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Graphene exfoliated through phytochemicals-compounds containing cathecolic-moieties as a functional nanomaterial for sensors

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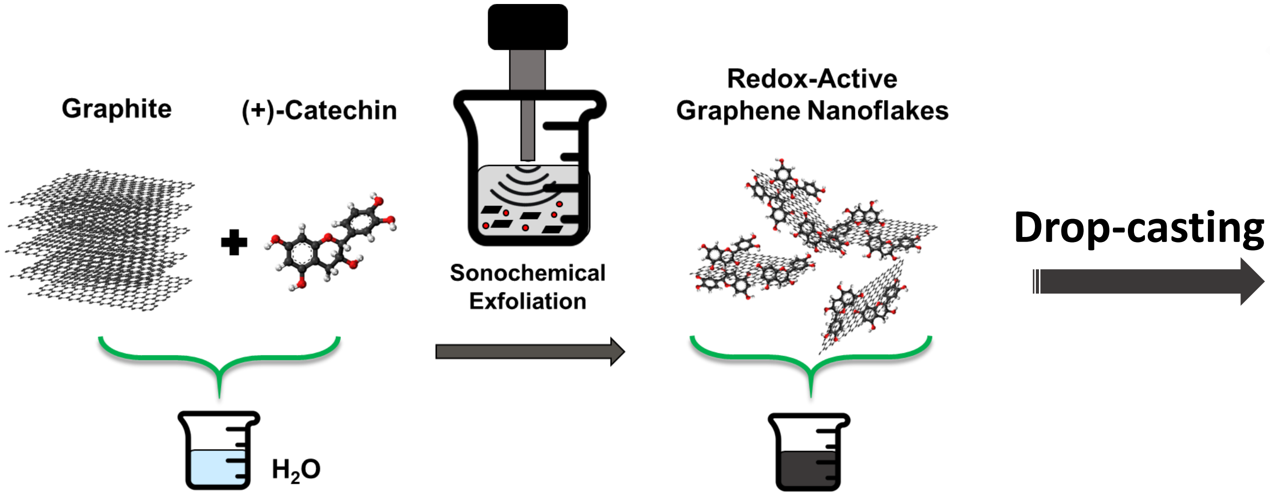
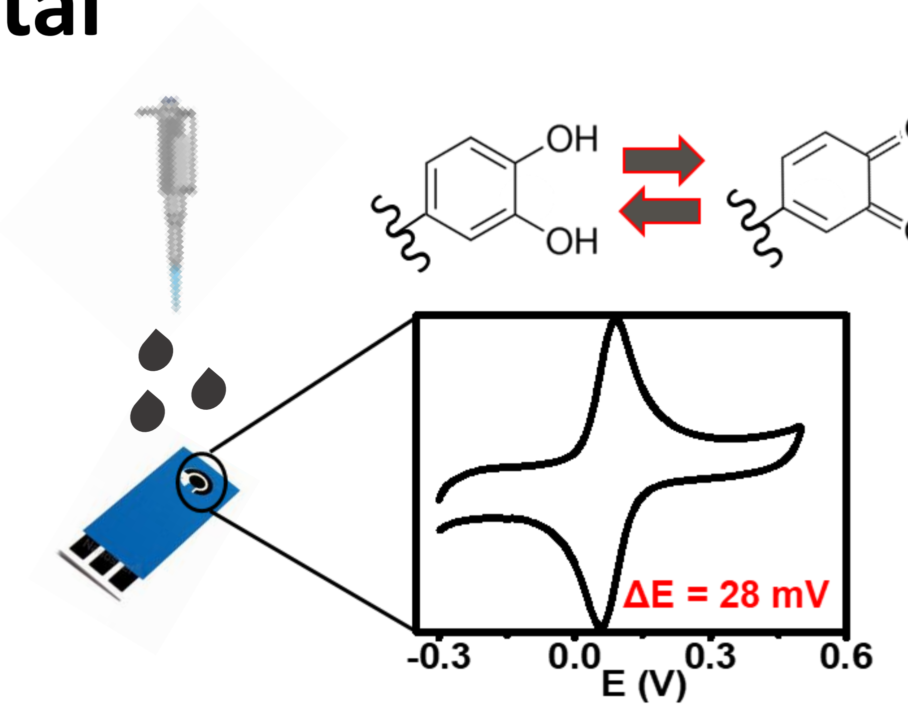
State of art

The green revolution on-course pumps towards the use of phytochemicals instead of chemicals and solvents. Among phytochemicals, polyphenols (PPs) have been employed to perform the synthesis of nanomaterials, especially in the analytical and nanobiotechnological fields. In this context, PPs have been quite used to assist exfoliation of graphite through liquid phase exfoliation (LPE). Noteworthy, exploiting the complex electrochemistry of PPs [1,2], some of them are able to act as surface modifiers resulting in activated phenols, which can work as redox-mediators [3]. Herein, we demonstrated that among natural PPs, a natural flavonol namely catechin (CT), allows exfoliation of graphite in water, giving rise to stable graphene nanoflakes (GF-CT) integrating well-defined electroactive quinonid adducts, resulting in a redox-active functional nanomaterial.

Experimental

Liquid phase exfoliation (LPE)

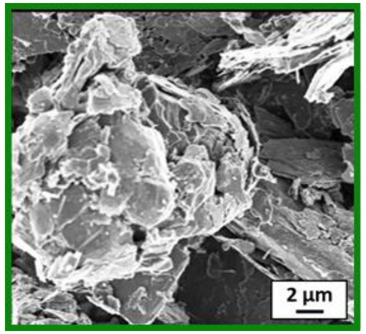




Results

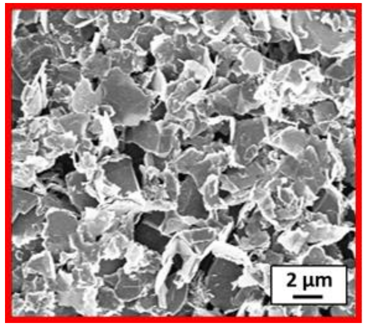
Morphological characterization

Bulk graphite

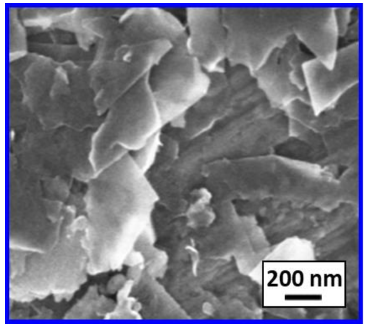


LPE

Graphene-catechin nanoflakes (GF-CT)



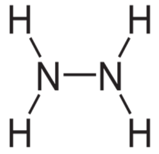
Graphene-sodium cholate nanoflakes (GF-SC)



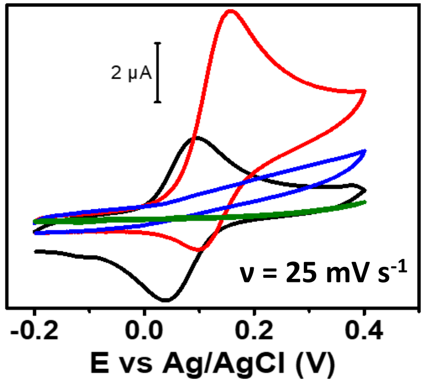
Electrochemical performance

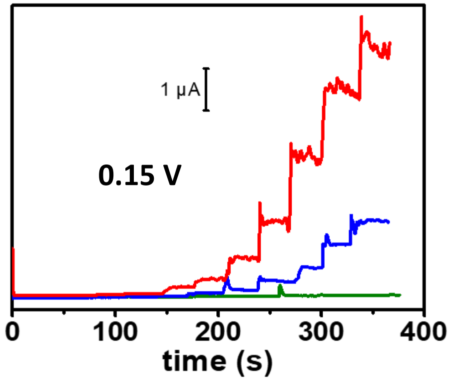
Cyclic voltammetry

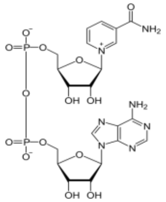
Amperometry calibration



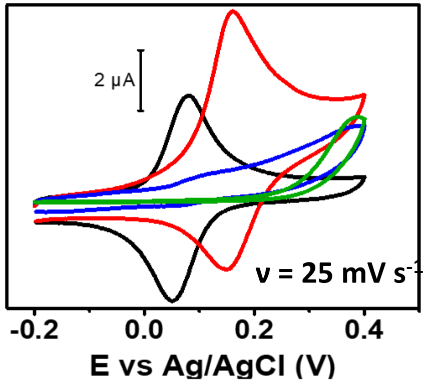
[HY] = 100 µM

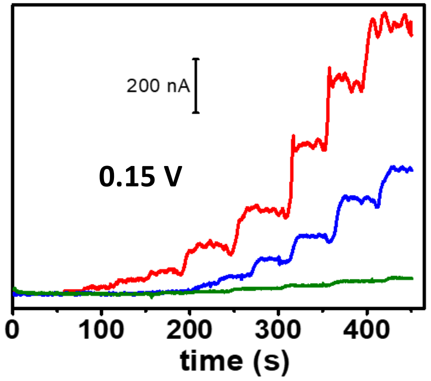






[NADH] = 250 µM





Red: GF-CT
Blue: GF-SC
Green: graphite SPE

HY

- LOD: 0.1 µM
- L.R.: 0.1-150 µM

NADH

- LOD: 0.65 µM
- L.R.: 2.5-200 µM

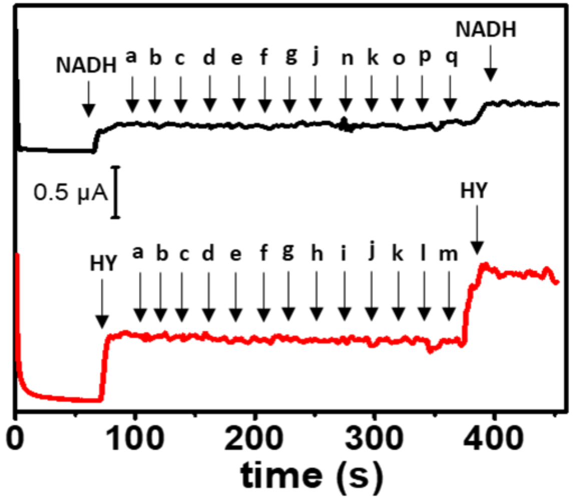
Results

Interference study

Working potential: 0.15 V

[HY] = 100 µM

[NADH] = 50 µM



a K^+ 1 mM, **b** Na^+ 1 mM, **c** Ca^{2+} 1 mM, **d** Mg^{2+} 1 mM, **e** Cl^- 1 mM, **f** CO^{3-} 1 mM, **g** PO^{4-} 1 mM, **h** NO^{3-} 200 µM, **i** NO^{2-} 100 µM, **j** glucose 2 mM, **k** urea 1 mM, **l** sodium acetate 100 µM, **m** sodium citrate 50 µM, **n** dopamine 1 µM, **o** L-tyrosine 50 µM, **p** ascorbic acid 50 µM, **q** uric acid 10 µM.

Sample analysis

Hydrazine					NADH				
Samples	Added µM	Found µM	Recovery %	RSD %	**Samples**	Added µM	Found µM	Recovery %	RSD %
	-	-	-	-		-	-	-	-
	10	10.5	105.1	1.0		10	10.7	107.0	5.9
River	25	26.3	105.2	0.2	**Serum 1**	25	25.6	102.2	6.7
	50	53.0	106.1	0.3		50	47.8	95.6	4.8
	-	-	-	-		-	-	-	-
	10	9.8	97.7	1.2		10.0	10.0	100.0	7.7
Lake	25	25.6	102.2	1.0	**Serum 2**	25	26.6	106.5	6.4
	50	51.1	102.2	1.8		50	52.8	105.7	7.3
	-	-	-	-		-	-	-	-
	10	9.4	94.2	1.3		10	10.0	100.0	3.3
Well	25	25.3	101.0	0.5	**Serum 3**	25	26.3	105.0	6.7
	50	48.0	96.0	0.5		50	52.6	105.2	8.0

HY → **Environmental waters**

NADH → **Human serum**

RSD < 8 %

Recoveries: 94-107 %

Conclusions

- The CT-assisted LPE of graphite provided redox-active graphene nanoflakes.
- The integrated quinoid mediator achieved enhanced performance for HY and NADH electrochemical detection
- GF-CT based sensor allowed accurate and selective NADH and HY determination in real matrices

Future perspectives

- Realization of exclusively based GF-CT conductive nanofilm
- Integration of GF-CT film into modular-flexible devices
- Development of bio-sensing platforms, exploiting the redox and mediator-activity of the GF-CT integrated catechol-quinone moieties

References

1. Wang Y, Shi Z and Yin J 2011 Facile Synthesis of Soluble Graphene via a Green Reduction of Graphene Oxide in Tea Solution and Its Biocomposites *ACS Appl. Mater. Interfaces* **3** 1127–33
2. Liao R, Tang Z, Lei Y and Guo B 2011 Polyphenol-Reduced Graphene Oxide : Mechanism and Derivatization *J. Phys. Chem.* **115** 20740–6
3. Yu Z, Shi Z, Xu H, Ma X, Tian M and Yin J 2017 Co-assembly of tannin-assisted exfoliated low-defect graphene and epoxy natural rubber latex to form soft and elastic nacre-like fi lm with good electrical conductivity *Carbon N. Y.* **114** 649–60