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Supplementary Information

Enhanced Photoelectrochemical Water Splitting using Carbon Cloth Functionalized with ZnO Nanostructures via Polydopamine Assisted Electroless Deposition

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S1: iR compensation

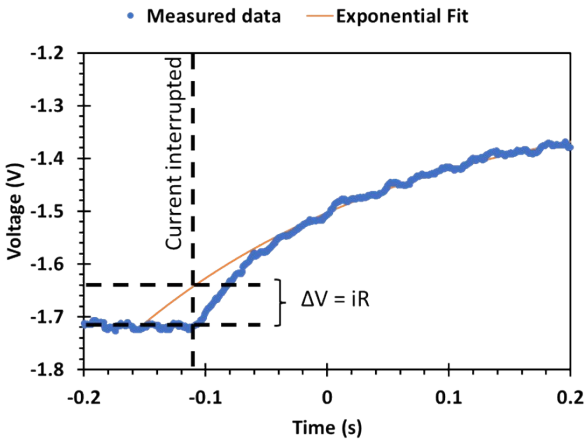

Figure S1: Estimation of iR contribution by the 'current-interrupt' method. Data is shown for Ni/CC cathode under 3-electrode chronoamperometry testing.

The ohmic (iR) contribution was measured by the 'current interrupt' method[1,2]. This was performed by measuring the transient change in voltage across the working and reference electrodes when the current was abrupted interrupted during chronoamperometry measurements by the potentiostat (see example in Fig. S1). The transient change in voltage was measured using an oscilloscope (MDO 3014, Tektronix), at a resolution of 10^{-4} s^{-1}. The

transient voltage data after current interruption was fitted with an exponential function, which was extrapolated to the point of current interruption to estimate the iR drop, from which the ohmic resistance of the circuit can be determined. Accordingly, the ohmic resistances R of the Ni/Cu and Ni/CC cathodes were measured to be 1.25 and 2.3 ohms respectively. These values were used to perform 'after-the-scan' correction to the voltage values in Fig. 6A-B by $V_{comp} = V_{exp} - iR$, where V_{exp} and i are the experimentally-obtained voltage and currents respectively.

S2: ZnO nanorod growth on carbon cloth without polydopamine and seeding

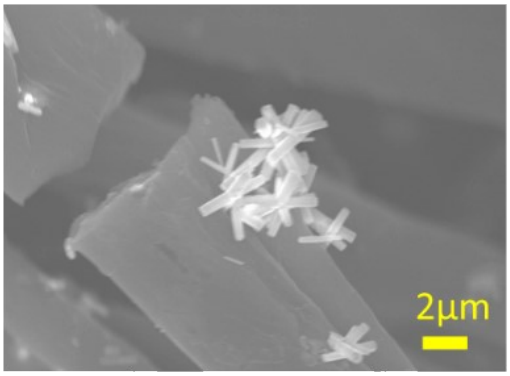

Figure S2: Direct hydrothermal growth of ZnO on carbon cloth without polydopamine or ZnO seed.

S3: Raman spectra of ZnO nanorods before and after cyclic voltammetry

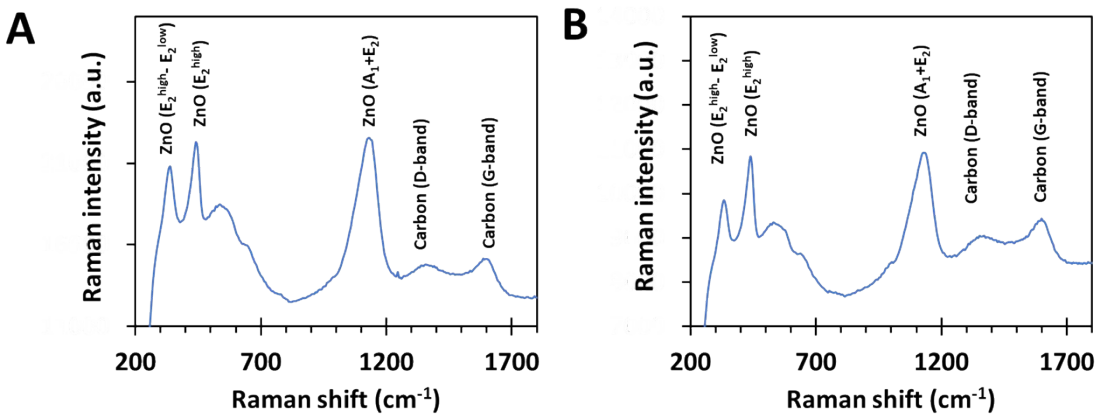

Figure S3: Raman spectra of ZnO nanorods grown on carbon cloth (A) before and (B) after 150 cycles of cyclic voltammetry.

S4: Details of energy band diagram

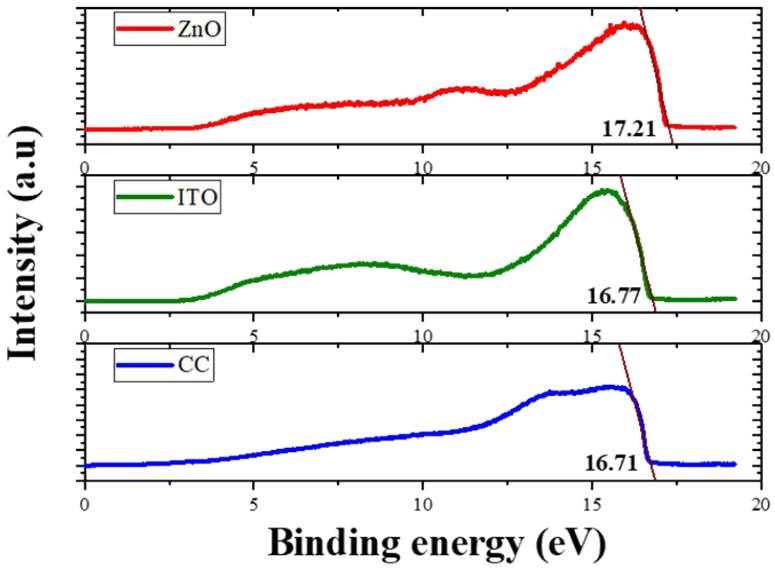

Figure S4: Ultraviolet photoelectron spectroscopy (UPS) measurements of work functions of ZnO, ITO, and carbon cloth samples.

The work functions (Φ_s) of carbon cloth, ITO, and ZnO were measured from ultraviolet photoelectron spectroscopy (UPS) spectra collected using a Kratos AXIS Supra instrument

with He(I) monochromatic light source. From the UPS spectra shown in Fig. S4, the work functions (Φ_s) of Carbon Cloth (CC), ITO and ZnO were calculated as 4.51, 4.45 and 4.01 eV using the following equation:

$$\Phi_s = photon\ energy - secondary\ electron\ cutoff\ energy \quad \text{(S1)}$$

where photon energy of He(I) source was 21.22 eV and the secondary electron cutoff energy for each sample is shown in the figure.

ZnO's band gap (3.26 eV) and position of its conduction band edge (3.87eV) were obtained from Hwang et al. [3], while the band gap (0.80 eV) of polydopamine (polyD) and its LUMO position (3.92 eV) were obtained from Zou et al. [4]. The Fermi level of polydopamine is assumed to be midway between the LUMO and HOMO. These data, together with the work function measurements from UPS, were used to construct the energy band diagram (Fig. S5), which is also shown in the main text.

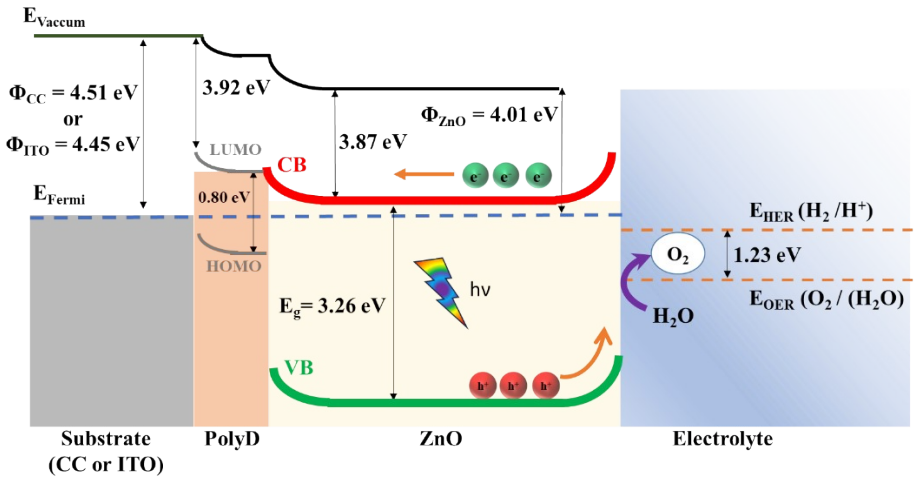

Figure S5: Band diagram of the heterostructures in the photoanode.

References

1. Oelßner, W., Berthold, F. & Guth, U. The iR drop – well-known but often underestimated in electrochemical polarization measurements and corrosion testing. *Mater. Corros.* **57**, 455–466 (2006).
2. iR Compensation: Potentiostat Fundamentals / Basics of EIS Gamry Instruments. https://www.gamry.com/application-notes/instrumentation/understanding-ir-compensation/.
3. Hwang, J. O. *et al.* Vertical ZnO nanowires/graphene hybrids for transparent and flexible field emission. *J. Mater. Chem.* **21**, 3432–3437 (2011).
4. Zou, Y. *et al.* Regulating the absorption spectrum of polydopamine. *Sci. Adv.* **6**, eabb4696 (2020).