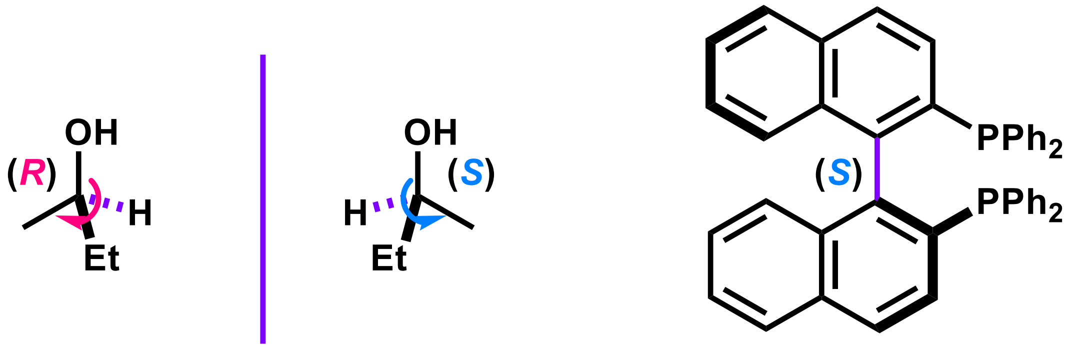
Spin-Controlled Electron by Chirality

2024.6.1.

Shu Nakamura

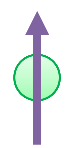
Contents

Chirality



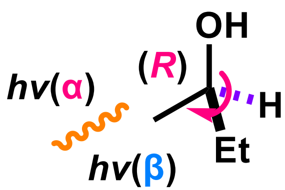
Right **and** ***Left*** **are not same. → Chirality**

*** Right and Left are defined by one vector.**



The minimal chirality is spin.

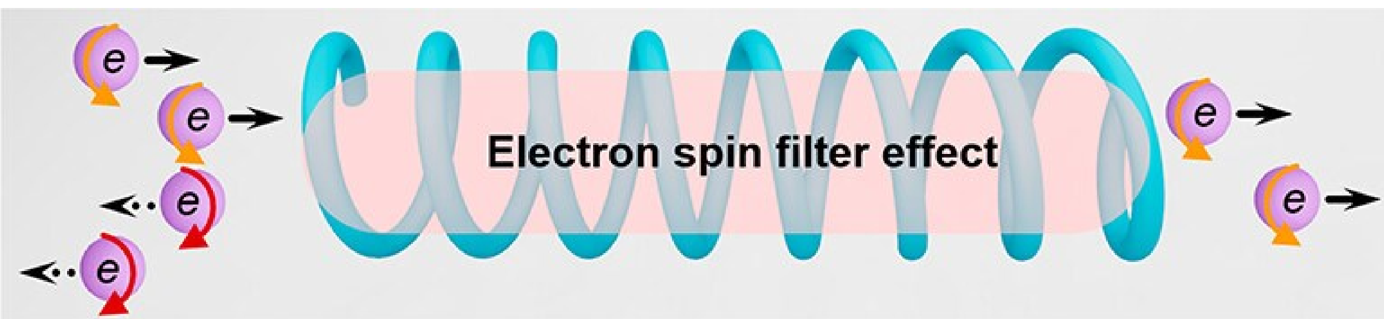
Chiral-Chiral Interaction



Photons are chiral. (circular polarized lights; CPL)
* Linear polarized light can be described as a sum of CPL.

→ Different ***n*** (reflactive index): **optical rotation**

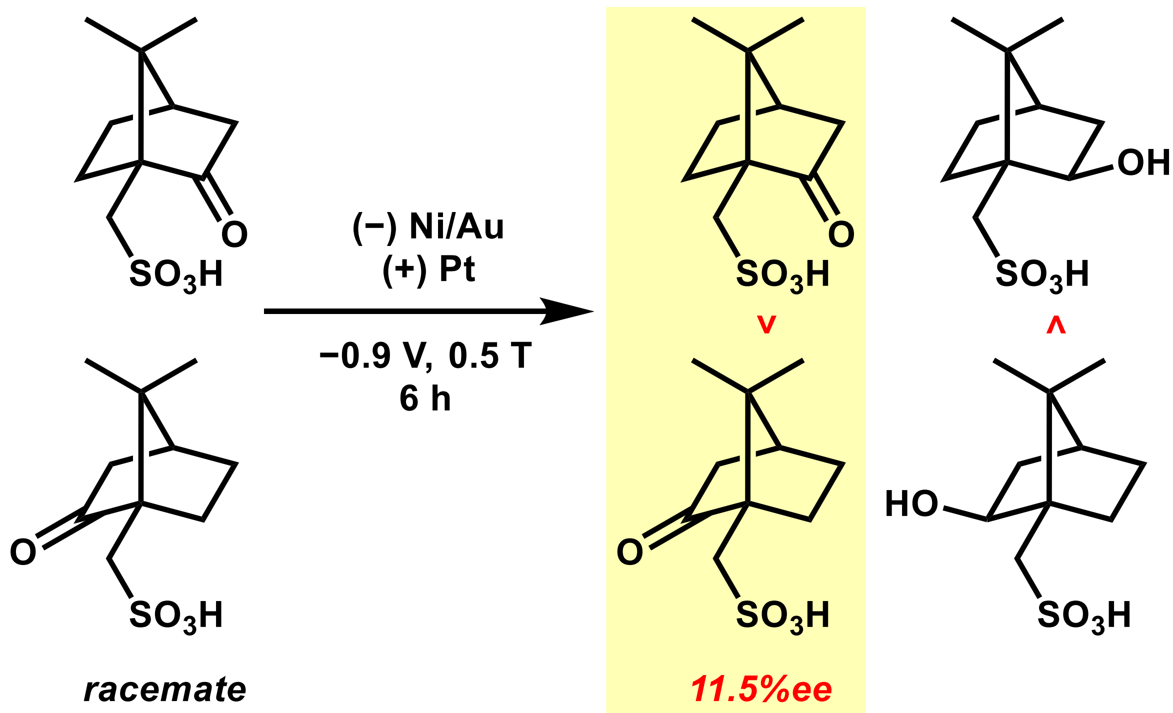
→ Different ***ε*** (absorbance): **circular dichroism** (**CD**)



Electrons with different spins could interact with chiral molecules differently.
→ **Chiral-Induced Spin Selectivity (CISS)**

1) Metzger, T. S.; Mishra, S.; Bloom, B. P.; Goren, N.; Neubauer, A.; Shmul, G.; Wei, J.; Yochelis, S.; Tassinari, F.; Fontanesi, C.; Waldeck, D. H.; Paltiel, Y.; Naaman, R. *Angew. Chem., Int. Ed.* **2020**, *59*, 1653.

Spin as a Chiral Source



1) Metzger, T. S.; Mishra, S.; Bloom, B. P.; Goren, N.; Neubauer, A.; Shmul, G.; Wei, J.; Yochelis, S.; Tassinari, F.; Fontanesi, C.; Waldeck, D. H.; Paltiel, Y.; Naaman, R. *Angew. Chem., Int. Ed.* **2020**, *59*, 1653.

Introduction of Authors

Masayuki Suda

2009 Ph.D @ Keio University
(Assoc. Prof. Yasuaki Einaga)
2010 Special Postdoctoral Researchers @ RIKEN
(Head, Chief: Reizo Kato)
2012 Assistant Professor @ Graduate University for Advanced Studies
2020-Associate Professor @ Kyoto University

Research topic: nanotechnology, materials

Prof. Peng-peng Wang

2014 Ph.D @ Tsinghua University (Prof. Xun Wang)
2014 Postdoctral fellow @ University of Maryland
(Prof. Min Ouyang)
2019-Professor @ Xi'an Jiaotong University

Research topic: nanostructures

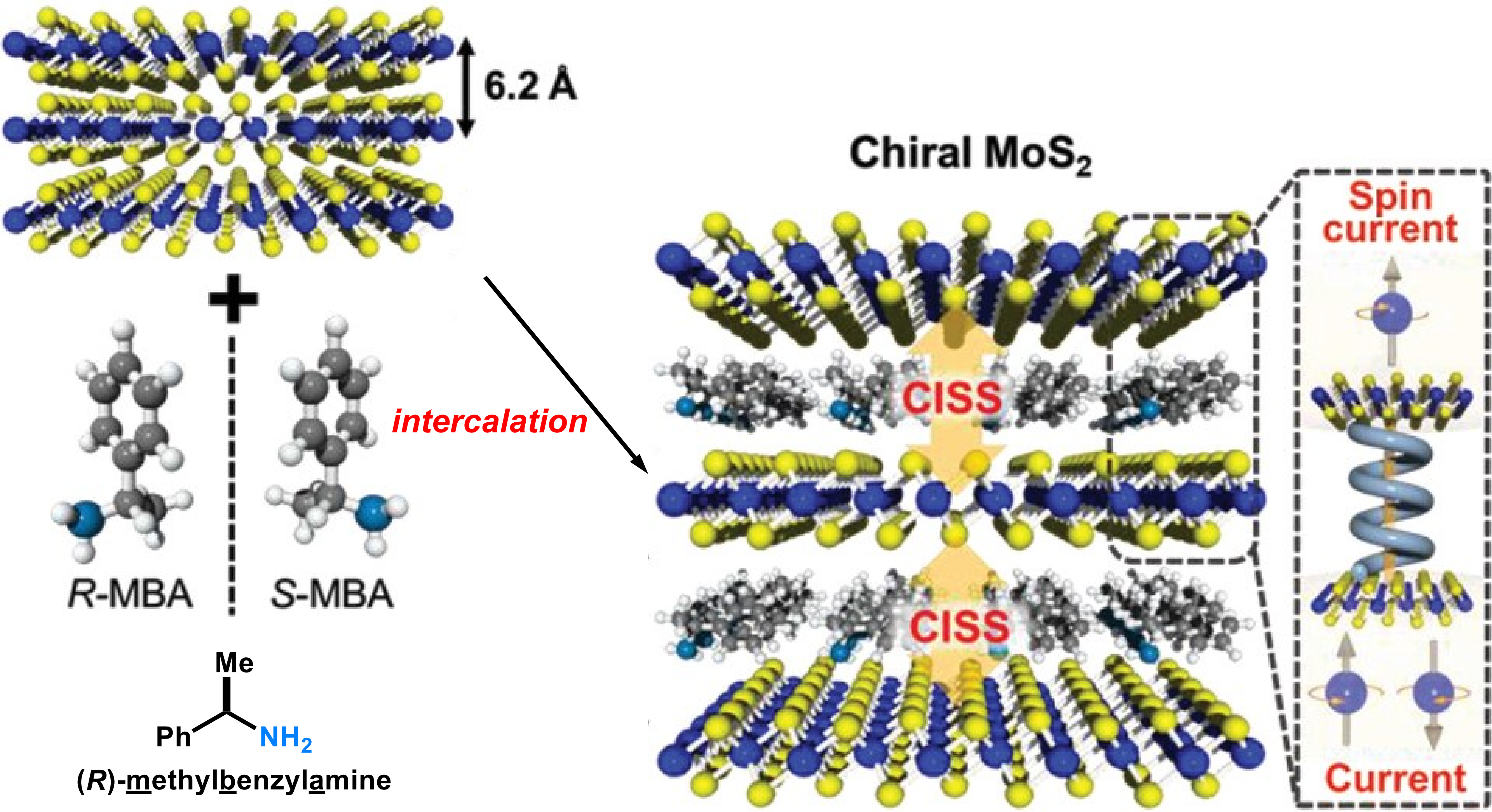
1) https://www2.riken.jp/lab/molecule/old-member/suda/suda.html
2) https://yamamoto.ims.ac.jp/en/node
3) https://orcid.org/0000-0003-4054-8903, 4) http://thuwangxungroup.com/Prior%20Members.html

Contents

Molybdenum Disulfide (MoS_2)

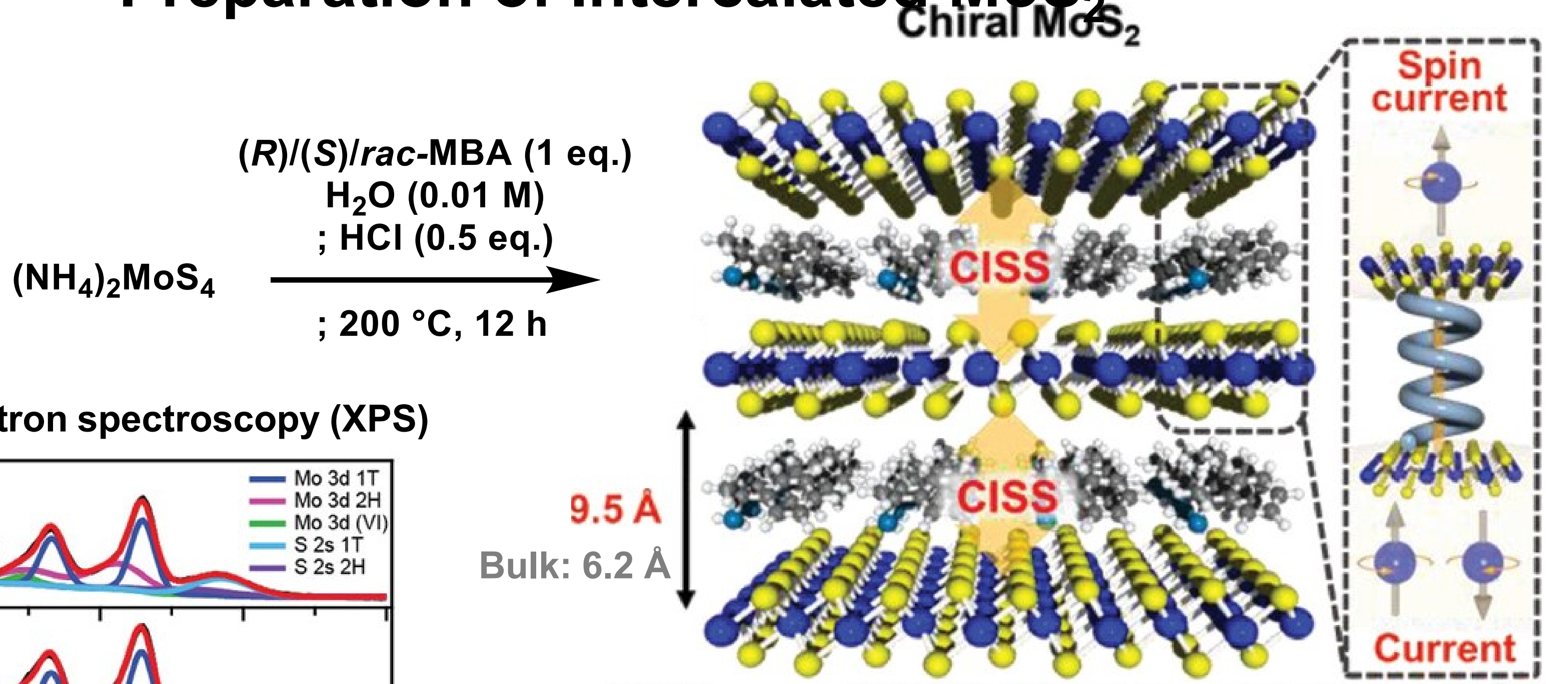
Bulk MoS_2

Semiconductor
Hexagonal graphite-like layered structure

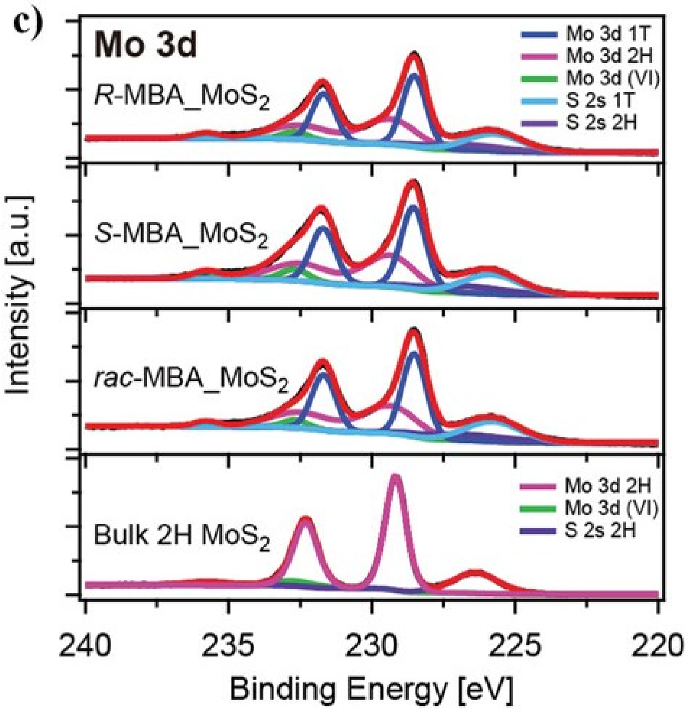


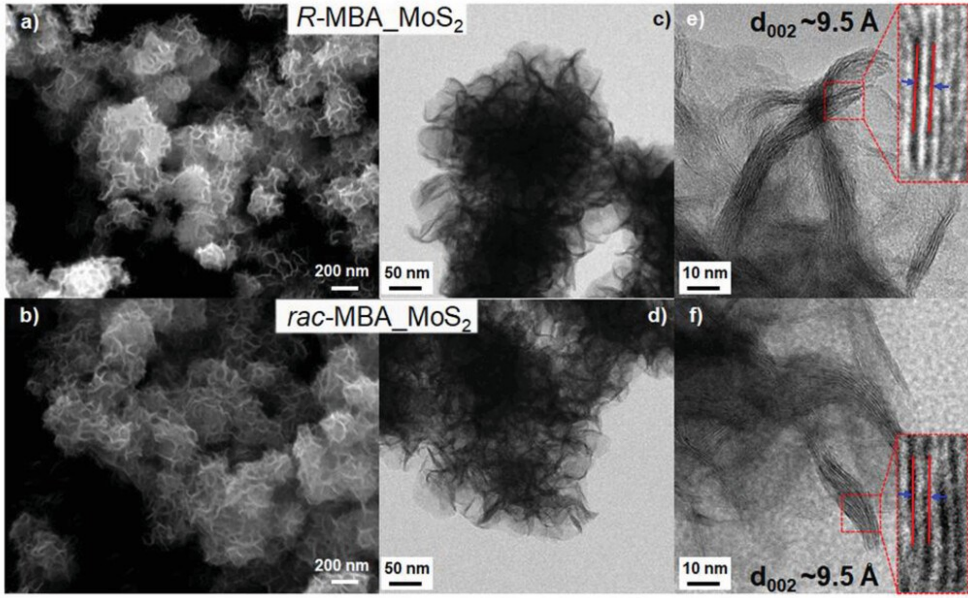
1) Bain, Z.; Kato, K.; Ogoshi, T.; Cui, Z.; Sa, B.; Tsutsui, Y.; Seki, S.; Suda, M. *Adv. Sci.* **2022**, *9*, 2201063.

Preparation of Intercalated MoS_2



X-ray photoelectron spectroscopy (XPS)



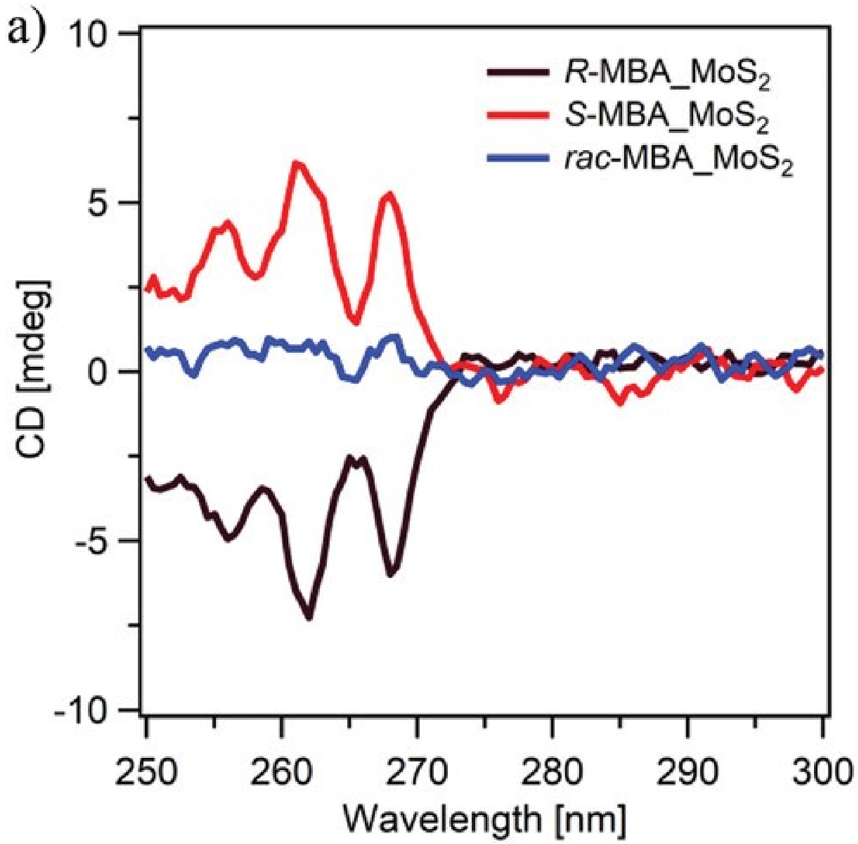


1T' phase (=intercalated) detected. (1T' : 2H ≒ 5 :3)

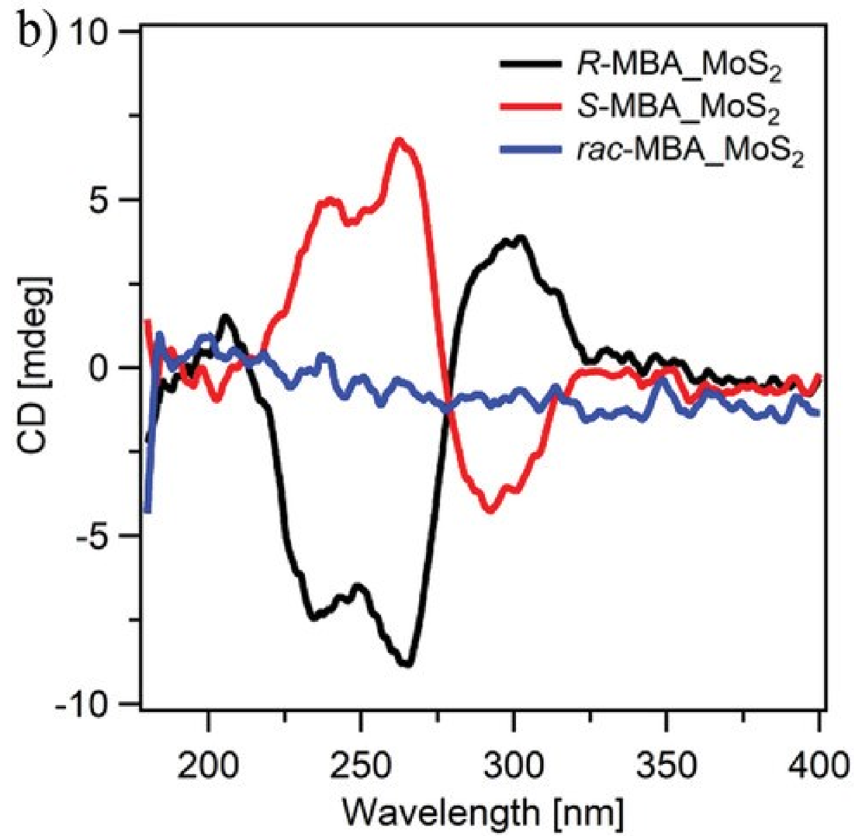
1) Bain, Z.; Kato, K.; Ogoshi, T.; Cui, Z.; Sa, B.; Tsutsui, Y.; Seki, S.; Suda, M. *Adv. Sci.* **2022**, *9*, 2201063.

Chirality of Intercalated MoS_2

CD spectra of MBA



CD spectra of MBA_MoS_2

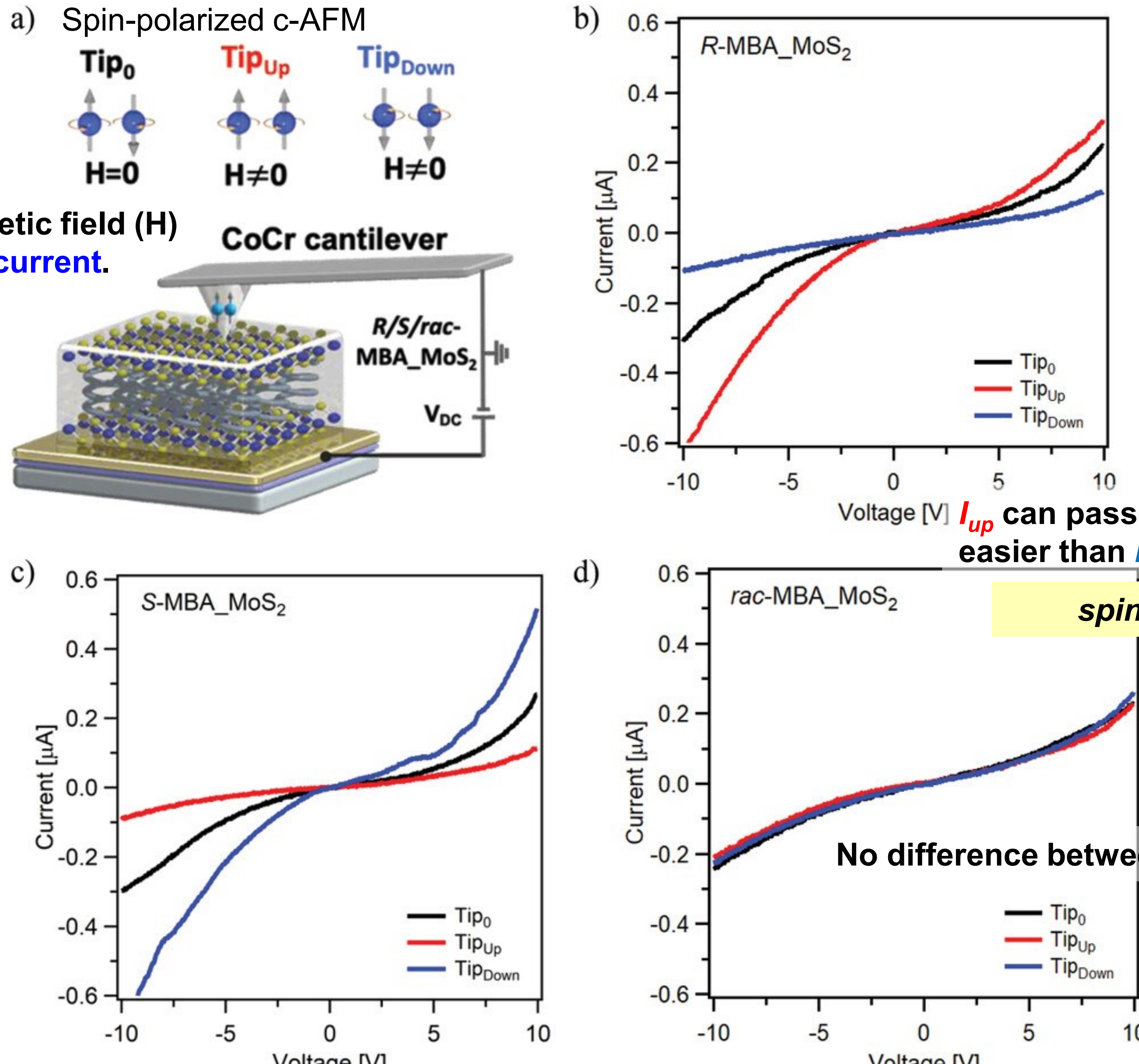


The chirality of intercalated MoS_2 did not only derive from chiral MBA.

1) Bain, Z.; Kato, K.; Ogoshi, T.; Cui, Z.; Sa, B.; Tsutsui, Y.; Seki, S.; Suda, M. *Adv. Sci.* **2022**, *9*, 2201063.

Spin Selectivity of Intercalated MoS_2 — c-AFM measurement

External magnetic field (H) enriches spin current.



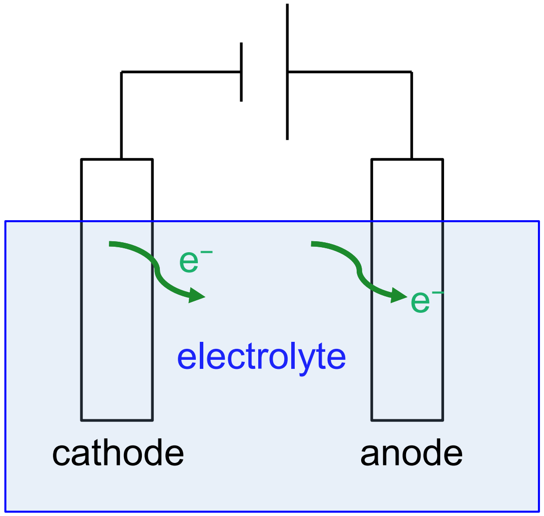
I_{up} can pass through *R*-MoS_2 easier than I_{down}.

spin filtering

No difference between I_{up} and I_{down}.

1) Bain, Z.; Kato, K.; Ogoshi, T.; Cui, Z.; Sa, B.; Tsutsui, Y.; Seki, S.; Suda, M. *Adv. Sci.* **2022**, 9, 2201063.

Electrolysis



Standard Electrode Potential (Standard Reduction Potential)

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ $\Delta_r G^0$ = −476 kJ/mol
= 1.23 V × 4·(−96500 C/mol)

$$E^0 = \frac{\Delta_r G^0}{-n\mathrm{F}}$$

***E*^{0}: standard electrode potential**
F: Faraday constant (≒96500 C/mol)
n: the number of electrons in the half reaction

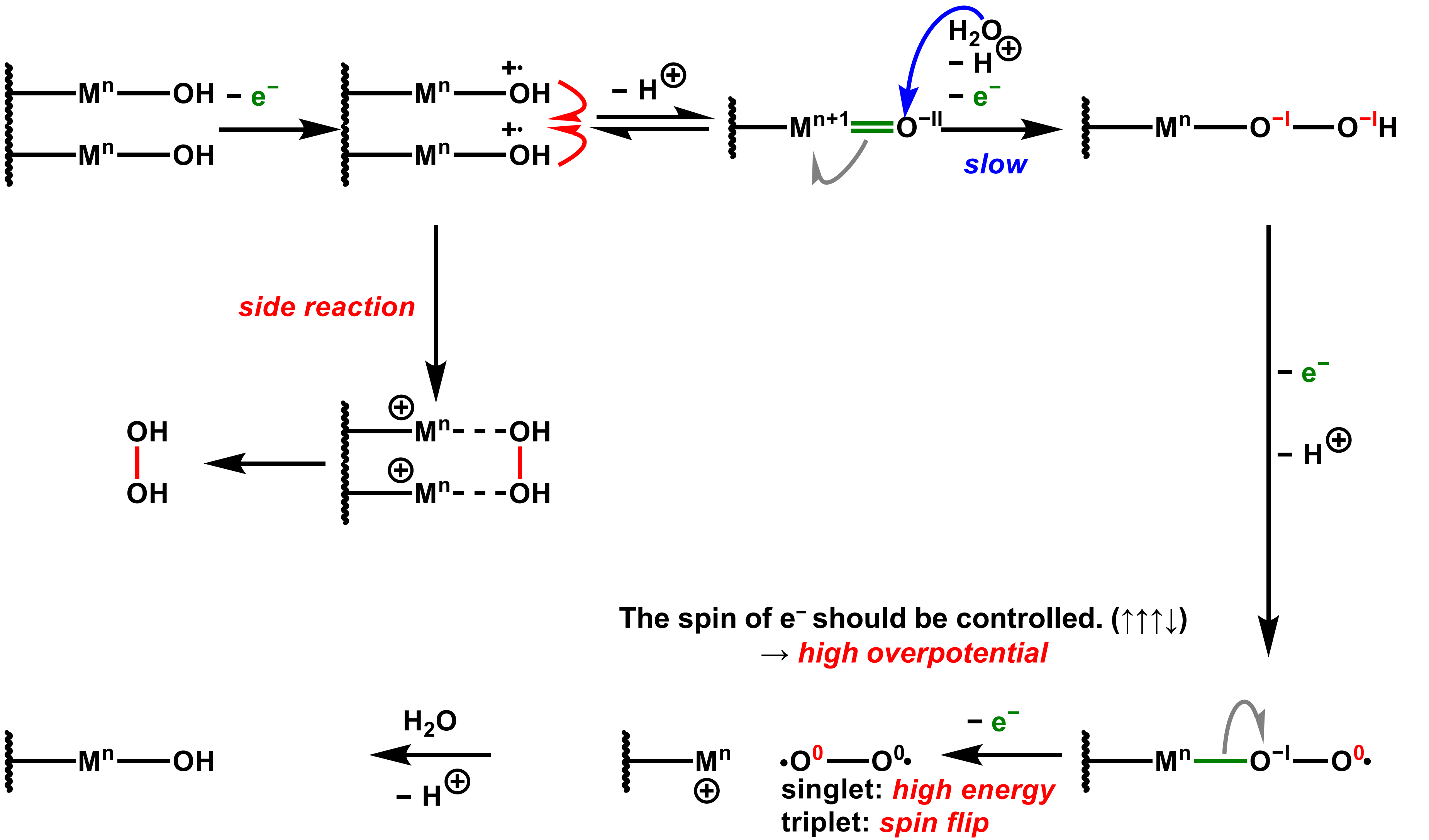
thermodynamic parameter

→ Usually, **overpotential** is necessary to overcome the activation energy.

Oxygen Evolution Reaction (OER)

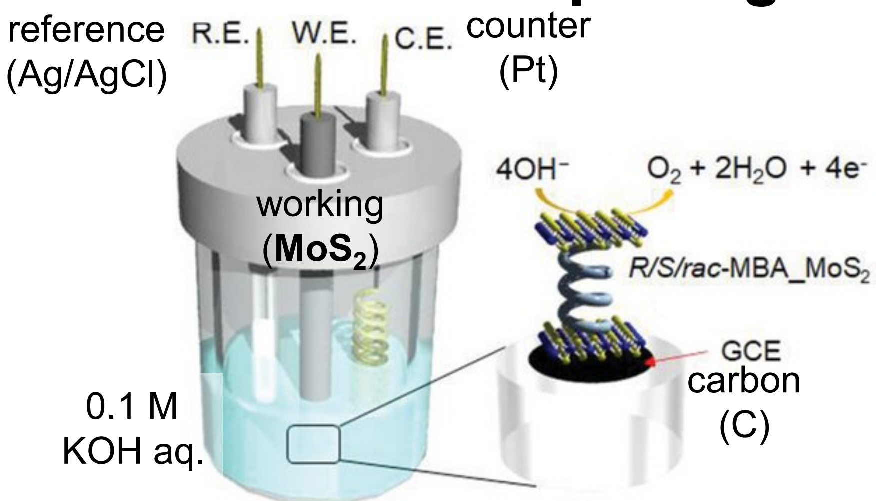
$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

Oxidation numbers are described.

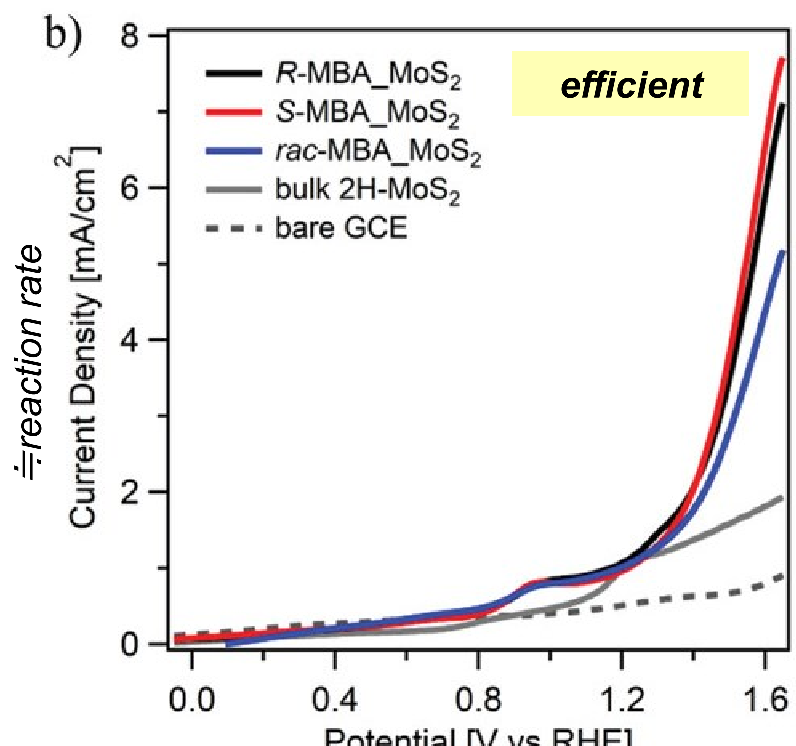


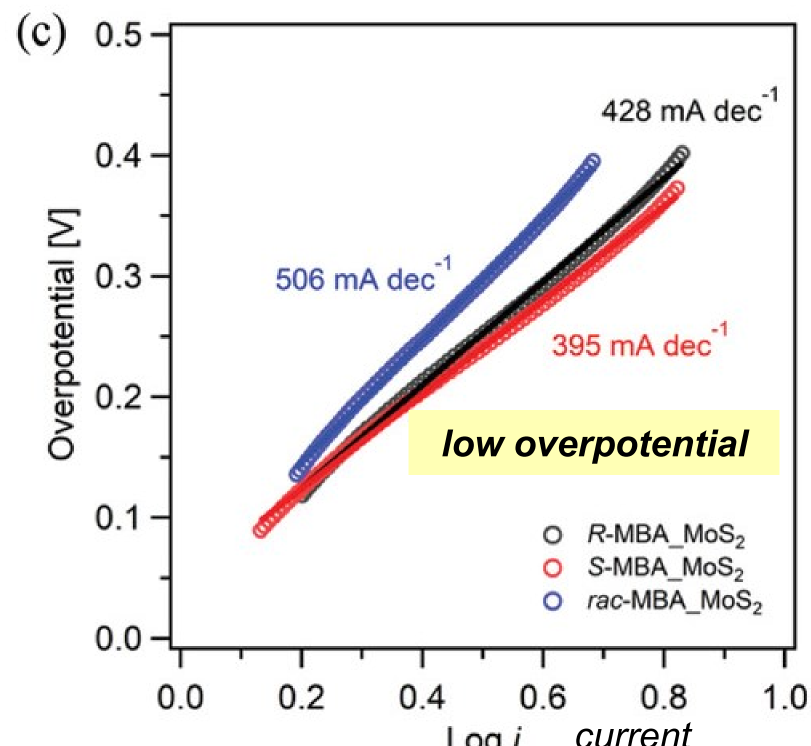
1) Wu, T.; Xu, Z. J. *Curr. Opin. Electrochem.* **2021**, *30*, 100804.
2) Vadakkayil, A.; Clever, C.; Kunzler, K. N.; Tan, S.; Bloom, B. P.; Waldeck, D. H. *Nat. Commun.* **2023**, *14*, 1067.

Water Splitting on Intercalated MoS_2 (1)



Chiral MoS_2 effectively induce electrolysis of OH^- than racemic one.

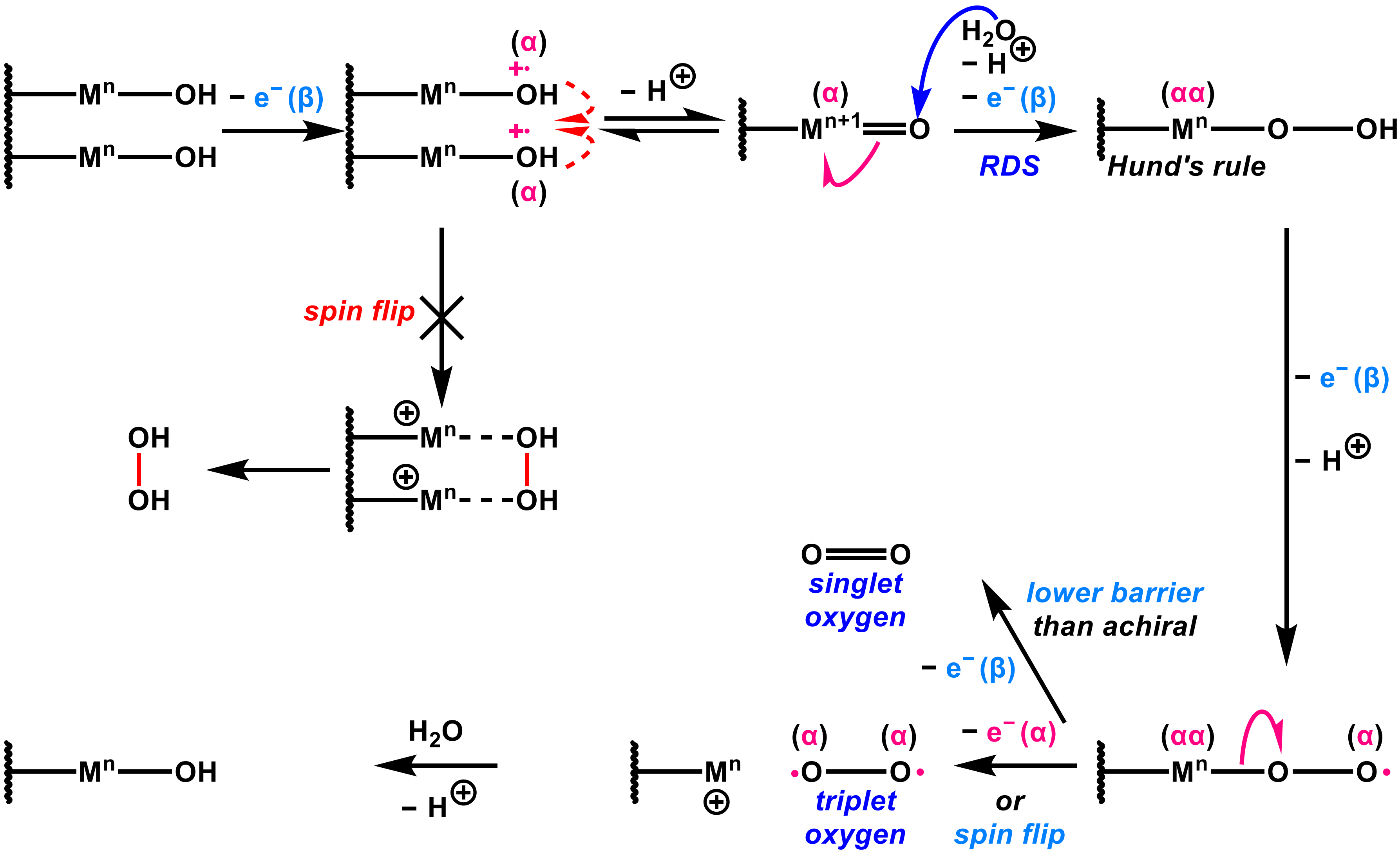




1) Bain, Z.; Kato, K.; Ogoshi, T.; Cui, Z.; Sa, B.; Tsutsui, Y.; Seki, S.; Suda, M. *Adv. Sci.* **2022**, 9, 2201063.

Spin-controlling OER

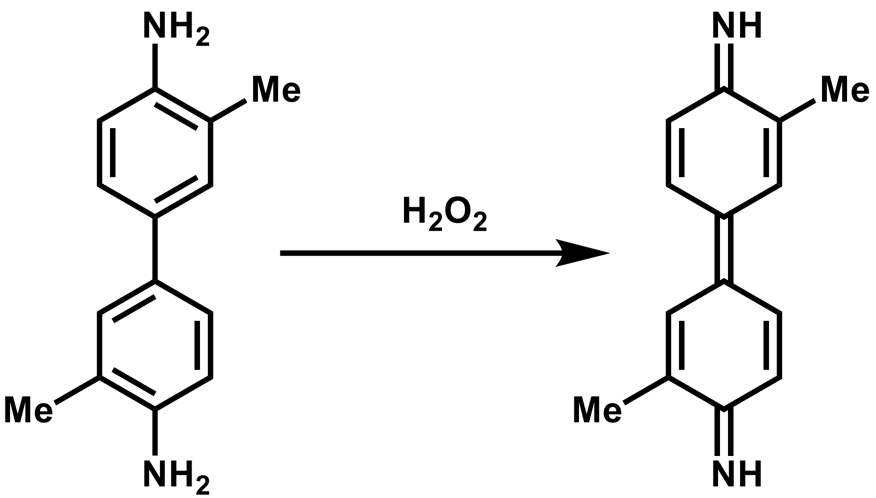
$2H_2O \rightarrow O_2$ (*triplet*, 2α) + $4H^+$ + $4e^-$(βββα)



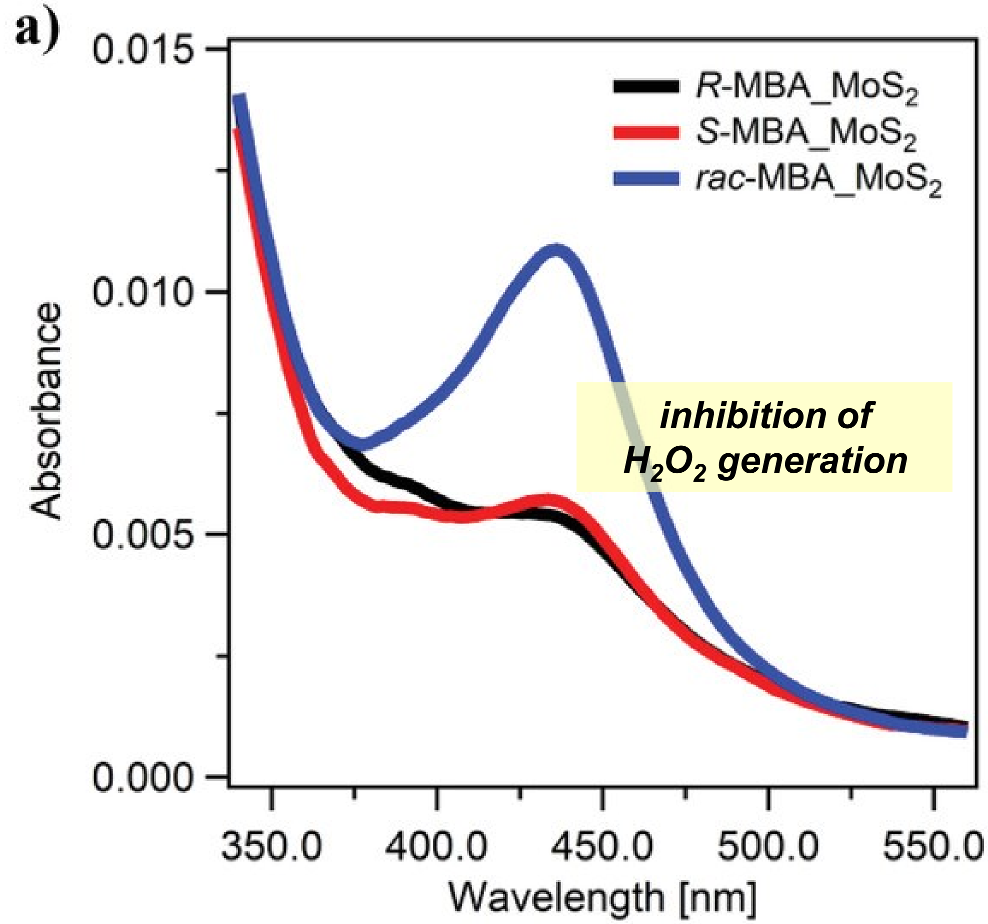
1) Wu, T.; Xu, Z. J. *Curr. Opin. Electrochem.* **2021**, *30*, 100804.
2) Vadakkayil, A.; Clever, C.; Kunzler, K. N.; Tan, S.; Bloom, B. P.; Waldeck, D. H. *Nat. Commun.* **2023**, *14*, 1067.

Water Splitting on Intercalated MoS_2 (2)

The major byproduct H_2O_2 was titrated using *o*-tolidine after the electrolysis in aq. Na_2SO_4.



***λ*: 437 nm**
detection of H_2O_2



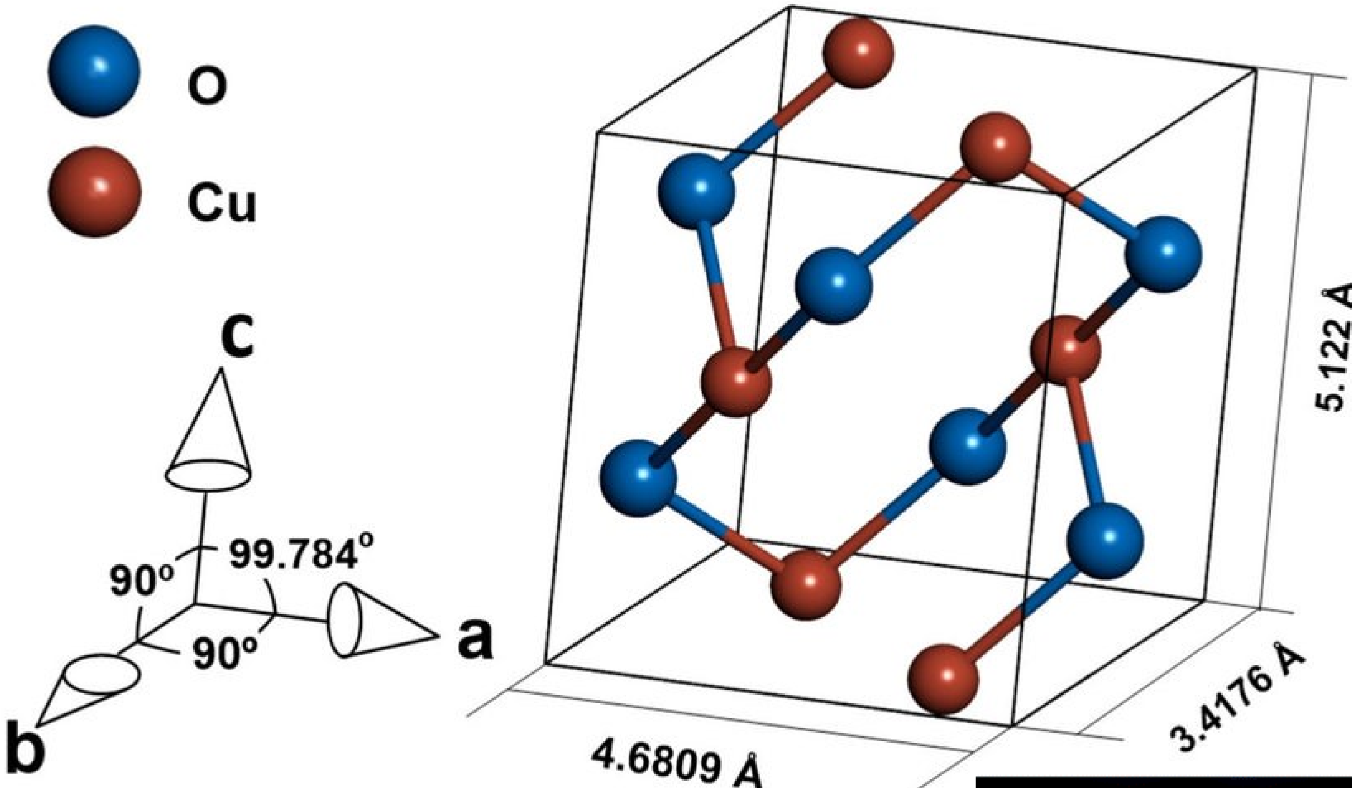
Chiral MoS_2 electrode…
- **enhance O_2 production**
- **suppress H_2O_2 generating side reaction**

by controlling the spin of the electrons…?

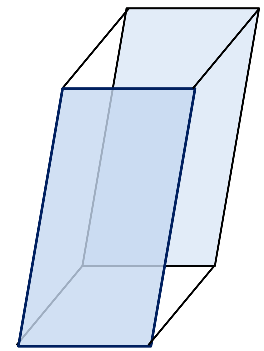
1) Bain, Z.; Kato, K.; Ogoshi, T.; Cui, Z.; Sa, B.; Tsutsui, Y.; Seki, S.; Suda, M. *Adv. Sci.* **2022**, 9, 2201063.

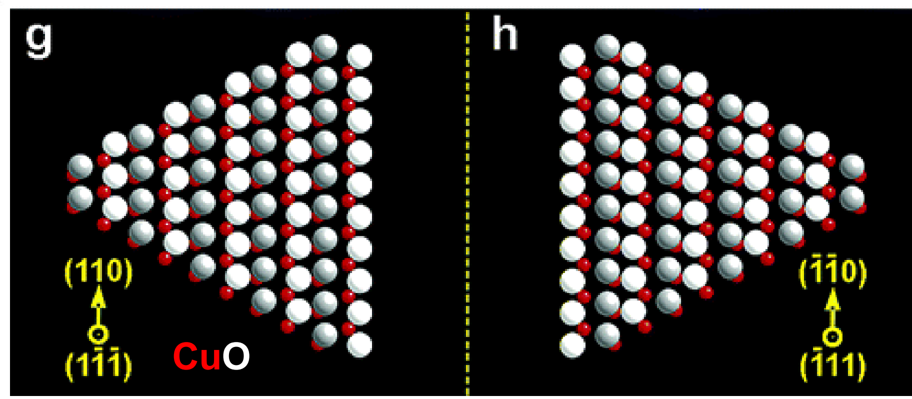
Contents

Simplest Chiral Electrode: Chiral CuO Nanocrystals



monoclinic crystal structure





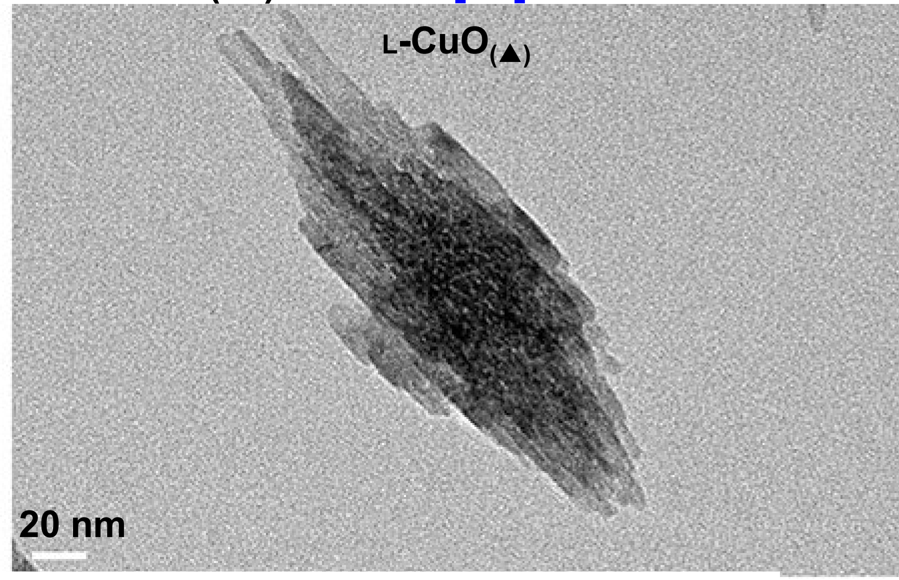
1) Ungeheuer, K.; Maraszalek, K. W.; Mitura-Nowak, M.;; Perzanowski, M.; Jelen, P.; Marszalek, M.; Sitarz, M. *Int. J. Mol. Sci.* **2022**, *23*, 4541. 2) Widmer, R.; Haug, F.-J.; Ruffieux, P.; Gröning, O.; Bielmann, M.; Gröning, P.; Fasel, R. *J. Am. Chem. Soc.* **2006**, *128*, 14103.

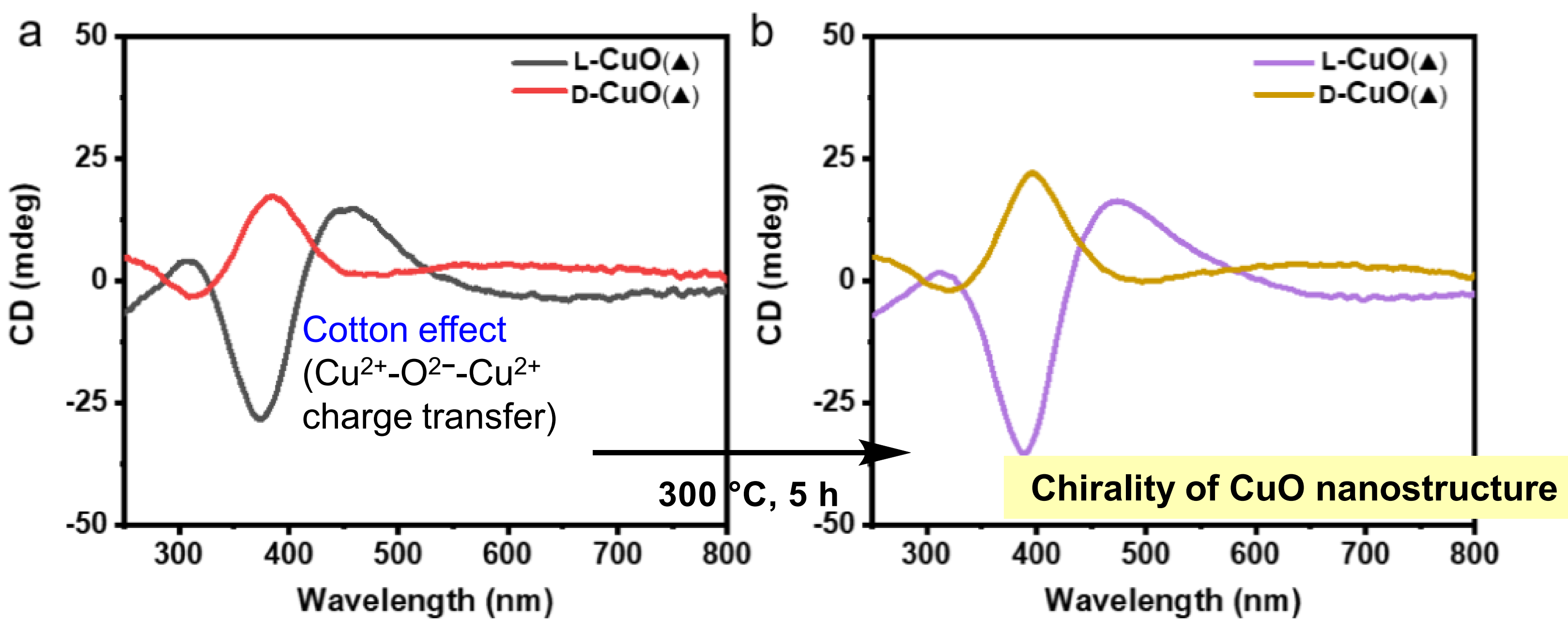
Preparation of Chiral $CuO_{(▲)}$ (CuO[12])

L/D/DL-Cysteine (0.25 eq.)
H_2O (0.02 M)
; pH 12 (by 1 M NaOH)

$CuCl_2$ ⟶ $CuO_{(▲)}$

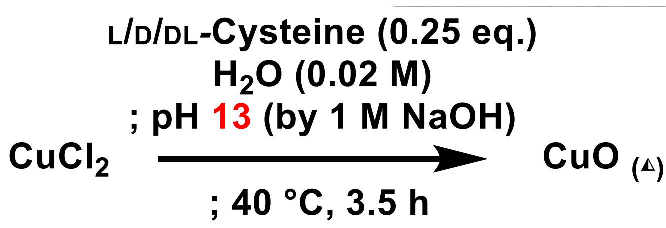
; 40 °C, 3.5 h

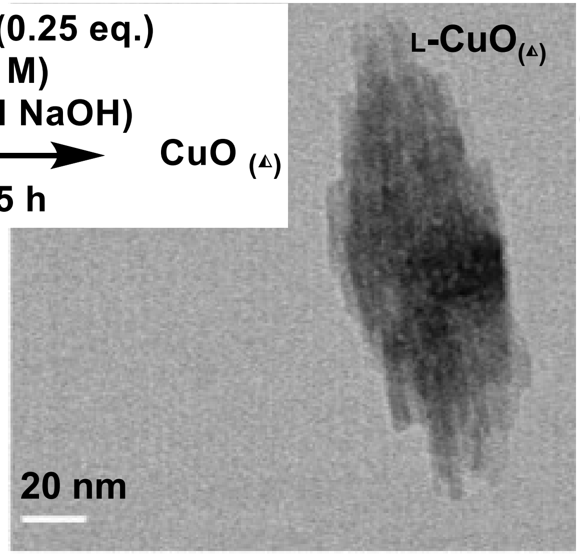


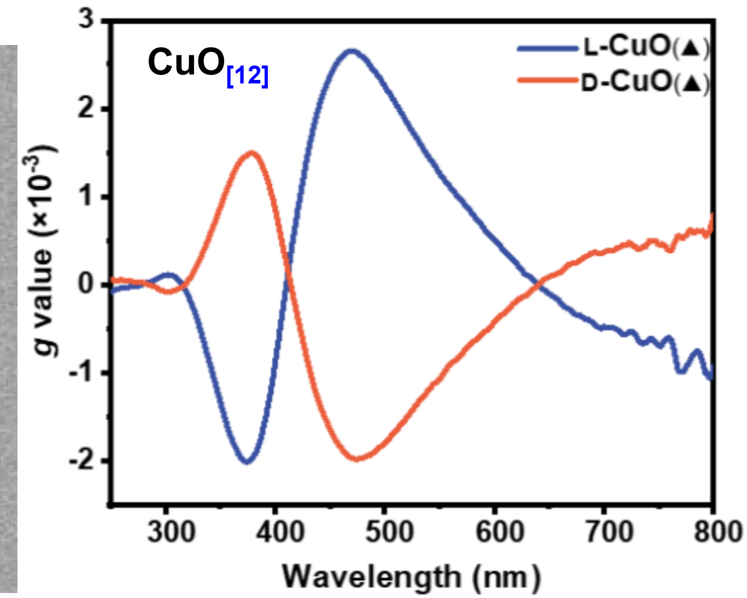


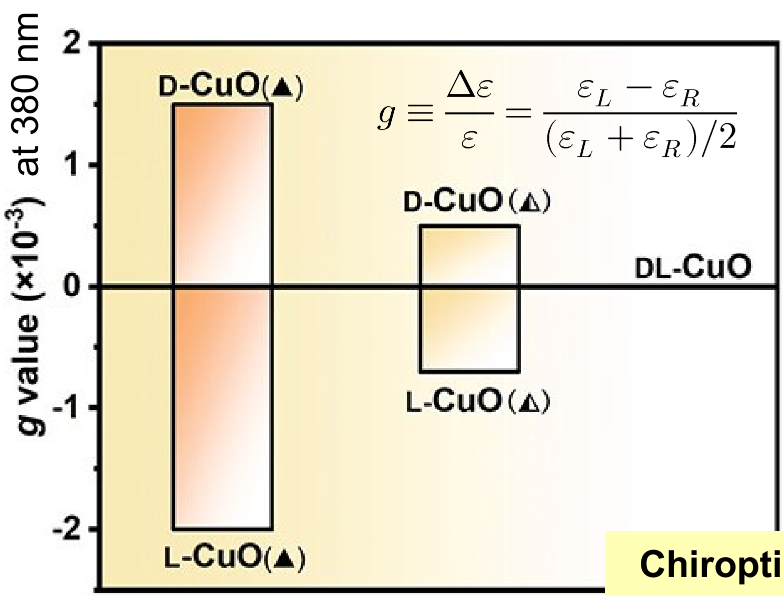
1) Jin, Y.; Fu, W.; Wen, Z.;Tan, L.; Chen, Z.; Wu, H.; Wang, P.-P. *J. Am. Chem. Soc.* **2024**, *146*, 2798.

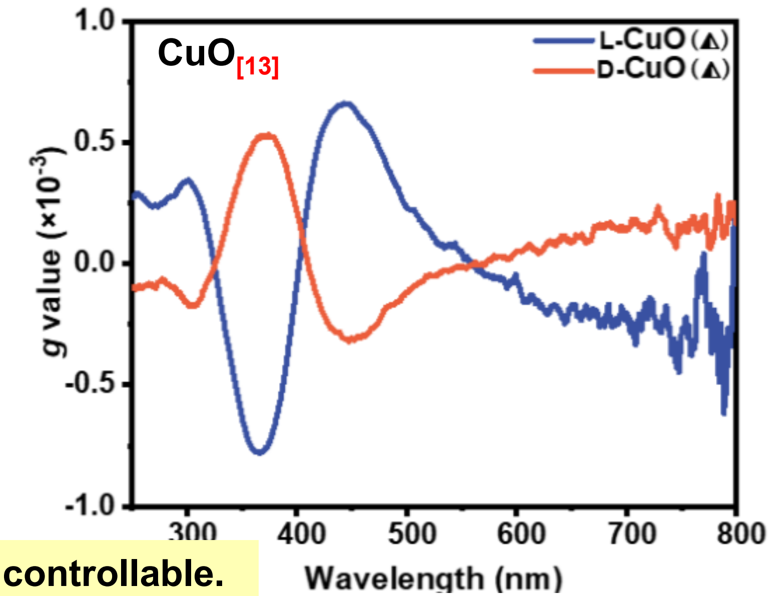
Preparation of Chiral CuO(▲) (CuO[13])







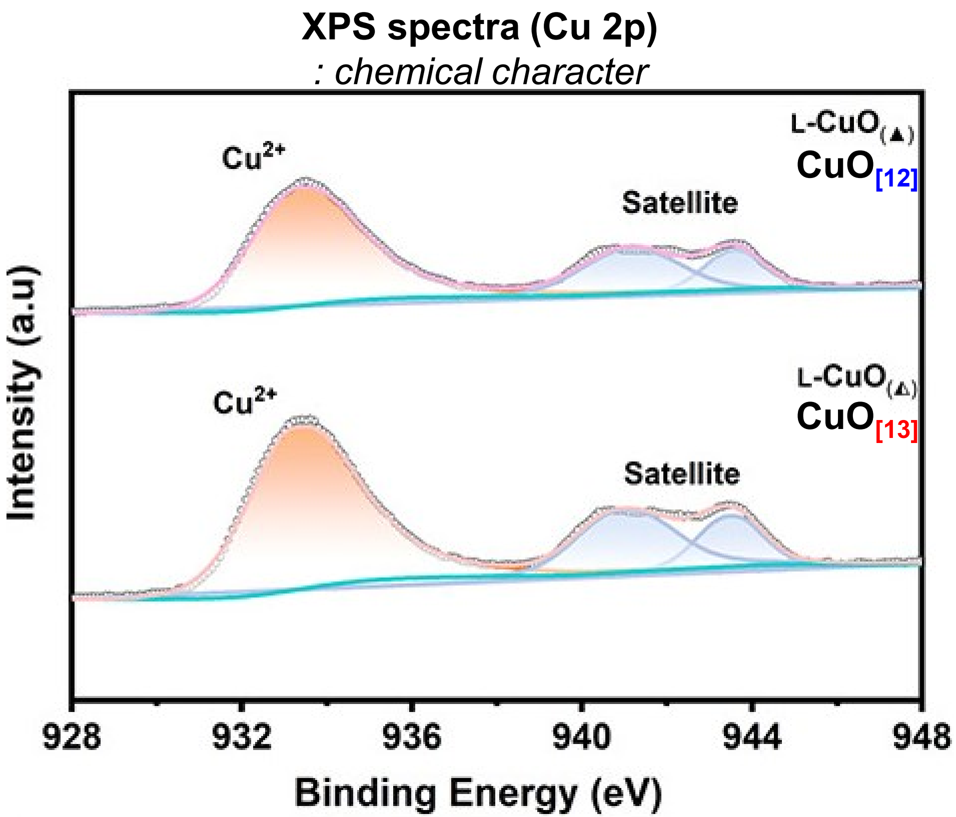


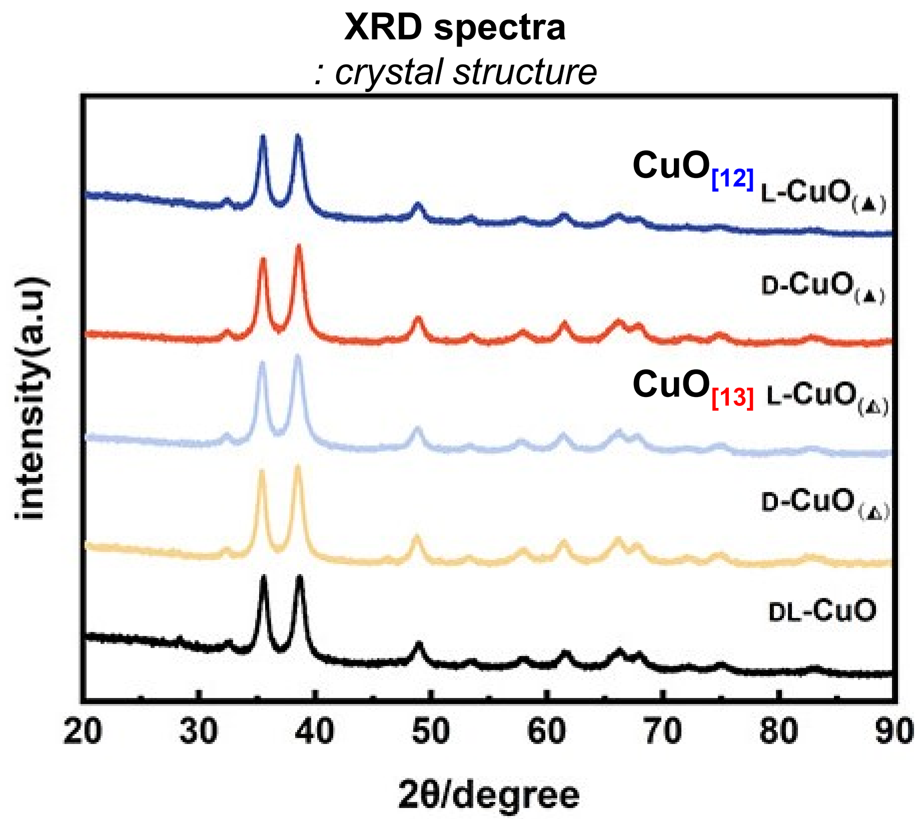


Chiroptical magnitude (*g*) is controllable.

1) Jin, Y.; Fu, W.; Wen, Z.;Tan, L.; Chen, Z.; Wu, H.; Wang, P.-P. *J. Am. Chem. Soc.* **2024**, *146*, 2798.

Material Characterization of CuOs





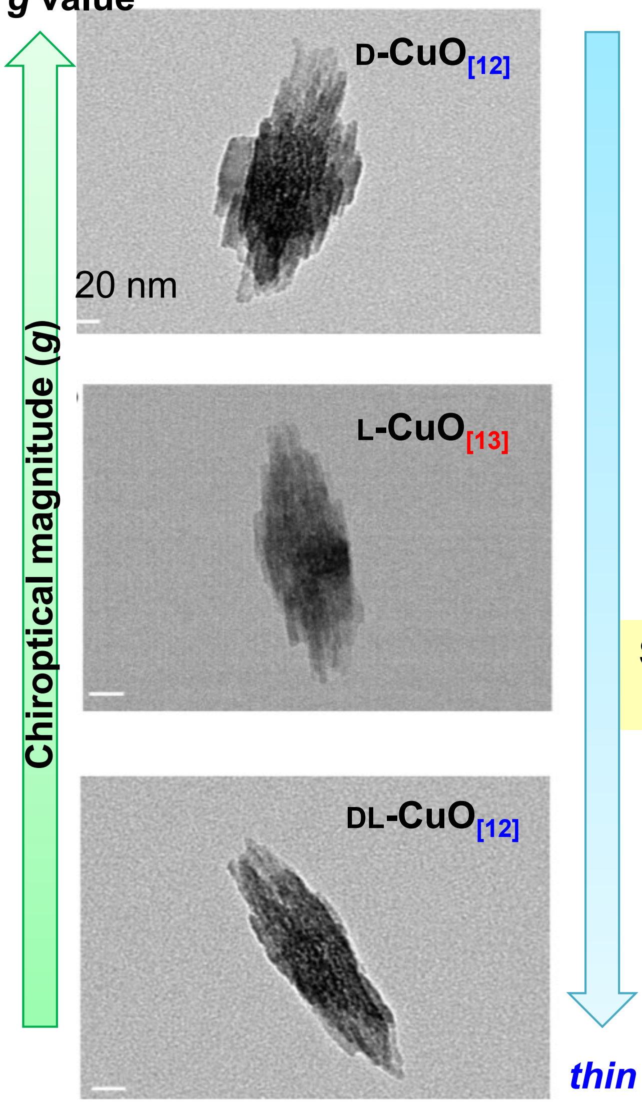
All CuOs show the same chemical/crystalline characters except for chiroptical properties.

1) Jin, Y.; Fu, W.; Wen, Z.;Tan, L.; Chen, Z.; Wu, H.; Wang, P.-P. *J. Am. Chem. Soc.* **2024**, *146*, 2798.

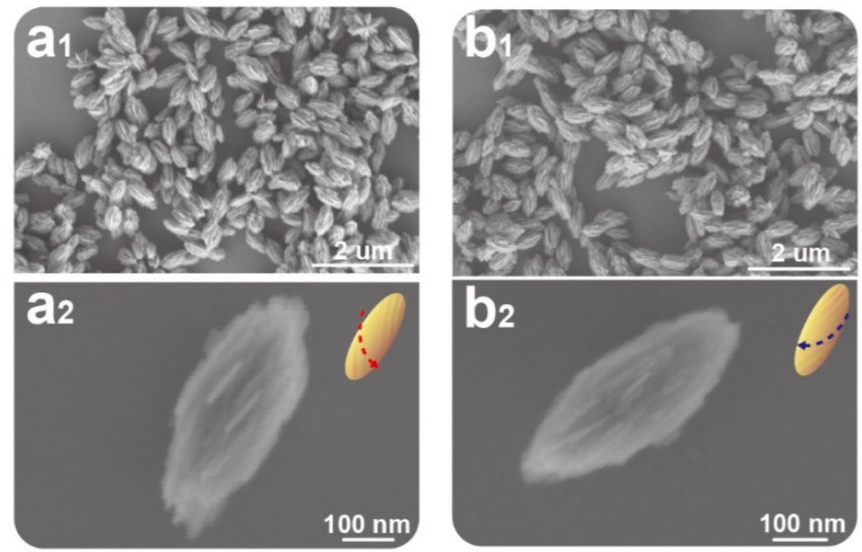
Possibility of Chiroptical Tuning (1)

Superstructure

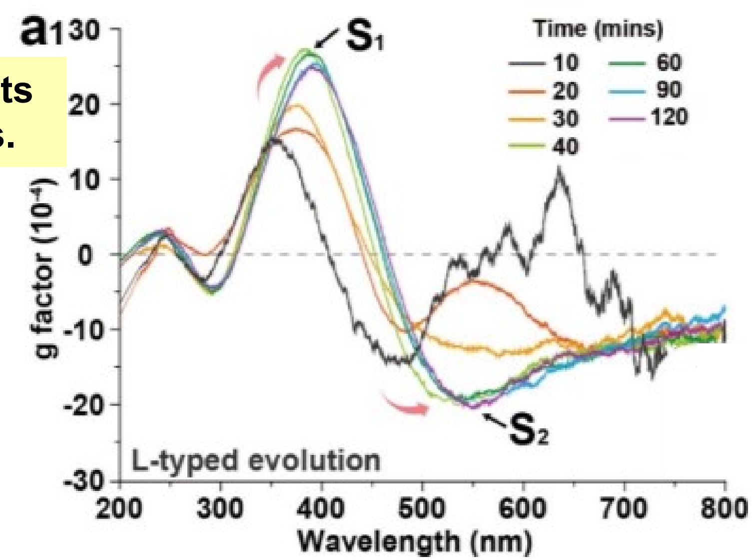
g value



chiral super structure



Super structure also affects the chiroptical properties.

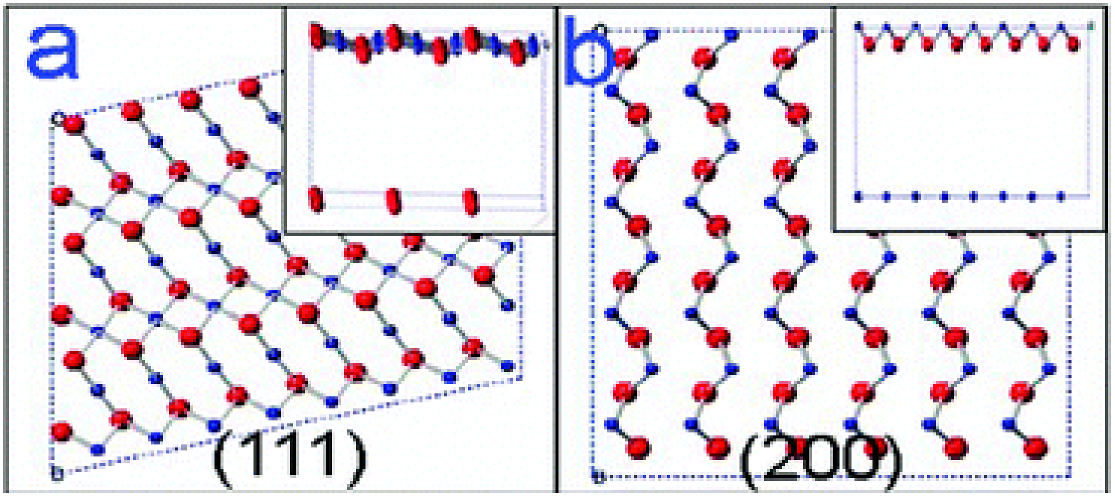


1) Jin, Y.; Fu, W.; Wen, Z.;Tan, L.; Chen, Z.; Wu, H.; Wang, P.-P. *J. Am. Chem. Soc.* **2024**, *146*, 2798.

2) Zhang, J.; Vallée, R. A. L.; Kochovski, Z,; Zhang, W.; Shen, C.; Bertram, F.; Pinna, N. *Angew. Chem., Int. Ed.* **2023**, *62*, e202305353.

Possibility of Chiroptical Tuning (2)

Assembly Direction



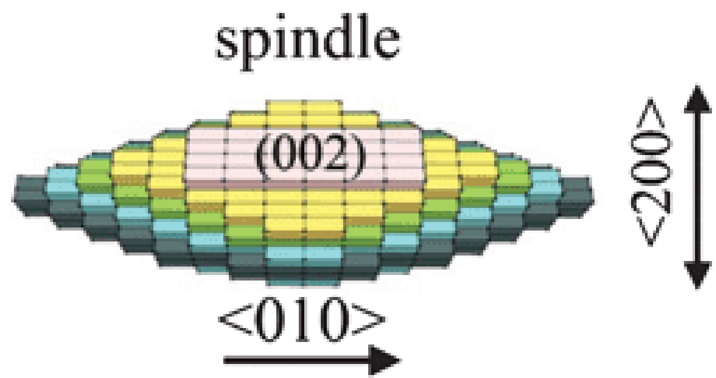
O^{2-} exposed

Cu^{2+} exposed

↓

OH^{-} will cap this face.

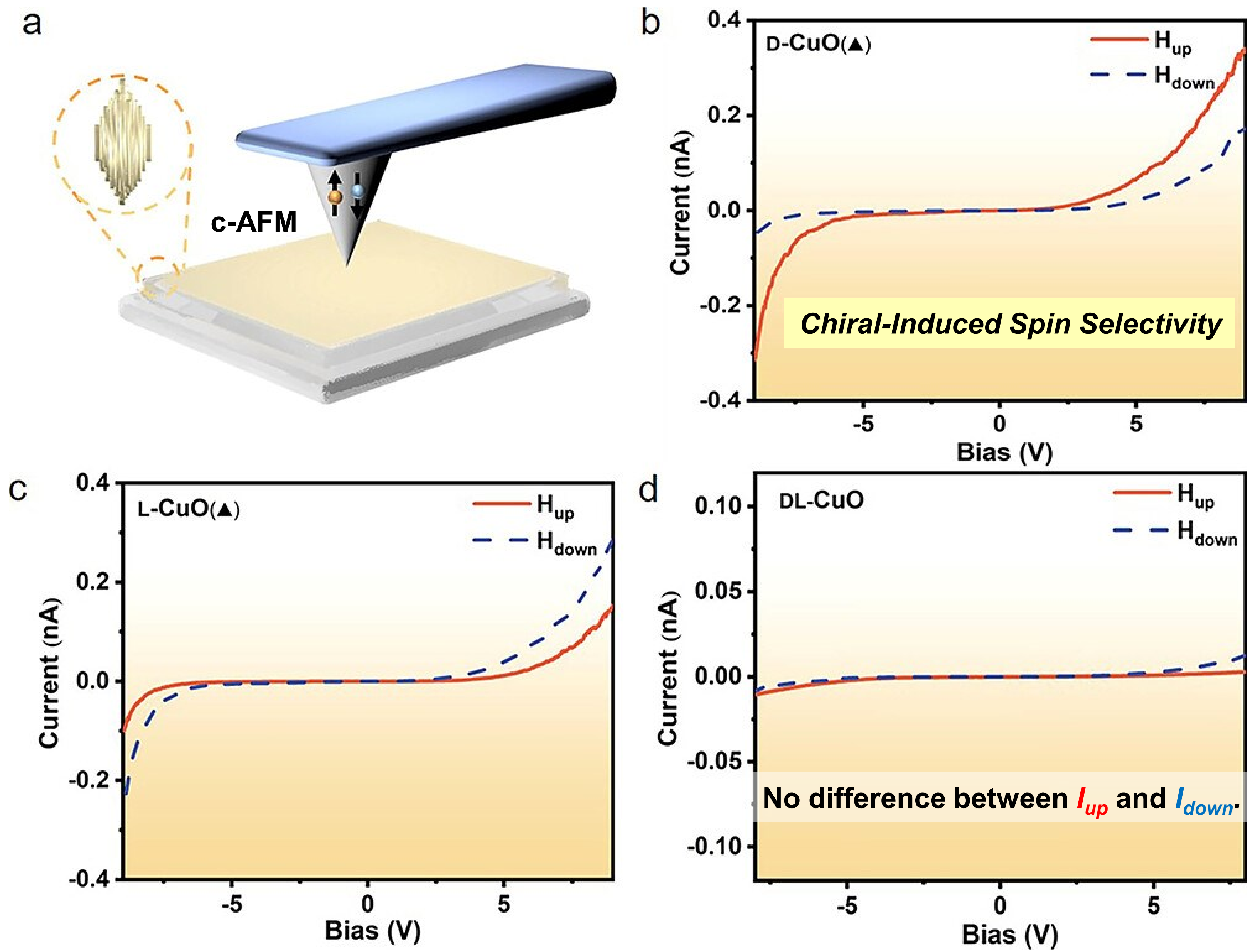
OH^{-} will control the assembly rates on some faces and the superstructure's shape.



(200) face would have a great impact on chiropticity ?

1) Fei, Z.; Lu, P.; Feng, X.; Sun, B.; Ji, W. *Catal. Sci. Technol.* **2012**, *2*, 1705.
2) Sun, S.; Zhang, X.; Zhang, J.; Wang, L.; Song, X.; Yang, Z. *CrystEngComm* **2013**, *15*, 867.
3) Zhang, Z.; Sun, H.; Shao, X.; Li, D.; Yu, H.; Han, M. *Adv. Mater.* **2005**, *17*, 42.

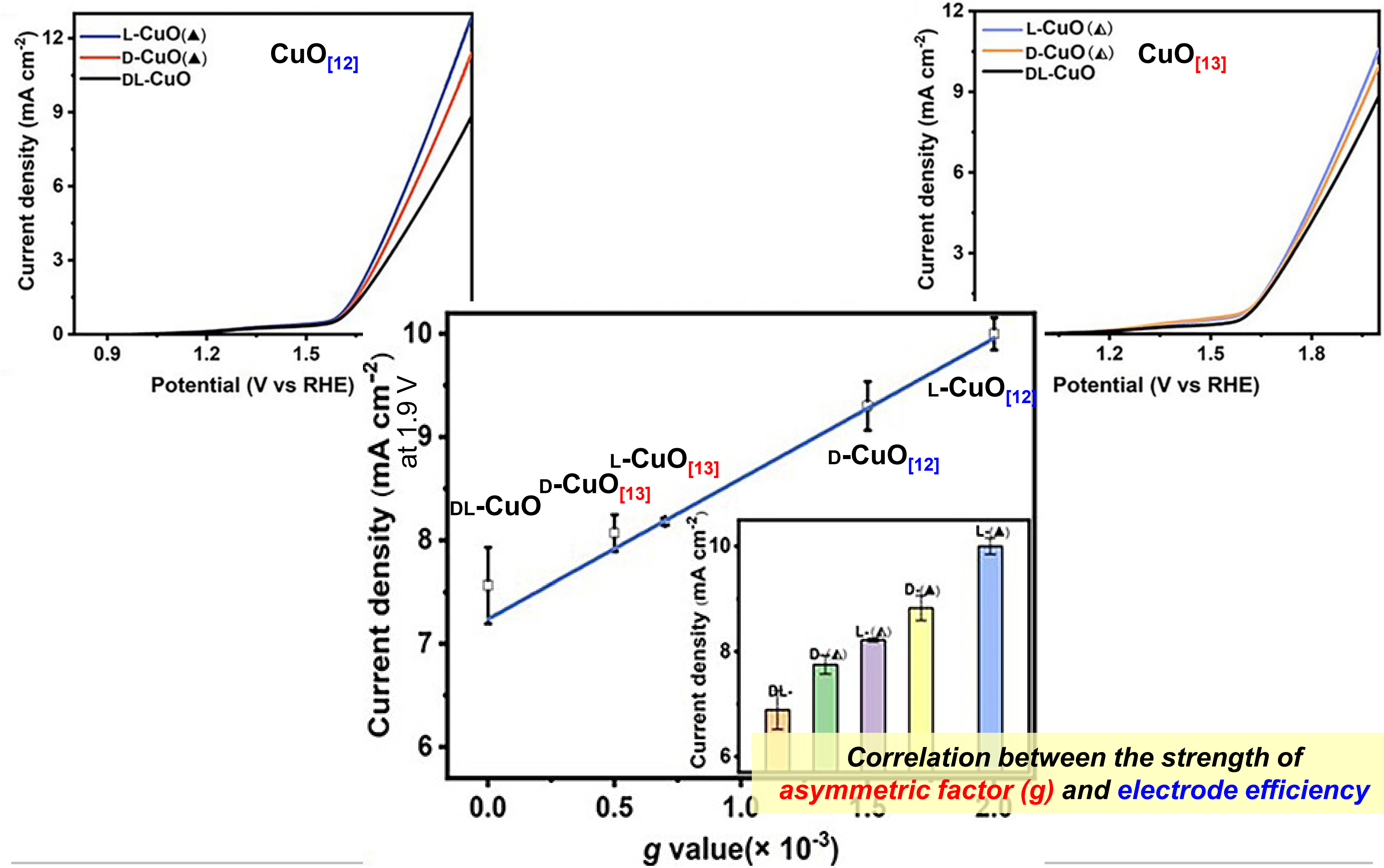
Spin Selectivity of Chiral CuO



1) Jin, Y.; Fu, W.; Wen, Z.;Tan, L.; Chen, Z.; Wu, H.; Wang, P.-P. *J. Am. Chem. Soc.* **2024**, *146*, 2798.

Water Splitting on Chiral CuO (1)

Current density (≒reaction rate) of the electrolysis of 0.1 M KOH aq.

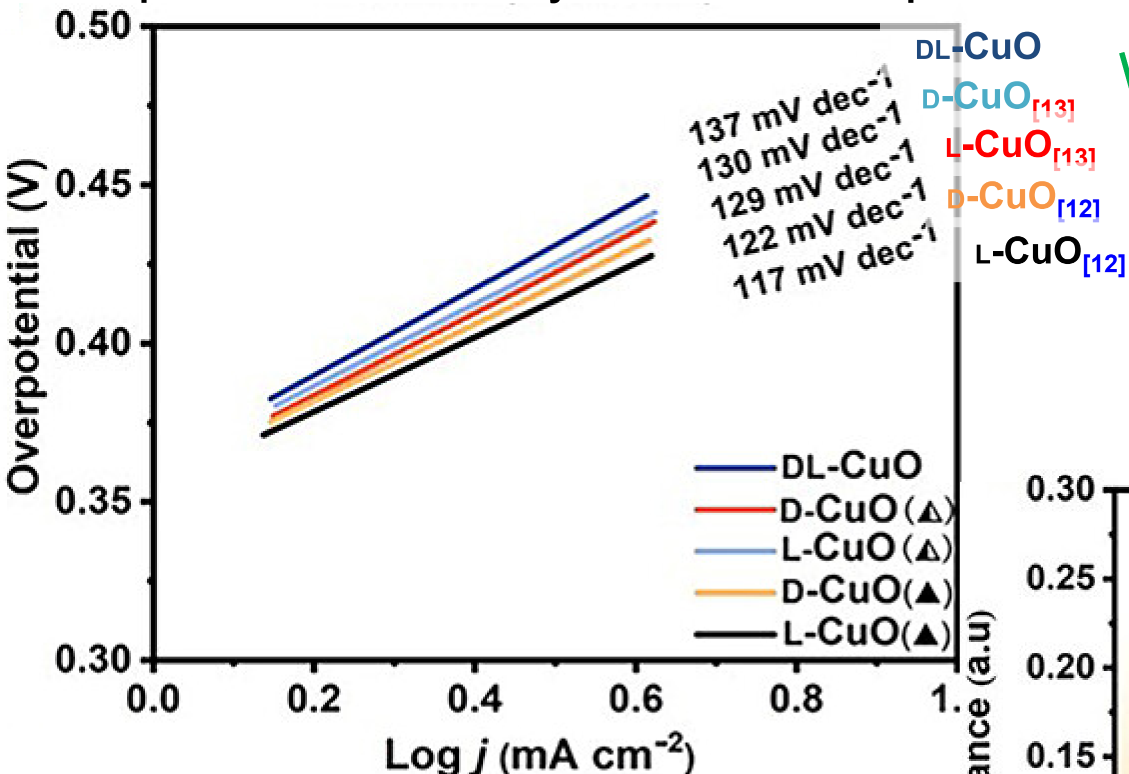


Correlation between the strength of asymmetric factor (g) and electrode efficiency

1) Jin, Y.; Fu, W.; Wen, Z.;Tan, L.; Chen, Z.; Wu, H.; Wang, P.-P. *J. Am. Chem. Soc.* **2024**, *146*, 2798.

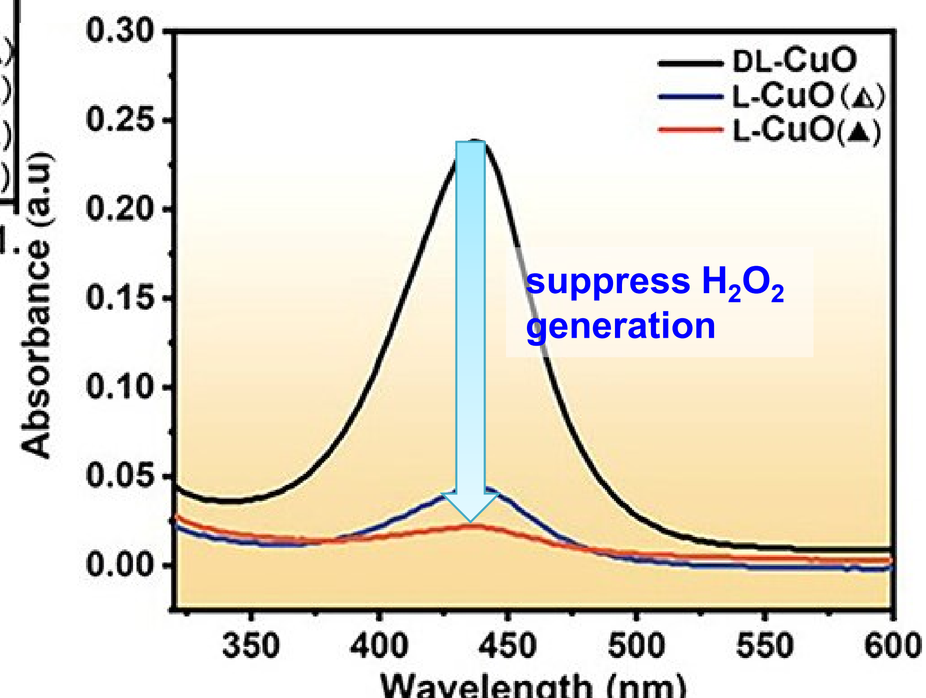
Water Splitting on Chiral CuO (2)

Overpotential of the electrolysis of 0.1 M KOH aq.



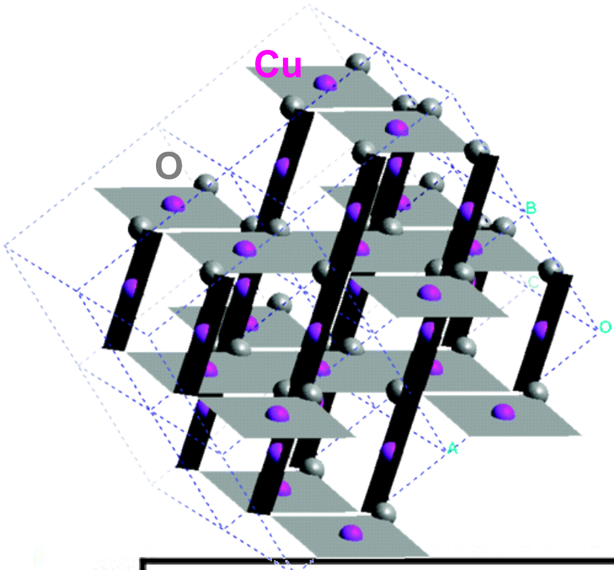
high g
low overpotential

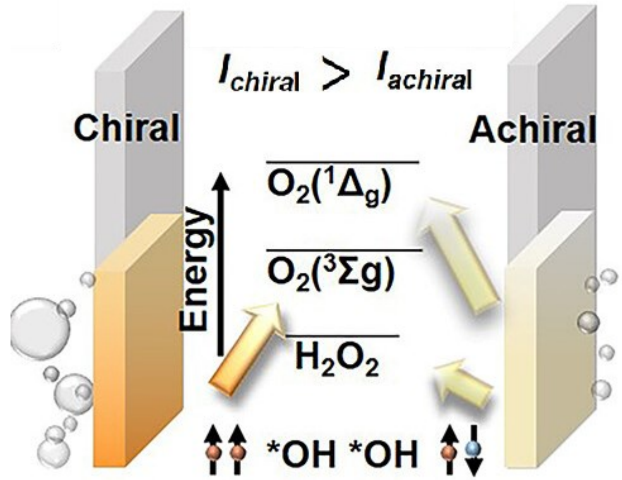
detection of H_2O_2 by *o*-tolidine after the electrolysis in 0.1 M Na_2SO_4

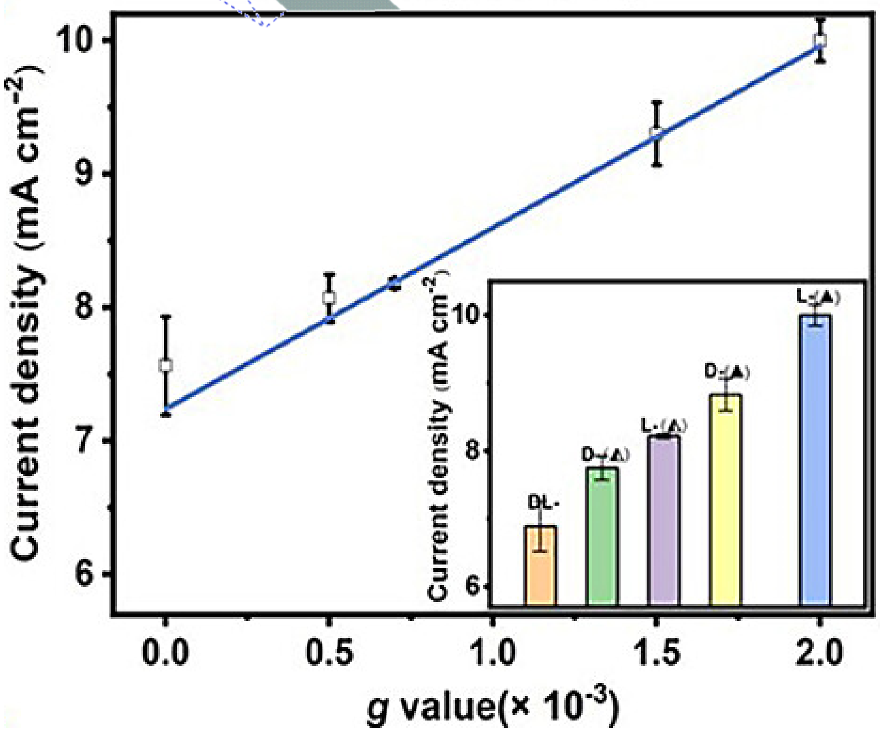


1) Jin, Y.; Fu, W.; Wen, Z.;Tan, L.; Chen, Z.; Wu, H.; Wang, P.-P. *J. Am. Chem. Soc.* **2024**, *146*, 2798.

Summary







2e⁻ reductant: $LiAlH_4$

1e⁻ reductant: SmI_2

1e⁻(β) reductant: *spin current (?)*

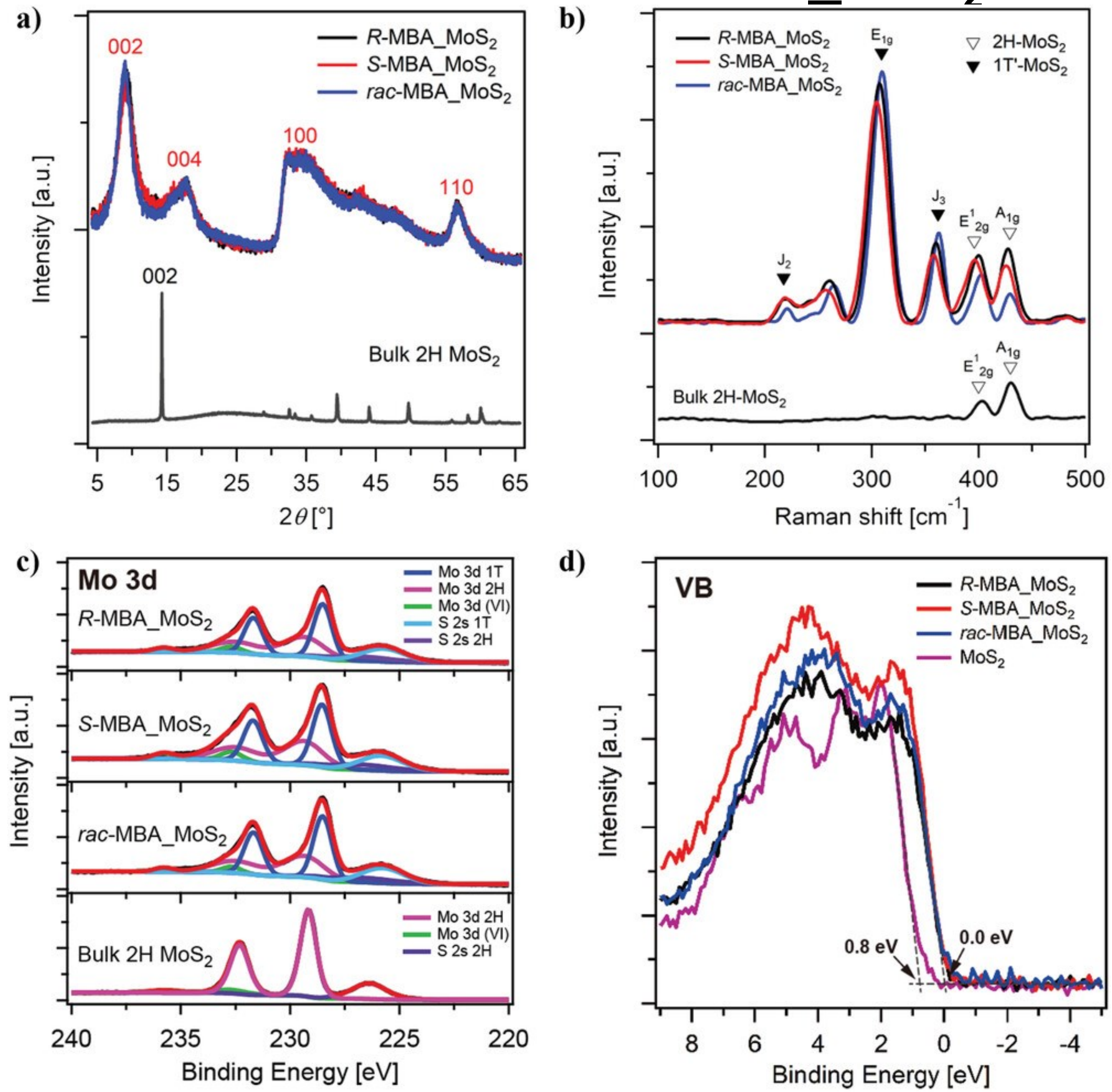
1) Jin, Y.; Fu, W.; Wen, Z.;Tan, L.; Chen, Z.; Wu, H.; Wang, P.-P. *J. Am. Chem. Soc.* **2024**, *146*, 2798.
2) Switzer, J. A. et al. *Chem. Mater.* **2004**, *16*, 4232.

Appendix

Characterization of MBA_MoS_2

XRD

Raman spectra



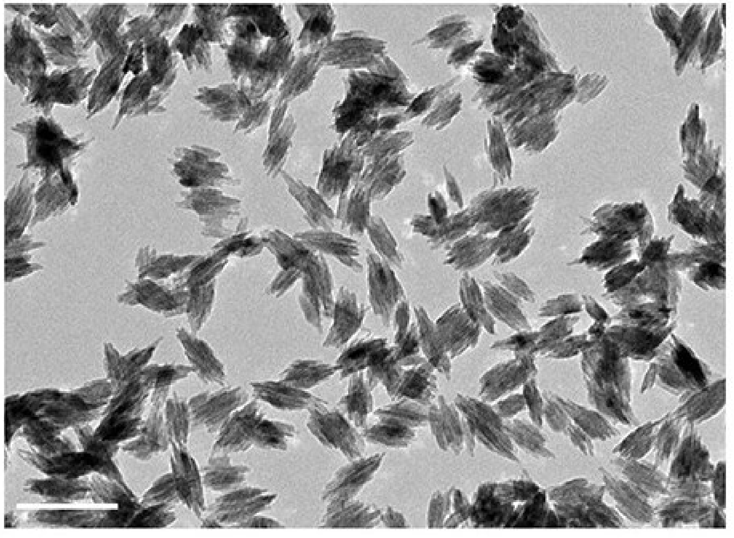
XPS

Valance band spectra

1) Bain, Z.; Kato, K.; Ogoshi, T.; Cui, Z.; Sa, B.; Tsutsui, Y.; Seki, S.; Suda, M. *Adv. Sci.* **2022**, *9*, 2201063.

TEM Image of CuO

D-CuO[13]

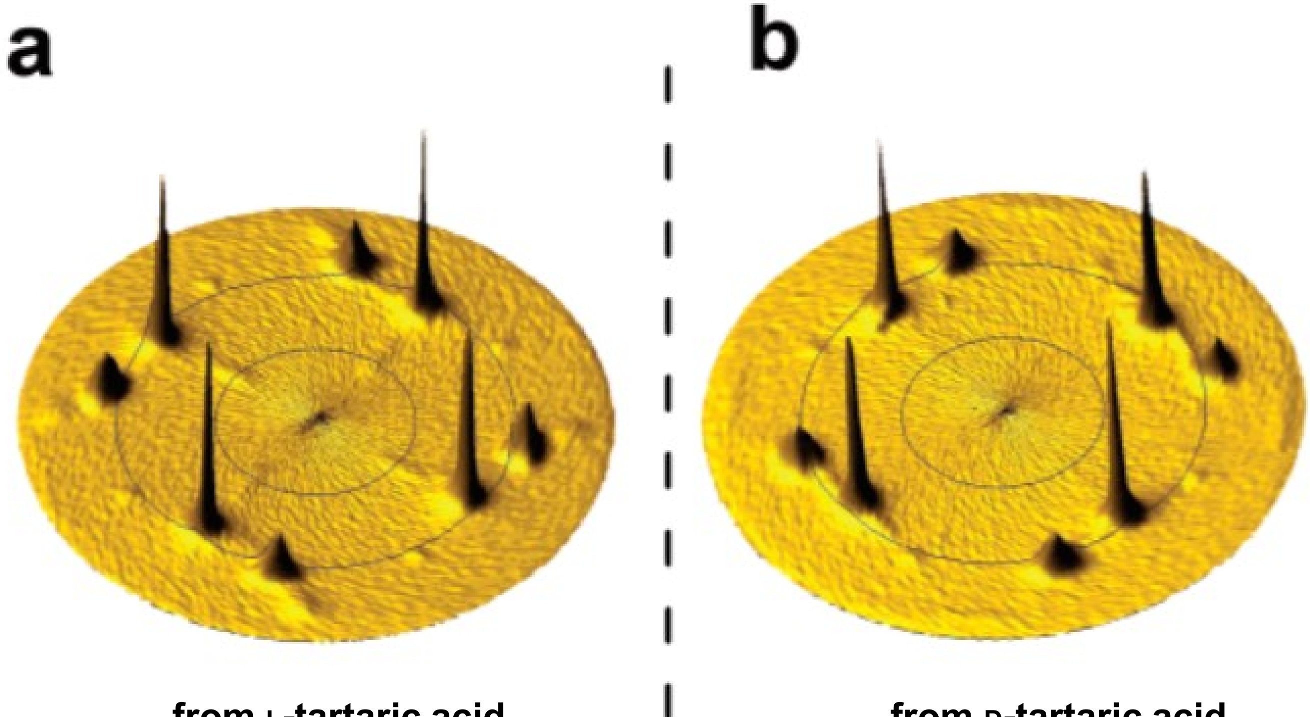


200 nm

L-CuO[12]

1) Jin, Y.; Fu, W.; Wen, Z.;Tan, L.; Chen, Z.; Wu, H.; Wang, P.-P. *J. Am. Chem. Soc.* **2024**, *146*, 2798.

Chiral CuO



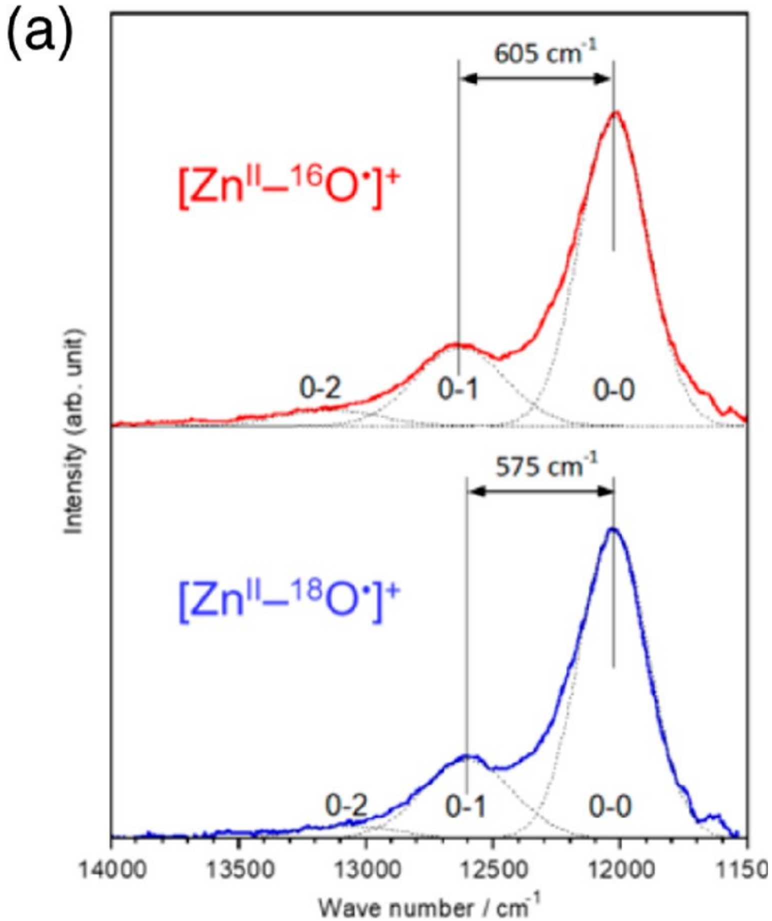
from L-tartaric acid

from D-tartaric acid

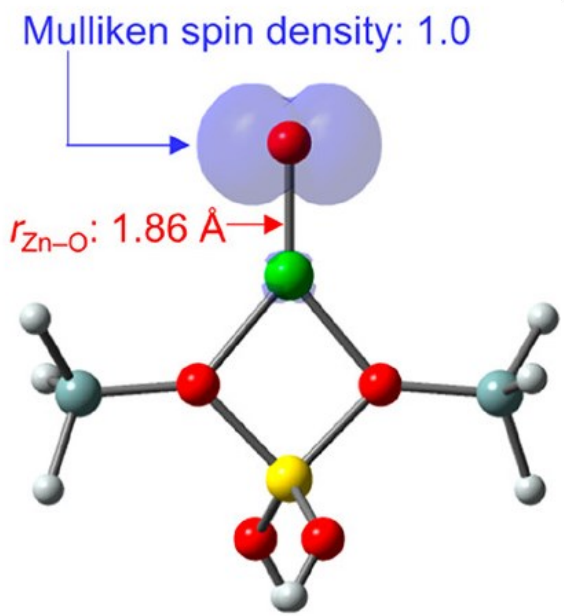
CuO(111) pole figure

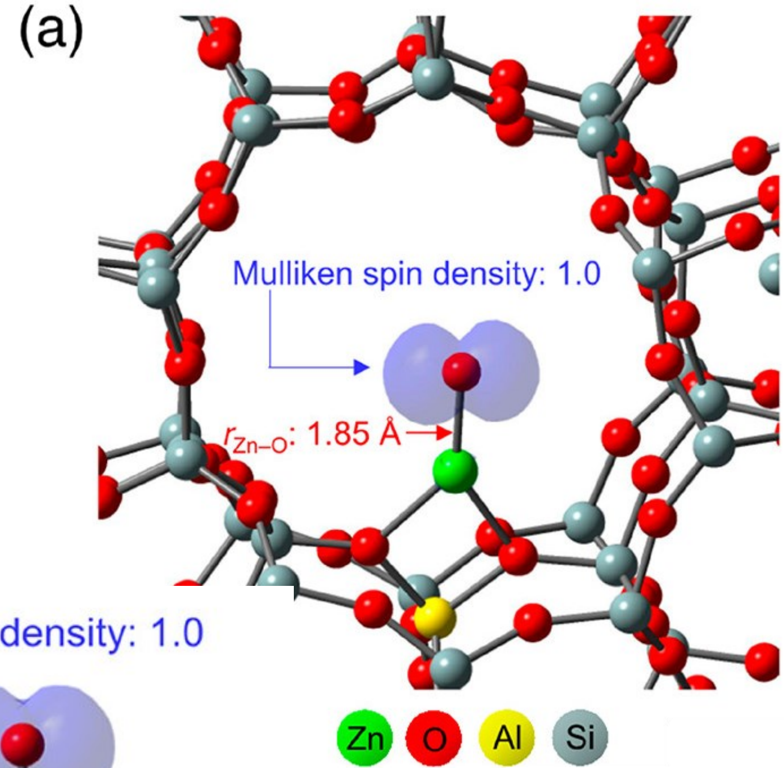
1) Kothari, H. M.; Kulp, E. A.; Boonsalee, S.; Nikiforov, M. P.; Bohannan, E. W.; Poizot, P.; Nakanishi, S.; Switzer, J. A. *Chem. Mater.* **2004**, *16*, 4232.

Example for Oxyl-complex



IR (and isotope effect) indicates Zn-O single bond.





This species can oxidize CH_4 into CH_3OH.

1) Shimoyama, Y.; Kojima, T. *Inorg. Chem.* **2019**, *58*, 9517.
2) Oda, A.; Ohkubo, T.; Yumura, T.; Kobayashi, H.; Kuroda, Y. *Inorg. Chem.* **2019**, *58*, 327.