

Supporting Information

Crumpled Graphene Decorated with Manganese Ferrite Nanoparticles for Hydrogen Peroxide Sensing and Electrochemical Supercapacitors

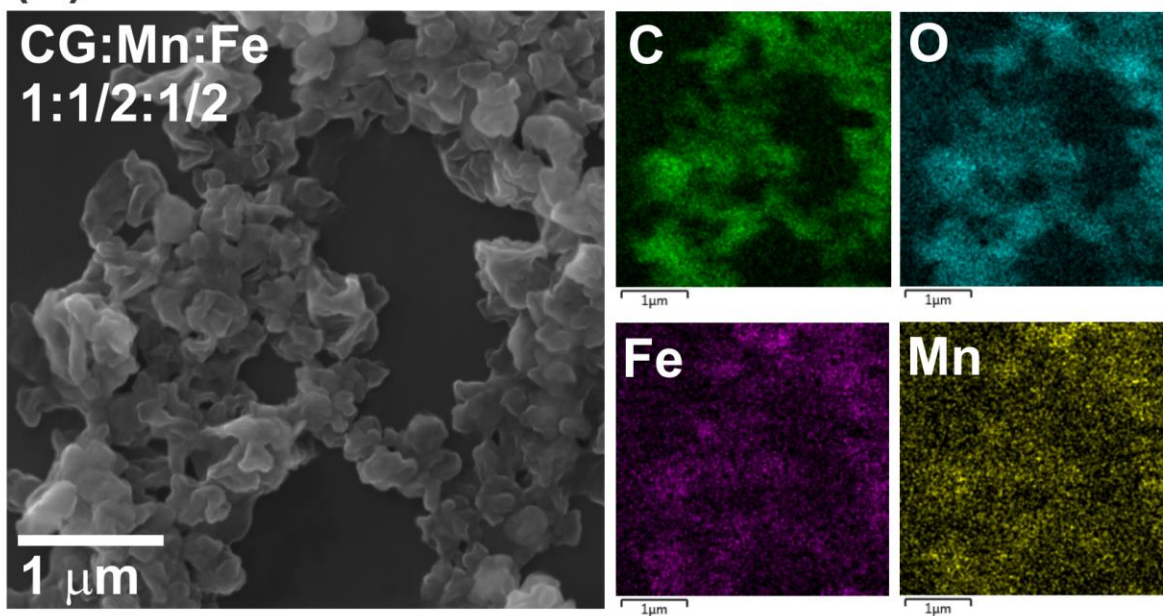
Larissa H. Nonaka[†]; Thiago S.D. Almeida[†]; Caroline B. Aquino[‡]; Sergio H. Domingues[‡]; Rodrigo V. Salvatierra[§]; Victor H.R. Souza^{†*}

[†]Faculty of Exact Science and Technology, Universidade Federal da Grande Dourados, Dourados, MS, Brazil

[‡]MackGraphe – Graphene and Nanomaterial Research Center, Mackenzie Presbyterian University, 01302-907 São Paulo, Brazil.

[§]Department of Chemistry, The NanoCarbon Center, and Department of Materials Science and NanoEngineering, Rice University, 6100 Main Street, Houston, Texas 77005, United States

(A)



(B)

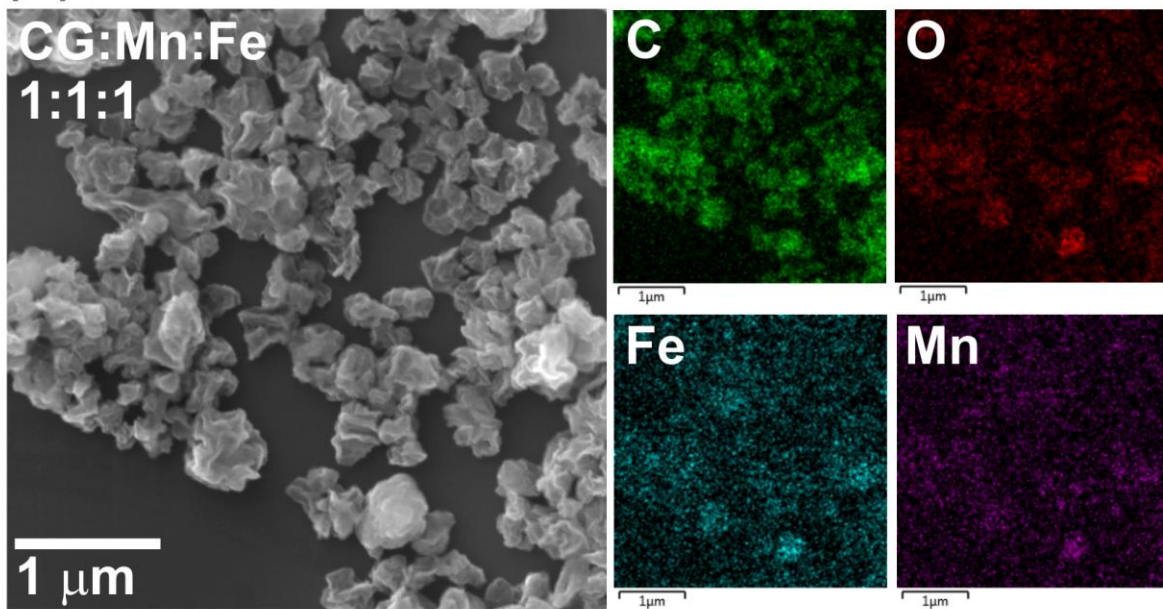


Figure S1 - SEM and EDS mapping images of the samples CG:Mn:Fe (A) 1:¹/₂:¹/₂, and (B) 1:1:1.

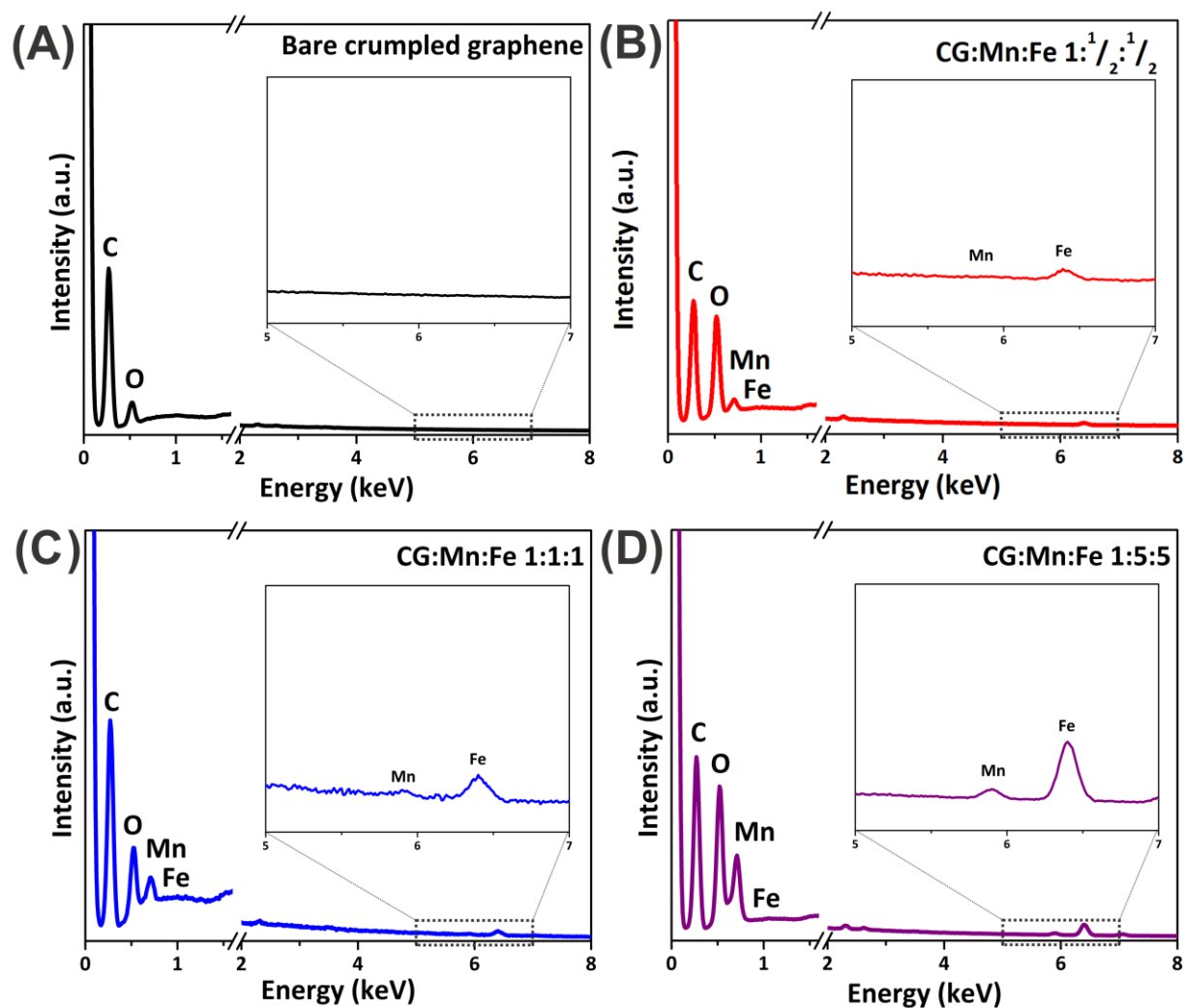


Figure S2 – EDS spectra and inset region from 5 to 7 keV for bare CG (A) and composites 1:1/2:1/2 (B), 1:1:1 (C), and 1:5:5 (D). The region corresponding to the peak of silicon was removed from all spectra.

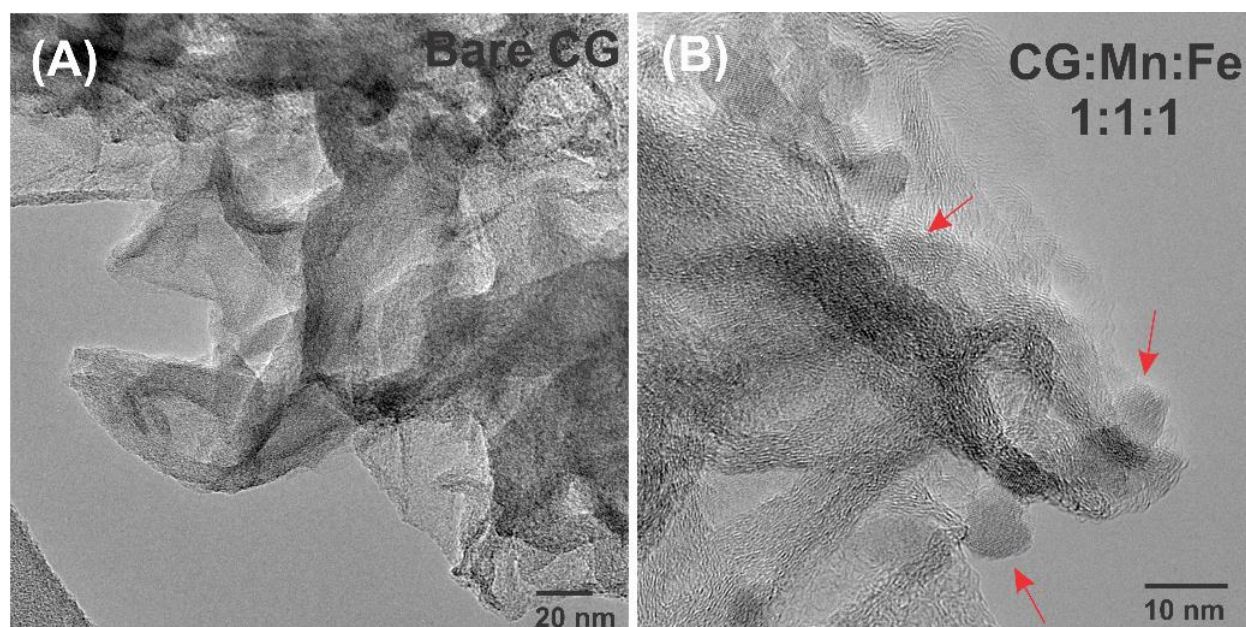


Figure S3 – HRTEM images for (A) bare CG, and (B) CG:Mn:Fe 1:1:1.

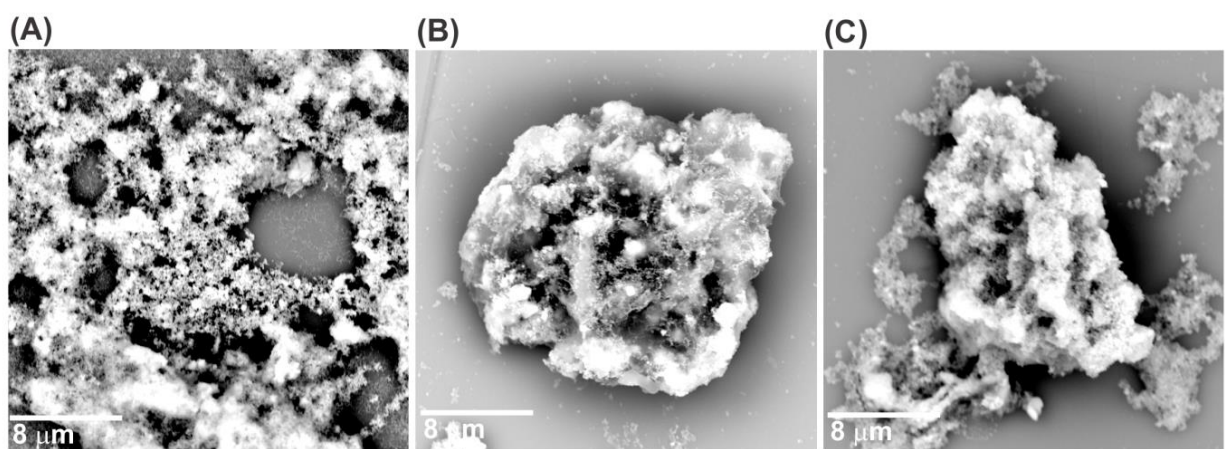


Figure S4 - SEM images of (A) bare MnFe₂O₄, (B) flat rGO:MnFe₂O₄ 1:1:1, and (C) flat rGO:MnFe₂O₄ 1:5:5.

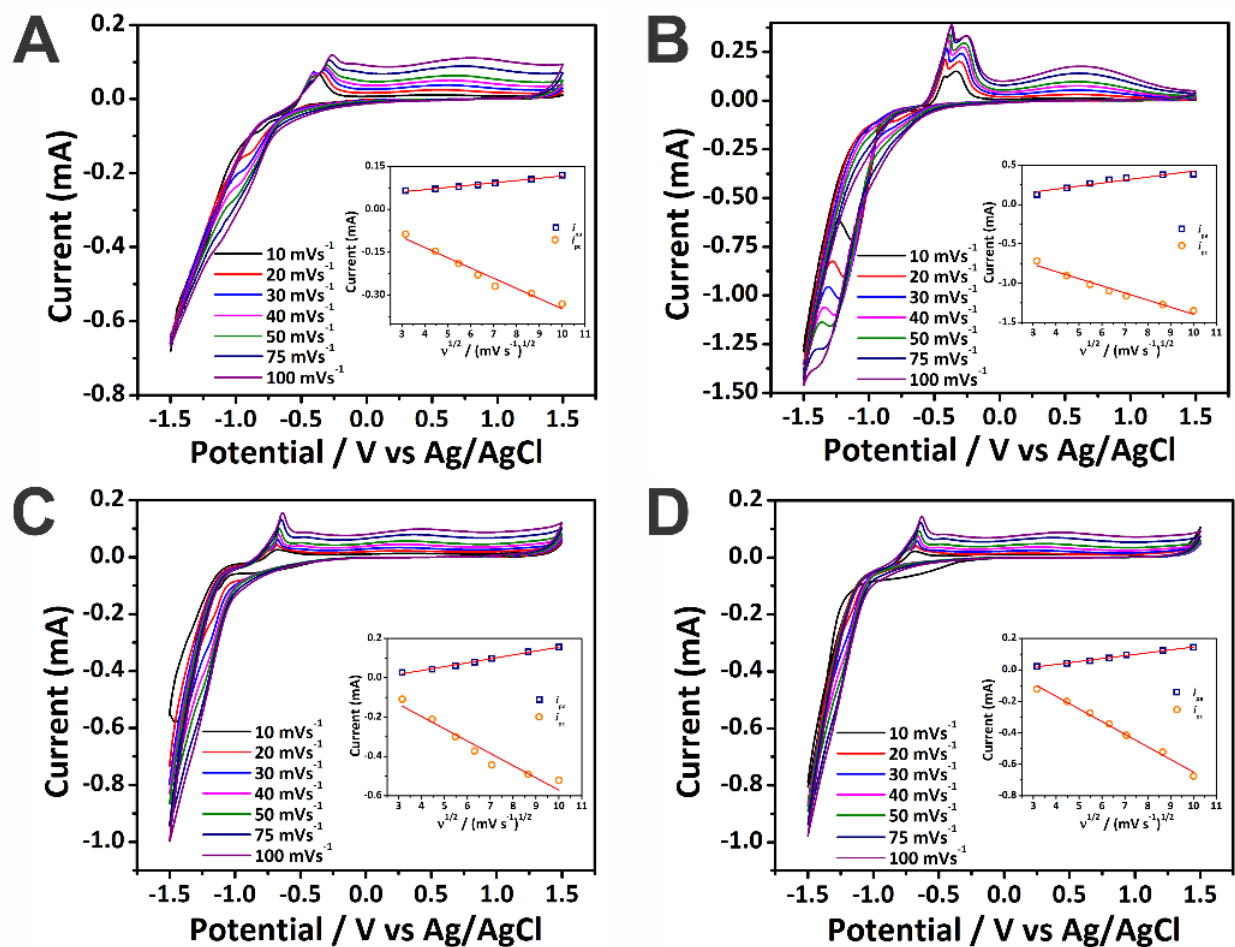


Figure S5 – CV curves at different scan rates, including the i vs. $v^{1/2}$ curves at the inset for (A) bare CG; (B) CG:Mn:Fe 1:1/2:1/2, (C) 1:1:1, and (D) 1:5:5.

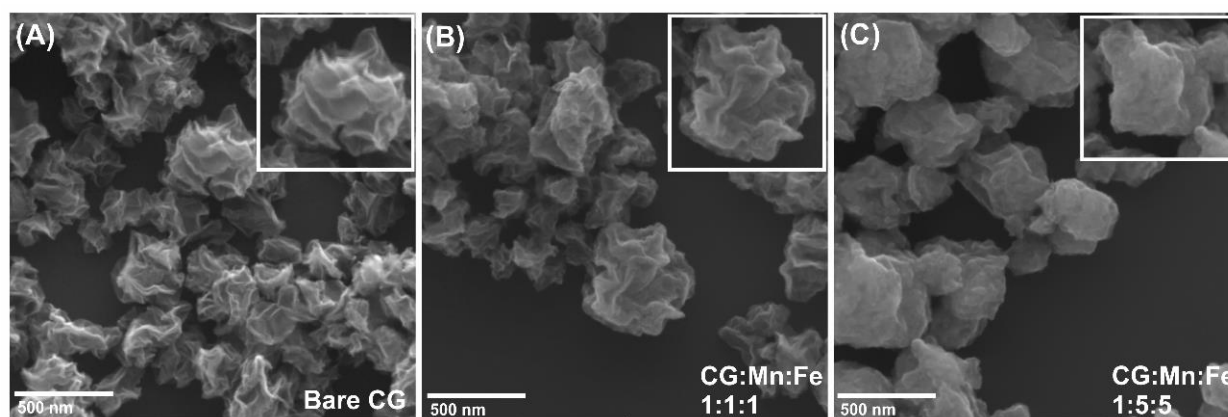


Figure S6 – SEM images of (A) bare CG, and composites (B) 1:1:1, (C) 1:5:5, showing the evolution of the morphology increasing the manganese ferrite nanoparticles decorating CG surface.

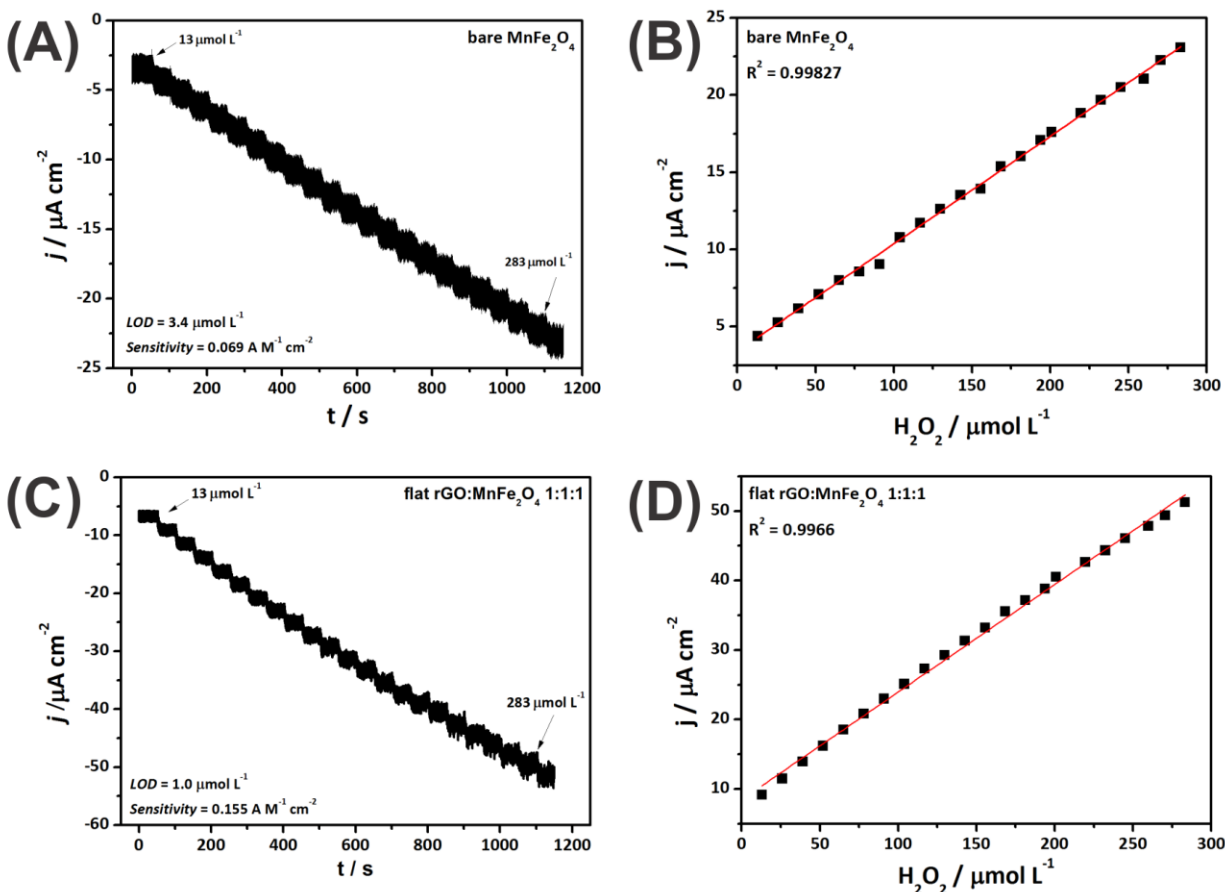


Figure S7 – (A) Chronoamperometric response of bare MnFe_2O_4 for H_2O_2 determination in a range from 13 to $283 \mu\text{mol L}^{-1}$, and (B) Analytical curve from the previous measure showing current density as a function of H_2O_2 concentration. (C) Chronoamperometric response of flat $\text{rGO:MnFe}_2\text{O}_4$ 1:1:1 for H_2O_2 determination in a range from 13 to $283 \mu\text{mol L}^{-1}$, and (D) Analytical curve from the previous measure showing current density as a function of H_2O_2 concentration.

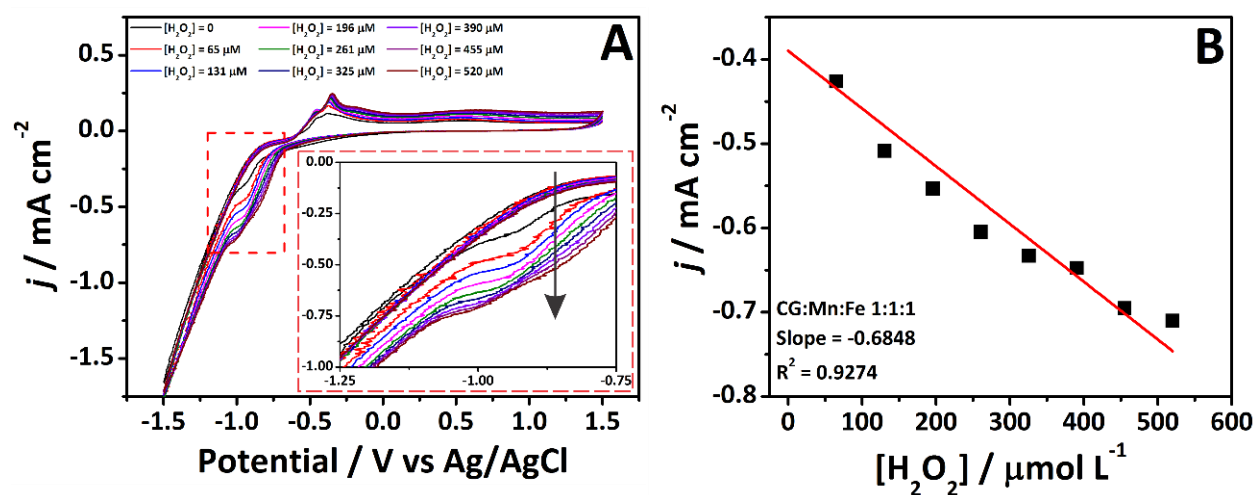


Figure S8 – H_2O_2 determination by CV measurements, including the evolution of cathodic peak with H_2O_2 concentration in the inset (A), and analytical curve using current density in function of H_2O_2 concentration (B).

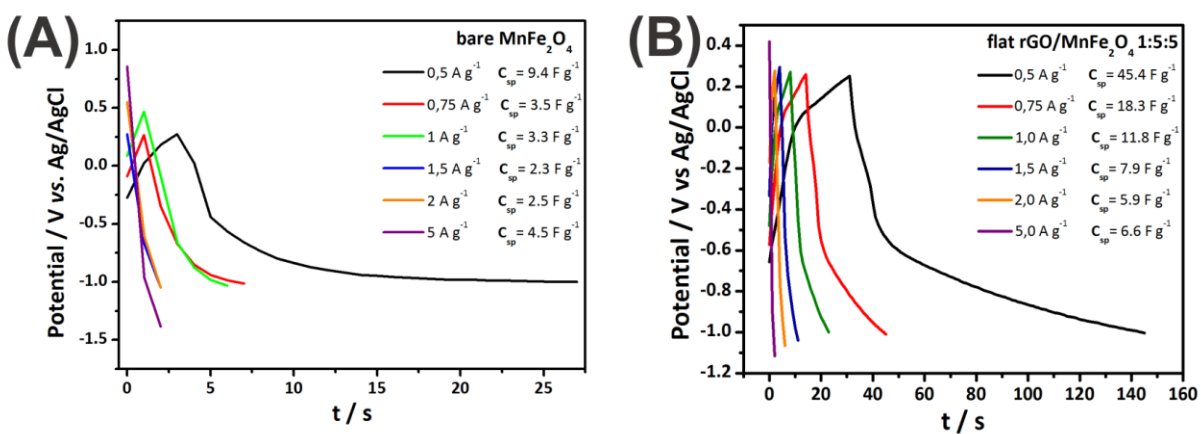
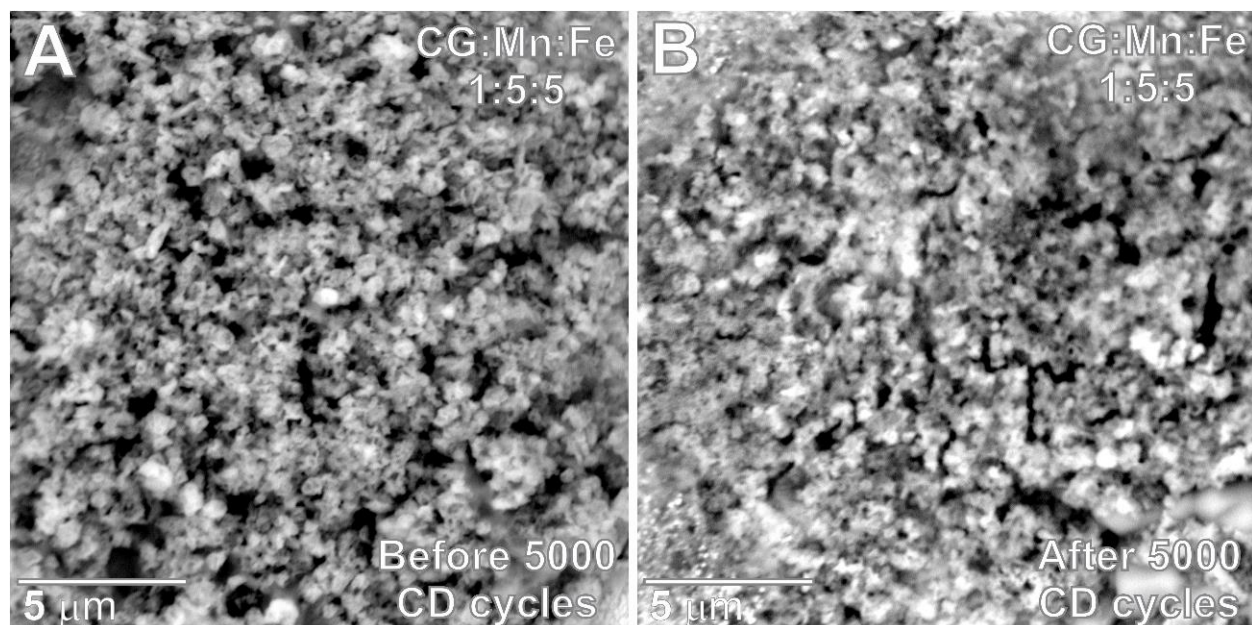


Figure S9 - Charge/discharge curves (3rd cycle) at different current densities for (A) bare MnFe_2O_4 , and (B) flat rGO: MnFe_2O_4 1:5:5.



S10 – SEM images of CG:Mn:Fe 1:5:5 before (A) and after (B) 5000 charge/discharge cycles.

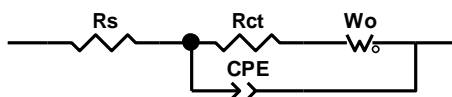


Figure S11 – Randles equivalent circuit used in this work.

Table S1 - Analytical parameters of the different materials produced in this work for H_2O_2 determination.

Sample	Limit of detection ($\mu\text{mol L}^{-1}$)	Sensitivity ($\text{A M}^{-1} \text{cm}^{-2}$)
Bare CG	3.51	0.04523
1:¹/₂:¹/₂	2.74	0.05802
1:1:1	1.63	0.09745
1:5:5	2.50	0.06343

TABLE S2 - Comparison of Coulombic efficiency* (%) and cycle life of MnFe₂O₄-based capacitors.

Material	CE% at current density (mA cm ⁻²) + aqueous electrolyte	Completed cycles	Reference
MnFe₂O₄ /graphene	~ 300% (0.3 A g ⁻¹) – 3 -electrode ~ 130% (0.3 A g ⁻¹) – 3-electrode ~ 50% (0.5 A g ⁻¹) – 2-electrode Electrolyte: PVA/H ₂ SO ₄	1000 to 5000 cycles (at 5 A g ⁻¹)	[9]
MnFe₂O₄/ polyaniline /graphene *polyaniline is electro-chemically active	~ 105 % (0.2 A g ⁻¹) – 3-electrode Electrolyte: 1 M KOH	5000 cycles (2 A g ⁻¹)	[5]
Cu-doped MnFe₂O₄/ graphene	N/A	1000 cycles (CV)	[8]
MnFe₂O₄ NPs	~ 52% (0.2 A g ⁻¹) – 2-electrode ~ 81% (0.4 A g ⁻¹) – 2-electrode Electrolyte: 3.5 M KOH	10000 cycles (3 A g ⁻¹)	[6]
MnFe₂O₄ NPs	~ 50% (0.2 A g ⁻¹) (2 M Na ₂ SO ₄) ~ 93% (0.2 A g ⁻¹) (2 M KOH) ~ 99% (0.2 A g ⁻¹) (2 M LiOH) ~ 99% (0.2 A g ⁻¹) (2 M NaOH) All 2-electrode	N/A	[40]
Crumpled graphene with MnFe₂O₄ NPs	~ 275% (0.5 A g ⁻¹) – 3-electrode ~ 125% (0.7 A g ⁻¹) – 3-electrode Electrolyte: 0.05M KCl	5000 cycles (2 A g ⁻¹)	This work

*CE was calculated as ratio of discharge to charge capacity in the galvanostatic measurement.