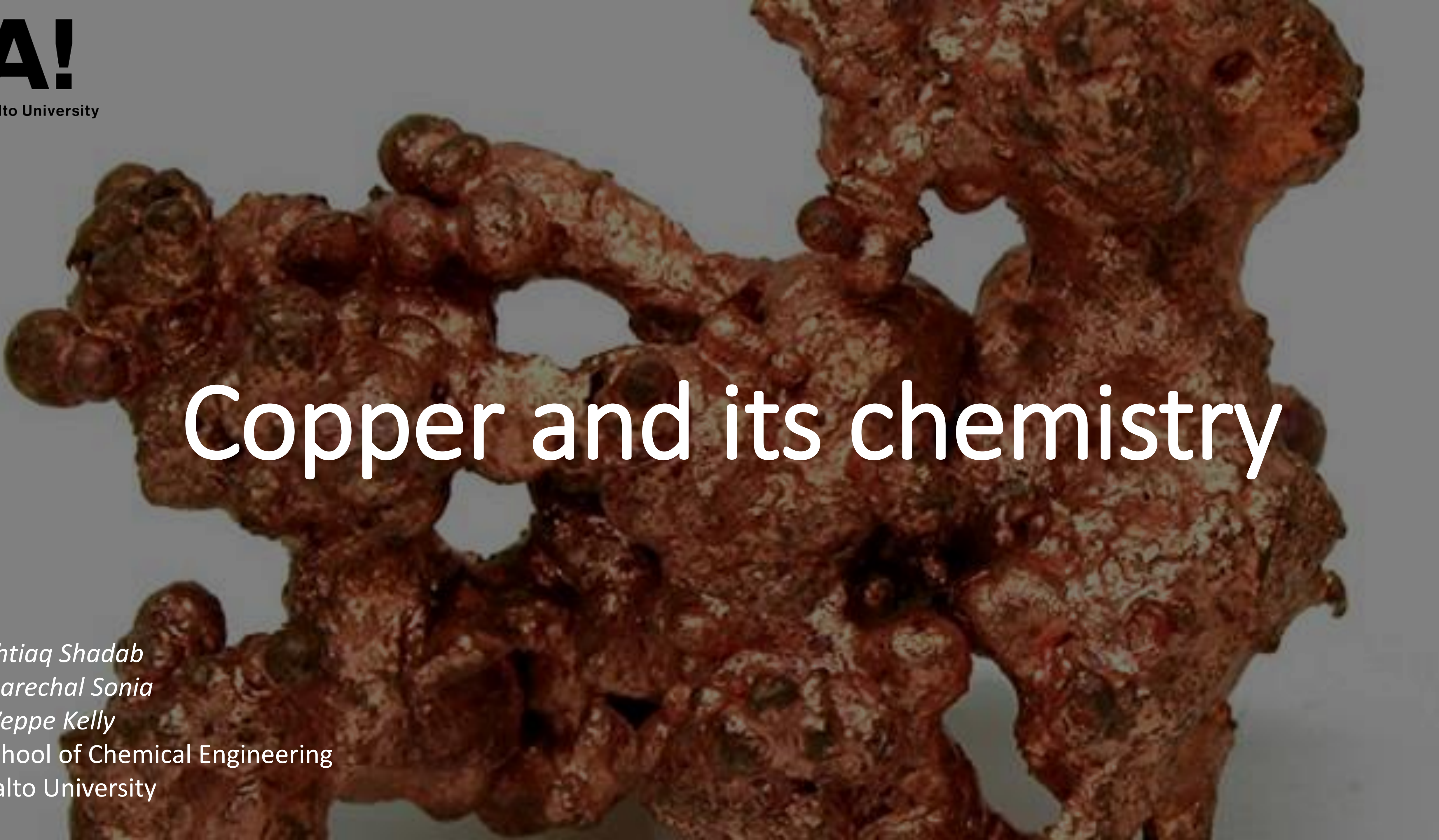

Copper and its chemistry

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School of Chemical Engineering
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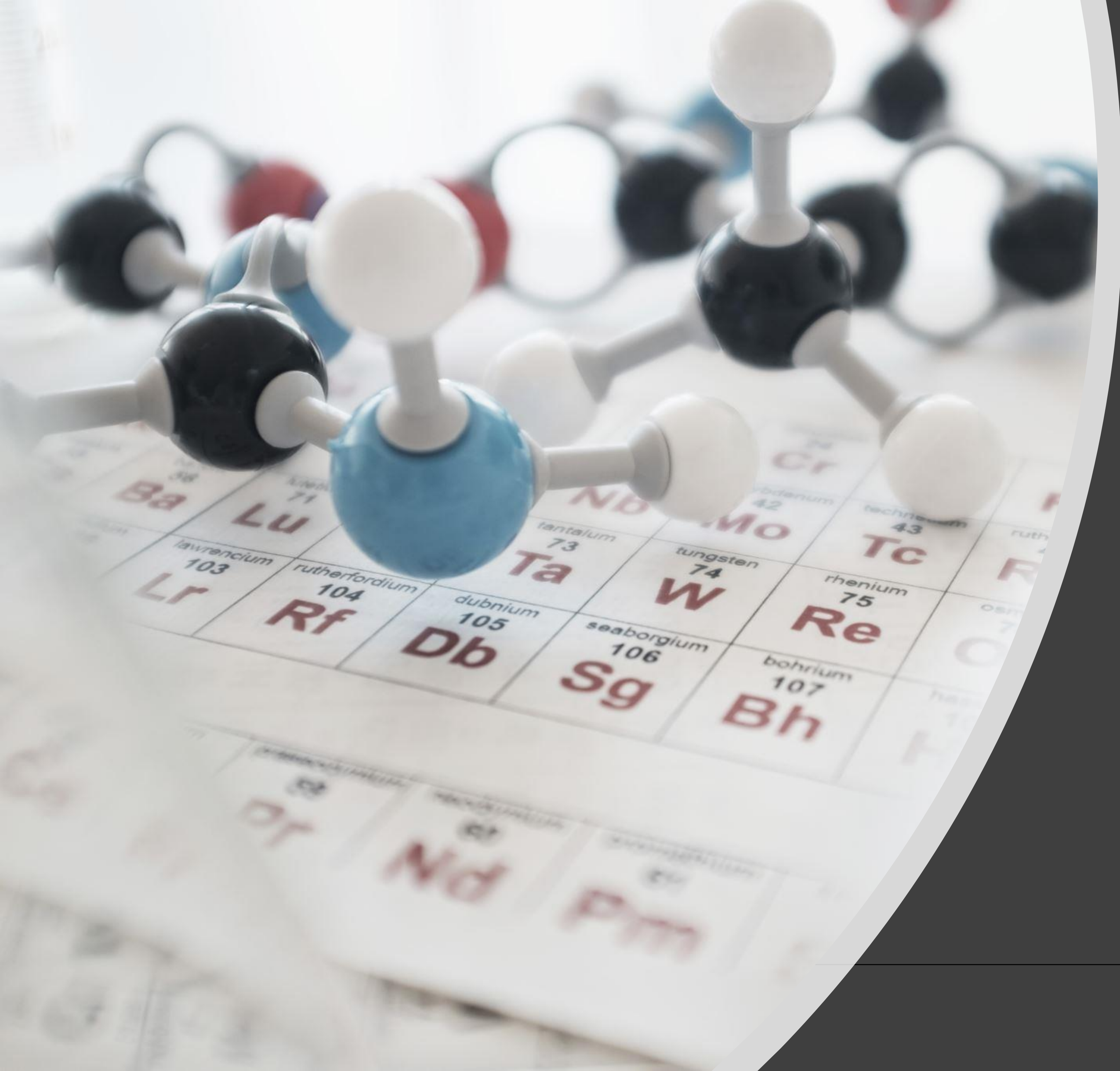
Overview

Element

Chemistry

Compounds

Applications



Element

Origin - Abundancy - Properties - Production

Presentation

- The oldest traces :
  - first half of the 5th millennium BC ,
  - 6 000 years ago : copper ores mining
- Name comes from the Latin cyprium (island of Cyprus)
- 26th most abundant element in the earth's crust (50 ppm)
- Properties :
  - Reddish color
  - very good thermal and electrical conductivity
  - resistant to atmospheric and marine corrosion
  - very malleable, tough and ductile and relatively soft
- Copper ores come in two main chemical forms :
  - Sulphide: CuFeS2, Cu5FeS4, Cu2S --> 80% of world production
  - Oxidised : CuCO3,Cu(OH)2, 2CuCO3,Cu(OH)2, Cu2O

- The element copper, from the ores, is obtained by two metallurgical methods :
  - Pyrometallurgy (sulphide ores)
    - $Cu_2O + FeS = Cu_2S + FeO$
    - $Cu_2S + 3/2\ O_2 = Cu_2O + SO_2$
    - $2\ Cu_2O + Cu_2S = 6\ Cu + SO_2$
  - Hydrometallurgy (oxidised or poor sulphide ores)
    - A dissolution
    - Solvent extraction
    - Electrolysis

Export and import

Mining production

Chile 5733

Peru 2145

China 1855

In thousand tones of Copper content (2021)

Importing countries

China 4 009

USA 930

Italia 631

In thousand tones (2021)

Mainly used in :

- Equipment
- Construction
- Transport
- Industry

Metal production

China 10 021

Chile 2329

Japan 1583

In thousand tones (2021)

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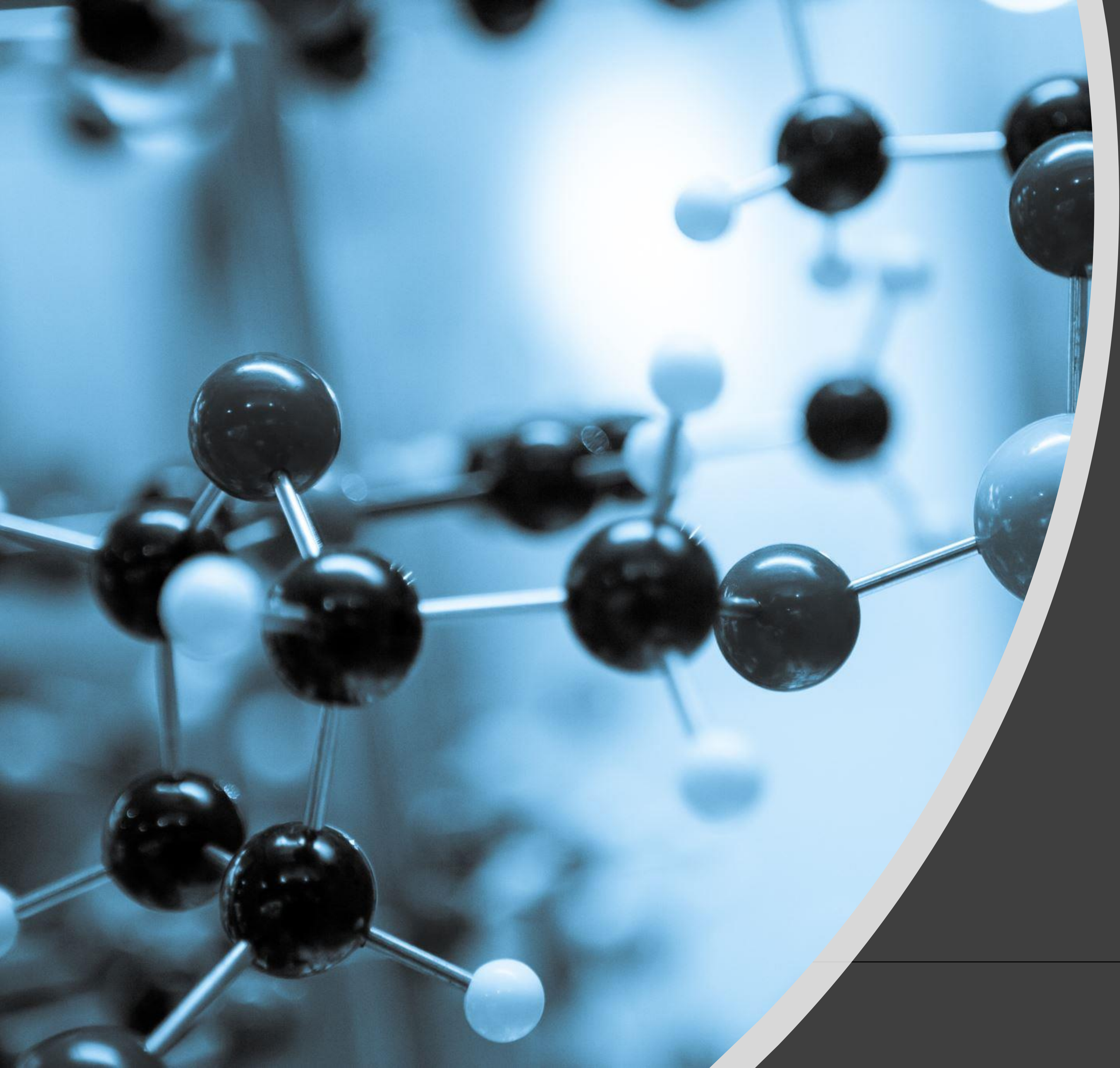
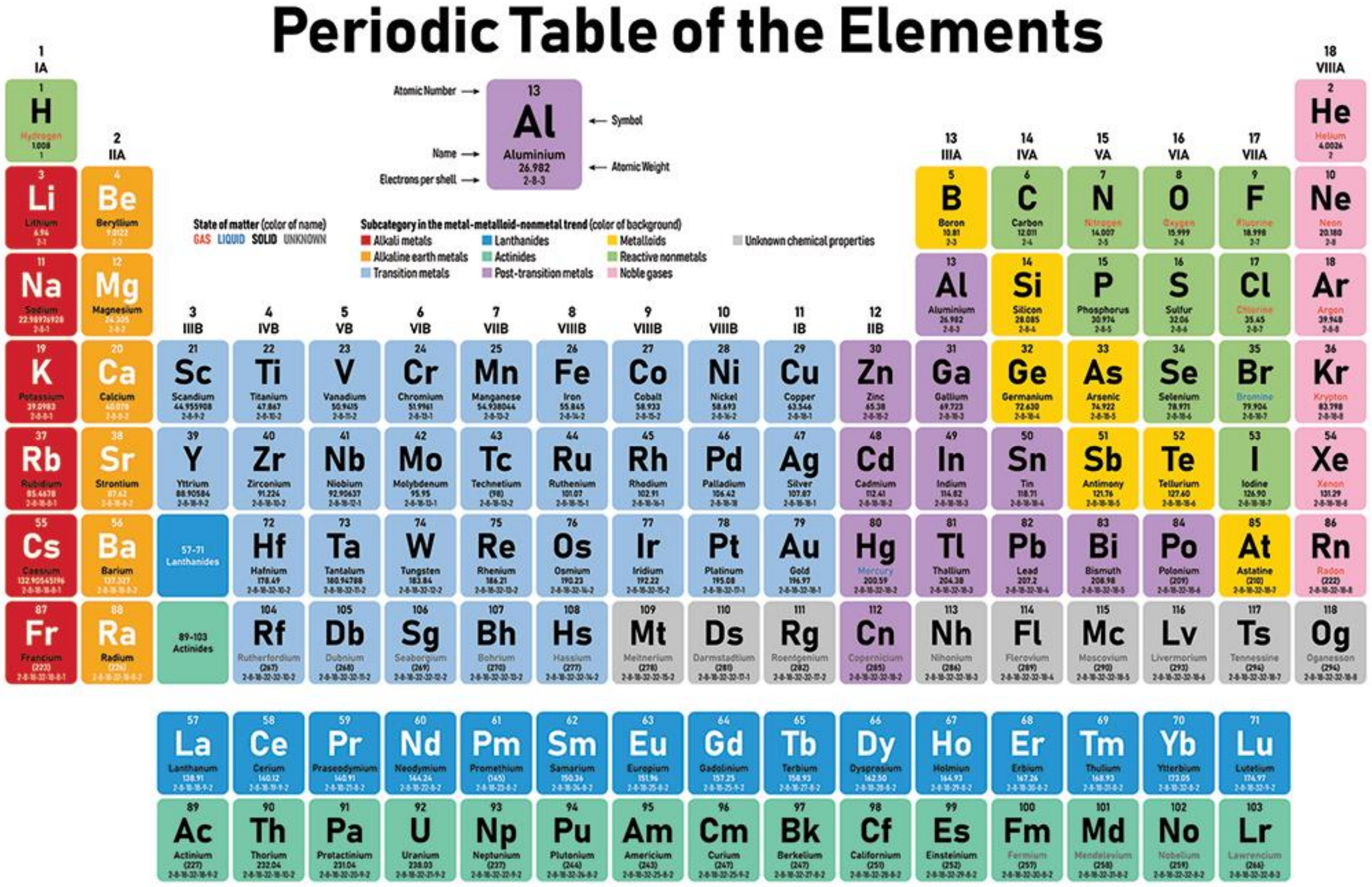


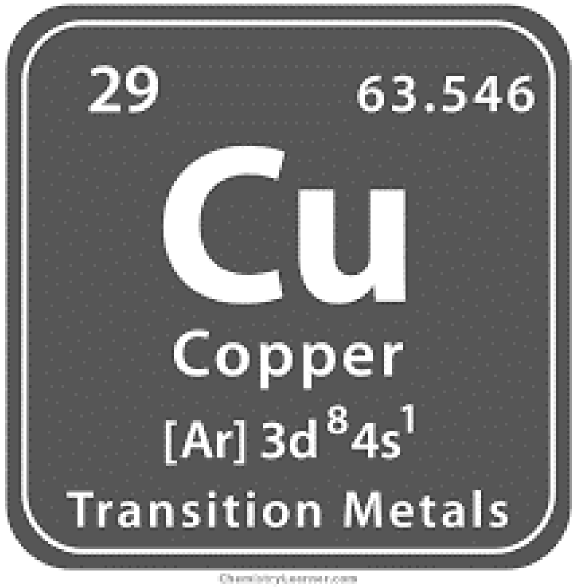
Chemistry

Electronic configuration – Oxidation state - Reactivity

Chemistry



Electronic configuration



Exception to the Klechkowski's rule

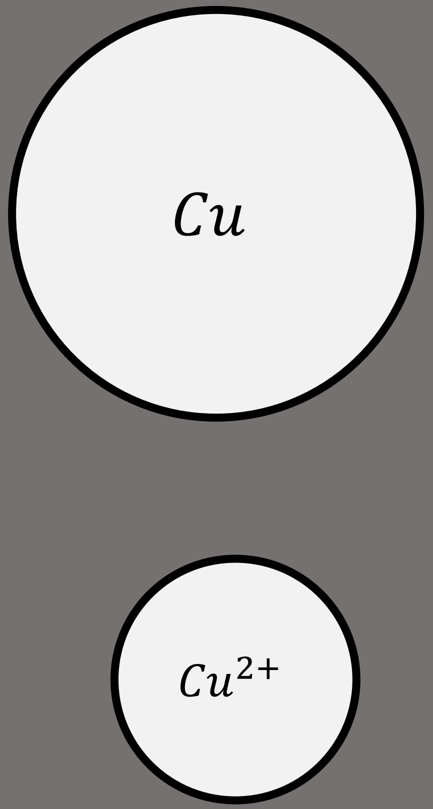
Chemistry

Oxidation states

- Most common oxidation state **+2** $(CuCl_2, Cu\mathrm{O}, CuSO_4)$, less common **+1** $(CuCl, Cu_2S, Cu_2O)$,
- Can have oxidation state of **+3** $(KCuO_2, K_3CuF_6)$ and **+4** (Cs_2CuF_6),
- **Copper (I) compounds :** cuprous compounds**,** diamagnetic, colourless, tetrahedral or square planar geometry, more stable state in solid compounds at moderate temperatures
- **Copper (II) compounds :** cupric compounds, usually coloured, affected by Jahn Teller distortions, more stable state in aqueous solutions

Metallic and ionic sizes

- 135pm and 71-87pm



Chemistry

Reactivity

- No reaction with water
- Slowly react whit atmospheric oxygen → green layer of verdigris (copper carbonate)
- Protection of the underlying metal from further corrosion = **passivation**
- In the absence of CO2, oxidation in air begins at 120 °C
- Reacts with hydrogen sulphide to form various copper sulphides
- low reactivity + malleability = ideal for architecture

https://en.wikipedia.org/w/index.php?title=Copper&oldid=11103143/

Compounds

Properties and Applications

Compounds of copper in +1 Oxidation

Cuprous oxide, (Cu_2O)

- Melting point of 1235 °C, and diamagnetic
- It is used in pigments, fungicides, in rectifier diodes before the use of silicon (due to semiconducting properties)

Cuprous chloride, (Cu_2Cl_2)

- Whitish to greyish solid, moist air converts into greenish color
- Cuprous chloride is used as catalyst in organic reactions, condensing agent for soap and fats

Cuprous sulfide, (Cu_2S)

- Occurs in the form of black powder or lumps, and melting point is 1130 °C
- Most used in industries such as luminous paints, solar cells, electrodes and solid lubricants

https://nanografi.com/blog/cuprous-copper-oxide-properties-and-applications/

Compounds of copper in +2 Oxidation

Cupric oxide, (CuO)

- Appear as brownish black powder, with melting point of 1201 °C.
- Used in glass industry, porcelain glazes, and artificial gems. Also use as an oxidation catalyst.

Cupric chloride ($CuCl_2$)

- It is yellowish to brown powder, with 498 °C melting point.
- Use in wood preservative, dyeing and printing of fibers, pigments of glass.

Cupric sulfate ($CuSO_4$)

- It also exist as hydrated form $CuSO_4 \cdot 5H_2O$ and known as blue vitriol.
- For agriculture purposes, as a pesticides, germicides, soil additive, also in medicines.

Compounds of copper

Other compounds of copper

- **ON = +3**: Examples are $KCuO_2$
- **ON = +4**: An example is Cs_2CuF_6
- Copper acetate $Cu(CH_3COO)_2$
- Copper nitrate $Cu(NO_3)_2$
- Copper oxychloride $Cu_2(OH)_3Cl$
- Copper cyanide CuCN
- Copper bromide $CuBr_2$

Applications

Atomic Layer Deposition of Copper Metal Films

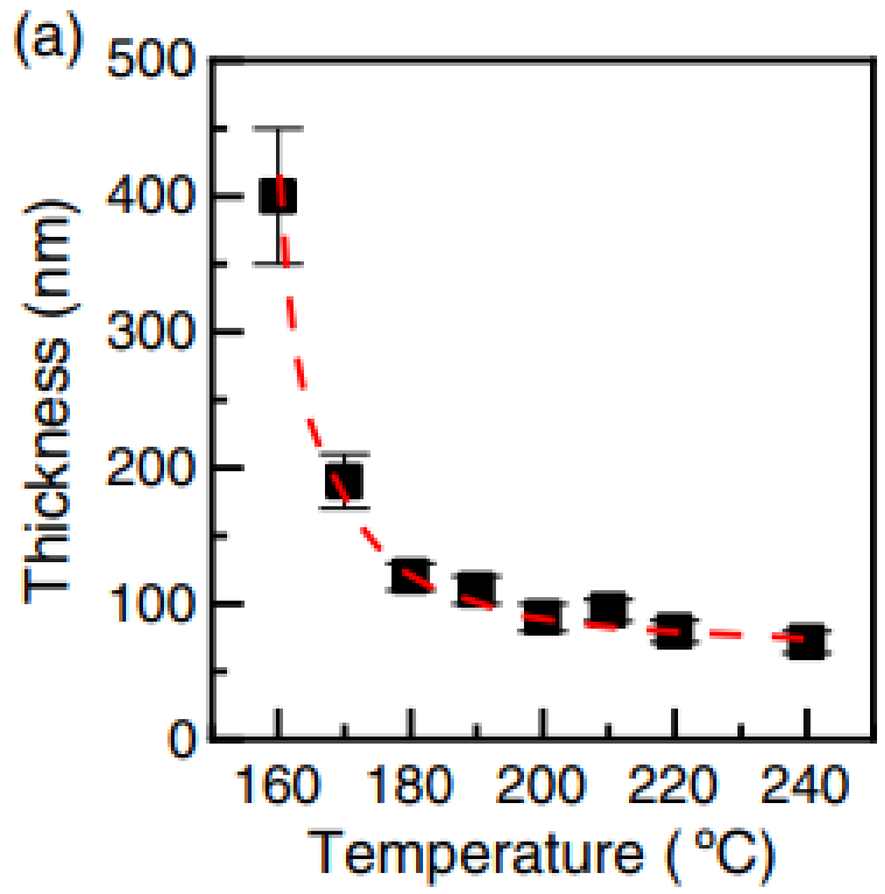
Atomic Layer Deposition of Copper Metal Films

ALD of Cu(acac)2 and Hydroquinone Reductant

- Copper has low sensitivity and high resistance to electromigration
- The process of ALD takes place at low temperature
- Band gap of 2.0 eV
- High growth rate of 1.8 Å/cycle

Uses

- Microelectronic devices
- Integrated circuits
- Printed circuit boards



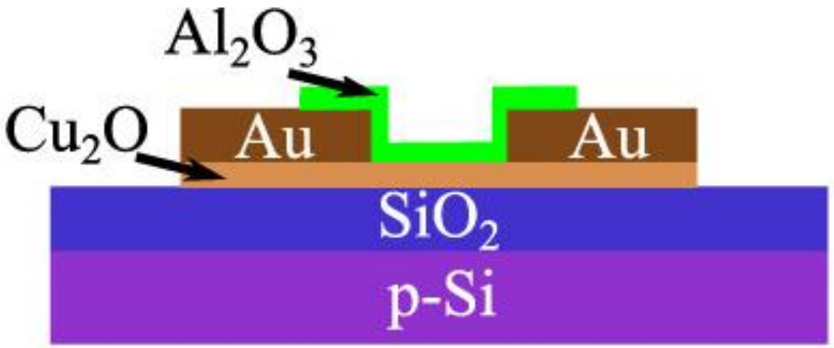
Atomic Layer Deposition of Copper Metal Films

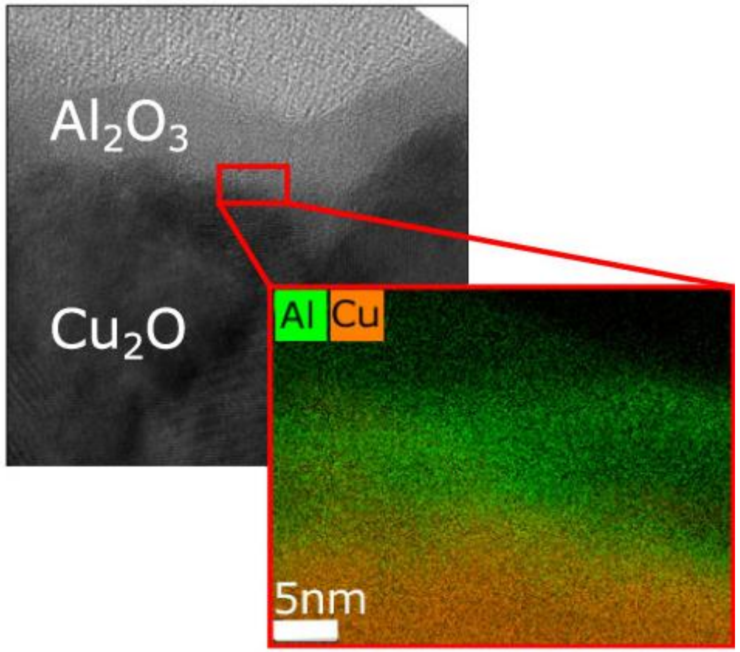
Improvement of oxidation resistance of copper

- Al_2O_3 films were deposited by the atomic layer deposition (ALD) technique onto pure copper
- Following Improvements achieved
- Denser structure
- Hardness

Applications

- Brightness enhancement films for liquid crystal displays (LCD)
- Micro-lens arrays for antireflective polymer optical films





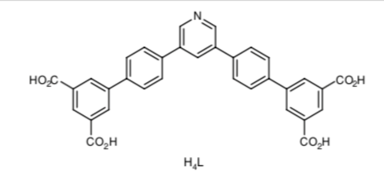
Reversible coordinative binding and separation of sulfur dioxide in a robust metal–organic framework with open copper sites

Context

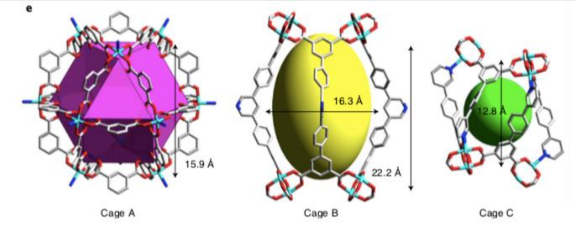
- **Challenge** : reduce SO2 emissions (anthropogenic sources account for >87% of global emissions)

Development of dry regenerable SO2 sorbents operating under ambient conditions

- **First idea** : Organometallic structure (MOF) sorbent but reversibility and/or limited stability in contact with highly corrosive SO2
- **Second idea** : Organometallic structure (MOF) with Open Metal Sites (OMS) : [Cu2(L)] (where L is H4L = 4′,4‴-(pyridine-3,5-diyl)bis([1,1′-biphenyl]-3,5- dicarboxylic acid)), named MFM-170.



Structure of H4L (ligand)



Structure of MFM-170 from single-crystal X-ray diffraction data

- **Efficiency of OMS :**

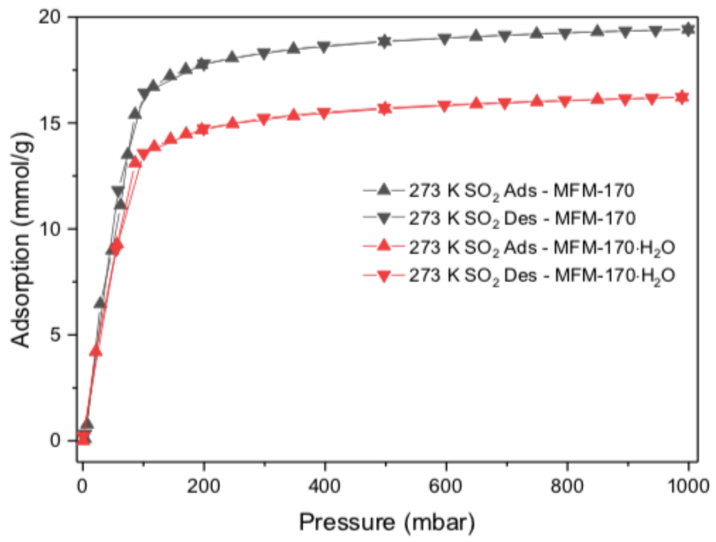


Fig. S15. Comparison of SO_2 isotherms up to 1 bar for MFM-170 (black) and MFM-170·H_2O (red) at 273 K. MFM-170·H_2O was activated by evacuation at room temperature until the mass was stable. MFM-170 was activated by heating at 423 K under vacuum until the mass was stable.

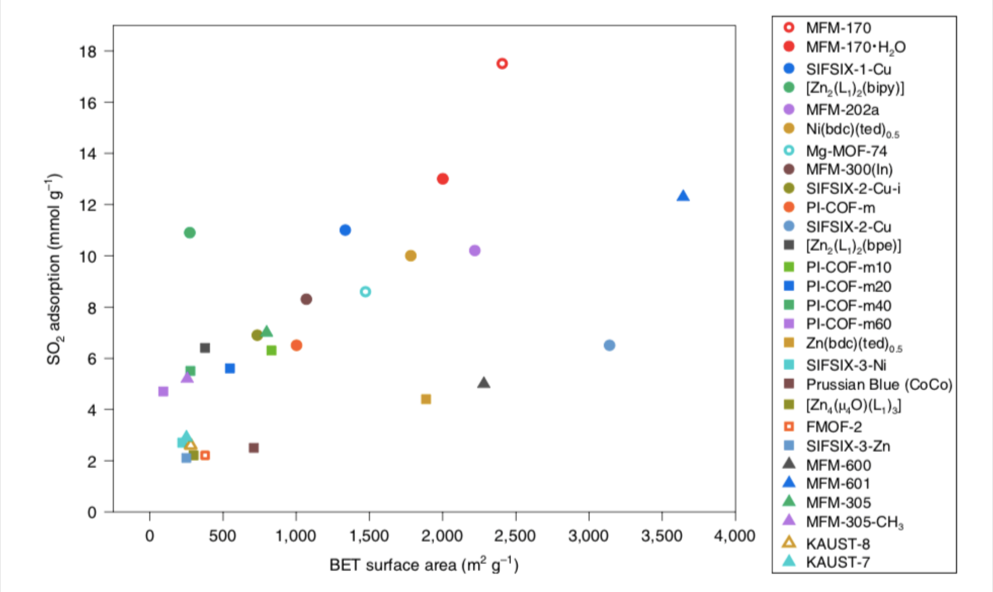
Isotherms were measured for the material saturated with MFM- 170·H2O (no OMS) and MFM-170 (with OMS°

The difference corresponds to about twice the density of open Cu(ii) sites (1.46mmolg-1)

Smith, Gemma L., et al. « Reversible Coordinative Binding and Separation of Sulfur Dioxide in a Robust Metal–Organic Framework with Open Copper Sites ». *Nature Materials*, vol. 18, nº 12, décembre 2019, p. 1358-65. *DOI.org (Crossref)*

Properties

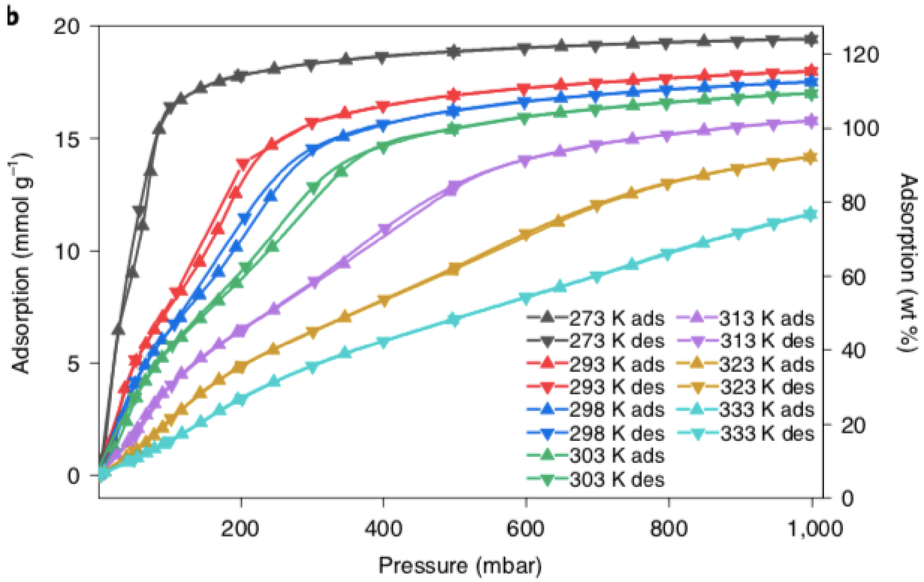
- **High SO2 adsorption**



SO2 adsorption capacity at 298 K and 1.0 bar :

- MFM-170 : 17.5 mmolg-1 at 298 K and 1.0 bar
- MFM-601 : 12.3 mmolg-1
- SIFSIX-1-Cu : 11.0 mmolg-1
- [Zn2(L1)2(bipy)] : 10.9 mmolg-1 at 293

Strong SO2 adsorption at high temperatures and at low and high pressure (11.6 mmol g-1 at 333 K and 1bar) :



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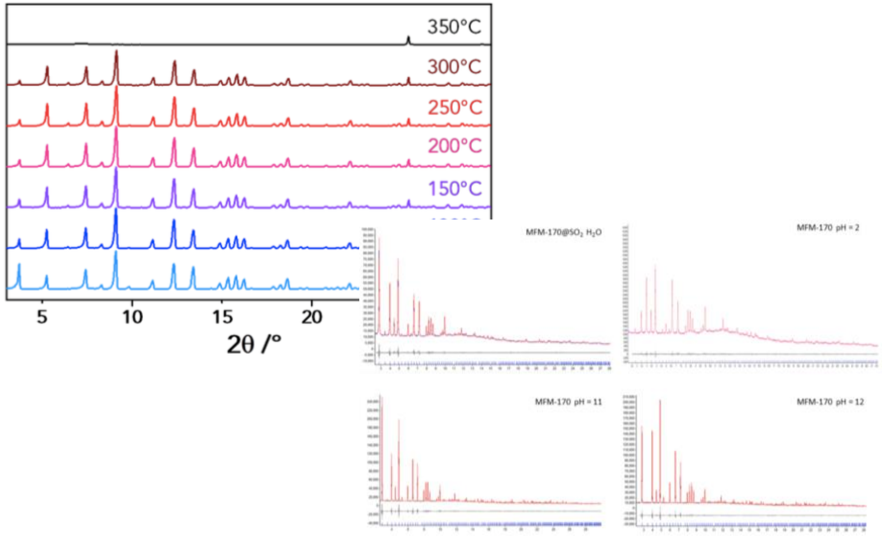
Smith, Gemma L., et al. « Reversible Coordinative Binding and Separation of Sulfur Dioxide in a Robust Metal–Organic Framework with Open Copper Sites ». *Nature Materials*, vol. 18, nº 12, décembre 2019, p. 1358-65. *DOI.org (Crossref)*

Properties

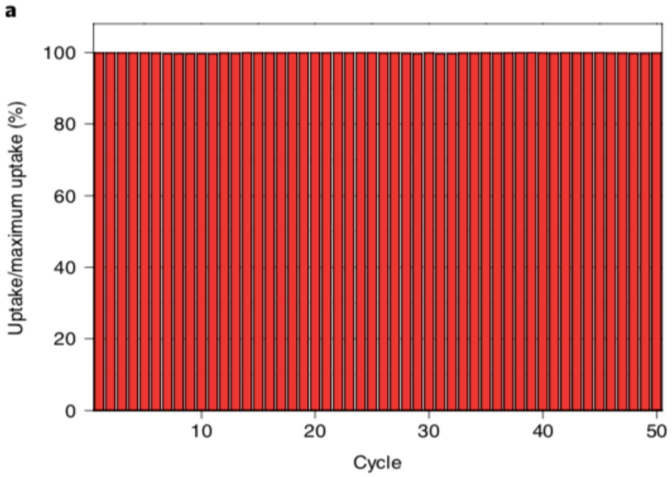
- **High thermal and chemical stability**

Stable towards heat, water and acidic and basic conditions : no loss of crystallinity or changes in the structure of the material. This is attributed to the unusual connectivity of the structure, where the axially coordinated pyridyl N-donors lock the two cubic lattices and block one of the two axial Cu(ii) sites.



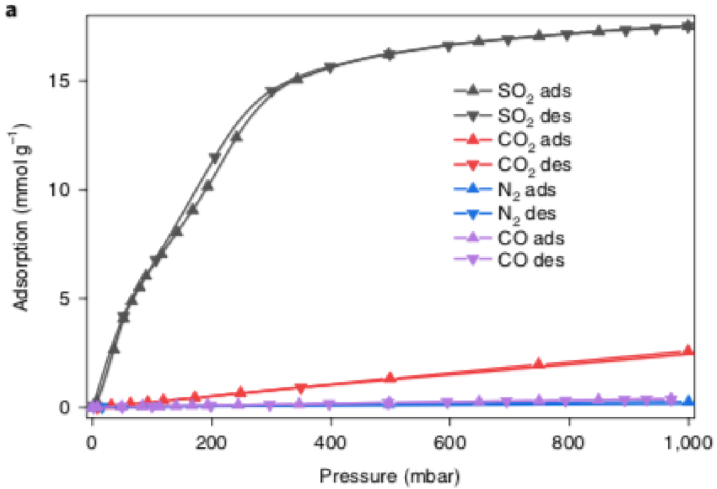
- **High separation properties**

Reversible type I isotherm : MFM-170 can be fully regenerated under varying pressure conditions many times over
Efficient separation of SO2 even in the presence of water and at elevated temperatures :



- **High selectivity**

At 1bar and 298K: MFM-170 shows an uptake of :
3.04mmo/g1 of CO2
1.33mmol/g of CH4
0.38mmol/g of CO
0.28mmol/g of N2
(17,5 mmol/g of SO2)

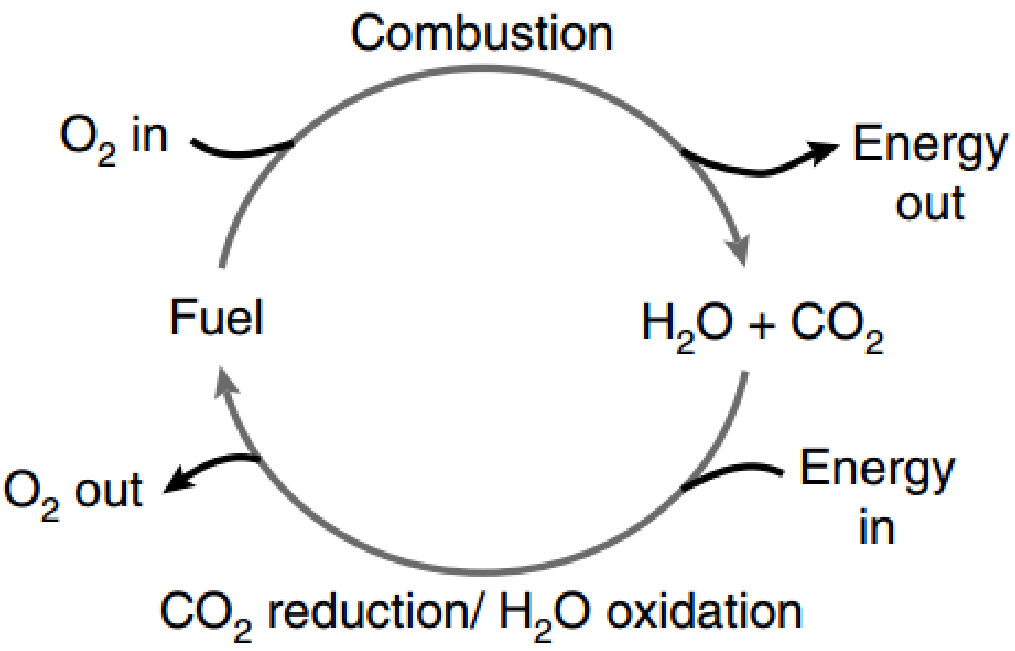


Bio-inspired hydrophobicity promotes CO_2 reduction on a Cu surface

Bio-inspired hydrophobicity promotes CO2 reduction on a Cu surface

Hydrophobic Cu dendrite preparation and characterization

- Theorized sustainable energy cycle → relief to numerous environmental concerns and curtail dependency on fossil fuel
- Cycle driven through aqueous CO2 electrolysis
- Cu = efficient and inexpensive catalyst for the CO2 reduction
- Hydrophobic surfaces trap appreciable amount of gas
- Microscale and nanoscale surface structuration



, et al. "Bio-Inspired Hydrophobicity Promotes CO2 Reduction on a Cu Surface". *Nature Materials,* vol. 18, n°11, novembre 2019, p. 1222-27

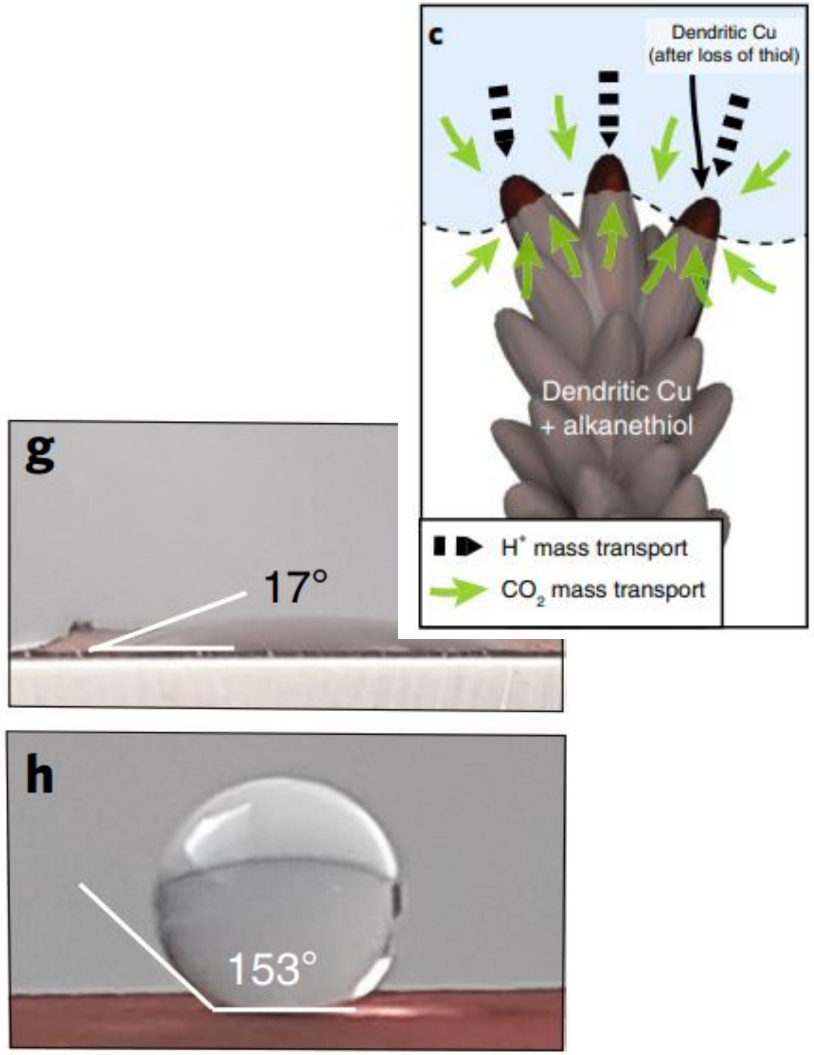
Bio-inspired hydrophobicity promotes CO2 reduction on a Cu surface

Catalytic activity of hydrophobic and wettable Cu dendrites

- Hydrophobic treatment : submersing dendritic Cu into liquid 1-octadecanethiol
- Without treatment : surface hydrophilic
- Decrease in electrochemically active surface area (ECSA)
- Hydrophobic dendrite : 3,10-3 cm2
- Wettable dendrite : 21 cm2
- Gas trapping → decrease in ECSA

Conclusion

- Hydrophobic dendritic Cu → increase in the CO2 reduction selectivity
- Gaseous layer trapped at the surface of the electrode
- Governing factor of CO2 reduction selectivity on Cu



, et al. “Bio-Inspired Hydrophobicity Promotes CO2 Reduction on a Cu Surface”. *Nature Materials,* vol. 18, n°11, novembre 2019, p. 1222-27

Thank you for your attention

Questions ?