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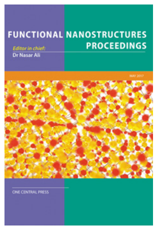

Carbon nanomaterials as glassy carbon modifiers for electrochemical devices with boosted activity

Domenica Tonelli*, Isacco Gualandi and Ylea Vlamidis

Department of Industrial Chemistry "Toso Montanari", University of Bologna, Viale del Risorgimento 4, 40137 Bologna, Italy.
**corresponding author*

ABSTRACT

Glassy carbon electrodes (GCEs) modified with a composite made of multi-walled carbon nanotubes (MWCNTs) and electrochemically reduced graphene oxide (ERGO) were employed to investigate the electroactivity of dopamine (DA) an catechol (CA) which resulted into a significant improvement of the analytical performances. The same composite was used to support tyrosinase or laccase in order to fabricate amperometric biosensors for determining total polyphenols in juice samples, based on the reduction of the enzymatically produced quinone. Carbon based nanomaterials were also exploited to induce the electrosynthesis of layered double hydroxides (LDHs). Using glucose as target, electrocatalytic activity was found to be higher than when LDH was deposited on bare GCE.

I. INTRODUCTION

The glassy carbon electrode is popular in electroanalysis for its wide potential range, low cost, availability, and chemical inertness in most electrolytes. However, during the oxidation of many analytes the reproducibility and sensitivity of its response deteriorate due to the fouling of its surface [1]. CNTs and many other carbon based materials have been very popular in electrochemical applications through the years. More recently, graphene (G) has attracted a great deal of attention owing to its highly accessible surface area, good electrical conductivity, chemical and thermal stability, mechanical strength and excellent electrochemical activity [2]. To obtain large quantities of graphene in the least expensive way several strategies have been developed. One of these is the oxidation of graphite to obtain the electrically insulating graphene oxide (GO) whose conductivity can be partially restored by reduction, employing both chemical and electrochemical methods [3]. In literature, the electrochemical reduction of GO has been performed on different electrode materials to obtain ERGO. It has been verified that coupling CNTs with reduced graphene oxide (rGO) can lead to composites that exploit the characteristics of both nanomaterials, thanks to a synergetic effect, thus leading to more outstanding features [4] which have been also exploited in the field of the electrochemical sensing [5]. We studied the modification by drop casting of a GCE with ERGO and MWCNTs to develop amperometric (bio)sensors with boosted performances and to induce the electrosynthesis of LDHs to be applied as redox mediators.

II. RESULTS AND DISCUSSION

Besides the single nanomaterials (MWCNTs and ERGO) three configurations were investigated, namely, a Composite obtained by mixing MWCNTs and ERGO and two bi-layers composed of the single components. In the former MWCNTs were deposited directly on the GC support with GO on the top (Bil-1), while the latter was obtained by swapping the order of the nanomaterials (Bil-2). The resulting modified electrodes were submitted to an electrochemical reduction treatment so that to convert GO to ERGO, i.e a green approach was followed to restore the conductivity. Then they were employed to perform the oxidation of CA and DA in aqueous solutions at different pHs to find out the configuration which allows for the maximum contact of the two nanomaterials so that to optimise the electron transfer process of the two analytes [6]. They were chosen since catechol was considered representative of polyphenols, a class of molecules that plays a key role in the defense against the dangerous effect of reactive oxygen and nitrogen radicals, and dopamine, which is a catecholamine, for its outstanding properties as neurotransmitter. When ERGO and MWCNTs were used as single components to modify GCE, the lowest currents were recorded which were of the same order of those displayed by bare GCE. Only slightly increased currents were observed when the nanomaterials were in the Bil-2 configuration, whereas the highest responses to CA and DA were obtained for Bil-1 and Composite configurations, both at pHs 4 and 7. In particular, these two configurations display a peak current which is about 3-4 times greater than the value recorded when the nanomaterials are casted alone on GCE or when the bare GCE is used. These results mean that MWCNTs and ERGO exhibit the stronger synergetic effect, due to the destacking of graphene sheets, when they are present in Bil-1 or Composite configurations. Since the modification of the electrode is easier and faster for the Composite than for Bil-1 and is even more reproducible, this configuration was further investigated to find out the best conditions for the determination of the two analytes. The choice was also supported from the consideration of a less extent of fouling effects at Composite, which always occur during phenols oxidation.

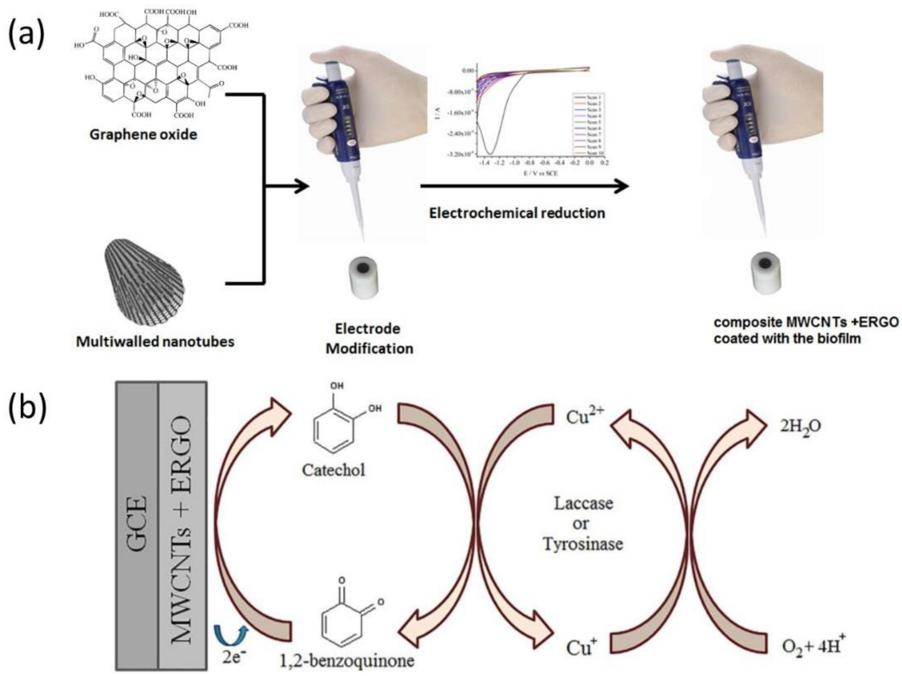

Figure 1 Preparation steps of the biosensors based on Tyr or Lac (a) and schematic of the reactions occurring within the biofilm and at the interface with the modified GCE (b).

Furthermore, Composite was also employed to develop biosensors based on laccase (Lac) or tyrosinase (Tyr) for total polyphenol determination in food samples [7]. The construction of biosensors or electrodes for biofuel cells working with redox enzymes requires a close contact between the active site of the enzyme and the surface of the electrode so that direct electron transfer (DET) can occur. The enzyme immobilization on the modified GCE was optimised employing different agents (bovine serum albumin and glutaraldehyde as crosslinking agent, chitosan, or Nafion). The conditions for the fabrication and the storage of the biosensors were established in order to obtain good enzyme retention, high sensitivities and long-life devices. A schematic of the biosensors fabrication is shown in Fig. 1. The DET occurrence was verified for both enzymes which had been drop casted on the GCE modified with the Composite. The biosensors were used for the determination of catechol and other polyphenols, i.e., pyrogallol, epicatechin, gallic acid, 1,2-dihydroxybenzoic acid, caffeic acid, chlorogenic acid, rutin, catechin and dopamine. Eventually, the biosensors reliability was demonstrated by estimating the total polyphenols concentration in juice samples, expressed as epicatechin equivalents.

Another interesting application of GCEs modified with carbon nanomaterials is the electrosynthesis of LDHs. This study, which is still in progress, was carried out to verify if the presence of hybrid systems based on ERGO and MWCNTs or of the single components can affect the deposition and the catalytic activity of Ni centres of a Ni/Al LDH employed to electrocatalyse the glucose oxidation. Preliminary results show that the electrosyntesis of the clay, which is well known to involve the increase of pH due to the cathodic reduction of nitrates, requires lower overvoltage than at the bare GCE and the Ni redox reaction occurs at less anodic potentials in the case of the two bilayers than in the case of the othe modified electrodes. These results are interesting not only for sensing of glucose but also in view of the development of more efficient and stable anodes for fuel cells. As to the electrocatalytic performance of the LDH towards the glucose oxidation, the results show that the highest activity was displayed by the electrode modified with the Composite.

III. REFERENCES

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