Room Temperature Electrochemical Synthesis of Nanostructured Cu_2O Thin Films

Presented By: Akhilender Jeet Singh
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Ways to produce Hydrogen

1. Steam Methane Reforming

$$CH_4 + H_2O\ (+\text{heat}) \rightarrow CO + 3H_2$$

$$CO + H_2O \rightarrow CO_2 + H_2\ (+\text{small amount of heat})$$

2. Electrocatalytic Water Splitting

$$2H_2O \rightarrow O_2 + 2H_2 \qquad E^0 = -1.23\,V$$

3. Photo-electrochemical Water Splitting

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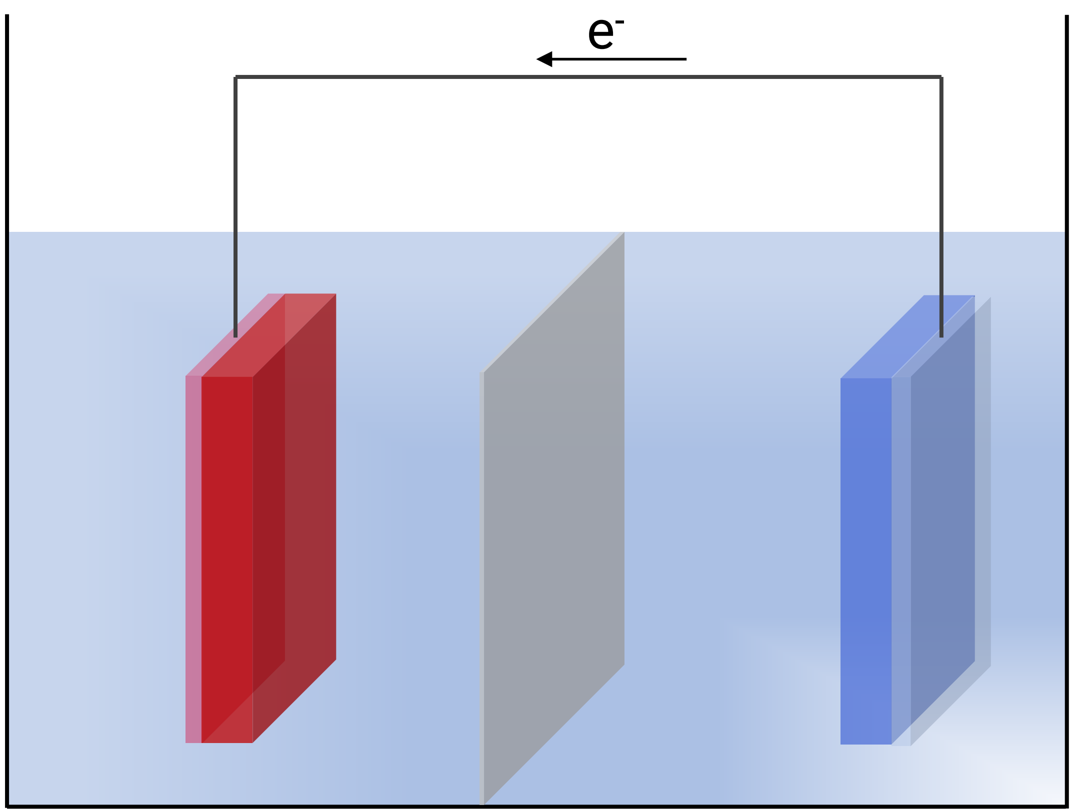

Photoelectrochemical (PEC) Cell

$$\Delta G^0 = +237.14\ \text{kJ/mol}$$
$$E_i = h\nu = 1.23\ \text{eV}$$
$$2h\nu \longrightarrow 2e^- + 2h^\bullet$$

Photoanode: Water Oxidation

$$2h^\bullet + H_2O \longrightarrow \frac{1}{2}O_2(g) + 2H^+$$

Photocathode: Water Reduction

$$2H^+ + 2e^- \longrightarrow H_2(g)$$

Overall reaction:

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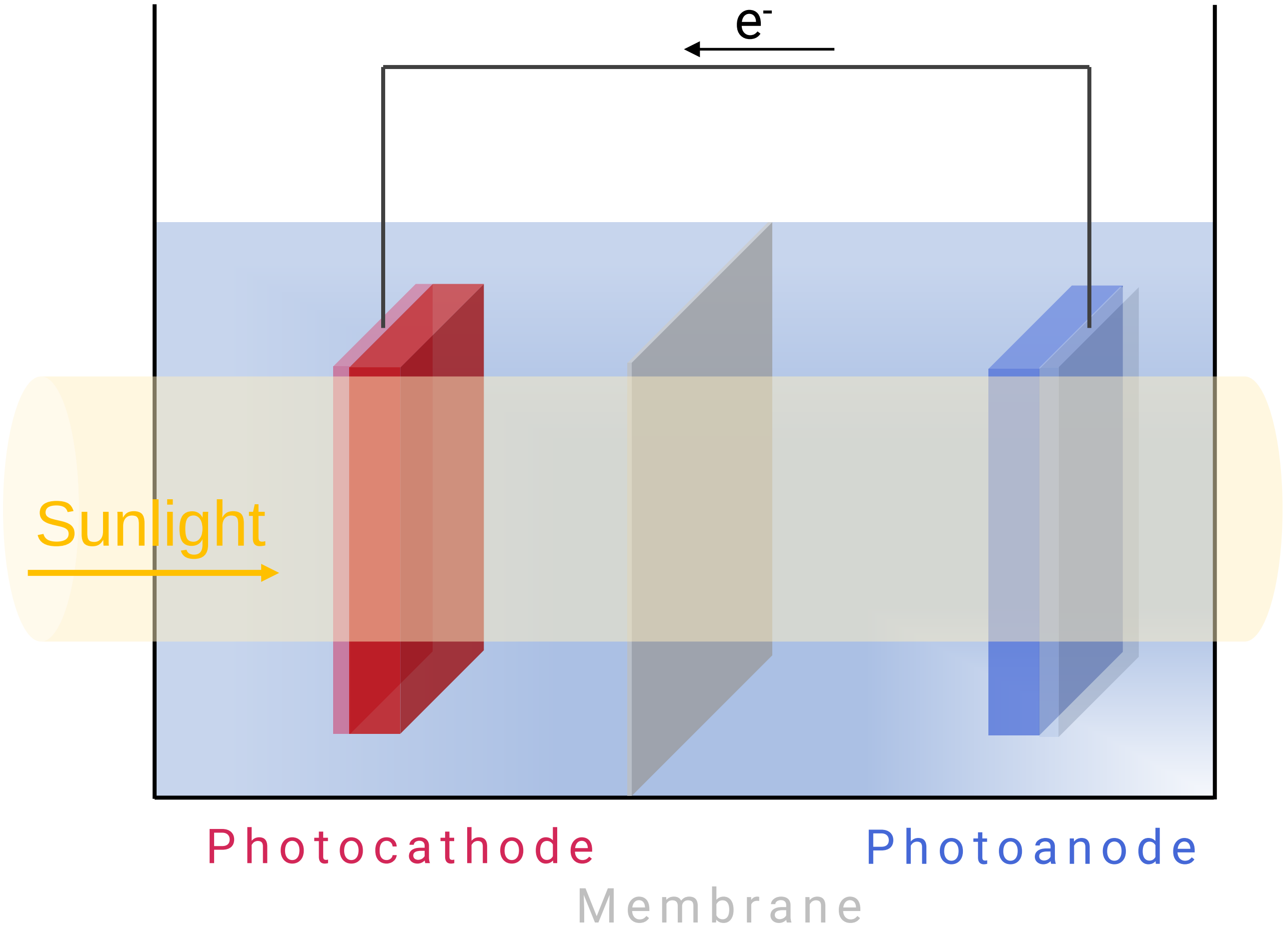

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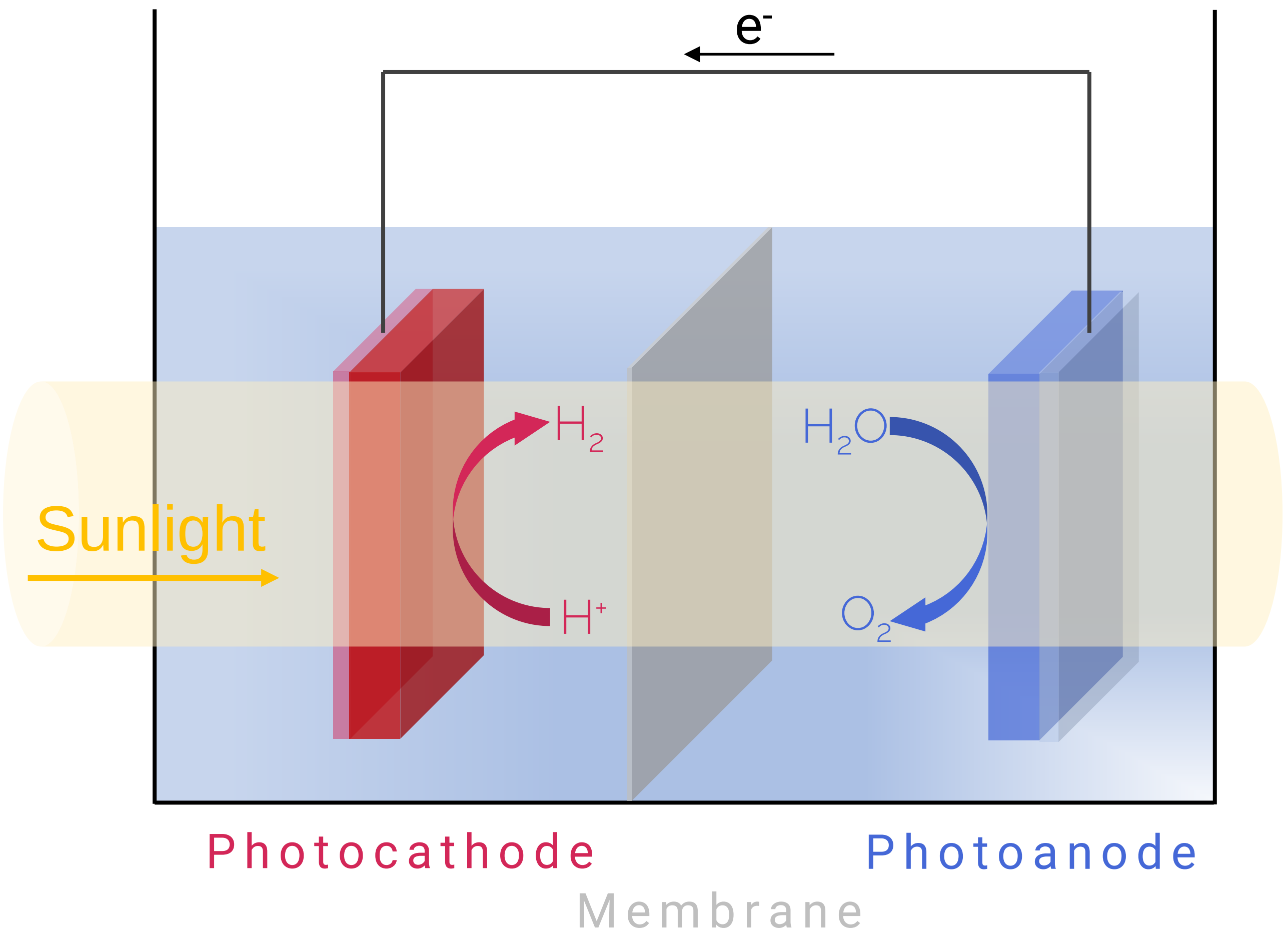

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Photoelectrode Materials

Material Requirements

Bandgap: ~ 1.8 - 2.0 eV

Band Alignment

Adsorption Coefficient

Stable in water

High diffusion length and mobility

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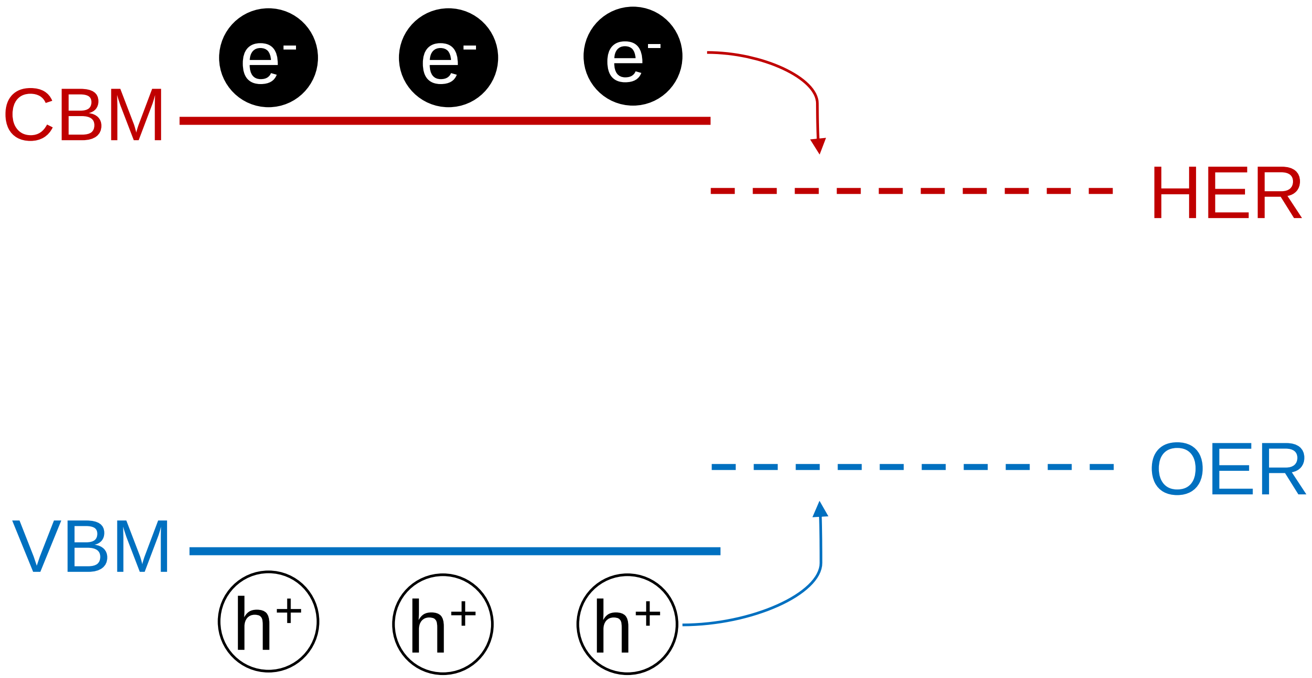

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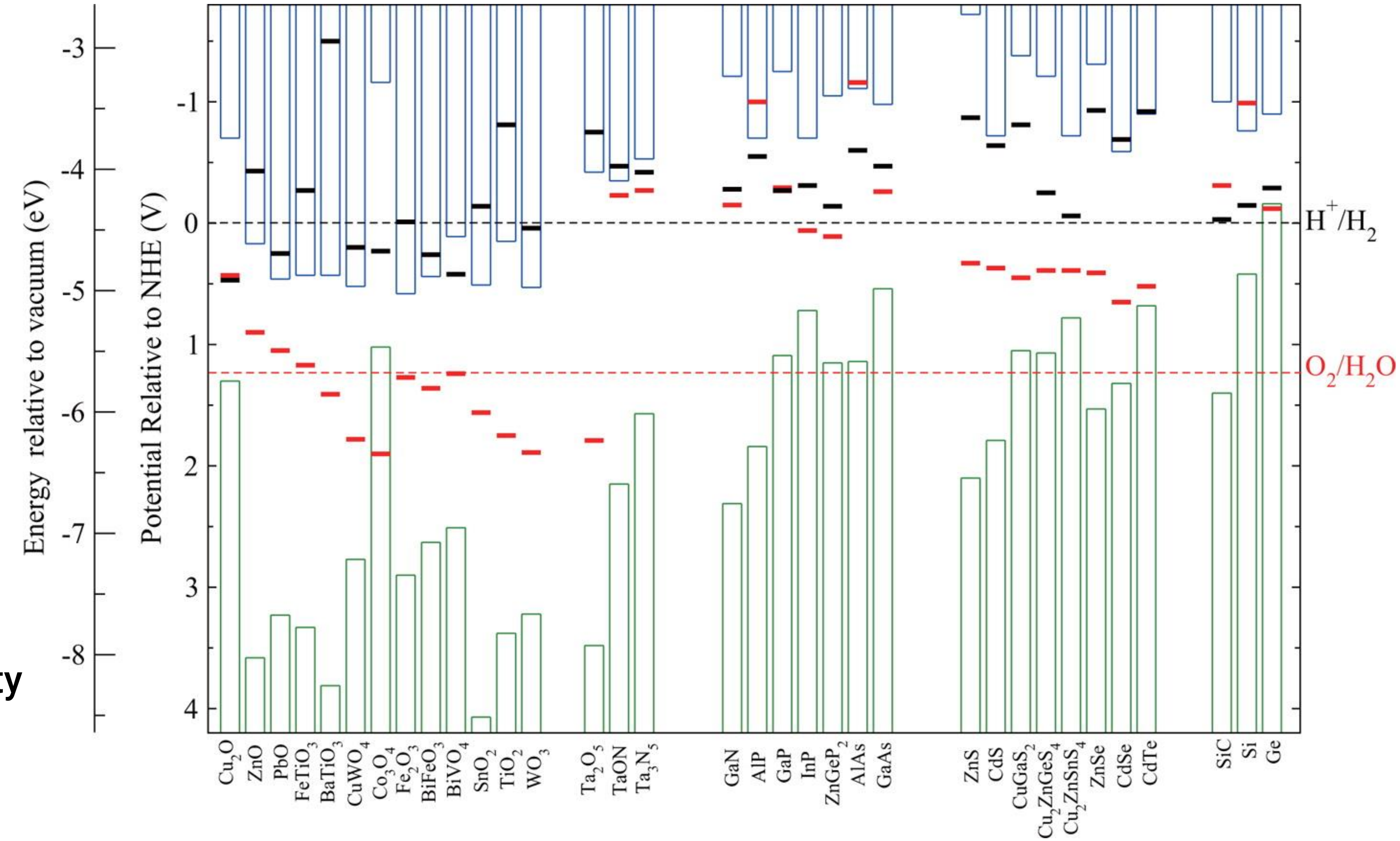

Chem. Mater. 2012, 24, 18, 3659−3666

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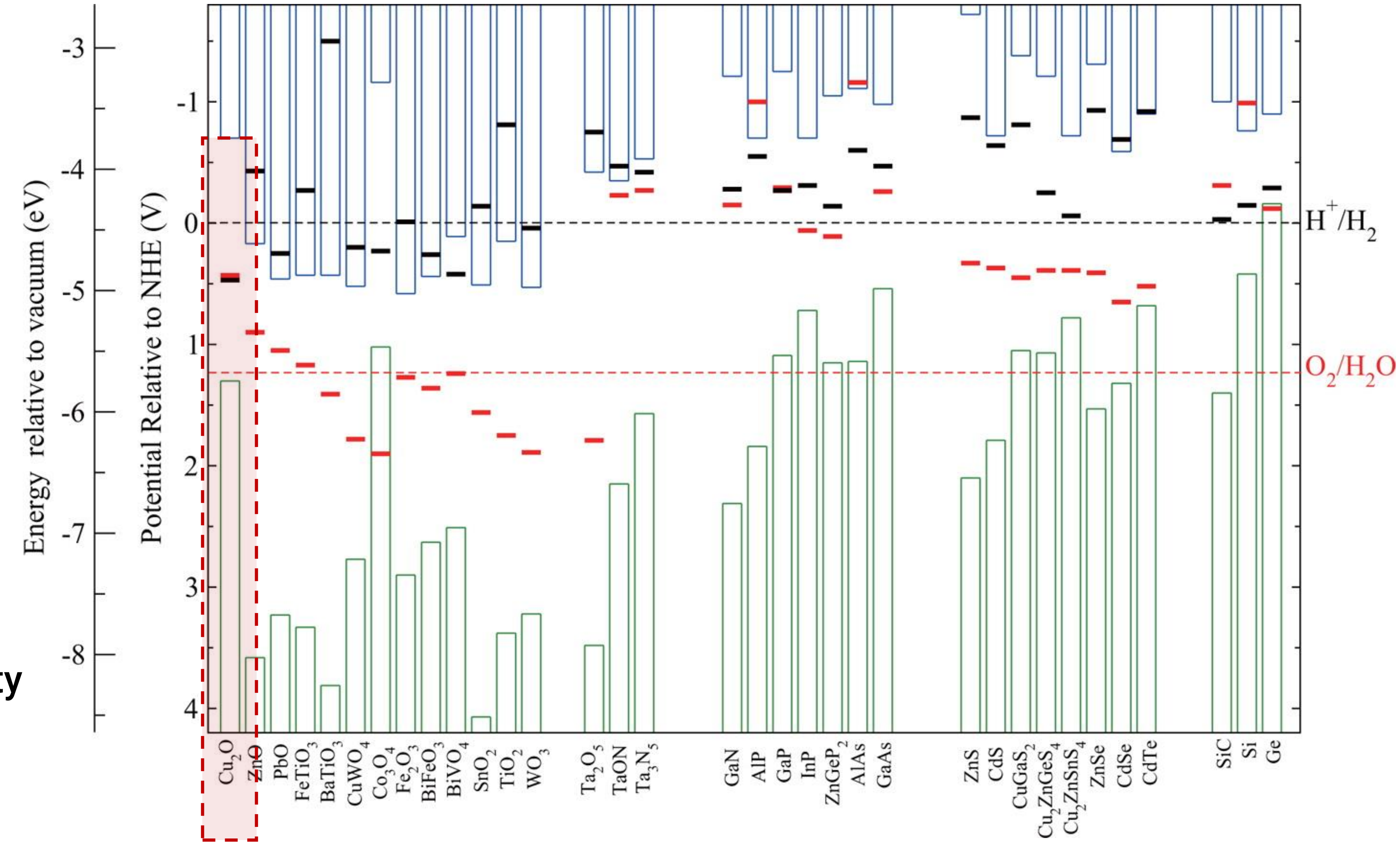

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Cu_2O Photocathode

CBM negative of $E^0_{H^+/H_2}$: **Photocathode**

Band gap: **2.0 eV**

Absorption Coefficient: **10^4 cm^{-1}**

Max. photocurrent: **-14.7 $mA\text{-}cm^{-2}$**

Solar to Hydrogen (STH) efficiency: **18 %**

Challenges:

- Photo-corrosion
- Low minority carrier diffusion length

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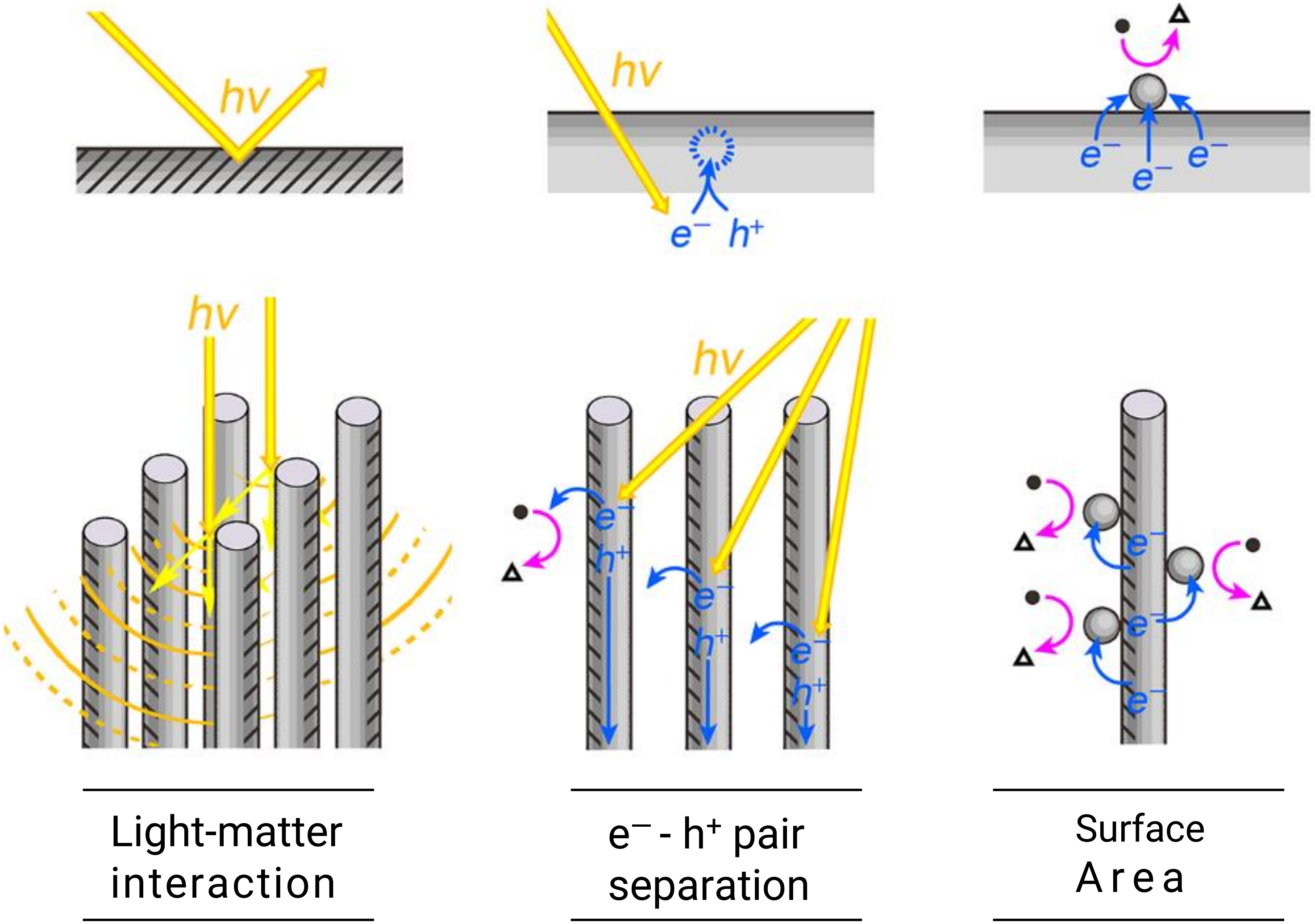


Nature nanotechnology 11, no. 7 (2016): 609-612

Strategy

Cu_2O Electrodeposition

Nanostructuring

Simple Electrochemical Synthesis

Synthesis of porous Cu_2O

Solution:
0.2 M $CuSO_4$ + 3M Lactic Acid + 0.1M K_2HPO_4 Buffer

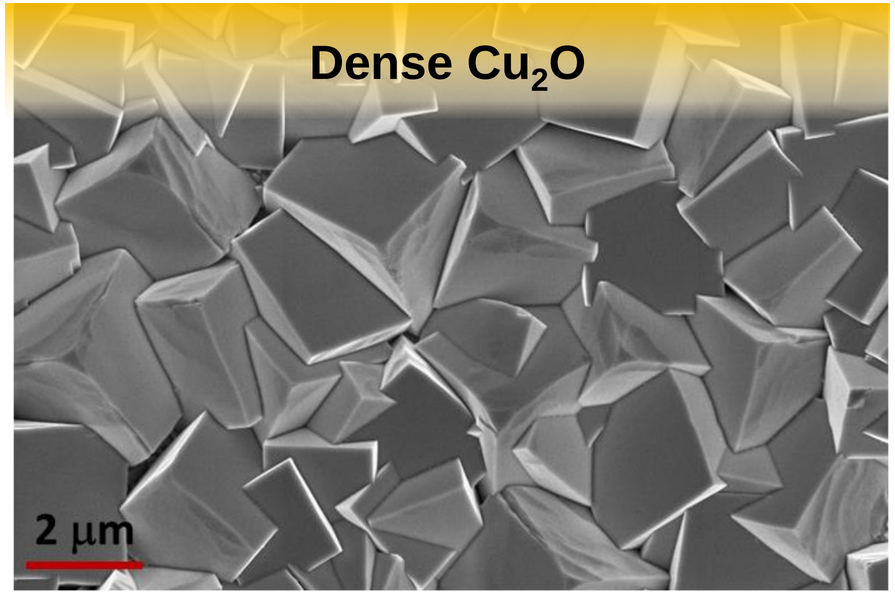
pH: 12 (Maintained by addition of 2M KOH)

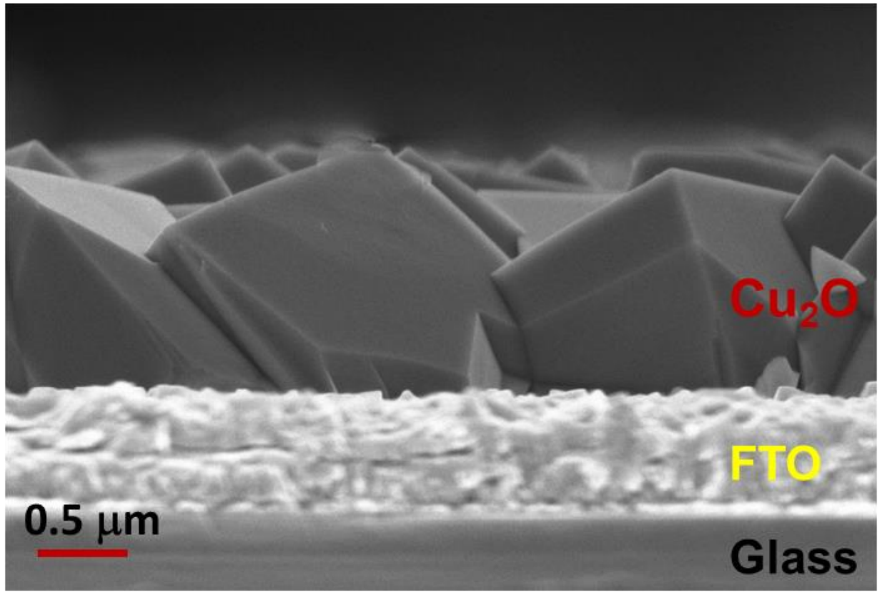
Potential: -0.35 V (vs. Ag/AgCl)

Bath temperature: 55 ^{0}C

Duration: 15 min

Thickness: 1 μm approx.





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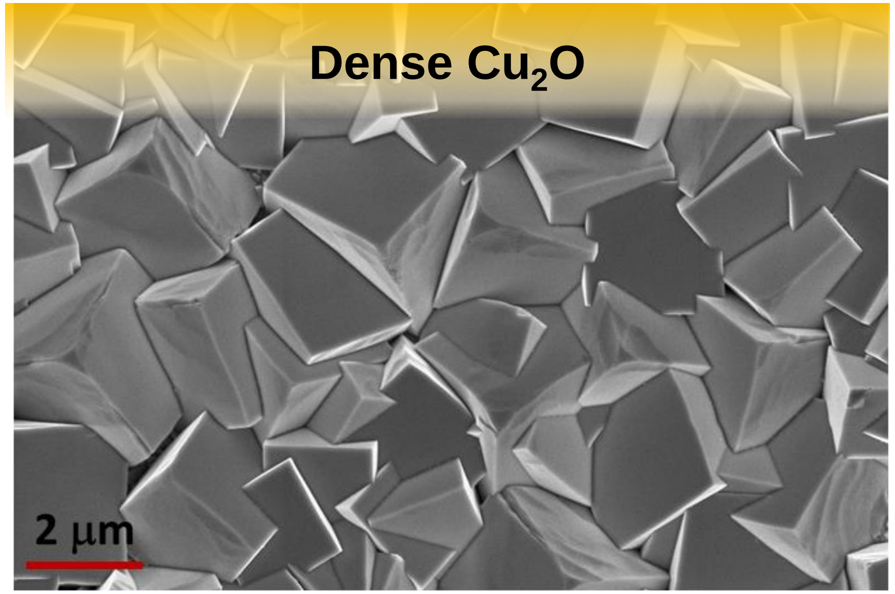
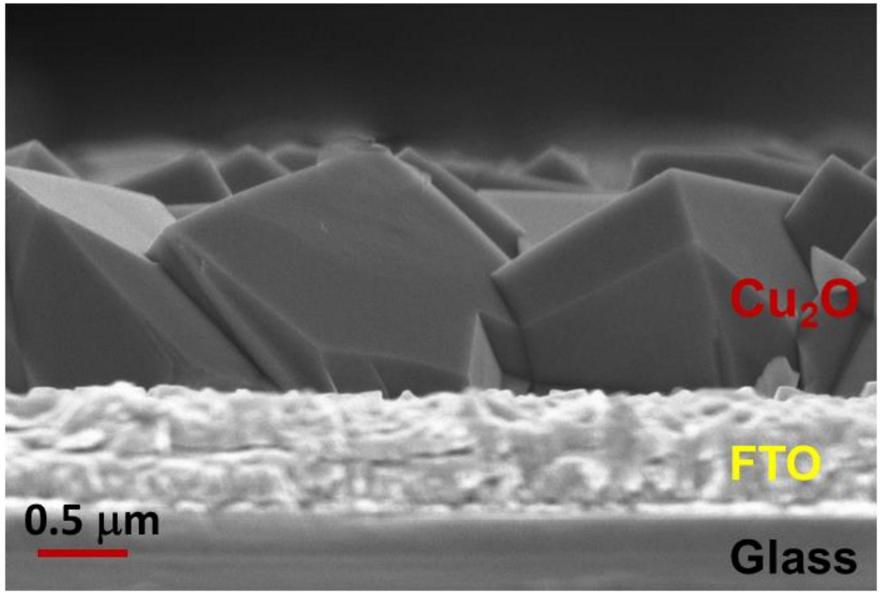
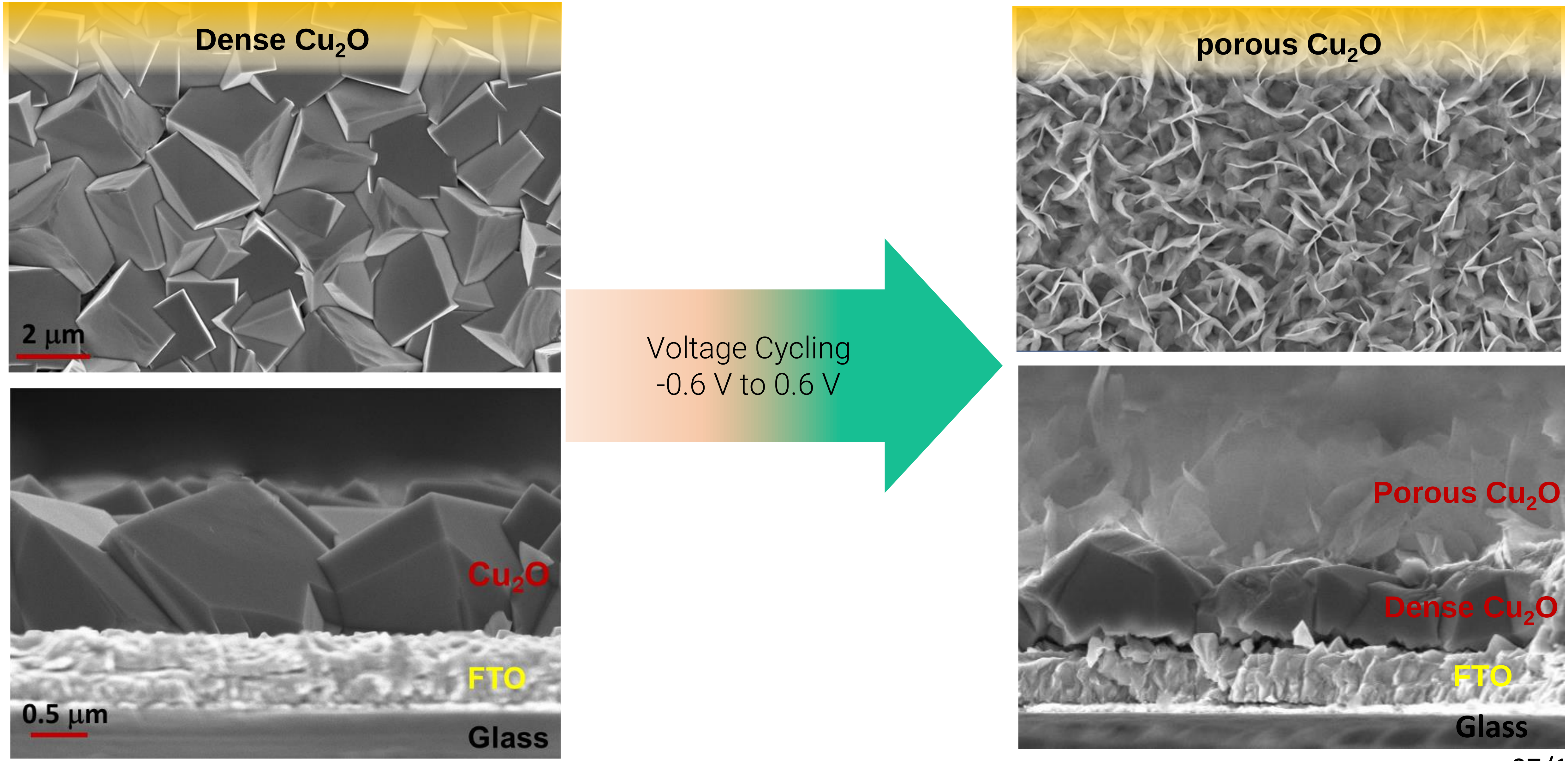


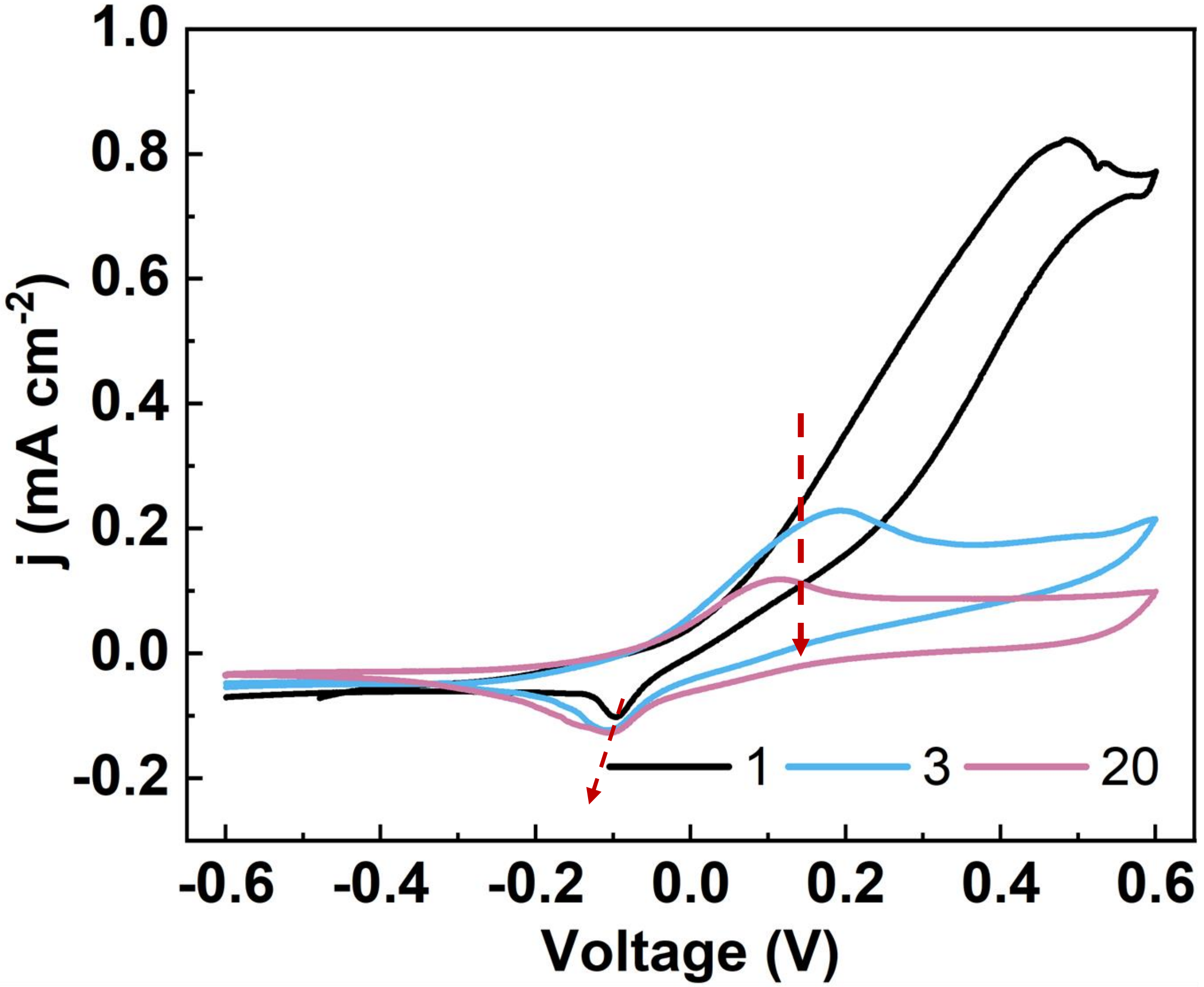


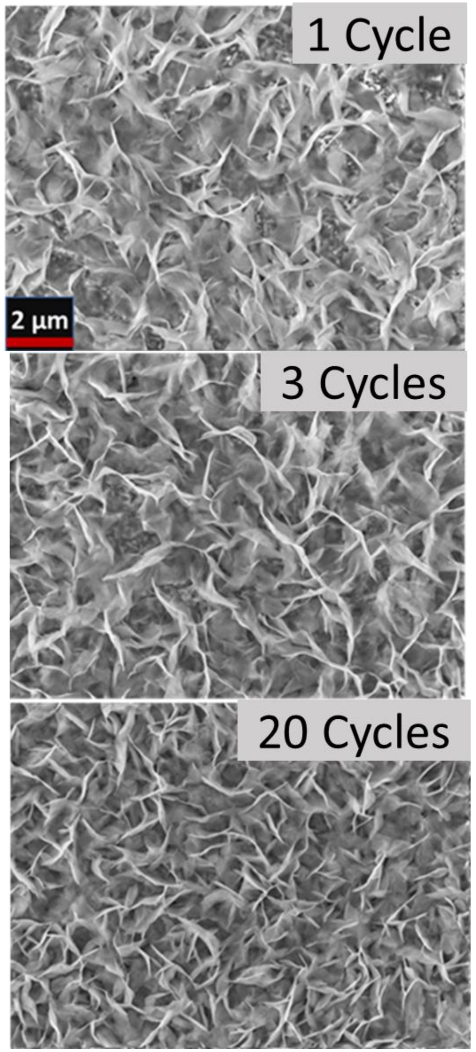
Voltage Cycling
-0.6 V to 0.6 V

Synthesis of porous Cu_2O



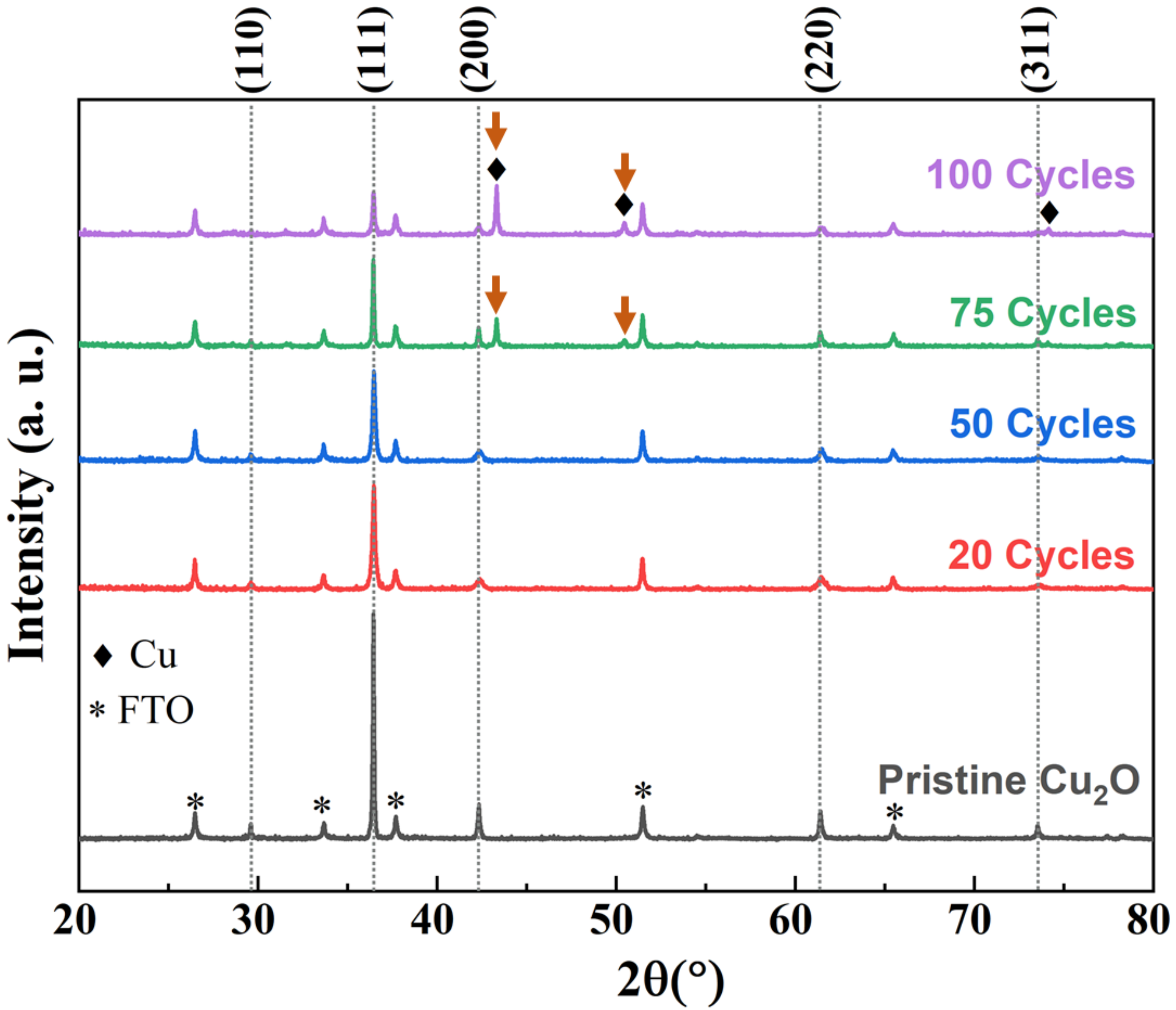
Morphology Evolution





- Porous morphology forms within first cycle
- After 5 cycles complete coverage

Etching and Formation of Cu-impurity



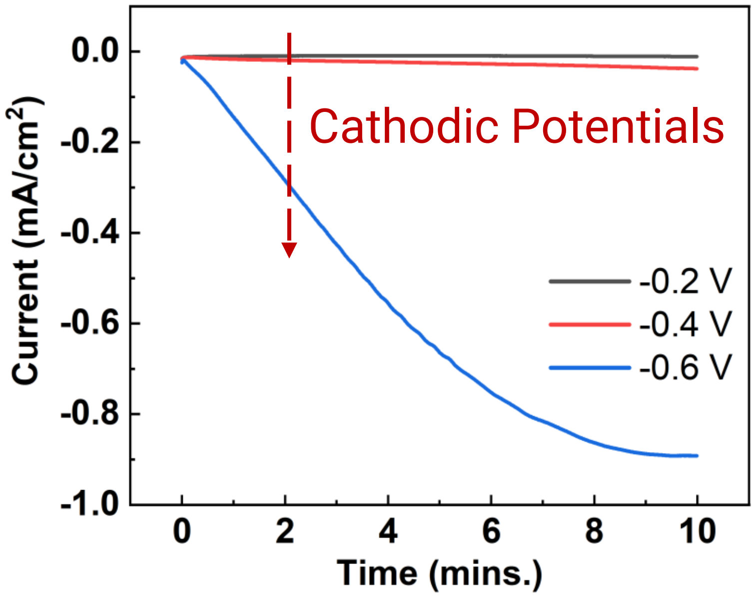
Reduction in Cu_2O peaks: Indication of etching

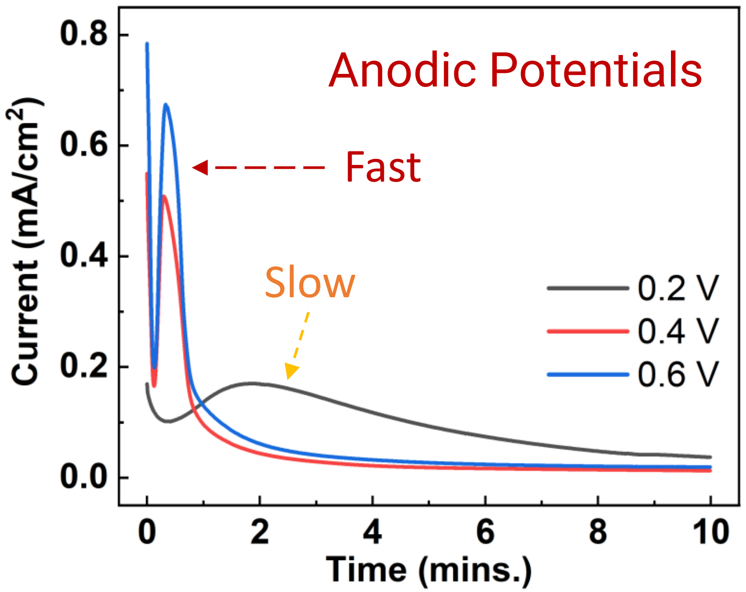
	Cu_2O (111)	FTO (110)	Ratio
Pristine Cu_2O/FTO	3482	540	6.45
Porous (20 cycle)	2800	522	5.36

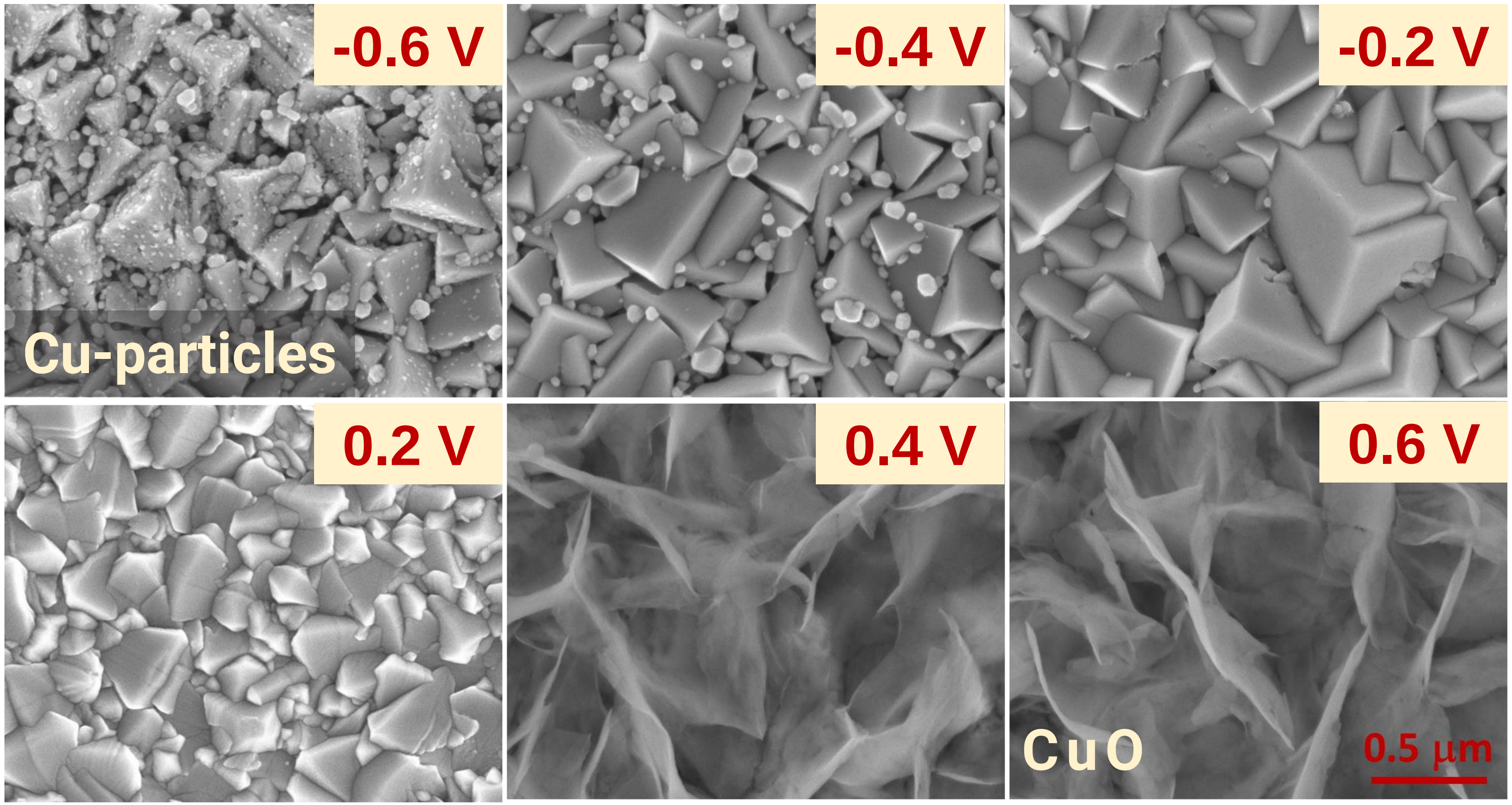
Presence of Cu impurity after 50 cycles:

Slow reduction kinetics

Potentiostatic hold

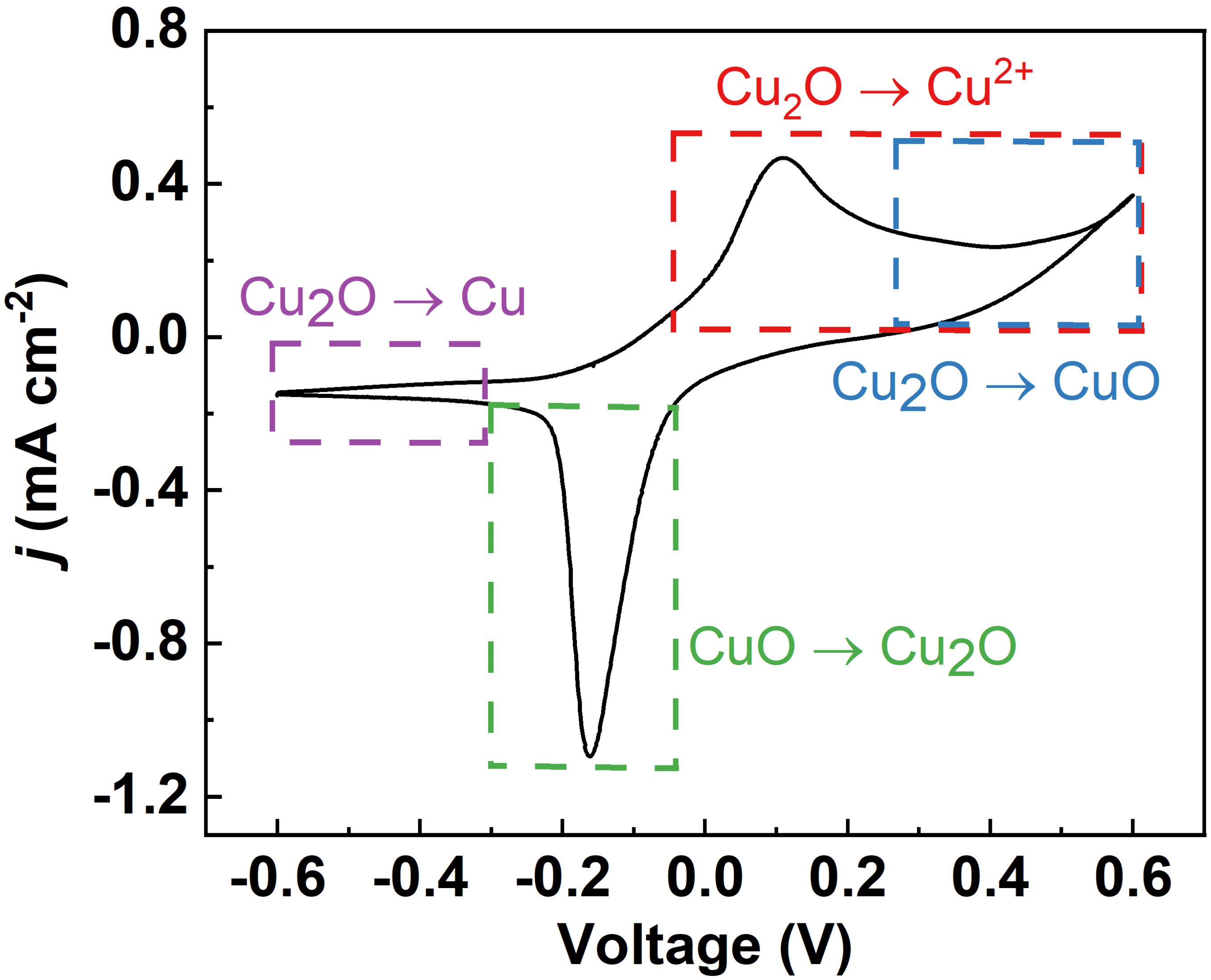






- Etching is observed during Potentiostatic hold at 0.2 V
- Cu_2O oxidized to either CuO or $Cu(OH)_2$
- Formation of a porous blocking layer at higher anodic potentials

Formation mechanism of porous Cu_2O



0.0 V to 0.6 V: XRD & ICP-AES
$Cu_2O + 2H^+ \rightarrow 2Cu^{2+} + H_2O + 2e^-$

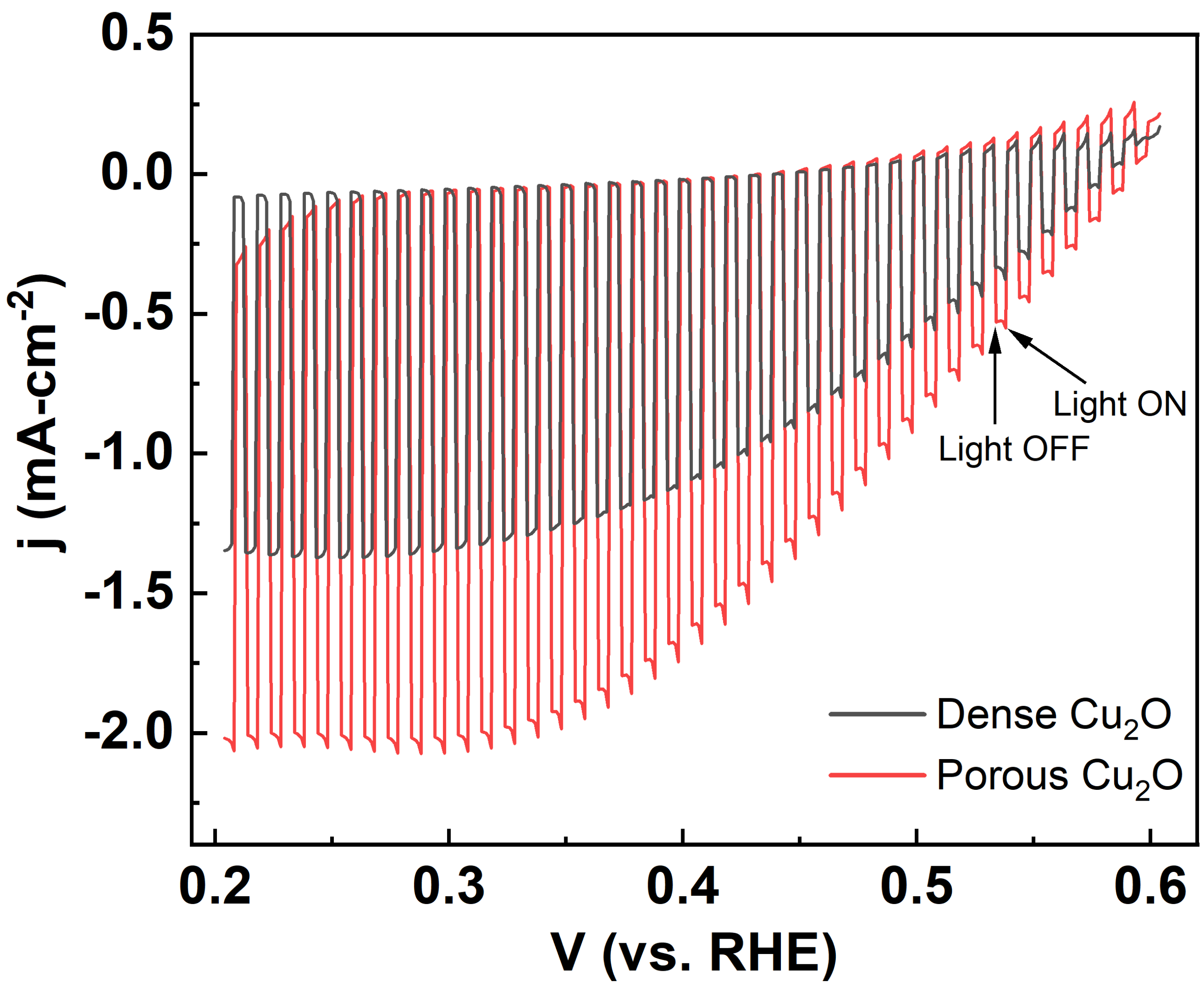
0.3 V to 0.6 V: CuO LSV & Pot. hold
$Cu_2O + 2OH^- + 2h^+ \rightarrow 2CuO + H_2O$

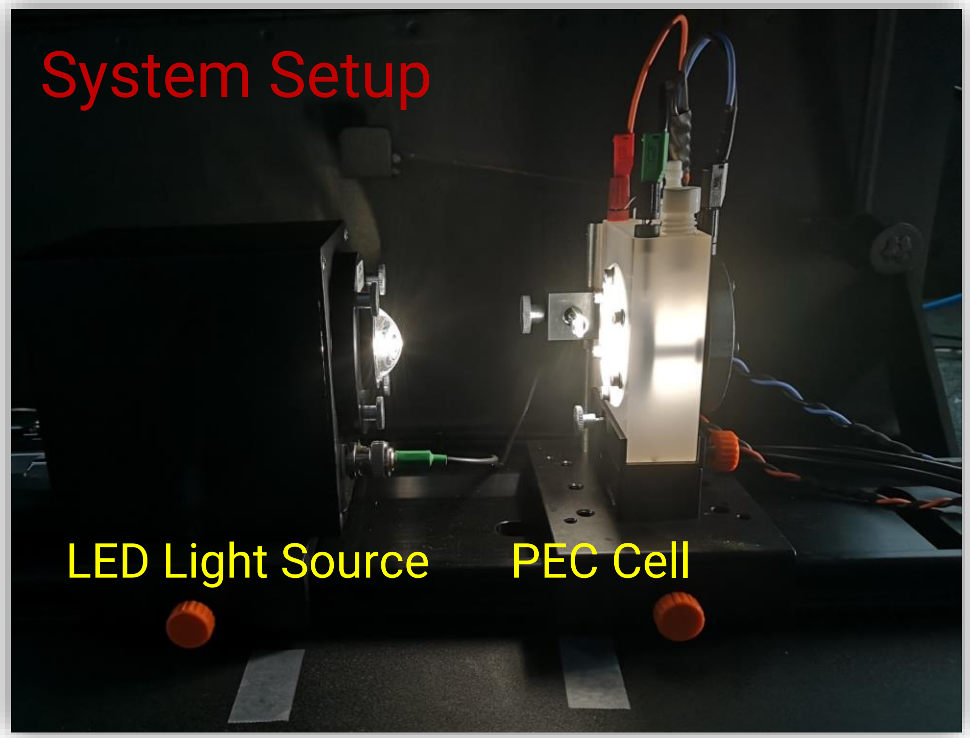
0.0 to -0.3 V: LSV analysis of CuO & Cu_2O
$2CuO + 2H^+ + 2e^- \rightarrow Cu_2O + H_2O$

-0.3 V to -0.6 V: Pot. Hold
$Cu_2O + 2H^+ + e^- \rightarrow 2Cu + H_2O$

- Etching
- Cu_2O oxidation to CuO
- CuO reduction to Cu_2O
- Cu_2O reduction to Cu

PEC Performance





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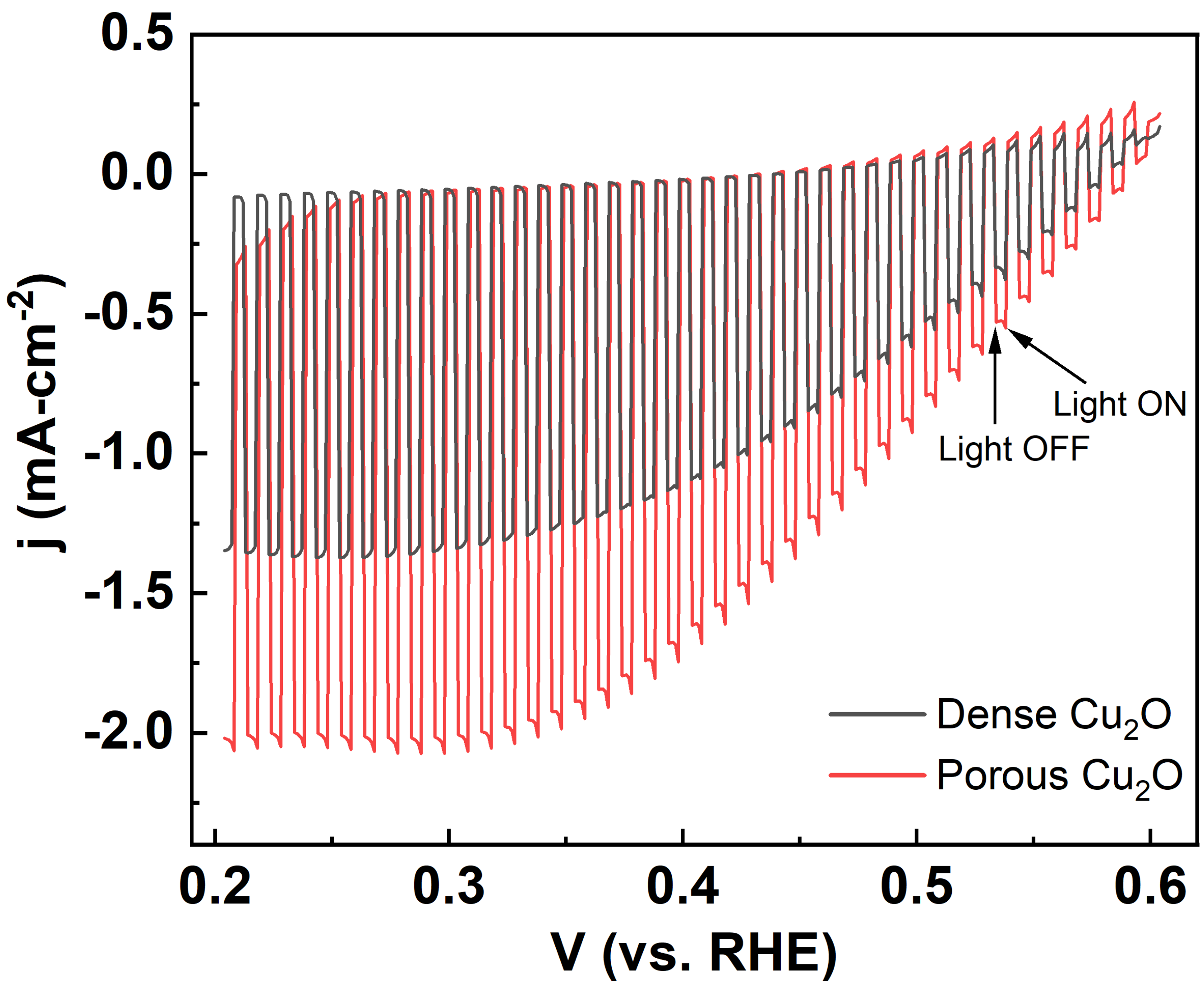

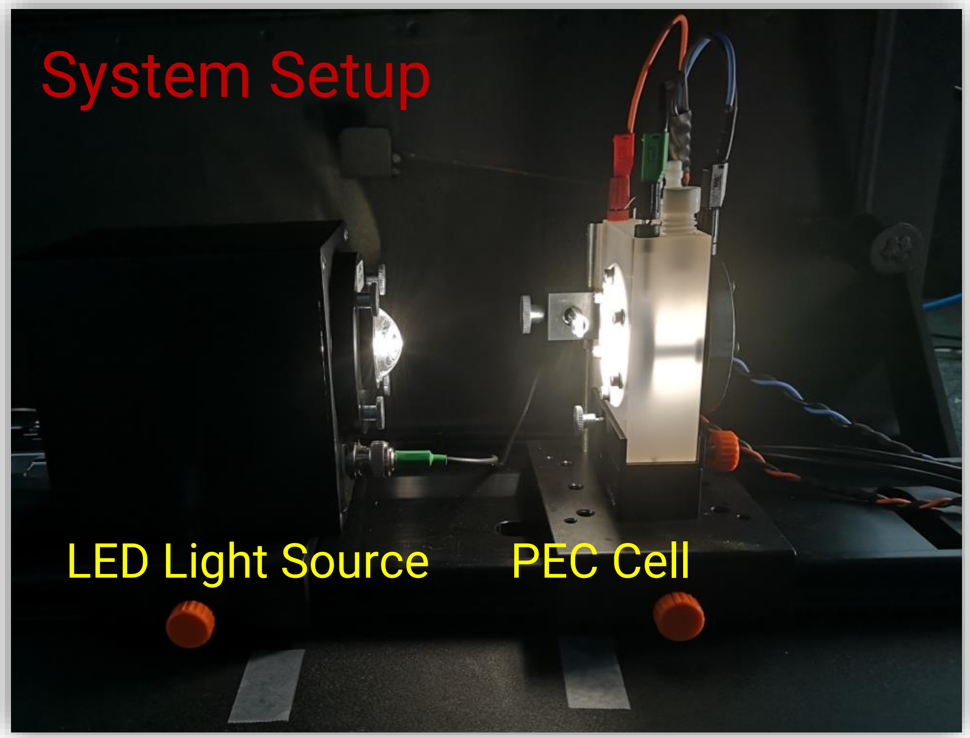

Photocurrent enhancement due to:

- Better light trapping
- Orthogonal charge separation
- Increased electrode-electrolyte contact area

Conclusions

- **Two step electrochemical synthesis of nanostructured Cu_2O thin films**
- **Nanostructured thin films show a photocurrent enhancement of 50% compared to dense film**

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Chandan Das

Garima Aggrawal

Suren Patwardhan

Sushobhita Chawala

Gurudayal Behera

Faleela

Thank You !!

Questions ??

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