Supporting Information

Photo-Responsive Doped 3D-Printed Copper Electrodes for Water Splitting: Refractory One-Pot Doping Dramatically Enhances the Performance

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Potential conversion

In this work, two reference electrodes, an Ag/AgCl 1M KCl for the macroscopic and an Ag/AgCl 3M KCl for the microscopic photoelectrochemical experiments, were used. For a uniform presentation, the potentials were converted in respect to reversible hydrogen electrode (RHE) using Equations 1-3, with pH = 13 (c(NaOH) = 0.1 M).

$$E(NHE) = E(Ag/AgCl\,3M\,KCl) + 0.197\,V \quad (1)$$

$$E(NHE) = E(Ag/AgCl\,1M\,KCl) + 0.222\,V \quad (2)$$

$$E(RHE) = E(NHE) + pH * 0.059V \quad (3)$$

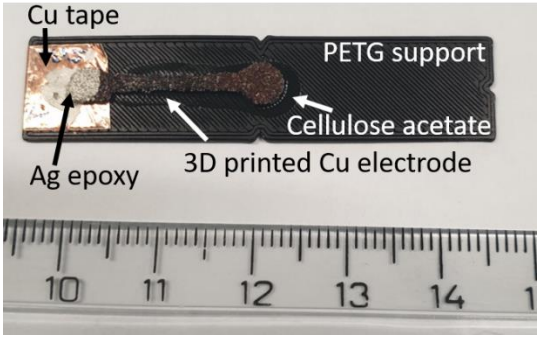


Figure S1: Optical image of a prepared 3D-printed Cu electrode sintered with Al_2O_3 for the photoelectrochemical water splitting. (Scale in cm)

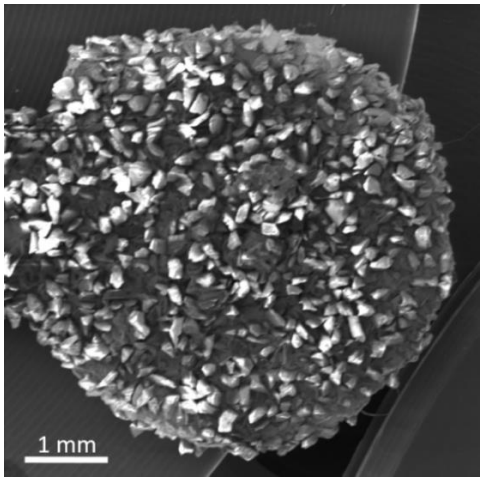


Figure S2: Scanning electron micrograph of the 3D printed Cu electrode sintered with Al_2O_3 as refractory.

Table S1: Number (N) of investigated electrodes for macroscopic photoelectrochemical experiments.

Wavelength / nm	Reaction	N(C/3DCu)	N(TiO_2/3DCu)	N(Al_2O_3/3DCu)
365	HER	3	3	4
365	OER	3	3	4
660	HER	3	3	7
660	OER	4	3	7

Table S2: Chemical composition of the sintered 3DCu electrodes determined by XPS wide spectra.

Electrode	Cu (%at)	C (%at)	Ti (%at)	Al (%at)	O (%at)
C/3DCu	2.27	64.92	-	25.23	7.58
TiO_2/3DCu	4.6	38.51	2.59	36.08	18.02
Al_2O_3/3DCu	5.21	16.86	-	45.06	32.87

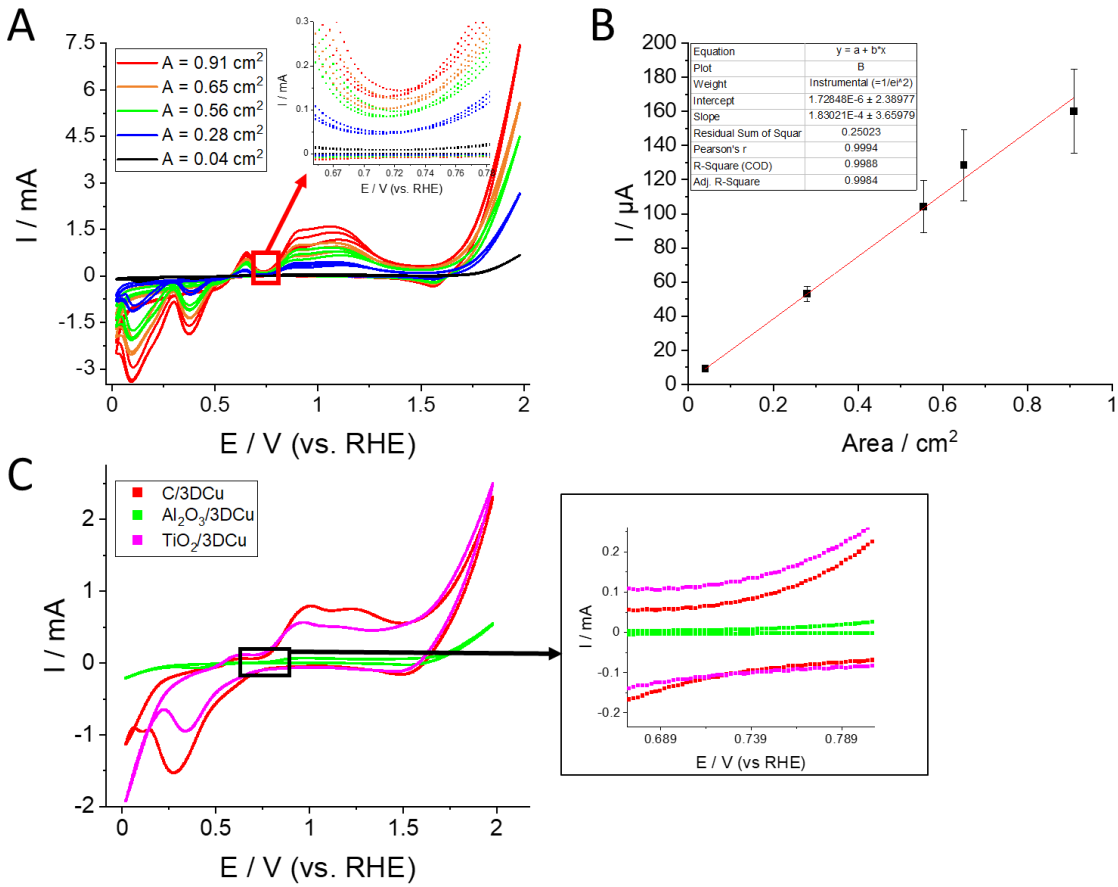


Figure S3: Correlation of the double layer charging current to the surface area. A) CV of Cu electrodes with known surfaces areas. (black: 0.04 cm^2; blue: 0.26 cm^2, green: 0.56 cm^2, yellow: 0.65 cm^2, red: 0.91 cm^2). B) Current/area correlation for Cu electrodes with known surface area. C) The double layer charging current of the samples. (Electrolyte: 0.1 M NaOH, Scan rate: 0.1 V s^{-1})

Direct H_2 detection *via* SPECM

To demonstrate that the observed photocurrents were the result of H_2 generation and not of photo-corrosion, SPECM was performed at a similar potential. For the direct H_2 detection, SPECM was performed at a similar potential (*E*(HER)= 0.06 V) as used in the photoelectrochemical on/off experiments. The results are depicted in Figure S4. The bFB image (Figure S4A) shows the location of the Al_2O_3/3DCu electrode cross-section, and the SG/TC image (Figure S4B) shows the HER at this potential located at the interface between Al_2O_3 and 3DCu. This demonstrates that at the used potentials H_2 was generated.

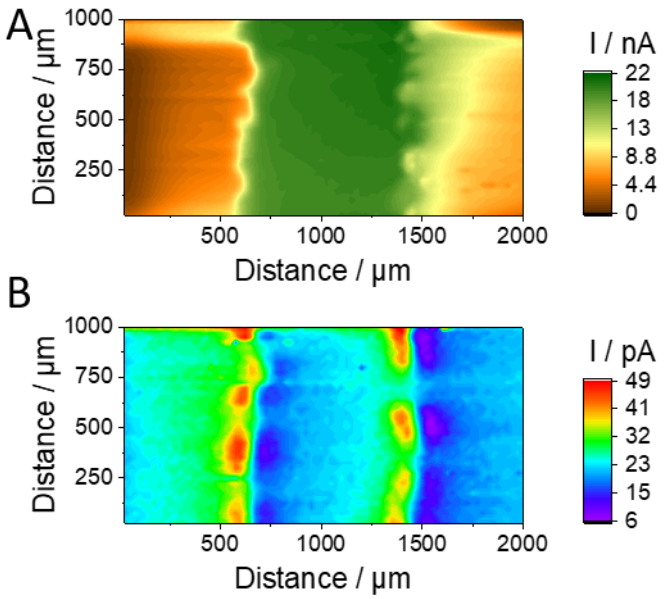


Figure S4: Scanning electrochemical microscopic examination of the electrochemical hydrogen evolution at a 3D printed Cu electrode sintered with Al_2O_3 as refractory. The SECM images were recorded in biased feedback mode (A) and SG/TC mode (B). (Experimental conditions: 0.1 M NaOH; E(HER)= 0.06 V; E_{UME}= 1.06 V vs RHE; pixel size: 25 µm).

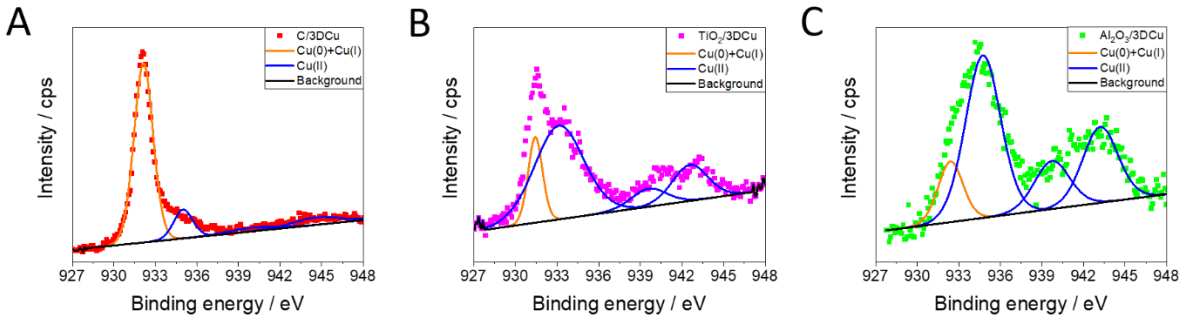


Figure S5: X-Ray photoelectron spectroscopic of Cu $2p_{3/2}$ region of the C/3DCu (A), TiO_2/3DCu (B), and Al_2O_3/3DCu (C) photoelectrodes after photoelectrochemical experiments.

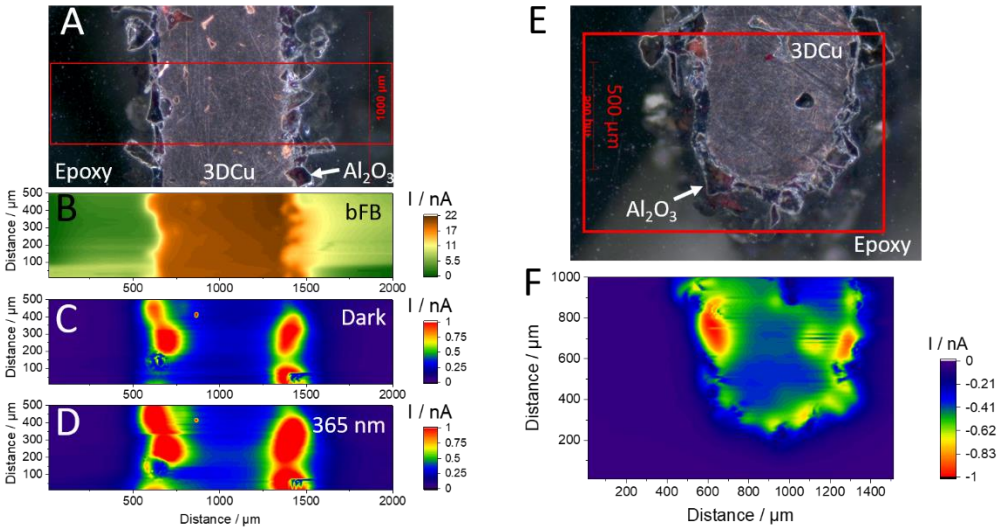


Figure S6: A) Optical image and B) bFB image of the Al_2O_3/3DCu cross-section imaged for HER. C) SG/TC image of the HER without light and D) with illumination. E) Optical image of the cross-section of Al_2O_3/3DCu imaged for OER. F) SG/TC image of the OER with illumination. The red squares indicate the SPECM imaged areas. Experimental conditions: 0.1 M NaOH; λ = 365 nm; HER: E(HER) = -0.29 V; E_{UME} = 1.06 V; OER: E(OER) = 1.91 V; E_{UME} = 0.86 V.

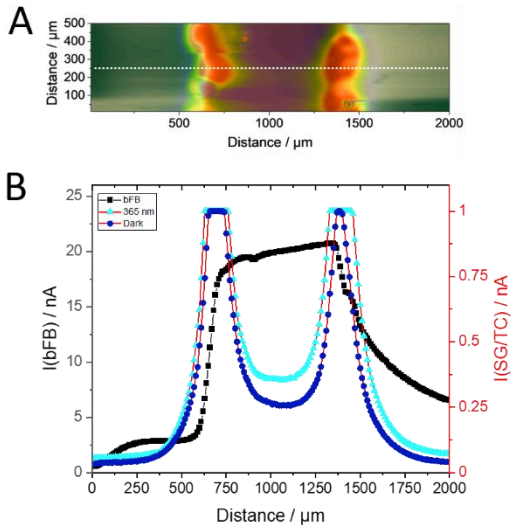


Figure S7: Composed overlay image of the bFB (from Figure S5B) and the SG/TC image of the HER with illumination (from Figure S5D). B) Overlay of the extracted line scans indicated by the white line in A).