Supporting Information

Charge Separation in Facet Engineered Chalcogenide Photocatalyst: A Selective Photocorrosion Approach**

Naixu Li,^[a] Maochang Liu,^[b] Zhaohui Zhou,^[b] Jiancheng Zhou,^{*[a]} Yueming Sun,^[a] and Liejin Guo^{*[b]}

- [a] Prof. J. Zhou, Prof. Y. Sun, N. Li
 School of Chemistry and Chemical Engineering
 Southeast University, Nanjing, Jiangsu, 211189 (P. R. China)
 E-mail: jczhou@seu.edu.cn
- [b] Prof. L. Guo, Dr. M. Liu, Dr. Z. Zhou International Research Center for Renewable Energy State Key Laboratory of Multiphase Flow Xi'an Jiaotong University, Xi'an, Shaanxi 710049 (P. R. China) E-mail: lj-guo@mail.xjtu.edu.cn



Figure S1. A) XRD pattern, and B) UV-vis spectrum of Cu_2WS_4 photocatalyst. Inset in (B) shows the photo of Cu_2WS_4 powder. XRD pattern with dominating diffraction peaks of 002 and 101, to some degree, indicate an exposure of {001} and {101} facets. The band gap of the photocatalyst was calculated to be about 2.1 eV according to the Kubelka-Munk method from the UV-vis spectrum.^[1,2]



Figure S2. A) TEM image viewed from [010] direction, and B) corresponding selected-area electron diffraction (SAED) pattern in the marked area.



Figure S3. Partial density of states (DOS) of S, W, and Cu on the (A-C) {001} and (E-F) {101} facets of *I*-Cu₂WS₄. This picture clearly shows the composition of the valence band and conduction band in Cu₂WS₄.



Figure S4. High-resolution XPS spectra of A) Pt and B) Ru of 5 wt% Pt/Cu_2WS_4 and 5 wt% Ru/Cu_2WS_4 photocatalysts. As indicated by the XPS analysis, Pt and Ru are mainly confirmed in their valence states of zero.^[1]



Figure S5. Time-coursed photocatalytic hydrogen production over Cu₂WS₄ decahedra with biggest {001} facets.



Figure S6. SEM image of recovered Pt-Cu₂WS₄ sample after the reaction shown in Figure S5.

References

[1] C. D. Wagner, Handbook of x-ray photoelectron spectroscopy: a reference book of standard data for use in x-ray photoelectron spectroscopy, Physical Electronics Division, Perkin-Elmer Corp., **1979**.

[2] II Y. Kim, S. Atherton, E. S. Brigham, T. E. Mallouk, J. Phys. Chem. 1993, 97, 11802.