2D Nanomaterial – Based Electrocatalyst for Water Soluble Hydroperoxide Reduction

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Supplementary information

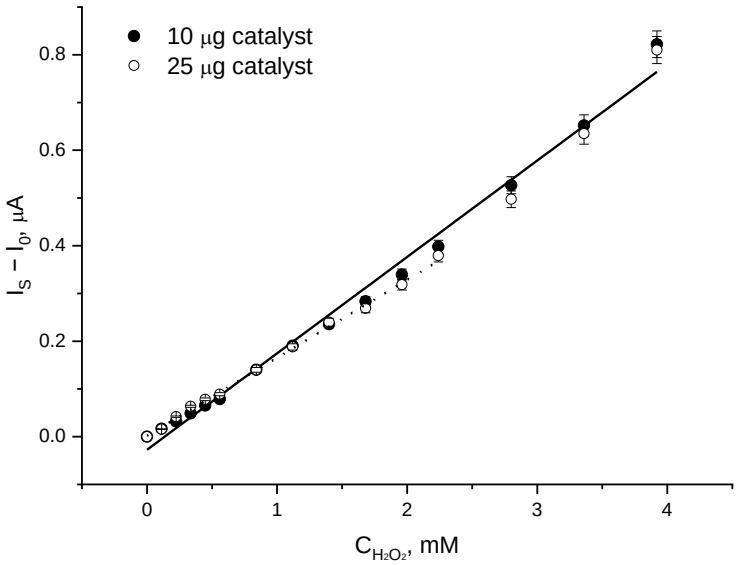


Fig. S1. Dependence of the electrode response on peroxide concentration at a constant operating potential for GCE modified with Co-doped g-C_3N_4 suspensions with catalyst load 0.01 mg (closed circles) and 0.025 mg (open circles).

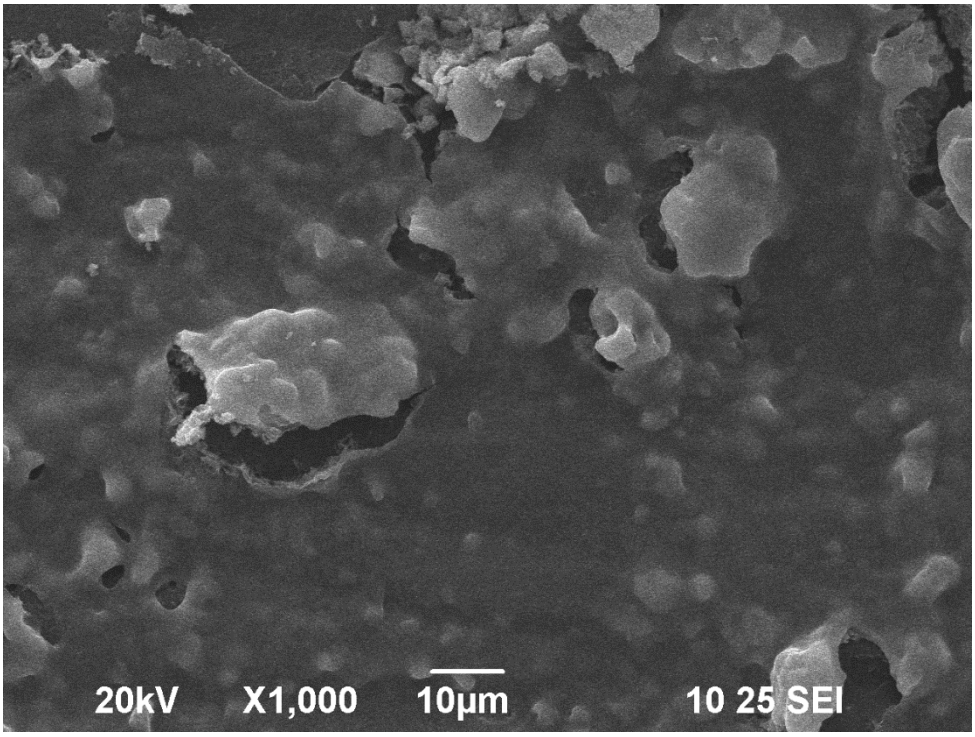
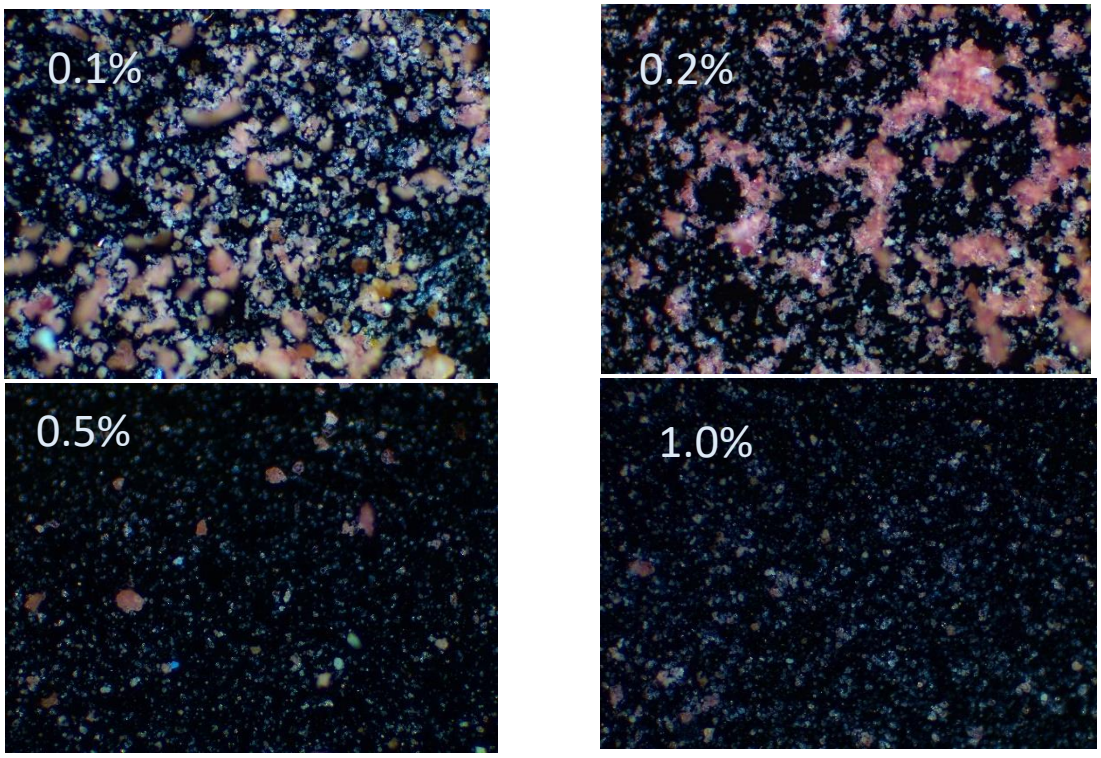


Fig S2. SEM images of the surface of a standard glassy carbon electrode modified with Co-g-C_3N_4 dispersed in 0.2 % Nafion aqueous suspension (0.01 mg load).

A



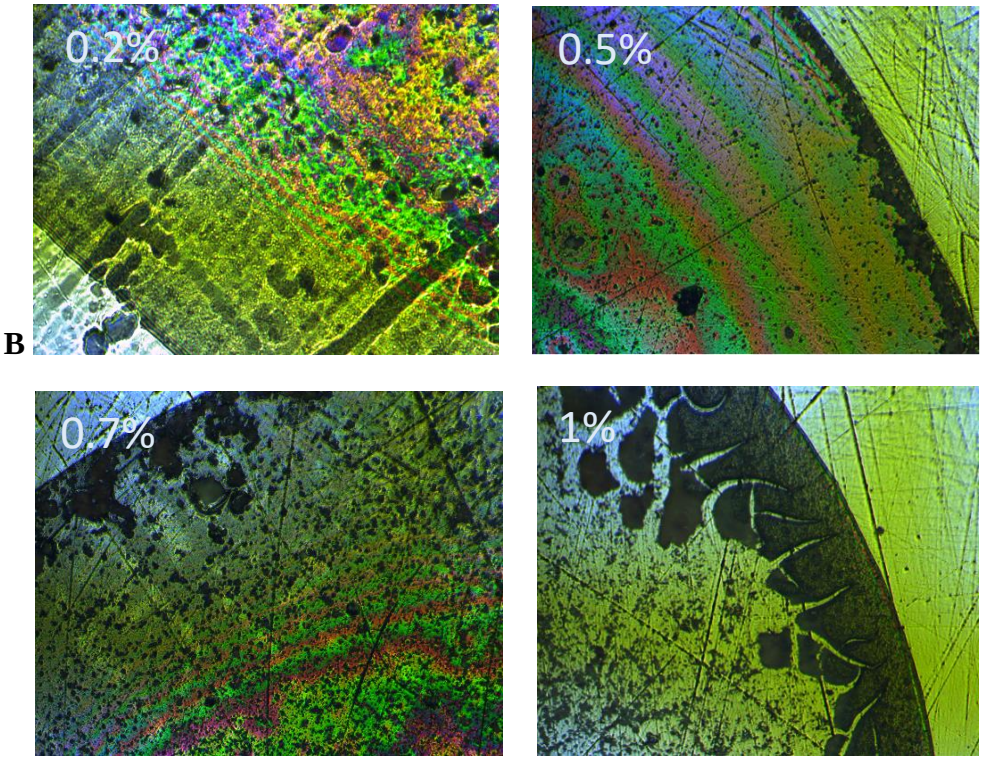


Fig. S3. Microscopic images of glassy carbon surface modified with Co-g-C_3N_4 (0.01 mg) dispersed in polymer suspension with different Nafion™ content. Magnification × 20; A) polarized light microscopy ; and B) reflected light photographs of the boundary regions.

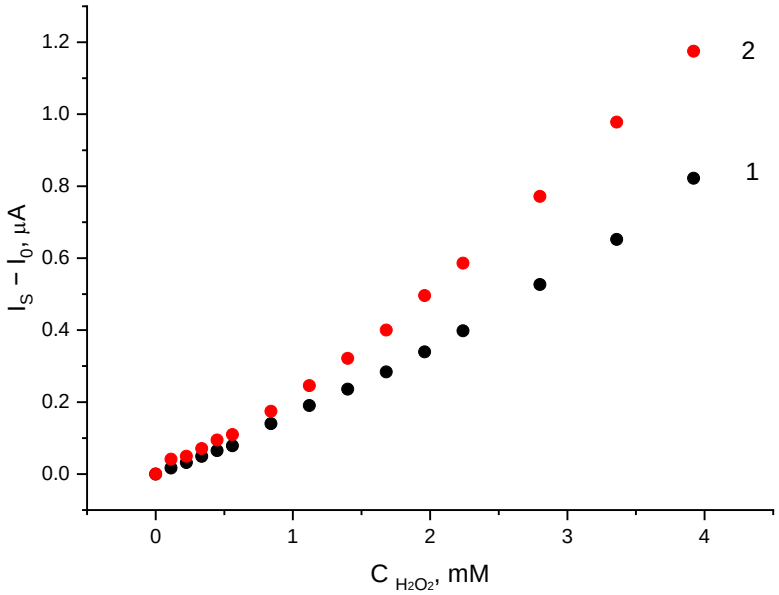


Fig. S4. Dependence of the electrode response on H_2O_2 concentration: 1) freshly prepared; and 2) after 3 days of continuous use; Electrode modifying phase deposited from a dispersion containing 2 mg/ml Co-g-C_3N_4 and 0.5% binding polymer Nafion (0.01 mg catalyst load).

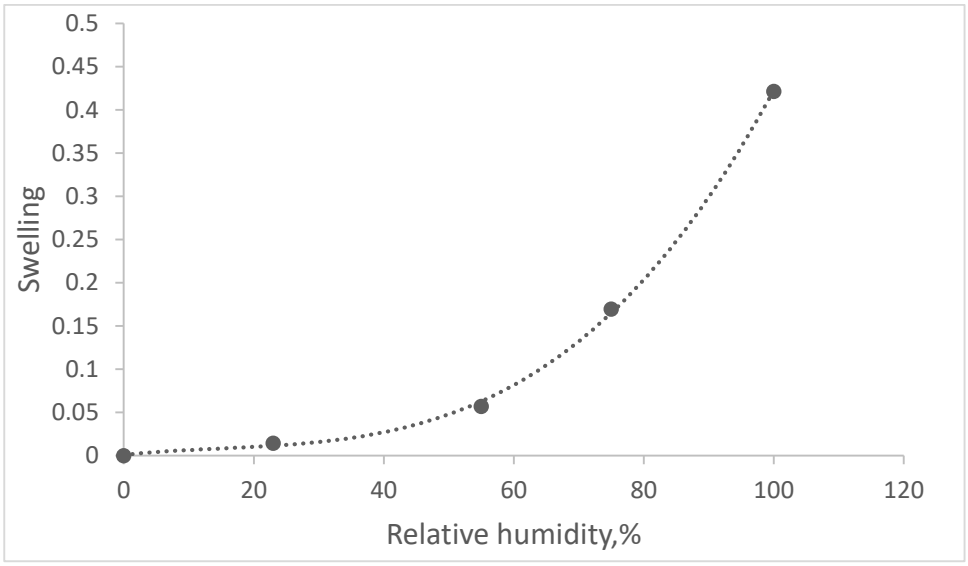


Fig. S5. Swelling of the Nafion polymer layer as a function of relative humidity of the air.

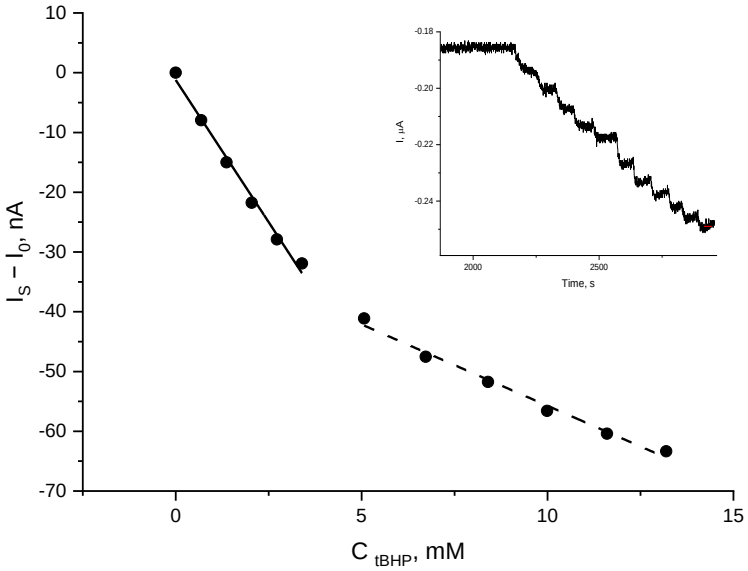


Fig. S6. Dependence of current variation on tBHP concentration at a constant potential of –0.3 V vs. Ag|AgCl. Inset: chronoamperometric record of GC electrode modified with Nafion™ upon addition of aliquots of tBHP; background electrolyte: phosphate buffer, pH = 7.0, reference electrode Ag|AgCl (KCl sat); operating potential: –0.3 V; catalyst load – 0.01 mg; room temperature.

By means of constant potential amperometry (at an applied potential of –0.3 V vs. Ag|AgCl) it has been observed that a reductive current flows upon the addition of hydroperoxide aliquots that reaches a steady – state value in 35-40 seconds (Fig.S6, Inset). When adding the next hydroperoxide aliquot the current changes stepwise until a new steady-state is reached. It shall be noted that the record is rather noisy and the noise level vastly increases with shifting to the less-negative operating potentials (e.g. –0.2 V) so that it was not possible to discriminate between the noise and the signal at potentials less-negative than –0.3 V.

The corresponding calibration plot drawn on the basis of chronoamperometric data (Fig. S6, Inset) is composed of two linear sections – a steeper segment (Fig. S6, solid line) going up to 3.5 mM, followed by a linear dependence with ca. 3 times smaller slope spanning over the region from 5 to 13 mM. The equation resulting from the linear regression analysis of the initial part of the calibration plot was $I_S - I_0$ = (1.21848E-

9 ± 9.22605E-10) + (-9.51616E-6 ± 4.47841E-7)·C_{tBHP}. The existence of two linear parts of the plot most probably results from the hampered penetration of tBHP through the polymer layer, most visible at concentrations exceeding 3.5 mM.

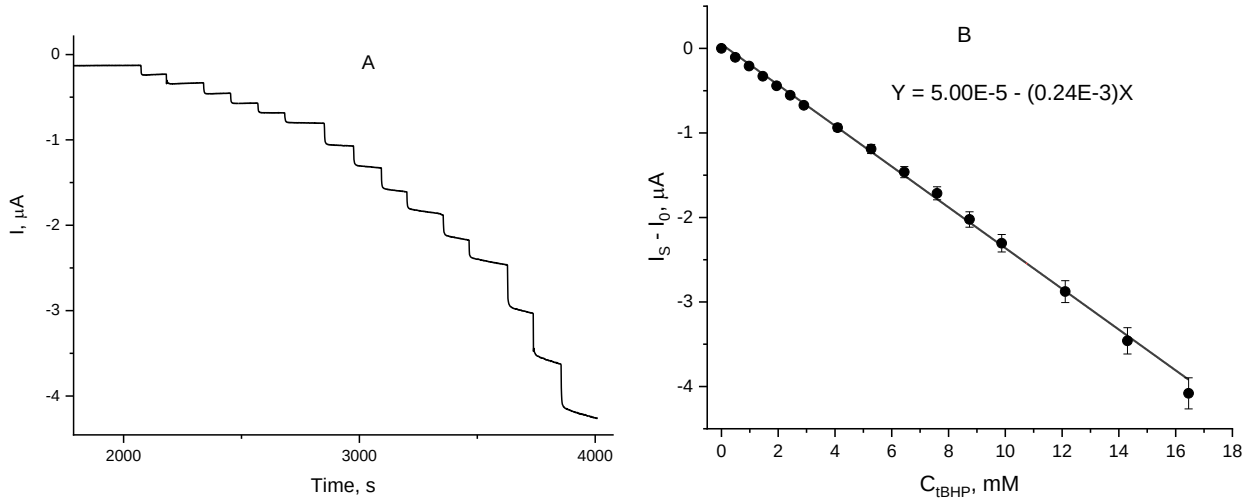


Fig.S7. Chronoamperometric record (A) and the corresponding calibration plots (B) of GC electrode modified with Co - g-C_3N_4/ Nafion™ upon addition of aliquots of tBHP; background electrolyte: phosphate buffer, pH = 7.0, reference electrode Ag|AgCl (KCl sat); operating potential: – 0.3 V)