SUPPLEMENTARY INFORMATION

Dry hydrogen production in tandem CRM-free water photoelectrolysis cell using a hydrophobic gas-diffusion backing layer

Stefano Trocino[1]*, Carmelo Lo Vecchio[1], Sabrina Campagna Zignani[1], Alessandra Carbone[1], Ada Saccà[1], Vincenzo Baglio[1], Roberto Gómez[2] and Antonino Salvatore Aricò[1]

1 Consiglio Nazionale delle Ricerche, Istituto di Tecnologie Avanzate per l'Energia "Nicola Giordano", CNR-ITAE, Via Salita Santa Lucia sopra Contesse 5, 98126 Messina, Italy; carmelo.lovecchio@itae.cnr.it (C.L.V.); sabrina.zignani@itae.cnr.it (S.C.Z.); alessandra.carbone@itae.cnr.it (A.C.); ada.sacca@itae.cnr.it (A.S.); vincenzo.baglio@itae.cnr.it (V.B.); antonino.arico@itae.cnr.it (A.S.A.).

2 Departament de Química Física i Institut Universitari d'Electroquímica, Universitat d'Alacant, Apartat 99, E-03080 Alicante, Spain; Roberto.Gomez@ua.es (R.G.)

* Correspondence: stefano.trocino@itae.cnr.it;; Tel.: +39090624270

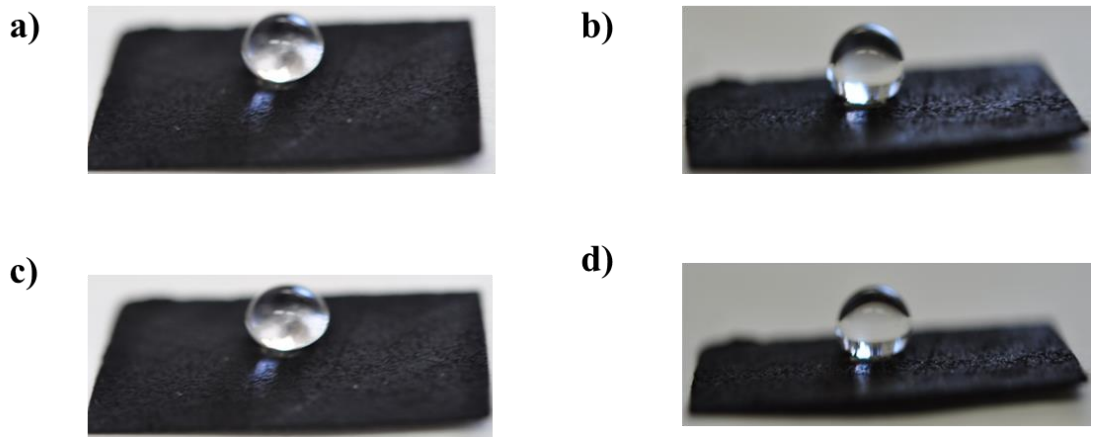

Figure S1. Photos of photocathode substrates Sigracet 35BC (on the left) and Sigracet 35BC + FEP 7% (on the right) after 0 s (a, b) and after 1800 s (c, d).

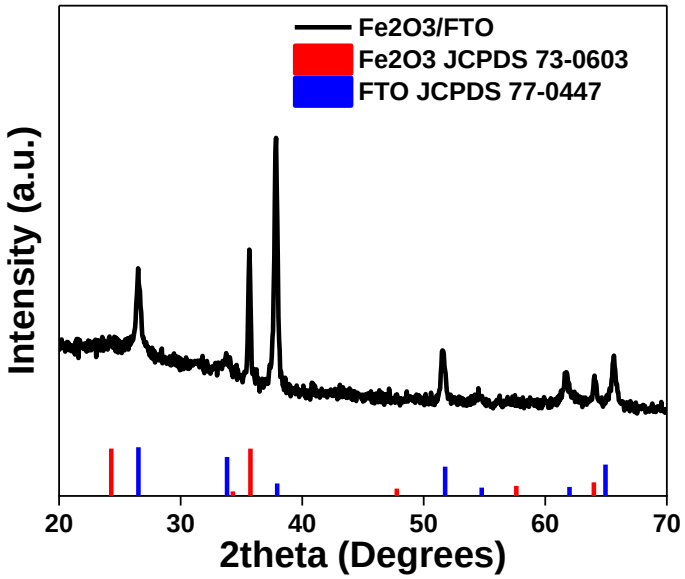

Figure S2. XRD pattern of synthesized anodic semiconductor Fe_2O_3 deposited on FTO glass and relative JCPDS cards.

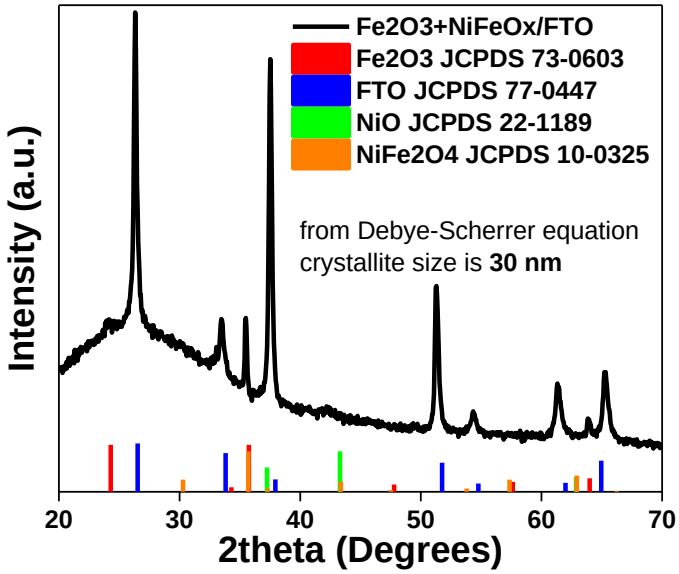

Figure S3. XRD pattern of synthesized anodic semiconductor Fe_2O_3 + NiFeOx deposited on FTO glass and relative JCPDS cards.

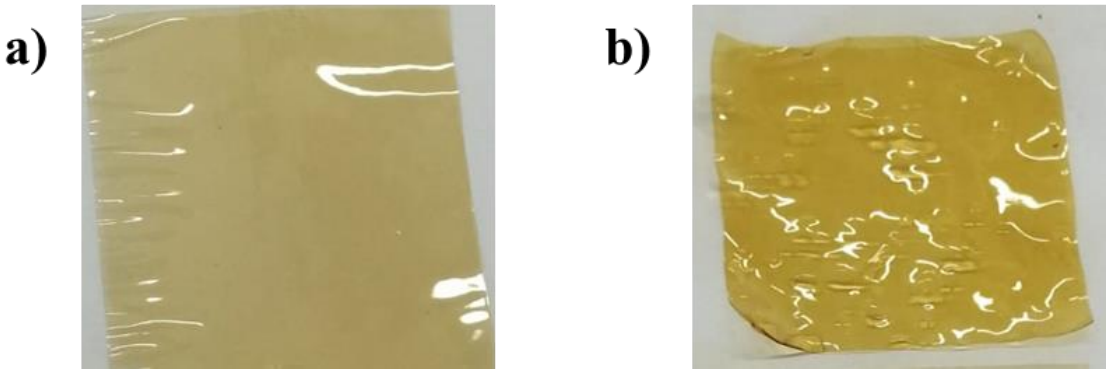

Figure S4. Photographs of transparent anionic membrane FAA-3 either dry (a) or wet (b).

The cathode stream was analysed by means of a mass spectrometer ThermoStar™ GSD320 (Pfeiffer, Ablar, Germany), under dark and light operation (Figure S5). We have analysed the output stream at the cathode with reference to H_2 and CO signals. The ionic current related to hydrogen increases during illumination at -0.6 V showing large oscillations whereas the CO signal is not affected (Figure S5).

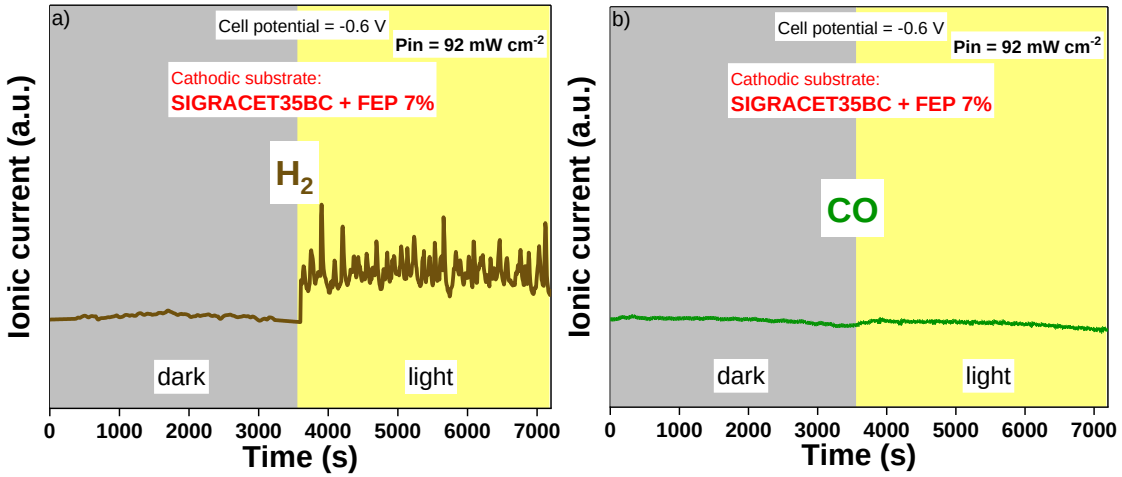

Figure S5. Mass spectrometry analysis during potentiostatic test (applied cell bias of -0.6 V) of the PEC cell (glass+FTO+Fe_2O_3+$NiFeO_x$+ionomer/FAA-3/ionomer+CuO+ Sigracet 35BC+FEP7%): H_2 ionic current (a) and CO ionic current (b).

No traces of humidity were detected by placing a small piece of filter paper below the cathode backing layer providing a clear indication that no water traces are permeating through this substrate.

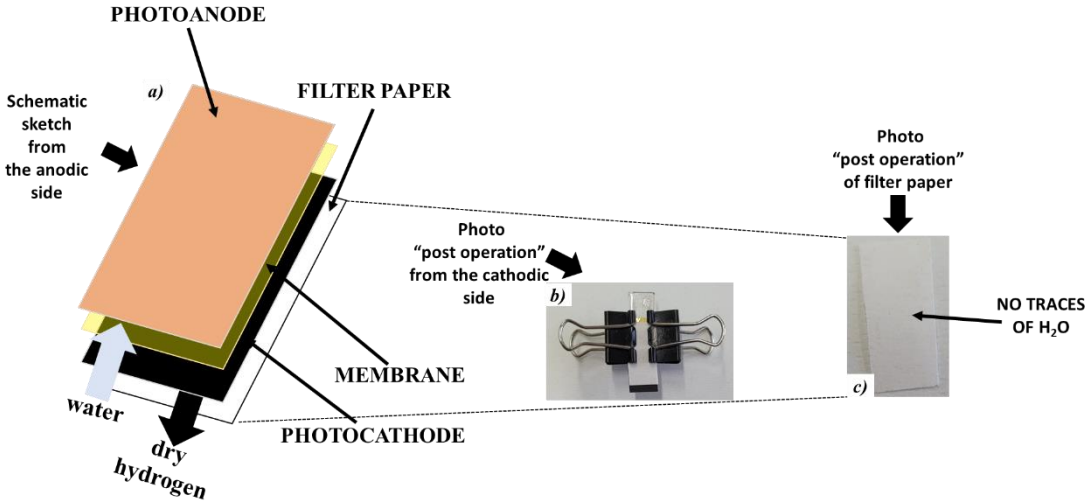

Figure S6. Schematic sketch (a) and photograph (b) of the photoelectrochemical cell (PEC) with carbonaceous gas diffusion layer as cathode substrate and filter paper to highlight any traces of water (left); (c) photograph of filter paper "post operation".

In order to understand if the hydrophobic carbonaceous substrate-based photocathode was able to block water diffusion towards the external hydrogen flow, an experiment was carried out by using a burette full of water pressed onto the CuO+ Sigracet 35BC+FEP7% electrode. It can be seen that also after about 4 hours the water did not cross the hydrophobic substrate. It is pointed out that the hydrostatic pressure applied by the burette inside the burette is much larger than the pressure of PEC.

Figure S7. Images of a 60 cm water column (about 60 mbar) in a burette placed perpendicular to a CuO/ Sigracet 35BC + FEP 7% sample at the beginning (a), after 1800 s (b), after 15000 s (c).

The morphological characteristic of NiFeOx-doped hematite on FTO are shown in Figure S8a, before the durability test, and in Figure S8b after the durability. Hematite appears in nanocolumnar structure, before and after durability test, with nanocolumns of about 90 nm of diameter. The NiFeOx promoter is also evident as agglomerate of nanoparticles which are indicated by the arrows in Fig. S8. No modifications have been observed.

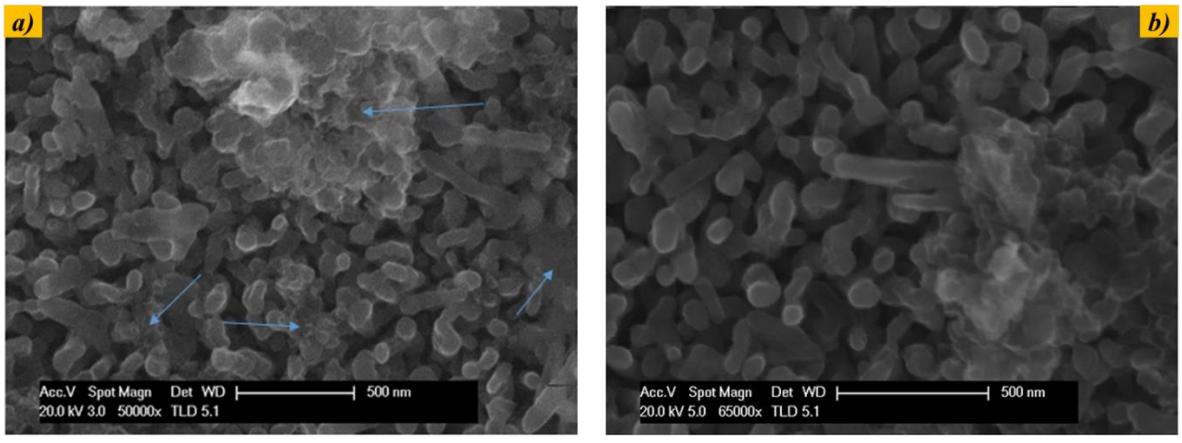

Figure S8. SEM images of the outer NiFeOx-coated hematite photoanode surface, before (a) and after (b) the durability test.