

Supplementary Materials

# Synthesis and Characterization of $p$ - $n$ Junction Ternary Mixed Oxides for Photocatalytic Coprocessing of CO<sub>2</sub> and H<sub>2</sub>O

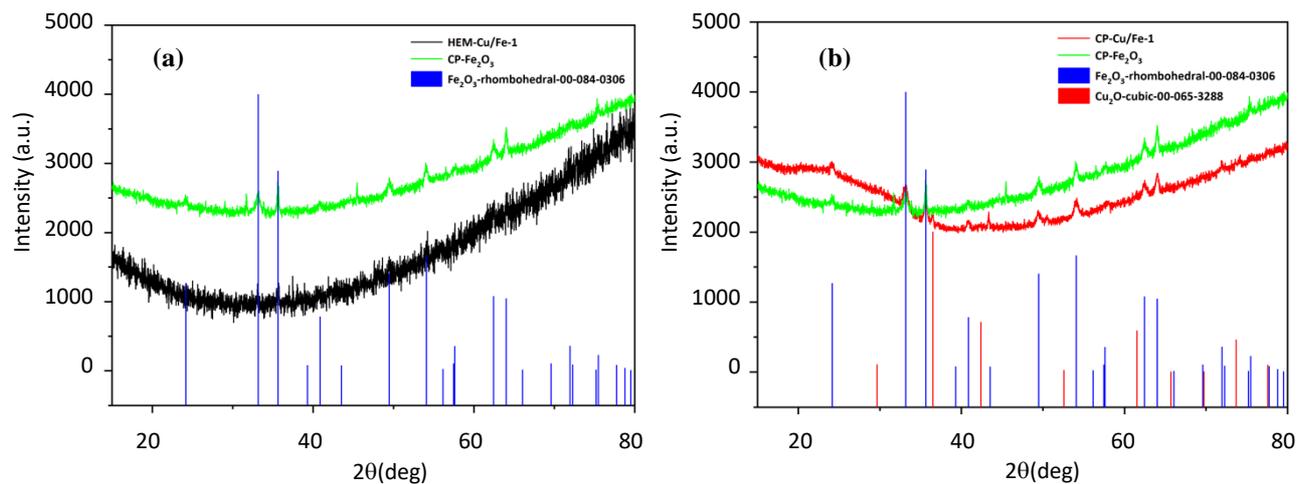
Davide M. S. Marcolongo <sup>1</sup>, Francesco Nocito <sup>1</sup>, Nicoletta Ditaranto <sup>1</sup>, Michele Aresta <sup>2</sup> and Angela Dibenedetto <sup>1,3,\*</sup>

<sup>1</sup> Dipartimento di Chimica, Università degli Studi di Bari, Via Orabona, 4, 70125 Bari, Italy; davide.marcolongo@uniba.it (D.M.S.M.); francesco.nocito@uniba.it (F.N.); nicoletta.ditaranto@uniba.it (N.D.)

<sup>2</sup> IC2R srl, Tecnopolis, Via Casamassima km 3, Valenzano, 70010 Bari, Italy; michele.aresta@ic2r.com

<sup>3</sup> CIRCC-Interuniversity Consortium on Chemical reactivity and Catalysis, Via Celso Ulpiani, 27, 70126 Bari, Italy

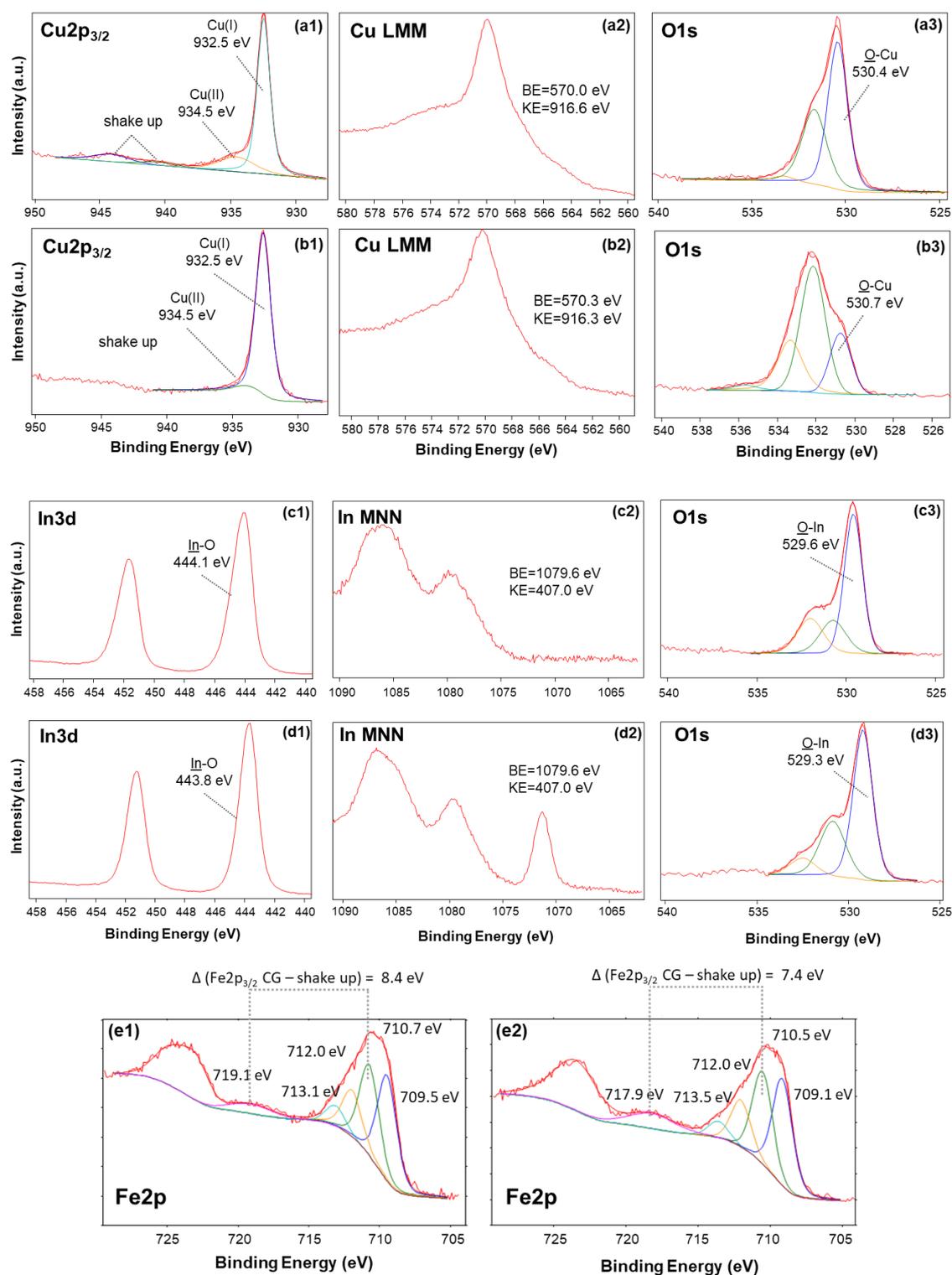
\* Correspondence: angela.dibenedetto@uniba.it; Tel.: +39-080-544-3606



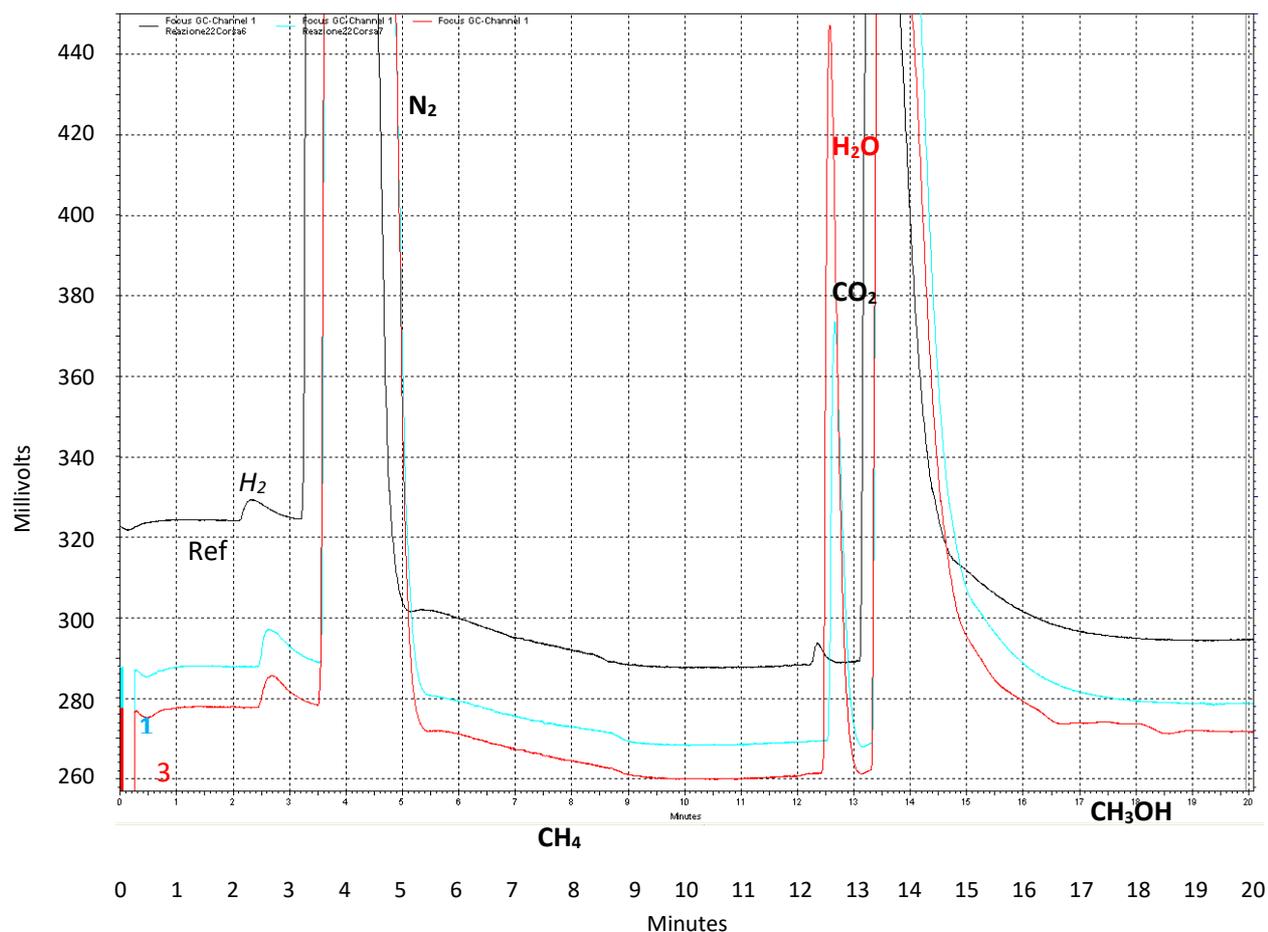
**Figure S1.** Comparison of CP-Fe<sub>2</sub>O<sub>3</sub> XRD patterns with and HEM-Cu/Fe-1 (a) and CP-Cu/Fe-1 (b) along with peak positions for reference diffraction patterns.

In Figure S1 (a), diffractogram for HEM-Cu/Fe-1 (black) is compared to that for S-Fe<sub>2</sub>O<sub>3</sub> (green) and to literature data (blue). No peaks are evident and phase identification is not possible, suggesting that the HEM prepared sample misses any crystallinity.

Figure S1 (b) shows the comparison of the diffractogram for CP-Cu/Fe-1 sample (red) with that of S-Fe<sub>2</sub>O<sub>3</sub> (green) and reference peaks for Fe<sub>2</sub>O<sub>3</sub> (blue lines) and Cu<sub>2</sub>O (red lines). Correspondence is here found for peaks relative to Fe<sub>2</sub>O<sub>3</sub>, for experimental and reference pattern. Also, low intensity peaks well indexed with cubic Cu<sub>2</sub>O are evident in the XRD of CP-Cu/Fe-1. Experimental peaks again suggest small particles (nano-size) and some amorphous phase presence.



**Figure S2.** High resolution XPS spectra of all the samples. (a) C-Cu<sub>2</sub>O sample: (a1) Cu 2p<sub>3/2</sub> spectral region, (a2) Cu LMM Auger transition, (a3) O1s spectral region. (b) S-Cu<sub>2</sub>O sample: (b1) Cu 2p<sub>3/2</sub> spectral region, (b2) Cu-LMM Auger transition, (b3) O1s spectral region. (c) C-In<sub>2</sub>O<sub>3</sub> sample: (c1) In 3d spectral region, (c2) In MNN Auger transition, (c3) O1s spectral region. (d) S-In<sub>2</sub>O<sub>3</sub> sample: (d1) In 3d spectral region, (d2) In MNN Auger transition, (d3) O1s spectral region. (e) Fe 2p spectral region: (e1) C-Fe<sub>2</sub>O<sub>3</sub>, (e2) S-Fe<sub>2</sub>O<sub>3</sub>.



**Figure S3.** H<sub>2</sub> evolution with time by using CP-Cu/In mixed oxides under VIS light irradiation reactor C. Hydrogen is formed after 1+ h and can be measured 2+h after irradiation. Methane is visible after 5+ h (red line).

GCs of samples taken up to 6 h irradiation are represented. The catalyst was still active at the end of 6 h irradiation. Black line: reference CO<sub>2</sub>-H<sub>2</sub>O-H<sub>2</sub>. Blue line: reaction gas after 2.4 h irradiation; Red line: Reaction gas after 5.4 h irradiation.

Sampling number	Time from reaction start (hour)	H <sub>2</sub> produced (mmol)	H <sub>2</sub> produced (mmol/g)	CH <sub>4</sub> (mmol/g)	CH <sub>3</sub> OH (mmol/g)
1	2.4	0.000111	0.001057		
3	5.4	0.000341	0.003257	0.000143	0.000115

Catalyst Amount: 0.1047g.