# Supplementary Information

CO2 capture and photocatalytic reduction using bifunctional TiO2/MOF nanocomposites under UV-visible irradiation

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Figure S1. Photocatalytic gas/solid reactor setup used to evaluate photocatalytic CO2 reduction: 1) CO2 cylinder, 2) H2 generator, 3) mass flow controllers, 4) non‑return valves, 5) photoreactor, 6) xenon arc lamp, 7) pressure transducer, 8) gas chromatograph, 9) vacuum pump.



**Figure S2. Thermogravimetric curves of TiO2, NH2‑UiO‑66 and TiO2/NH2‑UiO‑66 nanocomposites (x‑TiMOF) under N2 atmosphere.**

**Table S1. Thermal gravimetric analysis of of TiO2, NH2‑UiO‑66 and TiO2/NH2‑UiO‑66 composites (x-TiMOF).**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | **Final mass (% mass)** | **Δmass lossa (% mass)** | **xTiO2*b* (% mass)** | **xNH2-UiO-66*c* (% mass)** | **xTiO2Theo*d* (% mass)** |
| TiO2 | 97.2 |  | 100.0 | 0.0 | 100.0 |
| 1-TiMOF | 89.0 | 35.1% | 81.0 | 19.0 | 80.0 |
| 2-TiMOF | 88.8 | 35.3% | 80.5 | 18.5 | 70.0 |
| 3-TiMOF | 86.6 | 32.7% | 75.5 | 24.5 | 60.0 |
| 4-TiMOF | 81.3 | 27.4% | 63.2 | 16.8 | 45.0 |
| NH2-UiO-66 | 53.9 |  | 0.0 | 100.0 | 0.0 |

*a*. Calculated: Δmass loss = TiO2 Final mass – Final mass, *b*. Calculated: xTiO2 = (Δmass loss)/(TiO2 Final mass – NH2‑UiO‑66Final mass), *c*. xNH2-UiO-66 = 1 - xTiO2, *d*. xTiO2 theo is the expected TiO2 content base on the unmodified NH2‑UiO‑66 synthesise yield



Figure S3. XPS survey spectra of the pure NH2-UiO-66 and TiO2 and the 2-TiMOF nanocomposite.



**Figure S4. High resolution XPS spectra in the region of : a) C1s, b) N1s and c) O 1s.**

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Figure S5. N2 adsorption-desorption isotherms at -196 °C.

Table S2. Experimental and calculated BET surface areas for the photocatalysts.

|  |  |  |
| --- | --- | --- |
|  | **BETexp (m2 g-1)** | **BETcalca (m2 g-1)** |
| TiO2 | 42 | 42 |
| 1-TiMOF | 173 | 200 |
| 2-TiMOF | 202 | 204 |
| 3-TiMOF | 268 | 245 |
| 4-TiMOF | 284 | 347 |
| NH2-UiO-66 | 871 | 871 |

*a.* BETcalc = xNH2-UiO-66.BETNH2-UiO-66 + xTiO2.BETTiO2

Table S3. CO evolution rates for photocatalysts.

|  |  |  |
| --- | --- | --- |
|  | **CO (µmol g-1 h-1)***a* | **CO (µmol cm-2 h-1)***b* |
| TiO2 | 2.85 | 0.0019 |
| 1-TiMOF | 3.74 | 0.0025 |
| 2-TiMOF | 4.24 | 0.0028 |
| 3-TiMOF | 3.37 | 0.0022 |
| 4-TiMOF | 2.85 | 0.0019 |
| NH2-UiO-66 | 1.50 | 0.0010 |

*a.* 3 mg photocatalyst mass used, *b.* photocatalyst illumination area 4.5 cm2



Figure S6. a) Kulbelka-Munk absorption spectra and b) Tauc plot of TiO2, NH2‑UiO‑66 and TiO2/NH2‑UiO‑66 composites.



Figure S7. 2-TiMOF photocatalytic CO evolution as a function of time.



Figure S8. 2-TiMOF CO evolution repeated for three 6 h photocatalytic cycles.



Figure S9. 2-TiMOF XRD patterns before and after photocatalytic testing.



Figure S10. Transient absorption spectroscopy of pure TiO2 (A & D), NH2-UiO-66 MOF (B & E) and a composite 2-TiMOF (C & F) showing the transient absorption spectra at select times from 10 µs to 900 ms after a laser pulse (A-C) and the kinetics of charge carrier recombination at numerous wavelengths from 500 – 900 nm (D-F), [λexc = 355 nm, ~2 mJ.cm-2, 6 ns pulse width, 0.6 Hz].