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Substrate and pH-dependent homogeneous electrocatalysis using riboflavin for oxygen reduction

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Abstract

Homogeneous, aqueous solutions of the natural compound riboflavin were investigated for their electrocatalytic oxygen to hydrogen peroxide (H₂O₂) reduction performance using cyclic voltammetry and electrolysis. In addition to pH dependencies, interestingly the choice of carbon-based electrode material had a strong impact on the electrocatalytic performance. Therefore, the three electrode materials, glassy carbon, carbon paper (CP), and carbon felt were electrochemically compared and afterwards investigated with scanning electron microscopy. Attributed to the deprotonation of riboflavin, pH = 13 was identified as the best performing condition. Using CP at pH = 13, the addition of riboflavin enhanced the H₂O₂ production by a factor of 14 up to 355 μmol after 6 h at an average faradaic efficiency of around 80%.

KEYWORDS

carbon electrode materials, electrocatalysis, oxygen reduction reaction, riboflavin

1 | INTRODUCTION

Riboflavin, also known as vitamin B₂, is a versatile and naturally occurring organic redox-active molecule.^[1] In addition to its biomedical use, there are numerous technical applications based on riboflavin's redox properties such as mediator for electrochemical sensing^[2,3], photochemical pollutant removal,^[4–6] and organic cathode material for metal-ion batteries.^[7–9] Already in 1968, the group of Alan Bard investigated the reduced states of riboflavin with cyclic voltammetry (CV) and electron paramagnetic resonance studies, confirming two separated one-electron reduction steps in aprotic media.^[10] Some years later, the interaction of reduced riboflavin and natural analogs like the flavin monophosphate and flavin adenine dinucleotide with oxygen (O₂) gained increased attention from bio-

chemists and electrochemists. In the 1990s, several groups investigated and reported such interactions of flavins with O₂,^[11,12] which is nowadays known as an electrocatalytic oxygen reduction reaction (ORR). Although the initial investigations were mainly describing homogeneous systems, pioneer work regarding the ORR forming hydrogen peroxide (H₂O₂) via two-electron reduction was mainly done on adsorbed flavins^[13–15] or mixtures of riboflavin and carbon support materials.^[16] In addition to non-covalent chemisorption techniques, already in early times, covalent linking to silica substrates,^[17] glassy carbon (GC) substrates^[18] or via oxidative electropolymerization onto carbon electrodes^[19,20] have been studied. Following this covalent approach on GC, Manisankar *et al.* reported such systems as an electron mediator for oxygen reduction electrocatalysis using quinone molecules.^[21,22] Although

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many of the initial reports were investigating the effects of O_2 on CV curves and reported rate constant values from rotating disc electrode experiments, only very few papers like the one by Wang *et al.*^[16] reported quantified analysis of H_2O_2 produced. Two recent papers by Kormányos *et al.*^[23,24] reported fully synthetic flavin derivatives for homogeneous as well as heterogeneous electrocatalytic O_2 reduction. It should be mentioned here that the target of this present work is the investigation of homogeneous solutions of the natural riboflavin. Nevertheless, similar to the work of Kormányos *et al.*^[23,24] great scientific effort is made for synthesizing variations of flavin analogs with tailored properties for applications as organic semiconductors.^[25–27]

In the field of electrocatalytic ORR, the choice of electrode material is crucial, due to the high catalytic effects of many carbon-based electrode materials themselves.^[28,29] Besides boron-doped diamond, all graphitic carbon electrode materials are reported to show significant ORR forming H_2O_2 in a potential range similar to organic carbonyl-bearing electrocatalysts.^[29–35] This background electrocatalytic effect of any carbon electrode material always has to be considered throughout electrocatalytic studies. Recently we have reported, that simply by changing the carbon electrode from GC to a carbon paper (CP) electrode, we could significantly alter the electrocatalytic H_2O_2 production performance.^[36] This strong impact of the exact type of carbon material used is known for electrocatalysis,^[33] for energy storage applications like redox-flow batteries,^[37,38] and for organic cathode material batteries.^[39] In this respect, recently Werner *et al.*^[39] published a report by thoroughly comparing the molecular differences of CP and graphite composites on copper substrates for battery application and Li and Wu^[40] performed a comparative study on the use of graphite and amorphous carbon electrodes in dual-ion battery applications.

In this report, we investigated the electrocatalytic properties of natural riboflavin for H_2O_2 production with different electrode materials, similar to Mirzakulova *et al.* for water oxidation.^[41] In particular, we have comparatively studied GC, CP and carbon felt (CF) as electrode materials for the O_2 to H_2O_2 reduction with and without homogeneous riboflavin present in acidic, neutral, and alkaline conditions.

2 | EXPERIMENTAL SECTION

2.1 | Electrode preparation

GC plate with a thickness of 2 mm (Alfa Aesar) was cut to 1×4 cm and polished using Al_2O_3 paste (Buehler Micro-polish II deagglomerated) with a decreasing particle size of

1.0, 0.3, and $0.05 \mu\text{m}$. In between each polishing step, the plate was sonicated in 18 M Ω water for 15 min, followed by sonication in iso-propanol (VWR Chemicals) for an additional 15 min.

Prior to use, an electrochemical treatment was performed, where the potential was swept between 1.65 and -0.85 V versus standard hydrogen electrode (SHE) at a scan rate of 50 mV s^{-1} for 30 cycles in 0.5 M sulphuric acid (J. T. Baker).

Toray CP (TGP-H 60; Alfa Aesar) was used as received, cut into 1×2.5 cm rectangles. CF was cut into 1×2 cm rectangles, cut in half to decrease the thickness, and contacted with a Pt wire. Before use, the electrode was submerged in the corresponding electrolyte solution for proper wetting.

2.2 | Oxygen reduction reaction

Electrochemical measurements were performed with an IPS Jaissle Potentiostat/Galvanostat PGU 10 V - 100 mA for GC and CP and a Jaissle Potentiostat/Galvanostat 1030 PC.T for measurements using CF. The electrolysis measurements were performed in a two-compartment cell separated by a Nafion membrane (117) (Alfa Aesar), while CV measurements were performed in a one-compartment cell. The geometrical electrode area was used for the calculation of the current densities.

As electrode solution, a 0.1 M phosphate buffer was used prepared from H_3PO_4 (Sigma Aldrich) and NaH_2PO_4 (Sigma-Aldrich) at $\text{pH} = 2$ and prepared from NaH_2PO_4 (Sigma-Aldrich) and Na_2HPO_4 (Sigma-Aldrich) at $\text{pH} = 7$. A 0.1 M NaOH (Alfa Aesar) solution was used at $\text{pH} = 13$. (-)-Riboflavin was purchased from Sigma Aldrich and used as received.

For electrolysis measurements, at first, both compartments were flushed with N_2 for 30 min, followed by 30 min flushing with O_2 . To ensure saturated conditions a CV was measured after each gasification. A Pt foil as a counter electrode and a commercial Ag/AgCl (3 M KCl) (BASi) reference electrode were used with the respective working electrode (WE). For the electrolysis, a constant potential of -0.25 V versus SHE for GC and -0.4 V versus SHE for CF and CP was applied for 6 h. Over the duration of the experiment, an aliquot of $100 \mu\text{l}$ was removed at the set points after 0, 1, 2, 4, and 6 h.

Quantification of H_2O_2 produced while chronoamperometry was done spectroscopically, following a method published by Apaydin *et al.*^[42] and Su *et al.*^[43] A 4 mM *p*-nitrobenzeneboronic acid (Alfa Aesar) solution in DMSO (VWR) was mixed in a 1:1 volumetric ratio with a 150 mM $Na_2CO_3/NaHCO_3$ (Fluka & Sigma Aldrich) buffer solution at $\text{pH} = 9$. The resulting mixture was filtered via a

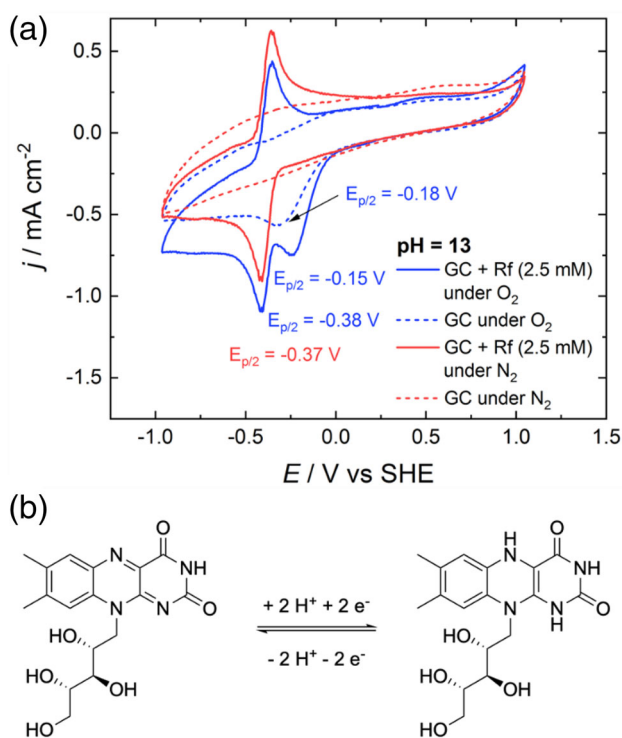


FIGURE 1 (a) Cyclic voltammetry (CV) under N_2 (red) and O_2 (blue) as well as $E_{p/2}$ for a solution of 2.5 mM riboflavin in NaOH at pH = 13 at 50 mV s^{-1} using a glassy carbon (GC) working electrode (WE) and (b) reduction scheme of riboflavin

syringe filter (Chromafil RC-45/15 MS, Macherey-Nagel) and afterwards mixed with the target samples. Under dark conditions, the reaction was left for 36 min before the UV-Visible (UV-VIS) absorbance at 411 nm was recorded with a Thermo Fischer Multiskan Go Microplate Spectrophotometer. For the calibration, several H_2O_2 standard solutions (Merck) were prepared and measured (See Figure S1 for calibration curve).

2.3 | Electrode characterization

The surface morphology of the electrodes was examined using scanning electron microscopy (SEM). A JEOL JSM-6360LV SEM was used at a high vacuum, at an acceleration voltage of 7.0 kV. UV-VIS spectra were recorded using a Perkin Elmer Lambda 1050 spectrometer and fluorescence spectra using a PTI QuantaMaster 40.

3 | RESULTS AND DISCUSSION

Figure 1 shows the CV graphs of blank GC (in dotted lines) in 0.1 M NaOH in comparison with a 2.5 mM solution of riboflavin in 0.1 M NaOH under nitrogen (N_2) and oxygen

(O_2) saturated conditions. Whereas bare GC does not show any redox feature under N_2 , a broad reduction peak at $E_{p/2} = -0.18 \text{ V}$ occurs under O_2 as a result of electrocatalytic ORR. Riboflavin under N_2 shows a well-resolved and reversible peak at -0.37 V undergoing the proposed reduction mechanism as depicted in Figure 1b. Under oxygen saturated conditions, the same redox peak is observed with an additional reduction peak at -0.15 V which can be attributed to the ORR. Although this peak is overlapping with the ORR peak of blank GC, the higher current density and more positive potential indicate an electrocatalytic behavior of riboflavin, which is in accordance with a comparable CV graph of a synthetic flavin derivative by the first paper by Kormányos *et al.*^[23] In comparison to previous reports^[16,34,35,44] on anthraquinone-based molecules for electrocatalytic ORR, these results using riboflavin look very promising. We prepared homogeneous solutions of riboflavin for investigating their electrocatalytic O_2 to H_2O_2 reduction. As Zhang *et al.*^[14] already reported a pH dependency on the electrocatalytic behavior of riboflavin, we thus prepared the experiments in three different solutions at pH = 2, pH = 7, and pH = 13. These results from electrolysis over 6 h using again a GC-WE are depicted in the following Figure 2 whereas accordingly CV graphs are shown in Figure 3.

According to Figure 2, blank GC produces nearly the same $60 \mu\text{mol}$ of H_2O_2 during the whole electrolysis time neutral and alkaline conditions, whereas in acidic pH = 2 with around $43 \mu\text{mol}$ significantly less H_2O_2 is produced. Referring to the faradaic efficiency (FE) values for the H_2O_2 produced, the neutral conditions seem to be favorable with around 77% in comparison to 70% in alkaline and 60% in acidic conditions. Upon addition of 0.3 mM riboflavin in alkaline conditions, an increased FE of roughly 83% was observed. Interestingly, at pH = 7 the riboflavin system produced significantly less H_2O_2 compared to blank GC but at an elevated FE of around 88%. The higher solubility and apparently higher ORR activity of riboflavin in alkaline solutions can be explained by means of deprotonation. The reaction equation for this deprotonation reaction with a pK_a value of 9.75, according to literature,^[45] and spectroscopic characterization of the neutral and deprotonated riboflavin species can be found in Figure S2. UV-VIS absorption and emission spectra clearly revealed that in alkaline solution a different, deprotonated species is present compared to neutral aqueous and aprotic DMF solution.

Recently we realized that the kind of graphitic carbon-based electrode material with the same electrocatalysts has a huge impact on the electrocatalytic ORR behavior of conductive polymers.^[36] In addition to this effect observed for ORR, similar effects were also reported for the electrocatalytic CO_2 reduction reaction.^[46] Regard-

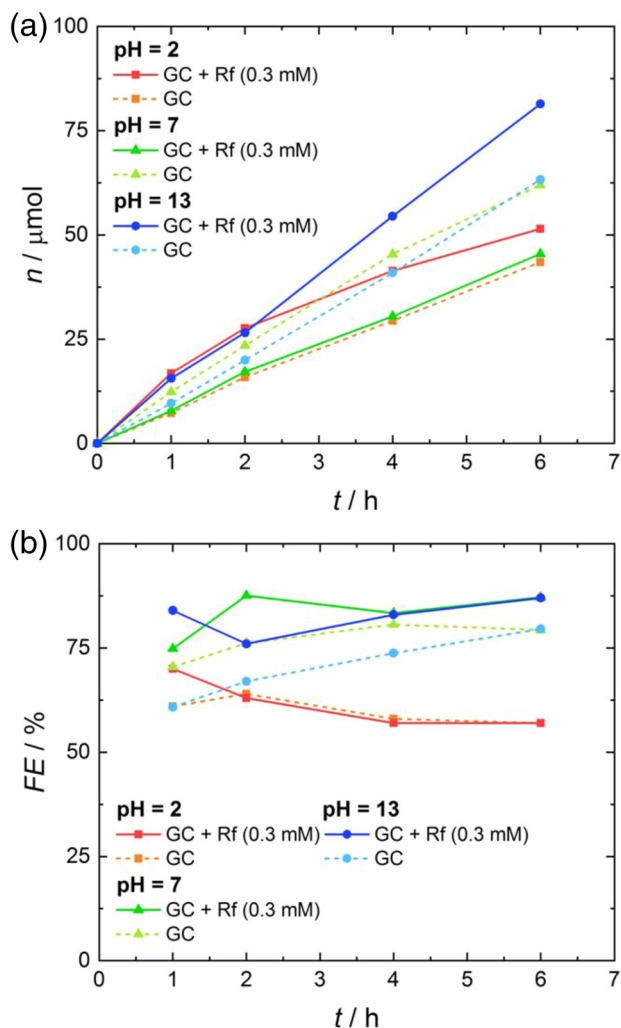


FIGURE 2 (a) Amount of H_2O_2 produced over the course of 6 h as well as (b) faradaic efficiency (FE) of electrolysis using a glassy carbon (GC) plate WE at pH = 2, 7, and 13 during constant potential electrolysis at -0.25 V versus standard hydrogen electrode (SHE)

ing organic battery application, recently remarkably large differences between two similar carbon-based electrode materials were reported by Werner *et al.* and thoroughly investigated.^[39] Therefore, in addition to GC, CP and CF were also used in our electrocatalytic studies. These results, recorded at a constant potential of -0.4 V versus SHE as a result of the respective current onsets in the CV graphs in Figure 4 are depicted in the following Figure 5.

Not only referring to the CV graphs in Figure 4 but also comparing the results from electrolysis in Figure 5 reveal a noteworthy difference to the smooth GC electrode surface. In acidic pH = 2, electrolysis using CP and CF yielded lower amounts of H_2O_2 compared to the accordingly blank experiments. However, the FE was increased upon the addition of riboflavin to the system. Especially the experiments performed in alkaline pH = 13 solutions, revealed a similar trend for all three carbon electrode

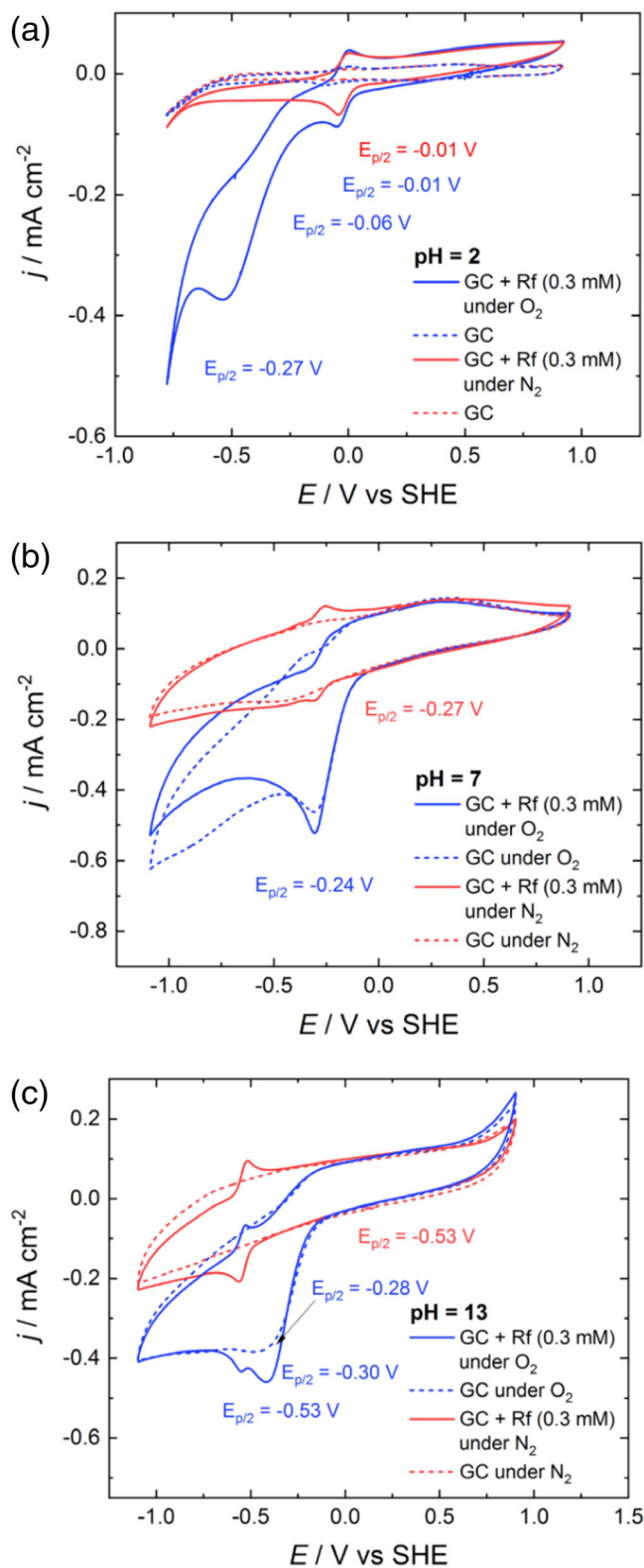


FIGURE 3 Cyclic voltammetry (CV) under N_2 (red) and O_2 (blue) as well as $E_{p/2}$ for a solution of 0.3 mM riboflavin in phosphate buffer at (a) pH = 2, (b) pH = 7, and (c) in NaOH at pH = 13 at 25 mV s^{-1} using a GC-WE

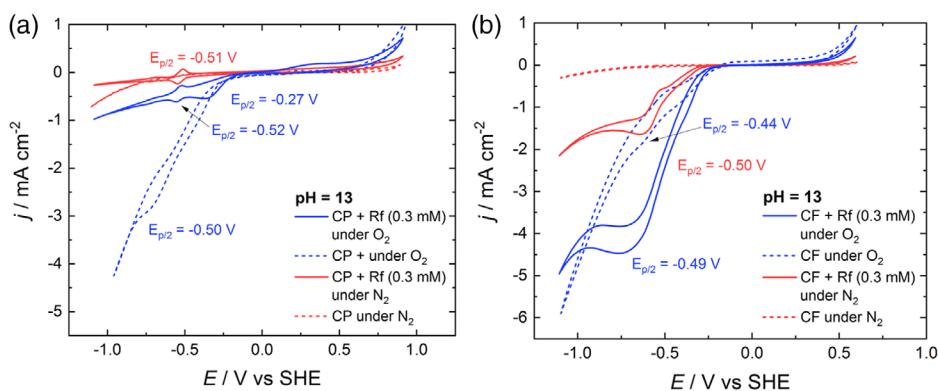


FIGURE 4 Cyclic voltammetry (CV) under N_2 (red) and O_2 (blue) as well as $E_{p/2}$ for a solution of 0.3 mM riboflavin in NaOH at pH = 13 and 25 mV s^{-1} using (a) carbon paper (CP) and (b) carbon felt (CF) working electrode (WE)

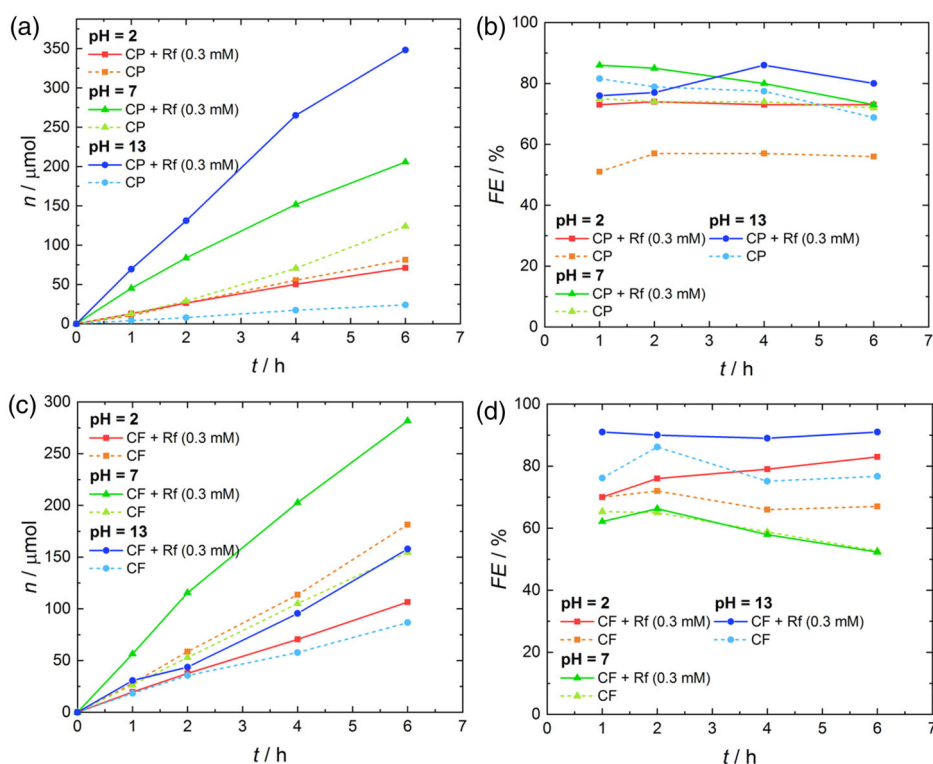


FIGURE 5 (a) Amount of H_2O_2 produced over the course of 6 h as well as (b) faradaic efficiency (FE) of electrolysis at -0.4 V using a carbon paper (CP) working electrode (WE) at pH = 2, 7, and 13, as well as respective measurements with (c) amount of H_2O_2 and (d) FE of electrolysis at -0.4 V using a carbon felt (CF) working electrode (WE)

materials used, that homogenous riboflavin significantly enhanced the moles H_2O_2 produced with higher FE . This is clear evidence for the electrocatalytic action of the deprotonated riboflavin. According to Figure 5a, using the 0.3 mM riboflavin solution in 0.1 M NaOH with a CP electrode produced $348 \mu\text{mol}$ of H_2O_2 after 6 h at an average FE of 80%. As the respective blank electrolysis only yielded $25 \mu\text{mol}$, this corresponds to increased production by a factor of 14. Interestingly, on CP and CF in neutral solu-

tion pH = 7 showed both an increased H_2O_2 production compared to the blank experiments, which is opposite to the trend observed for GC in Figure 2. Using riboflavin and CF at pH = 7, an outstanding amount of $282 \mu\text{mol}$ H_2O_2 was produced in contrast to $155 \mu\text{mol}$ without riboflavin, although the FE remained nearly unchanged at average values of around 60%. A summary of the moles H_2O_2 produced as well as the FE can be found in Table 1.

TABLE 1 Moles H_2O_2 produced as well as faradaic efficiencies for electrolysis measurements over the course of 6 h at pH = 2, 7 and 13

Electrode material	Blank measurements		0.3 mM riboflavin	
	n (μmol)	FE (%)	n (μmol)	FE (%)
pH = 2				
Glassy carbon	43	60	52	62
Carbon paper	81	55	71	73
Carbon felt	181	69	107	77
pH = 7				
Glassy carbon	62	77	45	88
Carbon paper	124	74	206	81
Carbon felt	155	60	282	60
pH = 13				
Glassy carbon	63	70	81	83
Carbon paper	25	77	348	80
Carbon felt	87	79	158	94

Summing up, CF was determined to show the highest moles H_2O_2 produced during blank experiments, but the lowest faradaic efficiencies in contrast to GC and CP. CF with riboflavin at pH = 7 resulted in the highest H_2O_2 moles produced of all CF experiments whereas in the case of CP the alkaline riboflavin conditions outperformed all other experiments. Upon comparing the different pH values among each other, with respect to all electrode materials used for alkaline solutions at pH = 13 riboflavin always induced an increase in the molar H_2O_2

production and the FE . This result is in accordance with related literature^[14,19,23] and can be seen as a hint that the deprotonated riboflavin species is more active towards the electrocatalytic oxygen to H_2O_2 reduction. As a result of the enhanced solubility of riboflavin in NaOH solution, also electrolytic experiments using 2.5 mM riboflavin solutions were performed as depicted in Figure S3. In the case of GC and CP, slightly less moles H_2O_2 were produced compared to the lower riboflavin concentrations of 0.3 mM, whereas in the case of CP with 130 μmol H_2O_2 only half of the amount was produced in comparison to 0.3 mM riboflavin. These results clearly illustrate a strong concentration dependence of the electrocatalytic effect of riboflavin in alkaline solutions, which are a subject for future research.

According to literature,^[14,47] organic molecules like riboflavin might adsorb on carbon electrode surfaces and thereby exhibit an electrocatalytic behavior that differs from a purely diffusion-controlled homogeneous system. Although investigations on a molecular level like scanning tunneling microscopy are beyond the scope of this work, the microscopic morphology changes of GC, CP, and CF were investigated before and after electrolysis using SEM as depicted in the following Figure 6.

Besides small brightness changes in the samples in Figure 6 no changes on GC and CP were observed after blank electrolysis at pH = 2 in SEM measurements. After electrolysis in pH = 2 with 0.3 mM riboflavin, a yellow deposit was observed by eye on all the carbon electrodes. According to the SEM images, the riboflavin appeared to precipitate during the electrochemical treat-

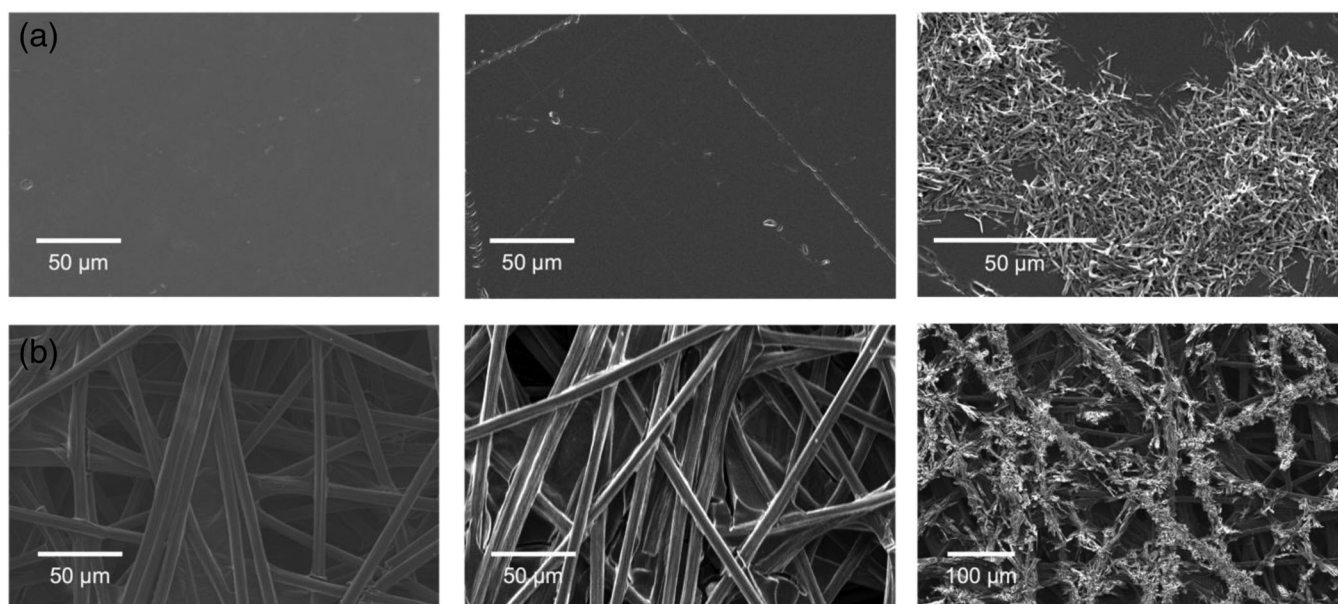


FIGURE 6 Scanning electron microscopy (SEM) images of (a) a glassy carbon (GC) plate, (b) a carbon paper (CP) prior to any use, after blank electrolysis at pH = 2, and electrolysis containing 0.3 mM riboflavin at pH = 2

ment in a micro-needle type structure. Such structures are reported in the literature for similar molecules like synthetic flavins,^[15,27] anthraquinones,^[48,49] or other organic pigments.^[50,51] This deposited layer might be an explanation for the comparably low H₂O₂ production with riboflavin at pH = 2. In contrast to pH = 2, investigations of the carbon electrodes after electrolysis in neutral and alkaline conditions (see Figure S4) did not show any microscopic changes or depositions. As concluded from these SEM studies, riboflavin precipitation in pH = 2 is a potential cause of the low H₂O₂ production. Details on whether riboflavin is adsorbing onto the carbon electrode materials on a nanoscopic or molecular level are subject to future studies with more advanced techniques. However, some literature reports suggest adsorption phenomena via π - π stacking to sp² hybridized carbon electrodes^[13,14] as used here in this study, but also to sp³ hybridized diamond electrodes.^[52]

4 | CONCLUSIONS

In our studies on the homogeneous electrocatalysis of riboflavin, we used GC, CP, and CF as electrically conductive carbon electrode materials for the electrochemical oxygen to H₂O₂ reduction. Furthermore, we compared different pH media. It was confirmed that without any riboflavin added, an ORR was occurring on these blank electrodes. The pH-dependent studies revealed a significant difference in the moles H₂O₂ produced and the corresponding *FE* for these blank responses. Literature reports identified the different molecular structures and the microscopic structures with respect to the electrochemically active surface area as the main reasons.

Upon addition of riboflavin into the electrolyte for homogeneous electrocatalysis of oxygen reduction, we also observed significant differences between these three different carbon electrode materials. In accordance with the literature, neutral to alkaline solutions are preferable for riboflavin catalyzed H₂O₂ production as at pH = 2, riboflavin precipitation was observed. In the case of all three electrode materials used, alkaline solutions showed increased performance for riboflavin catalyzed H₂O₂ production. CP in 0.3 mM riboflavin in 0.1 M NaOH solution produced an outstanding 348 μ mol of H₂O₂ at an average *FE* of 80%, which is the 14-fold amount in comparison to blank CP. On CF, homogenous riboflavin solutions showed the highest H₂O₂ production at neutral pH = 7.

Overall, we have demonstrated in this systematic study the homogeneous electrocatalytic activity of the naturally occurring vitamin riboflavin in addition to the mainly heterogenized or adsorbed previous studies reported.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

Data available in article supplementary material.

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