

Optimizing CuO p-type dye-sensitized solar cells by using a comprehensive electrochemical impedance spectroscopic study

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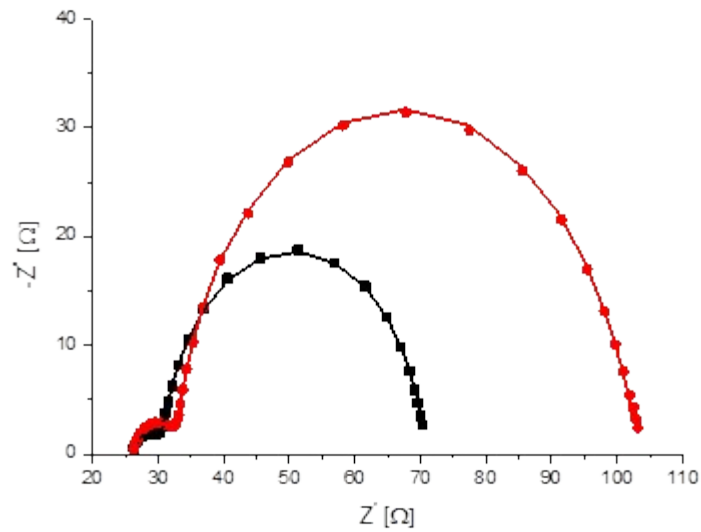


Figure S1: Upper part - Nyquist plot (circles) of CuO-DSSCs with the respective Kronig-Kramers test (solid line) under 1 sun illumination (black) and dark (red) recorded at V_{oc} conditions.

Table S1: Respective chi-square values of the Kronig-Kramers test for the imaginary ($-Z''$) and real part (Z') as well as the sum (Z) for the measured Nyquist plots under light and dark conditions.

Measurement condition	$\chi^2 [Z]$	$\chi^2 [Z']$	$\chi^2 [-Z'']$
light	2.11×10^{-6}	8.00×10^{-7}	1.3×10^{-6}
dark	9.94×10^{-6}	3.17×10^{-6}	6.77×10^{-6}

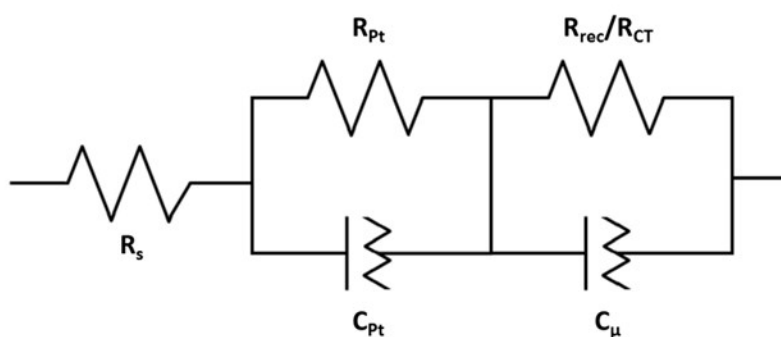
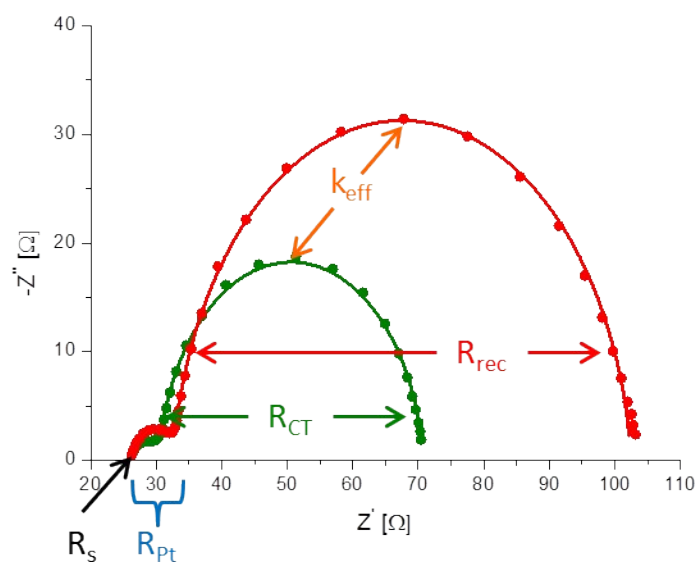


Figure S2: Upper part - Nyquist plot (circles) of CuO-DSSCs with the respective fitting (solid line) under 1 sun illumination (green) and dark (red) recorded at V_{oc} conditions. The resistances and the effective rate constant k_{eff} , which can be extracted from the Nyquist plots, are shown. Bottom part – Electrical circuit model used for EIS data fitting.

Table S2: Fitting results of the exemplary Nyquist plots of Fig S2 with the corresponding percental errors. $Y_{0,Pt}$, α_{Pt} , $Y_{0,\mu}$ and α_{μ} are used to calculate the capacitances C_{Pt} and C_{μ} of the constant-phase element – **Equation 2**.

Measurement condition	R_s [Ω]	R_{Pt} [Ω]	$Y_{0,Pt}$ [Ss^α]	α_{Pt}	$R_{CT/rec}$ [Ω]	$Y_{0,\mu}$ [Ss^α]	α_{μ}
light	26.16 (0.74%)	4.51 (6.59%)	3.91×10^{-5} (45.88%)	0.81 (6.05%)	39.99 (0.72%)	1.86×10^{-4} (3.10%)	0.95 (0.67%)
dark	27.56 (0.56%)	6.37 (3.66%)	1.19×10^{-5} (29.82%)	0.92 (3.44%)	69.77 (0.50%)	2.15×10^{-4} (2.22%)	0.94 (0.50%)

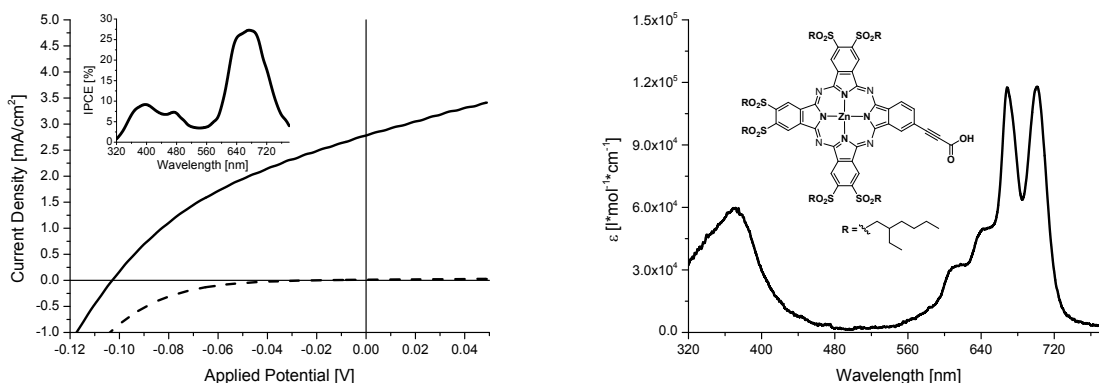


Figure S3: Left part: Current density vs. applied voltage under 1 sun and AM 1.5 illumination (line) and dark (dashed) conditions for a p-type CuO DSSC. Inset – IPCE spectra of the corresponding device. Right part: Absorption spectra and molecular structure of the electron-accepting phthalocyanine **ZnPc2**, which was used as a photosensitizer.

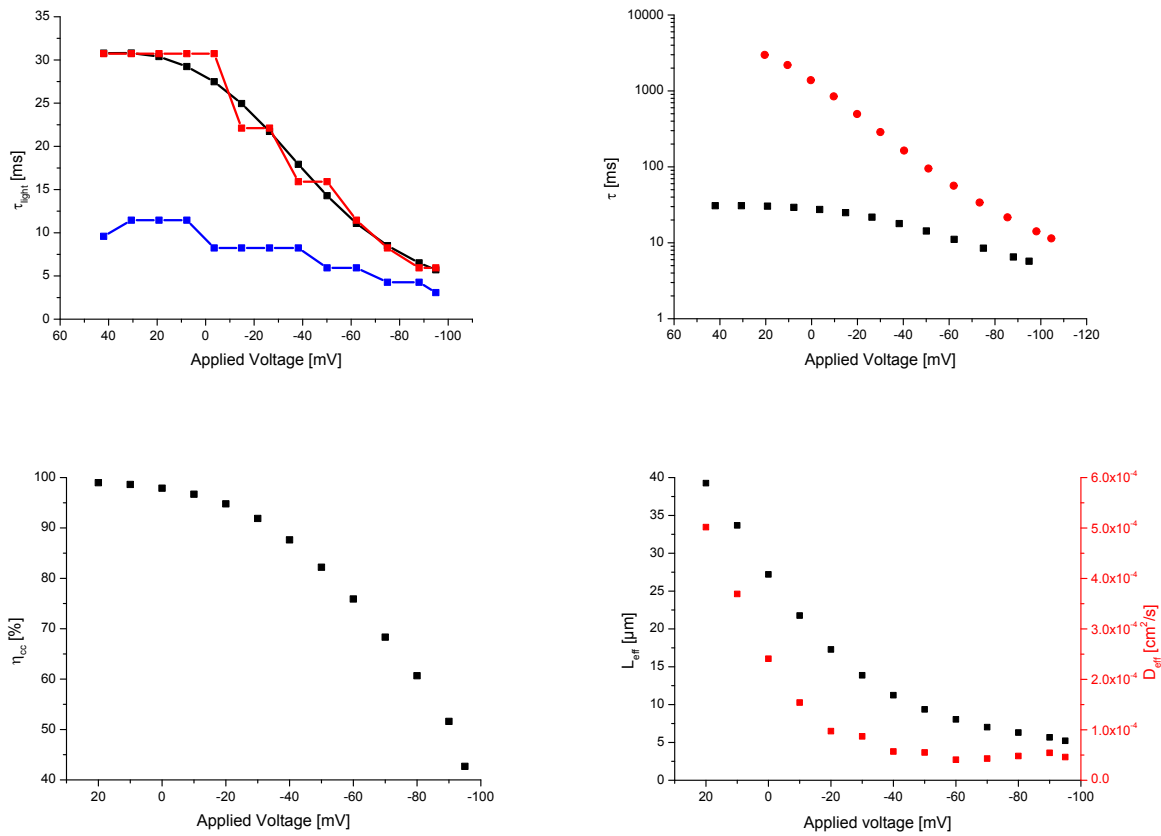


Figure S4: Top left – Time constants under light conditions derived via **Equation 3** (black), determined via **Equation 4** / the Nyquist plot maximum frequency (red), and via **Equation 4** / the frequency of the maximum in the bode phase plot (blue). Top right - τ_{light} (black) and τ_{dark} (red) determined by **Equation 3** for the whole voltage region. Bottom left - η_{cc} vs. applied voltage. Bottom right – L_{eff} (black) and D_{eff} (red) vs. applied voltage for a p-type CuO DSSCs.

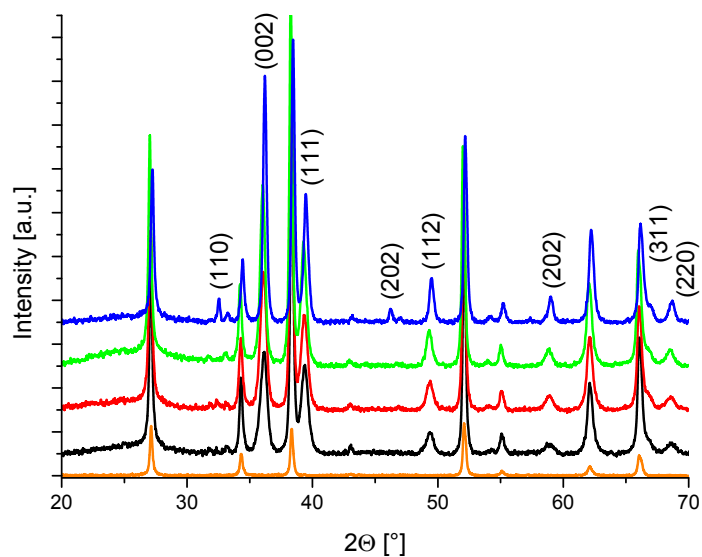


Figure S5: XRD spectra of CuO electrodes calcinated at 300, 350, 400, and 500°C in black, red, green, and blue, respectively, with the bare FTO substrate in orange and the corresponding crystal planes in brackets. Some of the spectra are offset in intensity for a better comparability.

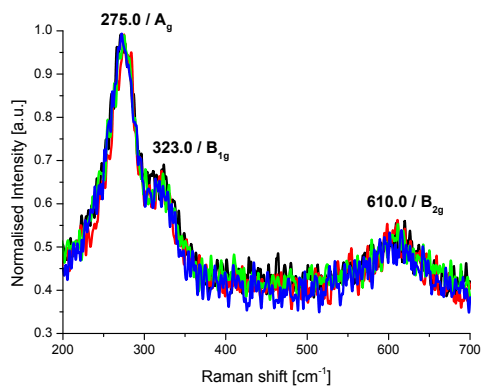


Figure S6: Normalised Raman spectra of CuO electrodes calcinated at 300 (black), 350 (red), 400 (green) and 500°C (blue) showing the three active raman modes A_g , B_{1g} and B_{2g} .

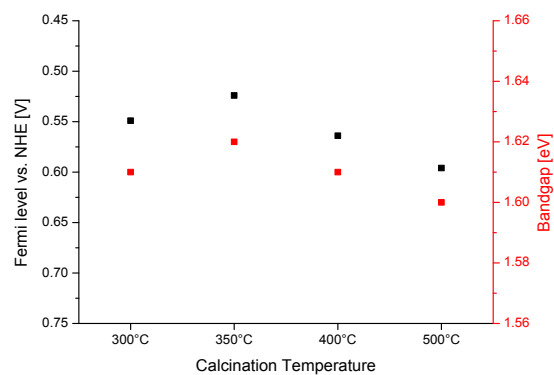


Figure S7: Variation of the Fermi level E_F (black) and the bandgap energy (red) for CuO electrodes calcinated at different temperatures.

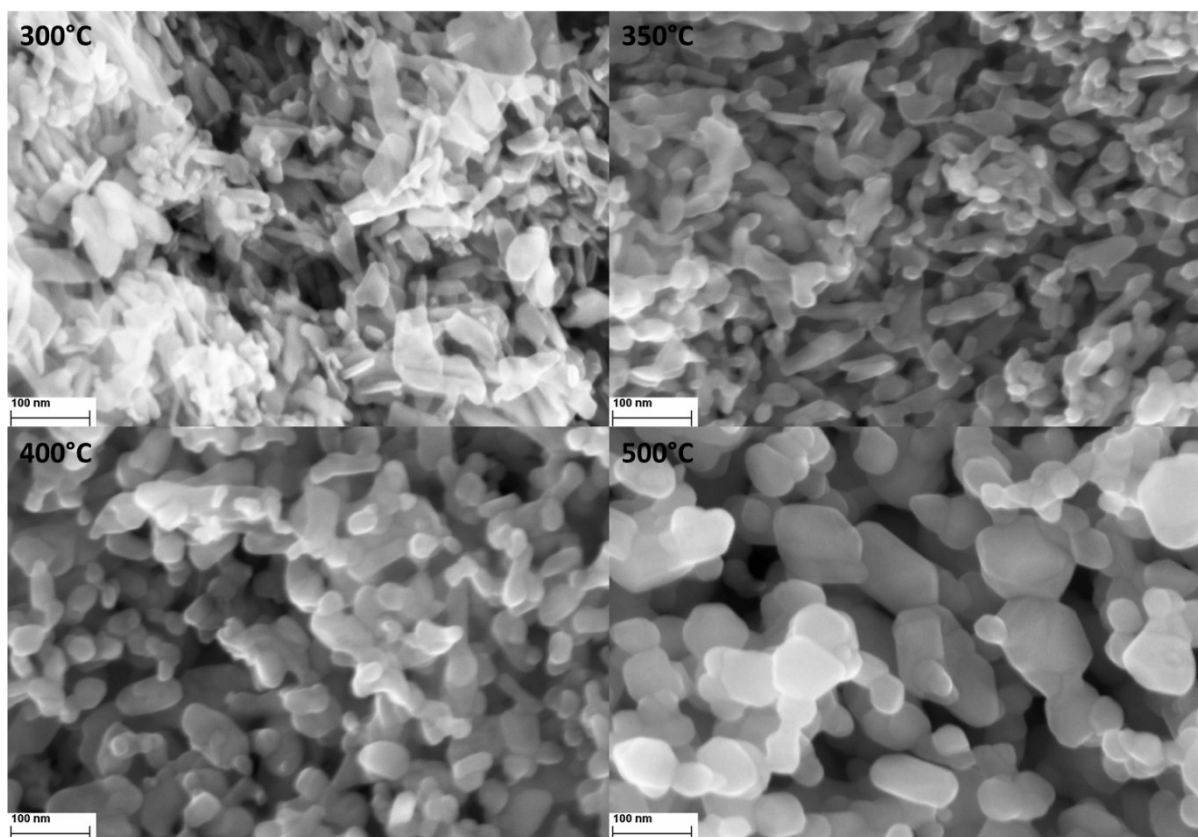


Figure S8: SEM images (150k magnification) of CuO electrodes calcinated at 300, 350, 400, and 500°C.

Table S3: Figures-of-merit of p-type CuO DSSCs for optimization of T_{sint} , the electrode thickness and the electrolyte ratio.

Devices			Figures-of-merit					
Sintering [°C]	Thickness [μm]	I/I ₂ ratio	Dye loading ^[a] [mol/cm ²]	V _{oc} [mV]	J _{sc} [mA/cm ²]	FF	η [%]	IPCE ^[b] [%]
Calcination temperature								
300	5.0	5:1	4.3	92.6	2.76	0.36	0.092	24.3
350	4.7	5:1	3.8	92.6	2.53	0.37	0.086	22.3
400	4.9	5:1	3.0	92.6	1.79	0.38	0.062	15.6
500	4.8	5:1	1.3	97.5	1.26	0.39	0.048	10.6
Electrode thickness								
300	1.5	5:1	0.9	112.2	2.01	0.38	0.087	17.7
300	5.0	5:1	4.3	92.6	2.76	0.36	0.092	24.3
300	9.0	5:1	13.8	82.9	3.08	0.34	0.087	25.5
Electrolyte ratio I/I₂⁻								
300	5.1	10:1	4.3	95.1	1.92	0.36	0.066	17.1
300	5.1	7.5:1	4.3	99.9	2.27	0.35	0.079	19.9
300	5.0	5:1	4.3	92.6	2.76	0.36	0.092	24.3
300	5.1	2.5:1	4.3	87.7	3.57	0.36	0.112	29.6

[a] All values multiplied by 10⁻⁹, [b] IPCE at 670 nm

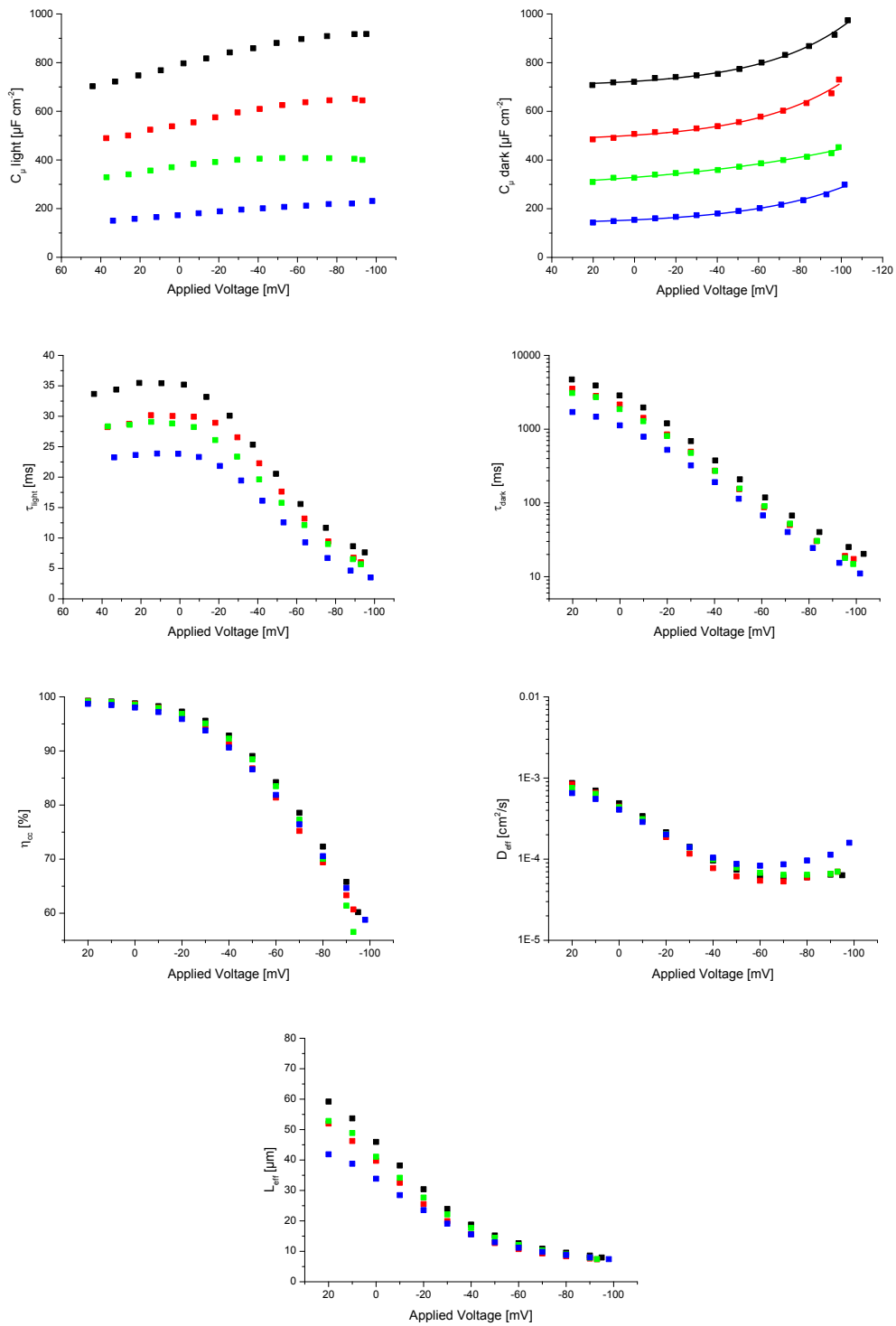
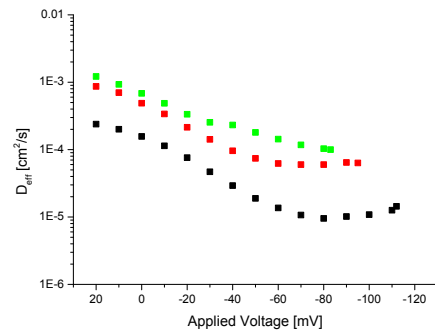
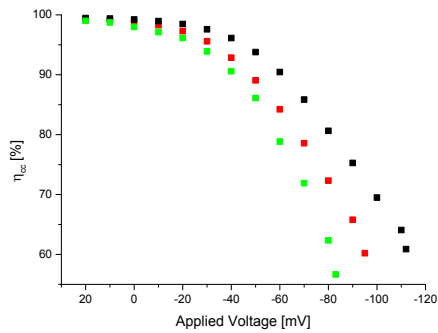
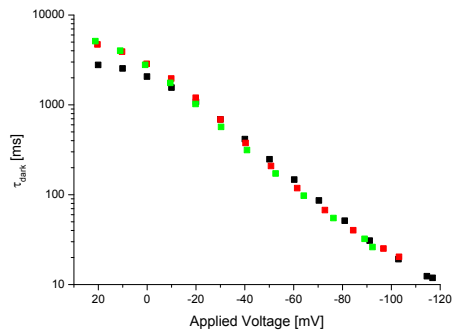
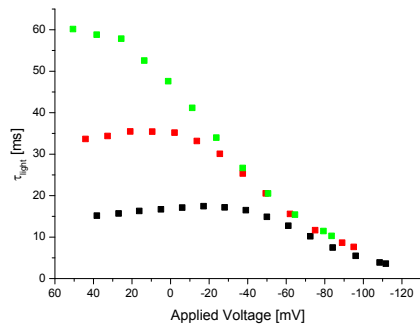
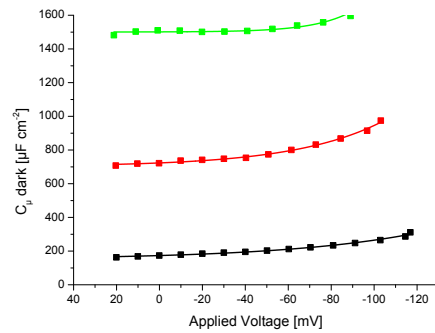
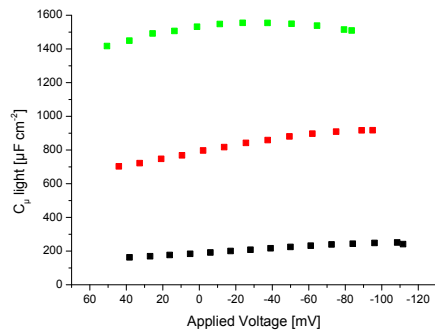


Figure S9: From top left to bottom right C_{μ}^{light} , C_{μ}^{dark} , τ_{light} , τ_{dark} , η_{cc} , D_{eff} and L_{eff} all vs. applied voltage for the different calcination temperatures 300 (black), 350 (red), 400 (green) and

500°C (blue). The fits of C_{μ} dark according to **Equation 9** are depicted as solid lines in the corresponding color.



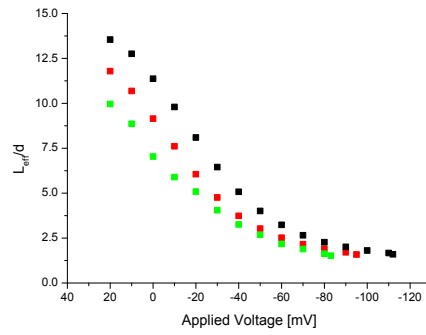
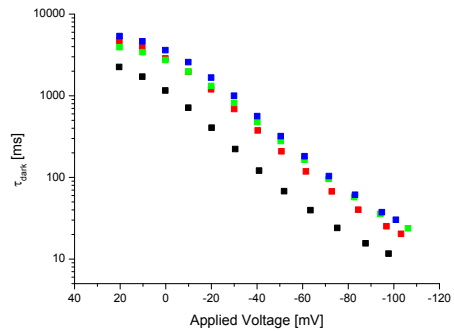
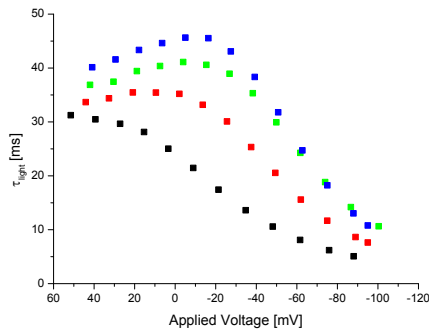
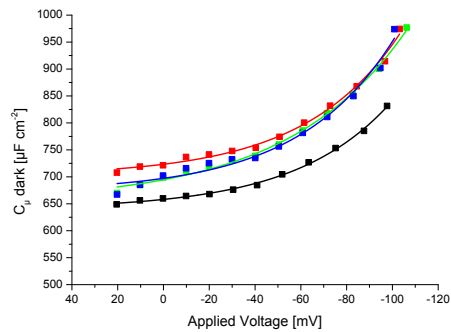
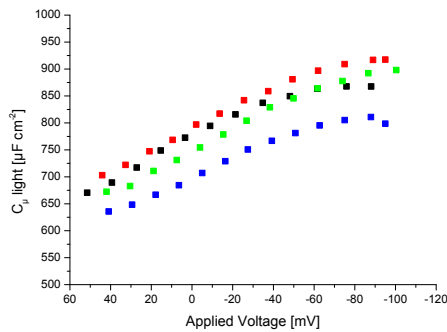


Figure S10: From top left to bottom right C_{μ} light, C_{μ} dark, τ_{light} , τ_{dark} , η_{cc} , D_{eff} and L_{eff}/d all vs. applied voltage for the different film thicknesses 1.5 μm (black), 5.0 μm (red) and 9.0 μm (green). The fits of C_{μ} dark according to **Equation 9** are depicted as solid lines in the corresponding color.



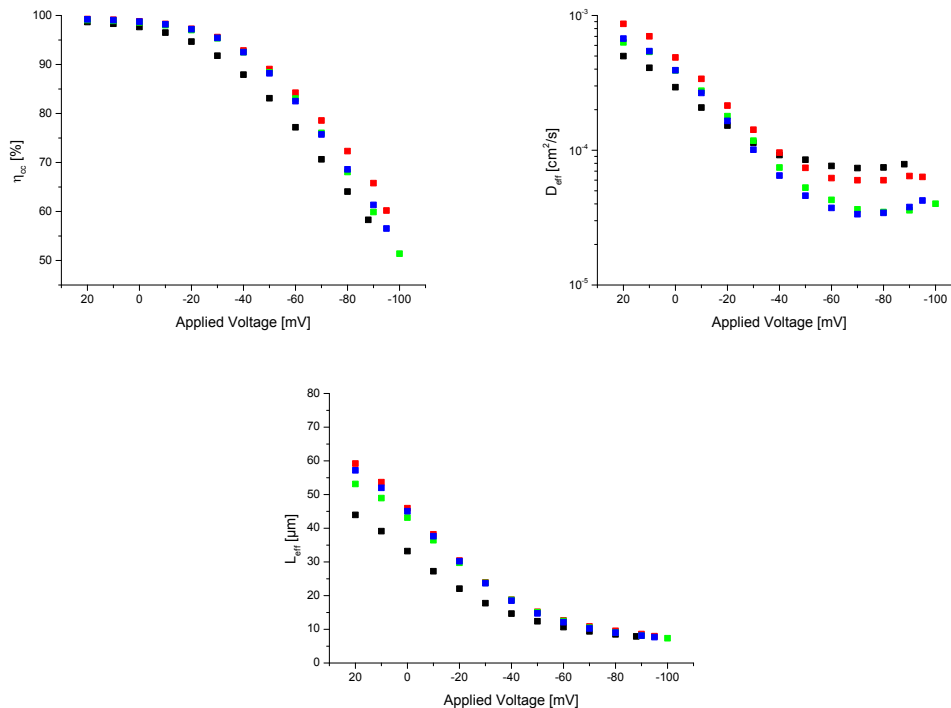
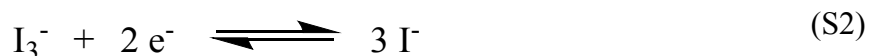


Figure S11: From top left to bottom right C_{μ} light, C_{μ} dark, τ_{light} , τ_{dark} , η_{cc} , D_{eff} and L_{eff} all vs. applied voltage for the electrolyte ratios 2.5:1 (black), 5:1 (red), 7.5:1 (green) and 10:1 (blue). The fits of C_{μ} dark according to **Equation 9** are depicted as solid lines in the corresponding color.

Calculation of the redox potential:

In solution iodine will undergo an equilibrium reaction with iodide to form triiodide with the reaction constant k_1 - Equation S1. Considering that k_1 is very large in acetonitrile ($\log(k_1/\text{M}^{-1}) = 6.76 \times 10^5$), basically all free iodine will react to triiodide.¹ From this we can approximate that the final triiodide concentration $[\text{I}_3^-]$ is almost equal to the initial concentration of iodine $[\text{I}_2]$. Furthermore, for every mol I_3^- that has been formed, an equimolar amount of iodine $[\text{I}^-]$ has been consumed – e.g., for an electrolyte with the initial concentrations of $[\text{I}^-] = 1.0\text{M}$ and $[\text{I}_2] = 0.1\text{M}$, the final concentrations of the active redox species will be $[\text{I}^-] = 0.9\text{M}$ and $[\text{I}_3^-] = 0.1\text{M}$. With Equation S1 and the aforementioned approximations at hand, we calculated the redox

potentials for the all the investigated electrolyte ratios. Equation S2 shows the redox reaction of the I⁻/I₃⁻ redox couple from which we can establish the corresponding Nernst-equation – Equation S3. From this we can calculate the redox potential (E_{redox}) of the investigated electrolytes using $E^0 (\text{I}_3^-/\text{I}^-) = 0.354 \text{ V vs. NHE}$ – Table S4 :¹



$$E_{\text{redox}} = E^0 + \frac{RT}{2F} \times \ln \frac{[\text{I}_3^-]}{[\text{I}^-]^3} \quad (\text{S3})$$

Table S4: Calculated redox potentials $E_{\text{redox}}(\text{I}_3^-/\text{I}^-)$ for the investigated electrolyte ratios

Ratio I:I ₂	[I ₃ ⁻] in M ^[a]	[I ⁻] in M ^[a]	$E_{\text{redox}} (\text{I}_3^-/\text{I}^-)$ in V vs. NHE ^[b]
10:1	0.1	0.9	0.331
7.5:1	0.13	0.87	0.335
5:1	0.2	0.8	0.343
2.5:1	0.4	0.6	0.361

[a] Concentration of the redox species after reaching the equilibrium - Equation S2, [b] calculated according to Equation S3

REFERENCES

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