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Review article

Bio(Sensing) devices based on ferrocene–functionalized graphene and carbon nanotubes

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ABSTRACT

Both carbon nanotubes (CNTs) and graphene are important pillars in the ongoing efforts to devise new applications in nanotechnology. One of their most promising applications is building devices such as sensors and biosensors, which is important step for the development of personalized medical healthcare devices. Mediators are usually used and sought to modify the physicochemical properties of these materials. In this review, we highlight the importance of the functionalization of CNT and graphene derivatives with redox molecules taking ferrocene derivatives as a model molecule. The employed techniques during (bio)sensing measurements using various functionalization strategies are also described. In addition, we discuss various aspects related to the applications of ferrocene–modified CNTs and graphene in electrochemical sensors and biosensors with a focus on the explanation of both CNTs/graphene and ferrocene contributions in the catalytic systems, which in turn enhance the analytical performance of the (bio)sensing devices.

Contents

Abbreviations: ACN, Acetonitrile; AFM, Atomic force microscopy; CNPE, Carbon nanotube paste electrode; CNT, Carbon nanotube; CPE, Carbon paste electrode; CS, Chitosan; CV, Cyclic voltammetry; DMF, Dimethylformamide; DNA, Deoxyribonucleic acid; DPV, Differential pulse voltammetry; DWCNT, Double–walled carbon nanotube; EDX, Energy–dispersive X–ray spectroscopy; ET, Electron–transfer; Fc, Ferrocene; Fcmc, Ferrocene monocarboxylic acid; FDMA, Ferrocenyldimethylamine; FEPA, (4–ferrocenylethyne)phenylamine; FTIR, Fourier transform infrared spectroscopy; GCE, Glassy carbon electrode; GO, Graphene oxide; HB, hydrogen–bonding; HBTU, N,N,N′,N′-Tetramethyl-O-(1H-benzotriazol-1-yl)uronium hexafluorophosphate; LBL, Layer–by–layer; MWCNT, Multi–walled carbon nanotube; NIR, near infra–red spectroscopy; PBS, Phosphate–buffered saline; PEG, Poly(ethyleneglycol); PEI, Polyethylenimine; PGE, Pyrolytic graphite electrode; rGO, Reduced graphene oxide; SEM, Scanning electron microscopy; SCE, Saturated calomel electrode; SWCNT, Single–walled carbon nanotube; TEM, Transmission electron microscopy; TGA, Thermogravimetric analysis; UV–Vis, Ultraviolet–visible spectroscopy; XPS, X–ray photoelectron spectroscopy; XRD, X–ray diffraction.

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1. Introduction

In field of carbon–based nanomaterials, graphene is now the rising star [1] while before there were and still are of interest carbon nanotubes (CNTs) and fullerenes [2–5]. The discovery of each of the carbon forms provokes a lot of excitement among scientists. The fascination toward carbon allotropes is essentially due to their unique physicochemical features such as their high electronic and thermal transport proprieties, thermal stabilities, etc. [6–11]. Also, economical considerations are equally important; their raw carbon material is the most abundant and cheapest element in Earth. So far, many chemical and physical methods have been devised to prepare single–walled carbon nanotubes (SWCNTs), multi–walled carbon nanotubes (MWCNTs), pristine graphene (G), graphene oxide (GO), reduced graphene oxide (rGO), and others derived materials and are well documented in many recent reviews [12–16].

CNTs and graphene are quite similar in many of their facets but different in some others. Both turn up to be attractive for many applications such as chemical sensors and especially in electrochemical biosensing [17,18]. They have also shown excellent performance in biofuel cells and polymer electrolyte membrane fuel cells [19], and in wide–range of electrical applications, for example in microelectronics [20], supercapacitors [21], solar cells [22], etc. The interest that initially has surrounded CNTs, however looks like it will be dwarfed by a swelled interest into graphene.

Nonetheless, there still is a huge contrast between the promising potential and the reality of using CNTs and graphene in practical applications on a large scale. The strong Van der Waals interactions among pristine carbon–based materials result in their bundling and aggregation, preventing their solubility in most of the organic and inorganic solvents. Therefore, in view of facilitating their solubility and their manipulation, many methods have been developed that can be divided into two categories, *i.e.*, (i) covalent and (ii) non–covalent functionalization [23,24]. These methods lead to functional materials with properties different from and sometimes even superior to the original products. For instance, chemical modification transforms an intrinsic zero band gap energy graphene into a semiconductor by opening up the band gap, thus enhancing the potential practical applications in electronics [25]. In this context, the functionalization of CNTs or graphene with redox molecules appears as an original approach to produce hybrid materials for various sensing and biomedical applications using electrochemical methods to monitor the recognition events.

One of the most promising applications is the use of graphene and CNTs to build biosensors for *in–vivo* usage since these carbon–derived materials has almost no toxicity [26]. Electrochemical biosensors proved to be highly sensitive, easily designable, cost–effective and can be readily miniaturized. Organometallics such as cobaltocene and nikelocene [27], organic based redox–active compounds such as tetrathiafulvalene derivatives [28], porphyrins [29] and phthalocyanines [30] and even some organic dyes such as methylene blue [31] have been used to tune the electronic and optoelectronic structure and transport properties of carbon nanomaterials. Still, ferrocene is one of the most exploited organometallic molecule in the development of electrochemical sensor devices owing to its well behaved and known redox chemistry. The attractive electrochemical characteristics exhibited by ferrocene *i.e.* fast electron–transfer rate, low oxidation potential and stability of two redox states [32] make it and its derivatives well–known substances as mediators [33]. And thus, the ferrocenyl moiety is usually used as a model redox molecule to characterize the effectiveness of the carbon nanomaterials modification as it has both chemical and electrochemical stability.

In this review, the goal is to highlight the importance of the functionalization of CNTs and graphene derivatives with redox molecule; we choose ferrocene as a model molecule because of its widespread use in literature. Firstly, we will discuss the covalent and non–covalent functionalization, which are used to introduce ferrocene. We will focus on the description of the techniques used for evidencing of each kind of functionalization. Then, incorporation of ferrocene derivatives in CNTs or graphene composites will be discussed. The application of modified CNTs and graphene in electrochemical sensors and biosensors will be highlighted, with an emphasis on some of the more significant examples, rather than trying to comprehensively cover all the work performed in this exciting field. The review also excludes works dealing with the use of ferrocene derivatives as labels where they are directly linked to biological species.