Supplementary Information

Fe clusters embedded on N-doped graphene as photothermal catalyst for selective CO_2 hydrogenation

Horatiu Szalad,[a] Lu Peng,[a] Ana Primo,[a] Josep Albero *[a] and Hermenegildo García*[a]

Experimental procedure:

Materials preparation:

1000 mg chitosan, 625 µL acetic acid and 5 mg of $Fe(OAc)_2$ or $Co(OAc)_2$, for Fe@(N)C and Co@(N)C, respectively, were added into 50 mL milli-Q water. After chitosan dissolved completely, the solution was introduced dropwise, with a syringe (0.8 mm diameter needle), in an aqueous solution of sodium hydroxide (0.1M). The gel microspheres were formed and immersed in NaOH solution for 2h, then profusely washed with distilled water to pH=7. Then the resulting hydrogel microspheres were washed by a series of ethanol/water baths with an increasing concentration of ethanol (10, 30, 50, 70, 90 and 100 vol%, respectively) for 15 minutes in each. After that, the microspheres were reduced with 500 mL $NaBH_4$-ethanol solution (0.05 M) overnight and exchanged by supercritical CO_2. The resulting microspheres were pyrolyzed under Ar flow (200 mL/min), increasing the temperature at a rate of 2 ^oC/min up to 200 ^oC for 2h and then to 900 ^oC for 2 h.

Characterization:

Powder X-ray diffraction (XRD) patterns were collected with a Shimadzu XRD-7000 diffractometer by using $Cu_{\kappa\alpha}$ radiation (λ=1.5418Å), operating at 40 kV and 40 mA at a scanning speed of 10^o per min in the 2–90^o 2θ range. Diffuse reflectance UV/Vis spectra (DRS) in the range of 200 - 800 nm were collected in a Varian Cary 5000 spectrophotometer from Varian. HRTEM images were made with a Philips CM300 FEG microscope operating at 200 kV. X-ray photoelectron spectra (XPS) were measured on a SPECS spectrometer equipped with a Phoibos 1509MCD detector using a non-monochromatic X-ray source (Al and Mg) operating at 200 W. The samples were evacuated in the pre-chamber of the spectrometer at 1×10^{-9} mbar. The measured intensity ratios of the components were obtained from the area of the corresponding peaks after nonlinear Shirley-type background subtraction and corrected by the transition function of the spectrometer. The work function of the apparatus was calibrated with Ag, Au and Cu resulting in a value 4.2440 eV.

Transient absorption spectra were recorded using the forth harmonic of a Q switched Nd:YAG laser (Quantel Brilliant, 266 nm, 15 mJ/pulse, 7 ns fwhm) coupled to a mLFP-122 Luzchem miniaturized detection equipment. This transient absorption spectrometer includes a 300 W ceramic xenon lamp, 125 mm monochromator, Tektronix TDS-2001C digitizer, compact photomultiplier and power supply, cell holder and fiber-optic connectors, computer interfaces, and a software package developed in the LabVIEW environment from National Instruments. The laser flash generates a 5 V trigger pulses with programmable frequency and delay. The rise time of the detector/digitizer is ~3 ns up to 300 MHz (2.5 GHz sampling). The monitoring beam is provided by a ceramic xenon lamp and delivered through fiber-optic cable. The laser pulse is probed by a fiber that synchronizes the photomultiplier detection system with the digitizer operating in the pre-trigger mode.

Photo-assisted tests:

A 40 mg quantity of photocatalyst was loaded into a cilindrical quartz photoreactor equipped with a nickel alloy thermocouple connected to a heating ribbon and a temperature controller. H_2 and CO_2 were introduced in 1:1 molar ratio up to achieve a final pressure of 1.4 bar. The photoreactor was heated at different temperatures prior irradiation and when the desired temperature was stabilized the photocatalyst was irradiated from the top (6 cm above) through a fiber optics with UV-Vis light from a 300 W Xe lamp. The evolved gases were analyzed using a gas chromatograph (Agilent 7890A) equipped with Carboxene 1010 column analysing CO_2, CO and up to C4 hydrocarbons. Quantification of the percentage of each gas was based on prior calibration of the system injecting mixtures with known percentage of gases.

Table SI1. Summary of the photothermal CO_2 hydrogenation results indicating the photocatalyst, temperature, light intensity and CO evolution.

Sample	*Temperature (°C)*	*Light intensity (mW/cm^2)*	*CO evolution (mmol/g)*
Fe@(N)C	245	120	319.4
Fe@(N)C	245	0	152.2
Co@(N)C	245	120	1805.1
Co@(N)C	245	0	1385.8
(N)C	245	120	49.8
Fe@(N)C	205	120	33.1
Fe@(N)C	205	0	19.5
Fe@(N)C	225	120	51.1
Fe@(N)C	225	0	27.9
Fe@(N)C	265	120	468.2
Fe@(N)C	265	0	246.1
Fe@(N)C	288	120	1578.9
Fe@(N)C	288	0	1287.2

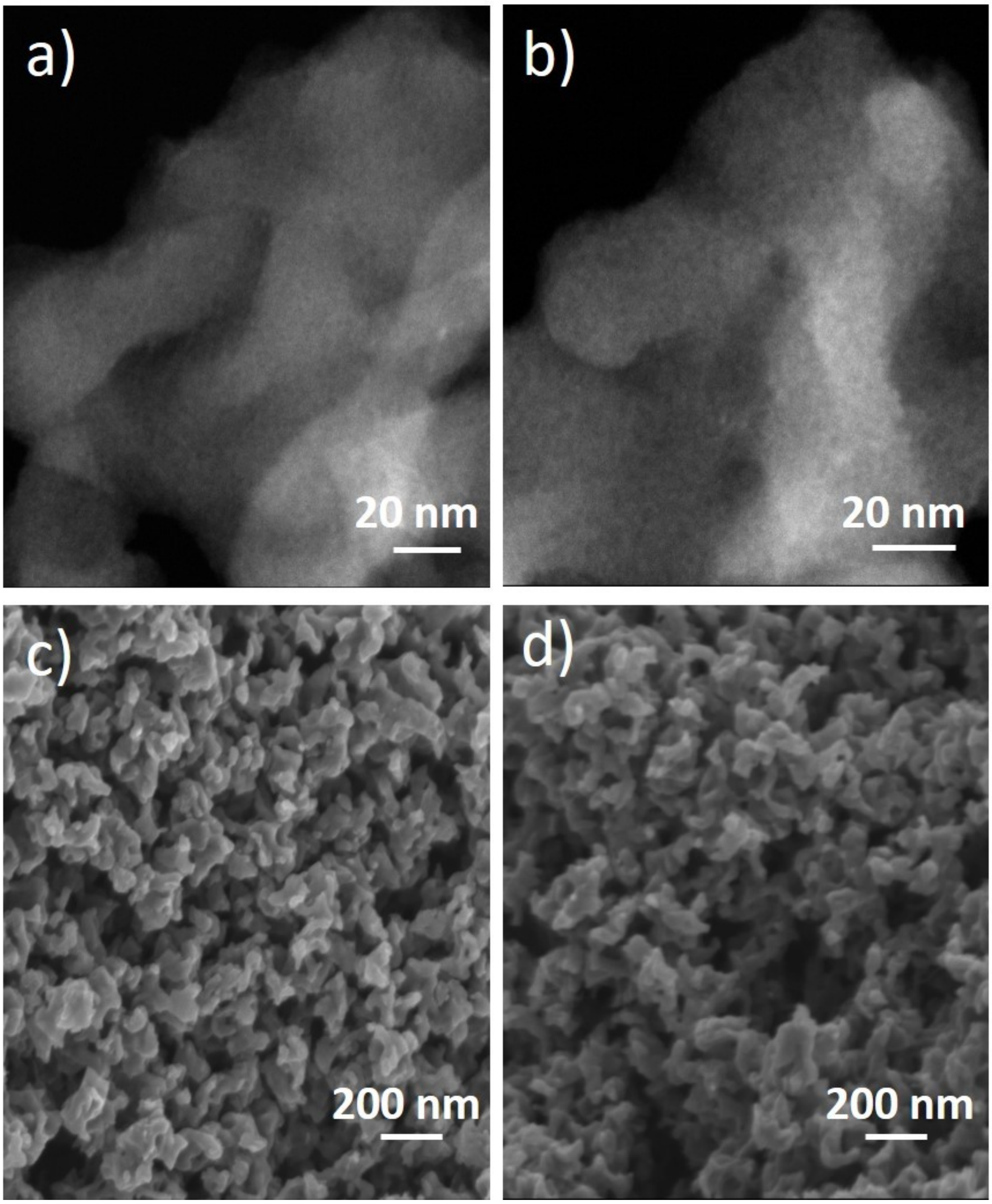


Figure SI1. ADF-STEM (a and b) and HRSEM (c and d) images of Fe@(N)C (a and c) and Co@(N)C (b and d) samples.

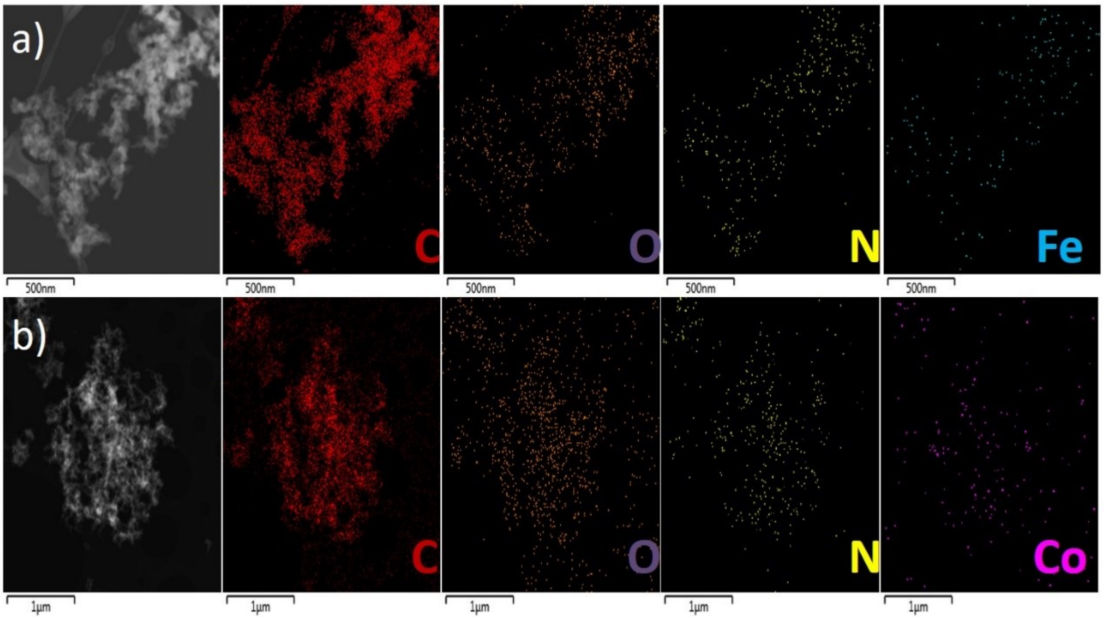


Figure SI2. Elemental mapping of representative Fe@(N)C (a) and Co@(N)C (b) STEM images.

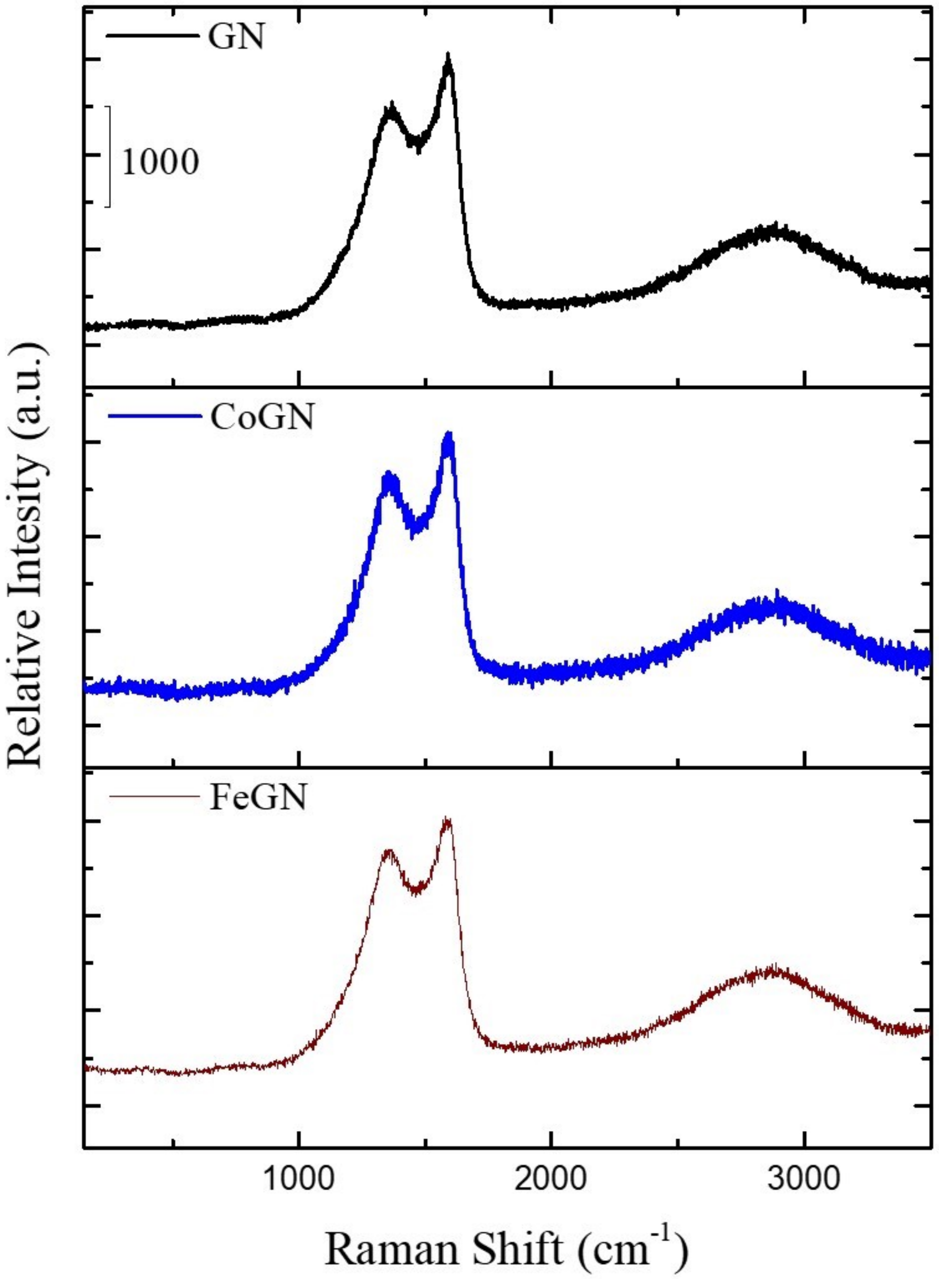


Figure SI3. Raman spectra of (N)C, Co@(N)C and Fe@(N)C.

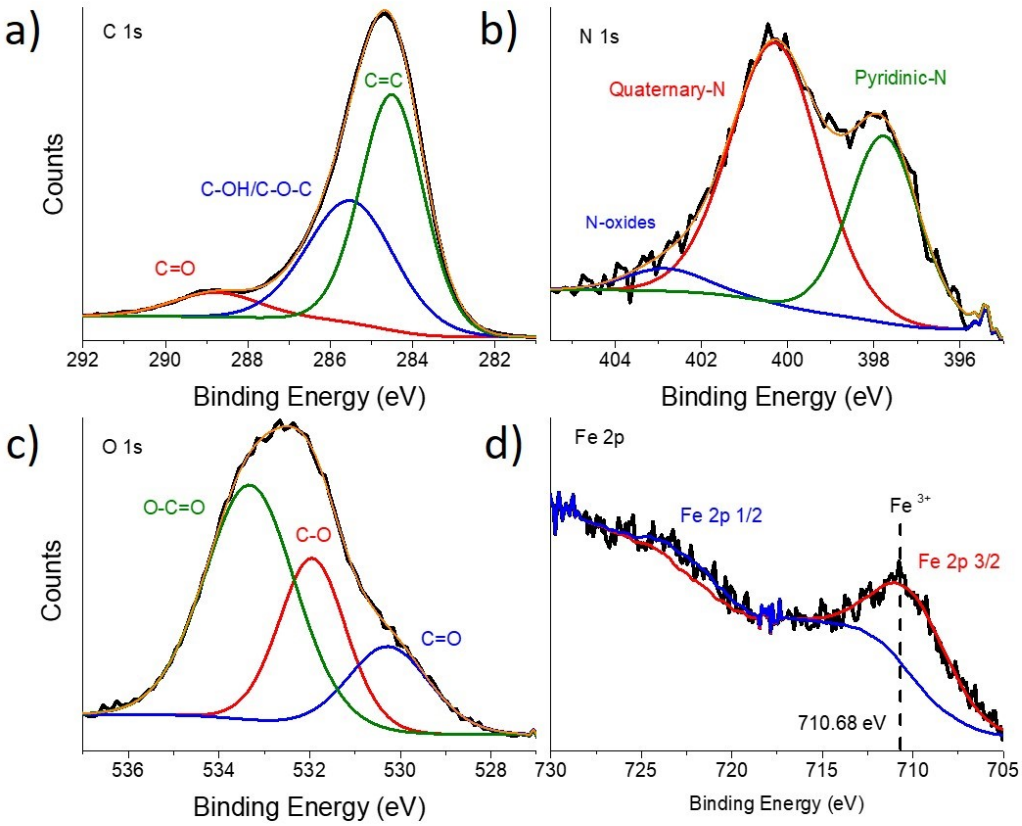


Figure SI 4. Experimental XPS a) C1s, b) N1s, c) O1s and d) Fe 2p peaks measured from Fe@(N)C sample.

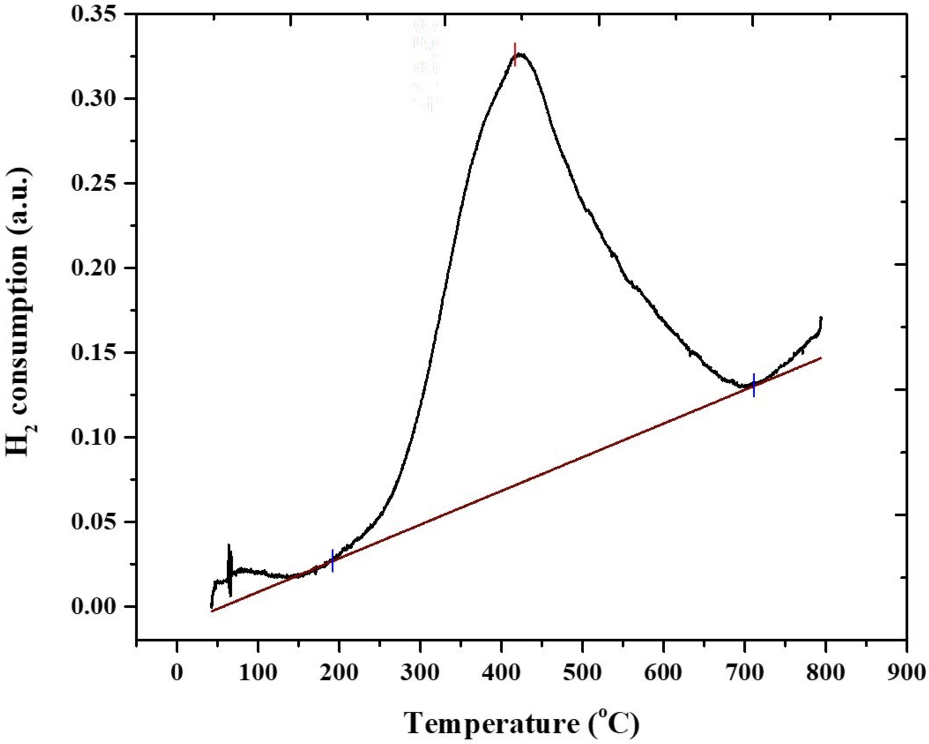


Figure SI5. TPR profile of Fe@(N)C.

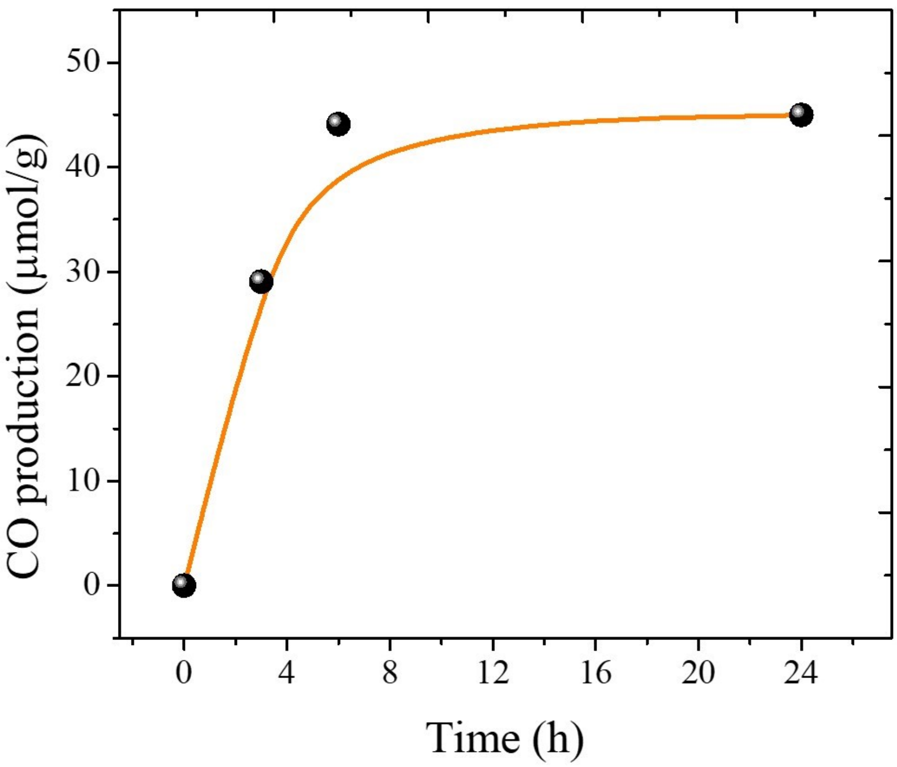


Figure SI6. CO evolution using (N)C sample at 245 ^oC and 120 mW/cm^2 light irradiation. 40 mg of each photocatalyst were used, partial pressures for H_2 and CO_2 was 0.7 bar. The red line only indicates the experimental trend.

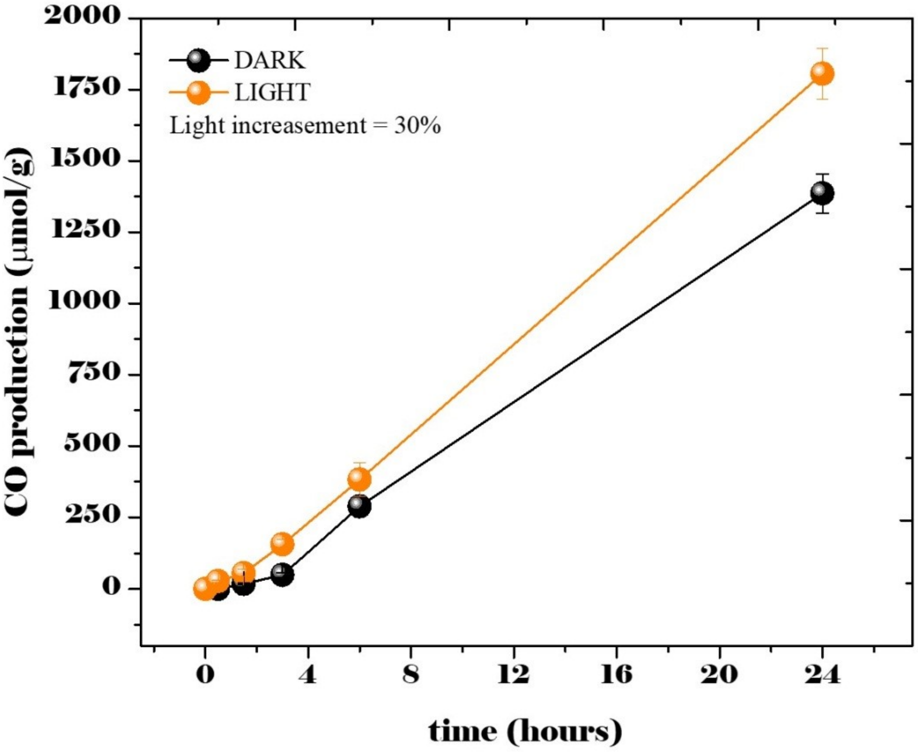
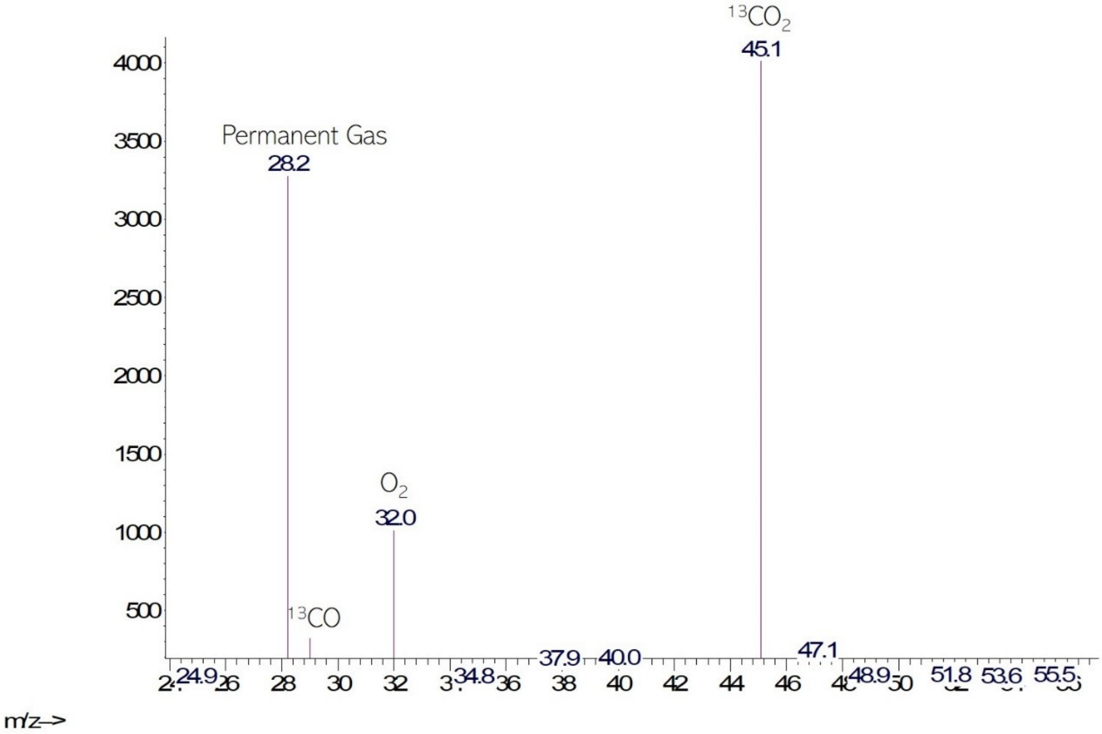


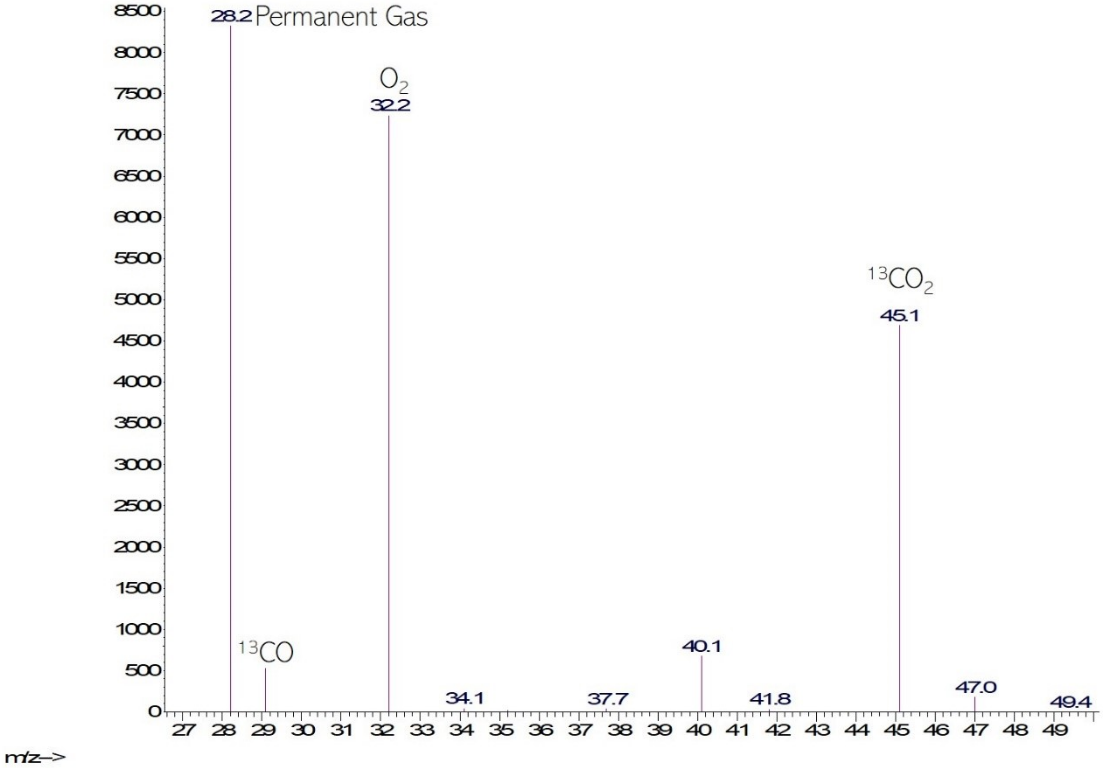
Fig. S7. CO evolution using Co@(N)C photocatalysts at 245 ^{o}C under 120 mW/cm^2 illumination (orange) and dark conditions (black). Reaction conditions: 40 mg of photocatalyst, partial pressures for H_2 and CO_2 0.7 bar. Lines between the experimental points just indicate the trend.

a)



$^{13}CO_2$
45.1
Permanent Gas
28.2
O_2
32.0
^{13}CO
24.9
34.8
37.9
40.0
47.1
48.9
51.8
53.6
55.5
4000
3500
3000
2500
2000
1500
1000
500
26
28
30
32
36
38
40
42
44
46
50
m/z-->

b)



28.2
Permanent Gas
O_2
32.2
$^{13}CO_2$
45.1
^{13}CO
40.1
34.1
37.7
41.8
47.0
49.4
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
m/z-->

c)

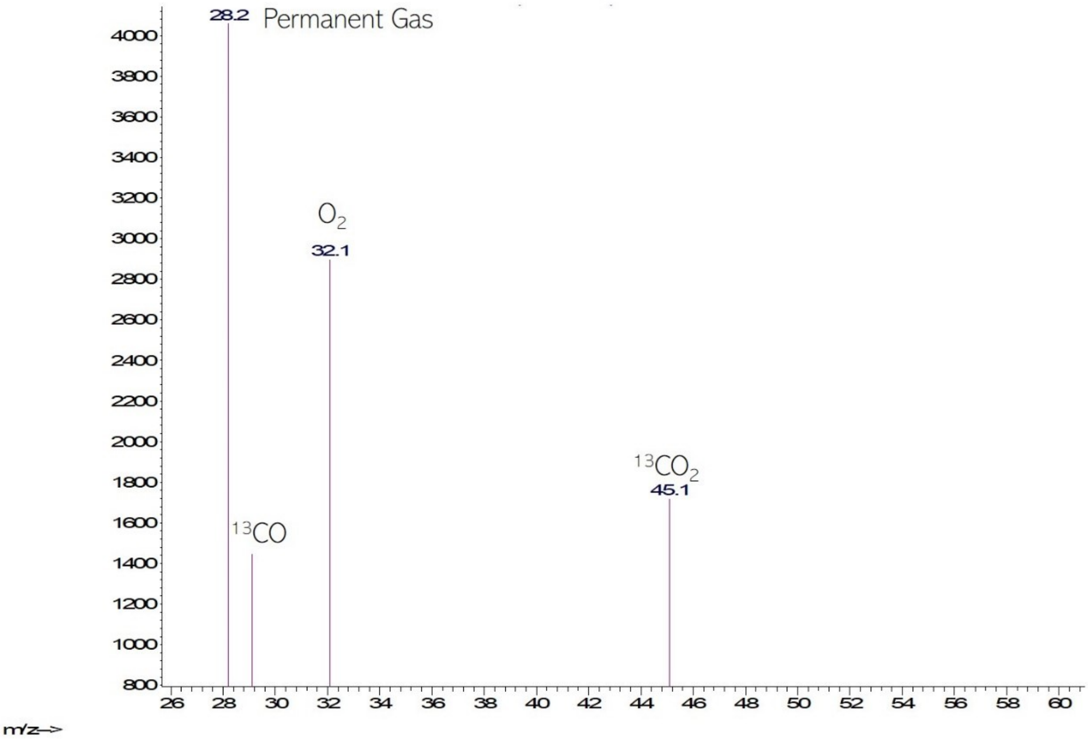


Figure SI8. Mass spectra of the reaction products from $^{13}CO_2$ and H_2 promoted by Fe@(N)C measured at 4 (a), 8 (b) and 24 h (c), showing than ^{13}CO is the main reaction product and it grows with time, as revealed by the relative peak at *m/z 29*.

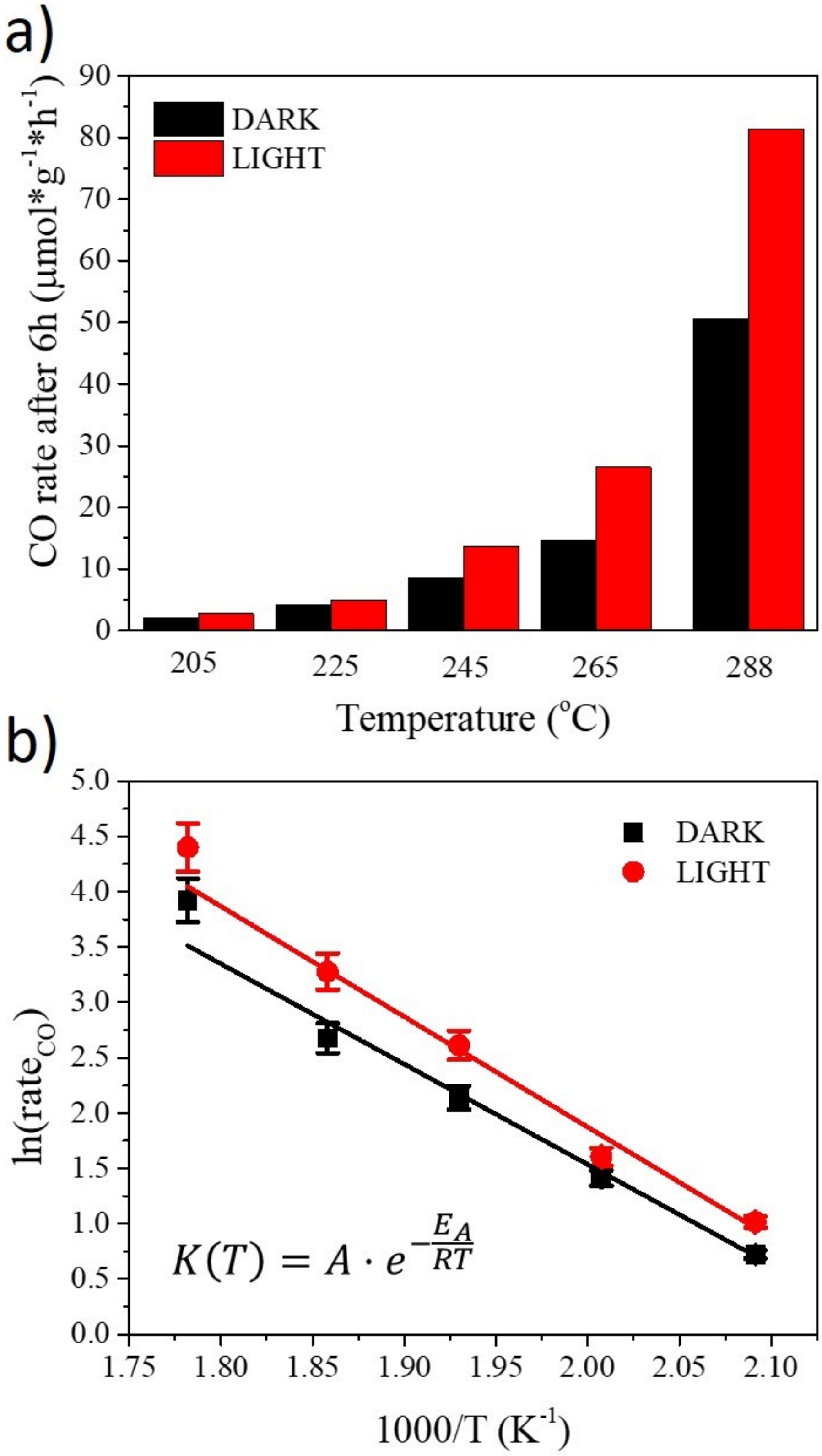


Figure SI9. CO production rate at different temperatures under light (120 mW/cm^2, orange) and dark (black) conditions using Fe@(N)C sample. (b) CO rate constant vs. temperature under light (orange) and dark (black) conditions. Solid lines correspond to the experimental data fitting to the Arrhenius equation (showed as inset). Error bars indicate standard deviation.

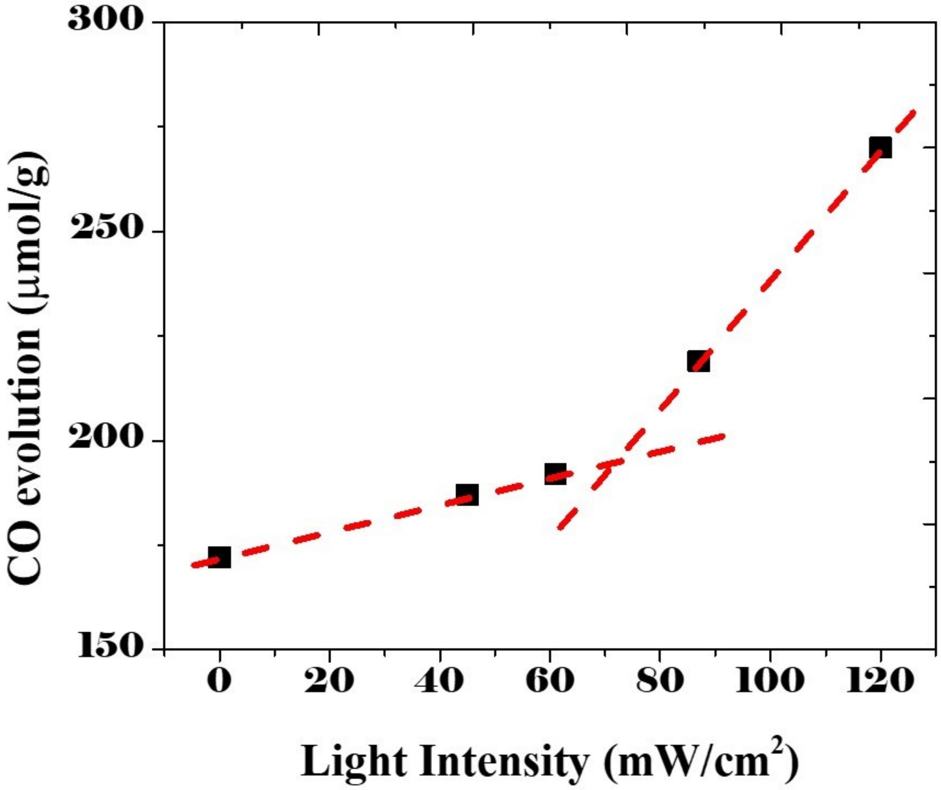


Figure SI10. CO evolution at 245 ^oC upon different light irradiation after 24 h reaction. 40 mg of each photocatalyst were used, partial pressures for H_2 and CO_2 was 0.7 bar. The red dashed lines only indicate the experimental trend.

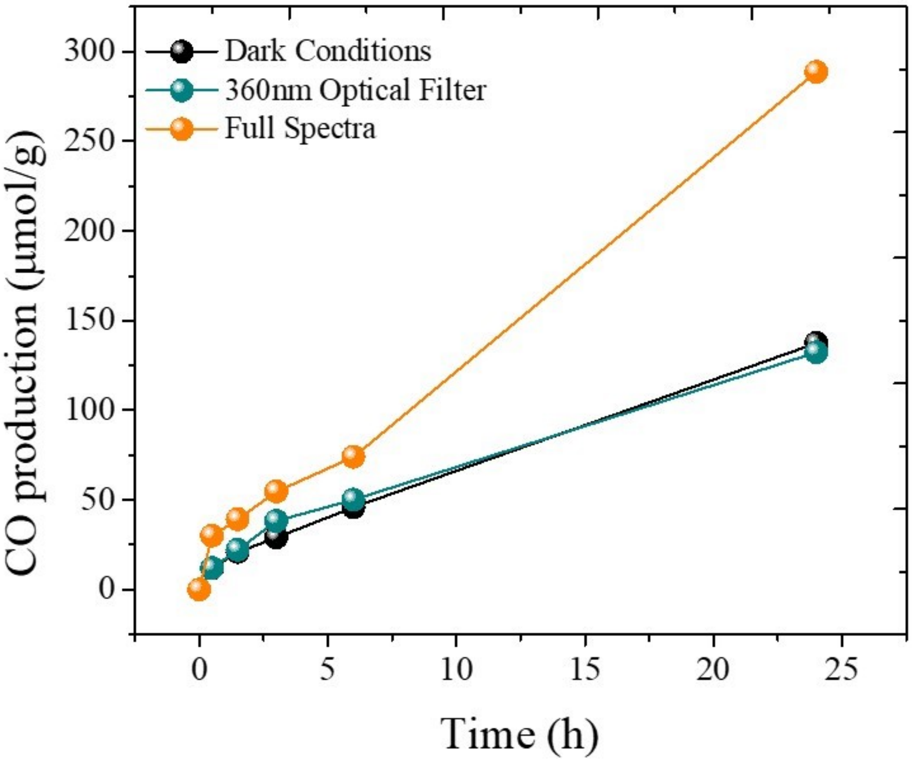


Fig. SI11. CO evolution using Fe@(N)C sample at 300 °C and full light spectrum (orange) (1200 W/m^2), UV light (cut-off filter 360 nm; blue), and in the dark (black). 40 mg of each photocatalyst were used, partial pressures for H_2 and CO_2 was 0.7 bar.

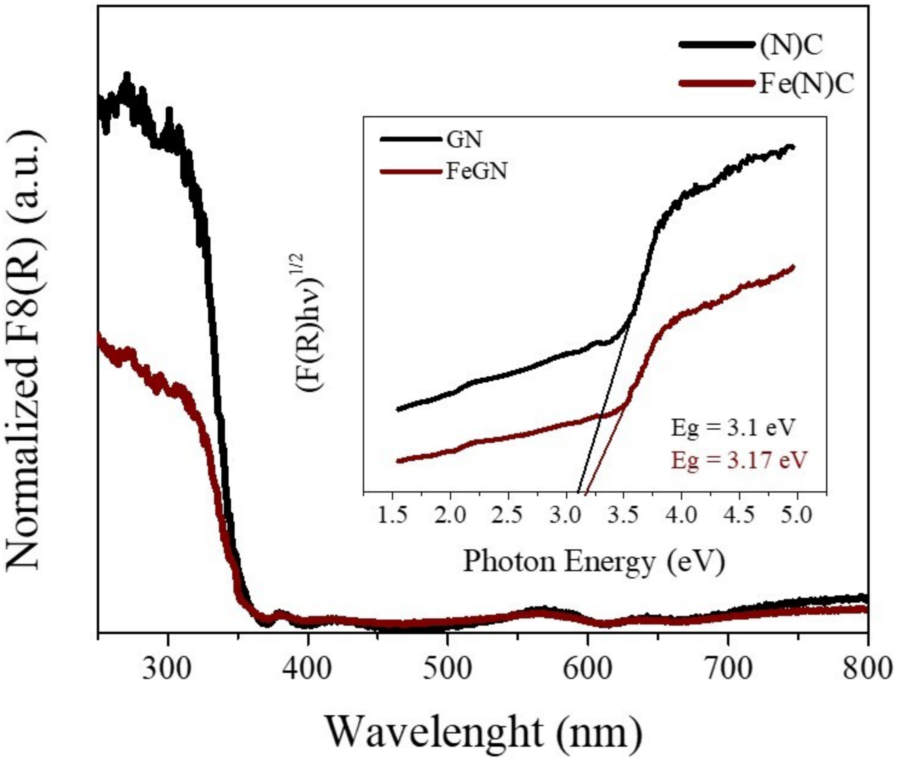


Figure SI12. Diffuse reflectance UV-Vis absorption spectra of (N)C and Fe@(N)C. Inset shows Tauc plot of (N)C and Fe@(N)C obtained from diffuse reflectance spectra, indicating the estimated band gaps.

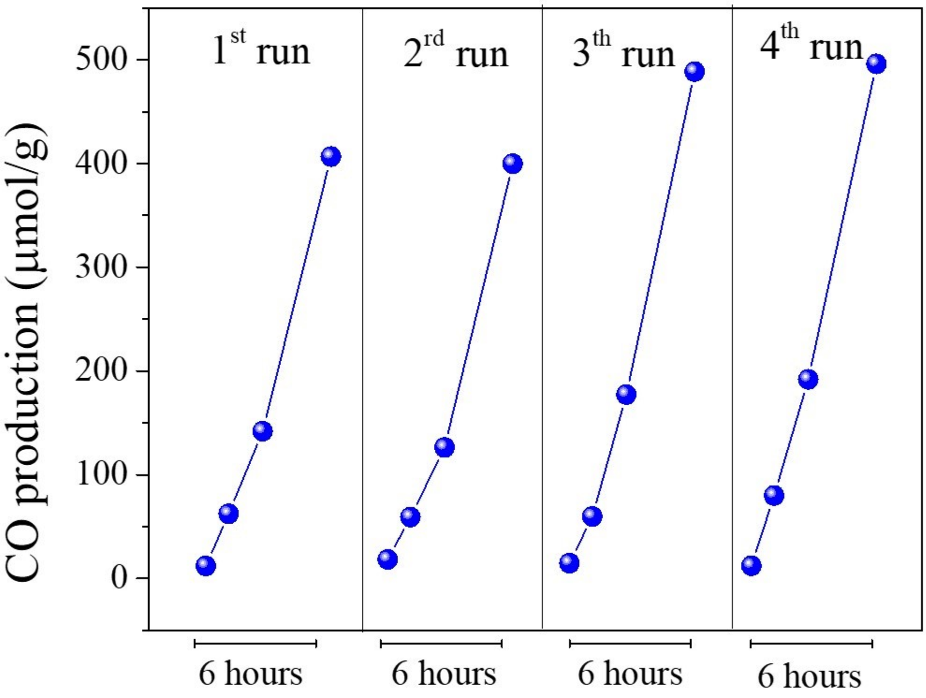


Fig. SI13. CO evolution using Fe@(N)C photocatalyst at 288 °C and 120 mW/cm^2 light irradiation after exhaustive Ar purging cycles. 40 mg of photocatalyst, partial pressures for H_2 and CO_2 was 0.7 bar in each cycle.

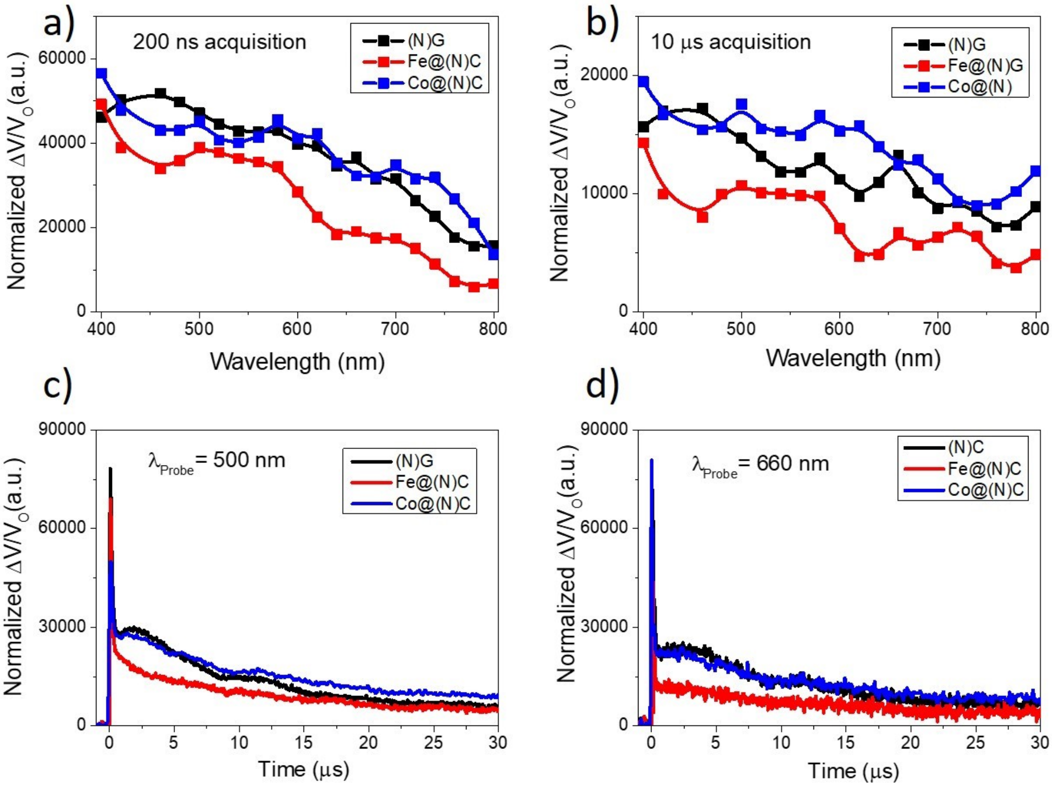


Figure SI14. Transient absorption spectra of (N)C (black), Fe@(N)C (red) and Co@(N)C (blue) iso-absorbing dispersions at 355 nm in acetonitrile acquired at 200 ns (a) and 10 µs (b), and signal decay monitored at 500 nm (c) and 660 nm (d).

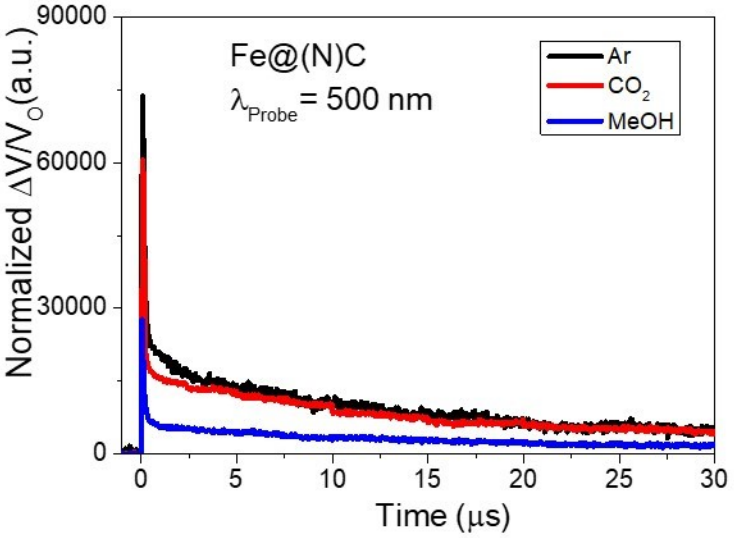


Figure SI15. Transient absorption signal decays monitored at 500 nm upn 355 nm laser excitation of Fe@(N)C under Ar atmosphere (black), CO_2 saturated (red) and acetonitrile:MeOH (85:15, v:v (blue) iso-absorbing dispersions at 355 nm.