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NANOMATERIAL-BASED SENSORS AND FOOD POLYPHENOLS: AN ANALYTICAL CHALLENGE AND A SOURCE OF USEFUL ELECTROCHEMICAL COMPOUNDS

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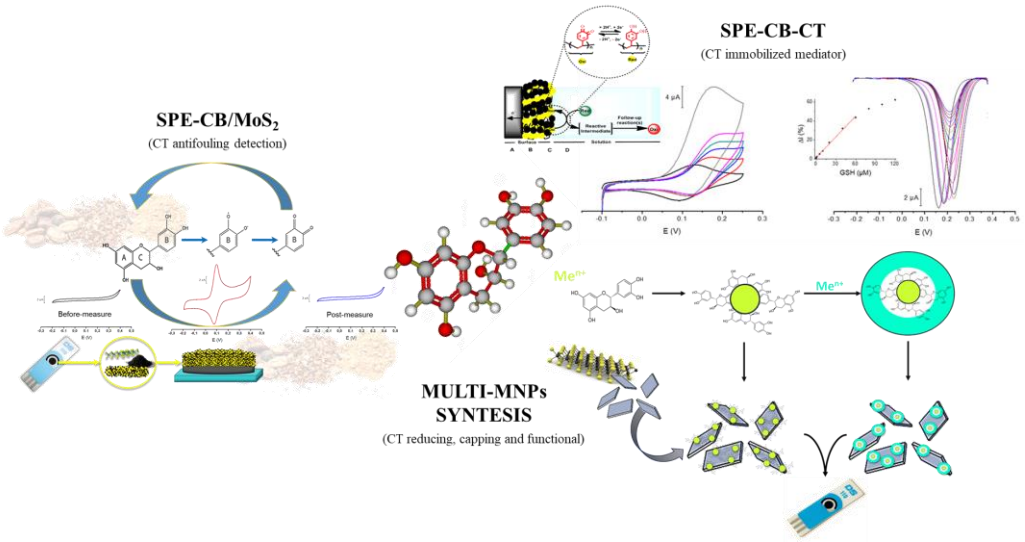
Nanomaterials (NMs) have become elective analytical tools able to improve the performances and give rise to new opportunities, for both constructions of analytical devices and implementation of analytical methods. On the other hands, polyphenolic compounds (PCs) still continue to attract exceptional attention, for their well-known health benefits, for their technological role and also marketing [1].
Thus, this work born with the idea to realize a regenerable and effective portable electrode able to directly allow the PCs quantification in foods. To this aim, different nanocomposites have been challenged, in particular, for the first time, 2D transition metal dichalcogenides (TMD) have been employed combined with carbon black nanoparticles, for the PCs analysis. In brief, a regenerable and totally anti-fouling (classical catechins/polyphenols analysis drawback) screen-printed electrode (SPE) based on TMD for the cocoa (CO) catechins (CT) rapid quantification has been realized, and at the same time, a new natural polyphenolic electrochemical mediator (CT) has been discovered, studied and exploited for a further nano-sensors realization.
Thus, firstly, the ability to detect catechins on a carbon black/molybdenum disulfide nanohybrid screen-printed electrode (SPE-CB/MoS_2) has been demonstrated. The SPE-CB/MoS_2 merge the ability of CB to improve the electrochemical response with the proprieties of MoS_2 to totally prevent catechins irreversible polymerization and absorption onto the electrode surface occurring at both bare and CB-modified SPEs. The latter, MoS_2 property has been proved in this study for the first time. The MoS_2 anti-fouling ability has been demonstrated using both flavanols standards and real samples. Moreover, the SPE-CB/MoS_2 proposed sensor allowed an improvement of sensitivity (LOD ≤ 0.17 µmol L^{-1}) of 100-folds compared to the bare SPE electrode, showing linear range between 0.12 and 25 µmol L^{-1} with good determination coefficients (R2 ≥ 0.998). 59 cocoa powder samples have been tested with the nanohybrid sensor developed and compared with the classical methods for polyphenols evaluation. The SPE-CB/MoS_2 allow to obtained repeatable (intra-electrode RSD = ip,a 0.9 % and Ep,a 5,2 %, n = 59) and reproducible (inter-electrode calibration slope RSD ≤ 4.1, n = 3) results, significantly correlated with classical methods for

the polyphenols evaluation (r= 0.95–0.97). Noteworthy, after the measurements of 59 cocoa samples the electrode was still active (recovery signal 99 %).
In a parallel track, during the study of nanomaterial reactivity towards cocoa catechins, carbon black demonstrated to act as catechins (CT) immobilization elective support. Indeed, upon the oxidation of CT to quinone, the cyclic voltammetry results demonstrated a pair of well-defined and reversible redox peaks. Surprisingly, the SPE-CB electrode after the CT measure (and after the washing-step), continues to show a pair of stable reversible redox peaks (RSD = ip,a 1.1 % and Ep,a 1,9 %, n = 20). Thus, was proven that the CT remain strongly attached to the electrode surface (SPE-CB) retaining a mediator-like electrochemical behavior. Thus, for the first time has been realized an electrochemical redox platform based on cocoa polyphenols, catechin-quinone (oxidized catechin), prepared by an in situ simple electrodeposition method onto a carbon black modified screen-printed electrode surface (SPE-CB/CT). The mediator (CT and cocoa extract) activity, has been studied, proved, and applied to glutathione (GSH) detection. The optimized SPE-CB/CT sensor exhibited a linear response to glutathione concentrations from 5 nM to 100 µM. As proof of concept, the fabricated SPE-CB/CT sensors, realized directly using cocoa extracts, were successfully employed for the determination of GSH and oxide glutathione (GSSG) in biological fluids.
In order to further prove the exploitability of the interaction between NMs and PCs, works are still in progress for the realization of TMD-based electrochemical platforms decorated with bimetallic nanoparticles, synthesized exploiting the PCs unique features. Definitely, this work contributes to further prove that nanomaterials (in this case TMDs and CB) are unique and useful analytical tools able to both tailor ‘customize sensors’ and giving rise to new analytical opportunities.



Graphical scheme of the main topics treated in this work

References

[1] Della Pelle, F., & Compagnone, D., Nanomaterial-based sensing and biosensing of phenolic compounds and related antioxidant capacity in food, Sensors, 2018, 18(2), 462.