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

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Cuprous oxide (Cu_2O) is a promising photoactive material for photoelectrodes used in water splitting and CO_2 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. Previous experimental study has shown that Cu_2O exhibits varying charge carrier dynamics depending on its crystallographic facet;[3] however, a quantum-level understanding of these variations remains elusive. In this study, we investigate facet-dependent charge carrier dynamics in Cu_2O using real-time quantum dynamics simulations. We performed semiclassical nonadiabatic dynamics simulation with the classical path approximation,[4] and elucidated the quantum mechanisms behind the slower carrier recombination observed at (111) facet, which leads to superior PEC performance.[3]

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[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. DOI: 10.1021/ja3010978.

[3] Pan, Linfeng, et al. "High carrier mobility along the [111] orientation in Cu2O photoelectrodes". *Nature* 628.8009 (2024), pp. 765-770. DOI: 10.1038/s41586-024-07273-8

[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. DOI: 10.1021/ct400641n