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Electronic Supporting information (ɫ)

Butterfly Shaped Organic Hetero-Junctional Photocatalyst for Effective Photocatalytic CO_2 Reduction

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2.1. Chemicals.

2,5-dibromothiophene (TP), Urea, received as of Sigma-Aldrich. All the organic solvents purchased from Sino pharm Chemical reagent Co., Ltd China. The predominant gas such as carbon dioxide (CO_2) and $^{13}CO_2$ were taken from Fuzhou Lianzhong Industrial Gases and Hess chemical gas center of Beijing.

2.2. Characterization.

FT-IR analysis characterized by using Nicolet 670 spectrometer, Powder X-ray diffraction (PXRD) were analyzed using Bruker D8 Advance diffractometer with Cu K 1 energy. The thermo ESCALAB 250 equipment including A1 Ka (200W) line source were utilized for the X-ray photoelectron spectroscopy (XPS) analysis of as-fabricated samples. UV-Visible analysis of the prepared samples was carried out using Varian Cary 500 scan UV-Visible spectrometer. The electron paramagnetic resonance denoted as EPR carried out via Bruker A 300 model, ^{13}C-NMR experiments were examined by using Bruker Advance III 500 instrument. Hitachi SU8010 field instrument utilized for emission scanning electron microscope (SEM) and same as the transmission electron microscopy (TEM) of the desired samples analyzed via JEOL-JEM 2010 Ex model. The Edinburgh FI-FSTCSPC 920 equipment were utilized for the emission spectra analysis. The elemental analysis of the samples was achieved from micrometer Vario EL cube for the detection (C, H, N) within the samples. The nitrogen adsorption and desorption isotherms experiment were conducted at 77 K using Micromeritics ASAP-2020. Density functional theory data measured via B3LYP 6-31 G (d, p) command on Gaussian program.

2.3. Photocatalytic test for CO_2 reduction.

Typically, the experiments remained achieved in an 80 ml Schlenk flask apparatus, by dispersing 30 mg of catalyst in 6 ml of solvent (water/acetonitrile=1ml/5ml). The reactor flask also contains the co-catalyst cobalt chloride 1µmol ($CoCl_2$), 15 mg of 2,2-bipyridine as a photosensitizer and 1mL TEOA. The reactor system remained expatriate several times and connecting by backfilling balloon of pure CO_2 (1 atm) by keeping on continuous moving for steady adsorption and desorption symmetry. Later, reactor flask was closed tightly and keeps under Xe arc lamp (500 W) as a radiation source, about 15 cm away from lamp. In order to maintain the temperature, the reaction system subjected with cooling water circulation and pressure was stabilized at 1 atm. The system was irradiated for 1 h and after the evolved gases were detected by an Agilent 7820A gas chromatography which is previously connected to the system. The long durability experiments were held under same condition and hence the wavelength experiments of the photocatalyst were performed by changing the filter cut of the Xe lamp (380, 400, 450, 470 and 500 nm) respectively.

2.4. Electrochemical Measurement.

In typical electrochemical measurement, we used fluoride tin oxide (FTO) glasses owing to its conducting surface property, these glasses were washed three times with continuous ultra-sonication and keep in an oven aimed at dry prior to fixative the sample on it. After, the well ground sample (50mg) remained dispersed into DMF (2 ml) with ultra-sonication. The side portions of glasses were covered by Scotch tape and deposit samples onto the glasses and keep at room temperature for dry. The glasses after dried were kept for calcinations into Air furnace at 200 ^{0}C for 2 h to improve adhesion. After calcinations, we obtained the FTO glasses of pure UCN and copolymerized UCN-$TP_{0.06}$ electrodes. The bare portion of as-prepared glasses electrodes were about 0.25cm^2 and hence epoxy resin was used to cover the uncoated area of each electrode.

The electrochemical experiments were carried out using CHI electrochemical equipment with as-prepared, Ag/AgCl and Pt plate as working, reference and counter electrodes respectively. About 0.2 M of sodium sulfate (Na_2SO_4) functioned as supporting electrolyte, later working electrodes were immersed into the electrolyte solution having counter plate (Pt) in addition reference Ag/AgCl electrodes. The electrochemical impedance spectroscopy (EIS) measurement of UCN and UCN-TP$_{0.06}$ were conducted in 50 mL 0.2 M Na_2SO_4 solution using Ag/AgCl (0.4 V) electrode in the dark. For EIS measurement the perturbation signal was 20mV besides frequency range was from 200 KHz to 10 Mhz.

In the photocurrent experiment, the working electrode remained illuminated from backside FTO toward semiconductor layer thickness effect diminishing and the episodic on-off photo-current response from UCN and UCN-TP$_{0.06}$ modified FTO, (-0.3V to 0.8V bias vs. Ag/AgCl), and the agitation signal was also 20 mV having frequency from 200 KHz to 100 Hz.

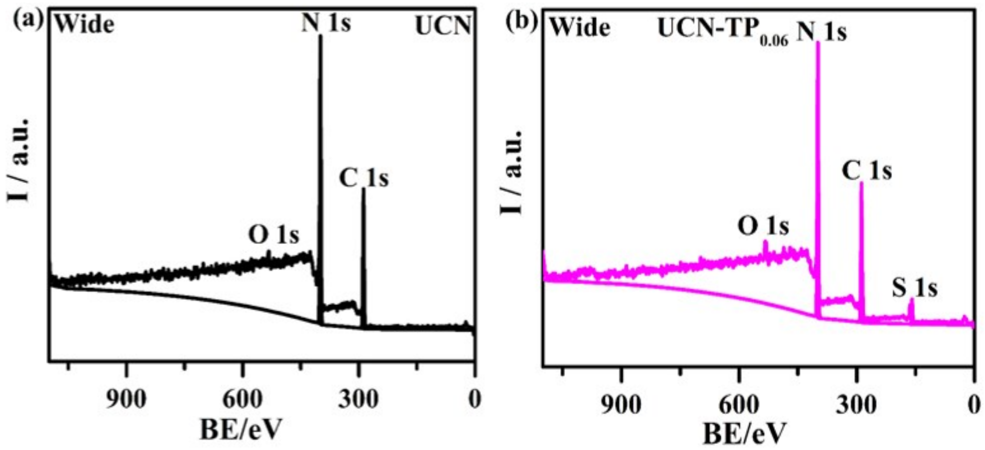

Fig.S1. (a) Wide spectrum of **(a)** UCN and **(b)** UCN-TP$_{0.06,}$ samples.

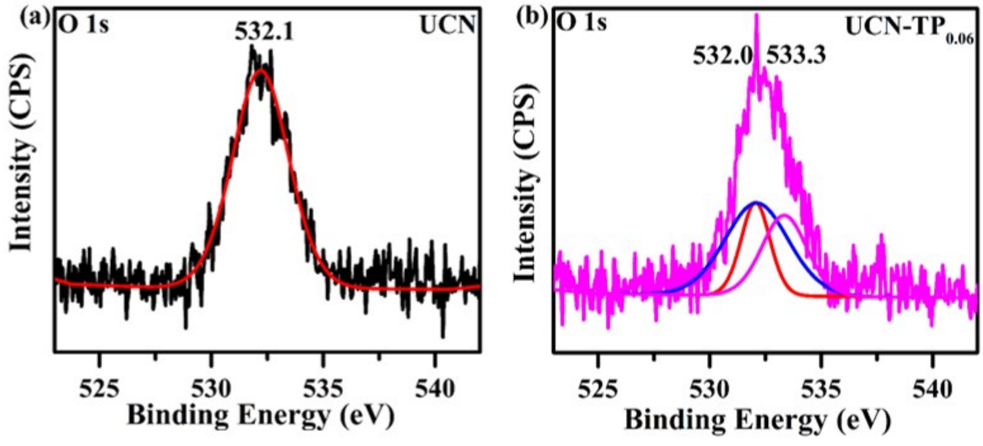

Fig.S2. O 1s XPS spectra of **(a)** UCN and **(b)** UCN-TP$_{0.06}$, samples.

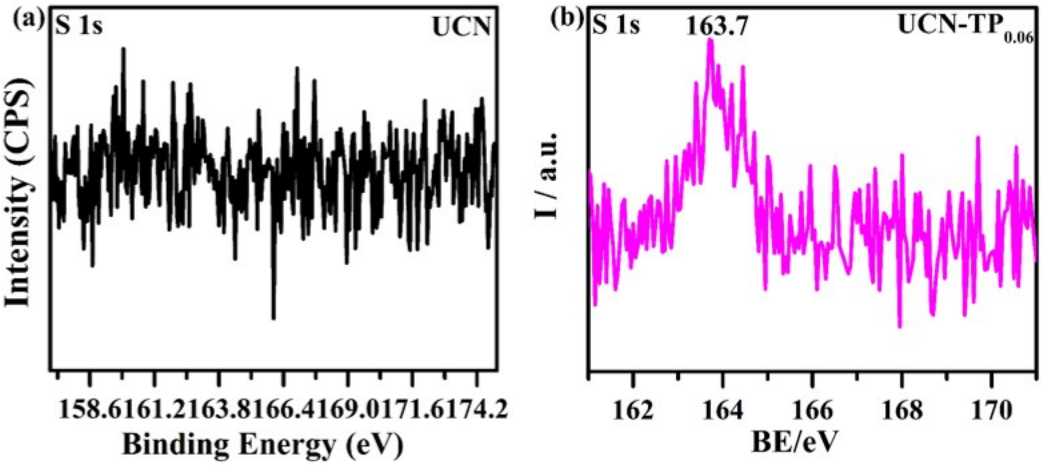

Fig.S3. S 1s XPS spectra of **(a)** UCN and **(b)** UCN-TP$_{0.06}$ samples.

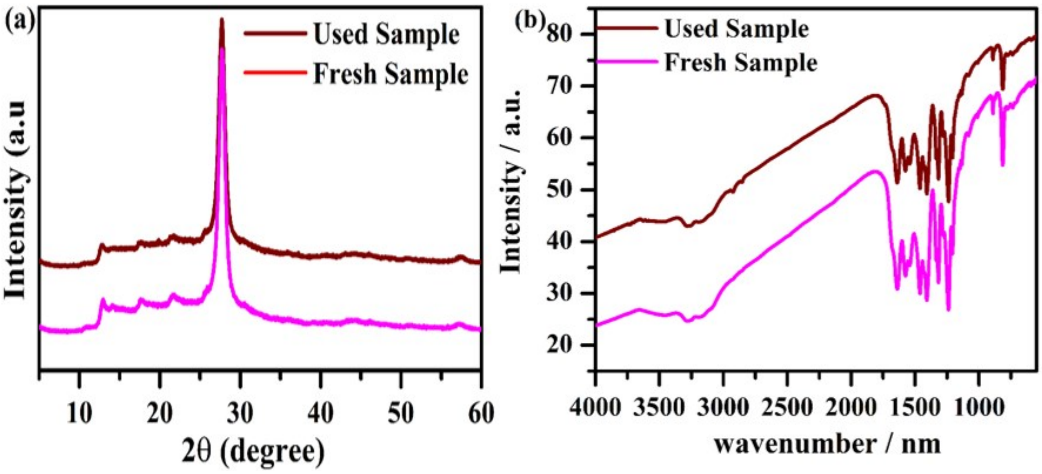

Fig.S4. (a). Powder XRD and **(b)** FT–IR patterns aimed at fresh along with used materials.

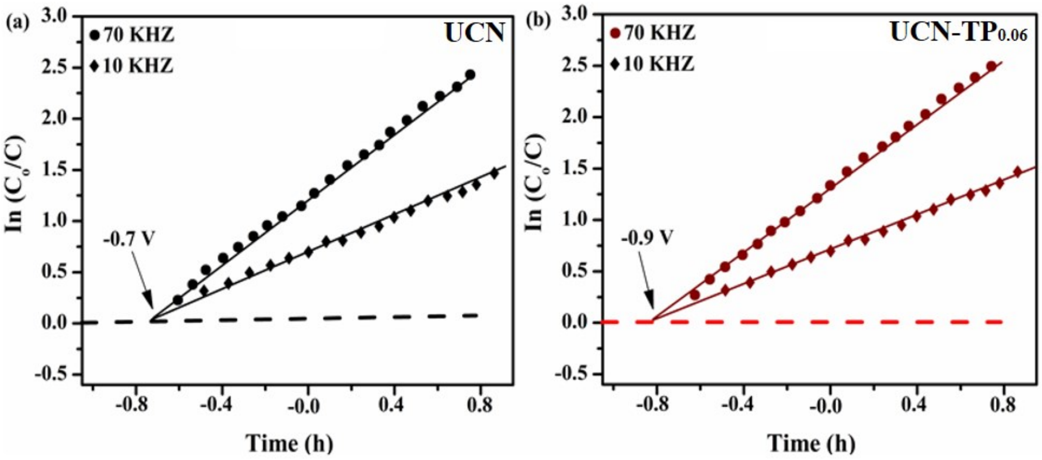

Fig.S5. Mott-Schottky plots for the Pure-UCN **(a)** and UCN-TP$_{0.06}$ **(b)** samples.

Table.S1. Physicochemical properties and CO and H_2 evolution during CO_2 reduction of as-prepared samples.

Sample	**Surface area BET m^2/g[a]**	**C/N ratio[b]**	**Band Gap (eV)[d]**	**CO[c] evolution (µmole/h^{-1})**	**H_2[c] evolution (µmole/h^{-1})**
UCN	58.1839	0.65	2.87 eV	2.72	0.51
UCN-TP$_{0.004}$	124.4193	0.68	2.62 eV	15.93	6.07
UCN-TP$_{0.008}$	197.2843	0.69	2.54 eV	25.01	4.87
UCN-TP$_{0.01}$	220.1454	0.70	2.52 eV	26.1	3.57
UCN-TP$_{0.06}$	**274.8190**	**0.71**	**2.49 eV**	**27.5**	**3.97**
UCN-TP$_{0.1}$	209.3285	0.69	2.51 eV	22.9	4.2
UCN-TP$_{0.3}$	149.3671	0.68	2.61 eV	11.5	5.97

Where, **[a]** the calculated after N_2 adsorption desorption isotherms. **[b]** Based on elemental analysis spectra. **[c]** From CO_2 reduction-controlled experiments and **[d]** from calculation.

Table.S2. Physicochemical properties of as-prepared samples with other precursors

Sample	**Surface area (m^2g^{-1})[a]**	**C/N molar ratio[b]**	**CO[c]evolution (µmole/h^{-1})**	**H_2[c] evolution (µmole/h^{-1})**
UCN-$TP_{0.06}$	**274.819**	**0.71**	**68.18**	**18.52**
DCN-$TP_{0.06}$	58.924	0.63	9.2	3.10
TCN-$TP_{0.06}$	45.632	0.61	7.4	2.21
ACN-$TP_{0.06}$	47.507	0.61	8.3	1.73

[a]The calculated after N_2 adsorption desorption isotherms.

[b] Based on elemental analysis spectra.

[c] From CO_2 reduction-controlled experiments under visible light.

Table.S3. Calculated values of Mullikan charge of copolymerized samples via DFT/ B3LYP/6-31G methods.

Atoms	UCN-TP_L	**Atoms**	UCN-TP_R

1 C	-1.0150	1 C	-2.0457
2 C	1.0342	2 C	1.5317
3 N	-0.5410	3 N	-1.2091
4 N	0.9818	4 N	3.1074
5 N	-0.5654	5 N	-1.4719
6 C	0.4218	6 C	0.4788
7 S	1.1245	7 S	1.2010
8 N	0.1229	8 N	-0.2287
9 H	0.4054	9 H	0.4068
10 H	0.4049	10 H	0.4052

Table.S4. Study of various conditions on controlled trials[a]

Entry	**CO(μmol)**	**H_2(μmol)**	**CO+H_2(μmol)**	**Sel.(%)[b]**	**TON[c]**
1	25.2	4.64	29.84	84.5	29.84
2[d]	ND.[e]	ND.	-	-	--
3[f]	ND.	ND.	-	-	-
4[g]	ND.	0.21	0.21	-	0.21
5[h]	ND.	0.56	-	-	-
6[i]	ND.	<0.1	<0.1	-	<0.1

7[j]	ND.	<0.1	<0.1	-	<0.1
8[k]	ND.	<0.1	<0.1	-	<0.1

Where, **[a]** Reaction conditions: UCN-TP$_{0.06}$ (30mg), bpy (15mg), COCl$_2$ (1μmol), TEOA (1ml), solvent (MeCN 7ml), and λ> 420nm, 30 °C, 1 hour. **[b]** Selectivity = nCO/n (CO+H$_2$) × 100. **[c]** Turn-over number (mol quantity of CO and H$_2$)/ (mol quantity of cobalt ion). [d] Without UCN-TP$_{0.06}$. **[e]** Not determined **[f]** In dark. **[g]** By means of Ar rather than CO$_2$. **[h]** Without TEOA **[i]** Without bpy. **[j]** Without CoCl$_2$. **[k]** Withoutbpy and CoCl$_2$.