Supporting Information

CO₂ conversion into methanol under ambient conditions using efficient nanocomposite photocatalyst/solar-energy materials in aqueous medium

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**Figure S1:** Optimum values of CNT content (3 wt. % of the photocatalyst) and Ni to Fe molar ratio (1:2) for photo-catalytic synthesis of methanol using CO₂ feed in aqueous medium.
Figure S2. XRD patterns of the composite materials under study, along with their components.
Figure S3. XPS diagram of the composite photocatalyst containing all components (For deconvolution of peaks, a smart background was used and fitting of data were performed with a Lorentzian/Gaussian [LG (30)] line-shape).
Figure S4. Raman spectrum of the composite photocatalyst containing all components: the spectrum consists of two parts, 1100-1900 cm$^{-1}$ (a) and 0-1100 cm$^{-1}$ (b), which are related to CNT and NiO/Fe$_2$O$_3$ components, respectively.

Here, D and G bands are the characteristic Raman peaks of CNT, verifying its presence in the composite material. The observation of $A_{1g}$ and $E_g$ indicates the formation of Fe$_2$O$_3$. The remaining peaks, i.e. LO, 2TO, LO+TO, and 2LO are ascribed to the synthesis of NiO component [Wang et al. Nanoscale Adv. 1, 1200–1206 (2019); Zhang et al. Energy Technol. 6, 263–272 (2018; DOI: 10.1002/ente.201700400); Lu et al. Opt. Express, 19, 16266–16272 (2011); Juma et al. J. Alloys Compd. 723, 866–872 (2017).].
Figure S5: Extra SEM images taken at higher magnification for the binary (first row; CNT/NiO) and ternary (second row; CNT/NiO/Fe$_2$O$_3$) composite photocatalysts.
Figure S6: Extra SEM evidence for nano-rod morphology due to Fe$_2$O$_3$ presence in the composite photocatalyst. The images were taken at two different magnifications from the ternary photocatalyst synthesized in the absence of NiO, i.e. CNT/Fe$_2$O$_3$. 
Figure S7: Nitrogen adsorption-desorption plots of the composite photocatalysts.
Figure S8: Diffuse reflectance spectra of CNT, NiO and CNT/NiO, depicted in a wide UV-Vis-NIR spectral region.

Figure S9: Diffuse reflectance spectrum of Fe$_2$O$_3$. 
**Figure S10:** Bandgap of the photocatalyst/solar-energy materials, determined through the Kubelka-Munk approach [$F(R)$ is defined as $(1-R)^2/2R$ and $R$ is reflectance; for more details, see references 22 and 26 of the main text].
Figure S11: Calibration diagrams of methanol, oxalic acid, acetic acid and formic acid aqueous solutions determined through HPLC analysis.
Figure S12: Non-liquid [gas phase] products (hydrogen, carbon monoxide and methane) generated during the CO\textsubscript{2} photoconversion process upon the binary and ternary photocatalysts [data were obtained using an online gas chromatograph (GC, SRI instruments 8610C) equipped with TCD and FID detectors connected to the reactor outlet].

No methane was detected for CNT/NiO, suggesting the lack of methyl formation, which is crucial in the synthesis of methane [Schouten et al, Chem. Sci., 2011, 2, 1902]. This evidence indicates by preventing the methane (methyl) formation, why the extent of methanol decreases for the binary photocatalyst [here, the only route for methanol production is CH\textsubscript{3}O/H\textsuperscript{•} reaction not CH\textsubscript{3}/OH one; see eq. 7 of the main text]. On the contrary, in the case of CNT/NiO/Fe\textsubscript{2}O\textsubscript{3}, both reaction pathways are available for the synthesis of methanol, and CH\textsubscript{4} (the result of CH\textsubscript{3}/H\textsuperscript{•} recombination) is the major gas-phase product.
Table S1. A comparison between this work and related studies reported for photocatalytic synthesis of methanol using CO$_2$ feed in aqueous media.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Methanol yield</th>
<th>Explanation</th>
<th>Ref.</th>
</tr>
</thead>
</table>
| CNT/NiO/Fe$_2$O$_3$ (50 mg in 50 ml H$_2$O)       | 4382 (μmol/l)  | 500 W Xenon  
Intensity: 100 mW.cm$^{-2}$, 2 h illumination                           | This work |
| CNT/NiO (50 mg in 50 ml H$_2$O)                    | 1655 (μmol/l)  | "                                                                           | "      |
| NiO/K$_2$Ta$_2$O$_6$ (20 mg in 20 ml H$_2$O)      | 1815 (μmol/l.g.h) | 250 W Mercury lamp  
(wavelength: 365 nm)                                                  | [1]    |
| CeO$_2$/Bi$_2$MoO$_z$ 50 mg in 50ml H$_2$O        | 32.5 (μmol/g)  | 300 W Xenon  
420 nm cut-off filter  
5 cm above the reactor, 4 h illumination | [2]    |
| rGO/InVO$_4$/Fe$_2$O$_3$ DMF/H$_2$O/Et$_3$N (3:1:1) | 16.9 (mmol/g) | 20 W LED  
Intensity: not mentioned, 24 h illumination                            | [3]    |
| o-BiVO$_4$ 0.2g in 160ml H$_2$O                    | 398.3 (μmol/g.hr) | 300 W Xenon  
Intensity: 100 mW.cm$^{-2}$                                            | [4]    |
| TiO$_2$ nanocrystals 0.05g in 30ml H$_2$O         | 2.5 (μmol/g)   | 500 W high-pressure Xenon  
Intensity: 2.5 mW.cm$^{-2}$ UV and 0.12 mW cm$^{-2}$ visible light, 10 h illumination | [5]    |
| CoPc-Rs/Fe$_2$O$_3$ NTs Composite film on Fe sheet, in 0.1 M KHCO$_3$ | 138 (μmol L$^{-1}$ cm$^{-2}$) | Visible light irradiation  
Intensity: not mentioned, 6.5 h illumination under cathodic bias (−1.3 V$_{SCE}$; photoelectrochemical) | [6]    |
| Fe$_2$O$_3$-TiO$_2$ (2 g/L in the presence of sulfite hole scavenger) | 319.42 (μmol/g) | 250 W Mercury lamp of UV high pressure  
Intensity: not mentioned, 7 h illumination at 90 °C | [7]    |
| SnO$_2$/Fe$_2$O$_3$ Photocatalyst film in 0.1M KHCO$_3$ | 0.69 (mmol L$^{-1}$ cm$^{-2}$) | Xenon lamp with a band-pass filter ($λ$= 420 nm, 100 mW.cm$^{-2}$), 6 h illumination | [8]    |
| MoS$_2$–TiO$_2$ (0.1 g in 200 mL of 1 M NaHCO$_3$) | 10.6 (μmol/g.hr) | 300 W xenon  
Intensity: not mentioned                                           | [9]    |
<table>
<thead>
<tr>
<th>Material</th>
<th>Concentration</th>
<th>Light Source/Condition</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/InTaO₄</td>
<td>0.02 g in 20 ml solution of acetonitrile, water and TEOA (3:1:1)</td>
<td>20 W white LED, 5 cm distance, 70 h illumination</td>
<td>[10]</td>
</tr>
<tr>
<td>In₂O₃-WO₃</td>
<td>(details: not mentioned)</td>
<td>355 high power laser beam, 1.5 cm distance</td>
<td>[11]</td>
</tr>
<tr>
<td>rGO/ SrTi₀.₉₅Fe₀.₀₅O₃₋₆</td>
<td>50 mg in 50 mL of RhB (10⁻⁵ M) and NaOH (0.02M).</td>
<td>300 W Xenon (320 nm≤ λ≥ 780 nm) Intensity: 160 mW.cm⁻²</td>
<td>[12]</td>
</tr>
<tr>
<td>g-C₃N₄/(Cu/TiO₂)</td>
<td>0.2 g in 400 ml 1M NaOH</td>
<td>254 nm UV light, 8 h illumination Intensity: 5.4 mW.cm⁻²</td>
<td>[13]</td>
</tr>
<tr>
<td>CdIn₂S₄/ g-C₃N₄</td>
<td>0.1 g in 100 ml 0.1M NaOH solution</td>
<td>300W Xenon with a UV cut-off filter (λ&gt;420nm) Intensity: 15 mW.cm⁻²</td>
<td>[14]</td>
</tr>
<tr>
<td>Bi₂WO₆</td>
<td>0.2 g in 100 ml H₂O</td>
<td>300 W Xenon Intensity: not mentioned</td>
<td>[15]</td>
</tr>
<tr>
<td>Bi₂S₃</td>
<td>20 mg in 80 ml H₂O</td>
<td>300W Xenon with a UV cut-off filter (λ&gt;420nm), 5 cm above the cell</td>
<td>[16]</td>
</tr>
<tr>
<td>Bi₂MoO₆</td>
<td>50 mg in 50 ml H₂O</td>
<td>300 W Xenon Intensity: not mentioned</td>
<td>[17]</td>
</tr>
<tr>
<td>WO₃</td>
<td>(details: not mentioned)</td>
<td>300W Xenon with a UV cut-off filter (λ&gt;420nm) Intensity: not mentioned</td>
<td>[18]</td>
</tr>
<tr>
<td>GrO/CuO</td>
<td>100 mg in 50 ml solution (DMF and H₂O)</td>
<td>20 W white cold LED Intensity: 85 W/m², 24 h illumination</td>
<td>[19]</td>
</tr>
<tr>
<td>CQD/Cu₂O</td>
<td>35 mg in 20 ml H₂O</td>
<td>300 W Xenon Intensity: not mentioned</td>
<td>[20]</td>
</tr>
<tr>
<td>GO-(TBA)₂Mo₆Br₈Br₄ₓ</td>
<td>100mg in 50 ml solution (10 ml H₂O and 40 ml DMF)</td>
<td>20 W white cold LED Intensity: 75 W/m²</td>
<td>[21]</td>
</tr>
<tr>
<td>System</td>
<td>Reaction Conditions</td>
<td>Catalytic Activity</td>
<td>Light Source</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>--------------------------------------------------------------------------------------</td>
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</tr>
<tr>
<td>g-C₃N₄/ZnO</td>
<td>100 mg in H₂O vapor, 0.12 g NaHCO₃, 0.25 ml HCl 4M</td>
<td>0.6 (μmol/g.h)</td>
<td>300 W Xenon</td>
</tr>
<tr>
<td>Cu/TiO₂ NFF</td>
<td>photocatalyst film in 100 ml H₂O</td>
<td>1.8 (μmol/cm² h)</td>
<td>500W Xenon lamp with a 420 nm cut-off filter</td>
</tr>
<tr>
<td>Bi₂S₃/CeO₂</td>
<td>10 mg in 100 ml H₂O</td>
<td>1346.8 (μmol/g)</td>
<td>300 W Xenon</td>
</tr>
<tr>
<td>Si/TiO₂</td>
<td>4.2 cm² in 0.4 ml DW</td>
<td>197 μM</td>
<td>300 W Xenon</td>
</tr>
<tr>
<td>Gr/TiO₂</td>
<td>0.05 g in 50ml NaHCO₃ (0.08 M)</td>
<td>0.680 (μmol /g.h)</td>
<td>500 W Xenon</td>
</tr>
<tr>
<td>3% NiOₓ–Ta₂O₅</td>
<td>0.2 g in 10 ml H₂O</td>
<td>50 (μmol)</td>
<td>400 W Halogen lamp</td>
</tr>
<tr>
<td>Lamellar BiVO₄</td>
<td>0.2 g in 100 ml H₂O</td>
<td>30 (μmol)</td>
<td>300 W Xenon</td>
</tr>
<tr>
<td>RuO₂-modified CuₓAgᵧInₓZnxSm</td>
<td>0.05 g in 50 ml H₂O</td>
<td>118.5 (μmol/g.h)</td>
<td>1000 W Xenon</td>
</tr>
<tr>
<td>Ni/NiO-loaded N-InTaO₄</td>
<td>0.1 g in 50 ml H₂O</td>
<td>350 (μmol/g)</td>
<td>Xenon lamp</td>
</tr>
<tr>
<td>NiO/InTaO₄</td>
<td>0.14 g in 50ml H₂O</td>
<td>1.3 (μmol.l⁻¹.h⁻¹.g⁻¹)</td>
<td>500 W Halogen lamp</td>
</tr>
</tbody>
</table>

References:


[27] Lv, X.J., Fu, W.F., Hu, C.Y., Chen, Y. and Zhou, W.B., 2013. Photocatalytic reduction of CO\textsubscript{2} with H\textsubscript{2}O over a graphene-modified NiO\textsubscript{x}–Ta\textsubscript{2}O\textsubscript{5} composite photocatalyst: coupling yields of methanol and hydrogen. RSC Advances, 3, pp.1753-1757.


[29] Liu, J.Y., Garg, B. and Ling, Y.C., 2011. Cu\textsubscript{x}Ag\textsubscript{y}In\textsubscript{z}Zn\textsubscript{k}S\textsubscript{m} solid solutions customized with RuO\textsubscript{2} or Rh\textsubscript{1.32}Cr\textsubscript{0.66}O\textsubscript{3} co-catalyst display visible light-driven catalytic activity for CO\textsubscript{2} reduction to CH\textsubscript{3}OH. Green Chemistry, 13(8), pp.2029-2031.
