Electronic Supplementary Information

**Dye-Sensitization of Boron-Doped Diamond Foam: Champion Photoelectrochemical Performance of Diamond Electrodes under Solar Light Illumination**

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**Fig. S1** SIMS analysis of a BDD foam electrode (one layer). The concentration of B-atoms is between $7 \times 10^{19}$ cm$^{-3}$ for the foam layer, which is about 500 nm thick (corresponding to one layer of templated hollow spheres). The compact layer underneath the porous film is highly doped to $>10^{21}$ cm$^{-3}$. 
Fig. S2 SEM images of B-doped diamond foam electrodes sensitized with BT-Rho. Holes in the diamond shell are obvious on the top-left image. Heavily damaged structures are seen on the bottom images. The multilayer morphology of the diamond foam electrodes is apparent from the top-right image.
Fig. S3 Raman spectra (at 458 nm excitation) of a pristine BDD foam electrode and those sensitized with CPDT-Fur and BT-Rho. The diamond peak is seen at 1330 cm\(^{-1}\). The main impurity peaks are trans-polyacetylene (1150 cm\(^{-1}\)) and a broad G-peak of sp\(^2\) carbon at ca. 1500 cm\(^{-1}\). The absence of features around 500 cm\(^{-1}\) indicates removal of SiO\(_2\) and low B-doping.
**Fig. S4a** Raman spectra (at 633 nm excitation) of a pristine flat BDD film electrode on a SiO$_2$ substrate and those sensitized with CPDT-Fur and BT-Rho.

**Fig. S4b** Raman spectrum of a pristine flat BDD film electrode on a Si substrate. Excitation wavelengths 633 nm (a), 488 nm (b). The Raman features from the substrate are marked with an asterisk.
Fig. S5 Adsorption isotherm of Kr at a pristine BDD foam electrode; geometric area 1 cm$^2$. From the found $S_{BET}$ of the sample and its projected geometric area, the roughness factor, $R_f$, equals 114.
Fig. S6 Cyclic voltammogram of a pristine BDD foam electrode in phosphate buffer pH 7 (Sigma Aldrich) at different scan rates (see annotation labels).
Fig. S7 Long-term chronoamperometric measurement of the diamond foam electrode sensitized with CPDT-Fur. Chopped white light illumination (100 mW/cm$^2$; simulated AM 1.5G solar spectrum, 5 min dark/light interval). Electrolyte solution: 5 mM methyl viologen in 0.1 M Na$_2$SO$_4$, pH 7. Applied potential bias: -0.3 V vs. Ag/AgCl.
**Fig. S8** Chronoamperometric measurement on a pure (non-sensitized) diamond foam compared to that on a pure (non-sensitized) flat diamond film. Chopped white light illumination (20 mW/cm$^2$; simulated AM 1.5G solar spectrum). Electrolyte solution: 5 mM methyl viologen in 0.1 M Na$_2$SO$_4$ pH 7. Applied potential bias: -0.3 V vs. Ag/AgCl.
**Fig. S9** Long-term chronoamperometric measurement of the ‘champion’ diamond foam electrode sensitized with **BT-Rho** (parallel experiment on another electrode – see main text). For comparison, the same plot for a blank (non-sensitized) diamond foam is also shown. Chopped white light illumination (100 mW/cm²; simulated AM 1.5G solar spectrum, 10 min dark/light interval). Electrolyte solution: 5 mM methyl viologen in 0.1 M Na₂SO₄ pH 7. Applied potential bias: -0.3 V vs. Ag/AgCl.
**Fig. S10** Detail of the photocurrent/time plot for a BDD diamond foam electrode sensitized with **BT-Rho** which passed ca. 42.6 hours of aging-activation (data from Fig. 4 in the main text). For comparison, the corresponding plot for a fresh **BT-Rho**-sensitized foam electrode is also shown (data from Fig. 3 in the main text, but with timescale offset). Chopped white light illumination (100 mW/cm²; simulated AM 1.5G solar spectrum). Electrolyte solution: 5 mM methyl viologen in 0.1 M Na₂SO₄ pH 7. Applied potential bias: -0.3 V vs. Ag/AgCl.
Fig. S11 Chronoamperometric measurement of a diamond foam electrode sensitized with CPDT-Fur. Chopped white light illumination (100 mW/cm\(^2\); simulated AM 1.5G solar spectrum). Electrolyte solution: 5 mM methyl viologen in 0.1 M Na\(_2\)SO\(_4\). Applied potential bias: -0.2 V vs. Ag/AgCl. Curves from top to bottom: (a) fresh electrode, 1 sun, (b) the same electrode after several tens of minutes at 1 sun, (c) the same electrode after ca. 5 hours at 1 sun. Red curves are for measurements after ca. 50 hours with four different light intensities.
Fig. S12 Chronoamperometric measurements of a diamond foam electrode sensitized with BT-Rho at different bias voltages. Chopped white light illumination (50 mW/cm²; simulated AM 1.5G solar spectrum). Electrolyte solution: 5 mM methyl viologen in 0.1 M Na₂SO₄. The applied bias voltages (vs. Ag/AgCl) are indicated in annotations.
Fig. S13 Long-term chronoamperometric measurement of a flat B-doped diamond electrode sensitized with BT-Rho. Chopped white light illumination (100 mW/cm²; simulated AM 1.5G solar spectrum, 10 min dark/light interval). Electrolyte solution: 5 mM methyl viologen in 0.1 M Na₂SO₄. Applied potential bias: -0.3 V vs. Ag/AgCl.
Fig. S14a  UV-Vis absorption spectrum of the pure BT-Rho dye in absolute ethanol (c = 50 µM, optical length 1 cm). The tested solution was purged with Ar. The optical cell was glass/glass interfaced to Pyrex tube. This tube was finally heat-sealed under vacuum (the solution was temporarily frozen by liquid nitrogen during evacuation). The figure shows a spectrum of a fresh solution and that after continuous illumination by white light (100 mW/cm$^2$; simulated AM 1.5G solar spectrum, non-chopped). The time of illumination (in hours) is labeled on each spectrum. The spectra are offset for clarity, but the absorbance scale is identical. (The absorbance at wavelengths from 550 to 700 nm can be considered as a baseline for each individual spectrum). Qualitatively the same spectral changes were found also in chloroform solution.
**Fig. S14b** UV-Vis absorption spectrum (referenced to air) of a solid film of the pure BT-Rho dye spin-coated from solution on a quartz substrate. The figure shows the spectrum of a fresh film and that after continuous illumination by white light (100 mW/cm²; simulated AM 1.5G solar spectrum, non-chopped) in air. The time of illumination (in hours) is labeled on each spectrum. The spectra are offset for clarity, but the absorbance scale is identical. (The absorbance at wavelengths near 800 nm can be considered as a baseline for each individual spectrum).