Article

Supplementary material to: Low-Cost Graphene-Based Composite Electrodes for Electro-Chemical Oxidation of Phenolic Dyes

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S1. UV-Vis Characterization of Degraded Dye Mixture Solution

Decolorization of dyes upon electrochemical degradation was tracked by UV-Vis spectrometry. UV-Vis absorption spectra of dyes mixture used in electooxidative degradation experiments (15 ppm dyes solution in 0.1 M Na_2SO_4) and 5 ppm solutions of each dye in 0.1 M Na_2SO_4 are shown in Figure S1.

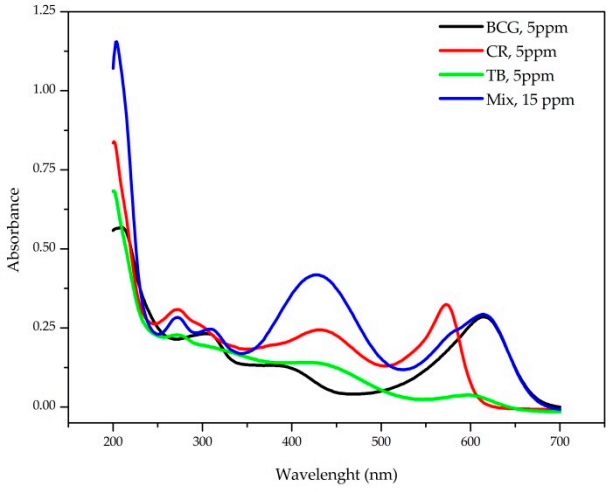


Figure S1. Comparison of the UV-Vis spectra of separate dyes (5 ppm of dye in 0.1 M Na_2SO_4) and dyes mixture (15 ppm of dyes in 0.1 M Na_2SO_4).

In order to establish experimental framework, 15 ppm dyes mixtures (solutions with 5 ppm of each dye in 0.1 M Na_2SO_4) were electrochemically treated for 150 min applying current density of 10 mA/cm^2. Figure S2 (left panels) represents resulting UV-Vis absorption spectra of the processes performed at (a) GNP@SS, (b) SnO_2/GNP@SS and (c) TiO_2/GNP@SS electrode. Absorption spectra of electrolyte solutions (0.1 M Na_2SO_4), that were electrochemically treated under the

same conditions at investigated electrodes, are presented for comparison on the right panels in Figure S2.

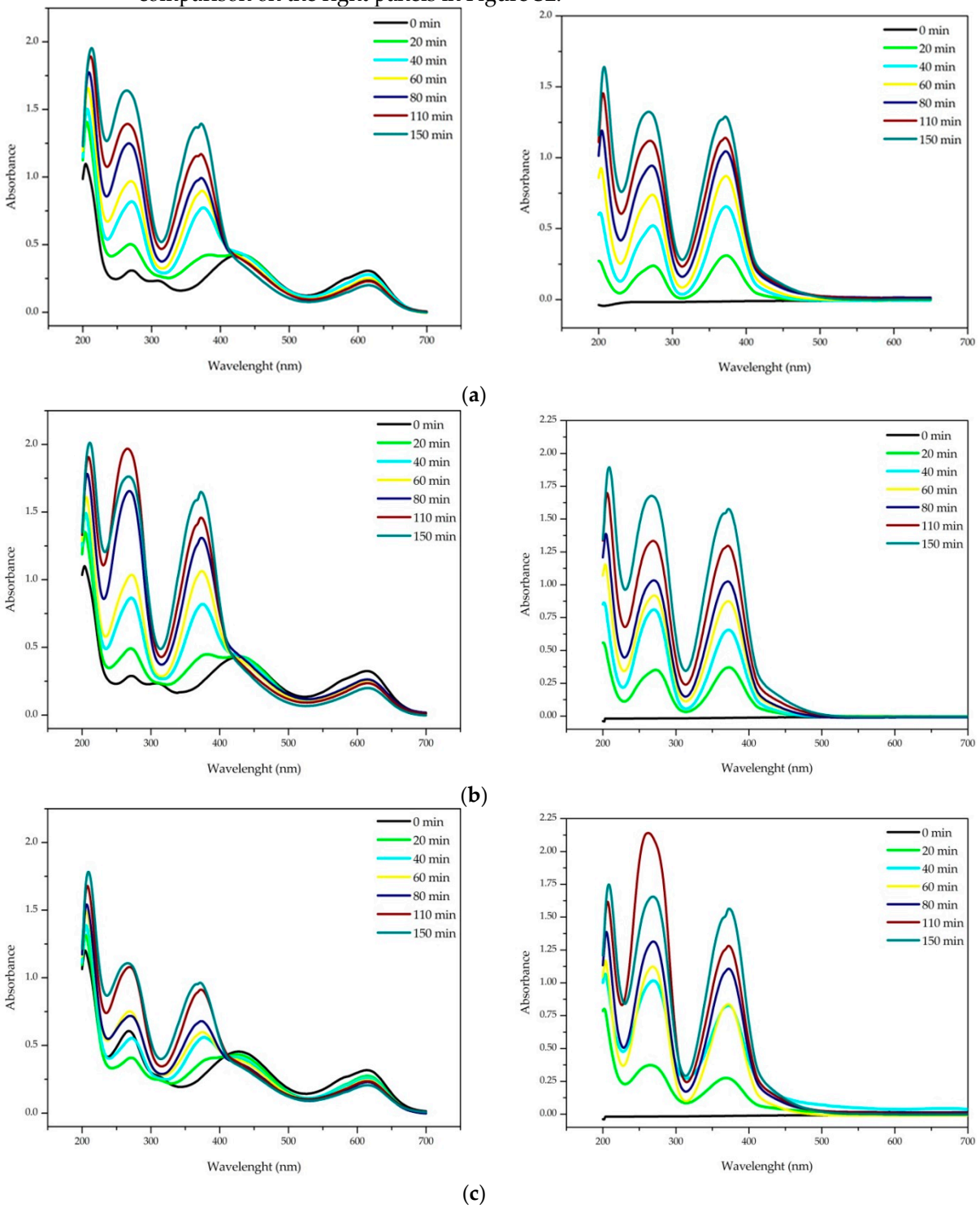


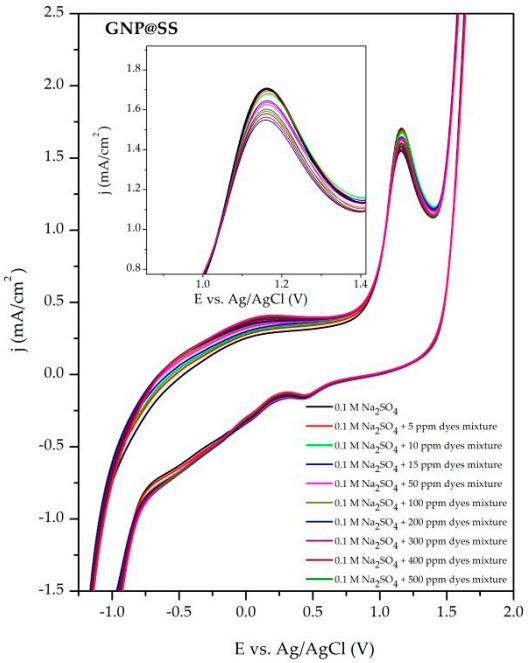
Figure S2. UV-Vis absorption spectra of 15 ppm dyes mixtures (5 ppm of each dye in 0.1 M Na_2SO_4) (left panels) and electrolyte solutions (0.1 M Na_2SO_4) (right panels) that were electrochemically treated for 150 min at current density of 10 mA/cm^2 at: (**a**) GNP@SS electrode; (**b**) SnO_2/GNP@SS electrode; (**c**) TiO_2/GNP@SS electrode.

The spectra exhibit an isosbestic point at 500 nm. At the wavelengths below 500 nm, the absorbance increase originates from the formation of yellowish feri-sulphate, as confirmed by blank assay electrolysis (Figure S2 (right panels)). The decrease of the absorbance

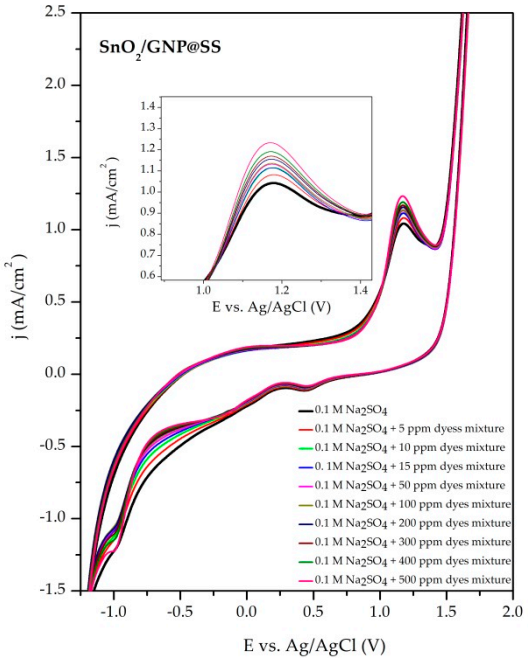
maximum at 615 nm within electrolysis is ascribed to the decolorization of BCG.

S2. Electrochemical Oxidation of the Dyes Mixture

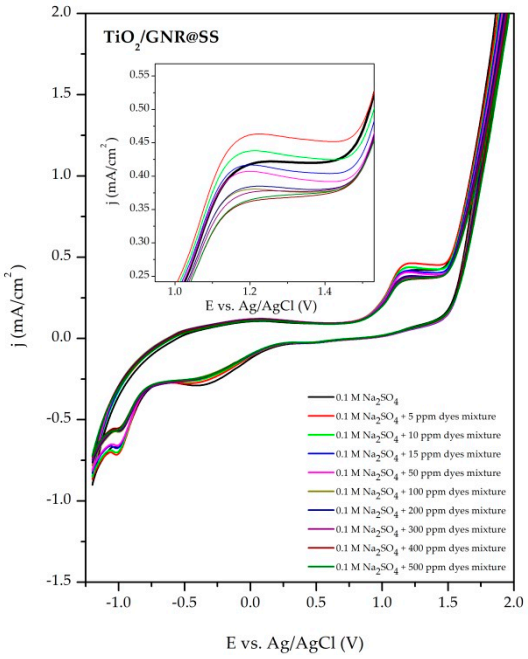
The electrochemical oxidation of the dyes mixtures at SnO_2/GNP@SS, and GNP@SS and TiO_2/GNP@SS electrodes was investigated by using cyclic voltammetry (CV) techniques. The experiments were performed in 0.1 M Na_2SO_4 as a supporting electrolyte. The total concentration of dyes mixtures treated was varied in range 0–500 ppm keeping the mass ratios of dyes in mixture equal (1 : 1 : 1). The results are presented in Figure S3.



(**a**)



(**b**)

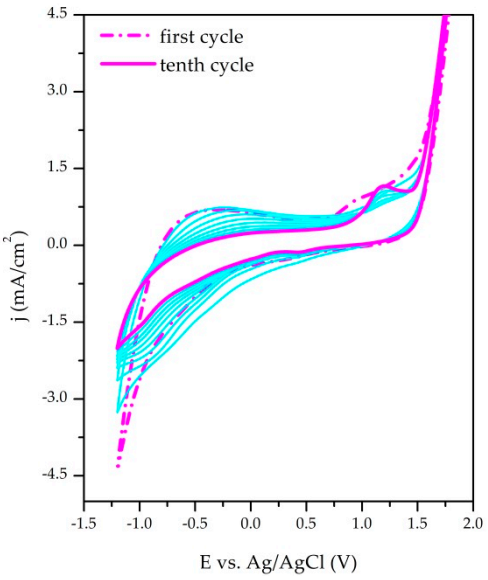


(**c**)

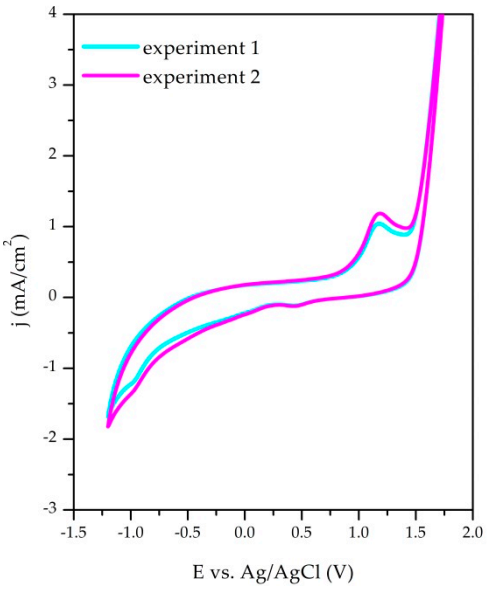
Figure S3. Cyclic voltammograms of (**a**) GNP@SS (**b**) SnO_2/GNP@SS; (**c**) TiO_2/GNP@SS electrodes in 0.1 M Na_2SO_4 with different dyes mixture concentration, at scan speed 100 mV/s.

S3. Stability, Repeatability and Reproducibility Studies

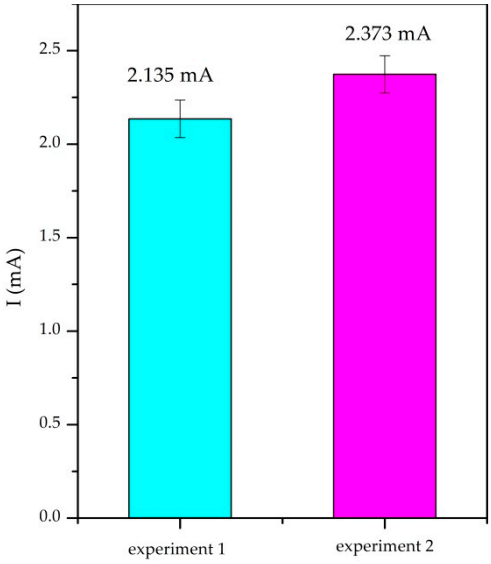
Within reproducibility studies, the performance of two independent SnO_2/GNP@SS electrodes was compared in Figure 5 (d). The results of cyclic stability and repeatability experiments that were performed using the second independent SnO_2/GNP@SS electrode (electrode 2) are presented in Figure S4. The change of peak current density from the first to the tenth cycle was estimated 1.7 % (Figure S4 (a)). The results of repeatability experiments showed similar curve shapes (Figure S4 (b)) and the obtained peak currents variation of 10 % (Figure S4 (c)).



(**a**)



(**b**)



(**c**)

Figure S4. Stability and repeatability studies of th second independantly investigated SnO_2/GNP@SS electrode: (**a**) cyclic stability; (**b**) repeatability – cyclic voltammograms of two individual experiments with the same electrode; (**c**) repeatability – peak currents comparison.

The results of chronopotentiometric measurements, performed concurrently with electrochemical degradation of dyes mixture, also prove the stability of used nanocomposite electrodes. The potential loss was estimated less than 3 % for all investigated electrodes after 6 h of electrochemical degradation (Figure S5).

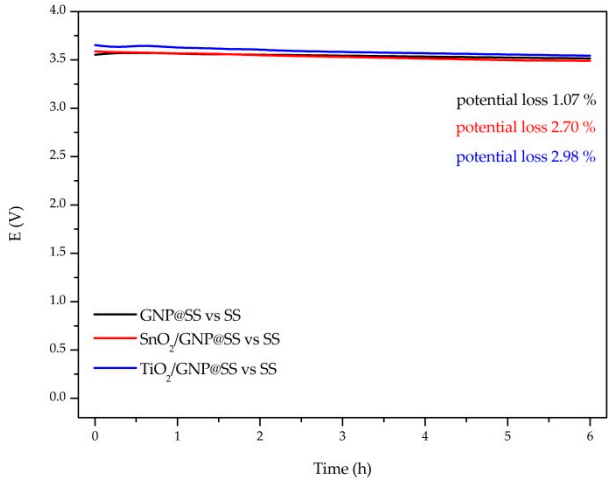


Figure S5. Chronopotentiograms of investigated nanocomposite electrodes, recorded during the degradation of dyes mixture (5 ppm of each dye in 0.1M Na_2SO_4, 15 ppm in total) at current density 10 mA/cm^2.

S3. GC-MS analysis

Chromatograms of aliquots, taken during the degradation of the dyes mixture at GNP electrode, are shown in Figure S6.

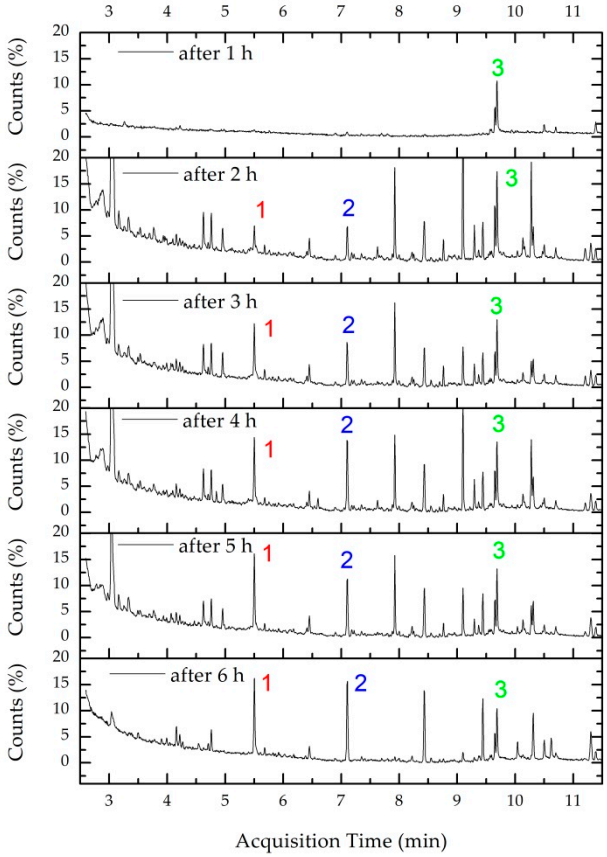


Figure S6. GC-MS analysis: chromatograms of solutions obtained during the degradation of dyes mixture at GNP electrode at current density 10 mA/cm^2. Identified products are numbered: peak 1 at 5.50 min corresponds to 6-acetyl-5-hydroxy-4-methylcyclohexa-2,4-dien-1-one, peak 2 at 7.10 min corresponds to 2,4-dimethylphenol and peak 3 at 9.63 min corresponds to 4-benzylidene-2-methyl-cyclohexa-2,5-dien-1-one.

S4. DFT Calculations

Calculated Fukui indices of radical attack for the most susceptible oxygen atoms are presented in Table S1.

Table S1. Fukui indices of radical attack susceptibility and Lowdin charges of all cresol red atoms.

atom	f_A^0	Lowdin charge
H	-0.0196	0.5443
H	-0.01805	0.7784
O	**-0.0444**	**6.3898**
H	-0.01805	0.7825
C	-0.00415	4.462
H	-0.0113	0.7782
C	-0.02845	3.6807
C	-0.02825	3.9378
H	-0.01945	0.7526
C	-0.0235	4.1144
C	-0.00855	4.1297
H	-0.00635	0.7907
C	-0.0122	4.0885
C	-0.0211	3.9335
H	-0.0078	0.7709
C	0.0009	3.7578
O	**-0.0172**	**6.4352**
H	-0.00795	0.7927
C	-0.0202	3.9446
C	-0.0124	4.1166
H	-0.0118	0.7853
H	-0.0169	0.7636
H	-0.0101	0.7658
C	-0.0117	4.1137
O	**-0.0464**	**6.6177**
C	-0.0246	4.1236
H	-0.019	0.7581
C	-0.00285	3.947
C	-0.02385	4.1157
C	-0.0314	3.9335
C	-0.02725	3.6845
C	-0.00995	3.9668
C	-0.00355	4.4566
O	**-0.0455**	**6.3923**
H	-0.02485	0.5455
C	-0.0292	4.1669
H	-0.0142	0.8044
C	0.00575	4.079
H	-0.0233	0.7597
C	-0.04465	6.624
H	-0.016	0.7594
O	**-0.04815**	**4.077**
C	-0.0213	4.0867
H	-0.02145	0.7474
H	-0.02225	0.7546