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Unifying CO₂-to-fuel and biomass valorization over metal-free 2D carbon nitride-fullerene

heterostructure: a solar-driven chemical circular economy

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1. Experimental section

1.1. Materials

Fullerene (C₆₀) was purchased from Sigma Aldrich. Thio-urea was purchased from TCI chemicals. *para*-Methoxy benzyl alcohol (*p*-MBA), Hydroxy methyl furfural (HMF), Cinnamyl alcohol (CA), Vanillyl alcohol (VNA), and Veratryl alcohol (VRA). Acetonitrile (ACN) HPLC grade solvent and Toluene were purchased from Sigma Aldrich. All the chemicals were used without further purification.

1.2. Synthesis procedure of TUCN

Thio-urea derived carbon nitride (hereafter denoted as TUCN) was prepared through a conventional calcination process. Typically, 20 g of thio-urea was transferred in to a covered alumina crucible. Then the heating treatment was conducted inside the Nabertherm box furnace at 550 °C for 3 h (heating rate 5 °C min⁻¹) under the flow of N₂. After the calcination, a yellow powder of TUCN was obtained which was grounded for further use.

1.3. Synthesis procedure of fullerene-TUCN (C₆₀/TUCN)

 C_{60} /TUCN was synthesized as follows: first in a 50 ml round bottom (RB) flask, 100 mg of as prepared TUCN and varied amount of C_{60} in mg (2.5, 5, 7.5, and 10) were transferred, separately. After that 20 ml Toluene was added to the RB flask and ultrasonicated for 30 minutes. Both solutions were mixed into the 100 ml beaker and kept under the probe ultrasonication for 1 h. The resultant dark purple solution was further transferred to the heating plate and the solvent (Toluene) was evaporated at 110 °C in the fumehood. The obtained solid residue was washed with toluene followed by iso-propyl alcohol (IPA) and dried at 80 °C in the oven. The corresponding $C_{60}/TUCN$ samples were marked as 2.5- $C_{60}/TUCN$, 5- $C_{60}/TUCN$, 7.5- $C_{60}/TUCN$, and 10- $C_{60}/TUCN$.

1.4. Analytical techniques

The diffraction patterns were determined by powder XRD using Bruker D8 Advance diffractometer equipped with a scintillation counter detector, with Cu-K α radiation (λ = 0.15418 nm) source operating at 40 kV and 40 mA. Agilent Cary 100 UV-Vis spectrophotometer was used to record absorbance spectra of powder samples. Photoluminescence spectra (PL) and Time Resolved Photoluminescence spectra (TRPL) were recorded on Horiba Fluorolog instrument. For surface area analysis, N₂ physisorption isotherm was obtained at 77 K using an Autosorb iQ2 instrument (Quantachrome) and the samples were degassed for 24 h at 120° C before the analysis. Elemental analysis (C, N, O and H elements) was carried out using Elementar Vario MACRO cube elemental analyzer. The morphology of prepared samples were investigated using Field emission scanning electron microscopy (FESEM) on the JEOL JSM-7610F Plus instrument. Transmission electron microscope (TEM) analysis was carried out using JEOL JEM-2100 operated at an accelerating voltage of 120 kV. X-ray photoelectron spectroscopy (XPS) was further corroborated to realize the chemical states and elemental compositions of the sample by using the Al K α X-ray source and a monochromator with ultra-high vacuum (7 x 10-9 torr) provided by Thermo Fisher Scientific. Electron paramagnetic resonance (EPR) analysis was carried using Bruker A300-9.5/12/S/W system at variable temperature (100-300 K). (Photo) electrochemical analysis was performed in a standard three-electrode, platinum electrode, Ag/AgCl (in saturated KCl) electrode, and glassy carbon electrode as a counter, reference and working electrode, respectively. The measurement was recorded via Metrohm Autolab (M204 multichannel potentiostat galvanostat). CO₂-temperature-programmed desorption (CO₂-TPD) analysis define the adsorption behavior of CO₂ over the surface of photocatalyst and was performed by using BELCAT II from MicrotracBEL Corp. After the reaction, an estimation of the gaseous product carbon monoxide (CO) was done by Gas Chromatography (Perkin Elmer Clarus 680) and the analysis of the liquid samples were estimated by Shimadzu Gas Chromatography-Mass Spectrometer (GC-MS) equipped with Stabilwax-MS column.

1.5. Computational Method

DFT were carried out with the Vienna ab initio simulation package (VASP)¹. The exchange correlation between electrons was treated using the generalized gradient approximation (GGA)² in the Perdew–Burke-Ernzerhof (PBE)³ and DFT-D2 method with Grimme van der Waals correction. A vacuum spacing of 15 Å was employed to eliminate the interactions between layers. The convergence threshold for energy and force are set at 10 eV and 0.03 eV/Å, respectively. The cut-off energy was set to be 520 eV with a total no. of 56 atoms of TUCN and 116 atoms of 5-C₆₀/TUCN, and a γ -centered K-point of 2 × 2 × 1 was used for geometry optimization and property calculations. The lattice constants of optimized structures are a = b = 14.27 Å.

Theoretical studies of model building heterostructure of spherical C₆₀ and 2D TUCN

In order to construct the heterostructure of spherical C_{60} and 2D TUCN,⁴ we took a 2 x 2 supercell of g- C_3N_4 , (Figure S11a), which in total contains 24 C atoms, 32 N atoms and M denotes the exact centre of the cavity in single-layered g- C_3N_4 . The optimized lattice constant of this 2D layer structure is calculated to be 14.18 Å. The side view and top view of the C_{60} molecular structure are plotted in (Figure S11b), and the two regular pentagons located in its uppermost and undermost planes. The geometrical structures of the C_{60} modified g- C_3N_4 hybrids is illustrated in Figure S11c. In the C_{60} /g- C_3N_4 nanocomposite, the pentagon in the C_{60} molecule is parallel to the g- C_3N_4 sheet. After the full structural relaxation, a strong bend occurs in the g- C_3N_4 monolayer.

1.6. General reaction procedure and photocatalytic activity

The photoredox performance of C_{60} /TUCN for simultaneous CO₂ reduction and biomass based *p*-MBA (model reaction) oxidation was scrutinized in a 10 ml RB flask under a solar simulator (AM 1.5), 100 mW.cm⁻². In a typical reaction, a certain amount of C_{60} /TUCN was pre-mixed in 3 ml of ACN (HPLC grade). Then, *p*-MBA (0.1 mmol) was added into the ACN solution mixture. Thereafter, the solution was thoroughly brimmed with CO₂ for 30 minutes to ensure the dissolution of enough CO₂ and kept under the solar simulator (AM 1.5), 100 mW.cm⁻². The reaction temperature was maintained at 25 °C, by using an external cooling circulation unit. After the reaction, the gaseous portion was analyzed by collecting the sample from the headspace of the RB with the help of gas tight syringe and quantified by injecting the gaseous sample in to the Gas Chromatography (Perkin Elmer Clarus 680, TCD detector, Argon as carrier gas). The liquid mixture was

centrifuged and segregated from the suspended catalyst and analyzed by Shimadzu Gas Chromatography-Mass Spectrometer (GC-MS). Moreover, the separated catalyst was collected and washed with copious amounts of water followed by IPA. Subsequently the washed catalyst was dried overnight in an oven at 80 °C and utilized for the further recycling experiments. The apparent quantum yield (AQY) of CO production was estimated at monochromatic wavelength (λ) of 450 nm. The details of AQY calculation is below:

(i) The number (*N*_{photons}) of absorbed photons:

$$N_{photon} = \frac{t(s) * P(W cm^{-2}) * \lambda(m) * S(cm^{2})}{h(J-s) * c (m s^{-1})}$$

Where, time (*t*, 10800 s), intensity (*P*, .00117 W cm⁻²), wavelength (λ , 450 * 10⁻⁹ m), irradiation area (*S*, 9.18 cm²), Planck's constant (*h*, 6.62 * 10⁻³⁴ *J*-*s*), and light velocity (c, 3 * 10⁸ ms⁻¹)

(ii) The AQY is obtained by following equation:

$$AQY = \frac{2 * nCO (mol) * N_A (mol^{-1})}{N_{photon}} * 100$$

Where, yield of CO (7.4 * 10^{-6} mol) and Avogadro number (N_A , 6.02 * 10^{23} mol⁻¹)

Table S1. Comparison of $5-C_{60}$ /TUCN and other reported photocatalytic systems for simultaneous CO₂ reduction and organic compounds oxidation.

S. No.	Catalyst	Organic substrate	Solvent	Light source	Oxidation product (Activity and sel. %)	Reduction product (Activity and sel. %)	Apparent quantum yield (AQY %) ^a	Ref.
1	CdS-TiO ₂	Cyclohexanol	Cyclohexa nol	250 W high pressure Hg lamp	Cyclohexanone (20 $\mu mol~h^{-1}g^{-1}$ and N.A.)	HCOOH (N.A. and N.A.), cyclohexyl formate (20.2 μmol h ⁻¹ g ⁻¹ and N.A.)	N.A.	5
2	Ag-TiO ₂	Benzyl Alcohol	CH ₃ CN	300 W Xe lamp	Benzaldehyde (N.A. and 98 %)	CH ₃ OH (7.47 μ mol h ⁻¹ g ⁻¹ and N.A.)	N.A.	6
3	Cu ₂ O/Cu	Benzyl Alcohol	CH ₃ CN	300 W Xe lamp, λ > 420 nm	Benzylacetate (116.7 μmol h ⁻¹ g ⁻¹ , and N.A)	CO (0.65 μmol h ⁻¹ g ⁻¹), H ₂ (20 μmol h ⁻¹ g ⁻¹), HCOOH (2.5 μmol h ⁻¹ g ^{-1,} and N.A.)	N.A.	7
4	Pd/TiO ₂	Ethane	Gas phase	300 W Xe Iamp UV light	Ethene (230.5 µmol h ⁻¹ g ⁻¹ and 95.42 %)	CO (120.4 μmol h ⁻¹ g ⁻¹ and 45 %), H ₂ (162.2 μmol h- 1g-1 and 55 %)	0.93 %	8
5	Cu/TiO ₂	Benzylamine	CH CN	High pressure Hg lamp λ > 365 nm	N-benzylidene-benzylamine (N.A. and 98 %)	CH OH (64.09 μ mol h ⁻¹ g ⁻¹ and N.A.)	N.A.	9
6	CdSe/CdS QDs	1-phenylethanol	DMF/Na ₂ C O ₃	λ =450 nm LED light	Pinacol (26.5 mmol g ⁻¹ h ⁻¹ and >96 %)	CO (27.63 mmol h ⁻¹ g ⁻¹ and ~94 %)	32.70 % ^b (λ = 450 nm)	10
7	$CsPbBr_{3}/Cs_{4}PbBr_{6}$	CH₃OH	CH ₃ CN/H ₂ O	300 W Xe lamp	HCOOH (56.50 μmol h ⁻¹ g ⁻¹ and N.A.)	CO (120.16 μmol h ⁻¹ g ⁻¹ and N.A.)	N.A.	11
8	g-CN/POM/[Re]	cyclohexene	CH ₃ CN	White LED light	1, 3 cyclohexadiene (272 μmolg ⁻¹ and N.A.), benzene (290 μmolg ⁻¹ and N.A.)	CO (510 μmolg ⁻¹ and N.A.)	N.A.	12
9	Py-PCN	Cyclohexene	Cyclohexe ne/NaHCO 3 as CO2 source	300 W Xe lamp	Cyclohexanol (0.28 μ mol h ⁻¹ and N.A.)	CO (0.28 μ mol h ⁻¹), HCOOH (0.55 μ mol h ⁻¹ and N.A.),	N.A.	13
10	3DOM CdSQD/NC	Benzylamine	CH₃CN/H₂ O	300 W Xe lamp, λ > 420 nm	N-benzylidene-benzylamine (9820 µmol g ⁻¹ h ⁻¹ and 95.3 %)	CO (5210 μmol g ⁻¹ h ⁻¹ and 89.6 %)	2.90 % (λ = 450 nm)	14
11	5-C ₆₀ /TUCN	<i>p</i> -methoxy benzyl alcohol	CH ₃ CN	350 W solar simulator, AM 1.5 G, 100 mW/cm ²	<i>P</i> -methoxy benzyaldehyde (0.65 mmol h ⁻¹ g ⁻¹ and >99 %)	CO (8.92 mmol h ⁻¹ g ⁻¹ and >95 %)	3.38 %ª (λ = 450 nm)	This work

N.A. - Not available.

 $^{\rm a}$ AQY % is calculated for the $\rm CO_2$ reduced product in presence of organic substrate.

 ${}^{\rm b}\text{AQY}$ % is calculated for the CO_2 reduced product in presence of strong TEA as electron donor.



Scheme S1. Schematic illustration of the $C_{60}/TUCN$ synthesis.



Figure S1. Fe-SEM images a) TUCN and b) $5-C_{60}/TUCN$.



Figure S2. a) BET, b) XPS survey scans, c) C1s XPS spectrum, and d) N1s XPS spectrum of TUCN and 5-C₆₀/TUCN.

Table S2: XPS-determined atomic percentage (%) and N/C ratio of TUCN and 5- $C_{_{60}}$ /T	FUCN
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		Elements							
Catalyst	С	N	0	N/C					
TUCN	44.54	52.68	2.78	1.18					
5-C ₆₀ /TUCN	47.77	49.25	2.99	1.03					

Table S3: CHNS analysis determined elemental percentage (%) and N/C ratio of TUCN and $5-C_{60}$ /TUCN

	Elements							
Catalyst	Н	С	N	S	N/C			
TUCN	1.47	35.33	69.58	1.03	1.96			
5-C ₆₀ /TUCN	0.025	38.44	63.45	0.66	1.65			



Figure S3. a) MS plot of TUCN, b) MS plot of $5-C_{60}/TUCN$, c) TPR of TUCN and $5-C_{60}/TUCN$, and d) Nyquist plot of TUCN and $5-C_{60}/TUCN$



Figure S4. CO₂-temperature-programmed desorption (CO₂-TPD) analysis of 5-C₆₀/TUCN



Scheme S2. Illustrative diagram of photocatalytic reaction setup



Figure S5. GC-MS liquid mixture profile snap-shot of $5-C_{60}/TUCN$ catalyzed *p*-MBA oxidation under CO₂ environment after 6 h.



Figure S6. Selective CO production during CO₂ photo reduction over the period of 6h.

Table S4: Substrate scope of biomass based aromatic alcohols to corresponding aldehydes integrated with CO generation via CO_2 photoreduction.

Entry Substrate		Conv.	Corresponding aldehyde	Production rate (mmol $h^{-1}g^{-1}$)			
	alcohol	% ^a	Sel. % [°]	СО	Corresponding aldehyde		
1	<i>p</i> -MBA	32	>99	8.92	0.53		
2	Cinnamyl alcohol	20	>99	1.60	0.33		
3	Vanillyl alcohol	13	>99	6.13	0.29		
4	Veratryl alcohol	31	>99	10.78	0.60		
5	HMF	7	>99	1.86	0.16		



Figure S7. Recycling studies of $5-C_{60}/TUCN$ catalyzed *p*-MBA oxidation under CO₂ environment, a) CO production rate, b) *p*-MBAL production rate and corresponding selectivity, c) XRD, and d) TEM analysis of $5-C_{60}/TUCN$ photocatalyst before and after catalysis.



Figure S8. a) ²⁹CO mass spectra and b) ²⁹CO mass fragmentation.

Table S5: p-MBA oxidation coupled with CO₂ photoreduction to CO under controlled experiments

Entry	Substrate	Conv.	Corresponding aldehyde	Production rate (mmol $h^{-1}g^{-1}$)		
	alconor	%	Sel. % ^ª	CO	<i>p</i> -MBAL	
1 ^b	<i>p</i> -MBA	5	>99	-	0.11	
2 ^c	<i>p</i> -MBA	9	>99	-	0.14	
3 ^d	<i>p</i> -MBA	<5	>99	15.42	0.06	

Reaction conditions: Catalyst (10 mg), CO_2 purging for 30 min, substrate (0.1 mmol), 3 mL ACN, reaction time 6 h, room temperature (25 °C) and Light source: solar simulator (AM 1.5 G, 100 mW/cm²). ^aThe conv. % and sel. % were obtained from GC-MS. ^b Under Argon. ^c Electron scavenger (AgNO₃), and ^d IPA as hole scavenger.



Figure S9. EPR spectra of $5-C_{60}$ /TUCN under varied atmospheric conditions.



Figure S10. Density of states (DOS) of TUCN and $5-C_{60}/TUCN$



Figure S11. Optimized geometric structures of a) TUCN monolayer, b) C_{60} molecule, and c) 5- C_{60} /TUCN heterostructure with top view and side view, here C and N atoms are represented by golden and blue color, respectively.

Table S6: Total energy (eV) directly obtained from DFT of the pristine TUCN and $5-C_{60}/TUCN$ single unit cell, corresponding intermediates and species

Materials	E _{DFT} (*)	E _{DFT} (COOH*)	E _{DFT} (CO*)	Е _{DFT} (С ₆₀)	E _{DFT} (HCOOH *)	E _{DFT} (CHO*)	E _{DFT} (CO ₂)	E _{DFT} (CO)	E _{DFT} (H ₂ O)	E _{DFT} (H ₂)
TUCN	-471.16	-496.08	-485.95	-	-	-	-22.96	-	-14.21	-6.76
5-C ₆₀	-	- 1027.39	-	-	-	-		14.78		

/TUCN	1003.37	1017.22	531.0	1033.18	1018.71		
			7				

Table S7: Gibbs free energy (Δ G) in eV of CO₂ photoreduction for the pristine TUCN and C₆₀/TUCN single unit cell and corresponding intermediates

Materials	ΔG _[COOH*]	ΔG _[CO*]	ΔG _[* + CO]	ΔG _[HCOOH*]	ΔG _[CHO*]
TUCN	1.43	0.731	0.732	-	-
5-C ₆₀ /TUCN	1.19	0.53	0.41	1.22	2.43

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