Reverse Semi-Combustion Driven by Titanium Dioxide-Ionic Liquid Hybrid Photocatalyst

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1. Preparation of TiO$_2$@IL catalysts

The TiO$_2$@[BMIm][Im] (around of 3 wt%) and [BMIm]Cl (around of 9 wt%), were prepared according to following procedure: The corresponding ionic liquid (IL) [BMIm][X] (X= Im, Cl) (6 g) was dissolved in distilled water (10 mL). The concentrated solution was mixture with 3 g of commercially available titania Evonix-P25 (TiO$_2$) under vigorous stirring for 30 minutes. The obtained solid was filtered and washed with distilled water (2 x 20 mL). The solid material was dried in vacuum for 3 h at 50 °C.

The others catalysts were prepared according to following procedure: The correspondent IL [BMIm][NTf$_2$], [BMPy][Im], [(But)$_3$EP][Im] (0.09 g) was added into a flask containing the TiO$_2$ (3 g). In the same flask 15 mL of CHCl$_3$ was add and the reaction was stirring for 30 minutes under ultrasound. After this time, the excess of solvent was removed by vacuum and the solid dried for 3 h at 50 °C.

![Figure S1. Structure and abbreviation of ILs used in this study.](image)

[BMIm][X]  [BMPy][Im]  [(But)$_3$EP][Im]  [NTf$_2$]  [Im]
2. NMR analysis of [BMIm][Im] IL before and after the photolysis

The NMR analyses were performed on a Bruker Avance 400 spectrometer, equipped with a BBO 5 mm probe with z-gradient operating at 400 MHz for 1H, and 100 MHz for 13C. The spectra were obtained at 298 K unless otherwise specified. Chemical shifts are reported in parts per million (ppm, δ) referenced to D2O and DMSO-d6 as an external reference (capillary).

Figure S2. 1H NMR (400 MHz, 25 °C) spectra of the aqueous solution of [BMIm][Im] IL: a) (D2O) before reaction; b) (DMSO-d6 capillary) after reaction (hv + CO2).
Figure S3. $^{13}$C-$^1$H NMR (100 MHz, 25 °C) spectra of the aqueous solution of [BMIm][m] IL (DMSO-d$_6$ capillary) after photoreaction ($h\nu +$ CO$_2$). No signal ~162 ppm of oxidized imidazolium ring (i.e 2-imidazolidinone) is observed, which exclude the possibilities that the unidentified products are the oxidized forms of the ionic liquid.

Figure S4. High zoom of $^1$H NMR (400 MHz, 25 °C) spectra of aqueous solution of [BMIm][m] IL (DMSO-d$_6$ capillary) after photoreaction ($h\nu +$ CO$_2$).
3. General Characterisation

Infra-Red (IR) analyses were conducted using a Bruker Alpha (Fourier transform infrared) FTIR spectrometer with an ATR attachment. Data collection utilised 256 cumulative scans with a resolution of 4 cm\(^{-1}\). CHN Elemental analysis of the ILs immobilized on the support surfaces was carried out on a CHN Exeter Analytical CE-440 using helium (99.997% purity) as a carrier and oxygen for the combustion (99.995% purity). Thermogravimetric (TGA) analyses were performed in a TA Instruments T5500 Thermogravimetric analyser in a stepwise programmed up to 1000 °C (10 °C/min) using a nitrogen (99.995% purity) flow of 25 mL min\(^{-1}\). Samples were held in Pt (high-temperature resistant) pans. Data analysis was processed using TRIOS Discovery program. N\(_2\) isotherms of the catalysts, previously degassed at 180 °C under vacuum for 18 h, were obtained using TriStar and 3Flex Micromeritics instruments. Specific surface areas were determined by the BET multipoint method, and average pore size was obtained by the BJH method.

![Figure S5. (a) FTIR absorbance and, (b) BET N\(_2\)-physisorption isotherms of pure TiO\(_2\) and TiO\(_2\) impregnated with [BMIm][Im], [BMIm][NTf\(_2\)], [BMIm]Cl, [BMPy][Im] and [(But)\(_3\)EP][Im].](image)

### Table S1. Textural properties of the TiO\(_2\) and hybrid TiO\(_2@IL\) materials.

| Entry | Photocatalyst | Ratio\(_{\text{Oct}}\)\(^{[a]}\) | IL\(^{[b]}\) wt. % | \(S_{\text{BET}}\)\(^{[c]}\) m\(^2\).g\(^{-1}\) | \(V_{\text{pore}}\)\(^{[d]}\) cm\(^3\).g\(^{-1}\) |
|-------|--------------|---------------------------------|----------------|-----------------|-----------------|
| 1     | TiO\(_2\)    | -                               | -              | 42.6\(^{[1]}\)   | 0.017           |
| 2     | TiO\(_2@\)BMIm][Im] | 2.8                            | 3.2            | 19.2            | 0.007           |
| 3     | TiO\(_2@\)BMIm][NTf\(_2\)] | 3.5                            | 5.5            | 18.9            | 0.008           |
| 4     | TiO\(_2@\)BMIm][Cl]   | 4.2                            | 8.9            | 20.8            | 0.009           |
| 5     | TiO\(_2@\)BMPy][Im]   | 2.8                            | 6.4            | 33.8            | 0.014           |
| 6     | TiO\(_2@\)[(But)\(_3\)EP][Im] | 7.2                            | 6.5            | 29.2            | 0.012           |

\(^{[a]}\) Determined by elemental analysis. \(^{[b]}\) Determined by TGA analysis. \(^{[c]}\) Determined by BET multipoint method and BJH method.

4. UV-Vis Diffuse Reflectance Spectroscopy

UV-Vis diffuse reflectance was performed by using a CARY 5000 spectrophotometer. TiO\(_2\) shows an expected band gap of 3.3 eV\(^{[1]}\) while the hybrid TiO\(_2@IL\) displayed a red shift of 0.2 eV independently of the IL.
5. Raman Spectroscopy

Raman spectroscopy was performed by using a Horiba-Jobin-Yvon LabRAM HR spectrometer, with a laser wavelength of 785 nm operating at a power of ca. 4 mW and a 600 lines mm⁻¹ grating. Spectra were collected by averaging 2 acquisitions of 15 s duration. The presence of Anatase phase was observed for all samples and no significantly shift/change was observed in the peak position and FWHM (143.3 ± 0.1 cm⁻¹ and 8.8 ± 0.1 cm⁻¹, respectively). The higher intensity displayed for the samples with IL may suggest a decrease of the scattering due to the hybrid morphology (Table S1) which might lead an enhancement of the Raman signal. Indeed, deeper investigations are necessary to fully understand the cause of the Raman signal enhancement to hybrid TiO₂@IL, which will be done in the future since this is not the aim of this work.

6. XPS Spectroscopy

XPS probes the upper surface of a material to depths of about 10 nm with XPS signal dominated by the surface of few nm. This allows the study of interface between TiO₂ and IL hybrid, and thus TiO₂@IL VB. Moreover, the area of analysed was ca. 0.5 mm² therefore probing TiO₂@IL average surface.

Powder sample were mounted on double sided tape (Sellotape) and pressed to ensure a good coverage of the tape with the powder. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Kratos AXIS Ultra DLD instrument. The chamber pressure during the measurements was 5 × 10⁻¹⁰ Torr. Wide energy range survey scans were collected at pass energy of 80 eV in hybrid slot lens mode and a step size of 0.5 eV. Wide scan and high-resolution data on the C 1s, O 1s, N 1s, F 1s, S 2p, P 2p Ti 2p and VB photoelectron peaks was collected at pass energy 20 eV over energy ranges suitable for each peak, and collection times of 5 min, step sizes of 0.1 eV. The charge neutraliser filament was used to prevent the sample charging over the irradiated area.

The X-ray source was a monochromated Al Kα emission, run at 10 mA and 12 kV (120 W). The energy range for each ‘pass energy’ (resolution) was calibrated using the Kratos Cu 2p₃/₂, Ag 3d₅/₂ and Au 4f₇/₂ three-point calibration method. The transmission function was calibrated using a clean gold sample method for all lens modes and the Kratos transmission generator software within Vision II. The data were processed with CASAXPS (Version 2.3.17). In XPS measurements an incorrect charge reference may induce misinterpretation of data, thus leading an equivocally explanation of the surface electronic structure of the materials. C 1s is the most used for charged reference XPS spectrum, however, for materials that contain a great amount of carbon in their composition (such as ionic liquids) the use of C 1s as reference is very uncertain. O 1s also can be used as charge reference, but can be very challenge to separate the contribution of the different oxidation states. Nonetheless, the C 1s and O
1s peaks are likely to contaminations such as adventitious carbon, water absorbed, etc. In this work, we have charged reference the XPS spectra using the Ti 2p at 458.9 eV\(^{[4]}\) (Figure 7), therefore, all the shifts observed in the VBM are relative to Ti 2p. Ti 2p displayed a high number of counts/resolution and very narrow peak (around 1.2 eV for all the samples). Moreover, a non-significantly shift of Ti 2p signal for TiO\(_2\)-modified surface electronic structure was reported\(^{[5]}\).
Figure S7. XPS wide scan and C 1s spectra of (a, b) TiO$_2$@[BMIm][Im]; (c, d) TiO$_2$@[BMIm][NTf$_2$]; (e, f) TiO$_2$@[BMIm][Cl]; (g, h) [BMPy][Im] and (i, j) [(But)$_3$EP][Im].
To ensure the appearance of new surfaces states found are ascribed only by the interaction between TiO$_2$ and IL, TiO$_2@[BMIm][Im]$ was annealed at 650 °C for 2 h under air to remove the IL contribution from the TiO$_2$ surface. In addition, bare TiO$_2$ was also annealed at the same conditions, since at 650 °C crystalline structure rearrangement might induce changes in the VB. As can be observed in the Figure S10 the VBM of the samples annealed are located at same position (ca. 7.5 eV), which shows that the absence of IL on TiO$_2$ surface reverses it to its bare counterpart confirming our hypothesis.

7. Electrochemistry measurements

All the electrochemistry measurements were performed using TiO$_2$ and TiO$_2@[BMIm][Im]$ films deposited on fluorine doped tin oxide (FTO) substrate, with each sample being prepared and measured three times to ensure the reproducibility of the measurements. Electrochemistry experiments were performed using an Autolab (PGSTAT 100N) potentiostat. The measurements were carried out in a quartz cell using a standard three-electrode configuration cell, with a platinum wire as the counter electrode, Ag/AgCl as the reference electrode and the photocatalyst as the working electrode; and 1 M NaOH media (pH 13.8). Mott Schottky measurements were performed in dark, in the frequency range of 100 kHz to 0.1 Hz at an amplitude of 10 mV.
Figure S10. Cyclic voltammetry of (a) bare TiO$_2$ and (b) TiO$_2$@[BMim][Im] using 1 M NaOH media, pH 14. (c) Cyclic voltammery in 1 M NaOH and 0.1 M of [BMim][Im] in 1 M NaOH were performed using Pt wires as working and counter electrodes. No additional peaks related to IL were observed in CVs, indicating IL possesses a wide electrochemical window. These results confirm the peaks observed for TiO$_2$@[BMim][Im] in CV (Figure 2a) are related to the structural defects in TiO$_2$ surface due to presence of IL.

8. Photocatalytic CO$_2$ Reduction

Typically, a Schlenk tube containing 40 mL of degassed distilled water was saturated with 50 bar of CO$_2$ gas. 2 mL of Water was poured in a quartz reactor vessel containing 0.02 g of catalyst under argon atmosphere. A small vacuum was made in the reactor in order to remove air and argon. Then, CO$_2$ was inserted in the reactor by a balloon and stirred the reaction mixture for 30 min. Afterward, the balloon was removed and the reactor was placed in front of 300 W Xe lamp. The temperature of the reactor was maintained at 25$^\circ$C by circulated the cool water through its water jacket. After desired time, gaseous products were analysed by Agilent GC and the liquid phase was analysed by $^1$H NMR.

Figure S11. GC-MS spectra of $^{13}$CO after photo-reduction of $^{13}$CO$_2$: (a) aqueous solution of [BMim][Im] IL. Reaction conditions: [BMim][Im] (40 mg), D$_2$O (2 mL), Temp. (25 $^\circ$C), Time (1 h), Xe Lamp (300 W) and (b) TiO$_2$@[BMim][Im] (30 mg), D$_2$O (2 mL), Temp. (25 $^\circ$C), Time (1 h) and Xe Lamp (300 W). Ions detection was obtained by a Secondary Electron Multiplier (SEM) type detector, using the Single Ion Monitoring (SIM) method.
Figure S12. (a) Experimental and simulated ESR spectra of imidazole radical obtained from photoreduction of CO\textsubscript{2} in aqueous solution using of [BMIm][Im] IL; (b) imidazolale radical obtained photoreduction of CO\textsubscript{2} in aqueous solution using [BMPy][Im] and [(But\textsubscript{3}EP)][Im] ILs.

Figure S13. Photocatalysis using TiO\textsubscript{2}@[BMIm][Im] in aqueous solution of formic acid (200 µl in 2 mL of H\textsubscript{2}O), temp. (25 °C) and Xe lamp (300 W).

8. Recyclability tests

Figure S14. The recycling tests for CO\textsubscript{2} photo-reduction by TiO\textsubscript{2}@[BMIm][Im] Reaction conditions: Cat. (20 mg, CO\textsubscript{2} (1 bar), H\textsubscript{2}O (2 mL), temp. (25 °C) and Xe lamp (300 W). After each cycle the argon was passed to remove the CO and CO\textsubscript{2}, then filled again the reactor with CO\textsubscript{2} and performed the reaction.
9. GC spectra of gaseous products

Figure S15. GC spectra of gaseous products after 2h reaction using TiO$_2$@[BMIm][Im].

Table S2. Recent examples of photocatalytic CO$_2$ conversions by TiO$_2$ based catalysts and ILs (main products).

| Entry | Photocatalyst | Medium | T | Irradiation | CO (µmol·g$^{-1}$·h$^{-1}$) | CH$_4$ | CH$_3$OH | C$_n$ | Ref. |
|-------|---------------|--------|---|-------------|---------------------------|-------|---------|------|------|
| 1     | TiO$_2$@[BMIm][Im] | CO$_2$+H$_2$O | RT | 240 W Xe arc lamp | 455±96 | - | - | - | This work |
| 2     | 5TC-OH/P25 | CO$_2$+H$_2$O | RT | 300 W Xe arc lamp | 11.7 | 16.6 | - | - | [8] |
| 3     | Pt/TiO$_2$ | CO$_2$+H$_2$O | 394 | 300 W Xe arc lamp | - | 0.0081 | - | - | [7] |
| 4     | Ru/TiO$_2$ | CO$_2$+H$_2$O | 394 | 300 W Xe arc lamp | - | 0.0053 | - | - | [7] |
| 5     | Au@STO/TiO$_2$ | CO$_2$+H$_2$O | RT | 300 W Xe arc lamp | 160 ppm·cm$^{-2}$·h$^{-1}$ | 1100 ppm·cm$^{-2}$·h$^{-1}$ | - | 70 ppm·cm$^{-2}$·h$^{-1}$ | [9] |
| 6     | Amine-TiO$_2$ | CO$_2$+H$_2$O | RT | Xe lamp | 100 ppm·h$^{-1}$ | 50 ppm·h$^{-1}$ | - | - | [10] |
| 7     | Pt/TiO$_2$ | CO$_2$+H$_2$O (2 bar CO$_2$) | 323 | 100 W Xe arc lamp | 1.1 | 5.2 | - | - | [11] |
| 8     | CoAl/TiO$_2$ NTs | CO$_2$+H$_2$O | NF* | 300 W Xe arc lamp | 4.6 | 0.4 | - | - | [11] |
| 9     | Ag/BaLa$_4$Ti$_15$O$_{48}$ | CO$_2$+H$_2$O | RT | 400 W Hg arc lamp | 73.3 | - | - | - | [12] |
| 10    | TiO$_2$ (TiB(He)-Brookite) | CO$_2$+H$_2$O | 303 | 90 mW/cm$^2$ AM 1.5G | - | 3 | 3.2 | - | [13] |
| 11    | 5TC-OH/TiO$_2$ | CO$_2$+H$_2$O | RT | 300 W Xe lamp | - | 11.7 | 16.6 | - | [14] |
| 12    | OMT-Au | CO$_2$+H$_2$O | NF* | 300 W Xe arc lamp | - | 1.8 | 0.4 | - | [15] |
| 13    | Pd-Cu/TiO$_2$ | CO$_2$+H$_2$O (0.2 MPa) | NF* | 2-mWcm$^{-2}$ - cut-off filter 400 nm | 1.9 | - | 19.6 | - | [16] |
| 14    | Pt-TiO$_2$ | CO$_2$+H$_2$O | 303 | Xe lamp, 19.6 mW/cm$^2$ | 200.0 µmol/g·cat·h | 1361.0 µmol/g·cat·h | - | - | [17] |
| 15    | TiO$_2$: 001-101 | CO$_2$+H$_2$O | 423 | 100 W mercury vapor lamp | - | - | - | - | [18] |
| 16    | TiO$_2$ (HF4.5) | CO$_2$+H$_2$O+4M HCl | NF* | 300 W Xe arc lamp | - | 1.4 | - | - | [19] |
| 17    | (Au, Cu)/TiO$_2$ (Au/Cu 1:2) | CO$_2$+H$_2$O (1.7 atm) | 333 | 1000 mWcm$^{-2}$ - filter AM1.5 | - | 2200.0 µmol/g·cat·h | - | - | [20] |
| 18    | G2-TiO$_2$ | CO$_2$+H$_2$O | NF* | 300 W Xe arc lamp | - | 8.0 | - | 16.8 | [21] |
| Entry | Photocatalyst | Medium | T (K) | Irradiation | CO | CH₄ | CH₃OH | Cₓ | Ref. |
|-------|---------------|--------|-------|-------------|----|-----|-------|----|------|
| 1     | Ru/Al₂O₃      | CO₂+H₂ | 394   | 300 W Xe arc lamp | -  | 18.2 x 10⁴ | trace | -  | [7]  |
| 2     | Ru/NaTaO₃     | CO₂+H₂O| 394   | 300 W UV-enhanced Xe | trace | 51.8 | -     | -  | [31] |
| 3     | Pt/NaTaO₃     | CO₂+H₂O| RT    | 300 W UV-enhanced Xe | 139.1 | trace | -     | -  | [31] |
| 4     | Ag/BaZrO₃     | CO₂+H₂O| RT    | 300 W Xe lamp       | -  | 0.9 | -     | -  | [32] |
| 5     | IL-Conjugated Polymer | CO₂+H₂O+TEOA | RT | Visible light | 47.4 | - | - | - | [33] |
| 6     | Ni(TPA/TEG)   | [Ru(bpy)₃]Cl₂·6H₂O + H₂O/acetetonitrile + TEAO + CO₂ | NF* | 300 W Xe lamp – visible light | 1.6 x 10⁴ | - | - | - | [34] |
| 7     | g-C₃N₄/ZnO    | CO₂+H₂O (vapor) | RT | 300 W Xe arc lamp | - | - | 0.6 | - | [35] |
| 8     | meso-CdSe     | CO₂+H₂O | RT | 300 W Xe arc lamp – cut-off filter 420 nm | 6.0 | 0.5 | - | - | [36] |
| 9     | Meso-ZnS      | CO₂+H₂O | RT | 300 W Xe arc lamp – cut-off filter 420 nm | 1.8 | 3.8 | - | - | [36] |
| 10    | NC@CoO₄       | [Ru(bpy)₃]Cl₂·6H₂O + H₂O/acetetonitrile + TEAO + CO₂ | 303 | 300 W Xe arc lamp – cut-off filter 420 nm | 2.6 x 10⁴ | - | - | - | [37] |
| 11    | α-FeO₃@g-C₃N₄ | CO₂+H₂O | RT | Xe lamp with a focus intensity of 0.21 W cm⁻² | 27.2 | - | - | - | [38] |
| 12    | 15CN-6Al-F(15CN-6Al-F) | CO₂+H₂O | NF* | 300 W Xe lamp | 24.0 | 6.0 | - | - | [39] |
| 13    | In₃S₂Cdln₃S₄ NTS | H₂O+CO₂+ACN+C o(bpy)₂⁺ (bpy=2′2′-bpyridine)+TEOA | 303 | Cut-off filter 400 nm | 825.0 | - | - | - | [40] |

Table S3. Recent examples of photocatalytic CO₂ conversions (main products).
14 O-doped g-C$_3$N$_4$  

\[
\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{NF}^* + 350 \text{ W Xe lamp - cut-off filter 420 nm}
\]
- - 0.88 - [41]

15 Ag/Er-modified Ga$_2$O$_3$  

\[
0.1 \text{M NaHCO}_3 \rightarrow \text{NF}^* + 400 \text{ W high-pressure mercury lamp}
\]
4.5 mmol of CO after 39 h photoradiation [42]

[Ru(bpy)$_3$]

16 Co$_3$-G nanosheets  

\[
\text{Co}_3\text{Cl}_2\cdot8\text{H}_2\text{O} \rightarrow \text{NF}^* + 22\text{-bipyridine} + \text{H}_2\text{O}/\text{triethanolamine/AC N}
\]
15 264.25 mW cm$^{-2}$ - cut-off filter 420 nm CO : TON of 350 in the first 3 h [42]

17 LaCo$_3$ perovskite  

\[
\text{CO}_2 + \text{OH}^- + \text{TEOA} + \text{MeCN} + \text{H}_2\text{O} \rightarrow \text{NF}^* + 300 \text{ W arc lamp - cut-off filter 420 nm}
\]
- 44.2 µmol h$^{-1}$ of CO [42]

18 BOC-OV  

\[
\text{CO}_2 + \text{OH}^- \rightarrow \text{RT}
\]
300 W high pressure xenon lamp 17.0 1.0 - - [42]

19 [EMIM][BF$_4$], H$_2$O, CO$_2$  

\[
\text{Ru(bpy)$_3$Cl}_2 \cdot 8\text{H}_2\text{O} \rightarrow \text{TEOA}
\]
300 W arc lamp - cut-off filter 420 nm 31.0 - - - [35]

20 g-C$_3$N$_4$ nanosheets  

\[
\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{NF}^* + 300 \text{ W arc lamp}
\]
- 1.4 1.9 - [42]

21 CeO$_2$ homojunction (CP2)  

\[
\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{NF}^* + 300 \text{ W arc lamp}
\]
- 0.86 - - [42]

22 Mg-In LDH  

\[
\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{NF}^* + 200 \text{ W Hg-Xe arc lamp}
\]
3.2 - - - [42]

23 MOF-525-Co  

\[
\text{CO}_2 + \text{MeCN/TEOA (4:1) - (80kPa)} \rightarrow \text{NF}^* + 300 \text{ W arc lamp - cut-off filter 400 nm <kl< 800 nm}
\]
200.6 36.8 - - - [42]

* Not found

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