Facet-dependent Carrier Dynamics of Cu_2O in Regulating the Photocatalytic H_2 Generation

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Project Background

❖ **Cuprous Oxide (Cu_2O):**
- Earth abundant & non-toxic
- Ease in forming numerous **well-defined morphologies**
- p-type semiconductor with **favourable band potentials** for redox reactions

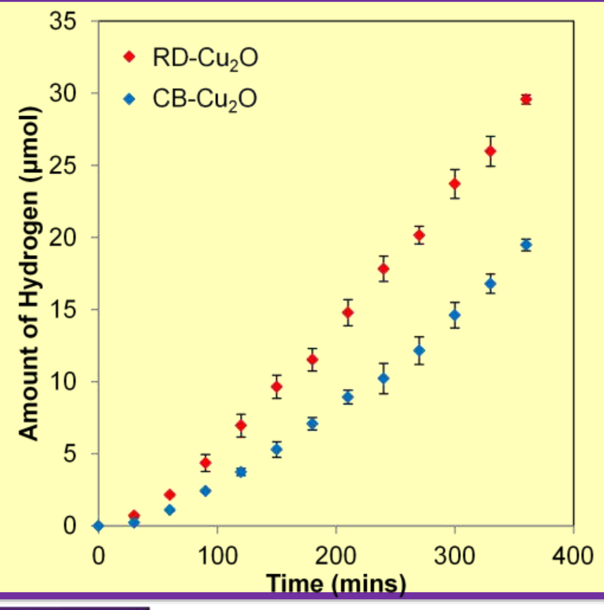
❖ **Facet-engineering of Cu_2O:**
- Facet-dependent properties
  - ✓ Surface adsorption ability
  - ✓ Surface electronic band structure
  - ✓ **Surface defect density**
- Influence the intrinsic carrier dynamics

Photoactivity

Photocatalytic H_2 Evolution

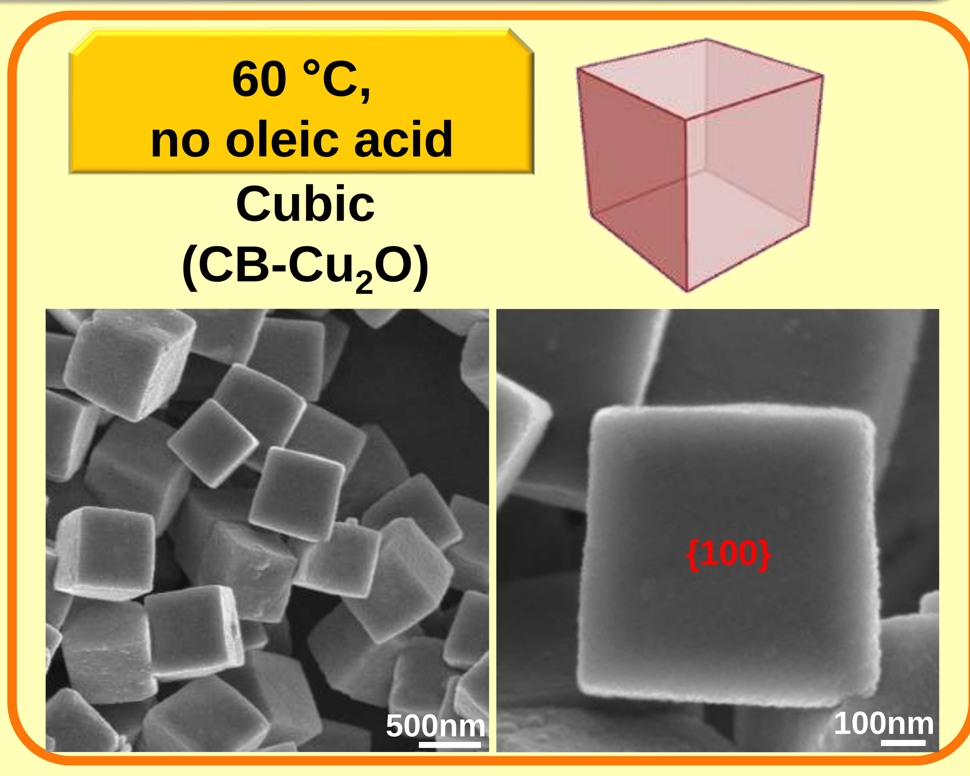
RD-Cu_2O: **29.6** µmol H_2
CB-Cu_2O: **19.5** µmol H_2

❖ RD-Cu_2O shows better performances.

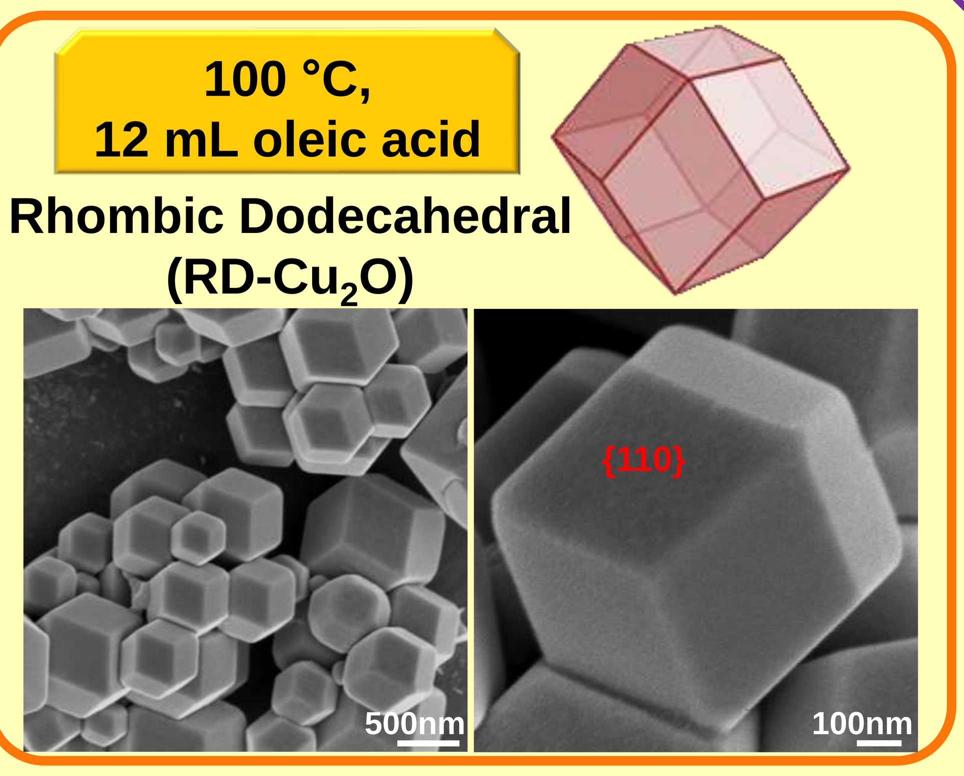


Morphology and Structure

60 °C, no oleic acid
Cubic (CB-Cu_2O)



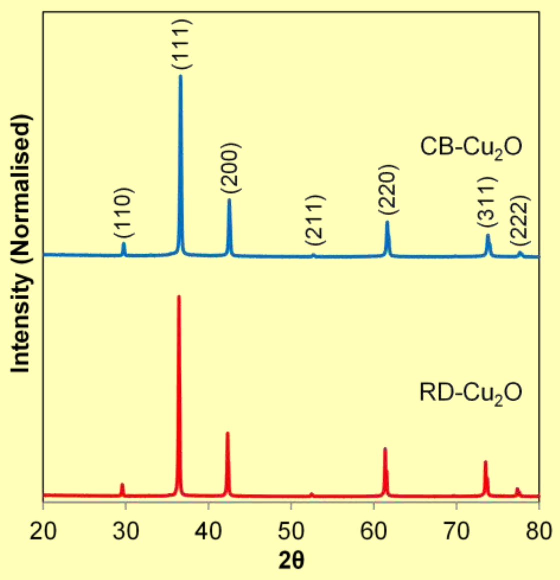
100 °C, 12 mL oleic acid
Rhombic Dodecahedral (RD-Cu_2O)



XRD

❖ Similar XRD patterns

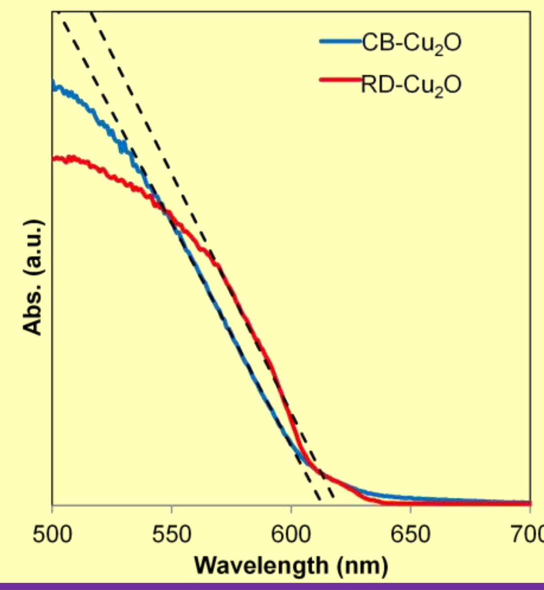
❖ Cubic crystalline Cu_2O



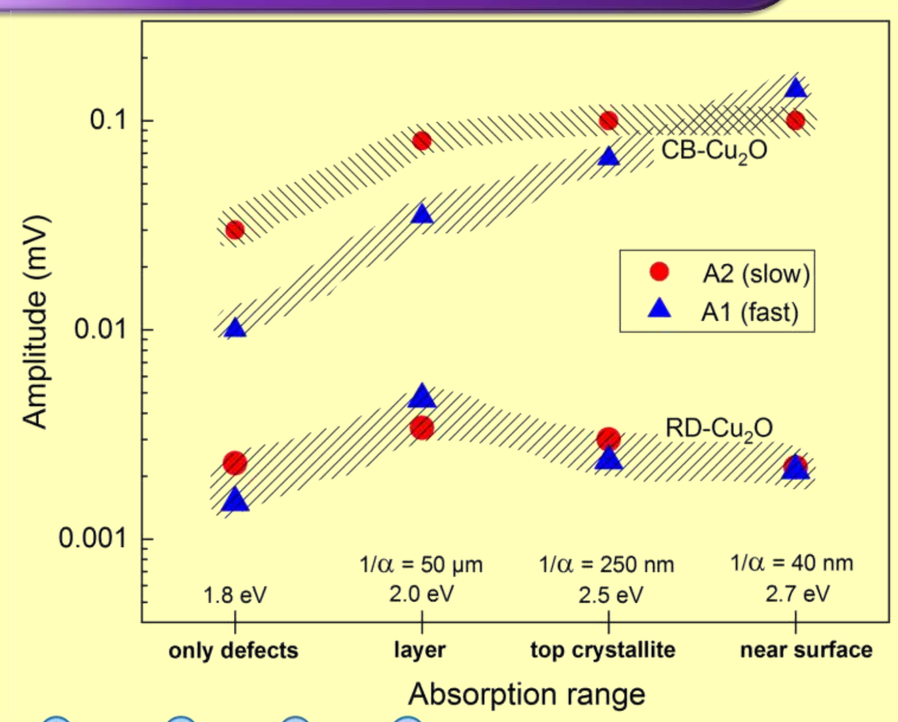
UV-Vis

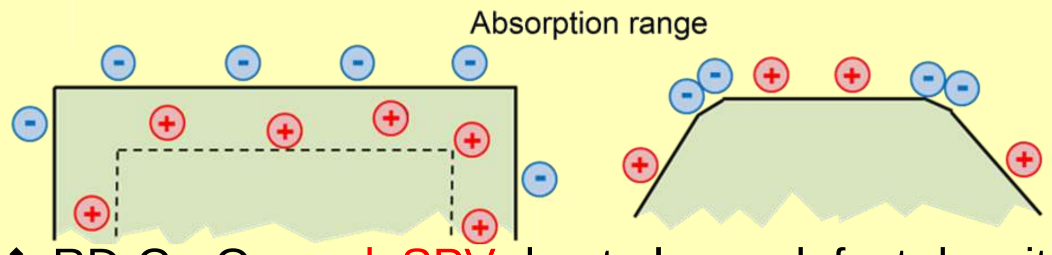
❖ Comparable absorption band edge

❖ Bandgap: ~2.0 eV



Surface Photovoltage Measurement



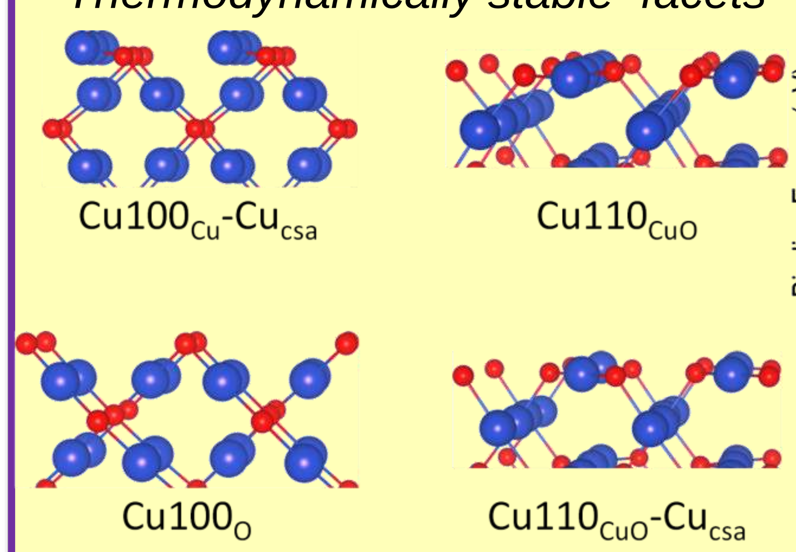


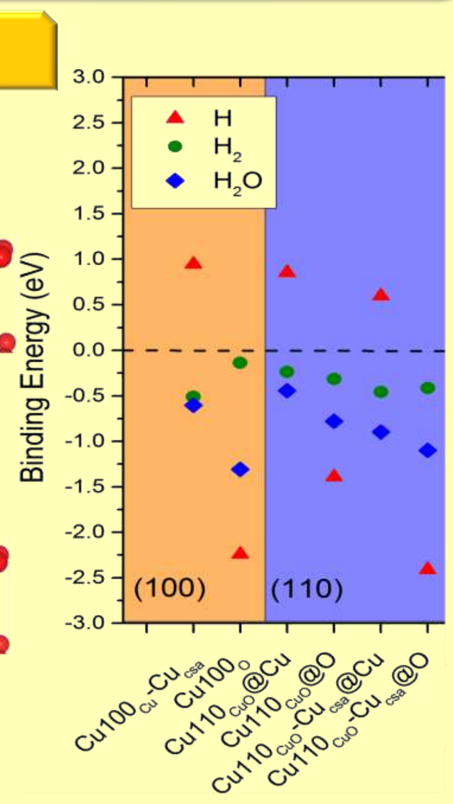
❖ RD-Cu_2O: weak SPV due to lower defect density.
❖ RD-Cu_2O: modulated charge distribution indicates better charge transfer.

Factors Influencing Photoactivity

Surface Absorption Ability

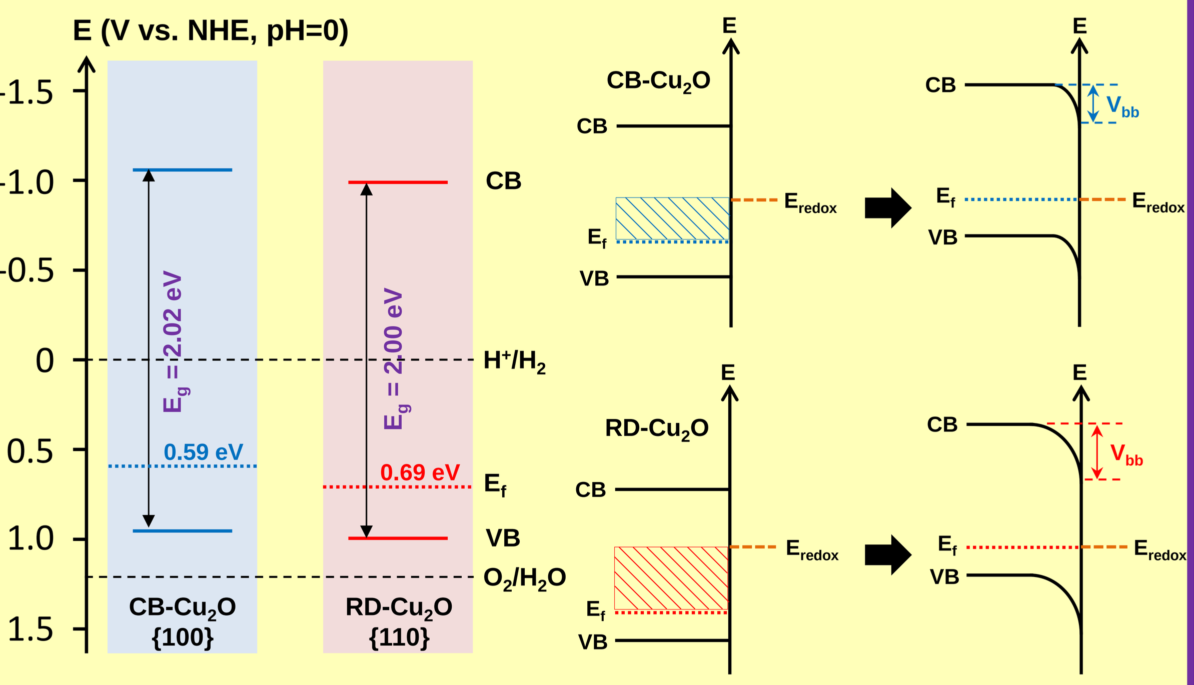
Thermodynamically stable facets





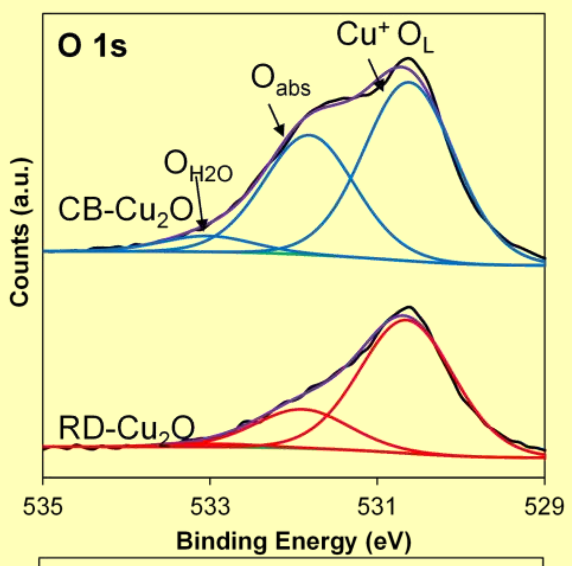
❖ Calculated using density of functional theory (DFT).
❖ By considering equal existence of these stable facets, surface adsorption ability of H, H_2 and H_2O could not be greatly differentiated.

Surface Electronic Structure

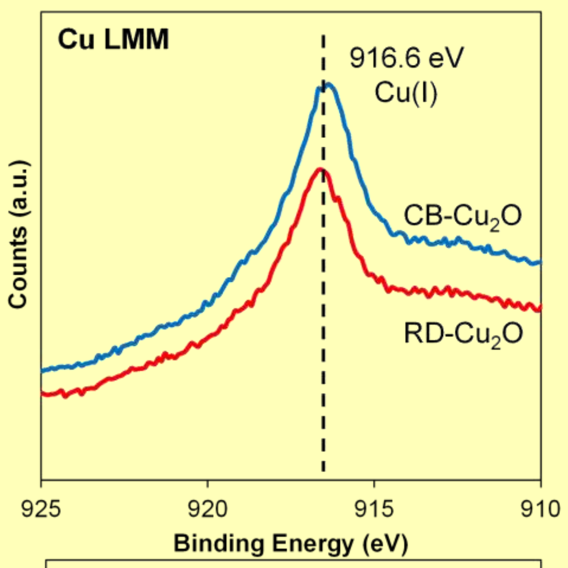


❖ Proposed band structures were identified by their bandgaps, valance bands computed from linear sweep voltammetry and valance XPS spectra.
❖ The larger band bending of RD-Cu2O indicates its better charge transfer when compared to CB-Cu_2O.

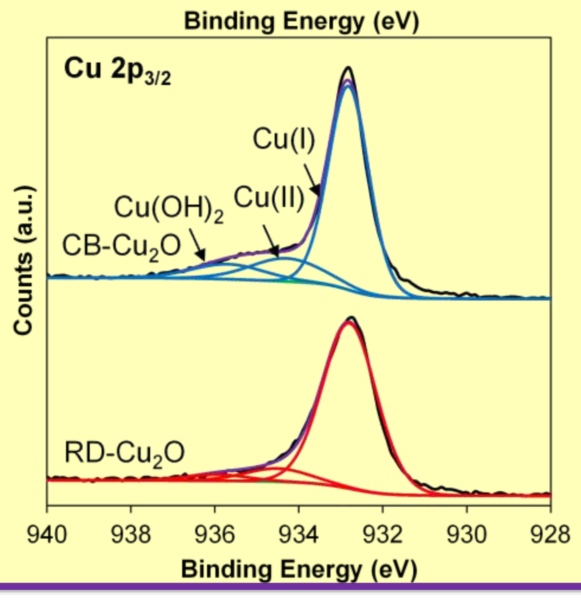
Surface Defect Density



❖ O_{abs} is associated to the oxygen vacancies.
❖ O 1s spectra show higher amount of oxygen vacancies in CB-Cu_2O.

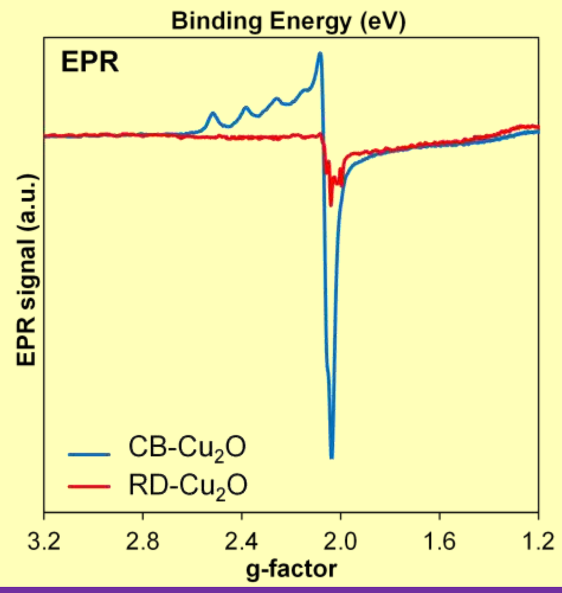


❖ 916.6 eV corresponded to Cu_2O is the only peak observed in Cu LMM auger spectra.
❖ No CuO species.



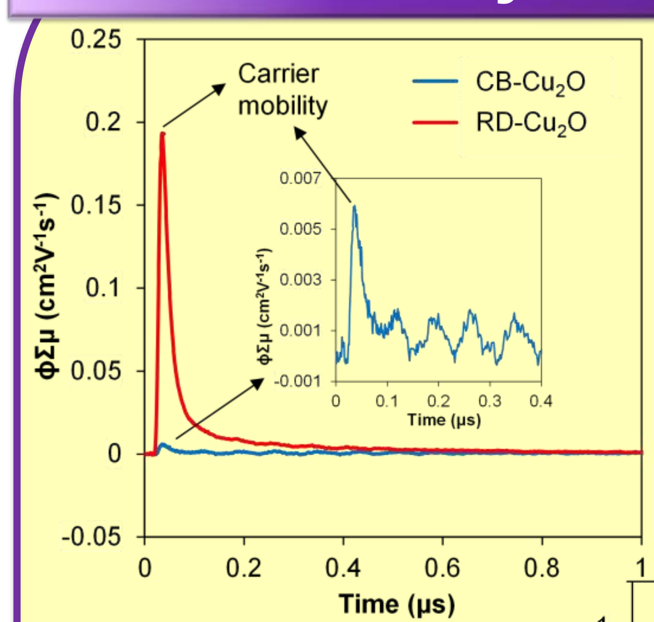
❖ Cu(II) indicates copper deficiency.
❖ Cu 2p spectra demonstrate larger amount of copper defect (Cu^{2+}) in CB-Cu_2O.

CB-Cu_2O has higher defect density than RD-Cu_2O.



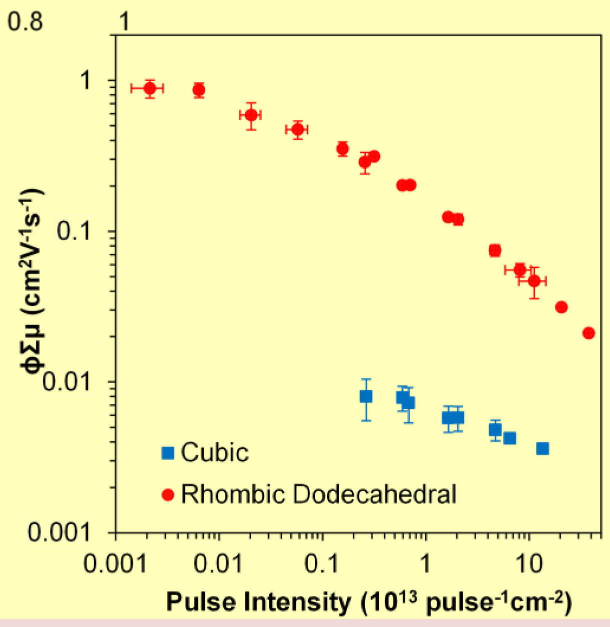
❖ Cu^{2+} is paramagnetic species and can be detected by electron paramagnetic resonance (EPR) spectroscopy.
❖ Intensified EPR signal (g-value: 2.06) of CB-Cu_2O indicates its higher amount of copper defect.

Time-resolve Microwave Conductivity Measurement

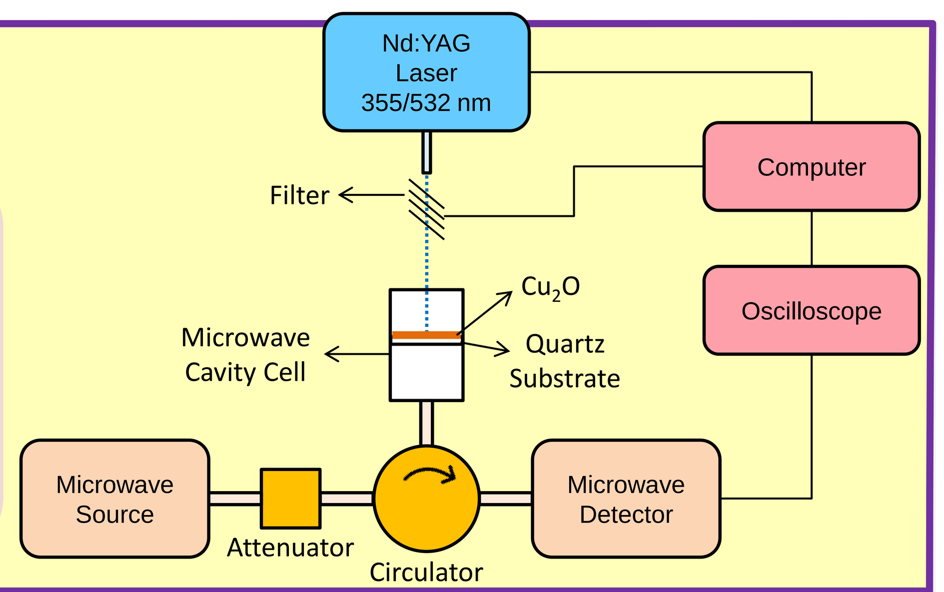


❖ RD-Cu_2O show higher carrier mobility.
❖ Fitted carrier lifetime of RD-Cu_2O is longer.

❖ RD-Cu_2O consistently show 2 orders of magnitude higher carrier mobility throughout different laser pulse intensity.



TRMC:
- Highly sensitive contactless approach that utilizes nanosecond pulsed laser to determine the carrier mobility and lifetime of a semiconductor.
- Measures the change in reflected microwave power which is expressed as product of internal quantum efficiency (ϕ) and the sum of carrier mobility (Σµ).



Summary

❖ **RD-Cu_2O > CB-Cu_2O**

❖ Attributed to its **higher carrier mobility and better charge separation,** which is associated to its **lower surface defect density and different surface exposed facets.**

❖ This study shows that the **charge carrier dynamics** have deciding influence on photoactivity.