Supplementary Materials: Effect of Sensitization on the Electrochemical Properties of Nanostructured NiO

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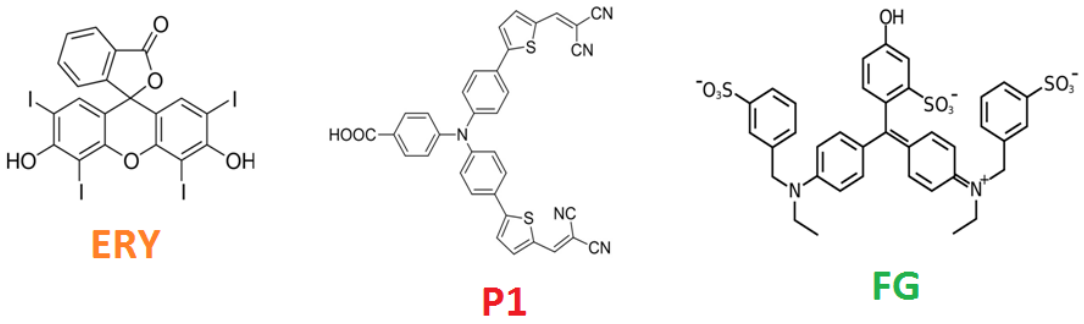

Figure S1. Structure of the commercial dyes here employed as sensitizers of screen-printed NiO photocathodes.

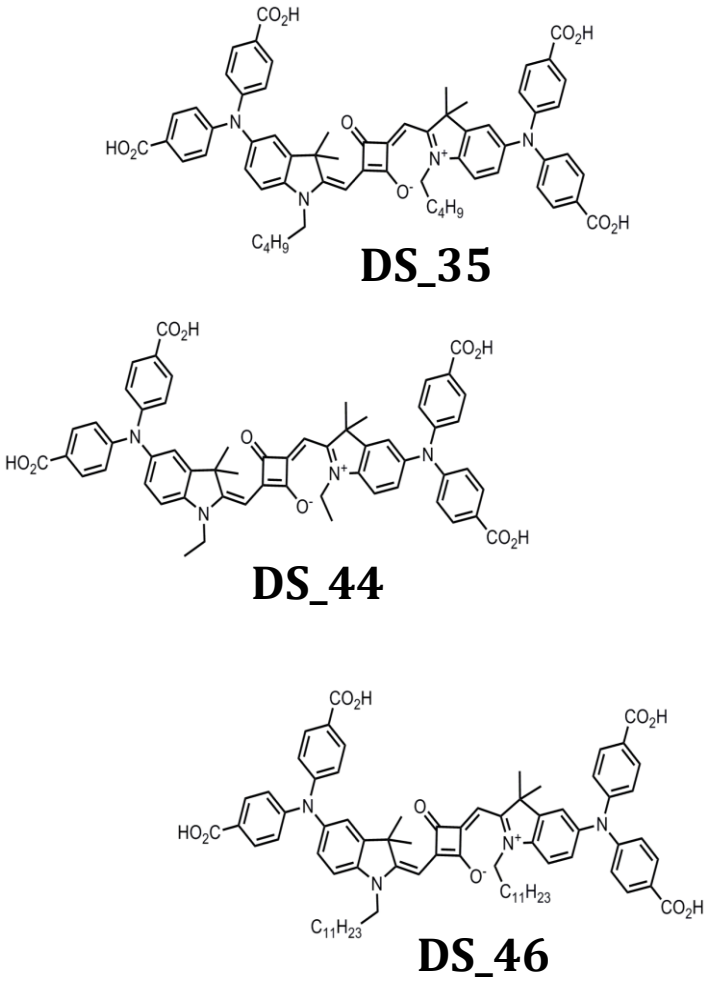

Figure S2. Structure of the three differently substituted squaraines DS_35, DS_44, and DS_46 here employed as sensitizers of screen-printed NiO photocathodes.

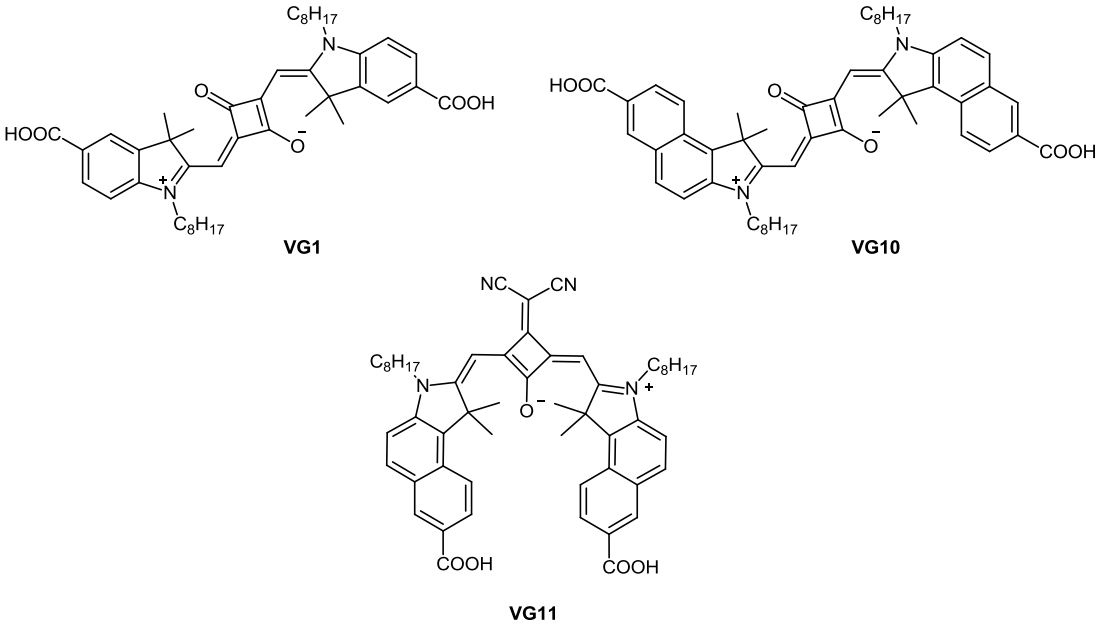

Figure S3. Structure of squaraines VG_1, VG_10, and VG_11 here employed as sensitizers of screen-printed NiO photocathodes.

Table S1. Procedure of the preparation of the paste P3 for the screen-printing deposition of NiO thin film cathodes.

Step 1	6 g of NiO nanopowders are grinded with 1 mL of concentrated HCl acid for 5 min (final volume of mixture: 1 mL).
Step 2	The addition of 1 mL of H_2O to the mixture obtained after Step 1 and grind for 1 min. This succession is repeated five times (final volume of mixture: 6 mL).
Step 3	The addition of 1 mL of ethanol to the mixture of Step 2 and grind for 1 min. This succession is repeated 15 times (final volume of the mixture: 21 mL).
Step 4	The addition of 2.5 mL of ethanol to the mixture of Step 3. This succession is repeated six times (final volume of the mixture: 36 mL).
Step 5	The transfer of the paste of Step 4 to a beaker using 100 mL of ethanol (final volume of the mixture: 136 mL).
Step 6	The mixture of Step 5 is stirred 1 min, successively sonicated for 2 min, and finally stirred again for 1 min.
Step 7	The addition of terpineol (20 g).
Step 8	The mixture of Step 7 is stirred 1 min, successively sonicated for 2 min, and finally stirred again for 1 min.
Step 9	The addition of a solution of ethyl cellulose to the mixture of Step 8. The added solution is formed by adding 3 g of ethyl cellulose in 30 g of a 10% v/v solution of ethanol in aqueous solvent.
Step 10	The mixture of Step 9 is stirred 1 min, successively sonicated for 2 min, and finally stirred again for 1 min. This succession of 4 min is repeated 3 times.
Step 11	The slow evaporation of the volatile components of the resulting mixture: The mixture of Step 10 is placed on hot plate at 50 °C for 9 h. Then, the NiO nanoparticle paste is cooled down to ambient temperature and is ready for being utilized in the screen-printing mode of deposition

Table S2. Variation of V_{OC} for the three-electrode cells with coumarin-sensitized NiO as the working electrode. The members of the coumarin family here considered were coumarin 343 (C343) and coumarin 153 (C153). The structures of the two coumarins are displayed in Figure S4. In the case of NiO sensitization with C343, the quasi constancy of V_{OC} in passing from the unpolarized state of the cell to the electrochemically cycled system is indicative of a low extent of sensitization and poor

tendency of C343 to detach from the NiO surface upon electrochemical oxidative treatment of the electrode.

Dye	V_{OC} (mV) vs. Ag/AgCl	$V_{OC,20}$ (mV) vs. Ag/AgCl
C343	280	270
C153	150	195

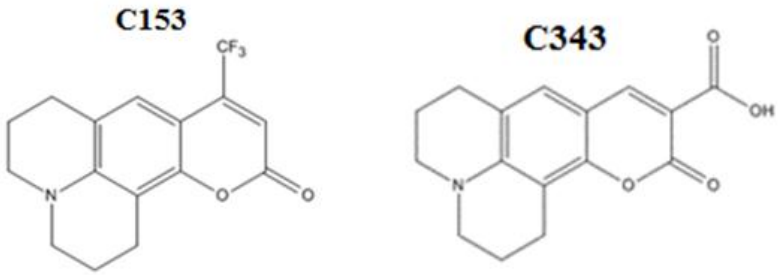

Figure S4. Structures of coumarins C153 and C343 here employed as sensitizers of screen-printed NiO photocathodes.

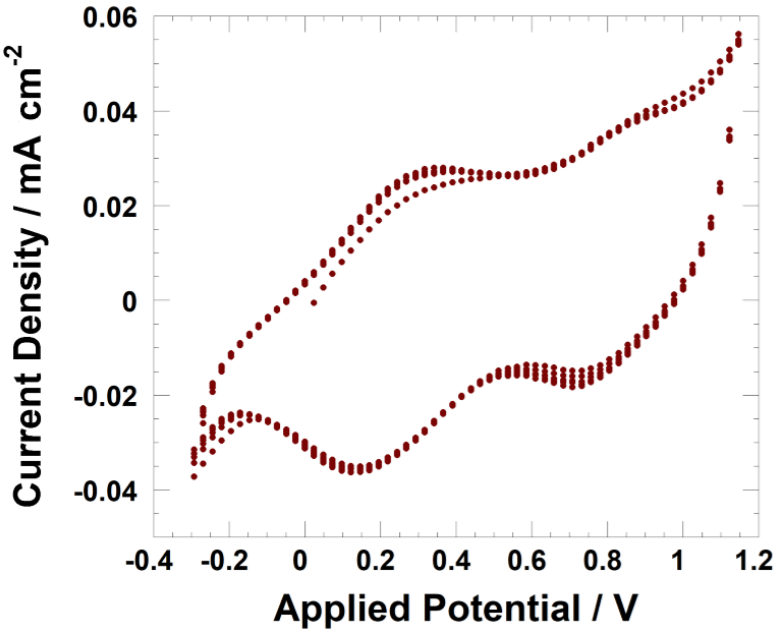

Figure S5. Voltammogram of bare NiO in the same electrolyte of Figure 2 (see main text). Scan rate: 100 mV s^{-1}.

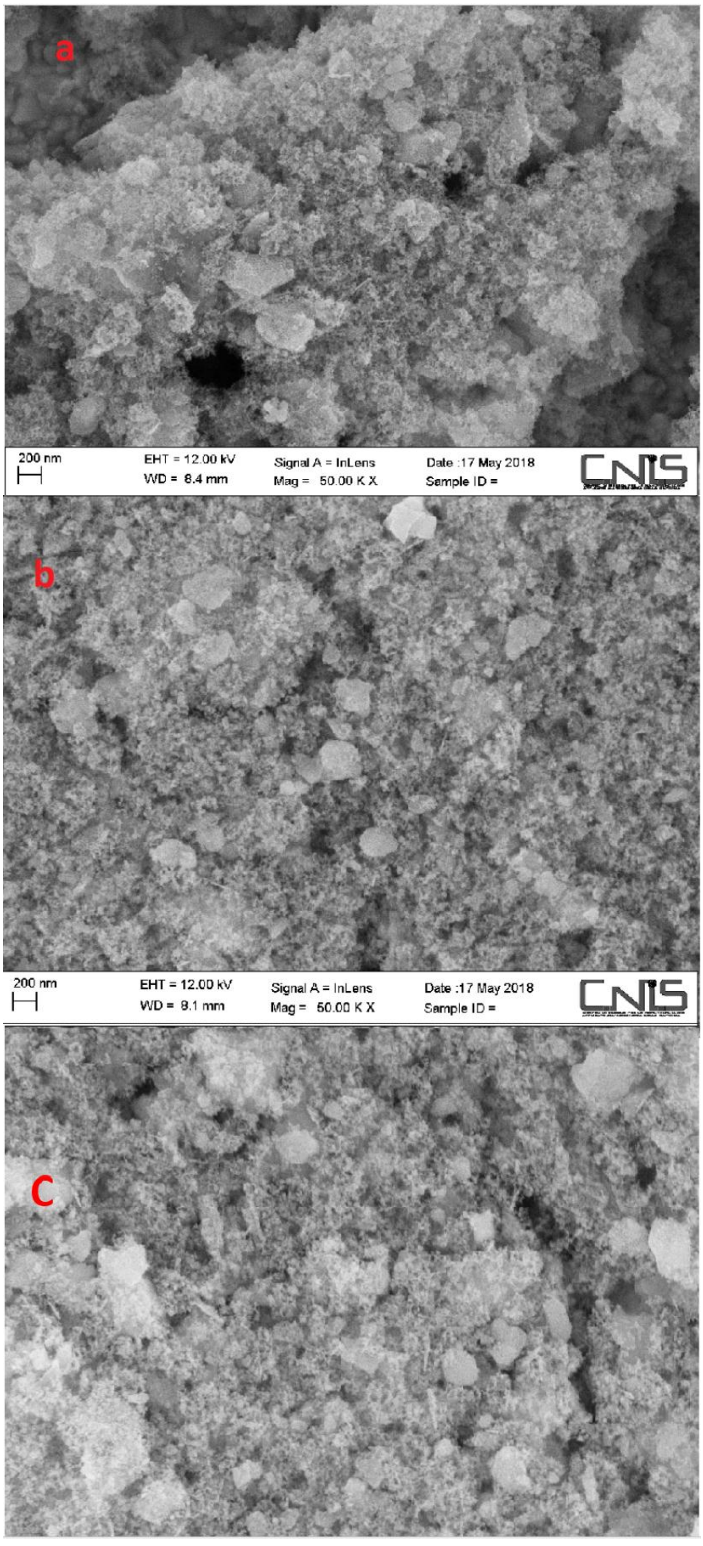

Figure S6. SEM images of sensitized electrode (**a**), unsensitized cycled electrode (**b**), and sensitized and then cycled electrode (**c**).

Table S3. EDX elemental analyses of sample reported in Figure S6.

Sample	Ni (at.%)	O (at.%)	C (at.%)	Cl (at.%)	Sn (at.%)
Sensitized	32.77	49.97	13.28	–	3.98
Bare-Cycled	37.04	51.59	8.60	0.34	2.43
Sensitized-Cycled	36.64	52.00	8.93	0.34	2.08

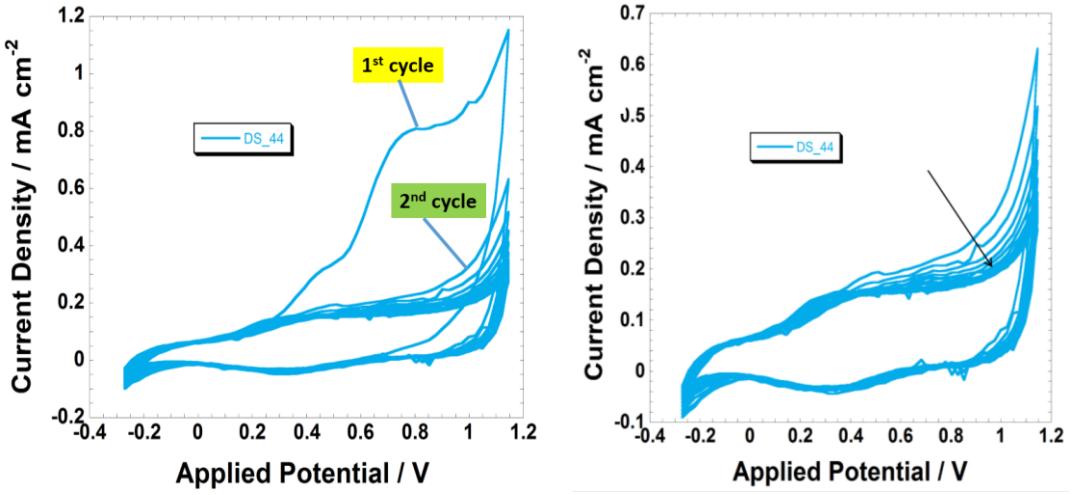

Figure S7. (**a**) First 20 voltammograms of DS_44-sensitized NiO electrode at the scan rate of 100 mV s^{-1}. The first two cycles are indicated. (**b**) Stabilization of the voltammogram of the DS_44-sensitized electrode after the first cycle (see (a)). The black arrow indicates the sense of variation of the current profile upon increase of the number of cycles. The applied potential is referred to the reference electrode Ag/AgCl.

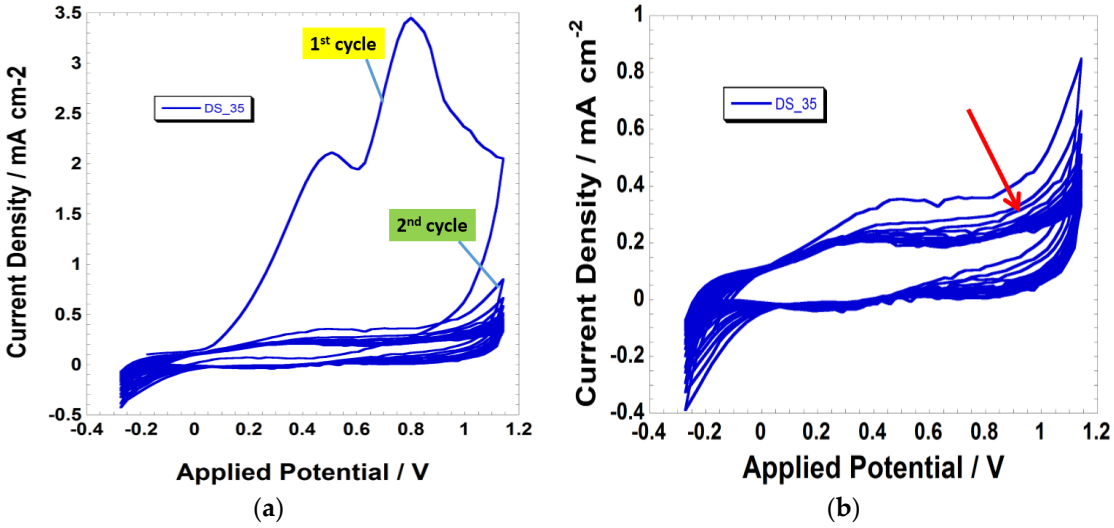

Figure S8. (**a**) First 20 voltammograms of DS_35-sensitized NiO electrode at the scan rate of 100 mV s^{-1}. The first two cycles are indicated. (**b**) Stabilization of the voltammogram of the DS_35-sensitized electrode after the first cycle (see (a)). The red arrow indicates the sense of variation of the current profile upon increase of the number of cycles. The applied potential is referred to the reference electrode Ag/AgCl.

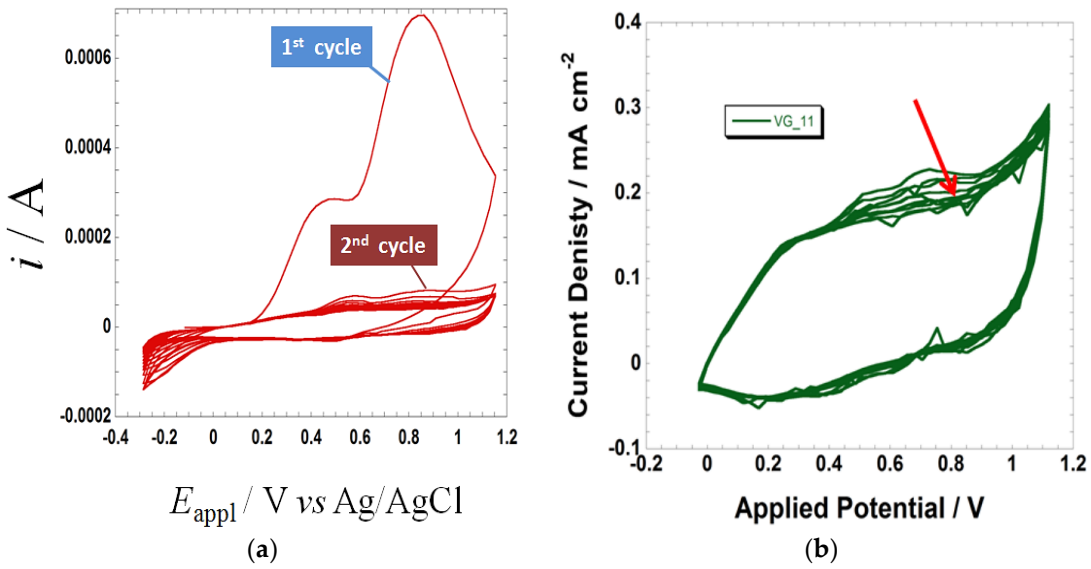

Figure S9. (**a**) Evolution of the voltammograms of VG_11-sensitized NiO electrode at the scan rate of 100 mV s^{-1}. The first two cycles are indicated. (**b**) Stabilization of the voltammogram of the VG_11-sensitized electrode after the first cycle (see (a)). The red arrow indicates the sense of variation of the current profile upon increase of the number of cycles. In the right plot, the applied potential is referred to the reference electrode Ag/AgCl.

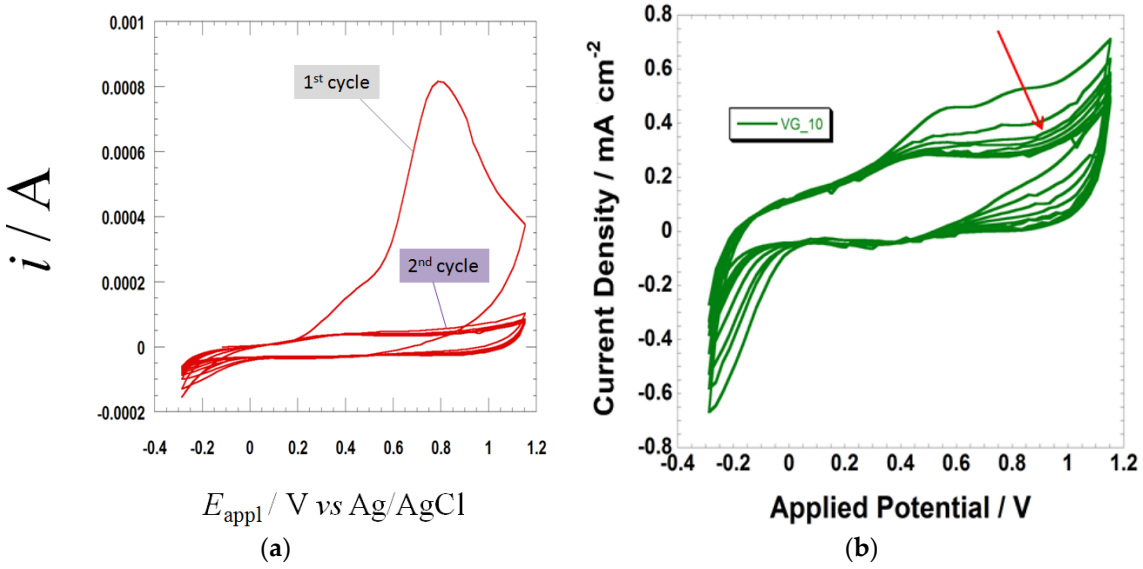

Figure S10. (**a**) evolution of the voltammograms of VG_10-sensitized NiO electrode at the scan rate of 100 mV s^{-1}. The first two cycles are indicated. (**b**) stabilization of the voltammogram of the VG_10-sensitized electrode after the first cycle (see (a)). The red arrow indicates the sense of variation of the current profile upon increase of the number of cycles. In the right plot the applied potential is referred to the reference electrode Ag/AgCl.

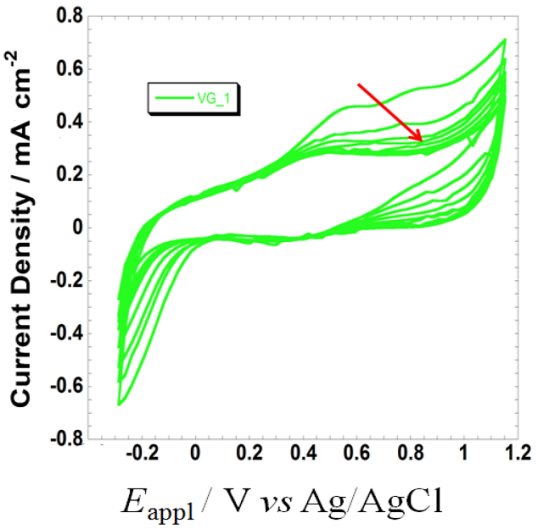

Figure S11. Evolution of the voltammograms of VG_1-sensitized NiO electrode at the scan rate of 100 mV s^{-1}. The red arrow indicates the sense of variation of the current profile upon increase of the number of cycles. First cycle is not shown.

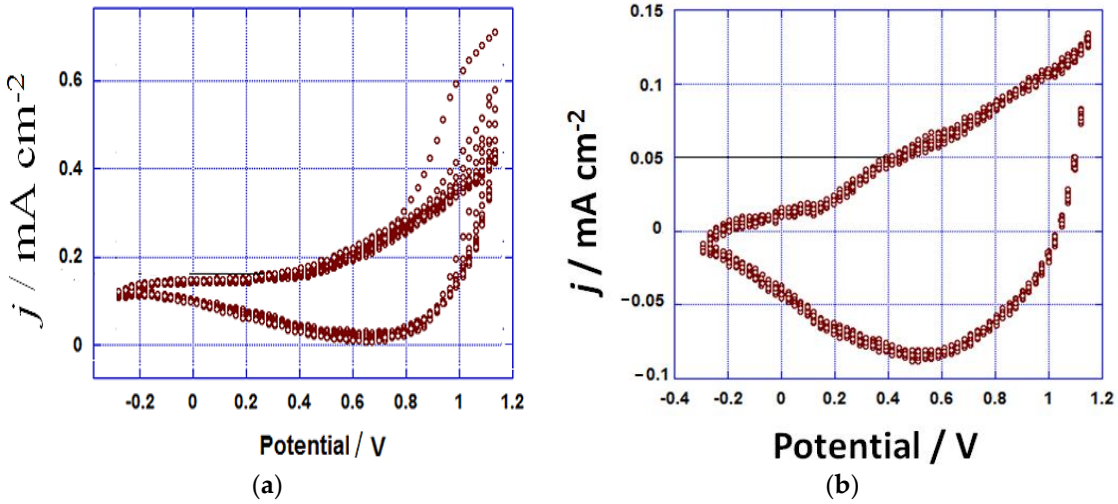

Figure S12. First 10 voltammograms of (**a**) C343- and (**b**) C153-sensitized NiO. Scan rate of 100 mV s^{-1}. The applied potential is referred to the reference electrode Ag/AgCl.

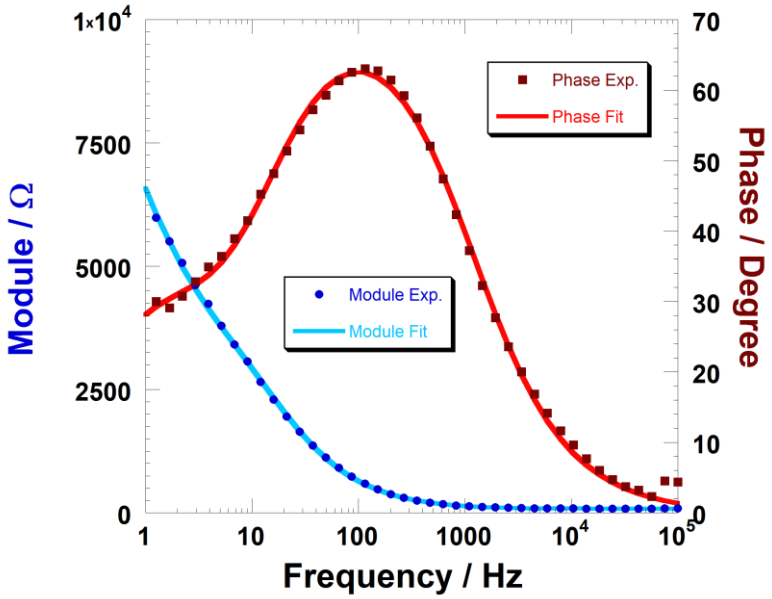

Figure S13. NiO bare: experimental EIS data (dots) and fitted curves (solid lane) for both module (in blue) and phase (red).

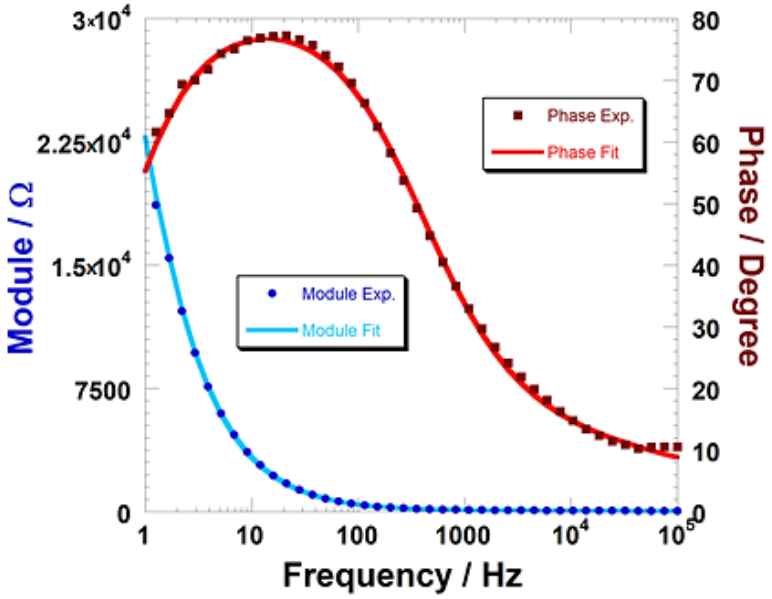

Figure S14. NiO sensitized with Fast Green: experimental EIS data (dots) and fitted curves (solid lane) for both module (in blue) and phase (red).

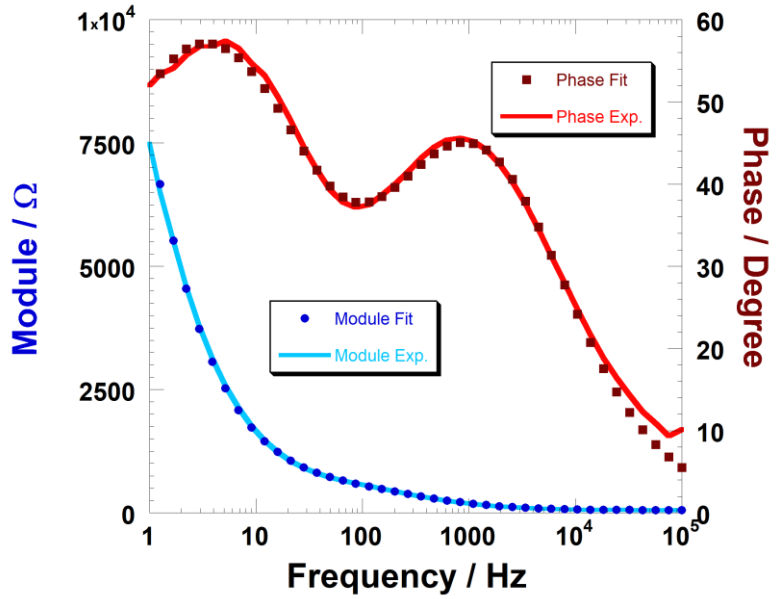

Figure S15. NiO sensitized with P1: experimental EIS data (dots) and fitted curves (solid lane) for both module (in blue) and phase (red).

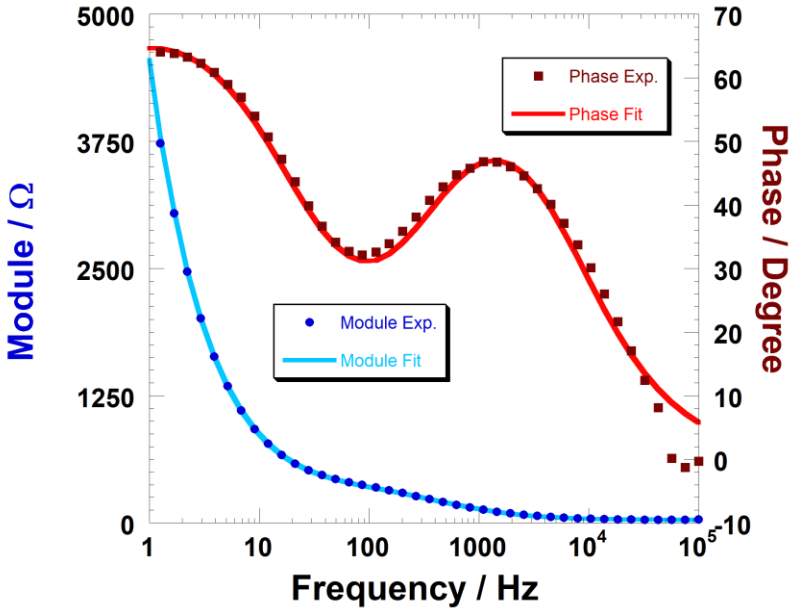

Figure S16. NiO sensitized with Erythrosine B: experimental EIS data (dots) and fitted curves (solid lane) for both module (in blue) and phase (red).

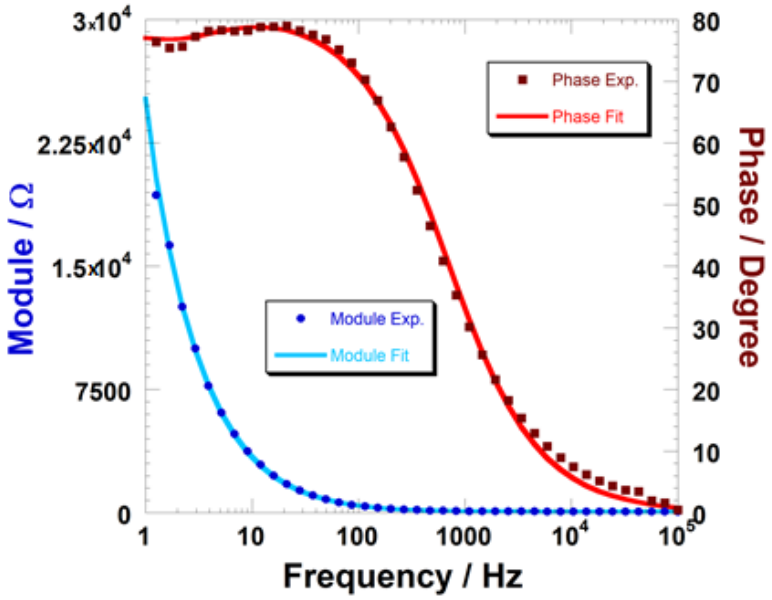

Figure S17. NiO sensitized with DS_44: experimental EIS data (dots) and fitted curves (solid lane) for both module (in blue) and phase (red).

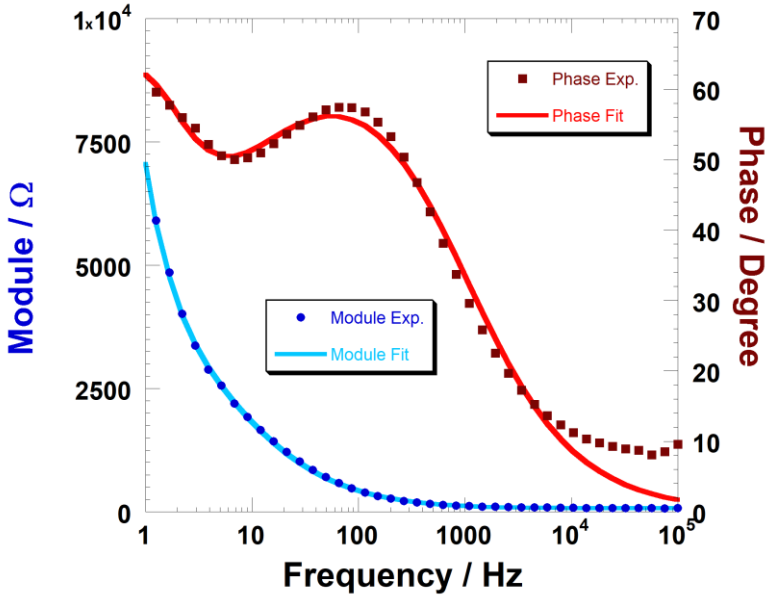

Figure S18. NiO sensitized with DS_35: experimental EIS data (dots) and fitted curves (solid lane) for both module (in blue) and phase (red).

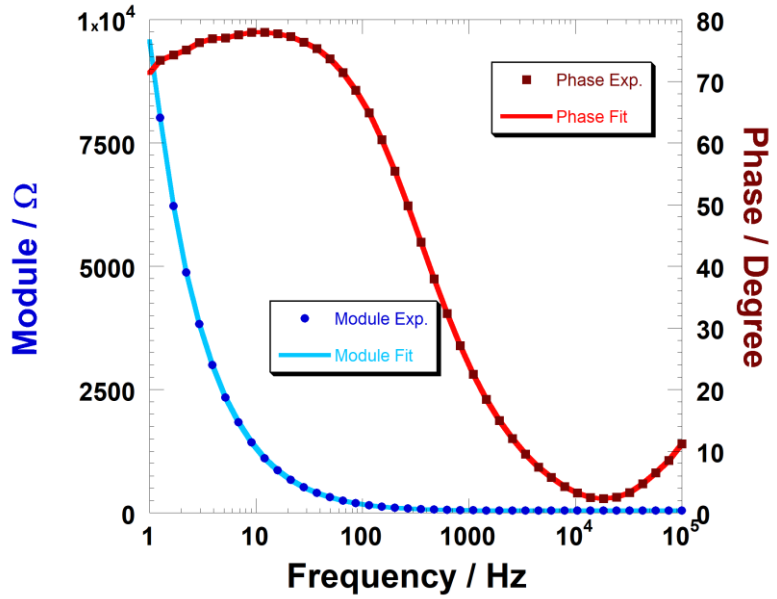

Figure S19. NiO sensitized with DS_46: experimental EIS data (dots) and fitted curves (solid lane) for both module (in blue) and phase (red).

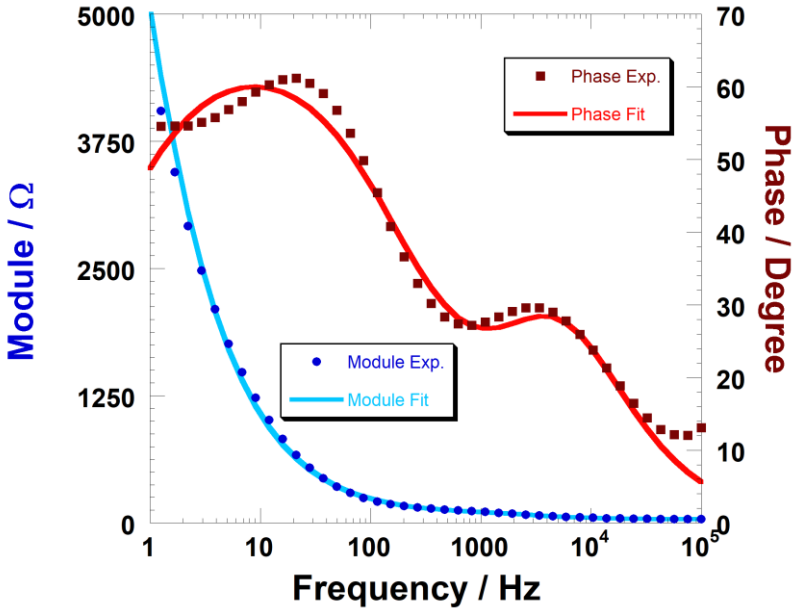

Figure S20. NiO sensitized with VG1: experimental EIS data (dots) and fitted curves (solid lane) for both module (in blue) and phase (red).

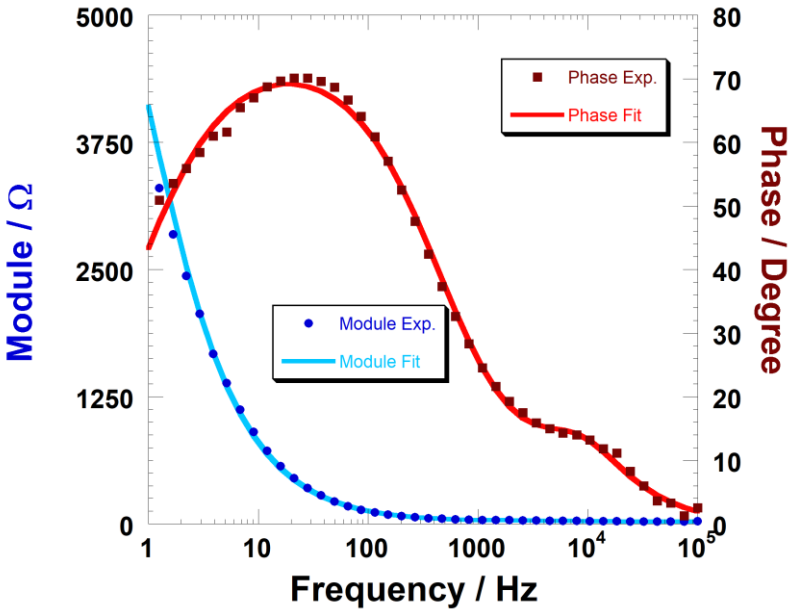

Figure S21. NiO sensitized with VG10: experimental EIS data (dots) and fitted curves (solid lane) for both module (in blue) and phase (red).

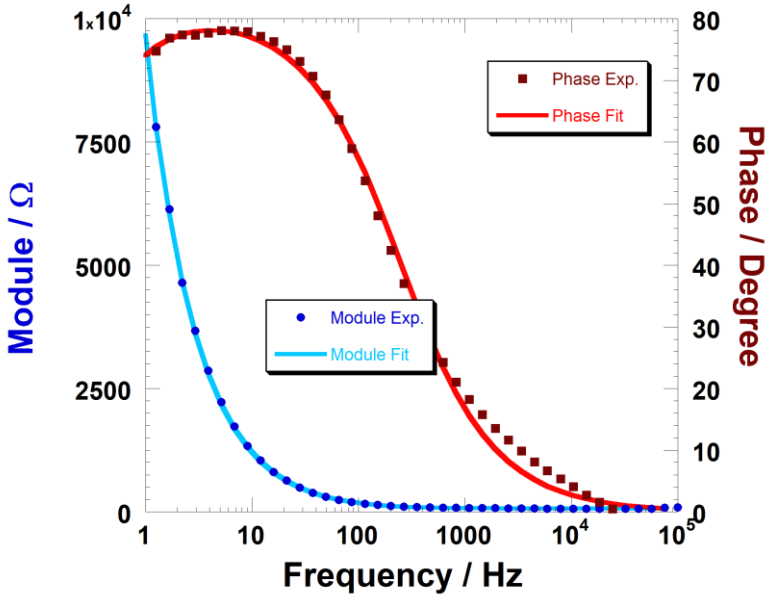

Figure S22. NiO sensitized with VG11: experimental EIS data (dots) and fitted curves (solid lane) for both module (in blue) and phase (red).