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Cu nanoparticles for CO_2 reduction: Benefits and challenges of synthesis via Gas Aggregation Source

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Motivation

- Enable use of Gas Aggregation Source for production of metallic nanoparticles as catalyst for CO_2 reduction in gas diffusion electrode (GDE)
- Tailoring of nanoparticle yield and morphology through substrate bias
- Gain insight into phenomena degrading catalytic performance
- Improve stability and product selectivity of catalyst over time

Nanoparticles

- Size between **1 and 100 nm** considered as **nanoparticles (NPs)**
- Properties **between single atoms** (discrete energy states) and **bulk materials**
- Possible practical **applications** include:
  → **Catalyst material** (fuel cells, CO2-reduction), **nanocomposites** [1],…
- Some **challenges** with nanoparticle applications include:
  → Often **not well bond** to surfaces
  → Most processes show **impurity** of resulting nanoparticles

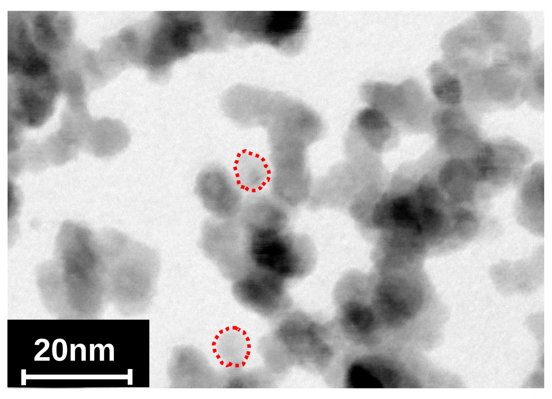


Figure 1: TEM micrograph of Cu NPs that were size-filtered at 8nm (provided by Michael Burtscher).

Gas Aggregation Source (GAS)

- **Magnetron Sputtering** in around **1mbar Ar** atmosphere
  → **Nucleation** of **nanoparticles (NPs)** through **3-body collisions**
  → Growth through additional collisions of atoms until **critical radius (≈ 10nm)**
- **Particles charge** in plasma → **Mass spectrometry** and filtering possible
- **Mass-filtering** (1-10nm) through **Quadrupole mass filter (QMF)** possible

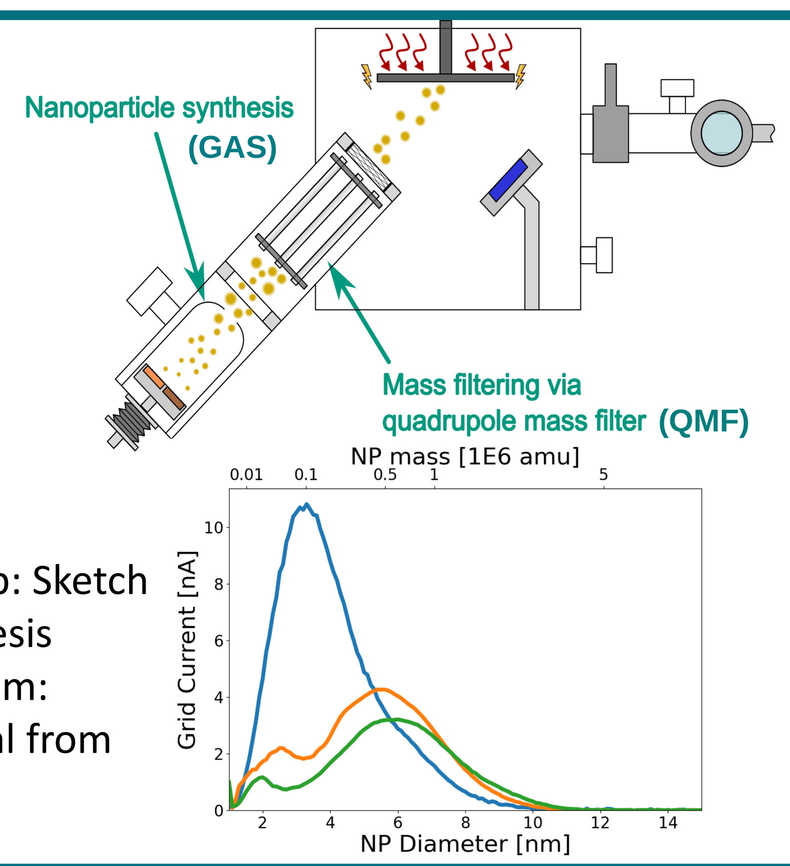


Figure 2: Top: Sketch of NP synthesis setup. Bottom: Typical signal from the QMF.

CO_2 reduction in Flow Cells

- **CO_2 reduced** in **electrolytic cell** with **aqueous solution**
- **Gas Diffusion Electrodes (GDEs)** enable gas flow to catalyst
  → **Fibrous carbon** body, **nanoporous Carbon support**
  → **Cu-nanoparticles (catalyst)** deposited onto Carbon support
- Cu enables **more complex reactions**, since CO adheres better than H
  → Multiple reactions expected in parallel

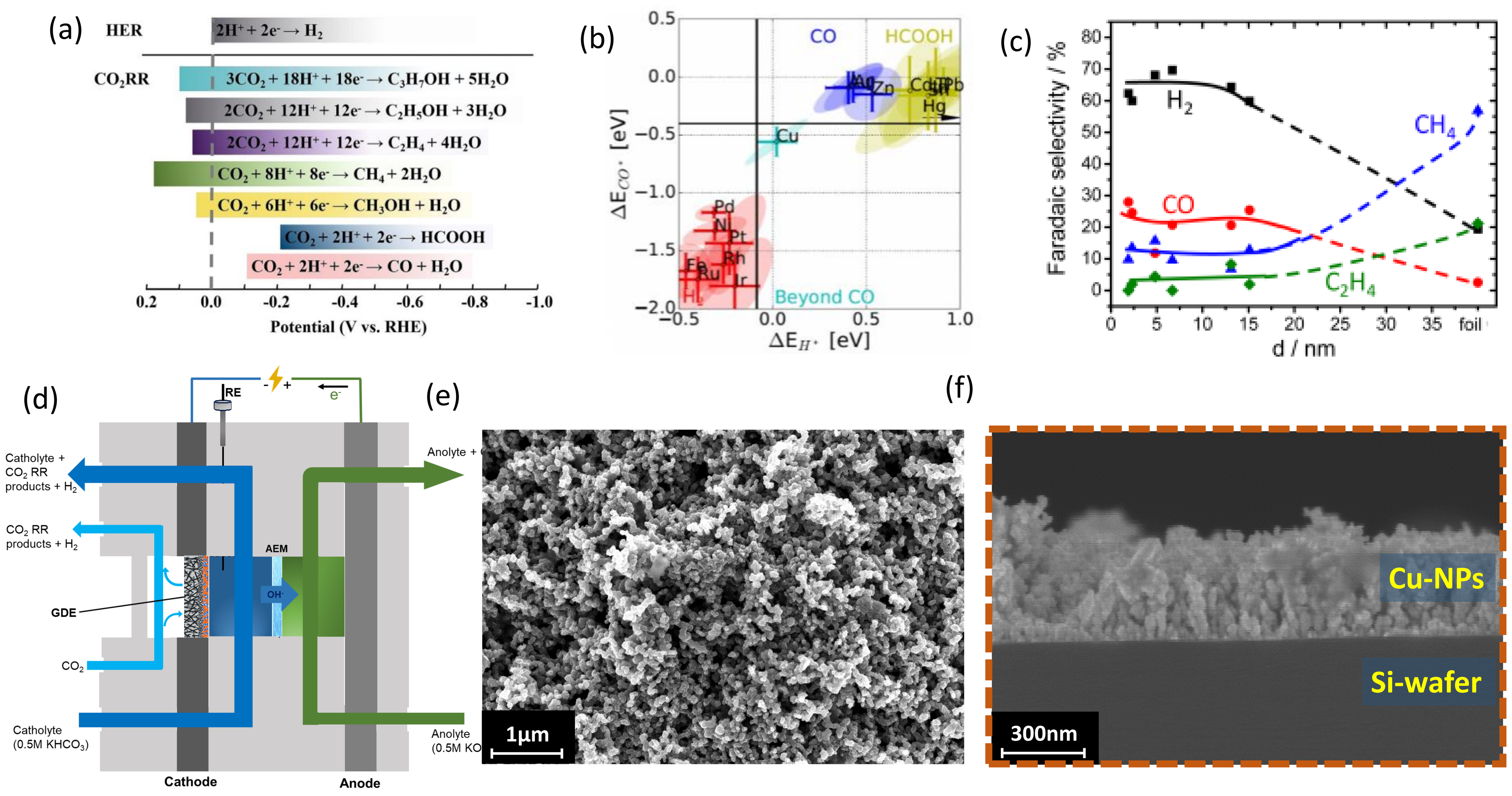
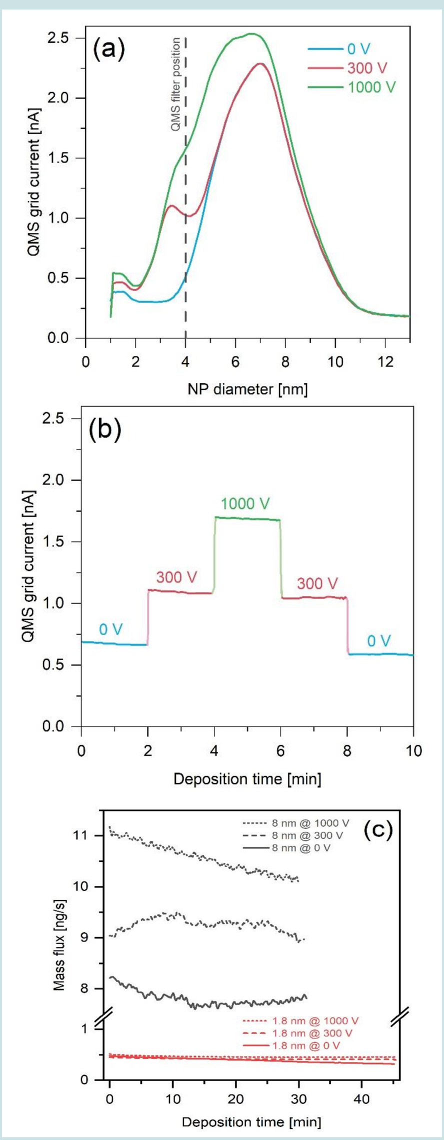


Figure 3: (a) Possible reactions on the catalyst in aqueous solutions [2]. (b) Anomality of Cu in respect to CO_2 reduction [3] and (c) the product selectivity of sub-monolayer deposition of different sizes of nanoparticles produced through inverse micelle encapsulation [4]
(d) Schematic of the flow cell setup. (e) and (f) show SEM micrographs of the top-view on Carbon support of the GDE and a side-view on a highly loaded catalyst on Si-substrate, respectively.

Results

Substrate bias changes deposition rate, impact energy and thin film morphology [5]



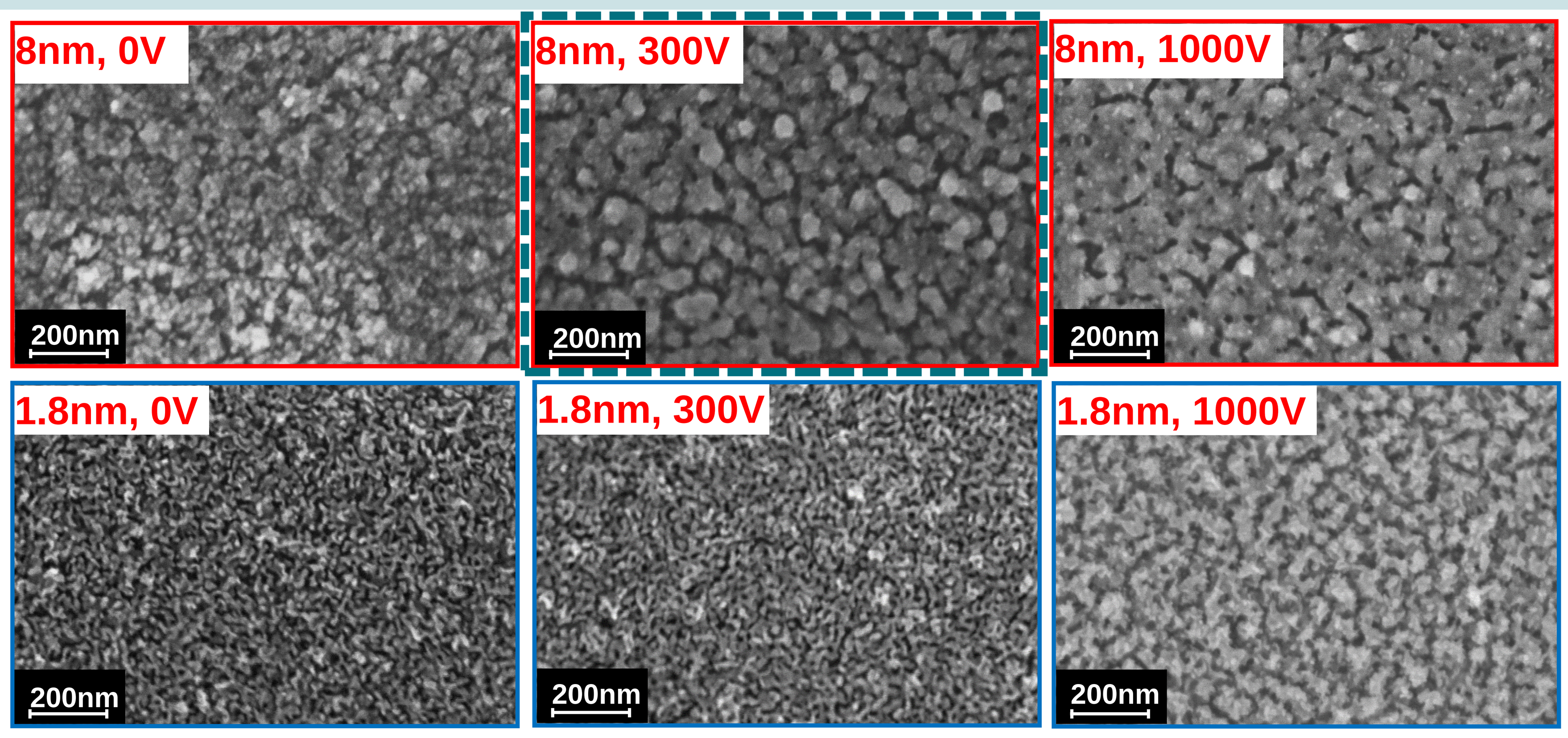


Figure 4: Left: QMF diameter profile (a), signal for 4nm filtered particles over time with bias (b) and derived mass flux of 1.8nm and 8nm filtered particles. Right: Top-view SEM micrographs to the depositions corresponding to the mass-flux graphs shown in Figure 3 (c)

Catalytic performance of different catalysts

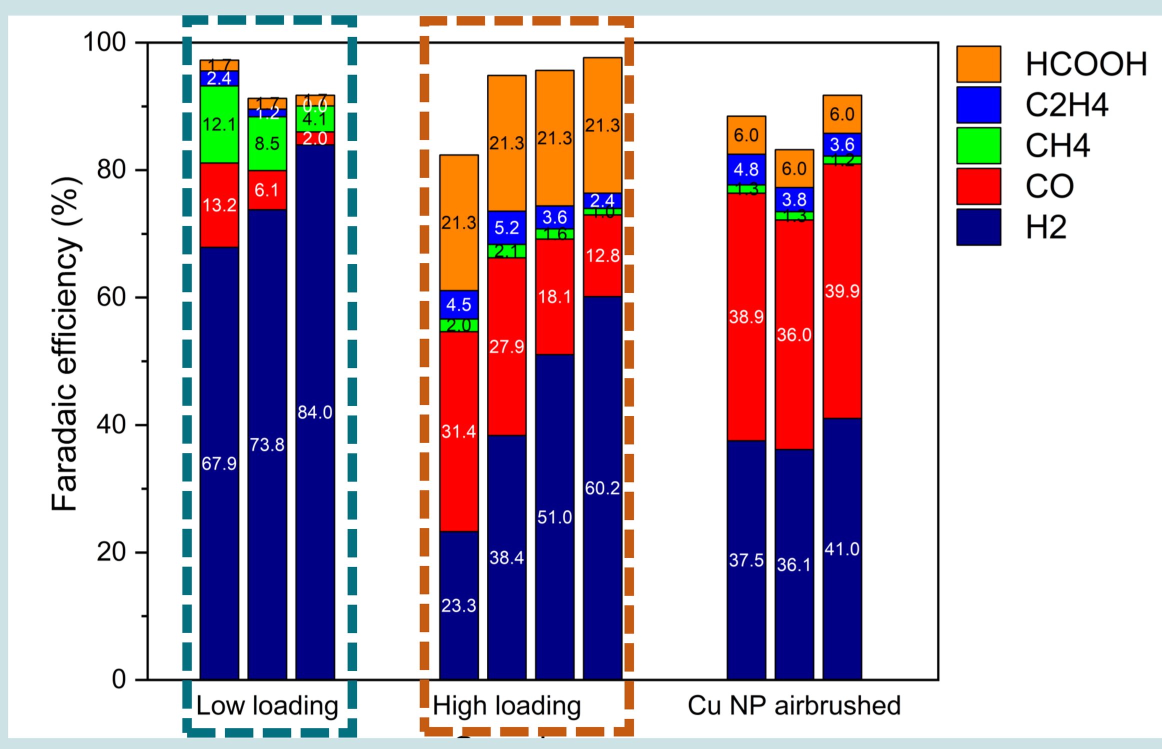


Figure 5: Faradaic efficiency of the catalyst over time for 3 different electrode designs. Changes over time demonstrate lack of catalyst stability in GAS-catalyst. The first catalyst corresponds to the 8nm, 300V bias deposition (Figure 4) and the second one to the cross-section (Figure 3)

Conclusion and outlook

Magnetron sputtering promising method to produce nanoparticles for catalysis due to:
→ **High purity** of catalyst material
→ **Morphology** and **loading** can be influenced
→ **Narrow size selection possible**

Challenges when using GAS:
→ Limited **reproducibility** and relatively low yield
→ Issues with **stability of catalyst** during CO_2-reduction

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References:
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