Electronic Supplementary Information

Vertically oriented CuO/ZnO nanorod arrays: from plasma-assisted synthesis to photocatalytic H_2 production

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Characterization

AFM investigation was performed using a NT-MDT SPM Solver P47H-PRO instrument operating in tapping mode in air. Root mean square roughness (R_{rms}) values were estimated on 2 × 2 μm^2 areas after a plane fitting procedure.

The AFM micrographs of Fig. S1a-c evidenced the formation of well-defined NR tips at the lowest RF-power. In a different way, at 10 and 15 W the system topography was characterized by a more pronounced grain interconnection, leading to flatter surfaces. The latter finding was confirmed not only by the peak-to-valley trends in the scan profiles of Fig. S1d-f, but also by roughness values, that displayed a linear decrease with the applied RF-power (see Fig. S1g). This phenomenon could be mainly related to ion bombardment during the sputtering process, leading to an increasing surface ablation/compaction of the obtained CuO/ZnO composites under more drastic plasma conditions.[1,2]

The spatial distribution of the *guest* CuO phase in the *host* ZnO matrix was investigated by EF-TEM (Fig. S2). EF-TEM analyses were carried out on a Philips CM30 microscope, equipped with a GIF 200 energy filter and operated at 300 kV. Energy filtered maps were acquired using the standard three-window method for O and Cu and the ratio method for Si and Zn.[3]
In line with the EDXS observations (Fig. 3d-f), maps enabled to unambiguously establish that CuO was located in the outermost sample region, and no appreciable diffusion into ZnO or along NRs grain boundaries took place. In addition, an increase in the overall CuO loading with the applied RF-power could be clearly detected, in agreement with XPS compositional analysis (Fig. 1d).

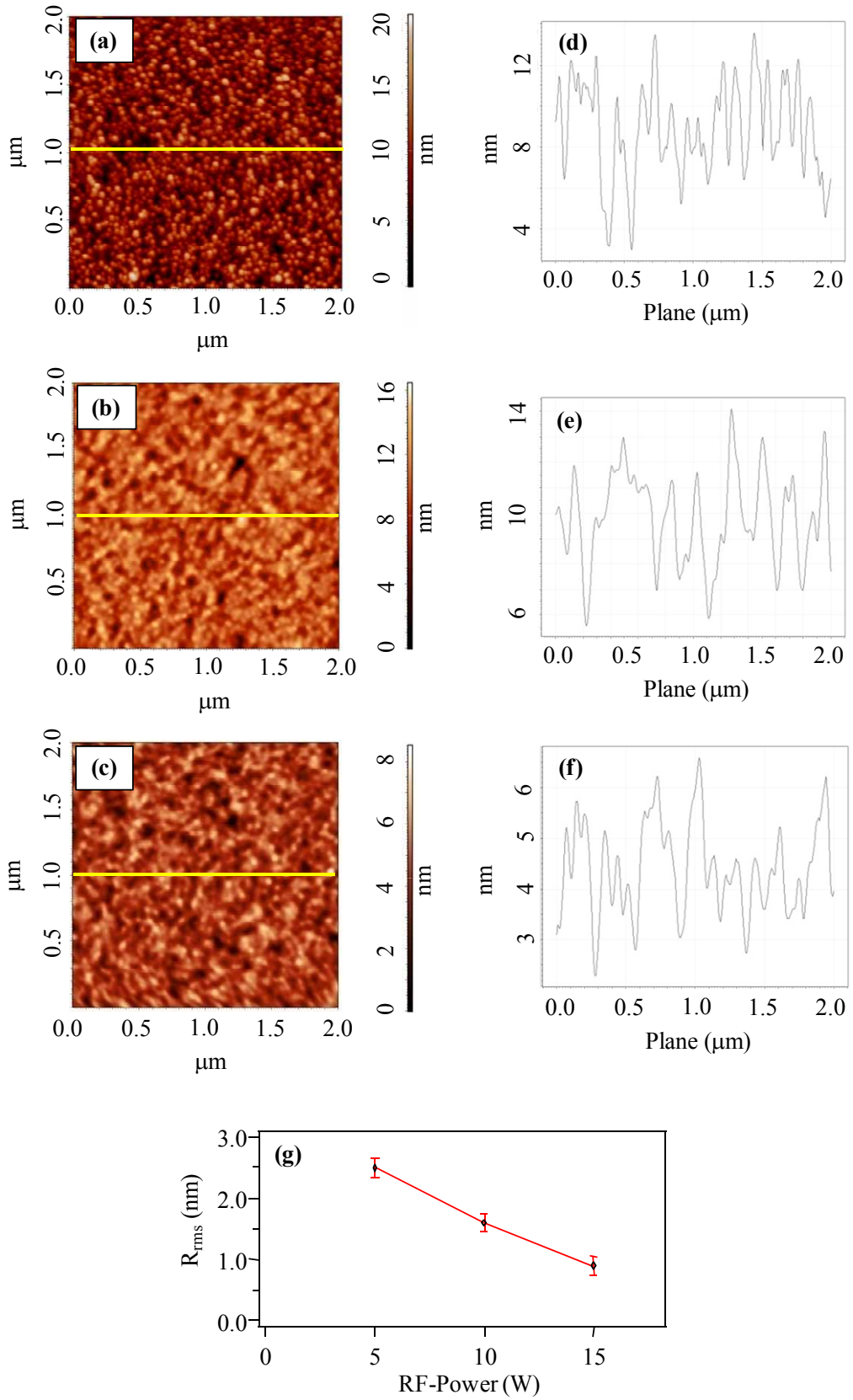

Fig. S1. AFM images and corresponding scan profiles along the marked lines for CuO/ZnO specimens obtained at RF-power values of 5 (a, d), 10 (b, e) and 15 W (c, f). Evolution of the root mean square roughness as a function of RF-power (g).

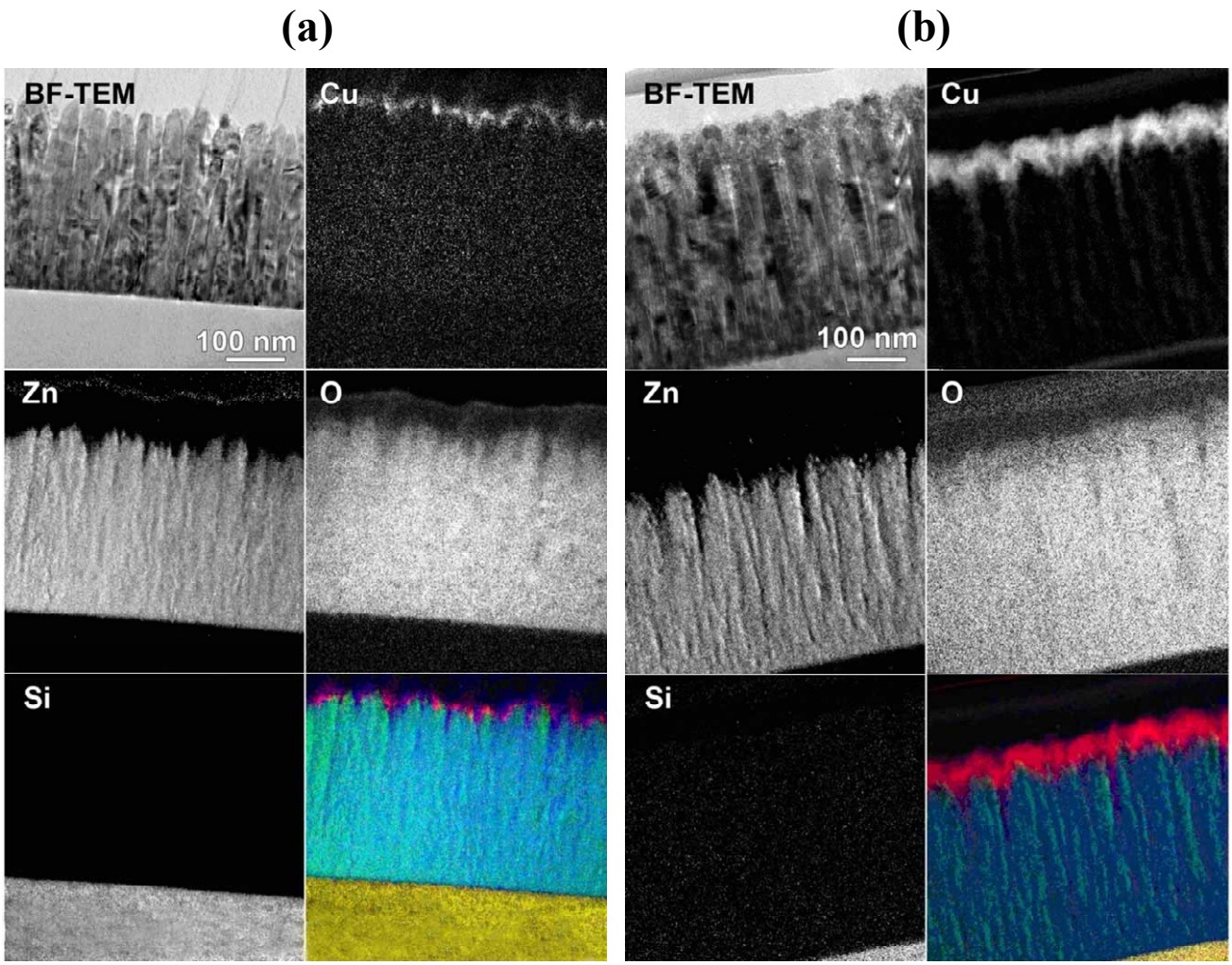

Fig. S2. Bright-field TEM images and elemental EF-TEM maps for Cu, Zn, O and Si for CuO/ZnO nanocomposites obtained with RF-power values of 5 (a) and 15 W (b). Color map codes: red = Cu, green = Zn, blue = O, yellow = Si.

H_2 production by photo-reforming

A schematic representation of the adopted experimental apparatus is shown in Fig. S3.

On-line detection of evolved gases was performed by an Agilent 7890 Gas Chromatographer (GC), equipped with a 10 way-two loop injection valve. A molecular sieve 5A column connected to Thermal Conductivity Detector (TCD) was used for H_2 analysis and a DB522-ms column connected to a Mass Spectrometry (MS) quadrupole detector was used for the analysis of CO_2 and volatile compounds in the gas flow. The same instrument, equipped with an auto-sampler, was used for the GC/MS analysis of the solutions recovered after photocatalytic experiments.

As concerns H_2 evolution, the measurement of the exposed CuO/ZnO surface is a critical issue.[2] As a consequence, the H_2 production rates displayed in Fig. 6 were normalized for the sample geometrical surface, which has indeed a practical meaning in terms of technological applications.

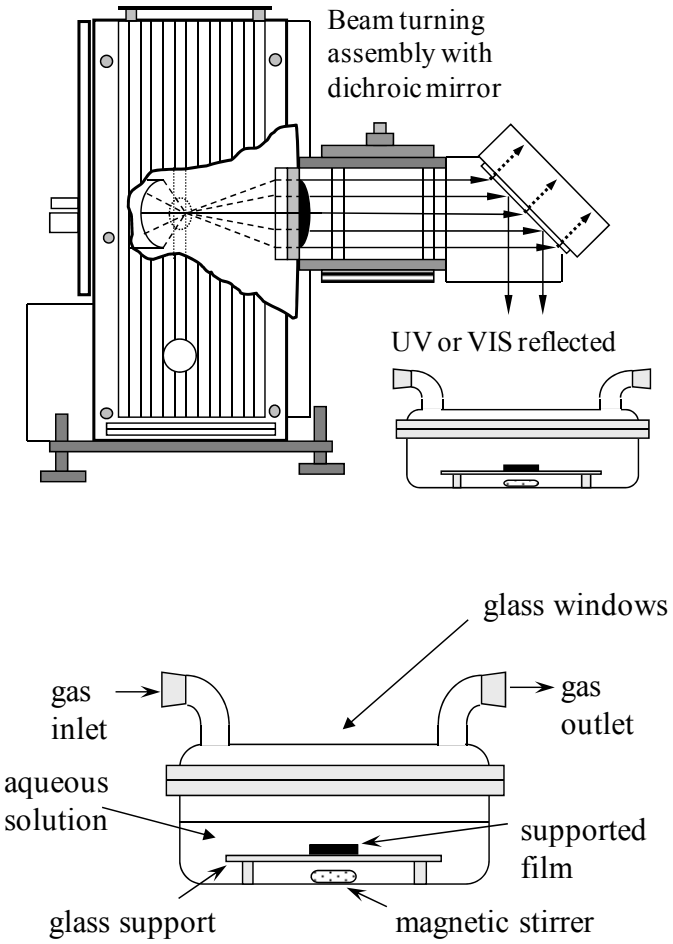

Fig. S3. Schematic representation of the experimental set-up for photo-reforming experiments under simulated solar radiation.

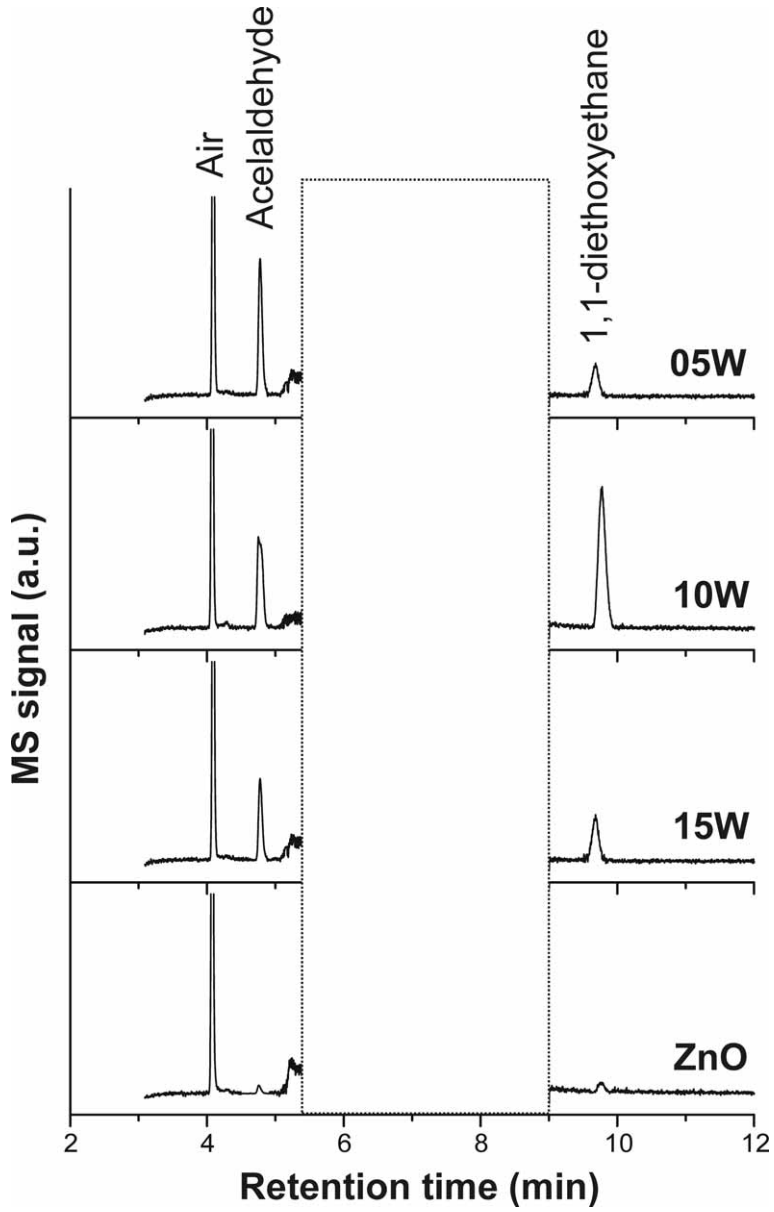

Fig. S4. GC/MS analysis of ethanol/water solutions recovered after photocatalytic experiments using CuO/ZnO samples prepared with different RF-power values. Data for bare ZnO are also displayed for comparison. The solvent peak (ethanol) was filtered by the MS quadrupole.

References

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