Prominent COF, g-C_3N_4, and Their Heterojunction Materials for Selective Photocatalytic CO_2 Reduction

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- **Keywords:** COF, g-C_3N_4, heterojunction, UV irradiation, CO_2 photoreduction

Supplementary Materials

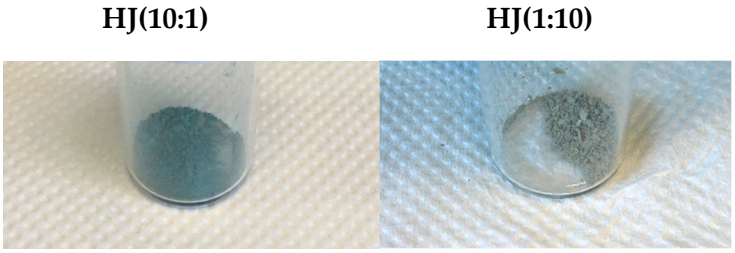


Figure S1. The synthesized green photocatalysts of HJ(10:1) and HJ(1:10).

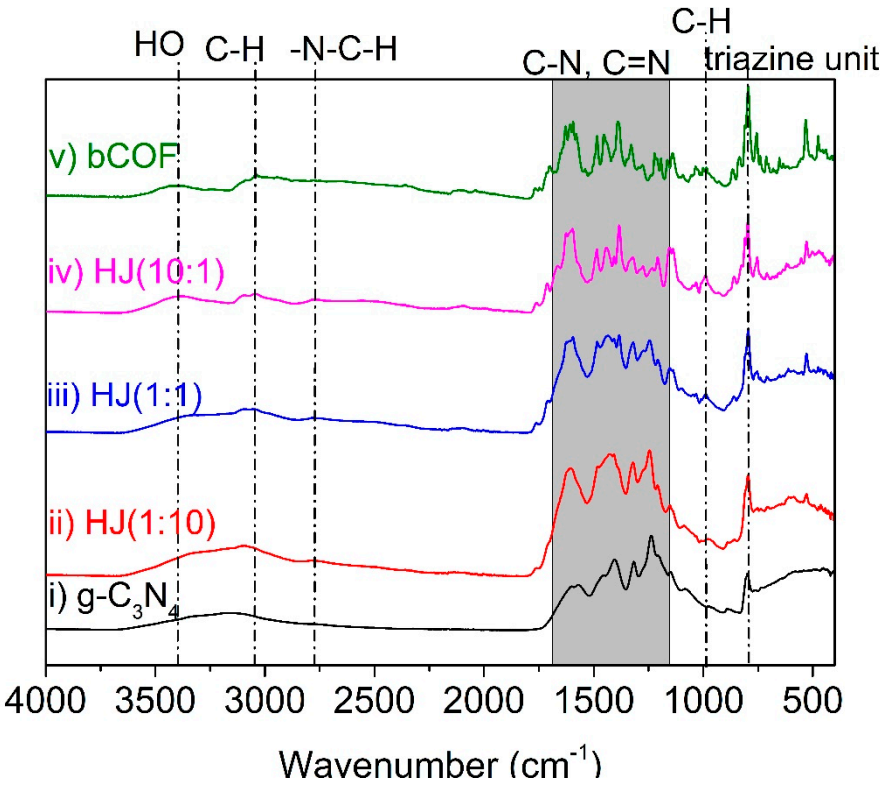


Figure S2. FTIR spectra in the range of 400 to 4000 cm^{-1} for the synthesized pristine (i, v) and heterojunction (ii, iii, iv) materials before the photocatalytic process.

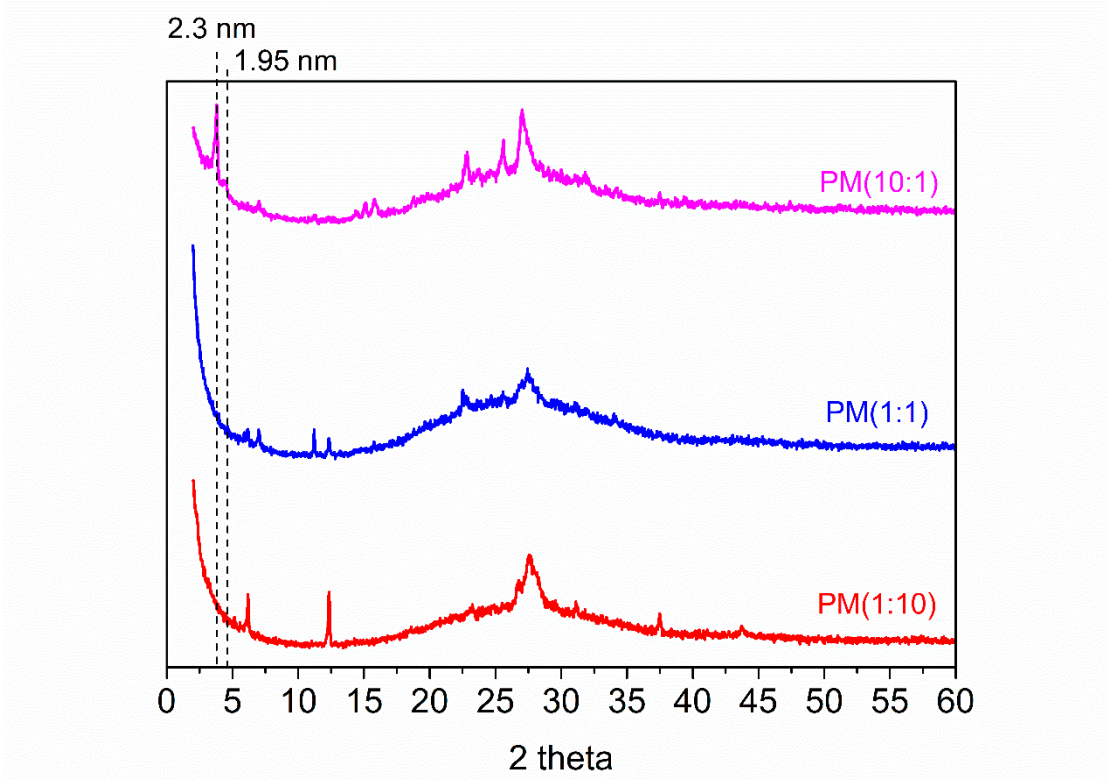


Figure S3. XRD of the physical mixed materials prior to CO_2 reduction process

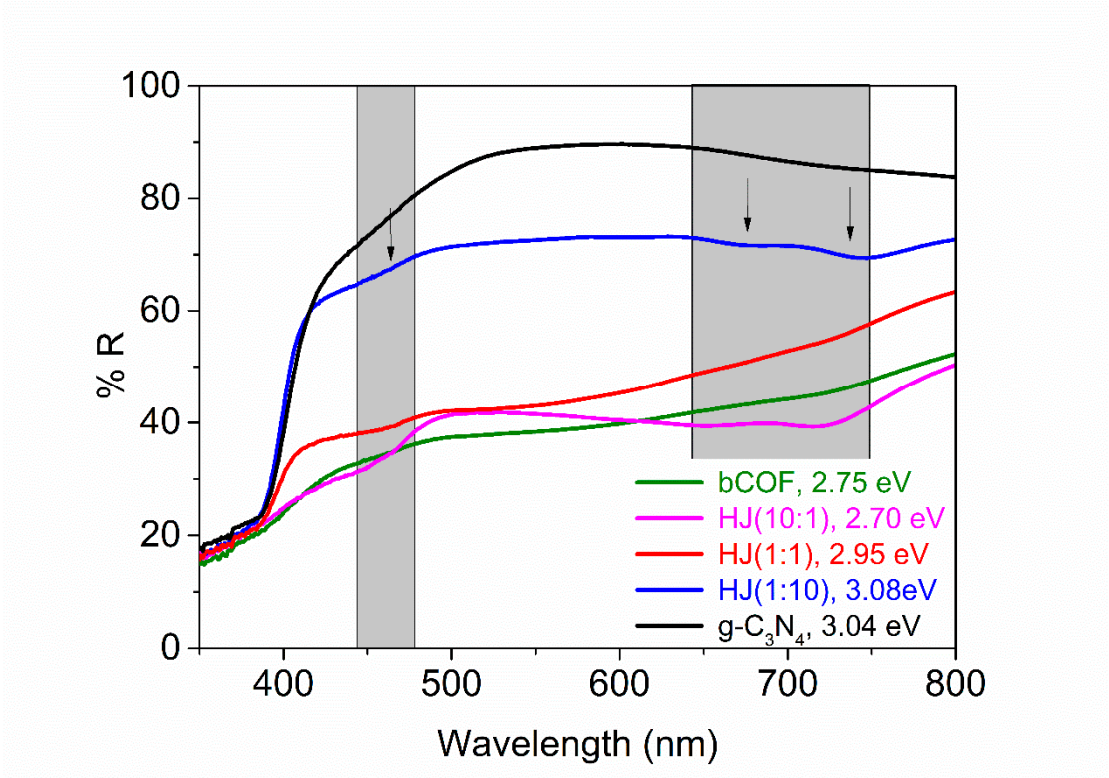
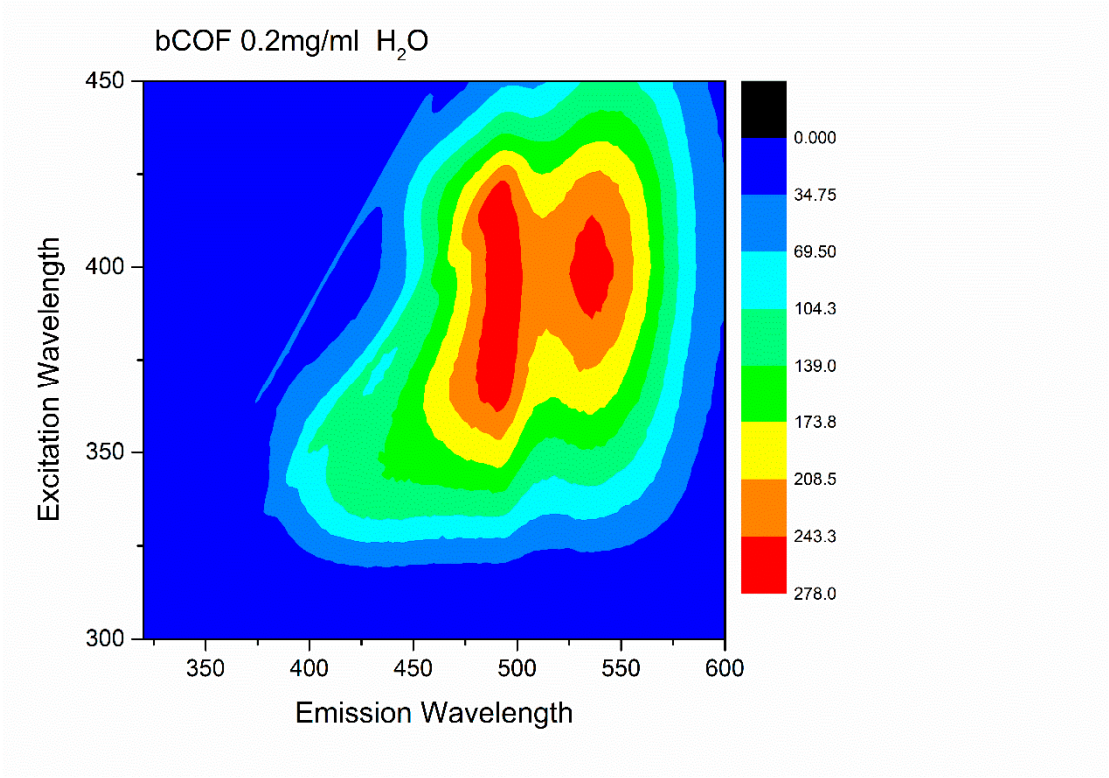
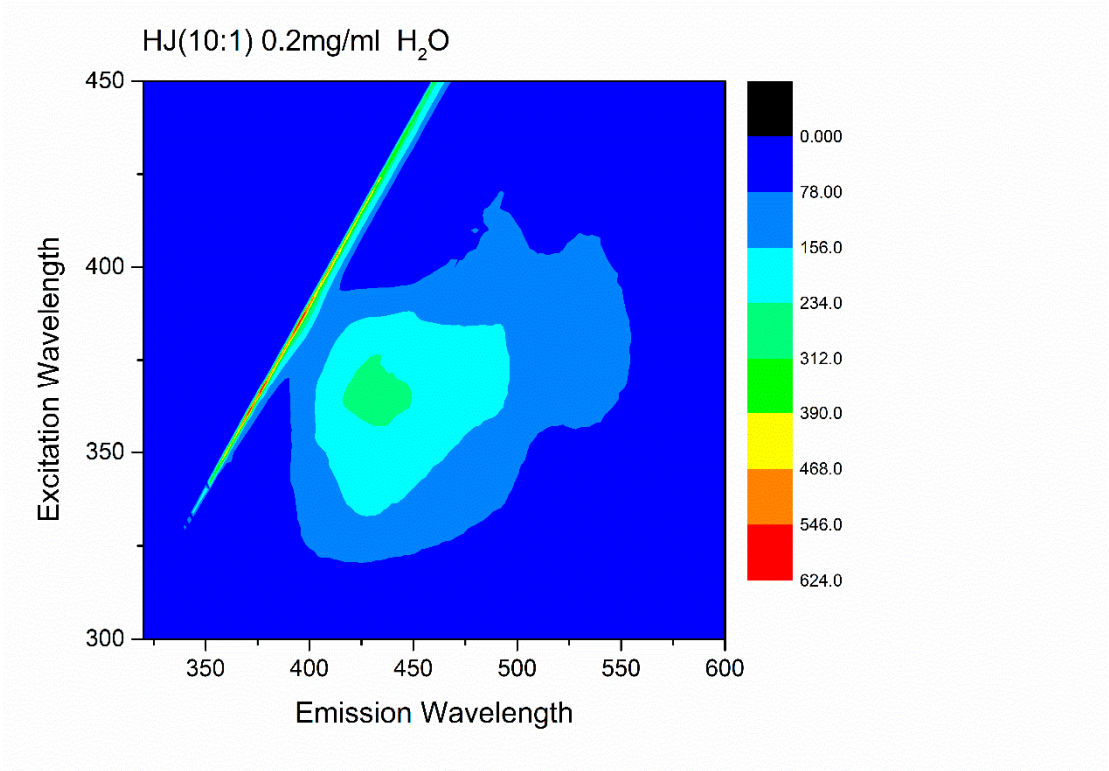
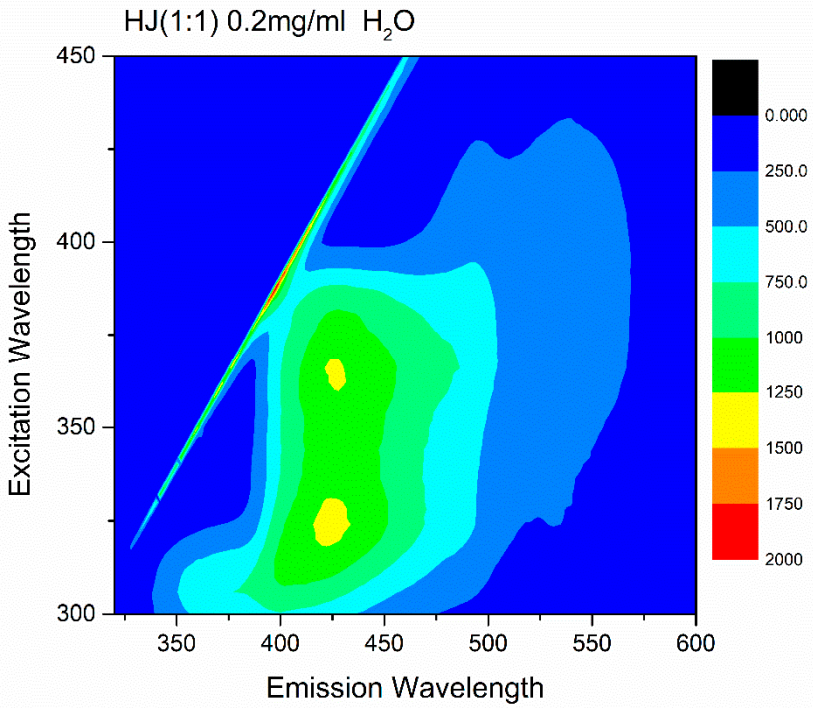
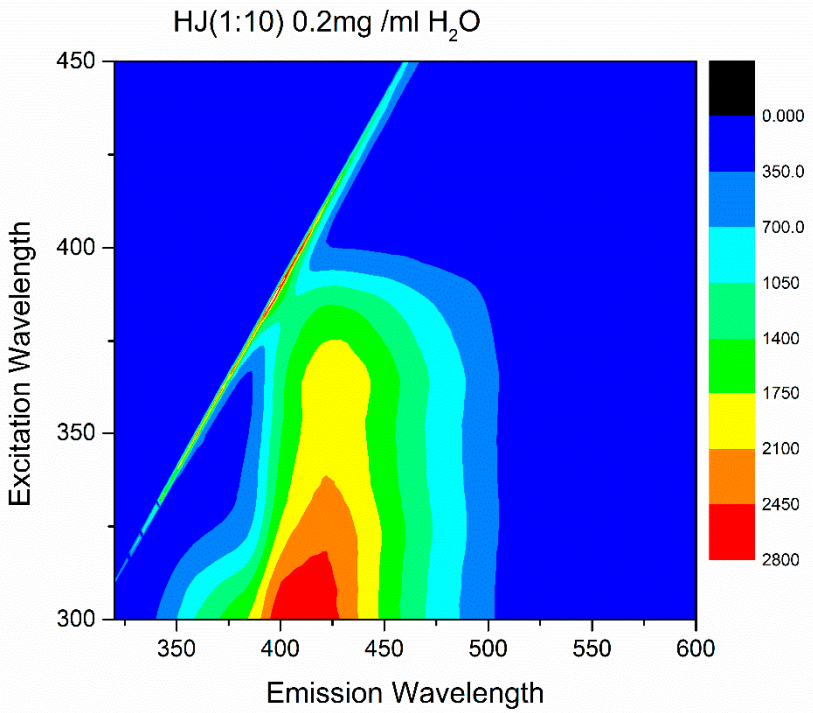


Figure S4. UV-Vis diffuse reflectance spectra of the synthesized pristine and heterojunction materials.


bCOF 0.2mg/ml H2O
Excitation Wavelength
Emission Wavelength
450
400
350
300
350
400
450
500
550
600
0.000
34.75
69.50
104.3
139.0
173.8
208.5
243.3
278.0


HJ(10:1) 0.2mg/ml H2O
Excitation Wavelength
Emission Wavelength
450
400
350
300
350
400
450
500
550
600
0.000
78.00
156.0
234.0
312.0
390.0
468.0
546.0
624.0


HJ(1:1) 0.2mg/ml H2O
Excitation Wavelength
Emission Wavelength
450
400
350
300
350
400
450
500
550
600
0.000
250.0
500.0
750.0
1000
1250
1500
1750
2000


HJ(1:10) 0.2mg /ml H2O
Excitation Wavelength
Emission Wavelength
450
400
350
300
350
400
450
500
550
600
0.000
350.0
700.0
1050
1400
1750
2100
2450
2800

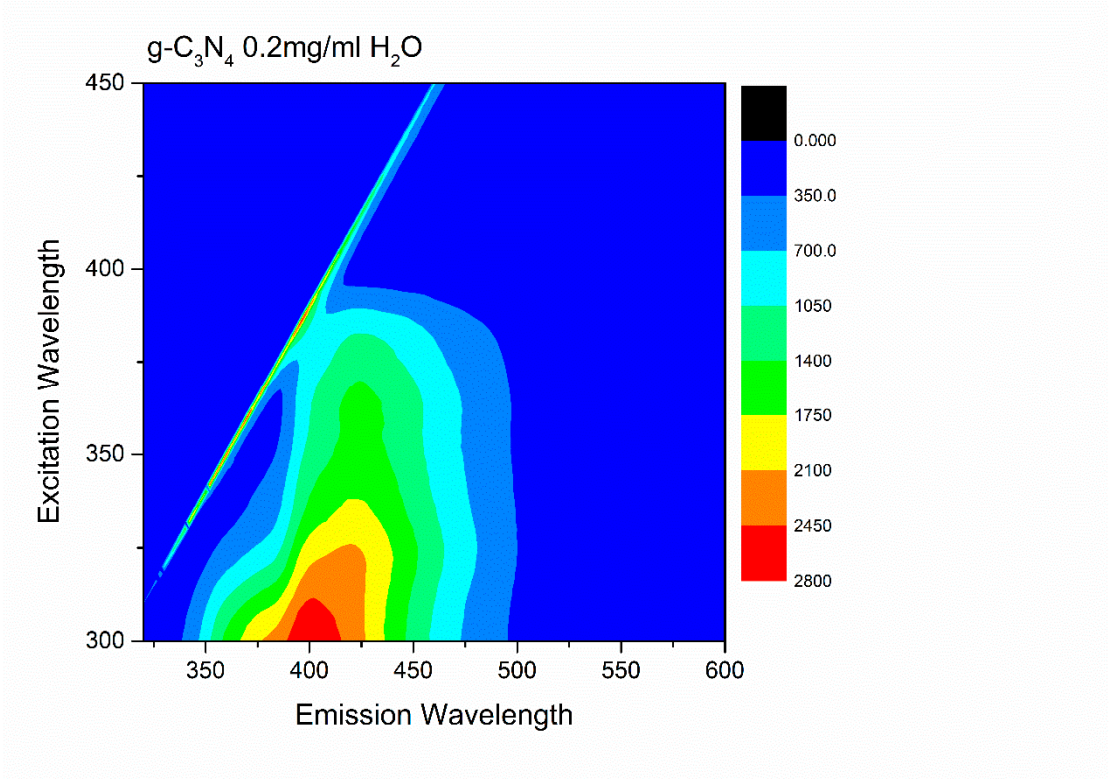


Figure S5. The excitation-dependent photoluminescence maps of the photocatalysts in aqueous dispersions. Concentration: 0.2 mg/ml. (Variations at the representation of the maximum in the color mapping occur also due to the scattering line provoked by the cuvette in the graphs.)

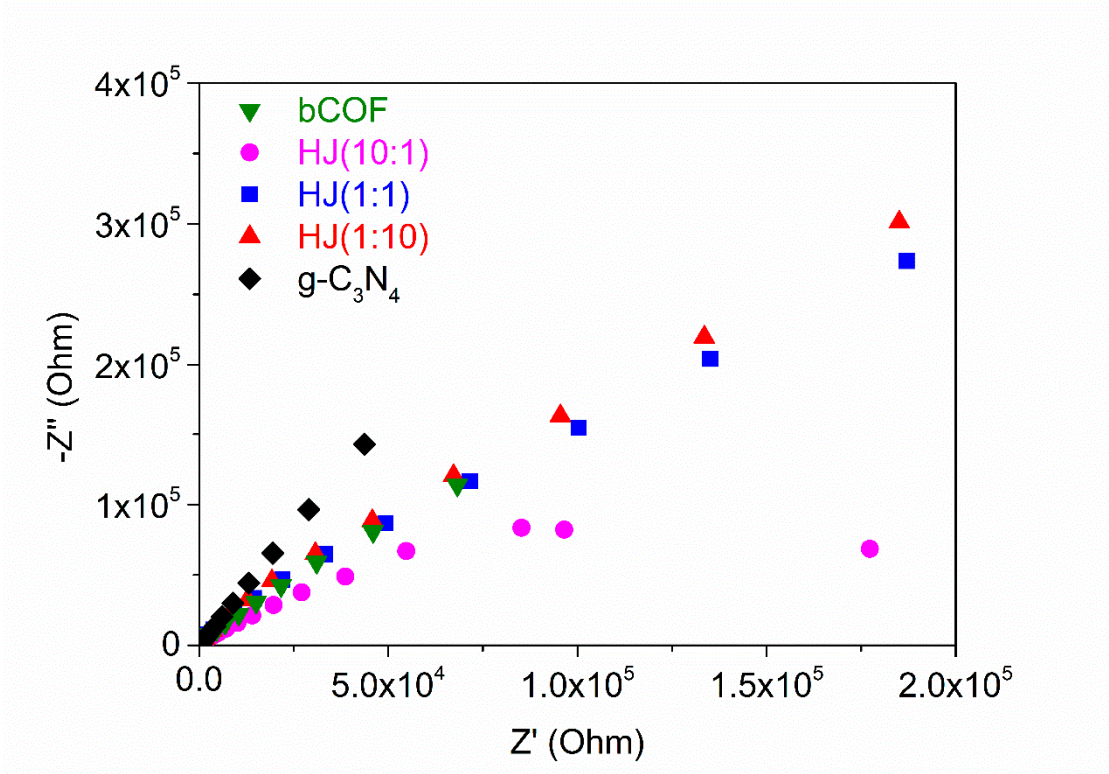
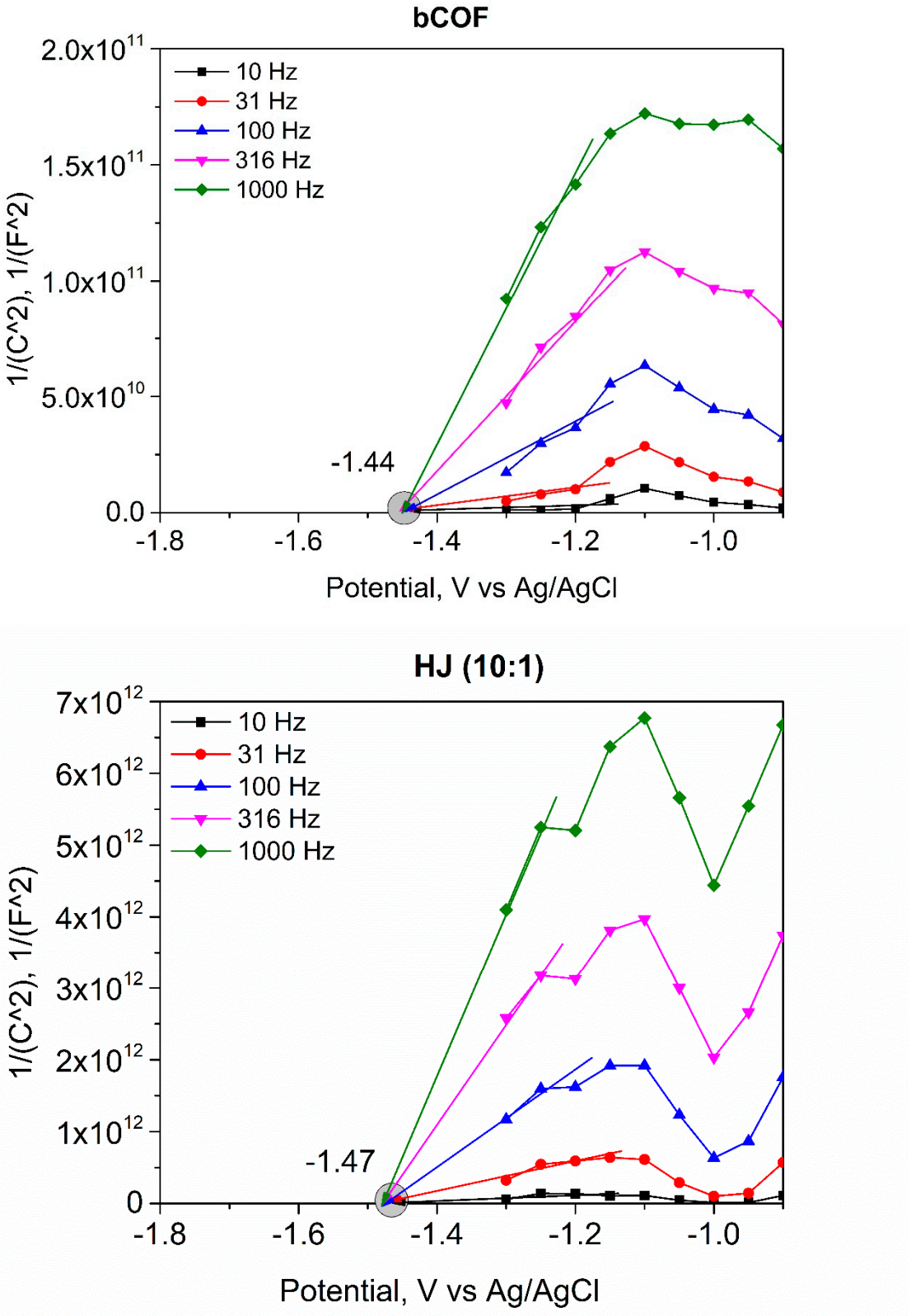


Figure S6. Electrochemical Impedance Spectroscopy measurements of the photocatalysts.



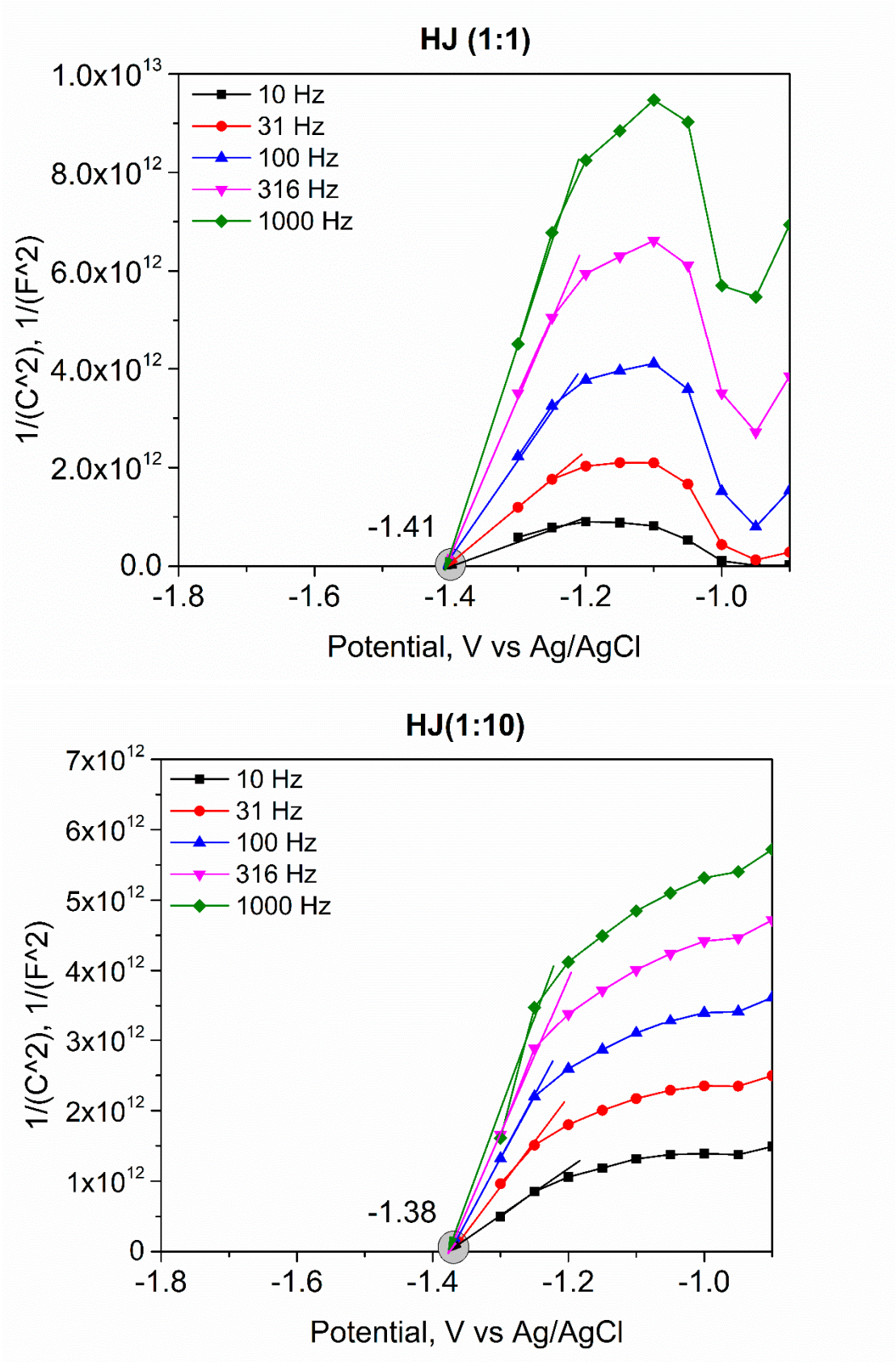


Figure S7. Mott-Schottky plots of the synthesized pristine and heterojunction materials.

Table S1. Multi-electron pathway for the CO_2 reduction: redox reaction and potentials.

	Redox reaction	Potential (V)
Photoreduction reactions	$CO_2 + e^- \rightarrow CO_2^{\cdot -}$	−1.90
	$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	−0.61
	$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	−0.53
	$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O$	−0.48
	$2H^+ + 2e^- \rightarrow H_2$	−0.41
	$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	−0.38
	$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	−0.24
Photooxidation reaction	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	+0.81

Table S2. The energy band gaps, the Mott-Schottky values and the band edge potentials of the photocatalysts.

vs. NHE, **pH=7**	E_g (eV)	Ag/AgCl	V_{CB}	V_{VB}
bCOF	2.75	-1.44	-1.30	1.45
HJ(10:1)	2.70	-1.47	-1.33	1.37
HJ(1:1)	2.95	-1.41	-1.27	1.68
HJ(1:10)	3.08	-1.38	-1.24	1.84
g-C_3N_4	3.04	-1.32	-1.18	1.86

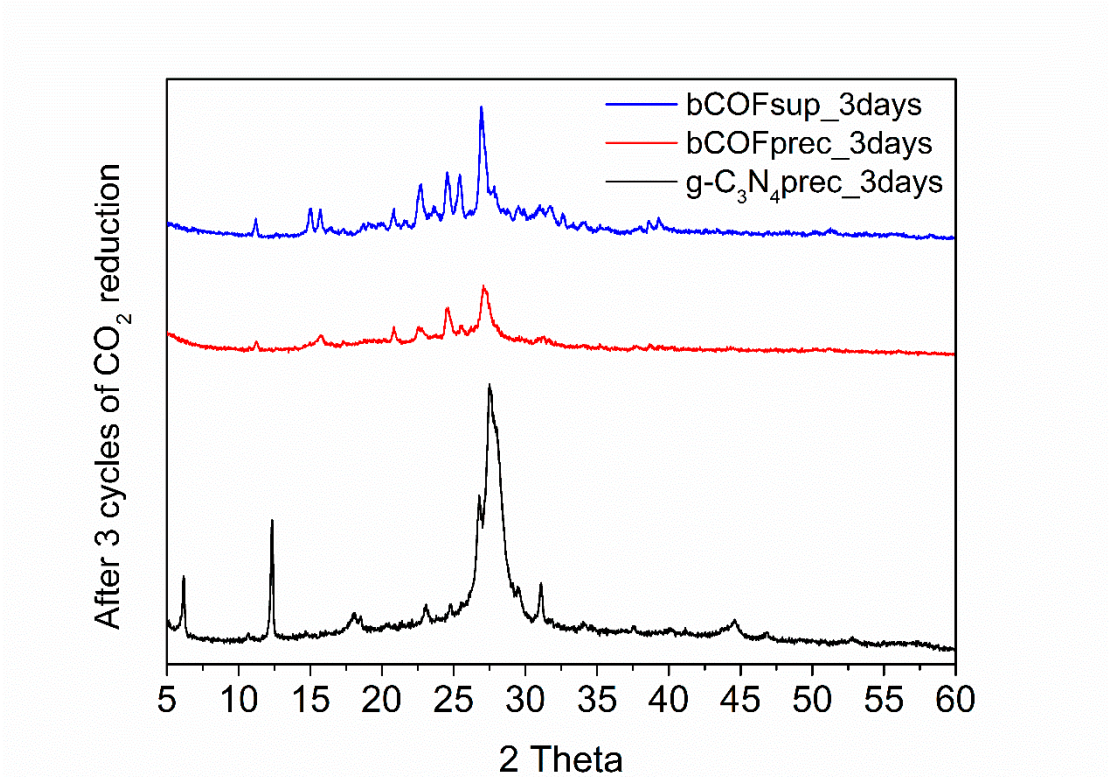


Figure S8. XRD patterns of the precipitate and supernatant pristine materials after the 3 days' sustainability cycle.

Table S3**.** Desorbed gaseous rates for the control experiment under Ar and UV irradiation for 18 h.

	H_2 (μmol g^{-1} h^{-1})	CO (μmol g^{-1} h^{-1})	CO_2 (μmol g^{-1} h^{-1})
bCOF	0.25	0.25	50.43
g-C_3N_4	1.07	1.32	27.80

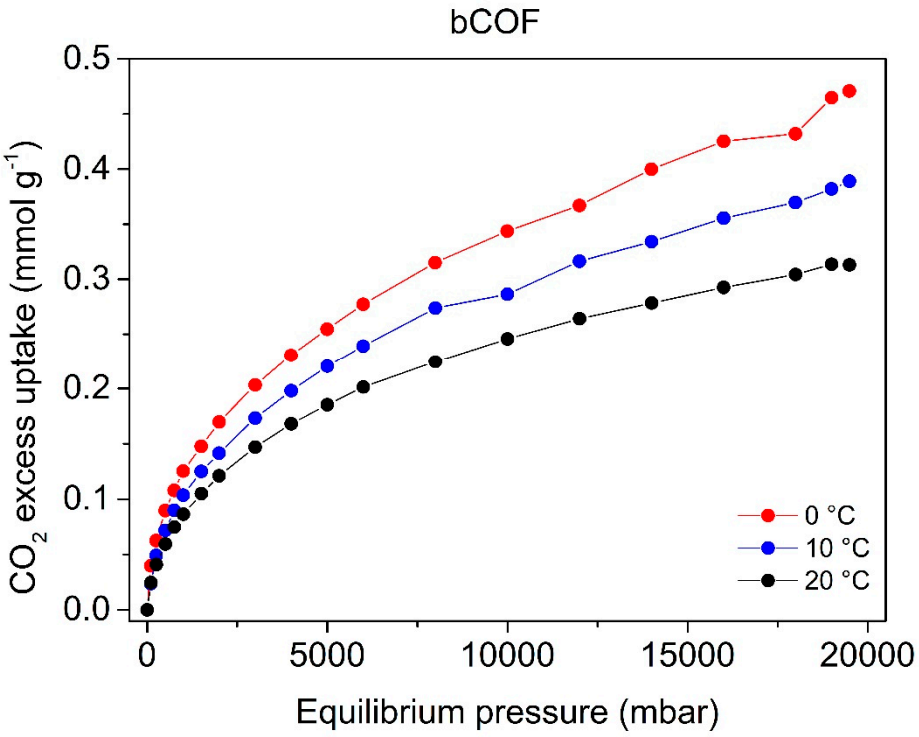


Figure S9. CO_2 sorption isotherms of bCOF measured at 0, 10 and 20 °C up to 20 bar.

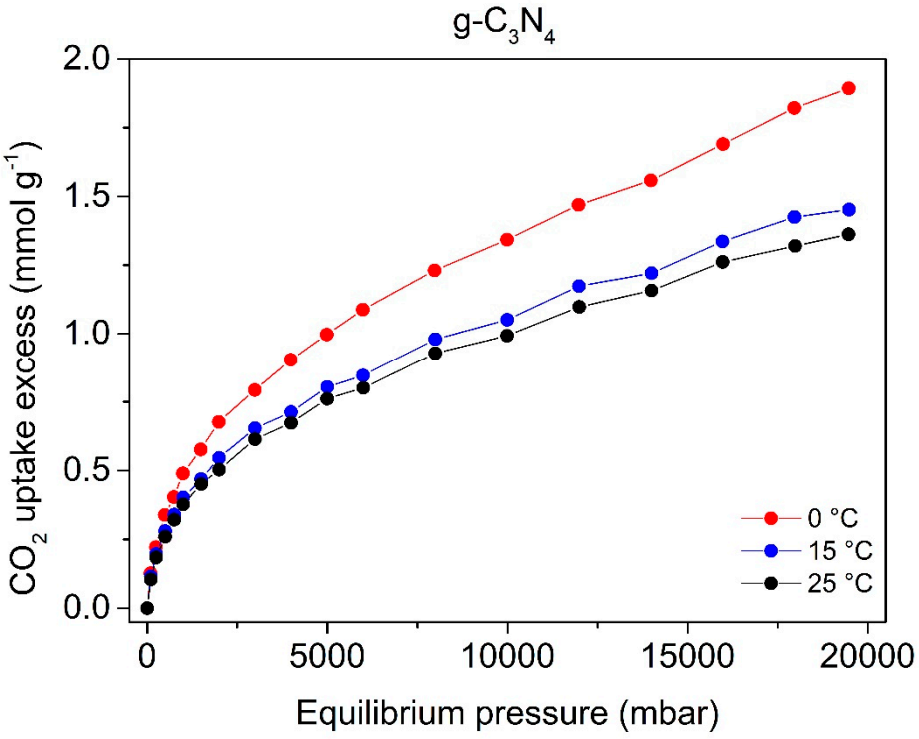


Figure S10. CO_2 sorption isotherms of g-C_3N_4 measured at 0, 10 and 25 °C, up to 20 bar.

Calculations for the formation rate of the products after CO_2 photoreduction.

The volume of the reactor is firstly calculated by its dimensions and then the occupied volume of the 100 ml of water is subtracted to determine the free volume filled with the gases. $V_{reactor}$= 242.11 ml, $V_{occupied}$=100 ml, V_{free}=141.11 ml

The total inlet CO_2 amount includes the gas of the free volume, where the pressure reaches 1.75 atm at 298.15 K and the soluble part into the aqueous dispersions. Through the ideal gas equation ($P_{total}V=n_{CO2}RT$) and Henrys' law ($S_{CO2}=kP$), the total inlet CO_2 is 0.0162 moles.

Based on the outlet molar ratio of CO and the partial pressure from the Dalton equation ($P_{CO}=xP_{total}$), the CO formation rate (μmol g^{-1} h^{-1}) is derived from further division with the mass of the photocatalyst and the hours of the photoreduction process.

As far as the H_2 production is concerned, the ideal gas equation is followed under the same conditions with P_{H2} the partial pressure combined with the outlet molar ratio. Then the outcome is divided by the mass of the photocatalyst and the hours of the photoreduction process to obtain the H_2 formation rate.

In the control experiments where CO_2 was substituted by argon in the reactor, the ideal gas equation was used to calculate the outlet amounts of H_2, CO and CO_2 gases under the same conditions.