Freestanding Films of Reduced Graphene Oxide Fully Decorated with Prussian Blue Nanoparticles for Hydrogen Peroxide Sensing

Vitor H.N. Martins†; Monize M. da Silva†; Daniel A. Gonçalves†; Volker Presser‡¥§, Samantha Husmann‡; Victor H.R. Souza†*

Ť	Faculty of Exact Science and Technology, Universidade Federal da Grande Dourados,
	Dourados, MS, Brazil

1 INM – Leibniz Institute for New Materials, Campus D2-2, 66123, Saarbrücken, Germany

Engineering, Saarland University, Campus D2 2,
66123, Saarbrücken, Germany

§ Saarene – Saarland Center for Energy Materials and Sustainability, Campus C4 2, 66123 Saarbrücken, Germany

* Corresponding author: victorsouza@ufgd.edu.br;



Figure S1. Photographic images of rGO/PAni/Fe₂O₃ freestanding films (a) as-synthesized, and (b) under mechanical deformation.



Figure S2. Electrochemical profile of PB growth over the graphene-based electrodes for samples PB5(a), PB10 (b), PB25 (c), and PB100 (d).



Figure S3. SEM image for rGO/PAni film.

Supporting information



Figure S4. Size distribution of PB cubes in samples PB5 (a), PB10 (b), PB25 (c), PB100 (d), and PB200 (e).



Figure S5. Cross-sectional images of the freestanding film before (a) and after (b) the electrodeposition of PB particles (PB100).



Figure S6. FTIR spectra of the bare electrode (rGO/PAni/Fe₂O₃) and samples PB10, PB25, and

PB100.

The FTIR spectra of the bare sample (rGO/PAni/Fe₂O₃) and PB10, PB25, and PB100 electrodes are depicted in Figure S5. The three main bands observed in all samples at 1236, 1090, and 888 cm⁻¹ correspond to v_{C-N} in benzenoid rings of PAni; $v_{-NH}^{+\bullet}$ of PAni, indicating the presence of the polymer in emeraldine salt protonated form, and γ_{C-H} of both 1,4 and 1,2,4 rings. All bands confirm the presence of PAni in its conductive form.¹⁻⁵

Supporting information

- 1. Trchová, M.; Stejskal, J. Polyaniline: The Infrared Spectroscopy of Conducting Polymer Nanotubes (IUPAC Technical Report). Pure Appl. Chem. 2011, 83, 1803–1817.
- Quillard, S.; Louarn, G.; Lefrant, S.; Macdiarmid, A. G. Vibrational Analysis of Polyaniline: A Comparative Study of Leucoemeraldine, Emeraldine, and Pernigraniline Bases. Phys. Rev. B: Condens. Matter Mater. Phys. 1994, 50, 12496–12508.
- Ping, Z.; Nauer, B. G. E.; Neugebauer, H.; Theiner, J.; Neckel, A.; Neckel, A. Protonation and Electrochemical Redox Doping Processes of Polyaniline in Aqueous Solutions: Investigations Using In Situ FTIR-ATR Spectroscopy and a New Doping System. J. Chem. Soc., Faraday Trans. 1997, 93, 121–129
- 4. Kang, E.; Neoh, K. G.; Tan, K. L. Polyaniline: A Polymer with Many Interesting Intrinsic Redox States. Prog. Polym. Sci. 1998, 23, 277–324.
- Martins, V. H. N., Siqueira, N. M. S., Fonsaca, J. E. S., Domingues, S. H. & Souza, V. H. R. Ternary Nanocomposites of Reduced Graphene Oxide, Polyaniline, and Iron Oxide Applied for Energy Storage. ACS Applied Nano Materials 2021, 4, 5553-5563.



Figure S7 – Anodic peak current *vs.* square root of the scan rate of rGO/PAni/Fe₂O₃ (a) and PB10 (b) electrodes. Insets: Cyclic voltammograms at different scan rates of rGO/PAni/Fe₂O₃ (i) and PB10 (ii) electrodes.



Figure S8. (a) Multiple chronoamperometric detections of H₂O₂ every 24 hours, and (b) the analytical curve calculated from (a).

Table S1. Electrochemical performance for H_2O_2 detection of the freestanding films synthesized in this work.

Sample	Limit of detection (µM)	Limits of quantification (µM)
rGO/PAni/Fe ₂ O ₃	25.0	85.0
PB5	5.0	15.0
PB10	2.0	7.0
PB25	4.0	10.0
PB100	20.0	80.0