Electronic Supplementary Information

A MOF-derived hierarchical CoP@$ZnIn_2S_4$ photocatalyst for visible light-driven hydrogen evolution

Boyuan Wu [a], Ning Liu [a], Lele Lu [a], Ruizhe Zhang [a], Runhao Zhang [a], Wei Shi *[ab] and Peng Cheng [ab]

[a] Department of Chemistry, Key Laboratory of Advanced Energy Materials Chemistry (MOE) and Renewable Energy Conversion and Storage Centre (RECAST), College of Chemistry, Nankai University, Tianjin 300071, China.

[b] Haihe Laboratory of Sustainable Chemical Transformations, Tianjin 300192, China

* Corresponding author. E-mail address: shiwei@nankai.edu.cn (W. Shi)

Experimental section

Materials

All chemicals were purchased from commercial sources and used without any further purification: $Co(NO_3)_2·6H_2O$ (99%, Aladdin), 2-methylimidazole (>98%, TCI), NaH_2PO_2 (99%, Macklin), $ZnCl_2$ (98%, TCI), $InCl_3·4H_2O$ (99.99% metal basis, Adamas-beta), thioacetamide (ACS, >99%, Aladdin), glycerol (99%, Aladdin), methanol and absolute ethanol (AR, Concord Technology).

Synthesis

Synthesis of ZIF-67: 0.582 g of $Co(NO_3)_2·6H_2O$ (2.0 mmol) and 0.656 g of 2-methylimidazole (8.0 mmol) were dissolved in 50 mL of methanol respectively to form two transparent solution, then the two solutions were quickly mixed under magnetic stirring. After stirring for 5 minutes, they were left to stand at room temperature for 24 hours. The purple solid was collected by centrifugation, washed with methanol for 3 times and dried at 60 °C overnight to obtain ZIF-67. The yield was 13.2 %.

Synthesis of MOF-derived CoP: 500 mg as-prepared ZIF-67 were placed in a covered crucible and calcined in a muffle furnace at 350 °C for 2 hours to experience a gentle oxidization process. Then 100 mg products and 2.0 g NaH_2PO_2 were put into two separated boats within a tube furnace, with NaH_2PO_2 placing at the upstream. The tube furnace was then heated at 300 °C for 2 hours with the ramping rate of 2 °C min^{-1} in Ar atomsphere. After cooling down to room temperature naturally, the black products were collected as CoP.

Synthesis of CoP@$ZnIn_2S_4$: $ZnIn_2S_4$ nanosheets were grown on the surface of CoP by hydrothermal method: 5 mg CoP were fully dispersed in the mixed solvent composed of 40 mL deionized water and 10 mL glycerol by magnetic stirring for 30 minutes after 5 minutes of ultrasonic treatment. Then, 132.6 mg $ZnCl_2$ (1.0 mmol), 586.5 mg $InCl_3·4H_2O$ (2.0 mmol) and 450.8 mg (6.0 mmol) thioacetamide (TAA) were added to the above dispersion. The mixture was reacted at 80 °C under magnetic stirring for 3 hours. The products were centrifuged to obtain the solids, which were washed three times with water and ethanol followed by drying at 60 °C for 12 hours, the products were labeled as CoP@$ZnIn_2S_4$-5. To prepare the CoP@$ZnIn_2S_4$-10 and CoP@$ZnIn_2S_4$-15, the addition amounts of CoP were changed to 10 mg and 15 mg with no change in other steps. In addition, pure $ZnIn_2S_4$ was synthesized without adding any CoP.

Characterizations

Powder X-ray diffraction (PXRD) patterns were obtained by a Rigaku Smartlab SE diffractometer using Cu-Kα radiation (λ= 1.54046 Å) with scan rate of 2° min^{-1}. The nitrogen adsorption-desorption isotherms were measured on a Micromeritics ASAP 2020 Plus HD88 surface area and porosity analyzer. ZEISS MERLIN COMPACT field-emission scanning electron microscope (SEM) and FEI Talos F200X G2 transmission electron microscope (TEM) were used to investigated the size and morphology of the materials. X-ray photoelectron spectroscopy (XPS) measurements were performed on Kratos Analytical Axis Ultra DLD detector using monochromated Al-Kα radiation as the excitation source. UV-vis diffuse reflectance spectra were recorded on a Shimadzu UV-2600 spectrophotometer.

Photocatalytic hydrogen evolution test

The photocatalytic hydrogen evolution experiments were conducted using Labsolar 6A system (Beijing PerfectLight Technology Co., Ltd.). A 300W Xe lamp (Microsolar300, Beijing PerfectLight Technology Co., Ltd.) with a UV-cutoff filter (λ ≥ 420 nm) is used as light source. 10 mg photocatalyst, 100 mL 10 vol% triethanolamine (TEOA) aqueous solution were added into a reaction vessel equipped with a top quartz window. Then the reactor was sealed and degassed 30 min to remove air before photocatalytic reaction. The initial pressure before starting photocatalytic reaction is ~1.0 kPa. During the reaction, the solution was continuously magnetically stirred and kept at 5 °C by a flow of cooling water. The evolved gas was analyzed by gas chromatography with a thermal conductive detector (TCD) and a 5 Å molecular sieve column using argon as the carrier gas.

Photoelectrochemical measurement

A CHI760E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd) was used to carry out photoelectrochemical measurements. Ag/AgCl served as the reference electrode and Pt plate served as the counter electrode, respectively. The electrolyte was 0.2 M Na_2SO_4 aqueous solution. The working electrodes were prepared according to the following procedure: at first, the FTO substrate was sonicated in acetone, absolute ethanol and distilled water for 30 min continuously. Then, 5 mg sample powder was dispersed in 500 μL ethanol and 50 μL Nafion solution under ultrasonication for 1 h. Finally, the as-prepared slurry was uniformly dropped onto a 1 cm×1 cm FTO and dried in air. Photocurrents of the samples were measured by using 300 W Xe lamp (Microsolar300, Beijing PerfectLight Technology Co., Ltd.) as light source with 0.5 V (versus Ag/AgCl) potential applied.[1] The electrochemical impedance spectroscopy (EIS) was performed in the frequency range from 10^5 to 10^{-1} Hz at the open-circuit voltage. Mott–Schottky plots were measured under a frequency of 1000, 2000 and 3000 Hz.

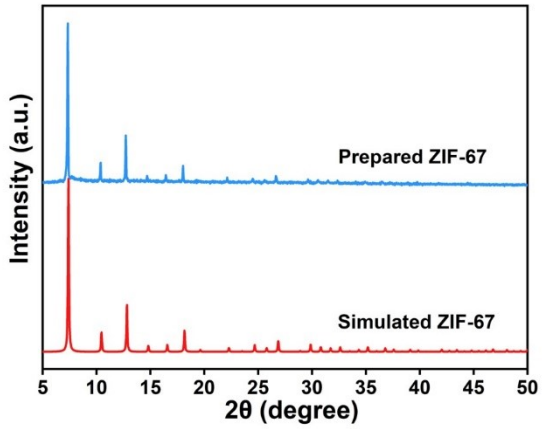

Fig. S1 PXRD patterns of prepared ZIF-67 and simulated ZIF-67.

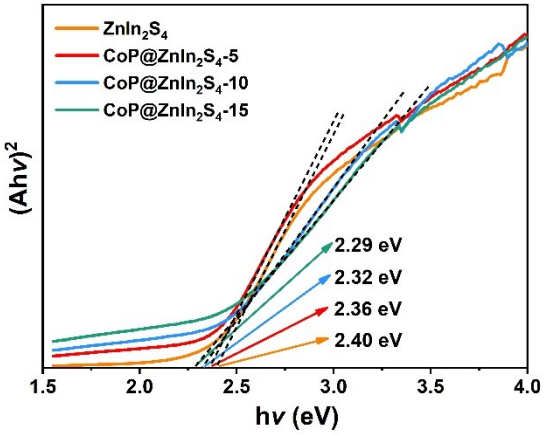

Fig. S2 Bandgap values of $ZnIn_2S_4$ and $CoP@ZnIn_2S_4$.

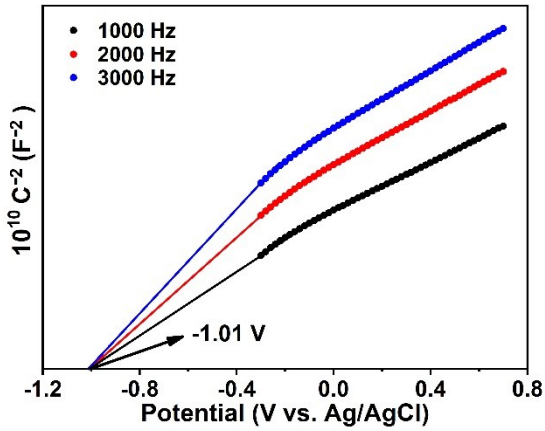

Fig. S3 Mott-Schottky plot of $ZnIn_2S_4$.

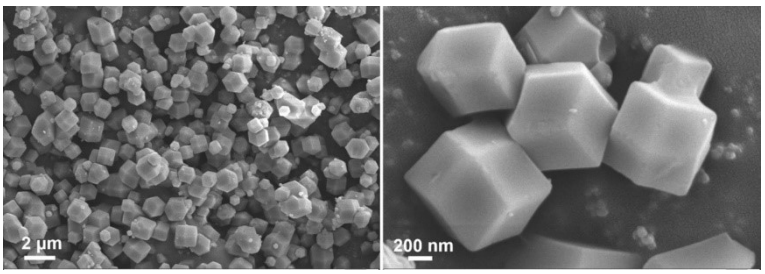

Fig. S4 SEM images of ZIF-67.

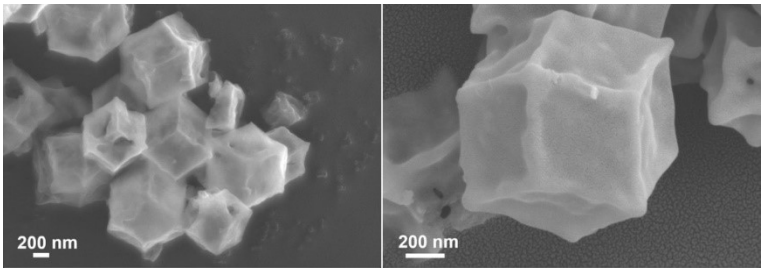

Fig. S5 SEM images of ZIF-67-derived CoP.

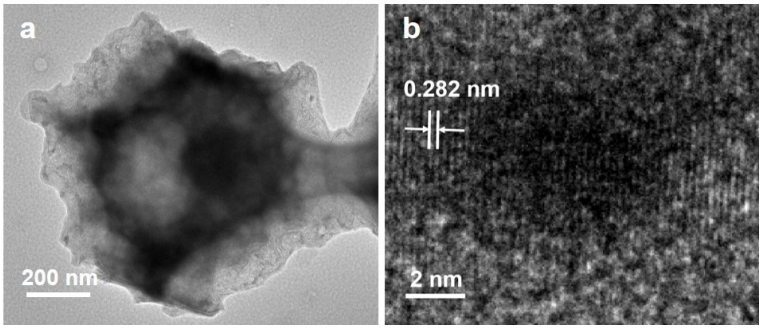

Fig. S6 (a) TEM image and (b) HRTEM image of ZIF-67-derived CoP.

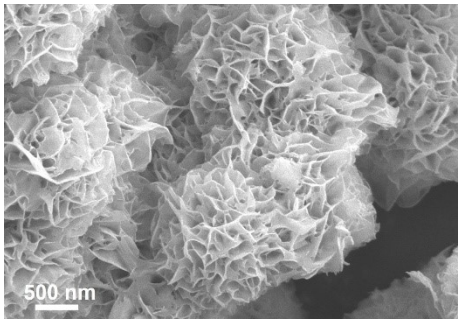

Fig. S7 SEM image of $ZnIn_2S_4$.

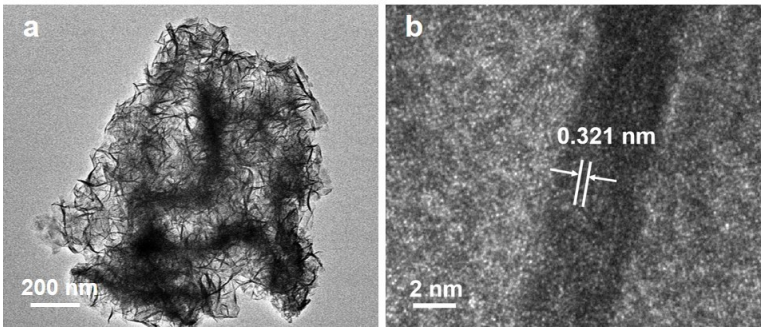

Fig. S8 (a) TEM image and (b) HRTEM image of $ZnIn_2S_4$.

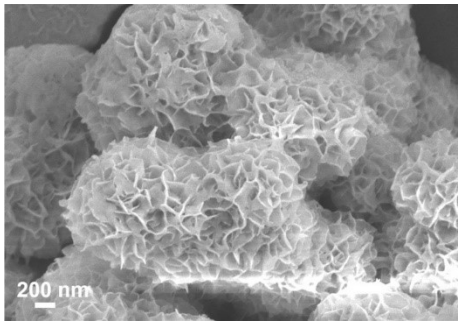

Fig. S9 SEM image of CoP@$ZnIn_2S_4$-5

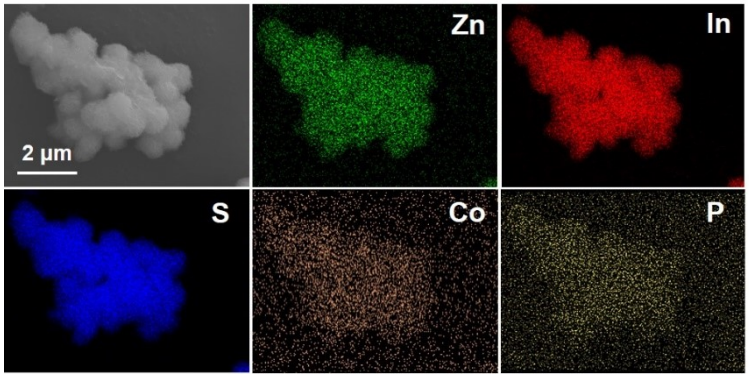

Fig. S10 SEM elemental mapping images of CoP@$ZnIn_2S_4$-5

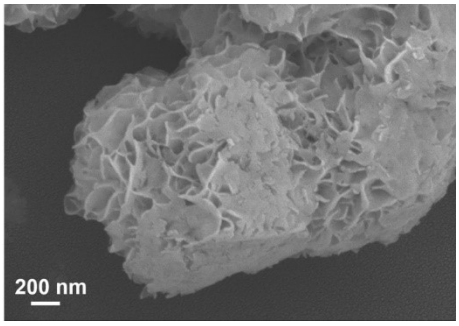

Fig. S11 SEM image of CoP@$ZnIn_2S_4$-10

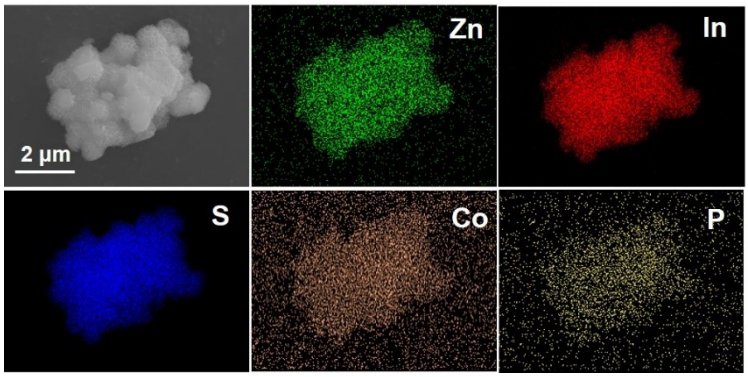

Fig. S12 SEM elemental mapping images of CoP@$ZnIn_2S_4$-10

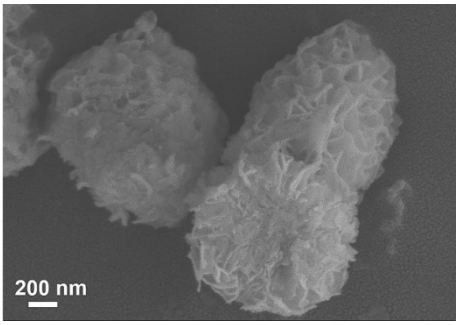

Fig. S13 SEM image of CoP@$ZnIn_2S_4$-15

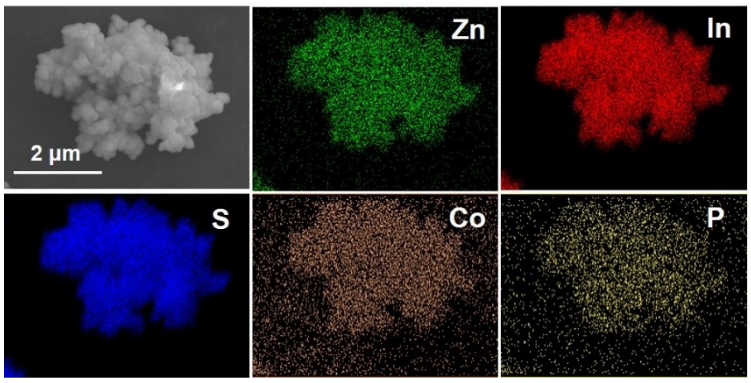

Fig. S14 SEM elemental mapping images of CoP@$ZnIn_2S_4$-15

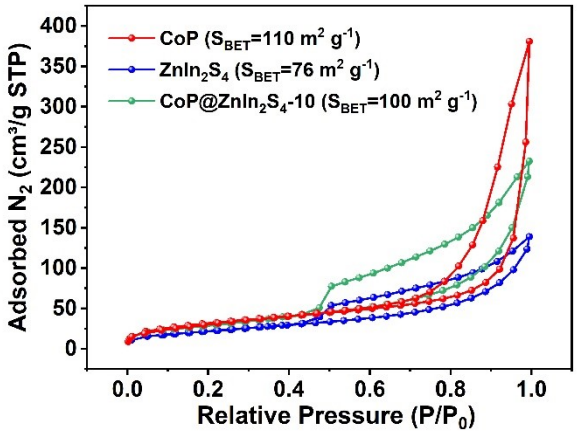

Fig. S15 N_2 adsoprtion-desorption isotherms of CoP, $ZnIn_2S_4$ and CoP@$ZnIn_2S_4$-10 (at 77 K).

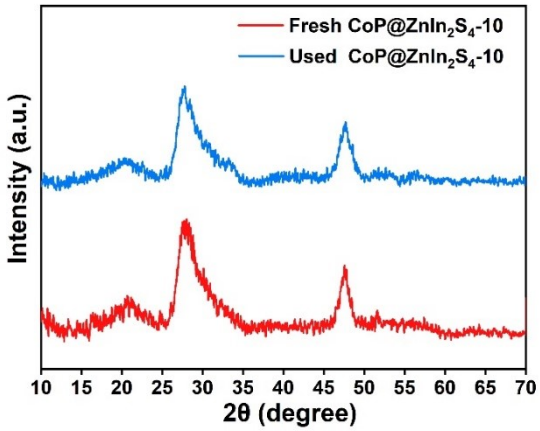

Fig. S16 PXRD patterns of fresh CoP@$ZnIn_2S_4$-10 and used CoP@$ZnIn_2S_4$-10.

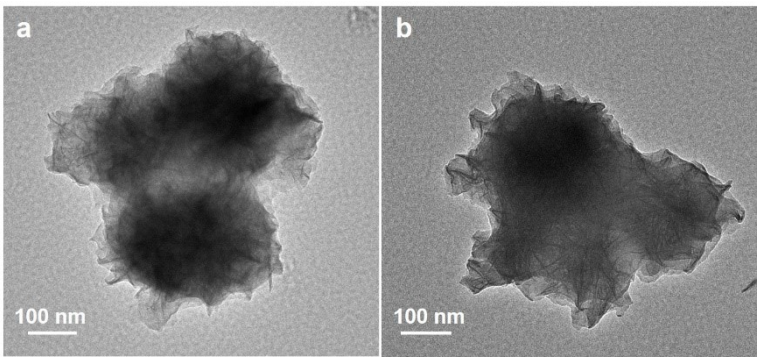

Fig. S17 TEM images of (a) fresh CoP@$ZnIn_2S_4$-10 and (b) used CoP@$ZnIn_2S_4$-10.

Table S1. Summary of some $ZnIn_2S_4$-based photocatalysts for hydrogen evolution reaction.

Photocatalyst	Sacrificial agent	Light source	Activity ($\mu mol\ h^{-1}\ g^{-1}$)	AQE	Ref.
$Au/MoS_2/ZnIn_2S_4$	Na_2SO_3 and Na_2S	150 W Xe lamp (>400 nm)	18955	—	2
$CdIn_2S_4/ZnIn_2S_4$	Na_2SO_3 and Na_2S	300 W Xe lamp (>420 nm)	12670	18.73% at 420 nm	3
$CoP@ZnIn_2S_4$	TEOA	300 W Xe lamp (>420 nm)	10310	16.3% at 420 nm	**This work**
$Co_9S_8/ZnIn_2S_4$	TEOA	300 W Xe lamp	9039	—	4
Ultrathin $MoS_2/ZnIn_2S_4$	TEOA	300 W Xe lamp (>400 nm)	8898	—	5
Protonated g-$C_3N_4/ZnIn_2S_4$	TEOA	300 W Xe lamp (>400 nm)	8601.16	0.92% at 400 nm	6
$Ni(OH)_2/ZnIn_2S_4$	TEOA	300 W Xe lamp (>400 nm)	8350	—	7
NH_2-UiO-66/$ZnIn_2S_4$	Na_2SO_3 and Na_2S	300 W Xe lamp (>420 nm)	7300	—	8
$ZnIn_2S_4/In(OH)_3$-NiS	lactic acid	300 W Xe lamp (>420 nm)	7010	14.3% at 420 nm	9
MIL-101/$ZnIn_2S_4$	lactic acid	300 W Xe lamp (>420 nm)	5800	10.93% at 420 nm	10
Ag_xAu_{1-x} alloy–$ZnIn_2S_4$	Na_2S and Na_2SO_3	300 W Xe lamp (>420 nm)	5400.7	8.06%	11
$SnSe/ZnIn_2S_4$	TEOA	300 W Xe lamp (400–800 nm)	5058	9% at 420 nm	12
$ZnIn_2S_4$/CDs	Na_2S and Na_2SO_3	300 W Xe lamp (>420 nm)	4150	—	13
$WO_3/ZnIn_2S_4$	TEOA	300 W Xe lamp (>420 nm)	3900	—	14
CoNi bimetal–$ZnIn_2S_4$	ascorbic acid	300 W Xe lamp (>420 nm)	3336	—	15
$CdS/ZnIn_2S_4$	Na_2S and Na_2SO_3	300 W Xe lamp (320–780 nm)	3072	15.9% at 420 nm	16
$WS_2/ZnIn_2S_4$ (3%)	lactic acid	300 W Xe lamp (>420 nm)	2550	3.2% at 420 nm	17
$ZnIn_2S_4@NH_2$-MIL-125(Ti)	Na_2S and Na_2SO_3	300 W Xe lamp (>420 nm)	2204.2	4.3% at 420 nm	18
$Ni_2P/ZnIn_2S_4$	lactic acid	300 W Xe lamp (>400 nm)	2066	—	19
Black phosphorus/$ZnIn_2S_4$	Na_2S and Na_2SO_3	300 W Xe lamp (>420 nm)	1278	0.25% at 450 nm	20
$Ti_3C_2@TiO_2/ZnIn_2S_4$	Na_2S and Na_2SO_3	300 W Xe lamp	1185.8	—	21

Table S2. Bi-exponential curve fitted parameters of TRPL spectra for as-prepared samples.

	A_1 (%)	τ_1 (ns)	A_2 (%)	τ_2 (ns)	τ_{ave} (ns)
$ZnIn_2S_4$	90.1	1.26	9.9	1.33	1.27
CoP@$ZnIn_2S_4$-5	87.3	1.25	12.7	5.79	3.08
CoP@$ZnIn_2S_4$-10	80.9	1.31	19.1	7.55	4.90
CoP@$ZnIn_2S_4$-15	84.2	1.27	15.8	6.24	3.65

The TRPL decay curves are fitted by bi-exponential fitting according to the following function:

$$I(t) = A_1 \cdot \exp(-t/\tau_1) + A_2 \cdot \exp(-t/\tau_2)$$

where, I is the normalized emission intensity, τ_1 and τ_2 are the lifetime values; A_1 and A_2 are corresponding constants indicating the amplitudes. Then, on the basis of the above fitting data, the average lifetime (τ_{ave}) is calculated by following: [22]

$$\tau_{\text{ave}} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2}$$

References

1. D. Gao, J. Xu, L. Wang, B. Zhu, H. Yu, J. Yu, *Adv. Mater.*, 2022, **34**, 2108475.
2. G. Swain, S. Sultana and K. Parida, *Inorg. Chem.*, 2019, **58**, 9941-9955.
3. X. Dang, M. Xie, F. Dai, J. Guo, J. Liu and X. Lu, *J. Mater. Chem. A*, 2021, **9**, 14888-14896.
4. G. Zhang, D. Chen, N. Li, Q. Xu, H. Li, J. He and J. Lu, *Angew. Chem. Int. Ed.*, 2020, **59**, 8255-8261.
5. W. Li, Z. Lin and G. Yang, *Nanoscale*, 2017, **9**, 18290-18298.
6. H. Yang, R. Cao, P. Sun, J. Yin, S. Zhang and X. Xu, *Appl. Catal. B,* 2019, **256**, 117862.
7. S. Li, D. Dai, L. Ge, Y. Gao, C. Han and N. Xiao, *Dalton Trans.*, 2017, **46**, 10620-10629.
8. C. Zhao, H. Jiang, Q. Liang, M. Zhou, Y. Zhang, Z. Li and S. Xu, *Solar Energy*, 2020, **207**, 599-608.
9. L. Ye, Z. Wen, Z. Li and H. Huang, *Solar RRL*, 2020, **4**, 2000027.
10. H. Chang, H. Wu, Y. Yang, L. Xie, W. Fan, M. Zou, G. Ma, Z. Jiang and Y. Zhang, *Int. J. Hydrogen Energy*, 2020, **45**, 30571-30582.
11. H. An, M. Li, R. Liu, Z. Gao and Z. Yin, *Chem. Eng. J.*, 2020, **382**, 122953.
12. C. Du, B. Yan and G. Yang, *Chem. Eng. J.*, 2021, **404**, 126477.
13. K. Lei, M. Kou, Z. Ma, Y. Deng, L. Ye and Y. Kong, *Colloids Surf. A*, 2019, **574**, 105-114.
14. L. Ye and Z. Wen, *Inter. J. Hydrogen Energy*, 2019, **44**, 3751-3759.
15. Z. Li, X. Wang, W. Tian, A. Meng and L. Yang, *ACS Sustainable Chem. Eng.*, 2019, **7**, 20190-20201.
16. Y. Zhu, J. Chen, L. Shao, X. Xia, Y. Liu and L. Wang, *Appl. Catal. B*, 2020, **268**, 118744.
17. M. Xiong, B. Chai, J. Yan, G. Fan and G. Song, *Appl. Surf. Sci.*, 2020, **514**, 145965.
18. H. Liu, J. Zhang and D. Ao, *Appl. Catal. B*, 2018, **221**, 433-442.
19. X.-l. Li, X.-j. Wang, J.-y. Zhu, Y.-p. Li, J. Zhao and F.-t. Li, *Chem. Eng. J.*, 2018, **353**, 15-24.
20. Q. Zhang, J. Zhang, L. Zhang, M. Cao, F. Yang and W.-L. Dai, *Appl. Surf. Sci.*, 2020, **504**, 144366.
21. K. Huang, C. Li and X. Meng, *J. Colloid Interface Sci.*, 2020, **580**, 669-680.
22. Z. Zhao, J. Wu, Y-Z. Zheng, N. Li, X. Li, X. Tao, *ACS Catal.*, 2019, 9, 8144–8152.