Electronic Supplementary Information

High-rate solar-light photoconversion of CO₂ to fuel: controllable transformation from C₁ to C₂ products

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**Fig. S1:** Depiction of experimental setup used for photocatalytic CO$_2$ reduction experiments, including online gas chromatography system for dynamic analysis of gaseous products.
Fig. S2: XRD of Pt sensitized Pt$_{\text{pct}}$-0.50-G/RBT samples, where Pt$_{\text{wt\%}}$ = 0.50, 1, 1.25 and 1.50 corresponding to theoretically calculated Pt wt. %
**Fig. S3:** Electron paramagnetic resonance (EPR) spectra of different samples.

**Explanation:** The 0.50-G/RBT peak of 1.99 is attributed to the presence of Ti$^{3+}$ states$^{1-3}$. The graphene-wrapping vacuum treatment promotes defects within the TiO$_2$ and facilitates formation of an intimate junction between Ti of TiO$_2$ and C present in G (Ti-O-C bonds), as confirmed by HR-TEM, PL, and XPS results.
**Fig. S4:** Band gap determination by Tauc plot analysis.

**Table S1.** Band gap values obtained from Tauc plot.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bandgap (eV)</th>
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<tbody>
<tr>
<td>P25</td>
<td>3.02</td>
</tr>
<tr>
<td>RBT</td>
<td>2.68</td>
</tr>
<tr>
<td>0.25-G/RBT</td>
<td>2.61</td>
</tr>
<tr>
<td>0.50-G/RBT</td>
<td>2.41</td>
</tr>
<tr>
<td>0.75-G/RBT</td>
<td>2.22</td>
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</table>
**Fig. S5**: Core level XPS spectra for representative sample 0.50-G/RBT with regions of: (a) C 1s, (b) O 1s; (c,d) shows the shift in XPS for Ti 2p and O 1s, respectively.

**Explanation**: XPS was utilized to confirm the interactions between RBT and graphene. **Fig. S5a** shows the C 1s XPS spectra of representative sample 0.50-G/RBT. The strong peak appearing at 284.60 eV is attributed to C-C bonds originating with the sp² carbon atoms of graphene. With deconvolution of the C 1s peak, two additional peaks positioned at 285.80 eV and 288.40 eV are observed. The peak at 285.80 eV corresponds to oxygenated carbon species such as C-O-R or O=C-OH. The peak appearing at 288.40 eV is due to Ti-O-C bonds formed by the Ti(OH)₂ and carboxyl group of graphene. **Fig. S5b** shows the deconvoluted peaks of O 1s. Three peaks are observed at 529.61 eV, 530.32 eV and 531.40 eV. The first peak at 529.61 eV is mainly due to the Ti-O-Ti bond. Shoulder peaks can be assigned to Ti-OH and Ti-O-C respectively. A peak shift was observed for 0.50-G/RBT as compared with RBT, indicating interaction between graphene and RBT (Fig. S5c and S5d). The XPS analysis confirms strong interaction between RBT and graphene, achieved by the vacuum annealing.
**Fig. S6**: Core level XPS data of Pt$_{1\%}$-0.50-G/RBT with regions showing: (a) presence of Pt, (b) Pt 4f, (c) Ti 2p, and (d) O 1s.

XPS measurements were conducted for all Pt sensitized samples, see **Fig. S7**; Pt is apparent in all samples.
Fig. S7: Pt 4f core level XPS spectra of Pt$_{\text{wt}}$%0.50-G/RBT, where Pt$_{\text{wt}}$% = 0.50, 1, 1.25 and 1.50 corresponding to theoretically calculated Pt wt. %.
Fig. S8: (a) Photoluminescence spectra of diverse samples, and (b) transient absorption spectroscopy of a Pt_{1\%}-0.50-G/RBT sample in which the hole-signature is quenched.
Fig. S9: HR-TEM and Pt particle size distribution of: (a) Pt$_{0.50\%}$-0.50-G/RBT, (b) Pt$_{1\%}$-0.50-G/RBT, (c) Pt$_{1.25\%}$-0.50-G/RBT, and (d) Pt$_{1.50\%}$-0.50-G/RBT.
Fig. S10: Photocatalytic control test results for a Pt_{1\%}-0.50-G/RBT sample under Ar/H_2O atmosphere, and blank reactor into which CO_2 and water vapour are introduced under AM 1.5G illumination.
**Fig. S11**: Cumulative amounts of methane (a,c) and ethane (b,d) by photocatalytic conversion of CO$_2$ and water vapour over different samples, indicating the effect Ti$^{3+}$ states (a,b) and graphene versus graphene oxide (c,d).
Fig. S12: Cumulative (a) methane, and (b) ethane evolution over different control samples in comparison with Pt_{1\%}-0.50-G/RBT.
Fig. S13 AM 1.5G photocatalytic activity and stability comparison of reduced blue titania (RBT), P25, and P25(VC) samples.

The results of Fig. S13 demonstrate P25 nanoparticles, which are only UV active, do not produce any appreciable amount of methane. Sample P25(VC), P25 nanoparticles annealed in a vacuum oven for 90 min at 230 °C produces 2.5 μmolg⁻¹ methane. The reduced blue titania (RBT) sample produces 8.1 μmolg⁻¹ methane. The RBT sample has superior photocatalytic activity with stable performance up to 3h, while the other two samples are rapidly deactivated. The superior activity of RBT is attributed to its enhanced light absorption and better charge separation, both properties arising from the presence of midgap states⁸,⁹, trivalent titanium ions¹⁻³, and disordered surface layers⁸,¹⁰.
Table S2. A comparison of previous works reporting simultaneous evolution of methane and ethane as CO₂ photoreduction products.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Test conditions</th>
<th>CH₄ yield</th>
<th>C₂H₆ yield</th>
<th>Stability</th>
<th>AQY (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au@TiO₂ yolk-shell hollow sphere¹¹</td>
<td>300 W Xe arc lamp</td>
<td>Over 10 h, 2.52 μmolg⁻¹h⁻¹</td>
<td>Over 10 h, 1.67 μmolg⁻¹h⁻¹</td>
<td>Not reported</td>
<td>Not reported</td>
</tr>
<tr>
<td>Nf/Pd-TiO₂¹²</td>
<td>UV, 300 W Xe arc lamp (λ &gt; 300 nm, pH=1)</td>
<td>Over 5 h, 1.4 μmolg⁻¹h⁻¹</td>
<td>Over 1 h, 0.7 μmolg⁻¹h⁻¹</td>
<td>CH₄ evolution stable for 18 h; C₂H₆ =1 h</td>
<td>Not reported</td>
</tr>
<tr>
<td>G-TiO₂¹³</td>
<td>300 W Xe arc lamp</td>
<td>Over 4 h, 10.1 μmolg⁻¹h⁻¹</td>
<td>Over 4 h, 16.8 μmolg⁻¹h⁻¹</td>
<td>Not reported</td>
<td>Not reported</td>
</tr>
<tr>
<td>Current work</td>
<td>100 W Solar simulator (AM1.5G)</td>
<td>Over 7 h, 37 μmolg h⁻¹</td>
<td>Over 7 h, 11 μmolg⁻¹h⁻¹</td>
<td>Stable for 42 h</td>
<td>7.9 % (5.2 % CH₄, 2.7 % C₂H₆)</td>
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References