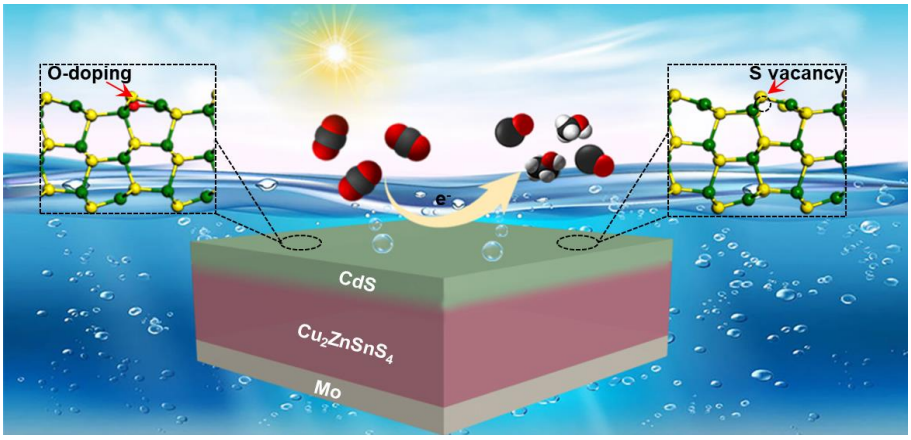
Accelerating Electron-Transfer and Tuning Product Selectivity Through Surficial Vacancy Engineering on CZTS/CdS for Photoelectrochemical CO_2 Reduction

Shujie Zhou, Xiaojing Hao, Rose Amal**

School of Chemical Engineering
University of New South Wales
Sydney, NSW, Australia
shujie.zhou@student.unsw.edu.au , xj.hao@unsw.edu.au, r.amal@unsw.edu.au

Photoelectrochemical (PEC) CO_2 reduction has attracted significant attention due to recent significant development of light harvesting semiconductors for direct solar into chemical energy conversion to address the energy crisis and global warming. Recently, copper-based chalcogenides have been considered as potential photocathode materials for PEC CO_2 reduction due to their excellent photovoltaic performance and favourable conduction band alignment with the CO_2 reduction potential.[1, 2] However, sluggish charge transfer kinetics and poor CO_2 reduction selectivity hinder their further development and optimization. Herein, a facile heat treatment (HT) of a Cu_2ZnSnS_4(CZTS)/CdS photocathode is demonstrated with enlarged photocurrent, as a result of the enhanced charge transfer and promoted band alignment originating from the elemental inter-diffusion at the CZTS/CdS interface. In addition, rationally regulated CO_2 reduction selectivity towards CO or alcohols can be obtained by tailoring the surficial sulfur vacancies by HT in different atmospheres (air and nitrogen). Sulfur vacancies replenished by O-doping (CZTS/CdS (HA)) is shown to favour CO adsorption and the C-C coupling pathway, and thereby produce methanol and ethanol, whilst the CdS surface with more S vacancies (CZTS/CdS (HN)) demonstrates promotes CO desorption capability with higher selectivity towards CO. The strategy in this work rationalizes the interface charge transfer optimization and surface vacancy engineering simultaneously, providing a new insight into PEC CO_2 reduction photocathode design.

Figure 1:



Schematic illustration of CZTS/CdS photocathode and surface modification caused by different HT condition: CZTS/CdS (HA) results in O-doped CdS while CZTS/CdS (HN) results in S-vacancy defected CdS.

References

[1] 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.
[2] Yoshida, T.; Yamaguchi, A.; Umezawa, N.; Miyauchi, M. *J. Phys. Chem. C* **2018,** 122 (38), 21695-21702.