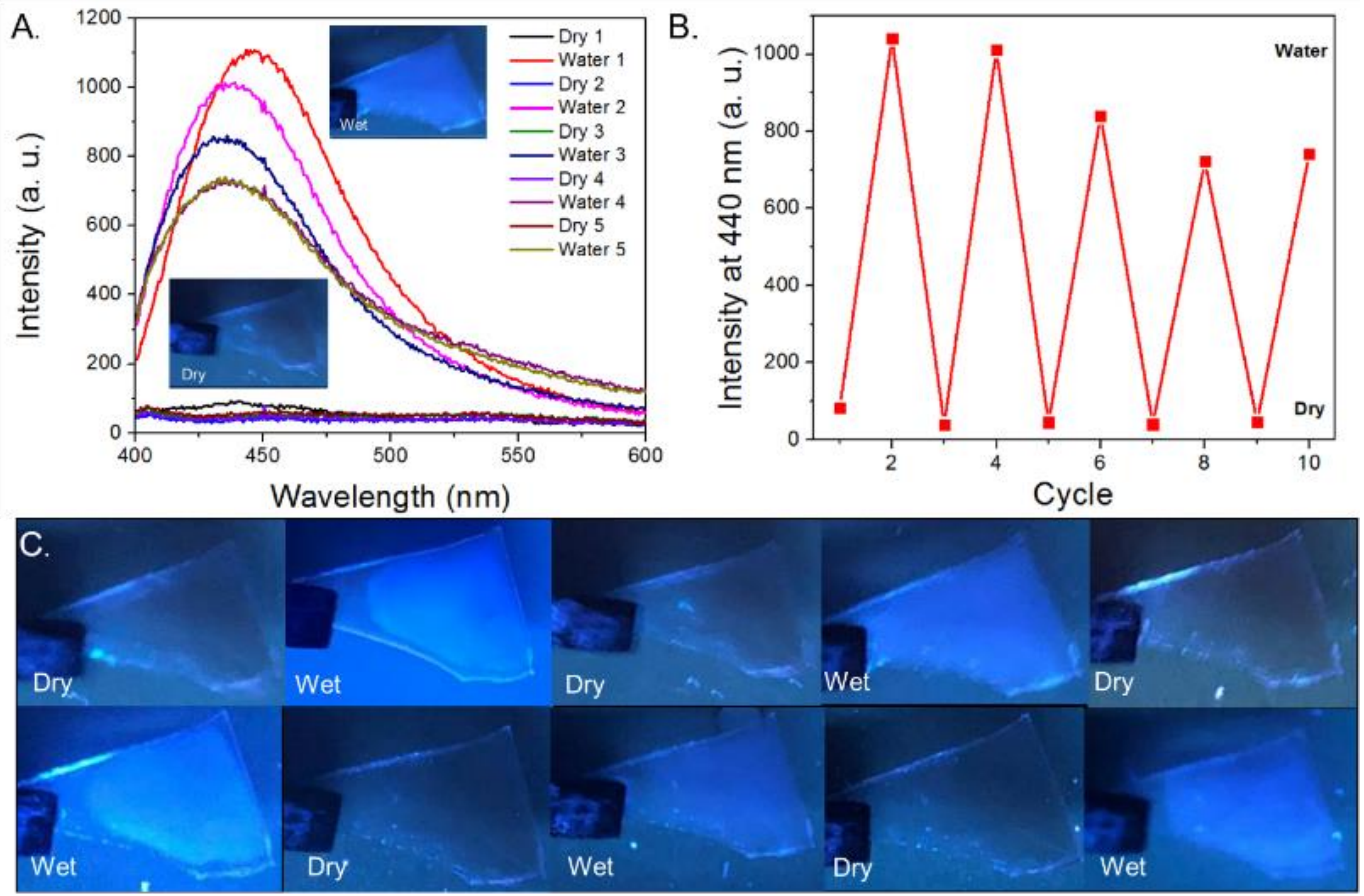
Solvent-Selective Luminescence

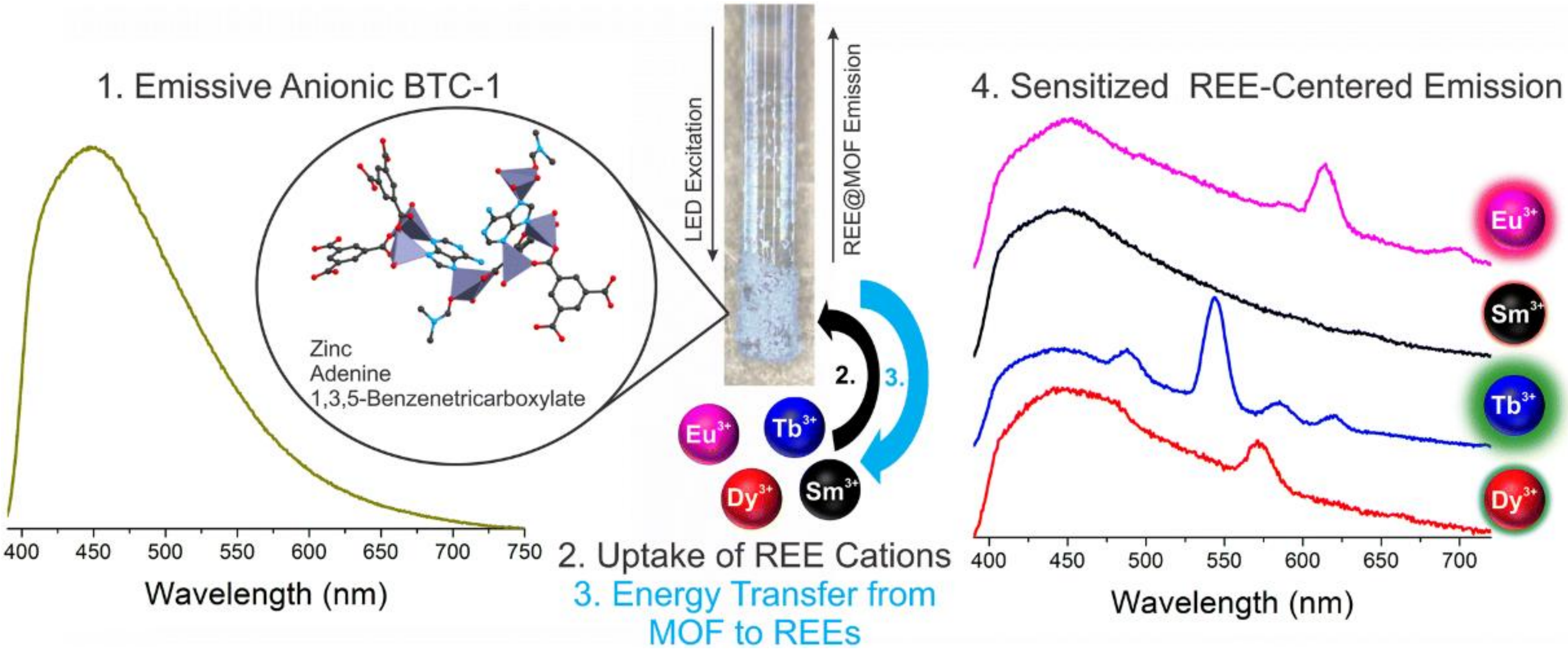


Crawford, S.E., Kim, K.J., Diemler, N, Baltrus, J.P, *ACS Appl. Opt. Mater.* **2023**, *1*(2), 587

Recyclable Response

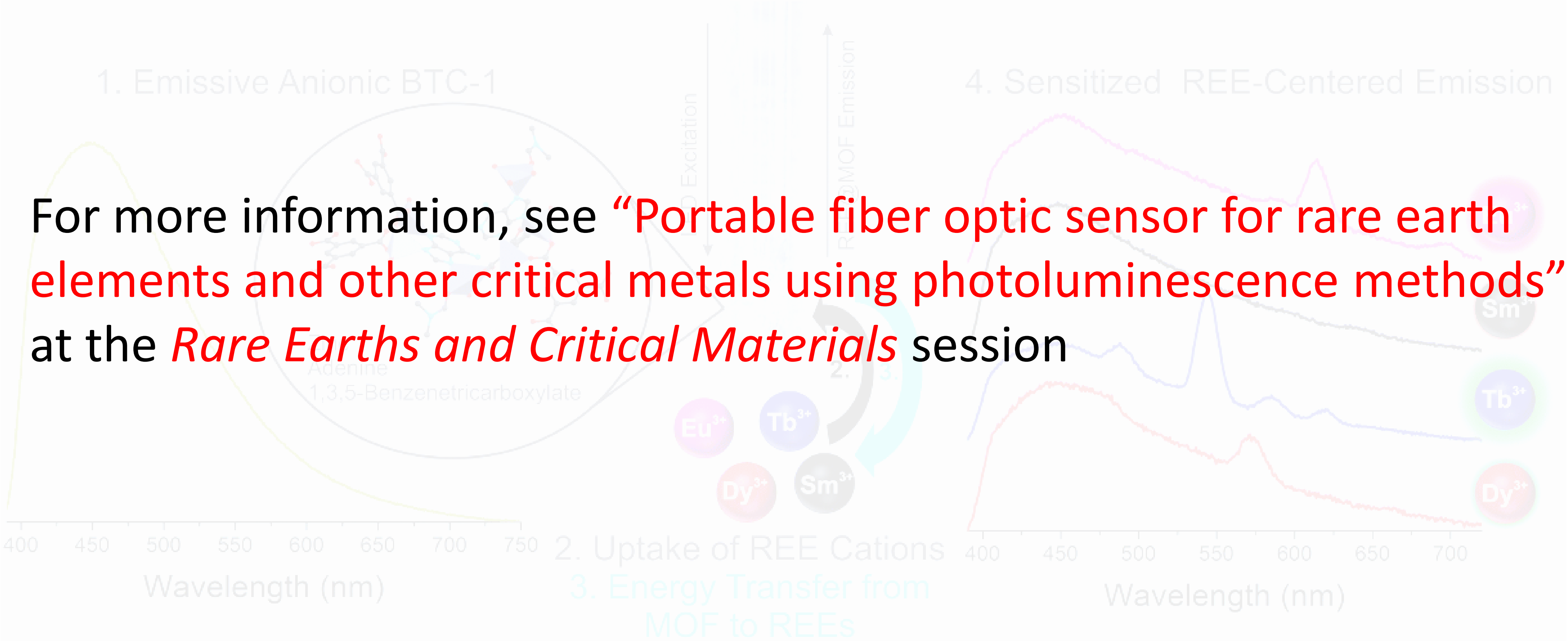


MOF Thin Film for Rare Earth Sensitization



Crawford, S., Burgess, W., Kim, K.-J., Baltrus, J., Diemler, N.; *RSC Appl. Int.* **2024**, *1*, 689

MOF Thin Film for Rare Earth Sensitization

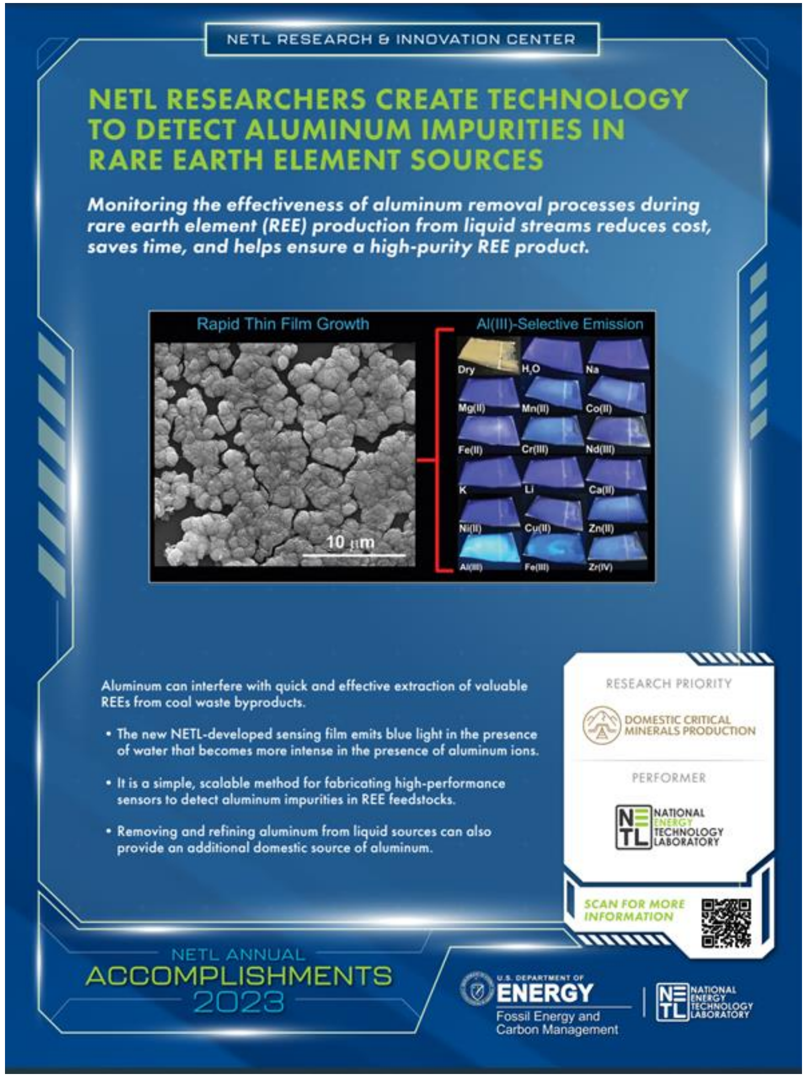


For more information, see "Portable fiber optic sensor for rare earth elements and other critical metals using photoluminescence methods" at the *Rare Earths and Critical Materials* session

Crawford, S., Burgess, W., Kim, K.-J., Baltrus, J., Diemler, N.; *RSC Appl. Int.* **2024**, *1*, 689

Concluding Thoughts

- Metal oxide templates offer a potentially scalable fabrication method for MOF thin films
- No expensive equipment or heating required
- Growth limited to AZO template---limits reagent waste
- Solvent conditions and anion can be used to tune MOF size, coverage density, and structure
- Exploited in luminescent, mass, and optical sensing applications for gasses and metal ions



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