Supporting Information

CO$_2$ 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 CO$_2$ 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 Fe₂O₃.
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$_2$ 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$_3$O/H$^*$ reaction not ČH$_3$/OH one; see eq. 7 of the main text]. On the contrary, in the case of CNT/NiO/Fe$_2$O$_3$, both reaction pathways are available for the synthesis of methanol, and CH$_4$ (the result of ČH$_3$/H$^*$ 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.

| Photocatalyst                        | Methanol yield | Explanation                                                                 | Ref.       |
|--------------------------------------|----------------|------------------------------------------------------------------------------|------------|
| 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 ($\lambda= 420$ 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]        |
| Material                  | Concentration | Reaction Details                                                                 | Productivity     | Source |
|--------------------------|---------------|----------------------------------------------------------------------------------|------------------|--------|
| Ni/InTaO<sub>4</sub>    | 0.02 g in 20 ml solution of acetonitrile, water and TEOA (3:1:1) | 200 (μmol/g) 20 W white LED, 5 cm distance, 70 h illumination | 20 (μmol/g.hr)  | [10]   |
| In<sub>2</sub>O<sub>3</sub>-WO<sub>3</sub>  | (details: not mentioned) | 496 (μmol/g.hr) 355 high power laser beam, 1.5 cm distance | 496 (μmol/g.hr) | [11]   |
| rGO/ SrTi<sub>0.95</sub>Fe<sub>0.05</sub>O<sub>3</sub>-δ | 50 mg in 50 mL of RhB (10<sup>-5</sup> M) and NaOH (0.02M). | 24.07 (μmol/g.hr) 300 W Xenon (320 nm ≤ λ ≥ 780 nm) Intensity: 160 mW.cm<sup>-2</sup> | 240.2 (μmol/g.hr) | [12]   |
| g-C<sub>3</sub>N<sub>4</sub>/(Cu/TiO<sub>2</sub>) | 0.2 g in 400 ml 1M NaOH | 2500 (μmol/g) 254 nm UV light, 8 h illumination Intensity: 5.4 mW.cm<sup>-2</sup> | 31 (μmol/g.hr)  | [13]   |
| CdIn<sub>2</sub>S<sub>4</sub>/ g-C<sub>3</sub>N<sub>4</sub> | 0.1 g in 100 ml 0.1M NaOH solution | 31 (μmol/g.hr) 300W Xenon with a UV cut-off filter (λ>420nm) Intensity: 15 mW.cm<sup>-2</sup> | 25 (μmol/g.hr)  | [14]   |
| Bi<sub>2</sub>WO<sub>6</sub> | 0.2 g in 100 ml H<sub>2</sub>O | 23 (μmol/g) 300 W Xenon Intensity: not mentioned | 23 (μmol/g)  | [15]   |
| Bi<sub>2</sub>S<sub>3</sub> | 20 mg in 80 ml H<sub>2</sub>O | 320.2 (μmol/g) 300W Xenon with a UV cut-off filter (λ>420nm), 5 cm above the cell | 320.2 (μmol/g)  | [16]   |
| Bi<sub>2</sub>MoO<sub>6</sub> | 50 mg in 50 ml H<sub>2</sub>O | 24.8 (μmol/g) 300 W Xenon Intensity: not mentioned | 24.8 (μmol/g)  | [17]   |
| WO<sub>3</sub>   | (details: not mentioned) | 9.77 (μmol/g) 300W Xenon with a UV cut-off filter (λ>420nm) Intensity: not mentioned | 9.77 (μmol/g)  | [18]   |
| GrO/CuO | 100 mg in 50 ml solution (DMF and H<sub>2</sub>O) | 1282 (μmol/g) 20 W white cold LED Intensity: 85 W/m<sup>2</sup>, 24 h illumination | 1282 (μmol/g)  | [19]   |
| CQD/Cu<sub>2</sub>O | 35 mg in 20 ml H<sub>2</sub>O | 55.7 (μmol/g.hr) 300 W Xenon Intensity: not mentioned | 55.7 (μmol/g.hr)  | [20]   |
| GO-(TBA)<sub>2</sub>Mo<sub>6</sub>Br<sub>8</sub>Br<sub>x</sub> | 100 mg in 50 ml solution (10 ml H<sub>2</sub>O and 40 ml DMF) | 1644 (μmol/g) 20 W white cold LED Intensity: 75 W/m<sup>2</sup> | 1644 (μmol/g)  | [21]   |
| Catalyst                  | Mass/Volume                  | Units                        | Conditions                                      | References |
|--------------------------|------------------------------|------------------------------|-------------------------------------------------|------------|
| g-C₃N₄/ZnO              | 100 mg in H₂O vapor, 0.12 g NaHCO₃, 0.25 ml HCl 4M | 0.6 (μmol/g.h)               | 300 W Xenon 10 cm apart (vertically positioned above the reactor chamber) | [22]       |
| Cu/TiO₂ NFF             | photocatalyst film in 100 ml H₂O | 1.8 (μmol/cm² h)             | 500W Xenon lamp with a 420 nm cut-off filter       | [23]       |
| Bi₂S₃/CeO₂              | 10 mg in 100 ml H₂O           | 1346.8 (μmol/g)              | 300 W Xenon 8 h illumination                     | [24]       |
| Si/TiO₂                  | 4.2 cm² in 0.4 ml DW         | 197 μM                      | 300 W Xenon 150 min illumination                 | [25]       |
| Gr/TiO₂                  | 0.05 g in 50ml NaHCO₃ (0.08 M) | 0.680 (μmol /g.h)            | 500 W Xenon Intensity: not mentioned             | [26]       |
| 3% NiOₓ–Ta₂O₅           | 0.2 g in 10 ml H₂O           | 50 (μmol)                   | 400 W Halogen lamp                               | [27]       |
| Lamellar BiVO₄          | 0.2 g in 100 ml H₂O          | 30 (μmol)                   | 300 W Xenon Intensity: not mentioned             | [28]       |
| RuO₂-modified CuₓAgₓInₓZnₓSmₓ | 0.05 g in 50 ml H₂O | 118.5 (μmol/g.h)            | 1000 W Xenon Intensity: not mentioned            | [29]       |
| Ni/NiO-loaded N-InTaO₄  | 0.1 g in 50 ml H₂O           | 350 (μmol/g)                | Xenon lamp Intensity: 100 mW                     | [30]       |
| NiO/InTaO₄              | 0.14 g in 50ml H₂O          | 1.3 (μmol.l⁻¹.h⁻¹.g⁻¹)      | 500 W Halogen lamp Intensity: not mentioned      | [31]       |

References:

[1] Shao, X., Yin, X. and Wang, J., 2018. Nanoheterostructures of potassium tantalate and nickel oxide for photocatalytic reduction of carbon dioxide to methanol in isopropanol. *Journal of colloid and interface science*, 512, pp.466-473.
[2] Dai, W., Hu, X., Wang, T., Xiong, W., Luo, X. and Zou, J., 2018. Hierarchical CeO$_2$/Bi$_2$MoO$_6$ heterostructured nanocomposites for photoreduction of CO$_2$ into hydrocarbons under visible light irradiation. *Applied Surface Science*, 434, pp.481-491.

[3] Kumar, A., Prajapati, P.K., Pal, U. and Jain, S.L., 2018. Ternary rGO/InVO$_4$/Fe$_2$O$_3$ Z-scheme heterostructured photocatalyst for CO$_2$ reduction under visible light irradiation. *ACS Sustainable Chemistry & Engineering*, 6, pp.8201-8211.

[4] Gao, S., Gu, B., Jiao, X., Sun, Y., Zu, X., Yang, F., Zhu, W., Wang, C., Feng, Z., Ye, B. and Xie, Y., 2017. Highly efficient and exceptionally durable CO$_2$ photoreduction to methanol over freestanding defective single-unit-cell bismuth vanadate layers. *Journal of the American Chemical Society*, 139, pp.3438-3445.

[5] Truong, Q.D., Hoa, H.T., Vo, D.V.N. and Le, T.S., 2017. Controlling the shape of anatase nanocrystals for enhanced photocatalytic reduction of CO$_2$ to methanol. *New Journal of Chemistry*, 41, pp.5660-5668.

[6] Yang, Z., Xu, J., Wu, C., Jing, H., Li, P., Yin, H., 2014. New insight into photoelectric converting CO$_2$ to CH$_3$OH on the one-dimensional ribbon CoPc enhanced Fe$_2$O$_3$ NTs. *Applied Catalysis B: Environmental*, pp.249-256.

[7] Wang, J., Liu, H., Xu, Y., Zhang, X., 2014. Preparation of Fe$_2$O$_3$-TiO$_2$ and its photocatalytic reduction of CO$_2$ to methanol. *Asian Journal of Chemistry*, 26, pp. 3875-3878.

[8] Yang, Z., Wang, H., Song, W., Wei, W., Mu, Q., Kong, B., Li, P. and Yin, H., 2017. One dimensional SnO$_2$ NRs/Fe$_2$O$_3$ NTs with dual synergistic effects for photoelectrocatalytic reduction CO$_2$ into methanol. *Journal of Colloid and Interface Science*, 486, pp.232-240.

[9] Tu, W., Li, Y., Kuai, L., Zhou, Y., Xu, Q., Li, H., Wang, X., Xiao, M. and Zou, Z., 2017. Construction of unique two-dimensional MoS$_2$–TiO$_2$ hybrid nanojunctions: MoS$_2$ as a promising cost-effective cocatalyst toward improved photocatalytic reduction of CO$_2$ to methanol. *Nanoscale*, 9(26), pp.9065-9070.

[10] Singhal, N., Goyal, R. and Kumar, U., 2017. Visible-light-assisted photocatalytic CO$_2$ reduction over InTaO$_4$: selective methanol formation. *Energy & Fuels*, 31(11), pp.12434-12438.

[11] Gondal, M.A., Dastageer, M.A., Oloore, L.E. and Baig, U., 2017. Laser induced selective photo-catalytic reduction of CO$_2$ into methanol using In$_2$O$_3$-WO$_3$ nano-composite. *Journal of Photochemistry and Photobiology A: Chemistry*, 343, pp.40-50.

[12] Dong, W.H., Wu, D.D., Luo, J.M., Xing, Q.J., Liu, H., Zou, J.P., Luo, X.B., Min, X.B., Liu, H.L., Luo, S.L. and Au, C.T., 2017. Coupling of photodegradation of RhB with photoreduction of CO$_2$ over rGO/StrTi$_{0.95}$Fe$_{0.05}$O$_{3-\delta}$ catalyst: A strategy for one-pot conversion of organic pollutants to methanol and ethanol. *Journal of Catalysis*, 349, pp.218-225.

[13] Adekoya, D.O., Tahir, M. and Amin, N.A.S., 2017. g-C$_3$N$_4$/Cu/TiO$_2$ nanocomposite for enhanced photoreduction of CO$_2$ to CH$_3$OH and HCOOH under UV/visible light. *Journal of CO$_2$ Utilization*, 18, pp.261-274.
[14] Liu, H., Zhang, Z., Meng, J. and Zhang, J., 2017. Novel visible-light-driven CdIn2S4/mesoporous g-C3N4 hybrids for efficient photocatalytic reduction of CO2 to methanol. *Molecular Catalysis, 430*, pp.9-19.

[15] Jiang, Z., Liang, X., Zheng, H., Liu, Y., Wang, Z., Wang, P., Zhang, X., Qin, X., Dai, Y., Whangbo, M.H. and Huang, B., 2017. Photocatalytic reduction of CO2 to methanol by three-dimensional hollow structures of Bi2WO6 quantum dots. *Applied Catalysis B: Environmental, 219*, pp.209-215.

[16] Jin, J. and He, T., 2017. Facile synthesis of Bi2S3 nanoribbons for photocatalytic reduction of CO2 into CH3OH. *Applied Surface Science, 394*, pp.364-370.

[17] Dai, W., Yu, J., Xu, H., Hu, X., Luo, X., Yang, L. and Tu, X., 2016. Synthesis of hierarchical flower-like Bi2MoO6 microspheres as efficient photocatalyst for photoreduction of CO2 into solar fuels under visible light. *CrystEngComm, 18*(19), pp.3472-3480.

[18] Wang, L., Wang, Y., Cheng, Y., Liu, Z., Guo, Q., Ha, M.N. and Zhao, Z., 2016. Hydrogen-treated mesoporous WO3 as a reducing agent of CO2 to fuels (CH4 and CH3OH) with enhanced photothermal catalytic performance. *Journal of Materials Chemistry A, 4*, pp.5314-5322.

[19] Gusain, R., Kumar, P., Sharma, O.P., Jain, S.L. and Khatri, O.P., 2016. Reduced graphene oxide–CuO nanocomposites for photocatalytic conversion of CO2 into methanol under visible light irradiation. *Applied Catalysis B: Environmental, 181*, pp.352-362.

[20] Li, H., Zhang, X. and MacFarlane, D.R., 2015. Carbon quantum dots/Cu2O heterostructures for solar-light-driven conversion of CO2 to methanol. *Advanced Energy Materials, 5*(5), p.1401077.

[21] Kumar, P., Mungse, H.P., Cordier, S., Boukherroub, R., Khatri, O.P. and Jain, S.L., 2015. Hexamolybdenum clusters supported on graphene oxide: Visible-light induced photocatalytic reduction of carbon dioxide into methanol. *Carbon, 94*, pp.91-100.

[22] Yu, W., Xu, D. and Peng, T., 2015. Enhanced photocatalytic activity of g-C3N4 for selective CO2 reduction to CH3OH via facile coupling of ZnO: a direct Z-scheme mechanism. *Journal of Materials Chemistry A, 3*, pp.19936-19947.

[23] Liu, E., Qi, L., Bian, J., Chen, Y., Hu, X., Fan, J., Liu, H., Zhu, C. and Wang, Q., 2015. A facile strategy to fabricate plasmonic Cu modified TiO2 nano-flower films for photocatalytic reduction of CO2 to methanol. *Materials Research Bulletin, 68*, pp.203-209.

[24] Ijaz, S., Ehsan, M.F., Ashiq, M.N. and He, T., 2015. Synthesis of a Bi2S3/CeO2 nanocatalyst and its visible light-driven conversion of CO2 into CH3OH and CH4. *Catalysis Science & Technology, 5*(12), pp.5208-5215.

[25] Liu, Y., Ji, G., Dastageer, M.A., Zhu, L., Wang, J., Zhang, B., Chang, X. and Gondal, M.A., 2014. Highly-active direct Z-scheme Si/TiO2 photocatalyst for boosted CO2 reduction into value-added methanol. *RSC Advances, 4*, pp.56961-56969.
[26] Baeissa, E.S., 2014. Green synthesis of methanol by photocatalytic reduction of CO$_2$ under visible light using a graphene and tourmaline co-doped titania nanocomposites. *Ceramics International, 40*(8), pp.12431-12438.

[27] Lv, X.J., Fu, W.F., Hu, C.Y., Chen, Y. and Zhou, W.B., 2013. Photocatalytic reduction of CO$_2$ with H$_2$O over a graphene-modified NiO$_x$–Ta$_2$O$_5$ composite photocatalyst: coupling yields of methanol and hydrogen. *RSC Advances, 3*, pp.1753-1757.

[28] Mao, J., Peng, T., Zhang, X., Li, K. and Zan, L., 2012. Selective methanol production from photocatalytic reduction of CO$_2$ on BiVO$_4$ under visible light irradiation. *Catalysis Communications, 28*, pp.38-41.

[29] Liu, J.Y., Garg, B. and Ling, Y.C., 2011. Cu$_x$Ag$_y$In$_z$Zn$_k$Sm$_m$ solid solutions customized with RuO$_2$ or Rh$_{1.32}$Cr$_{0.66}$O$_3$ co-catalyst display visible light-driven catalytic activity for CO$_2$ reduction to CH$_3$OH. *Green Chemistry, 13*(8), pp.2029-2031.

[30] Tsai, C.W., Chen, H.M., Liu, R.S., Asakura, K. and Chan, T.S., 2011. Ni@NiO core–shell structure-modified nitrogen-doped InTaO$_4$ for solar-driven highly efficient CO$_2$ reduction to methanol. *The Journal of Physical Chemistry C, 115*, pp.10180-10186.

[31] Pan, P.W. and Chen, Y.W., 2007. Photocatalytic reduction of carbon dioxide on NiO/InTaO$_4$ under visible light irradiation. *Catalysis Communications, 8*, pp.1546-1549.