Time-domain ab initio analysis of facet-dependent carrier dynamics in Cuprous oxide

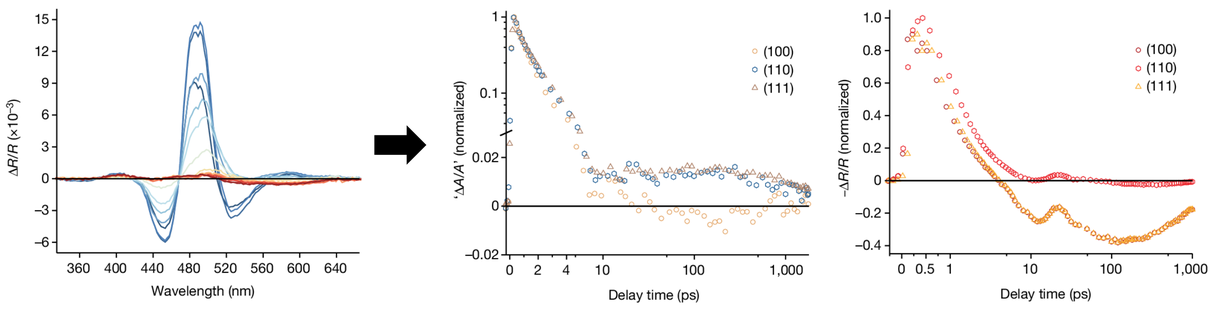
Minjae Kwen[1], Yoosang Son[1], and Hyungjun Kim[1*]

[1]Department of Chemistry, Korea Advanced Institute of Science and Technology

Introduction

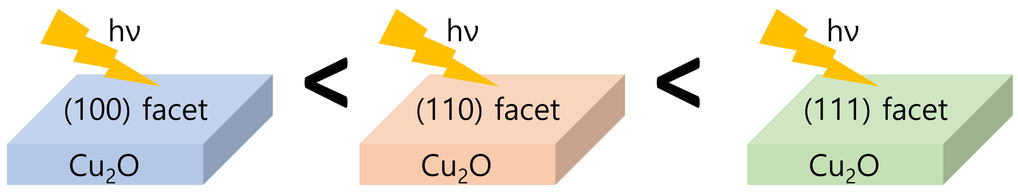
Cuprous oxide (Cu_2O) is a promising photoactive material for photoelectrodes used in water splitting and CO2 reduction.[1,2] A through characterization of **charge carrier mobility and recombination dynamics in Cu_2O** is important to crucial for understanding its photoelectrochemical (PEC) behavior.

Performance of the Cu_2O photoelectrode was studied by *Pan et al.*[3] Carrier dynamics of single crystalline Cu_2O films were examined using **ultrafast transient reflection spectroscopy**.



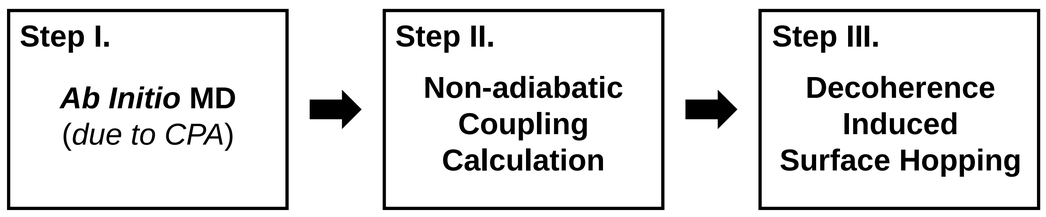
Figures from Fig 2a, 2d, 2e of *Nature* 628.8009 (2024): 765-770.[3]

Exciton lifetime and carrier diffusion lengths follows:



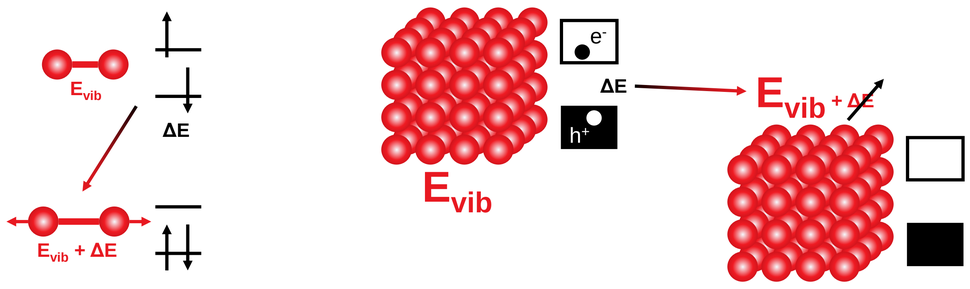
Calculational Methods

Surface hopping method with **classical path approximation (CPA)** was used for nonadiabatic dynamics simulation.



■ Classical Path Approximation (CPA)[4]

The CPA is the assumption that **the nuclear dynamics is unaffected by the electronic dynamics**. With CPA, **the nuclear trajectory is predetermined** during the surface hopping simulation.



■ Decoherence Induced Surface Hopping (DISH)[5]

(1) Time propagation of waveftn. → Coefficient calculation governed by TDSE

Using non-adiabatic coupling (NAC), $H_{ij} \equiv -i\hbar\left\langle \Phi_i \middle| \frac{\partial}{\partial t} \middle| \Phi_j \right\rangle$

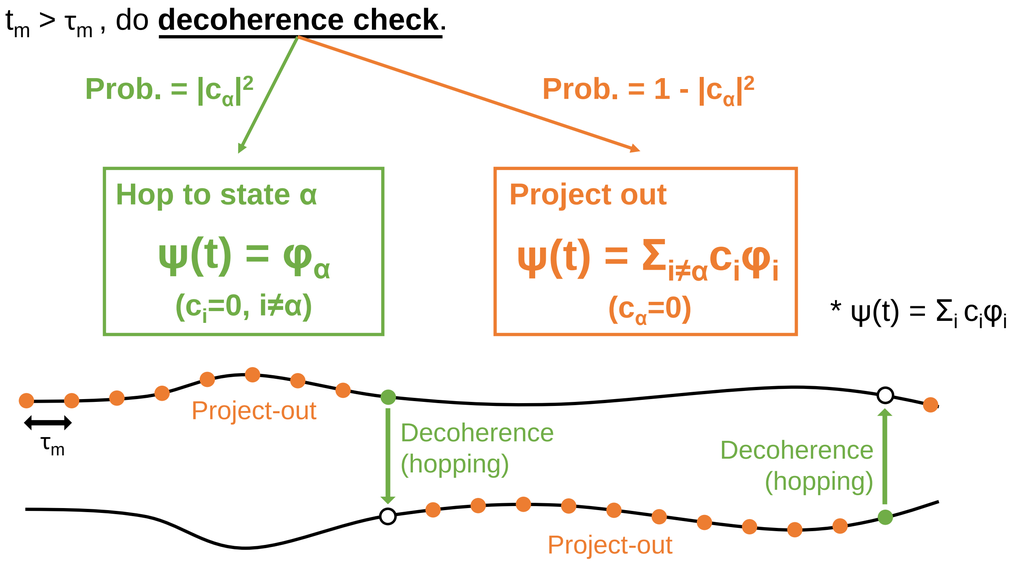
(2) Decoherence time (τ_m) calculation, from **the autocorrelation ftn. of energy gap**

$\frac{1}{\tau_\alpha}(t) = \sum_{i\neq\alpha}^{N} |c_i(t)|^2 r_{\alpha i}$, $r_{\alpha i}$ is the time constant of the decay of $J_{ij}(t) = \langle \Psi_i(t)|\Psi_j(t)\rangle$

$J_{ij}(t) \approx \langle J_{ij}(\mathbf{R}(t))\rangle_T \approx \exp\left[-\frac{1}{\hbar^2}\int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \langle \delta U(t)\cdot\delta U(t_0)\rangle_T\right]$, $\delta U(t) = \Delta E_{ij}(\mathbf{R}(t)) - \langle \Delta E_{ij}(\mathbf{R}(t))\rangle_T$

(3) Time from the recent decoherence check (t_m)

If $t_m > \tau_m$, do **decoherence check**.

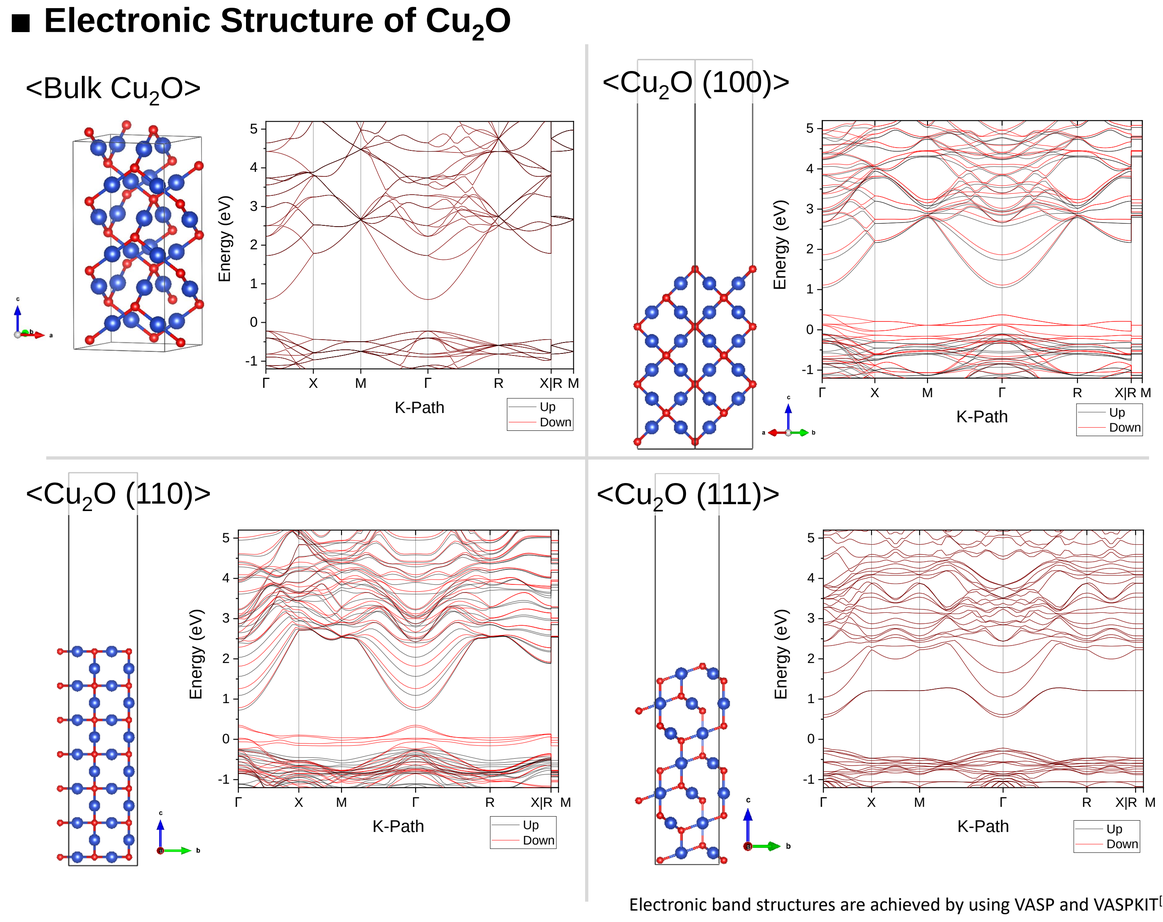


(4) Average for iterational surface hopping trajectories

(5) Ensemble Average for different nuclear trajectories

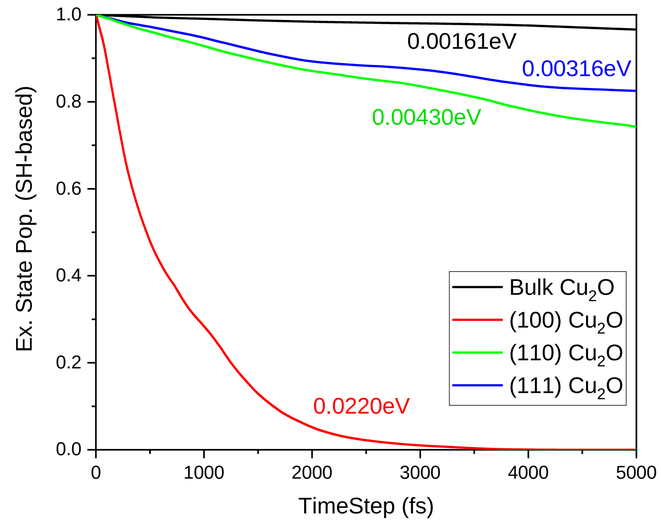
Results

■ Electronic Structure of Cu_2O



Electronic band structures are achieved by using VASP and VASPKIT[6]

■ Surface Hopping Simulation

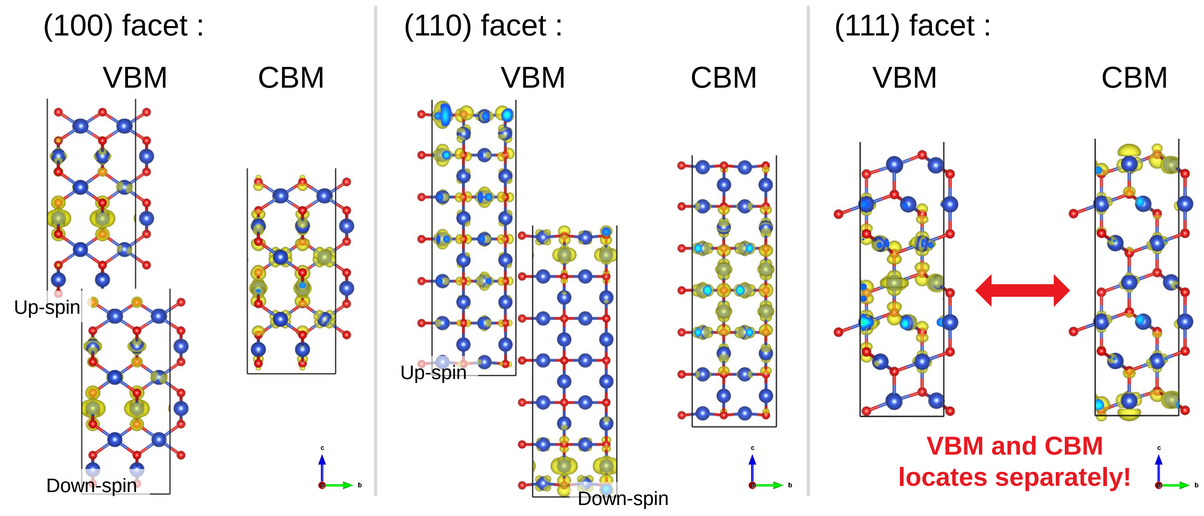


[Lifetime of exciton (ps)]

Bulk Cu_2O	(100) facet	(110) facet	(111) facet
148	0.730	16.1	22.4

Surface hopping simulation performed using Quantum Espresso and PYXAID[4]

■ Decomposed partial charge density



■ Effective Mass Calculation

From $\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{d^2\epsilon}{dk^2}$,

	Bulk Cu_2O	(100) facet	(110) facet	(111) facet
m_e^*/m_o on CBM	0.766	0.876 (Up) 0.890 (Down)	0.557 (Up) 0.573 (Down)	0.861
m_h^*/m_o on VBM	4.78	4.61 (Up) 5.33 (Down)	5.23 (Up) 10.1 (Down)	3.22

Conclusion

Using semiclassical nonadiabatic dynamics simulations, we elucidated the quantum mechanisms behind the **slower carrier recombination observed at (111) facet**. We also explicated this phenomenon with high band separation of VBM and CBM at (111) slab system.

References

[1] Paracchino, Adriana, *et al*. "Highly active oxide photocathode for photoelectrochemical water reduction". *Nature materials* 10.6 (2011), pp. 456-461.
[2] Li, Christina W., and Matthew W. Kanan. "CO2 reduction at low overpotential on Cu electrodes resulting from the reduction of thick Cu2O films". *Journal of the American Chemical Society* 134.17 (2012), pp. 7231-7234.
[3] Pan, Linfeng, *et al*. "High carrier mobility along the [111] orientation in Cu2O photoelectrodes". *Nature* 628.8009 (2024), pp. 765-770.
[4] Akimov, Alexey V., and Oleg V. Prezhdo. "The PYXAID program for non-adiabatic molecular dynamics in condensed matter systems". *Journal of chemical theory and computation* 9.11 (2013), pp. 4959-4972.
[5] Jaeger, Heather M., *et al*. "Decoherence-induced surface hopping." The Journal of chemical physics 137.22 (2012).
[6] Wang, V., *et al*. "A user-friendly interface facilitating high-throughput computing and analysis using VASP code., 2021, 267."