

# Gold nanoparticles decorated Reduced Graphene Oxide electrodes for detection of a cancer biomarker candidate

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The modification of graphene based materials with colloidal inorganic nanocrystals has recently attracted increasing attention.<sup>1,2</sup> A novel colloidal hybrid material, based on pyrene-carboxylic acid (PCA) functionalized Reduced Graphene Oxide (RGO) flakes, uniformly coated by a dense layer of organothiol-capped Au nanoparticles (NPs), is proposed. The Au NPs, 2-3 nm in size, have been synthesized with a reproducible control on size and shape by an *in situ* colloidal reduction method. The RGO flakes, which are achieved by exfoliation, in form of single- and few-layered sheets, allow to access the relevant structural properties of graphene, concomitantly permitting its solution processing, both for fundamental studies, and for achieving functional hybrid materials for advanced technological applications.<sup>3</sup>

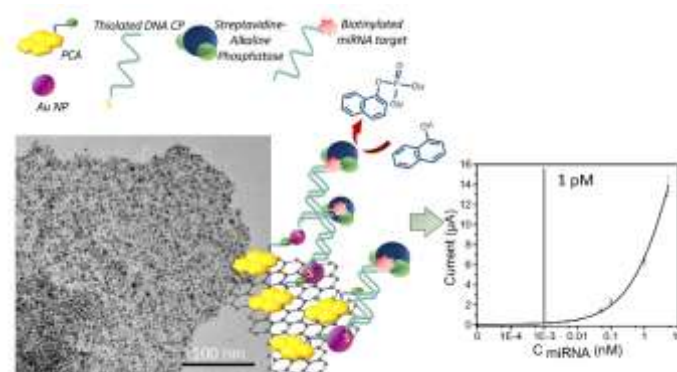
The synthesis of the novel colloidal hybrid material has been optimized, so as to be suited for its application upon modification of Screen-Printed Carbon Electrodes (SPCEs) in the detection of the miRNA-221 sequence, a cancer biomarker candidate overexpressed in lung and breast cancer.

Electrochemical measurements performed on the modified electrodes show that the hybrid Au NP decorated RGO provides a twofold increase of the electroactive surface area, faster heterogeneous electron transfer kinetics at the electrode/electrolyte interface with a decrease of the resistance of the electron transfer with respect to the unmodified electrodes.

The hybrid modified SPCEs demonstrate an improved electrocatalytic activity towards red/ox reactions of 1-naphthol, a typical reagent involved in the Alkaline Phosphatase-amplified bioassay, showing a great potential as platform for the

detection of the proposed cancer biomarker candidate.

The platforms have been found highly reliable and sensitive in the streptavidin-alkaline phosphatase catalyzed assay of the miRNA-221 sequence,<sup>4</sup> detected in spiked human blood serum samples with a LOD of 0.7 pM, and an average percentage standard deviation (RSD) of 13%, in a range of 1 – 5000 pM.



**Figure 1.** Electrochemical detection of miRNA-221 by a Streptavidin-Alkaline Phosphatase catalyzed assay. PCA-RGO/Au NP based SPCEs, modified by a thiolated DNA capture probe (CP) hybridized by the biotinylated mi-RNA 221target, upon exposure to 1-naphthyl phosphate, generate 1-naphthol, which is detected by DPV.

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## References

- [1] C. Ingrosso et al. *J. Mater. Chem. A* 2017, 5, 9307.
- [2] C. Ingrosso et al. *ACS Appl. Mater. & Interfaces* 2015, 7, 4151.
- [3] Novoselov K. S. et al. *Nature* 2012, 490, 192.
- [4] Bettazzi, F. et al. *Anal. Bioanal. Chem.* 2013, 405, 1025.