

Article

2D Nanomaterial—Based Electrocatalyst for Water Soluble Hydroperoxide Reduction

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Abstract: Hydroperoxides generated on lipid peroxidation are highly reactive compounds, tend to form free radicals, and their elevated levels indicate the deterioration of lipid samples. A good alternative to the classical methods for hydroperoxide monitoring are the electroanalytical methods (e.g., a catalytic electrode for their redox-transformation). For this purpose, a series of metal oxides—doped graphitic carbon nitride 2D nanomaterials—have been examined under mild conditions (pH = 7, room temperature) as catalysts for the electrochemical reduction of two water-soluble hydroperoxides: hydrogen peroxide and *tert*-butyl hydroperoxide. Composition of the electrode modifying phase has been optimized with respect to the catalyst load and binding polymer concentration. The resulting catalytic electrode has been characterized by impedance studies, cyclic voltammetry and chronoamperometry. Electrocatalytic effect of the Co-g-C₃N₄/Nafion modified electrode on the electrochemical reduction of both hydroperoxides has been proved by comparative studies. An optimal range of operating potentials from −0.215 V to −0.415 V (vs. RHE) was selected with the highest sensitivity achieved at −0.415 V (vs. RHE). At this operating potential, a linear dynamic range from 0.4 to 14 mM has been established by means of constant-potential chronoamperometry with a sensitivity, which is two orders of magnitude higher than that obtained with polymer-covered electrode.

Keywords: protonated 2D g-C₃N₄; Co₃O₄-doped g-C₃N₄; modified GC electrode; electrocatalysis; hydroperoxide electrochemical reduction



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1. Introduction

Peroxide compounds have the ability to easily generate radicals at ambient conditions (room temperature and atmospheric pressure), initiating a series of radical reactions. This predetermines their widespread industrial use in the process of textile and wood pulp bleaching, as polymerization initiators, in stain removing formulations (e.g., Vanish) etc. Peroxide compounds could be, however, undesired products resulting from the peroxidation of vegetable oils and fatty acids [1] and play a major role in aging, mutagenic processes, oxidative stress [2] and a number of diseases [3,4]. There are a number of known techniques for assaying peroxides, for example, titrimetry [5], chromatography [6] and fluorescence spectroscopy [7,8], most of them requiring costly equipment, painstaking sample pretreatment and highly qualified operators.

Due to their simplicity, high sensitivity and possibility to tune the operational potential, thus making the assay interference-free, an increased research interest in developing electrochemical methods for the determination of hydroperoxides [9–13] in various liquid samples have been seen over the last four decades. Most of the studies were focused on the determination of hydrogen peroxide, mostly because its widespread use as a disinfectant in food industry, or due to its natural occurrence as a byproduct of enzyme-catalyzed reactions. The latter means that a sensitive and selective catalytic peroxide electrode can be easily coupled with an immobilized oxidase to form an electrochemical biosensor [14–17].

Hydrogen peroxide can be either oxidized or reduced electrochemically and the reduction process is believed to be less-susceptible to interferences in complex media. A variety of catalysts have been researched for catalytic electroreduction of H_2O_2 ; mostly nanodimensional, such as nanoparticles of noble metals, metal oxide nanoparticles, carbon nanomaterials and others [9,10,18–20]. The advantages of using noble metal nanomaterials (Pt, Au, Ag, Rh and their hybrids) are their high catalytic activity, chemical stability and electrical conductivity [16,21], but the high cost of produced electrocatalysts has led to extensive research in order to develop alternative catalysts, including carbon nanomaterials and metal oxides nanoparticles [12,22].

Since the discovery of graphene in the 1990s, carbonaceous 2D nanomaterials have been attracting increasing attention from diverse technological and scientific areas ranging from electronics to biomedicine [23]. Their unique catalytic properties and large surface-to-volume ratio makes them suitable for a wide spectrum of applications, such as environmental catalysis [24], drug delivery, and sensory [23] and energy applications.

Graphitic carbon nitride ($g-C_3N_4$) is a carbonaceous 2D material, involving mostly covalent bonds (C-N) forming a π -conjugated polymer with high molecular weight and unique electron structure predetermining its semiconductor properties [25]. The 2D structure of $g-C_3N_4$ is composed of tri-s-triazine units and possesses a high degree of condensation, which regulates its great thermal and chemical stability [26]. All of these describe $g-C_3N_4$ as a multifunctional, heterogeneous, metal-free catalyst [27], of which its main drawback is a poorly developed specific surface area, despite its high biocompatibility [23].

Melamine has been used as a cost-effective precursor for the synthesis of graphitic carbon nitride [28] due to its low toxicity, ensuring at the same time increased surface area and volume of the pores. Another approach to enlarge the specific surface area of $g-C_3N_4$ is modification with the oxides of transition metals in the form of ultrafine dispersion, which are distributed between the nano-sheets of $g-C_3N_4$ and prevent their agglomeration [29]. Among transition metal oxides, a very promising catalyst exhibiting high catalytic activity and stability in electrochemical reactions are the oxides of Co (II and/or III) with a spinel structure, specifically Co_3O_4 [9].

Earlier [30] and preliminary studies (not published yet) of the group concerning the catalytic activity of pristine $g-C_3N_4$ and doped with either Co_3O_4 or $Co_3O_4-Bi_2O_3$ and Co_3O_4-MgO $g-C_3N_4$ in the process of peroxymonosulfate (PMS) activation (disruption of peroxide bond with the formation of sulfate anion radicals) have shown that their heterogeneous catalytic activity increases in the following order: $g-C_3N_4 < Co-g-C_3N_4$ ($g-C_3N_4$ doped with Co_3O_4) $< Co-Bi-g-C_3N_4$ ($g-C_3N_4$ doped with Co_3O_4 & Bi_2O_3) $< Co-Mg-g-C_3N_4$ ($g-C_3N_4$ doped with Co_3O_4 & MgO). In searching for a correlation between their activity and structural and morphological specifics, a thorough characterization has been performed using a set of experimental techniques: XRD, TEM, BET, ICP-OES and FT-IR [30–32]. The specific surface area has been identified as one of the factors affecting to a great extent the catalytic activity in disrupting the peroxide bond in PMS, as it increased exactly in the same order as the heterogeneous-catalytic activity (for the heterogeneous reactions, the rate is directly proportional to the contact surface). It has been found that the incorporation of metal oxides (spinel Co_3O_4 , alone or in combination with either MgO or Bi_2O_3) in between the carbon nitride sheets vastly affects their structure: the specific surface area of metal oxide-doped carbon nitride is much higher than the one of pristine $g-C_3N_4$ that could be attributed to the high dispersion of Co_3O_4 , MgO and Bi_2O_3 between the layers of $g-C_3N_4$, which prevents the agglomeration of the particles.

Taking this into account, we focused our research efforts on the studies of electrocatalytic activity of these composite 2D nanomaterials in the electrochemical reduction of hydroperoxide bonds containing compounds. Therefore, the purpose of this study is to develop and characterize a sensitive chemically modified glassy carbon electrode (GCE) for the determination of water-soluble peroxides such as hydrogen peroxide and *tert*-butyl hydroperoxide in aqueous media by using as a modifying phase graphitic carbon

nitride ($g\text{-C}_3\text{N}_4$) doped with metal oxides and NafionTM polymer suspension as a binding agent as a first step towards the development of an electrochemical peroxide test. Despite considerable research interest in the photocatalytic activity of metal oxide-doped $g\text{-C}_3\text{N}_4$, no literature precedent was found reporting on the electrocatalytic properties of these 2D nanomaterials.

2. Results

2.1. Electrocatalytic Activity of Pristine and Metal Oxide—Doped $g\text{-C}_3\text{N}_4$

Having in mind their heterogeneous-catalytic activity in peroxide bond cleavage, the metal oxide doped $g\text{-C}_3\text{N}_4$ composites, as well as the pristine $g\text{-C}_3\text{N}_4$ and spinel Co_3O_4 , have been examined as electrocatalysts in the process of electrochemical reduction of two water-soluble hydroperoxides: hydrogen peroxide and *tert*-butyl hydroperoxide (tBHP). For this purpose, a series of glassy carbon electrodes modified with each of the catalysts dispersed (by sonication) in Nafion aqueous suspension have been examined in the peroxide electroreduction process (Figure 1). The electrocatalytic activity has been measured under mild conditions (neutral pH, room temperature) as the electrode sensitivity, determined at a constant potential, where peroxide electroreduction takes place. Surprisingly, the electrochemical activity of these catalysts did not follow the same rationalities as in the heterogeneous catalysis. In the electroreduction process of either hydroperoxide, the highest electrocatalytic activity has been observed for Co_3O_4 -doped $g\text{-C}_3\text{N}_4$ (Co- $g\text{-C}_3\text{N}_4$). It has to be mentioned that its activity is much higher than the one of pristine $g\text{-C}_3\text{N}_4$ or Co_3O_4 , which suggests that there is a synergistic effect upon combining the two components of the composite catalyst. Not surprisingly, the most active composite (Co-Mg- $g\text{-C}_3\text{N}_4$) in the heterogeneous peroxide bond disruption which possesses the highest specific surface area shows very low activity in hydrogen peroxide electrochemical reduction (Figure 1, light blue series) and a lack of such in the electroreduction of tBHP (Figure 1, blue series). Upon its addition to concentrated (e.g., 6%) hydrogen peroxide, aqueous solution causes vigorous release of oxygen gas. This finding can explain its apparently low activity in hydroperoxides electrochemical reduction due to the purely heterogeneous-catalytic decomposition the actual concentration near the electrode surface sharply decreases, which, in turn, results in much lower electrode sensitivity. The second composite catalyst, Co-Bi- $g\text{-C}_3\text{N}_4$, the surface area of which is more than twice as high as the one of Co-doped $g\text{-C}_3\text{N}_4$, demonstrates ca 30% lower electrocatalytic activity at the electroreduction of hydrogen peroxide, and 60% lower activity at tBHP electroreduction than the latter, which can be explained similarly; the heterogeneous-catalytic decomposition of these hydroperoxides decreases its concentration near the electrode surface and apparently causes lower sensitivity.

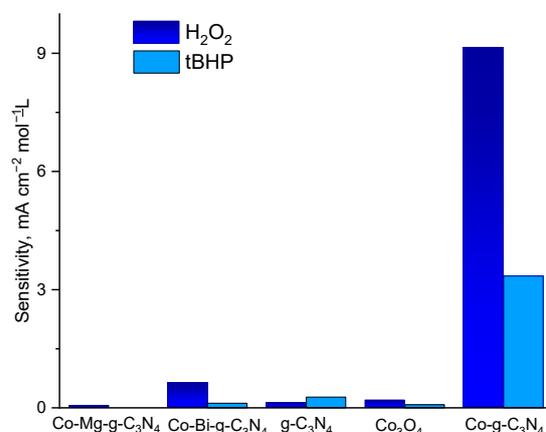


Figure 1. The sensitivity of a catalytic electrode upon electrochemical reduction of H_2O_2 (dark blue series) and *t*-butyl hydroperoxide (blue series) in neutral aqueous medium; operational potential -0.2 V (-0.415 V vs. RHE); reference electrode $\text{Ag}|\text{AgCl}$, sat. KCl; room temperature $21 \pm 1\text{ }^\circ\text{C}$. Catalyst load for all the electrodes: 0.01 mg.

Therefore, based on the above findings and its superior catalytic performance in electroreduction of the two hydroperoxides, the Co-g-C₃N₄ has been selected for further studies.

2.2. Optimization of the Polymer-Catalyst Ratio

Knowing that the catalyst is a large band-gap semiconductor that, if loaded in large amounts, can impede the electrocatalytic process, we aimed close to the monolayer surface coverage. For the purpose of electrode modification, Co-g-C₃N₄ was pre-dispersed in aqueous suspension of Nafion in amounts gradually decreasing from 10 mg/mL to 2 mg/mL, followed by the assay of electrode sensitivity. It should be pointed out that all dispersions were highly unstable, tending to sediment within several minutes after stopping sonication, which is most probably a consequence of the strong attraction forces acting between the g-C₃N₄ layers that trigger particle agglomeration in the absence of ultrasound treatment. It has been found that current variation depends linearly on peroxide concentration (measured at a constant potential) for the electrodes prepared with 2 mg/mL (0.01 mg catalyst load) and 5 mg/mL suspensions (0.025 mg catalyst load); however, the electrode sensitivity (slope of the dependence) decreases with increasing the catalyst's amount (Figure S1). Hence, the suspension of 2 mg/mL has been selected for further studies because it ensures a thin layer surface coverage, as can be seen in the SEM studies (Figure S2).

The content of the second component in the modifying phase, the polymer Nafion 117, has also been optimized in order to warrant not only good analyte penetrability and high sensitivity, but also durability of the modifier. The concentration of polymer suspension was varied from 0.1 to 1%. By means of polarization microscopy (Figure S3A), it has been observed that by decreasing polymer concentration from 1 to 0.1%, the catalyst's nanoparticles tend to agglomerate due to decreased viscosity of suspension. The catalyst particles were unevenly distributed within the modifying layer, since the hardness and Young's modulus (both measured by nanoindentation) showed very different values at different areas of the same sample. As a common feature, the larger the polymeric content, the more structures are disposed in the periphery of the studied sample (Figure S3B) that leads to the formation of cracks in the modifying phase and its destruction during the measurements. Moreover, with increasing the amount of the binding polymer in the modifier, the deviations from linearity of the dependence of the electrode response on hydroperoxide concentration become substantial (Figure S4, curve 1). It becomes even more noticeable upon continuous utilization of the modified electrode (Figure S4, curve 2) since the electrode response was found to gradually change to some extent during several measurements which most probably comes from the swelling of the polymer film. The larger the polymer content in the modifier, the more noticeable the electrode "activation effect". Studies on polymer swelling have shown that Nafion is a highly hydrophilic polymer that can absorb up to 43% of water in a 100% humid atmosphere (Figure S5), and the "activation effect" can be assigned to the increased conductivity of the modifying layer, because it is a polyelectrolyte material with ionic conductivity that increases proportionally according to the water content in the film [33].

The sensitivity of electrocatalytic hydroperoxide reduction (determined at a constant potential of -0.2 V (-0.415 V vs. RHE) where the electrocatalytic process takes place at a considerable rate) is virtually identical for the modifier with polymeric content of either 0.1% or 0.2%, whilst the preparation with 0.5% polymeric content demonstrates a decrease of the electrode sensitivity with ca 1/4 as compared with the former, the obvious reason for which is the troubled analyte penetration through a thicker modifying layer. These findings, together with the non-linear dependence of response on concentration, makes this polymer content non-optimal for analytical applications despite the mechanical stability of the polymer-enriched modifier is greater than the one with 0.1%-polymer content and a bit more stable than the electrode prepared with 0.2% Nafion as a binder. Therefore, for

fabrication of catalytic electrodes applicable in hydroperoxide assay, a 2 mg/mL Co-g-C₃N₄ dispersed in 0.2% Nafion aqueous suspension was selected as an optimal composition.

The electrochemical impedance spectroscopy (EIS) is a valuable alternating current technique that supplies information about the charge transfer at the electrode-solution interface, while changing the frequencies from high to low during the measuring process. The Nyquist plots (Figure 2) of a glassy carbon electrode modified with a layer of Nafion™ (Figure 2, series 1) and with Co-g-C₃N₄—Nafion™ composite (Figure 2, series 2) prepared with the optimized polymer-to-catalyst ratio is depicted. The first region in Figure 2, series 1 represents a semicircle, which appears within the high-frequencies range, followed by a linear “tail” sloped at ca. 45°, typical for the medium and low-frequencies region of the spectrum. The semicircular part of the EIS spectrum indicates the occurrence of charge-transfer resistance ($R \sim 3.9 \text{ k}\Omega$), whilst the linear part can be assigned to the diffusion process. Since the EIS spectra have been obtained in the presence of $\text{Fe}(\text{CN})_6^{3-/4-}$ as redox probe, the appearance of the charge transfer resistance can be associated with the electrostatic repulsion between the hexacyanoferrate anions and the polymer-coated glassy carbon surface, as the Nafion polymer contains numerous negatively charged fluoride/sulfonate side groups, providing it with a negative surface charge. The EIS spectrum of glassy carbon electrode modified with Co-g-C₃N₄—Nafion™ composite in 0.1 M KCl with 5 mM $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ has been recorded over the same frequency range: from 10^5 Hz to 1 Hz (Figure 2, series 2). On the EIS spectrum of Co-g-C₃N₄—Nafion™ modified electrode the semicircle region on the Nyquist plot is not detectable, as it represents a straight line tilted at an angle larger than 45°, which corresponds to the occupation of the electrode surface with numerous imperfect capacitors, similar to the behaviour of a graphene modified surface, as reported in [34]. Apparently, the charge transfer is not restricted over the high-frequencies region; however, the data analysis and simulations returned a value of the charge-transfer resistance, which is approximately 3–4 orders of magnitude higher, as can be expected due to the semiconductive nature of the catalyst Co-g-C₃N₄.

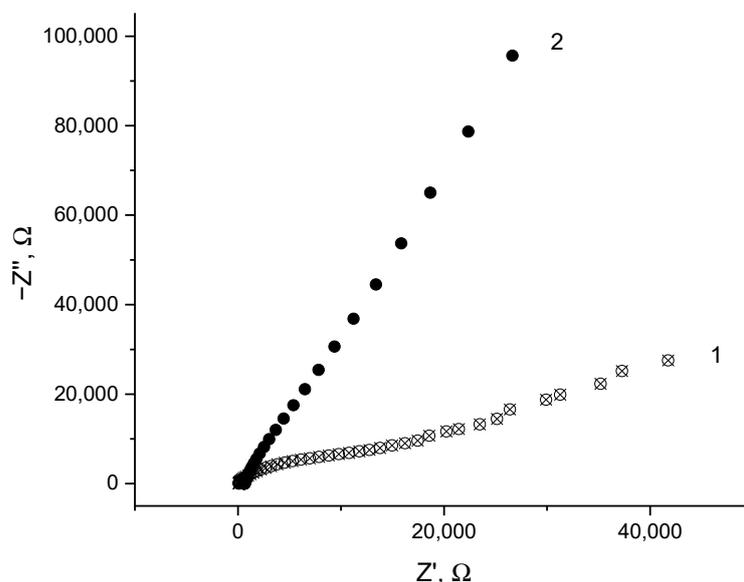


Figure 2. EIS spectra (Nyquist plot) of GC electrode, modified with Nafion™ (1) and with Co-g-C₃N₄—Nafion composite (2); reference electrode Ag | AgCl, sat KCl; electrolyte 0.1 M KCl with 5 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ redox probe.

2.3. Electrocatalytic Reduction of Hydroperoxides by Co-g-C₃N₄/Nafion Modified Electrode

The electrochemical behaviour of a Nafion-covered glassy carbon electrode in the absence and the presence of tBHP (which is much more stable at room temperature than hydrogen peroxide) has been explored by means of cyclic voltammetry, CV, over the

potential region, from -0.6 to 0.6 V vs. Ag | AgCl (Figure 3). It has been found that under the given experimental conditions, this hydroperoxide is susceptible to electrochemical reduction that takes place between -0.3 V and $+0.2$ V. At potentials more negative than -0.3 V the electrochemical reduction of tBHP overlaps with the oxygen electroreduction process.

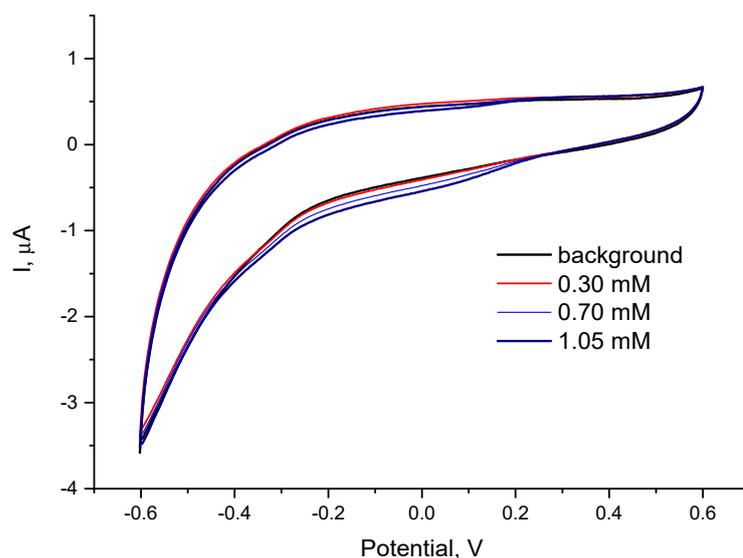


Figure 3. Cyclic voltammograms of GC electrode modified with Nafion™ in the absence and presence of tBHP); background electrolyte: phosphate buffer, pH = 7, reference electrode Ag | AgCl (KCl sat); scan rate 20 mV/s.).

The voltametric response of Co-g-C₃N₄/Nafion™-modified glassy carbon electrode in the absence and the presence of both water-soluble hydroperoxides: hydrogen peroxide (Figure 4A) and tBHP (Figure 4B) shows much more pronounced electroreduction waves starting at ca. $+0.2$ V (0.015 V vs. RHE) and going down to -0.4 V (-0.615 V vs. RHE) and further. The most clearly expressed difference between the background current and the current in the presence of either hydroperoxide was noticed at ca. -0.2 V (-0.415 V vs. RHE, reversible hydrogen electrode). Comparative studies performed in a completely deaerated medium have shown that over the modified electrode, the oxygen reduction starts at potentials more negative than -0.25 V (-0.465 V vs. RHE), and hence there is an overlap of the hydroperoxide reduction wave and the oxygen reduction one. This is an important finding because oxygen is produced during the hydroperoxides electroreduction process and, as such, it affects both the noise level and the sensitivity of the determination (the latter being taken as a measure of the electrocatalytic activity of modifying phase).

By means of constant potential chronoamperometry, the electrode response has been examined as a function of hydroperoxides concentration at -0.2 V, -0.1 and 0 V (-0.415 V, -0.315 V and -0.215 V vs. RHE, resp.) in a neutral medium (Figure 5). It can be seen that as the working potential goes in the negative direction, the electrode sensitivity increases slightly between 0 (-0.215 V vs. RHE) and -0.1 V (-0.315 V vs. RHE), however the slopes of the linear dependencies at -0.1 (-0.315 V vs. RHE) and -0.2 V (-0.415 V vs. RHE) differ drastically. At all these potentials, the current changes stepwise when introducing hydroperoxide aliquot and the noise levels were kept low. At potentials more negative than -0.2 V (-0.415 V vs. RHE), the sensitivity was found to increase, however, with a higher noise level. Therefore, further chronoamperometric experiments were performed at -0.2 V (-0.415 V vs. RHE) where the linear dynamic range determined spans over the interval from 0.4 to 14 mM peroxide concentration (see e.g., Figure S6).

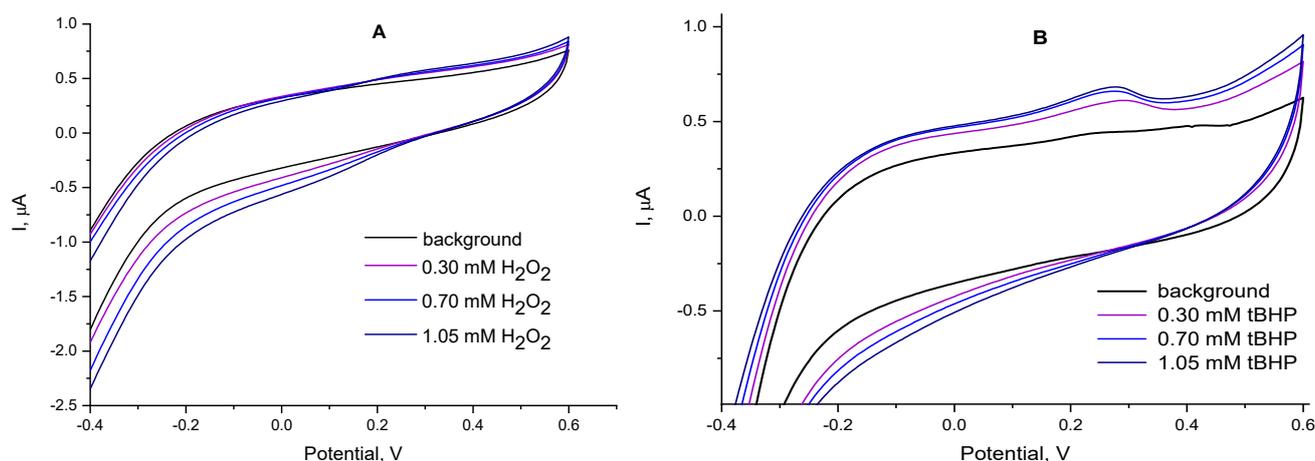


Figure 4. Cyclic voltammograms of GC electrode modified with Co-g-C₃N₄/Nafion™ in the absence and presence of H₂O₂ (A); in the absence and presence of tBHP (B); background electrolyte: phosphate buffer, pH = 7, reference electrode Ag | AgCl (KCl sat); scan rate 20 mV/s; catalyst load 0.01 mg.

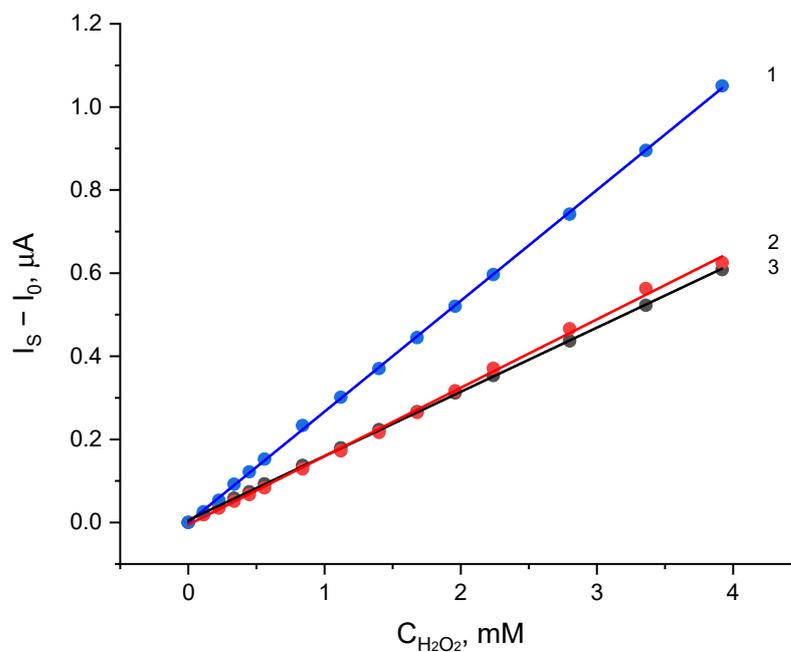


Figure 5. Calibration plots of GC electrode modified with Co-g-C₃N₄/Nafion™ dependence of electrode response on H₂O₂ concentration; background electrolyte: phosphate buffer, pH = 7.0, reference electrode Ag | AgCl (KCl sat); operating potentials: −0.2 V (curve 1); −0.1 V (curve 2) and 0.0 V (curve 3), resp.: −0.415 V; −0.315 V, and −0.215 V vs. RHE.

To justify the role of each component of the modifying phase, a series of chronoamperometric experiments with electrodes modified with only polymer, with only Co-g-C₃N₄ and with Co-g-C₃N₄/Nafion have been performed (Figure 6) at the potential where the highest sensitivity has been detected (−0.2 V vs. Ag | AgCl, sat. KCl or −0.415 V vs. RHE) in the presence of both studied hydroperoxides. The lowest electrocatalytic activity has been detected for the polymer-coated GCE, that can be assigned to the delayed penetration of the hydroperoxides through the polymer layer, as the studies with a bare GCE showed higher electrode sensitivity for the polymer-coated GCE. The solely catalyst-modified electrode manifests higher activity than the Nafion/GCE (however comparable with the one achieved on bare GCE), whilst the Co-g-C₃N₄/Nafion modified GCE shows a dramatic change in the H₂O₂ electroreduction rate which exceeds more than 10 times the sensitivity

registered over only Co-g-C₃N₄-modified GCE, and is about two orders of magnitude higher than the one found on polymer-coated GCE. All of these point toward a pronounced electrocatalytic effect of the modifying phase in the process of hydrogen peroxide electroreduction. Similarly, the response to tBHP at a constant potential of -0.2 V (vs. Ag/AgCl, KCl sat, or -0.415 V vs. RHE) of the Co-g-C₃N₄/NafionTM/GCE confirms the conclusion for electrocatalytic effect of the composite modifier, as its sensitivity is more than 50 times bigger than the one achieved with only the polymer coated electrode, and almost 5 times higher than the one of Co-g-C₃N₄-coated GCE. The authentic record (Figure S6) shows the stepwise current change when adding portions of hydroperoxide. The signal remains stable and noise-free, with the analyte concentration increase. The calibration graph drawn on the basis of chronoamperometric record, demonstrates the wide linear dynamic range of Co-g-C₃N₄/NafionTM catalytic electrode (Figure S6) kept strict up to 14 mM concentration of hydroperoxide with correlation coefficients of 0.997.

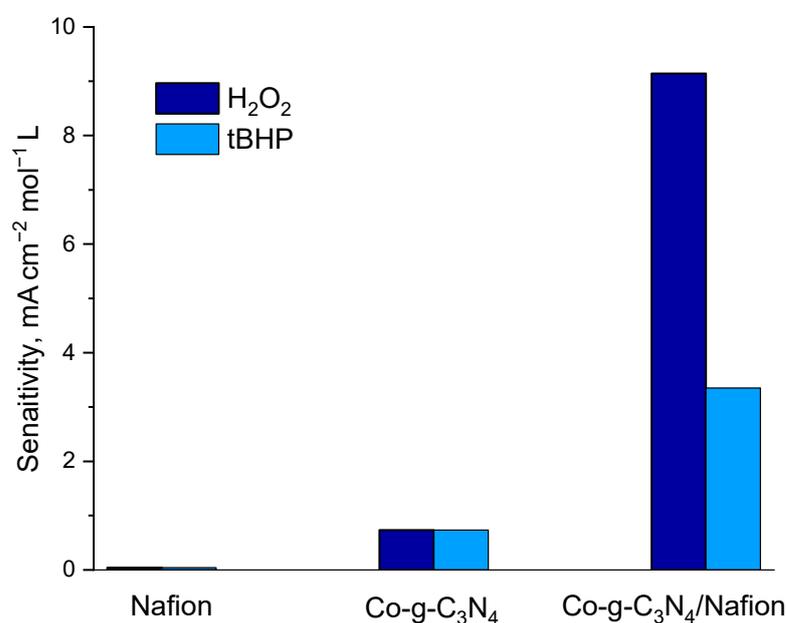


Figure 6. Electrode sensitivity determined at a constant potential of -0.2 V (vs. Ag|AgCl, sat. KCl or -0.415 V vs. RHE) for different electrode modifications: 0.2% Nafion—coated GCE; electrode modified with Co-g-C₃N₄ layer (2 mg/mL dispersed in water); and electrode modified with Co-g-C₃N₄/Nafion suspension (catalyst load 0.01 mg); working potential -0.2 V (-0.002 V vs. SHE); pH = 7.0, room temperature.

Keeping in mind that Nafion is an ionic conductor widely used in proton-exchange membranes for PEM, fuel cells, the effect of proton concentration on the electrode response has been explored. By increasing the concentration of H⁺ 100 times (to pH = 5), the electrode sensitivity almost doubled the one at neutral pH upon hydrogen peroxide electroreduction (Figure 7), whilst for the other analyte, tBHP the difference in the sensitivity was even bigger: ca. 3 times. A further decrease of the pH of the working medium to pH = 3 has led to an insignificant augmentation in the electroreduction rate of H₂O₂, and approximately a 30% rise of the one for tBHP electroreduction.

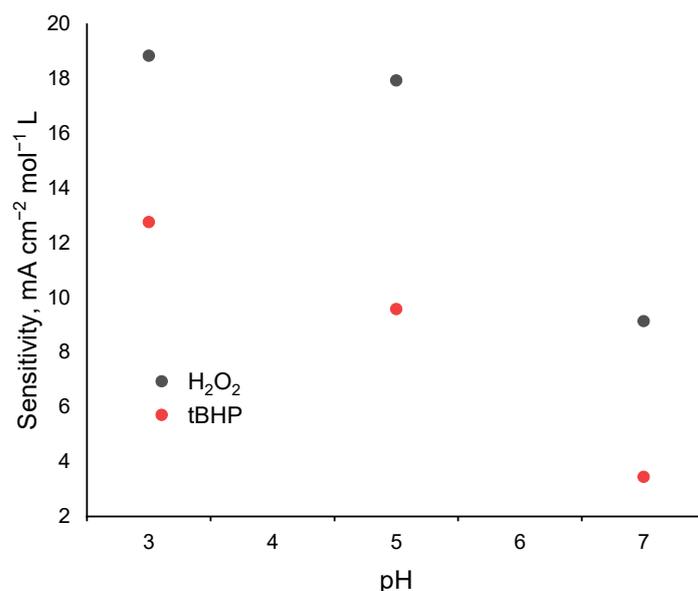


Figure 7. Dependence of the sensitivity of modified with Co-g-C₃N₄/Nafion glassy carbon electrode on pH of the operating medium; catalyst load of 0.01 mg; background electrolyte: phosphate buffer (pH = 3, pH = 5 and pH = 7), reference electrode Ag | AgCl (KCl sat); operating potential: −0.2 V vs. Ag | AgCl (−0.415 V vs. RHE).

2.4. Stability of the Co-Doped C₃N₄/Nafion Modified Electrode

Stability of the modified electrode with optimized polymer-catalyst ratio, has been found to depend strongly on the duration of the drying process (i.e., on the residual moisture in the polymer-composite deposit). Upon continuous drying (48–72 h at ambient temperature) the resulting catalytic electrode is stable for more than two weeks; however, an additional “activation” takes place, the electrode sensitivity raises with ca. 15–20% after 3–4 uses and decays again after 2–3 days of “dry” storage at ambient atmosphere. Most probably, the “activation” effect is due to the swelling of the polymer layer, which makes it more permeable for the analyte. The reproducibility of the response of already “activated” electrode is 96.5–97.0%.

3. Discussion

Screening for electrocatalytic activity of the modifying phase containing pristine g-C₃N₄, metal oxide—doped g-C₃N₄ or spinel Co₃O₄ showed that the most prospective g-C₃N₄-based 2D nanomaterial for developing catalytic electrodes applicable in the determination of water-soluble hydroperoxides is graphitic carbon nitride doped with Co₃O₄. The composite catalysts manifesting high heterogeneous-catalytic activity, e.g., Co-Mg-g-C₃N₄ and Co-Bi-g-C₃N₄, as well as the spinel Co₃O₄, were characterized with a poor electrocatalytic one and vice-versa. The plausible explanation of this finding is that under the given experimental conditions, the water-soluble hydroperoxides are consumed by two alternative ways: either electrocatalytic reduction on the surface of the catalyst-modified electrode, or entirely heterogeneous-catalytic decomposition to water or *t*-butyl alcohol with oxygen release. A similar situation has been observed in our previous studies dealing with the electrocatalytic activity of bimetallic Pd-Au codeposits on glassy carbon in varying proportions [35] examined in H₂O₂ electroreduction: by increasing the portion of the element possessing heterogeneous-catalytic activity in the target reaction, the electrocatalytic one declined. Therefore, purely heterogeneous-catalytic and electrochemical reactions take place concomitantly and compete for the hydroperoxide, thus the more active the heterogeneous catalyst, the lesser its electrocatalytic activity.

A comparison of the sensitivities of Co-g-C₃N₄/Nafion modified GCE with the most-active Pd-Au electrocatalyst reported earlier [35] and determined under equivalent ex-

perimental conditions indicates that the bimetallic noble metals deposits are only 18% more active than the composite electrocatalyst discussed here. Moreover, the analytical performance of Co-g-C₃N₄/Nafion modified GCE in terms of linear dynamic range, time for reaching a steady-state response and electrode stability are superior for the 2D-material based electrode. All these characteristics make the here reported modified electrode a good candidate for further development of a chemosensor for monitoring of peroxide levels in food, cosmetics and pharmaceuticals.

Comparative studies have shown that in the presence of the two studied hydroperoxides neither the Co-g-C₃N₄-modified GCE, nor the one coated with the binding polymer Nafion manifest some considerable electrocatalytic activity during the hydroperoxides electrochemical reduction (Figure 6). Moreover, the electroreduction rate on the polymer-coated GCE is suppressed as compared to the one registered on a bare GCE (the sensitivity is comparable with that of Co-g-C₃N₄ coated GCE), which is due to the hampered penetration of the studied hydroperoxides through the polymer film. However, upon combining the two components by putting a semiconductive material with heterojunction inside in proximal contact with an ionic conductor, a composite with pronounced electrocatalytic effect in the electrochemical reduction of both studied hydroperoxides (Figure 6) is formed. The optimization of the modifying phase showed that the catalyst being a large band-gap semiconductor, shall form a very thin layer to avoid insulation of the electrochemically active surface area (Figure S1); however, the addition of the conductive binding polymer allows the composite to form a 3D network where the electrode surface and the particles of Co-g-C₃N₄ are interconnected and the electron/ionic transport is facilitated.

Because the analyte diffusion through the polymer film seems to be the rate-limiting process, as it can be concluded from the comparison of electrode sensitivities for polymer-coated and Co-g-C₃N₄-modified electrodes, the notable increase of the sensitivity of the composite-modified electrode under acidic conditions (Figure 7) as compared to the neutral medium, is most probably due to the enhanced electrical conductivity of the polymer, similarly to the findings observed in [36]. Similarly, the observed “activation” of the Co-g-C₃N₄/Nafion—modified GCE when used continuously (Figure S4), can be explained with the swelling of the highly hydrophilic polymer, which in turn affects positively composite conductivity, and this way improves electrode sensitivity.

The irregular change of the electrocatalytic activity at the studied pHs (Figure 7) also supports the hypothesis for the enhanced conductivity of the polymer-catalyst layer at lower pHs: the catalytic activity in H₂O₂ electrochemical reduction is almost identical at pH = 3 and pH = 5 that speaks in the favor of better conductivity of the modifying phase in acidic medium. At the present stage one can only speculate about the reasons for observing such an electrochemical behaviour of the composite material; hence, further mechanistic studies are needed to reveal the exact causes of it.

Working potential has been found to affect to a great extent the rate of the electroreduction process as well (Figure 5); the escalation of the electroreduction rate with ~75% when shifting the operating potential from −0.1 V (−0.315 V vs. RHE) to −0.2 V (−0.415 V vs. RHE) evidences that the faradaic process reaches its maximum at the latter potential. The higher noise level noticed at working potentials more negative than −0.2 V (−0.415 V vs. RHE) can be due to a more intense oxygen evolution.

To the best of our knowledge, this work reports for the first time the electrocatalytic effect of metal oxide-doped g-C₃N₄ in combination with conductive polymer on the electrochemical reduction of H₂O₂ and tBHP, although its photocatalytic activity is a subject of considerable research interest, as pointed out above. The possibility that the composite material may act as a photocatalyst or photoelectrocatalyst has been checked by performing the hydroperoxide electroreduction in the dark as well. The comparison of the catalytic activity in the “light” and “dark” experiments showed negligible difference (of ca. 8%), suggesting that the photoelectrocatalytic effect, if any, is not substantial.

Summarizing, the results obtained so far indicate the possibility for creating an amperometric sensor to assay water-soluble tBHP and hydrogen peroxide in a wide range of

concentrations. In perspective, this catalytic electrode might be subjected to investigations under non-aqueous conditions, so to explore its electrocatalytic activity towards water-insoluble hydroperoxide compounds, and eventually will pave the way to the development of an electrochemical peroxide test.

4. Materials and Methods

4.1. Materials

The working electrodes were discs from glassy carbon with a diameter of the working surface $d = 2$ mm (Metrohm, Utrecht, The Netherlands); hydrogen peroxide H_2O_2 (Fluka); tert-Butyl hydroperoxide (Acros); Nafion™ 117, 5% suspension in water-alcohol mixture (Sigma-Aldrich, MI, USA); K_2HPO_4 and KH_2PO_4 (Acros) were of analytical grade and used without further purification. 0.1 M buffer solutions with $\text{pH} = 7$, $\text{pH} = 5$ and $\text{pH} = 3$, were prepared with monobasic and dibasic potassium phosphates dissolved in ultrapure water ($0.055 \mu\text{S cm}^{-1}$, B30 Adrona-Bio, Vilnius, Lithuania). Buffer solutions were adjusted to the desired pH with a pH-meter Easy Five (Mettler Toledo, OH, USA).

4.2. Apparatus and Measurements

All electrochemical measurements were performed in a conventional three-electrode cell (working volume 20–100 mL, Metrohm-Autolab, Utrecht, The Netherlands), with a catalyst-modified disc of glassy carbon (GCE) as working electrode, a $\text{Ag} | \text{AgCl}$ (KCl sat.) reference electrode and a platinum foil as auxiliary electrode. An electrochemical workstation PGSTAT Autolab 302N (Metrohm, Utrecht, The Netherlands) with Nova 2.1.5 software has been used in all experiments. Cyclic voltammograms (CVs) were recorded at a scan rate of 20 mV s^{-1} . Chronoamperometric measurements were performed under constant stirring.

The electrochemically accessible surface area was determined from cyclic voltammetry data, recorded at low scan rates (2–10 mV/s) in 5 mm $[\text{Fe}(\text{CN})_6]^{3+/4+}$ dissolved in 0.1 M KCl by using the Randles-Sevchik equation.

When necessary, the working medium was deaerated with argon gas (99.99% purity).

Electron microscopy was performed with a JEOL JSM 6390 (Oxford Instruments) scanning electron microscope.

4.3. Synthesis of Graphitic Carbon Nitride $g\text{-C}_3\text{N}_4$ and Co-Doped $g\text{-C}_3\text{N}_4$

The synthesis of graphitic carbon nitride ($g\text{-C}_3\text{N}_4$ protonated form—pm) is made by thermal condensation of protonated melamine, as described in [30,37]. In brief, 12 g of melamine dissolved into 100 cm^3 of methanol at 60°C were stirred for 10 min, then mixed with 100 mL of 0.2 M nitric acid added dropwise. The obtained white precipitate was separated out, washed several times with methanol (MeOH) and dried at 60°C for 12 h, and then calcined at 550°C for 2 h. The synthesis of the Co-doped $g\text{-C}_3\text{N}_4$ was carried out in one step method by thermal polycondensation on protonated melamine in the presence of salts of cobalt oxide (Co_3O_4) [29]. To reach Co 5% wt. in the final catalyst, a certain amount of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 50 cm^3 of methanol and added to the protonated melamine, under continuous stirring at 50 deg. until evaporation of the MeOH. The obtained solid was dried at 60°C for 10 h and calcined at 550°C for 2 h. Double metal oxide doped samples have been synthesised by a similar procedure.

4.4. Modification of Working Electrode

Before the modification, the glassy carbon electrode (GCE) surface was polished with $0.05 \mu\text{m}$ suspension of $\gamma\text{Al}_2\text{O}_3$ and rinsed with ultrapure water. The polishing step was followed by cleaning by ultra-sonication in distilled water for 3 min and followed by drying at room temperature. The modifying phase was prepared through dispersion of 2 mg of catalyst ($\text{Co-g-C}_3\text{N}_4$ or $g\text{-C}_3\text{N}_4$) in 1 mL of the polymer suspension Nafion assisted by ultrasonication for at least 45 min. After polishing, a $5 \mu\text{L}$ drop of the suspension was then cast onto the GCE surface, and was then dried at room temperature for 16 h.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal12080807/s1>, Figures S1–S7: Supplementary information.

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