Charge Assisted Hydrogel Based on Ga^{III}-MOC and $[Cu(en)_2(NO_3)_2]$: Application in Electrocatalytic CO_2 Reduction

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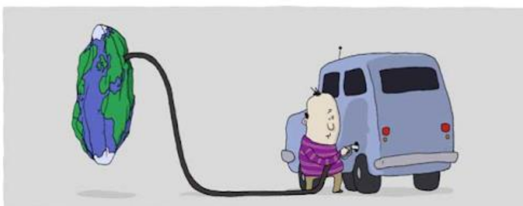
Introduction

➢ Fossil fuel consumption



- Global primary energy consumption by fossil fuels were measured to be 135, 807 TWh.
- Significant increase was observed over the past half-century, and it is still increasing.
- Not only coal, oil and natural gas demand is also growing quickly.

➢ Effects

- We now emit more than 35 billion tonnes of CO_2 every year.
- Rate of warming reach to 0.32 ^{o}F per decade.
- We will run out of oil by 2052.

➢ Solutions

- Plantation
- CO_2 capture and conversions to value added products
- Use of renewable energy source

➢ Ways of CO_2 reduction reaction

I. **Photochemical**

II. **Electrochemical**

III. **Photoelectrochemical**

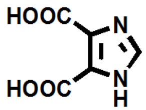
IV. **Thermal method**

V. **Photothermal method**

➢ Electrochemical CO_2 reduction reaction

- Mild operation technique
- Competition with HER
- Lower overpotential
- Single product faradic efficiency and higher current density
- Low cost operating system and catalyst durability

Synthetic strategy

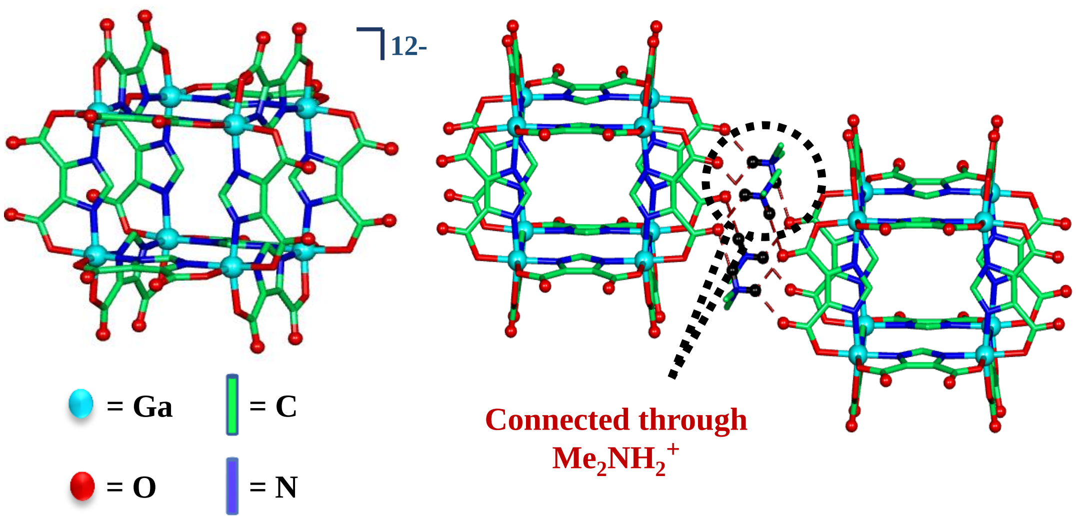
$Ga(NO_3)_3.6H_2O$ + 

DMF , NEt_3 → 120ºC $(Me_2NH_2)_{12}[Ga_8(4,5\text{-}ImDC)_{12}]\cdot DMF\cdot 29H_2O$

Ga-MOC

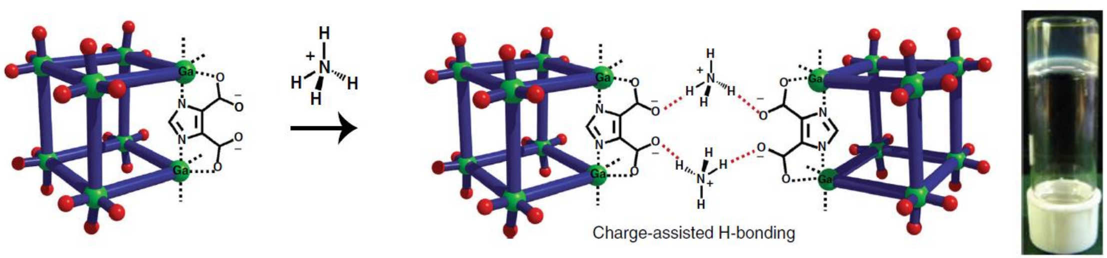
4,5-ImDC= 4,5-Imidazoledicarboxylic acid

➢ Structure of the MOC



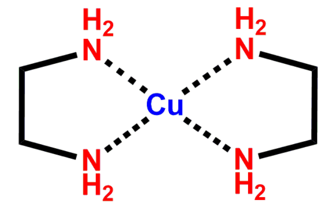
➢ Gelation with binder

Binder = NH_4^+



➢ Binder

- Redox active metal center
- Contains $–NH_2$ group



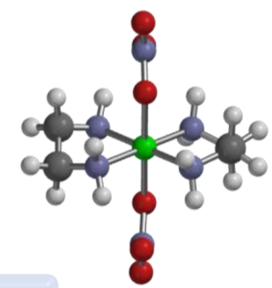
➢ Synthesis

$Cu(NO_3)_2.3H_2O$ in ethanol + 2 eq. of Ethylenediamine

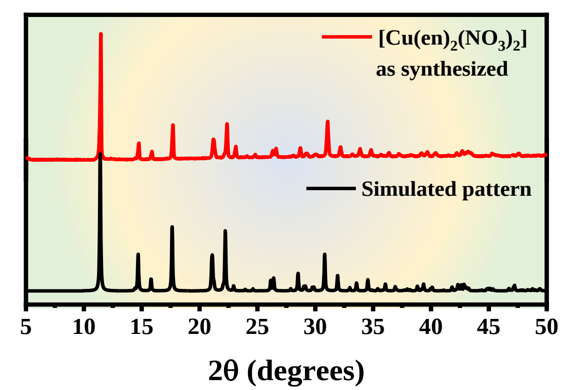
↓

$[Cu(en)_2(NO_3)_2]$

Cu-com

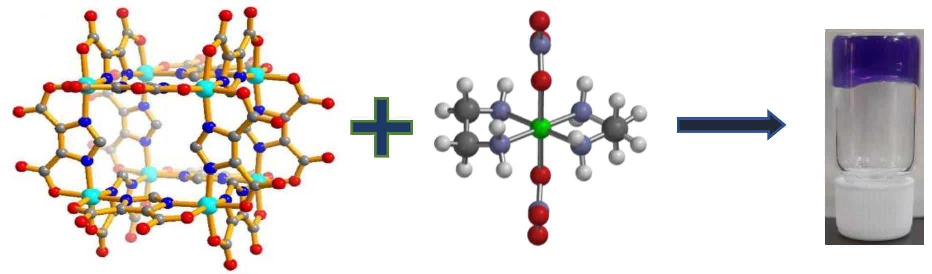


➢ PXRD of the binder



Characterization

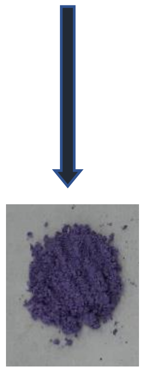
➢ Gelation



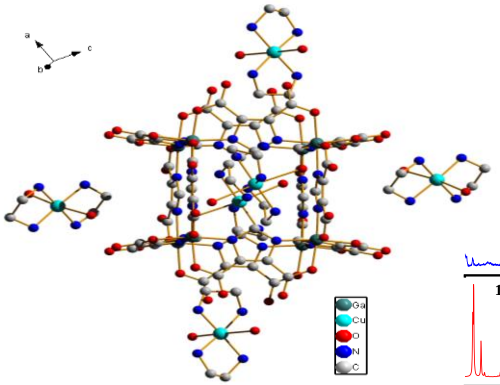
0.5mL 0.01(M) Ga-MOC

0.5mL 0.1(M) Cu-com

Ga-Cu gel

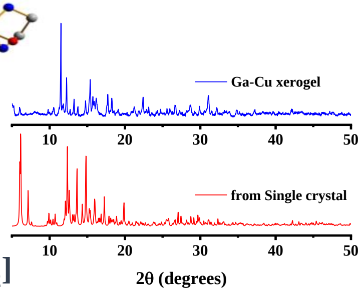


Ga-Cu xerogel

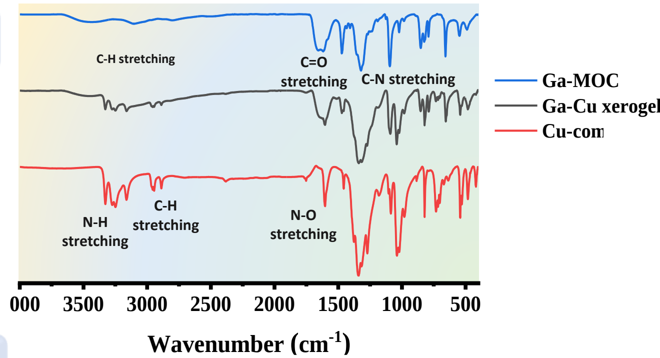


$[Cu(en)_2(H_2O)_2]_6[Ga_8(ImDC)_{12}]$

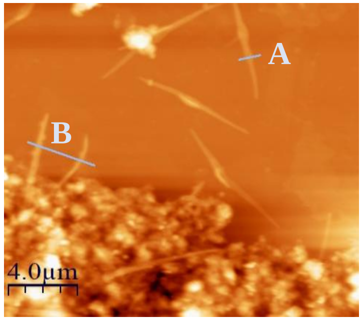
➢ PXRD

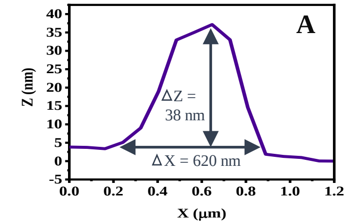


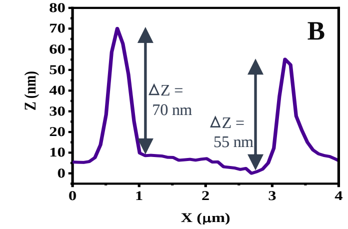
➢ FTIR



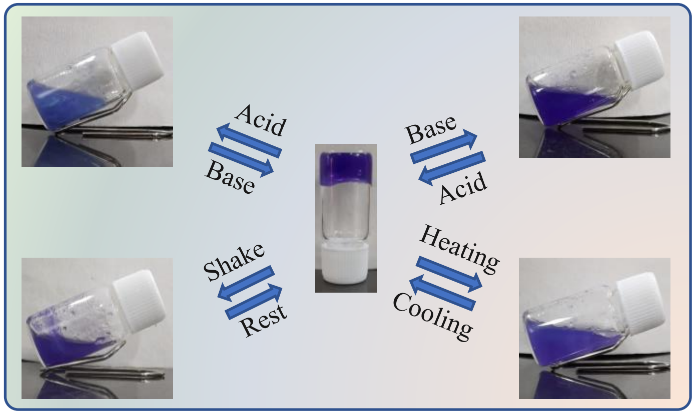
➢ AFM



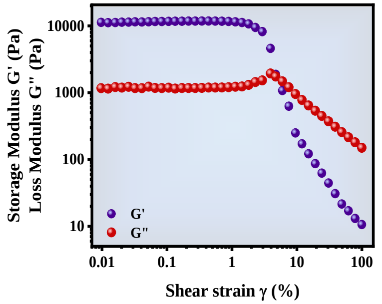


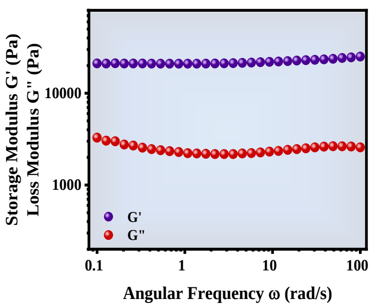


➢ Stimuli response



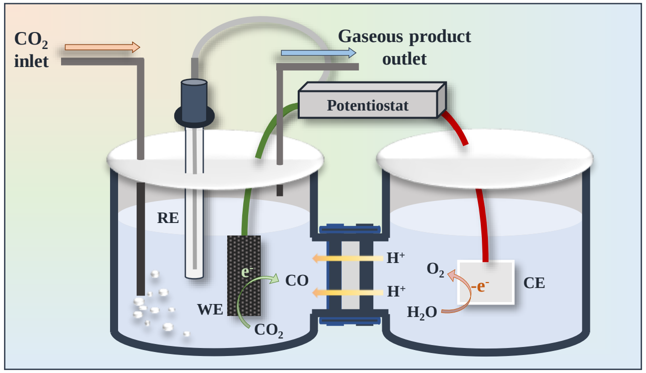
➢ Rheology





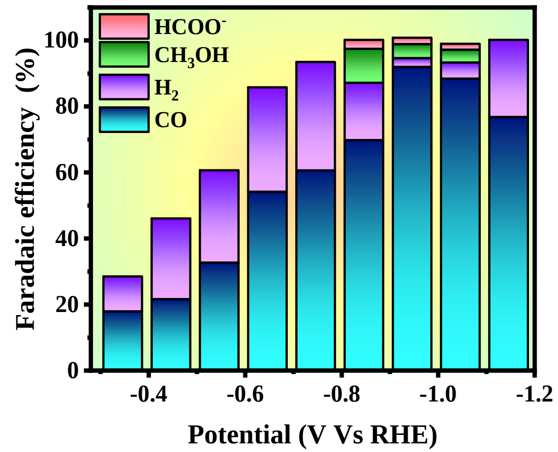
Electrochemical CO_2 reduction

Electrocatalytic setup

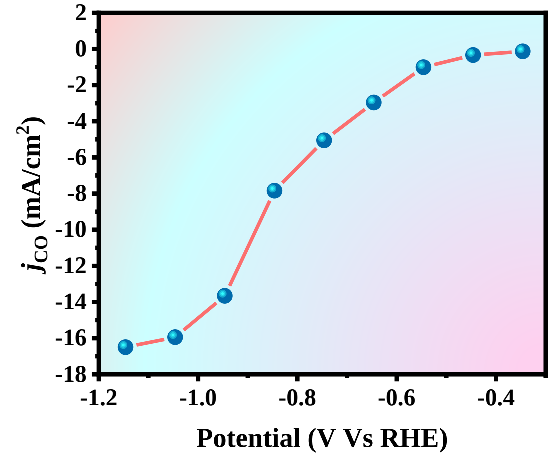


- Catalyst loaded carbon paper used as the WE
- Ag/AgCl as RE and
- Pt as the CE

Faradic efficiency

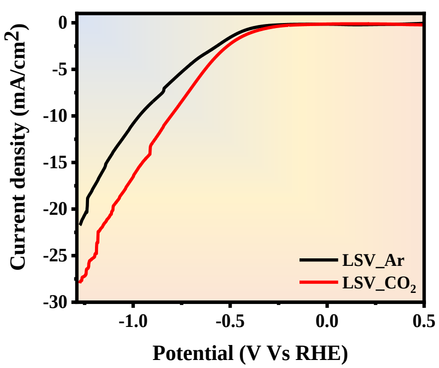


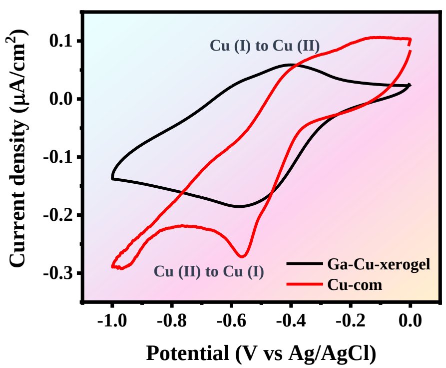
Partial current density



- 92 % faradaic efficiency was obtained for CO product at 0.95 V vs RHE
- At 0.95 V the partial current density for CO was 14 mA/cm^2

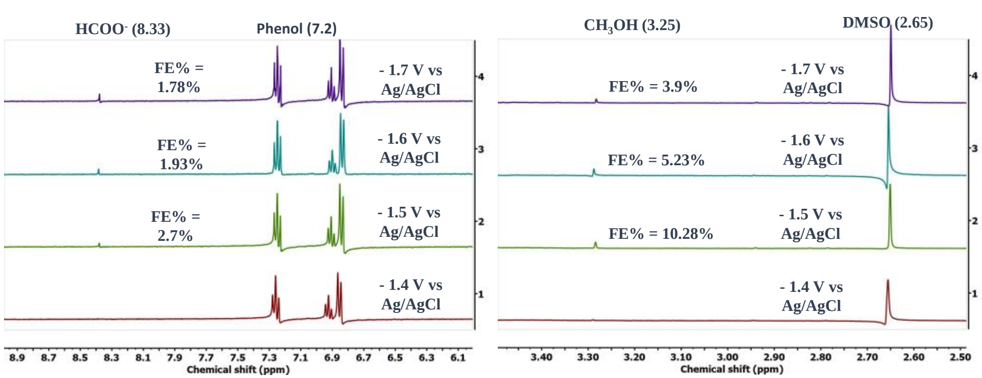
LSV and CV





- Theoretical redox potential of CO_2 to CO conversion = -0.1 V vs RHE
- Overpotential = (0.3-0.1) V = 200 mV
- 0.2 M $KHCO_3$ has been used as the electrolyte (pH = 7.1)
- Copper is the redox active center for this catalysis process

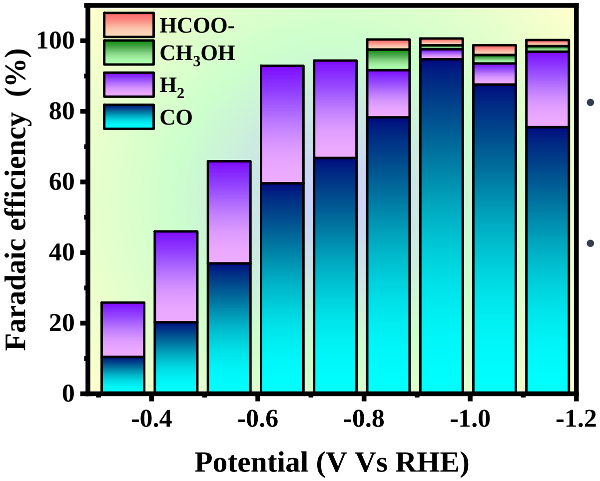
NMR analysis



- Minute amount of formate and methanol was obtained as liquid products

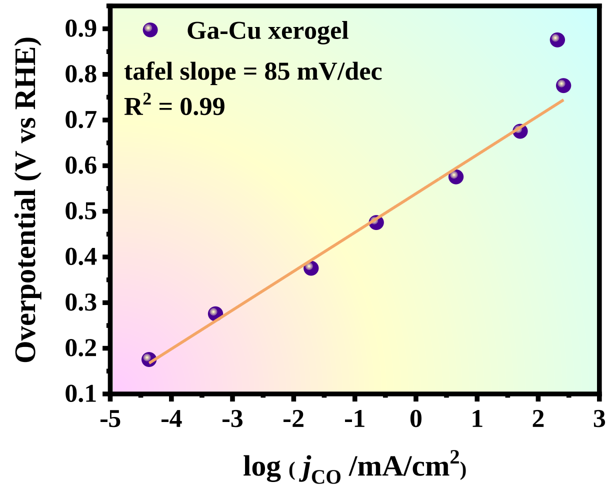
Electrochemical CO_2 reduction

➢ Electrocatalysis in gel state



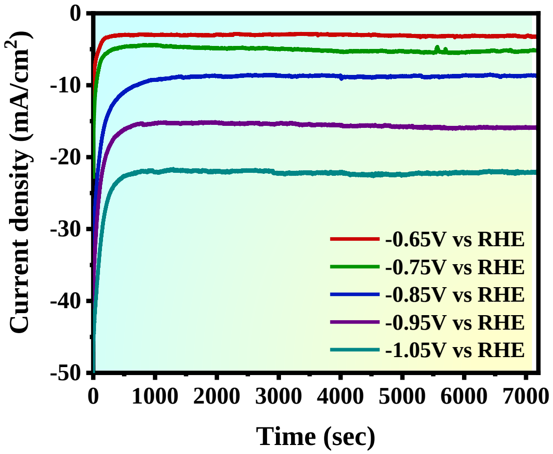
- Similar faradic efficiency was obtained as like the xerogel
- 94 % FE for CO at 0.95 V vs RHE

➢ Tafel slope



- Pathway
  $CO_2 + e^- + H^+ \longrightarrow$ HCOO (ad)
  HCOO (ad) $+ e^- + H^+ \longrightarrow CO + H_2O$
- Tafel slope indicates, second electron transfer process is the rate determining step

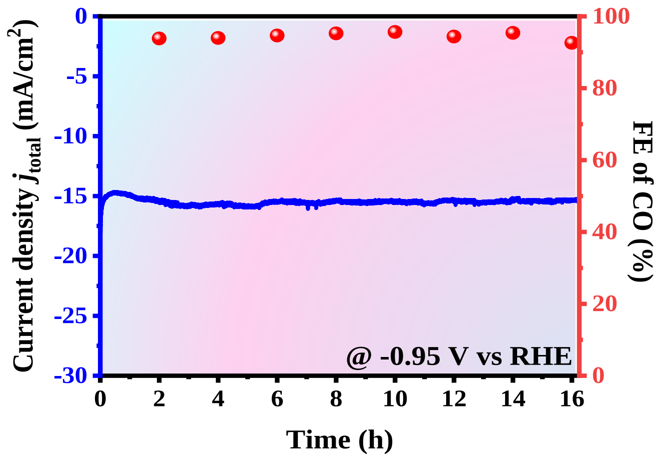
➢ i-t curve @ different potential

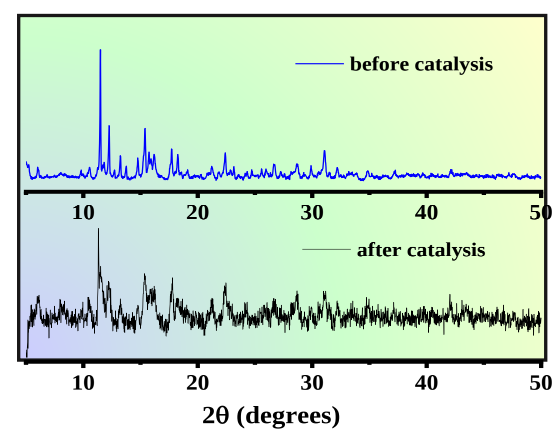


➢ Stability

TON = 1.52×10^{20} cm^{-2}h^{-1}

TOF = 987 h^{-1}





Conclusion

- **We have designed a hybrid soft material with a redox active metal centre.**
- **Bi-component gel to crystallisation process happens spontaneously without application of external stimuli.**
- **Low cost Cu^{2+} complex was used as the catalytic centre.**
- **CO_2 reduction reaction was obtained with low overpotential of 200 mV.**
- **CO Faradaic Efficiency was obtained 94% at -0.95 V vs RHE.**
- **It can couple the two way advantage of renewable energy uses and CO_2 removal.**

Acknowledgement

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सत्यमेव जयते
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➢ References

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