Supplementary Information

ETS-10 Modified with Cu_xO Nanoparticles and Their Application for the Conversion of CO_2 and Water into Oxygenates

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Photocatalytic reactor

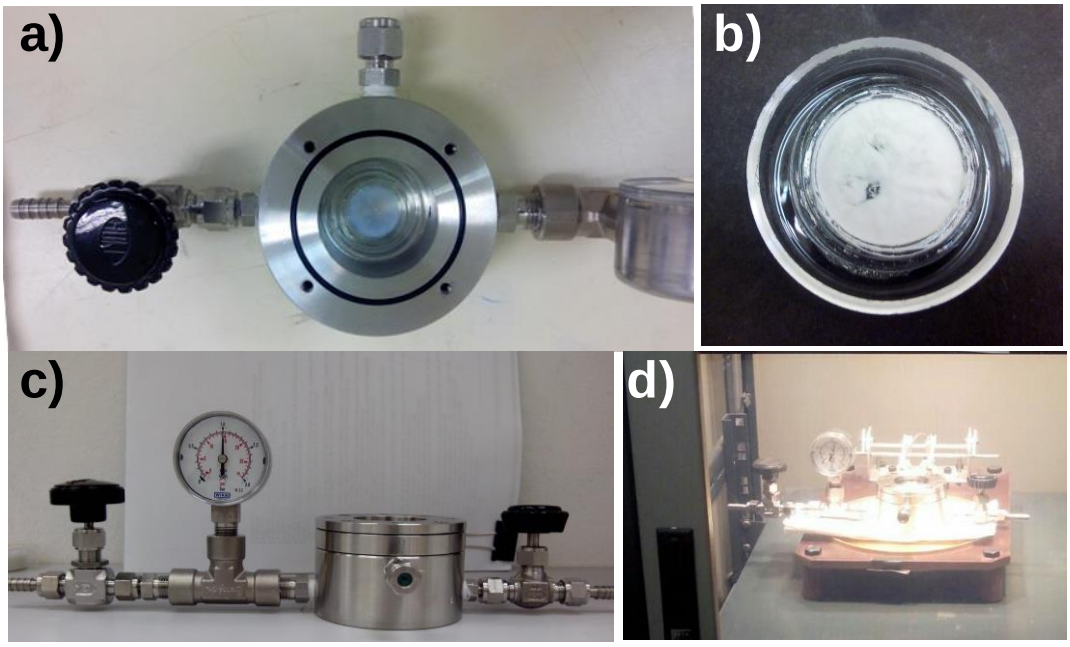

Figure S1. Reactor for photocatalytic reactions: (a) top view of the reactor with 50 mL total capacity; (b) glass support of powder and liquid water; (c) side view of the reactor; (d) reactor inside the solar simulator. Maximum temperature was 333 K.

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Analytical curve of methanol

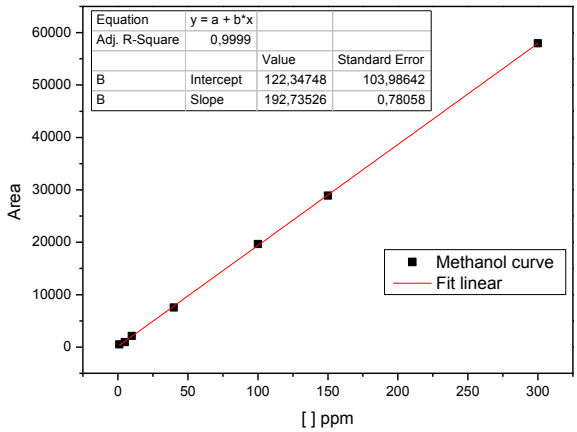


Figure S2. Calibration curve of methanol solutions obtained experimentally by gas chromatography-flame ionization detector (GC-FID).

High resolution transmission electron microscopy (HRTEM)

(a) (b)

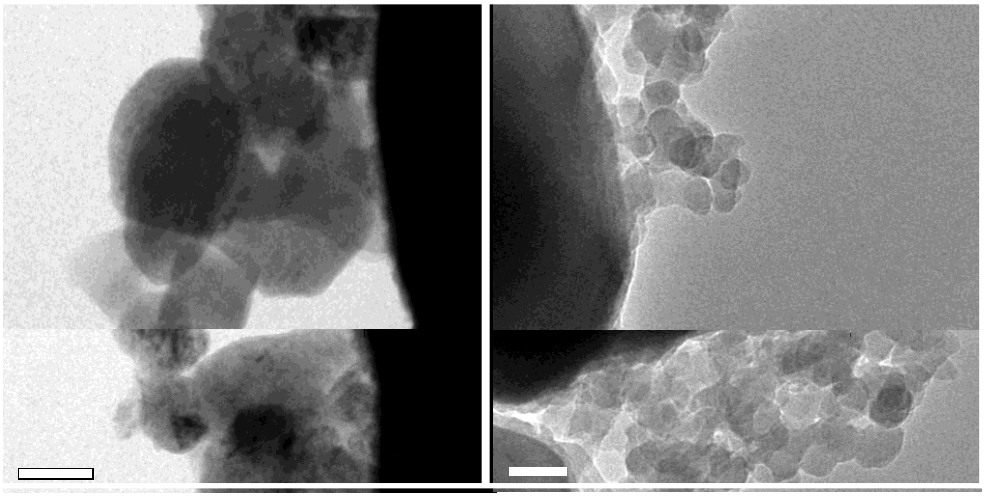


Figure S3. High resolution transmission electron micrographs of (a) Cu_2O nanoparticles and (b) CuO nanoparticles.

Direct band gap estimations by Tauc equation

The absorption spectra can be used to estimate the energy gap of the materials through Tauc's formula:[1]

$$(\alpha h\nu)\nu^{\eta} = B\,(h_0 - Eg) \qquad (S1)$$

where B is a constant related to the material; hν is the photon energy in eV, h is Planck's constant; ν is the frequency of the photon; Eg is the optical band gap in eV, η is an exponent that can take a value = 2 for a direct transition; α is the absorption coefficient and the value is proportional to the F(R ∞) = Kubelka Munk function. Moreover, the most common method to calculate the band gap energy (Eg) involves plotting $(a\ hn)^n$ *vs.* (hn), as shown in Figure S4.

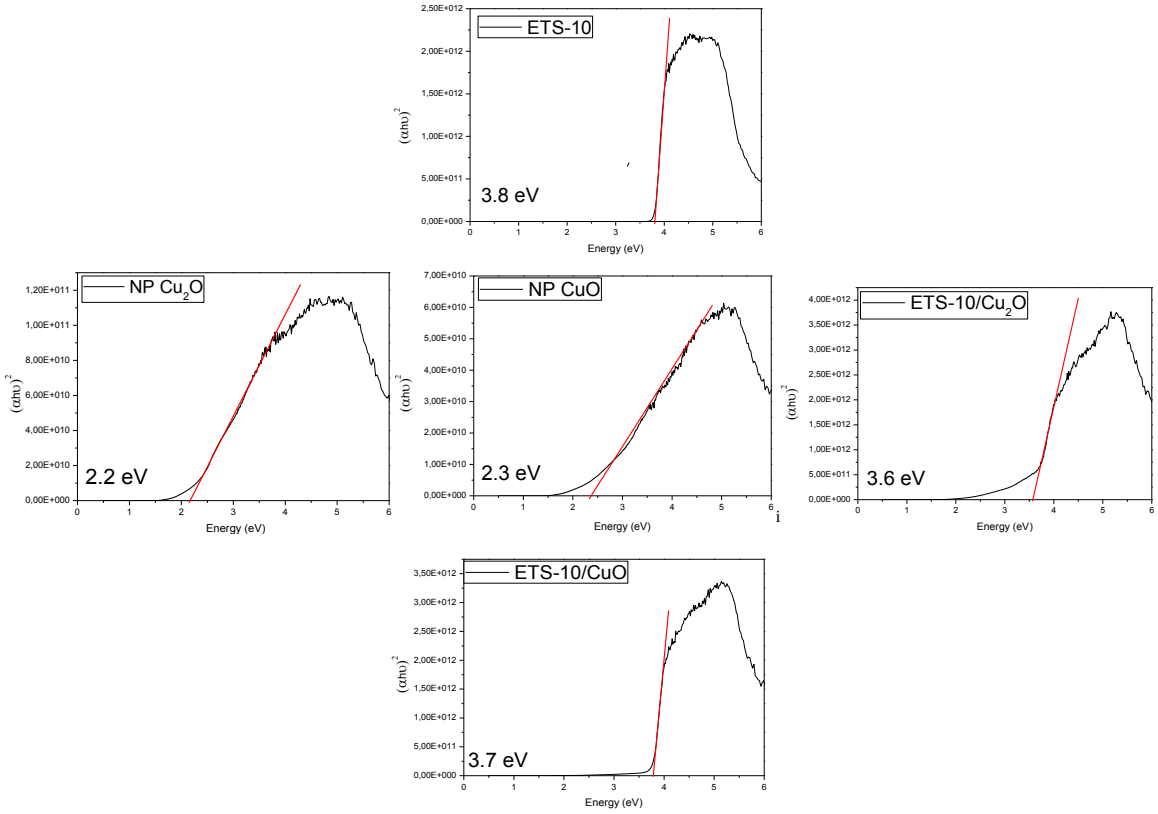
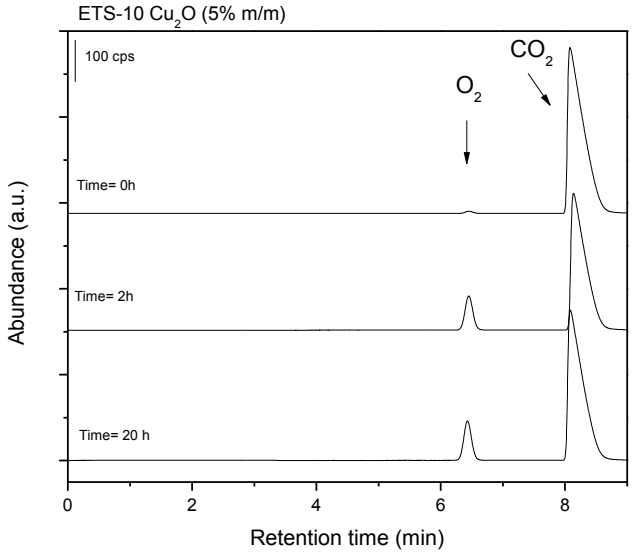


Figure S4. Direct band gap estimations of Cu_2O, CuO nanoparticles, titanosilicate ETS-10, ETS-10/Cu_2O and ETS-10/CuO by Tauc equation.

Gas phase chromatographic analysis

The gas phase was analyzed using a GC with TCD detector to determine O_2, CO and CO_2.



O_2 evolution after 20 h of irradiation

Gas	Peak area	Area / %
O_2	800.01483	12.22865
CO_2	5742.12207	87.77135

Figure S5. Chromatograms of photocatalytic reaction applying the catalyst ETS-10/Cu_2O obtained by GC-TCD analysis and relative areas. Gas carrier: He; isotherm: 100 °C.

Possible mechanisms of acetic acid formation

Srinivas *et al.*[2] proposed the mechanism for acetic acid formation in reaction media, associated to formic acid and methanol formation in contact of catalyst and irradiation, as follow:

$$\begin{aligned} {}^{\bullet}CO_2 + {}^{\bullet}CO_2^- &\longrightarrow CO + CO_3^{2-} \\ CO_2 + 2\,H^+ + e^- &\longrightarrow HCOOH \\ CH_3OH + {}^{\bullet}COOH + H^+ + e^- &\longrightarrow CH_3COOH \end{aligned} \qquad \text{(S2)}$$

Acetic acid formation occurs also by glyoxal pathway from CO_2 to CH_4. This mechanism was proposed by Shkrob *et al.*[3] using EPR technique. Methyl radicals can also be formed from acetaldehyde along a different pathway if the aldehyde is oxidized to acetic acid.

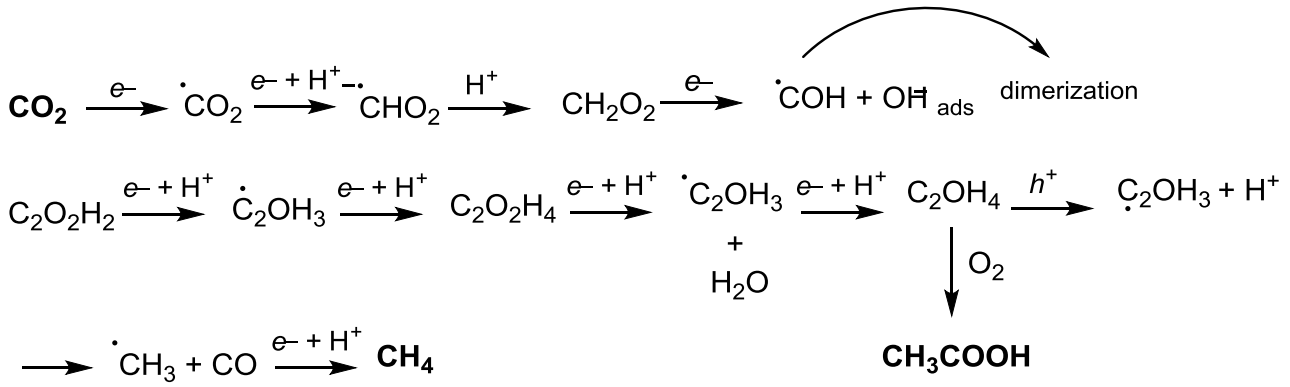


Figure S6. Possible pathways to acetic acid during photocatalytic reactions.

Catalytic activity

The catalytic activity can be calculate by equation:[4,5]

$$R = [\text{Product}] / \text{time}[\text{catalyst}] \quad \text{(S3)}$$

where [Product] are given in μmol or ppm.

For example:

ETS-10/CuO = R = [120] / (20 × 0.050) = 120 mol (mol h)$^{-1}$

Then, we divided the mol number of products for mol number of photoactive material on photocatalyst.

120 × 10^{-6} mol / (3.14 × 10^{-5} mol) = 3.82 $mol_{product}$ ($mol_{catalyst}$ h)$^{-1}$

References

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2. Srinivas, B.; Shubhamangala, B.; Lalitha, K.; Reddy, P. A. K.; Kumari, V. D.; Subrahmanyam, M.; De, B. R.; *Photochem. Photobiol.* **2011**, *87*, 995.

3. Dimitrijevic, N. M.; Shkrob, I. A.; Gosztola, D. J.; Rajh, T.; *J. Phys. Chem. C* **2012**, *116*, 878.

4. Habisreutinger, S. N.; Schmidt-Mende, L.; Stolarczyk, J. K.; *Angew. Chem., Int. Ed.* **2013**, *52*, 7372.

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