Accelerating electron-transfer and tuning product selectivity through surficial vacancy engineering on CZTS/CdS for photoelectrochemical CO_2 reduction

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Research background

- **Photoelectrochemical (PEC) CO_2 reduction reaction:**
  - One of the most promising alternatives to address the energy crisis and global warming. [1]
  - Direct conversion of sustainable solar energy to value added chemicals.

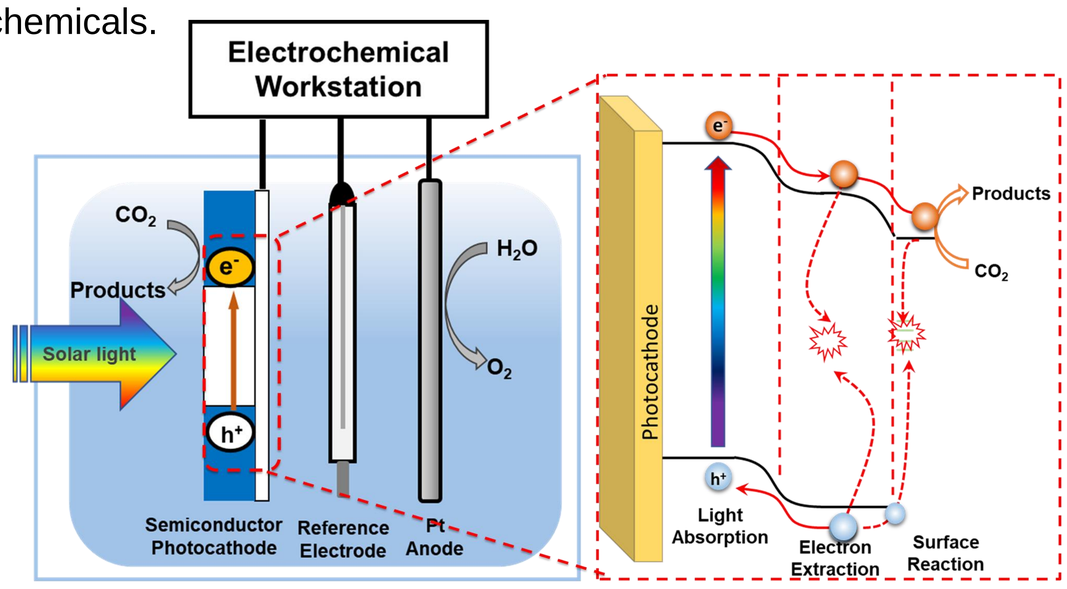


Fig.1 Schematic illustration of typical PEC CO_2 reduction device and the possible charge transfer route within the photocathode.

- **Cu_2ZnSnS_4(CZTS)-based photocathode**
  - CZTS: Well-known photovoltaic material with promising efficiency and good commercialization potential.[2]
- **Challenges of CZTS photocathode for PEC CO_2 reduction:[3]**
  - Serious charge recombination,
  - Uncontrollable CO_2 reduction selectivity and reaction pathway.

Strategy & Design

- **Heat treatment(HT) on CZTS/CdS photocathode**
  - HT in air: CZTS/CdS (HA) results in O-doped CdS
  - HT in N_2: CZTS/CdS (HN) results in CdS with S-vacancy.

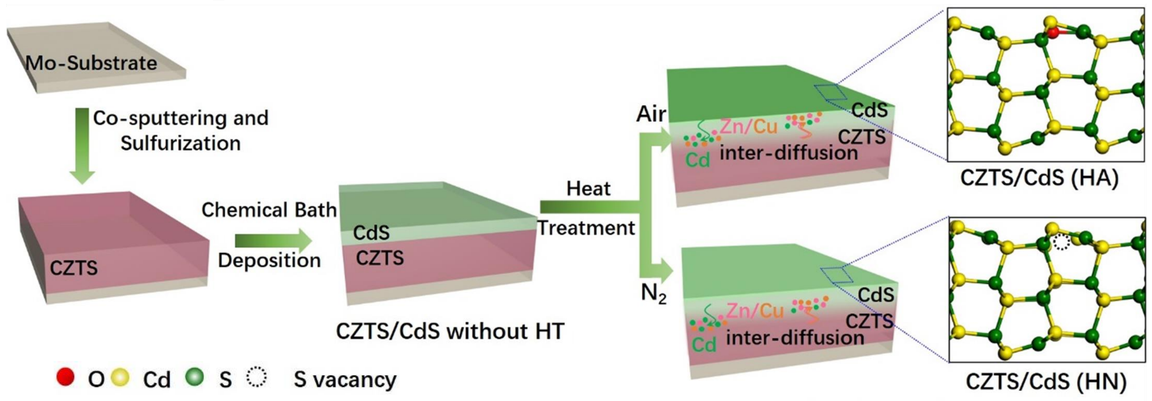
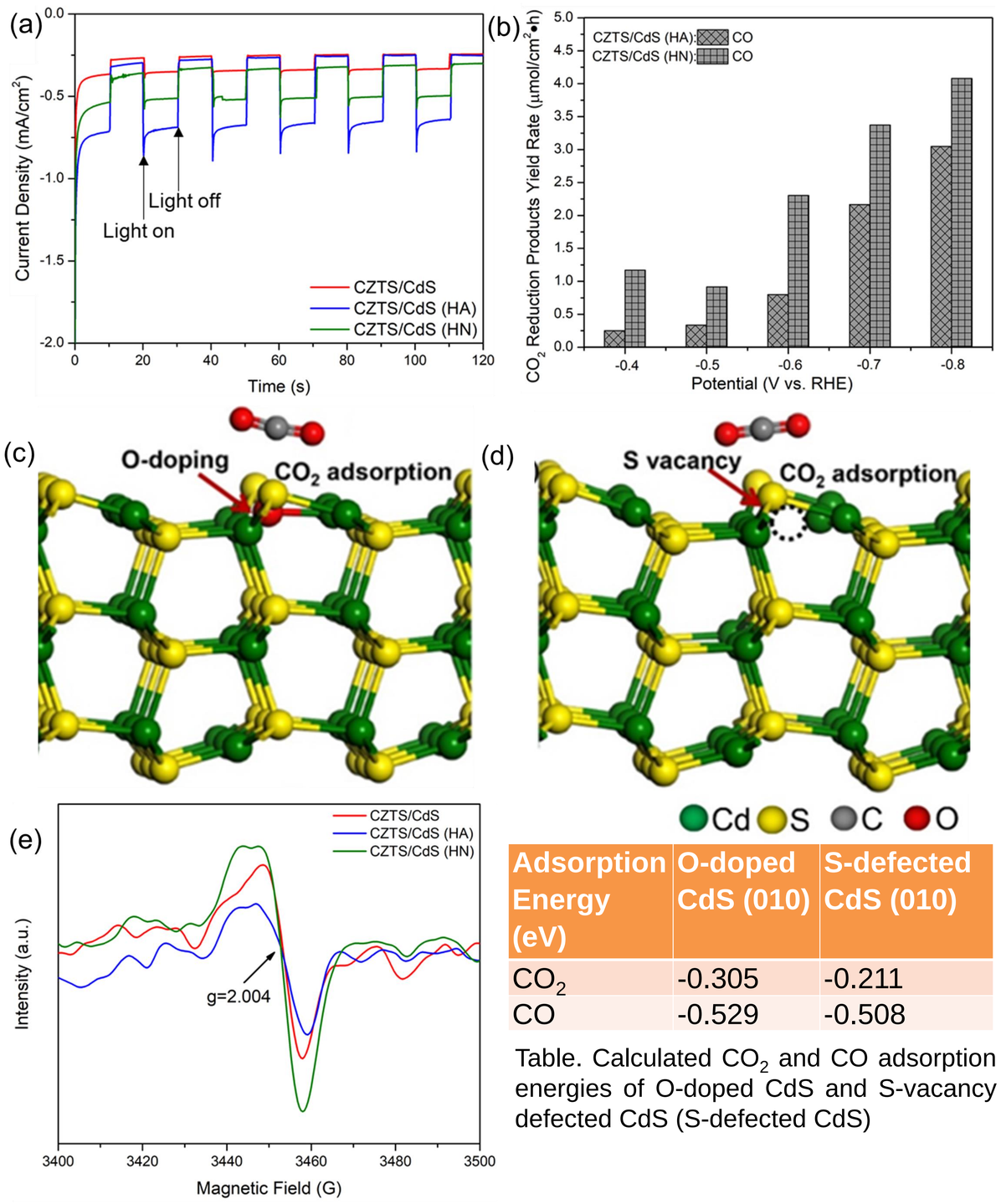


Fig.2 Schematic diagram of fabrication process of CZTS, CZTS/CdS, CZTS/CdS (HA) and CZTS/CdS (HN).

Surface defect engineering

- **Heat treatment(HT) in different atmospheres**
  - CZTS/CdS (HN) exhibits lower photocurrent density compared to CZTS/CdS (HA), but higher CO yield rate.
  - CZTS/CdS (HA) results in oxygen doped CdS, which favours the CO_2 and CO adsorption capability.
  - CZTS/CdS (HN) results in more S-vacancies, which facilitates the surficial CO desorption process.



Adsorption Energy (eV)	O-doped CdS (010)	S-defected CdS (010)
CO_2	-0.305	-0.211
CO	-0.529	-0.508

Table. Calculated CO_2 and CO adsorption energies of O-doped CdS and S-vacancy defected CdS (S-defected CdS)

Fig.4 (a-b) I-t curves of CZTS/CdS, CZTS/CdS (HA) and CZTS/CdS (HN). CO yield rates of CZTS/CdS (HA) and CZTS/CdS (HN). (c-d) DFT-optimized structures of CO_2 adsorbed on O-doped CdS and CdS with S-vacancy. (e) EPR spectra of CZTS/CdS, CZTS/CdS (HA) and CZTS/CdS (HN).

Interfacial elemental inter-diffusion

- **Inter-diffusion between Cd in CdS and Cu/Zn in CZTS**
  - More favourable band alignment with enlarged built-in potential.
  - Accelerated interfacial charge transfer after HT.

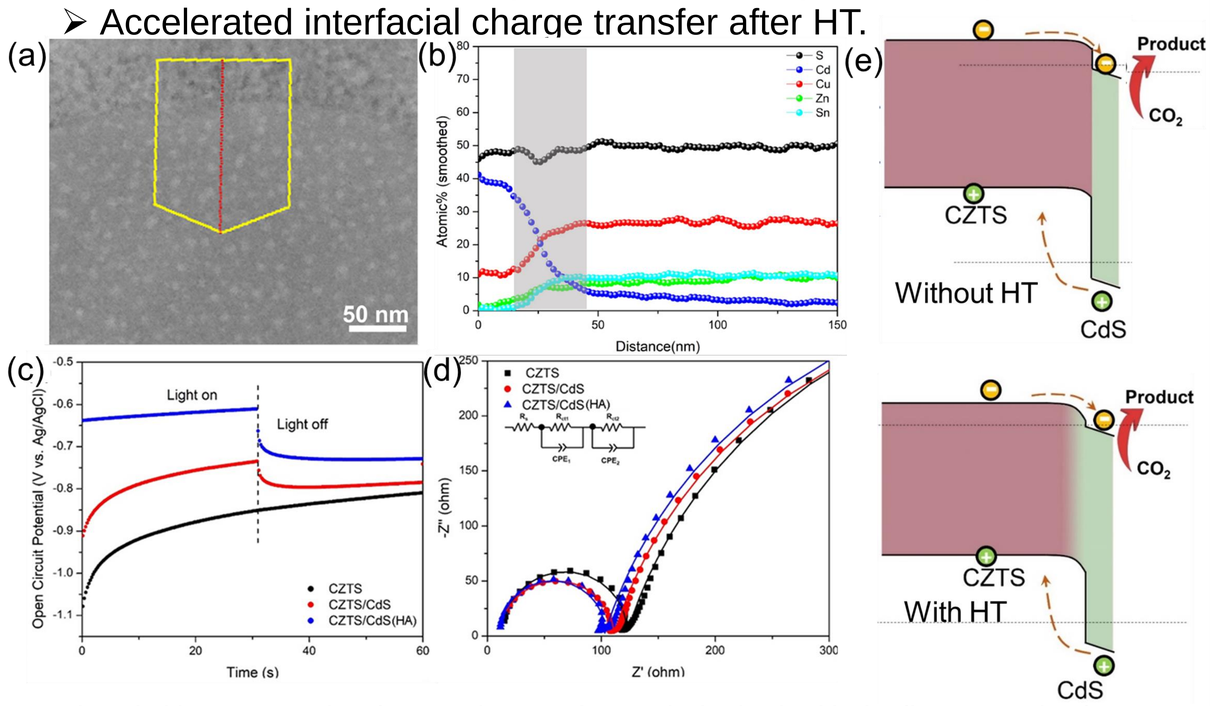


Fig.3 (a-b) Cross-sectional STEM image of CZTS/CdS (HA) with the linear atomic element distribution. (c-d) OCP and EIS curves of CZTS, CZTS/CdS and CZTS/CdS (HA). (e) Band alignment schemes of CZTS/CdS without HT and CZTS/CdS with.

Conclusion

- Elemental inter-diffusion between CdS and CZTS was observed after HT, contributing to a more favourable band alignment at the interface with enlarged built-in potential.
- HT in air, intrinsic S vacancies on CZTS/CdS surface can be replenished by oxygen (O-doping), resulting in better CO_2 and CO adsorption capability for alcohols production .
- HT in N_2, more S vacancies are generated on the surface, facilitating the surficial CO desorption process and leads to higher CO selectivity.

Reference

[1] Chang, X.; Wang, T.; Yang, P.; Zhang, G.; Gong, J. *Adv. Mater.* **2019,** 31 (31), 1804710.

[2] Yan, C.; Huang, J.; Sun, K.; Johnston, S.; Zhang, Y.; Sun, H.; Pu, A.; He, M.; Liu, F.; Eder, K. *Nat. Energy* **2018,** 3 (9), 764.

[3] Liu, L. Z.; Zhang, Y. H.; Huang, H. W. *Solar RRL* **2021,** 5 (2), 202000430.