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Fast charge transfer kinetics in an inorganic-organic S-scheme photocatalyst for cooperative hydrogen evolution and furfuryl alcohol upgrading

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1 Materials

4,4',4"-(1,3,5-triazine-2,4,6-triyl) trianiline (Tta), 1,3,5-triformylphloroglucinol (Tp), 2,2,6,6tetramethyl-1-piperidinyloxy (TEMPO), isopropanol (IPA) and ammonium oxalate (AO) were bought from Aladdin Industrial Corporation (Shanghai, China). Zinc chloride (ZnCl₂, \geq 99%), thioacetamide (CH₃CSNH₂, \geq 99%), Indium (III) chloride tetrahydrate (InCl₃.4H₂O, \geq 99.5%), dimethyl sulfoxide (DMSO) (C₂H₆OS, \geq 99%), glycerol (C₃H₈O₃, \geq 99.5%) were bought from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used without pass purification. All chemicals were obtained from commercial sources and used directly without further purification.

2 Experimental

2.1 Synthesis of ZnIn₂S₄

The $ZnIn_2S_4$ was prepared by a hydrothermal method. 10 mL of glycerol solution was added to 30 mL of DMF solution with continuous stirring for 10 min to make the mixture homogeneous. Then, 0.136 g (1 mmol) of $ZnCl_2$, 0.586 g (1 mmol) of $InCl_3.4H_2O$ and 0.3 g of thioacetamide were slowly added to the above mixed solution, and sonication was continued for 30 min. Finally, the solution was transferred to a 100 mL PTFE-lined stainless-steel autoclave and held at 180°C for 10 h. The cooled suspension was centrifuged to room temperature to obtain the precipitate, washed several times with distilled water and ethanol, and dried under vacuum overnight at 60°C. The resulting sample was collected and recorded as $ZnIn_2S_4$ (ZIS).

2.2 Synthesis of Tp-Tta COF

1,3,5-Triformylphloroglucinol (Tp, 0.13 mmol) and 4,4',4"-(1,3,5-triazine-2,4,6-triyl) trianiline (Tta, 0.07 mmol) were added in 5 mL dimethyl sulfoxide. Then, the mixture was heated and stirred at

120°C for 48 h under Ar atmosphere. After cooling down, the suspension liquid was washed thoroughly with methanol. Then, the sample was dried at 70°C for 8 h under vacuum. The preparation process is shown in Fig. S1a.

2.3 Preparation of 2D/2D ZnIn₂S₄/Tp-Tta COF (ZT-x) composite photocatalyst

The 2D/2D ZnIn₂S₄/Tp-Tta COF composite photocatalysts were obtained by growing ZnIn₂S₄ nanosheets on the prepared Tp-Tta COF flakes by a one-step hydrothermal method. Tp-Tta COF of different mass ratios was added to 10 mL of glycerol solution and 30 mL of DMF solution, and sonicated until well dispersed, then 0.136 g (1 mmol) ZnCl₂, 0.586 g (1 mmol) InCl₃.4H₂O and 0.3 g thioacetamide were added and stirred vigorously for 1 h. Finally, the solution was transferred to a 100 mL PTFE-lined stainless-steel autoclave and held at 180°C for 10 h. ZnIn₂S₄/Tp-Tta COF nanopowders were obtained by centrifuging the suspensions to obtain the precipitates with methanol and dried overnight at 60°C under vacuum. ZnIn₂S₄/Tp-Tta COF composites with different Tp-Tta COF mass ratios were labeled as ZT-3 (3 wt.%), ZT-5 (5 wt.%) and ZT-8 (8 wt.%).

3 Characterization techniques

The synthesized samples were tested by Powder X-ray diffraction (PXRD) with D/MAX-2550 (Rigaku) diffraction gauge with Cu K α radiation. The scanning rate is 5° min⁻¹. The crystal structure of a single sample and composite were studied.X-ray photoelectron spectroscopy (XPS) spectra were performed on a PHI ESCA-5000C (Perkin Elmer) system. ISI XPS (AXIS Supra) was carried out to test the charges transfer pathway on the photocatalyst. The test conditions were monochrome A1 Ka (hv = 1486.6 eV) with a power of 150 W and a 400 μ m beam spot. Finally, the test results were corrected by taking C1s as 284.8 eV. The morphological characteristics of the composite sample were

observed by JXA-840A (JEOL) field emission scanning electron microscopy (FE-SEM), (TEM, JEOL JEM-2100) high-resolution transmission electron microscope (HR-TEM), along with energy dispersive X-ray spectroscopy (EDX) element mapping data. Atomic force microscopy (AFM, Bruker, Dimension FastScan) together experiments were carried out using a multimode. Scanner type: threeaxis separated full closed-loop flatbed scanner. Scanner noise: xy-axis closed-loop noise 0.6 nm, nonlinearity less than 0.5%, z-axis closed-loop height noise less than 0.06 nm, non-linearity less than 2%. In order to investigate the light absorption ability of the samples, UV-visible diffuse reflectance absorbance tests were performed on the samples. The equipment used was an ultraviolet-visible photometer (UV-2600) from Shimadzu, Japan. The test conditions were: the substrate barium sulfate (BaSO₄), and the test wavelength range was 200-1400 nm. Time-resolved photoluminescence (TR-PL) decay spectra of the samples were recorded using an Edinburgh HORIBA SCIENTIFIC Fluorescence Lifetime System (DeltaPro) spectrophotometer of the ZnIn₂S₄, Tp-Tta COF and ZnIn₂S₄/Tp-Tta COF. The hydrophilicity of the catalysts was investigated using a contact angle meter (DSA100, KRUSS, Germany) by dropping water droplets or Furfuryl alcohol solution (15.0 µL) on the surface of the samples. Electron spin resonance (ESR) measurements were performed using a Bruker A300 instrument with 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as the radical trapping agent. For data recording, visible light (420-780 nm) was used as the light source. A BRUKE Tensor-27 spectrometer was used for obtaining the Fourier transformation infrared (FTIR) spectroscopy, with a resolution of 4 cm⁻¹. In order to investigate the specific surface area and pore size distribution of the samples, the samples were tested for specific surface area (BET) using a fully automated specific surface and pore size distribution analyzer (Mac 2460). Prior to gas adsorption treatment samples were degassed at 200°C for 12 h under vacuum. A surface photovoltage spectrometer (PL-SPS/IPCE1000)

was used to measure the steady-state surface photovoltage (SS-SPV) spectrum. Transient surface photovoltage (TS-SPV) response measurements were performed using a system equipped with a third harmonic Nd: YAG laser (Polaris II, New Wave Research, Inc.) and a 500 MHz digital fluorescence oscilloscope (TDS 5054, Tektronix).

4. (Photo)electrochemical tests

The electrochemical workstation (CHI-660E, China, Shanghai) of the standard three-electrode is used, wherein the Photocurrent density curve (i-t), electrochemical impedance spectroscopy (EIS) and Mott Schottky diagrams are obtained, wherein the Pt, Ag/AgCl and catalysts are respectively used as a reference electrode, Count electrodes and operating electrodes. 0.5 mol L⁻¹ Na₂SO₄ solution as supporting electrolyte. The specific steps of the working electrode of the photoelectric test sample are as follows: mix 250 μ L of ethanol, 250 μ L of ethylene glycol and 40 μ L of membrane solution (5% Nafion solution) into a mixed solution, then add 5 mg of the sample to be tested and disperse evenly by ultrasound. Apply the above solution evenly on conductive glass (make sure that the shape and area of coating on each glass are consistent), then bake at 60°C for 4 h.

5 Photocatalytic measurements of furfuryl alcohol into furfural and H₂

The Photothermal catalytic of furfuryl alcohol into furfural and H₂ test is carried out in a 100 mL of three flask reaction units. First, the H₂ production activity of all preparation catalysts was studied with 10 vol% furfuryl alcohol of aqueous solution. Typically, 10 mg of catalyst is uniformly dispersed in 80 ml of 10 vol% furfuryl alcohol of aqueous solution and is sonicated for 3 min. Before each reaction, the reaction flask containing the suspension was filled with N₂ and kept for 15 min. The sealed reaction bottle is placed under the light emitting diode light source (80 W LED, $\lambda = 420$ nm).

The evolved H₂ content was measured using a GC-8A (Shimadzu Co.) gas chromatograph equipped with a thermal conductivity detector. At the end of the light reaction, the organic liquid in the bottom layer was collected by extraction. The remaining solution was analyzed with an Agilent gas chromatograph (A91PLUS). In addition, the effects of different test conditions on the synergistic photocatalytic redox reaction were compared. The photocatalytic products of H₂ and furfural were prepared by a series of controlled experiments on ZT-5 photocatalyst. Normal reaction conditions:10 mg of catalyst, 72 mL of H₂O, 9.26 mmol of furfuryl alcohol, irradiated by LED (420 nm, 80 W) for 3h in N₂ atmosphere. By varying one condition of the photocatalytic experiment, such as the light, the amount of catalyst, and the reactants at the oxidation end, while other conditions were kept consistent with the photocatalytic experiment. In addition, we did a capture test of the redox reaction process of the photocatalyst with different scavengers added:10 mg of catalyst, 72 mL of H₂O, 9.26 mmol of furfuryl alcohol, 9.26 mmol of furfuryl alcohol, 9.26 mmol of phydrogen with furfural on ZT-5 photocatalyst with different scavengers added:10 mg of catalyst, 72 mL of H₂O, 9.26 mmol of furfuryl alcohol, 9.26 mmol of furfuryl alcohol, 9.26 mmol of furfuryl mathematicated by LED (420 nm, 80 W) for 3 h in N₂ atmosphere.

The total apparent quantum efficiency (AQY) for hydrogen generation is calculated according to the following equation:

 $AQY = [2 \times (Numbers of evolved H_2) + 2 \times (Numbers of produced furfural)] / (Numbers of incident photons) \times 100\%$ (1)

6. Supplementary figures



Fig. S1 (a) Schematic illustration for the preparation of Tp-Tta COF, (b) XRD pattern and (c) FTIR spectrum of Tp-Tta COF.



Fig. S2 The SEM images of (a) $ZnIn_2S_4$ and (b) Tp-Tta COF. (c) AFM image with the corresponding height profile of thin layer Tp-Tta COF.



Fig. S3 TEM image of ZnIn₂S₄.



Fig. S4 TEM image of Tp-Tta COF.



Fig. S5 (a) SEM and (b) amplificatory SEM images of Tp-Tta COF.



Fig. S6 SEM image of ZT-5.



Fig. S7 (a) HRTEM image and (b) the lattice spacing of corresponding region of ZT-5.



Fig. S8 XRD patterns of $ZnIn_2S_4$, Tp-Tta COF and ZT-x composites, respectively.



Fig. S9 FTIR spectra of $ZnIn_2S_4$, Tp-Tta COF and ZT-5, respectively.



Fig. S10 (a) DRS of ZnIn₂S₄, Tp-Tta COF and ZT-x composites. (b) The optical images of ZnIn₂S₄, Tp-Tta COF and ZT-x composites, respectively.



Fig. S11 XPS spectra of (a) Zn 2p (b) In 3d, (c) S 2p, (d) C 1s, (e) N 1s and (f) O 1s of ZnIn₂S₄, Tp-Tta COF and ZnIn₂S₄/Tp-Tta COF samples.



Fig. S12 In-situ irradiated XPS full spectra of ZnIn₂S₄, Tp-Tta COF and ZT-5 samples, respectively.



Fig. S13 Band gap of (a) $ZnIn_2S_4$ and (b) Tp-Tta COF samples.



Fig. S14 Mott–Schottky plots of (a) $ZnIn_2S_4$ and (b) Tp-Tta COF samples.



Fig. S15 N_2 adsorption-desorption isotherms and pore size distribution curves of (a, d) $ZnIn_2S_4$, (b, e) ZT-5 and (c, f) Tp-Tta COF, respectively.



Fig. S16 Contact angle of ZnIn₂S₄, ZT-5 and Tp-Tta COF, respectively, (a-c) in water and

(d-f) 10 vol% furfuryl alcohol aqueous solution.



Fig. S17 Reaction illustration of H_2 and furfural generation from furfural-alcohol aqueous solution.



Fig. S18 A series of control experiments over the ZT-5 sample.



Fig. S19 The irradiance spectrum of 80 W LED light source (420 nm).



Fig. S20 HRTEM images before and after the photocatalytic reaction of ZT-5 sample.



Fig. S21 XPS spectra before and after the photocatalytic reaction of ZT-5 sample.



Fig. S22 XRD patterns of ZT-5 before and after reaction.



Fig. S23 (a) H_2 evolution in benzyl alcohol aqueous solution, (b) comparison of H_2 evolution and benzaldehyde production rates over different samples. Under 80 W LED (λ =420 nm) irradiation, the reaction solution is 10 vol% benzyl alcohol aqueous solution.



Fig. S24 Photocatalytic performance of H_2 and furfural evolution over ZT-5 sample with different scavengers.

R_{ct} (k Ω) of samples	ZnIn ₂ S ₄	ZT-5	Tp-Tta COF
Without light irradiation	429.6	342.4	2060
Under light irradiation	255.6	118.6	1635.2



Fig. S25 The fitting results of EIS of $ZnIn_2S_4$, Tp-Tta COF and ZT-5 samples, respectively, with/without light irradiation.



Fig. S26 TS-SPV spectra of $ZnIn_2S_4$, Tp-Tta COF and ZT-5 samples, respectively.



Fig. S27 The charge separation efficiency of ZnIn₂S₄, Tp-Tta COF and ZT-5 samples, respectively.

Note: The photocurrent can be defined by the following equation (1):

$$J_{H_2O} = J_{max} \eta_{abs.} \eta_{sep.} \eta_{trans.}$$
(1)

When H_2O_2 is added into electrolyte solution, the surface charge transfer become extremely fast and the $\eta_{\text{trans.}}$ approximately reaches 100%, and then the photogenerated current can be expressed as equation (2):

$$J_{H_2 O_2} = J_{max} \eta_{abs.} \eta_{sep.} \tag{2}$$

Here, J_{max} , $\eta_{abs.}$, $\eta_{sep.}$ do not change in both J_{H_2O} and $J_{H_2O_2}$ system. Consequently, the $\eta_{trans.}$ can be conveyed as following equation (3):

$$\eta_{trans.} = \frac{J_{H_20}}{J_{H_20_2}}$$
(3)



Fig. S28 Surface photovoltage intensity of $ZnIn_2S_4$, Tp-Tta COF and ZT-5 samples, respectively.

7. Supplementary tables

Sampla	Surface area	Pore volume	Dono sizo (nm)
Sample	(m²/g)	(cm ³ /g)	r ore size (iiiii)
$ZnIn_2S_4$	94.05	0.28	7.32
ZT-5	137.11	0.31	7.67
Tp-Tta COF	577.42	0.86	9.14

Table S1. Specific surface area, pore volume and pore size of ZnIn₂S₄, Tp-Tta COF and ZT-5, respectively.

Table S2. Contact angles of $ZnIn_2S_4$, Tp-Tta COF and ZT-5 in water and 10 vol% furfuryl alcohol aqueous solution.

Sample	Water	10 vol% furfuryl alcohol aqueous solution
ZnIn ₂ S ₄	15.203	6.819
ZT-5	10.491	3.565
Tp-Tta COF	8.536	3.111

Table S3. Photocatalytic performance of H_2 and furfural production over the ZT-5 photocatalyst. Normal reaction conditions: 10 mg dosage, 72 mL H_2O , 9.26 mmol furfural alcohol, LED (420 nm, 80 W) irradiation for 3 h, N_2 atmosphere.

Entry	Reaction	H ₂ production	Furfural production		
	conditions		(mmol g ⁻¹ h ⁻¹)		
1	Normal	9.73	12.1		
2	No light	0	0		
3	No catalyst	0	0		
4	Pure water	0.067	0		
5	Pure furfuryl alcohol	1.2	1.37		

			Efficiency	D.C	
Catalyst	Light source	Substrate	(mmol g ⁻¹ ·h ⁻¹)	Ref.	
ZnIn ₂ S ₄ /	80 W LED	FA (H ₂ O)	H ₂ : 9.73 FAD: 12.1	This	
Tp-Tta COF	$\lambda = 420 \text{ nm}$	AQY: 6.2% (420 nm)		work	
$ZnIn_2S_4/$	80 W LED		H ₂ : 38.6	This	
Tp-Tta COF	$\lambda = 420 \text{ nm}$	BA (H ₂ O)	BAD: 14.4	work	
CoTiO ₃ /	White LED		H ₂ : 1.93	1	
$Zn_{0.5}Cd_{0.5}S$	white LED	$FA(\Pi_2 O)$	FAD :1.96	1	
LaVO /	200 W Valamp		H ₂ : 0.287		
$a \in \mathbf{N}$	(250 mW sm^{-2})	$FA(H_2O)$	FAD: 0.95	2	
g-C ₃ 1 v ₄	(230 mw cm)		AQY: 22.16% (420 nm)		
7CS/Dt	200 W Valamp		H ₂ : 1.05	2	
ZCS/Pt 300 W X	500 w Xe lamp	FA (11 ₂ O)	C =71%, S = 89%	3	
T; C Ty/CdS	3 W blue LED	FA H ₂ : 0.47 FAD: 0.481		4	
11 ₃ C ₂ 1 x/CuS	λ=420 nm			4	
MoS-/7IS	300 W Xe lamp	$FA(H_{1}O)$	H ₂ : 2.832	5	
10032/213	λ≥420 nm	I'A (II ₂ O)	FAD: 2.752	5	
Mag /719	300 W Xe lamp		H ₂ : 3.78	5	
WI052/215	λ≥420 nm	$BA(H_2O)$	BAD: 3.73	5	
N; D/	200 W Valamp		HER: 1.11		
$11_{12}F_{5}$	300 w Xe lamp	$BA (H_2O)$	BAD: 1.19	6	
ZIIII <u>1</u> 284	<i>λ</i> ∕420 IIII		AQY:11.73% (420 nm)		
Ni-718	300 W Xe lamp		HER: 1.46		
N1:ZIS	λ>420 nm	BAD: 3.61		/	
Zn In S. W	300 W Xe lamp		HER: 1.77	o	
$Zn_3In_2S_6$ -W	λ≥420 nm	da (Π ₂ υ)	BAD: 1.83	ð	

Table S4 Comparison of the performance of H_2 generation and alcohol oxidation of the reported works.

			AQY:5.46% (420 nm)	
Au/Zele S	300 W Xe lamp		HER: 1.63	0
Au/21111254	λ≥420 nm	$BA(\Pi_2 O)$	BAD: 1.76	
Ni/ZnC4S	300 W Xe lamp		HER: 18.99	10
N1/ZnCdS	λ≥420 nm	$BA(\Pi_2 O)$	BAD: 14.92	10
Co-MoS ₂ /	80 W LED		HER: 0.48	11
CN	λ=420 nm	$BA(H_2O)$	BAD: 0.31	11
BA: benzyl alcohol. BAD: benzaldehyde. FA: furfuryl alcohol. FD: furfuraldehyde.				

Table S5 Photocatalytic coproduction of H_2 and furfural over ZT-5 photocatalyst with adding different scavengers. Reaction conditions: 10 mg dosage, 72 mL H₂O, 9.26 mmol furfural alcohol, 9.26 mmol scavenger, LED (420 nm, 80 W) irradiation for 3 h, N₂ atmosphere.

Entry	Saavangan	Active	H ₂ production	Furfural production	
Entry Scavenger		species	(mmol g ⁻¹ h ⁻¹)	(mmol g ⁻¹ h ⁻¹)	
1	Normal	/	9.73	12.1	
2	IPA	∙ОН	6.8	3.53	
3	AO	h^+	8.80	4.04	
4	TEMPO	e-	0.63	4.95	

Sample	τ ₁ (ns)	τ ₂ (ns)	τ ₃ (ns)	A ₁ (%)	A ₂ (%)	A ₃ (%)	τ _{AV} (ns)
ZnIn ₂ S ₄	0.11	0.27	0.93	25.99	47.57	26.43	0.90
ZT-5	9.04	140.00	0.51	5.42	65.63	28.95	138.11
Tp-Tta COF	1.43	104.74	0.42	11.57	57.23	31.20	104.23

Table S6 Kinetic fitting parameters for TR-PL spectra.

The average life time of the samples was calculated using the formula of

$$\tau_{ave} = (A_1 \bullet \tau_1^2 + A_2 \bullet \tau_2^2 + A_3 \bullet \tau_3^2) / (A_1 \bullet \tau_1 + A_2 \bullet \tau_2 + A_3 \bullet \tau_3)$$
(4)

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