Electrochimica Acta 188 (2016) 574–581

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Novel carbon black-cobalt phthalocyanine nanocomposite as sensing platform to detect organophosphorus pollutants at screen-printed electrode

S. Cinti[a,b], D. Neagu[a,b], M. Carbone[a,b], I. Cacciotti[c,d], D. Moscone[a,b], F. Arduini[a,b,*]

[a] Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via della Ricerca Scientifica, 00133 Rome, Italy
[b] Consorzio Interuniversitario Biostrutture e Biosistemi "INBB", Viale Medaglie d'Oro, 305, Rome, Italy
[c] Università degli Studi di Roma "Niccolò Cusano", Via Don Carlo Gnocchi 3, 00166 Rome, Italy
[d] Consorzio Interuniversitario Nazionale Per La Scienza E Tecnologia Dei Materiali (INSTM), Italy

ARTICLE INFO

Article history:
Received 27 July 2015
Received in revised form 11 November 2015
Accepted 12 November 2015
Available online 1 December 2015

Keywords:
Biosensor
Hybrid Nanocomposite
Carbon Black
Cobalt Phthalocyanine
Organophosphorus pesticide

ABSTRACT

A facile "one-step" route to produce a homogenous and highly stable cobalt phthalocyanine (CoPc)-based dispersion by using carbon black (CB) as supporting material is reported. Herein, CB is proposed as effective material to load CoPc in order to obtain a CB/CoPc hybrid nanocomposite dispersion suitable for modifying screen-printed electrodes (SPEs) by an easy and automatable drop casting approach. CoPc resulted anchored to CB by a non-covalent physisorption, confirmed by IR and UV-visible spectroscopies, allowing to preserve the electrochemical performances of CoPc. The resulting CB/CoPc-modified SPE was tested as sensing tool to detect thiocholine, an enzymatic product of butyrylcholinesterase (BChE). The use of CB/CoPc leads to a highly sensitive thiocholine detection by applying a low potential (+0.05 V vs. internal reference) without fouling problem, a typical drawback that affects the thiol electrochemical detection. The favorable characteristics of the sensor were exploited for an easy BChE biosensor fabrication that renders this biosensor well suitable for mass-production. This electrochemical monoenzymatic biosensor was then challenged towards paraoxon, chosen as model organophosphorous pesticide, obtaining a low detection limit (18 nM). The suitability of the biosensor was tested in a waste water sample obtaining satisfactory recovery values, thus demonstrating its capability in such complex matrix.

1. Introduction

Carbon black (CB) appears as a fluffy fine powder with a large surface area. It is an industrially manufactured colloidal material that consists of approximately spherical elemental carbon particles with diameter comprised from 15 to 100 nm, which typically forms aggregates with sizes below a micrometer [1]. It is a nanomaterial used in a wide range of applications, e.g. tyre industry, batteries, fuel cells [2–4]. Lately, thanks to its electrically conductive properties and capability to electrocatalyze many oxidation/reduction processes, CB is increasingly emerging over the electroanalytical field [5,6]. Yet, unlike traditional electrochemical cells and bulky electrodes, the increasing demand of miniaturized and low cost devices is strongly focused towards screen-printing fabrication technique, which allows for obtaining electrodes printable on a large variety of materials, e.g. plastic, paper, gloves, skin, etc [7–9]. A wide variety of conductive inks as well as gold, silver, platinum, graphite, are frequently used. Particularly, graphite-based screen-printed electrodes (SPEs) exhibit a powerful suitability to be tailored with diverse (nano) materials, due to their resistance to a wide range of solvents, low background current, and broad potential windows of application. Our group was among the first ones to highlight the excellent electrocatalytic abilities of CB modified SPEs toward the determination of several clinically and environmentally-relevant compounds [5,10–12].

Nowadays, in the (bio) sensor field there is a rush to develop new catalysts exploiting the exceptional electronic properties of nanomaterials, that appear chemically and physically different from their bulk versions. A matter of example is well represented by metallic nanoparticles or carbon allotropes (graphene, carbon nanotubes) [13,14].

However, in addition to the fabrication of new materials with novel sensing properties, it is important to find solutions that allow a quick and cost-effective mass production of electrochemical

* Corresponding author. Tel.: +39 0672594404; fax: +39 0672594328.
E-mail address: fabiana.arduini@uniroma2.it (F. Arduini).

http://dx.doi.org/10.1016/j.electacta.2015.11.069
0013-4686/

platforms: CB certainly satisfies these requirements, being characterized by a low price (around 1 euro/kg), an easy procedure to obtain stable and homogeneous dispersions, and the feasibility to modify SPEs. Among the carbon nanomaterials, CB is widely adopted with satisfactory results, as also reported by the research group headed by Compton, who highlighted the improvements due to the direct application of CB on the electrode surface [15]. Recently, Vicentini et al. reported on the utilization of three different CB types as glassy-carbon electrode modifiers, showing significant improvements in the electrochemical performances compared to bare and edge-plane pyrolytic graphite electrodes [6]. As evidenced by our group, modification of SPEs by using CB dispersed in a dimethylformamide (DMF):water mixture appears to be a very simple and effective method to achieve fully automatable and cost-efficient procedure [5]. In particular, CB dispersions in aqueous mixtures of DMF are characterized by a long-term stability (more than one month) and allow the modifications of SPEs without the risk of removing conductive polymer-based inks and damaging the substrate (usually flexible polyester sheets), imparting to the electrodes great electrocatalytic properties comparable to reduced graphene oxide and nanotubes (CNTs) [12]. These latter are characterized by long fabrication/purification procedures and issues related to the obtainment of homogeneous and stable dispersion. Besides its strong sensing features, due to its large surface area, and the high number of defect site [10], CB also finds applications as an excellent supporting material capable of highly loading and dispersing different materials such as metallic nanoparticles or electrochemical mediators. Recently, we have demonstrated the suitability to modify SPEs with a film of CB covered by a layer of gold nanoparticles (AuNPs) for the determination of arsenic (III) [16], or by a thionine layer to detect bisphenol A [17]. The presence of a CB under-layer allowed a better dispersion and a more homogeneous deposition of the sensing and electrocatalytically active materials on the electrode surface, enabling a large electronic network between the adsorbed catalyst (i.e. AuNPs, thionine) and the electrode surface [16,17].

Herein, we chose to employ a different route to take advantage of the excellent adsorbing and dispersing properties related to CB: a "one-step" approach to obtain a stable dispersion of CB and cobalt phthalocyanine (CoPc), namely CB/CoPc, was adopted. It is well-established that CoPc represents an excellent electrochemical mediator that allows the determination of numerous high-interest (bio) chemical compounds [18]. However, its low solubility in aqueous mixture limits its application towards printed electrodes. To overcome this issue, the most employed method involves the introduction of the CoPc powder directly in the conductive ink as reported by Hart's group [19]. Yet, the use of bulk-approach often presents same drawbacks related to the amount of catalyst to produce an effective homogeneous ink. Relating to bulk-modified SPEs, as recently claimed by Banks' group [20], a typical issue during the fabrication approach could be represented by the amount of electrocatalyst (CoPc) which cannot be easily altered. Instead, drop casting SPEs with a CoPc nanoformulation allows to tailor sensor properties depending on the needs. In addition, in the case of the bulk modified CoPc, only the surface layer is accessible to the solution and hence the rest of the electrode containing the bulk of the incorporated CoPc is likely not wired electrically as reported by Banks' group [20].The powerful advantage of the proposed approach consists in the ease-to-custom dispersion in order to achieve the optimal analytical response. In addition, variable reproducibility can be readily enhanced by coupling these nanoformulations with automated dispensing systems, e.g. Biodot® (www.biodot.com).

A large number of papers have been reported in literature with the attempt to quickly and effectively modify electrodes with hybrid carbonaceous nanomaterial-CoPc dispersions to detect pesticides. Several approaches have been described using single-walled carbon nanotubes (SWCNTs) [21], derivatized SWCNTs [22], nitrogen-doped graphene [23]. However, even if these carbonaceous-based composites evinced satisfactory analytical properties, often their production requires long and costly synthesis procedures. Printed technology applied to the analytical field is aimed at the improvement of diagnostic devices for the easy monitoring of health and environmental pollution. Particularly in the case of developing countries, as proposed by the World Health Organization (WHO), these devices should meet the ASSURED (Affordable, Sensitive, Specific, User-friendly, Rapid and robust, Equipment free and Deliverable to end-users) criteria [24]. The chance to employ cost-effective raw materials coupled to unnecessary treatments (oxidation, reduction, derivatization) represents a big deal. Employing CB, instead of the more expensive graphene or CNTs, seems to provide advantages as recently shown by Paczosa-Bator et al. [25]. They reported on a significantly decrease of the membrane resistance, contributing to a substantial improvement in the reproducibility of a solid-contact ion-selective electrode toward potassium and nitrate ion detection, highlighting the role of CB as a supporting material for platinum nanoparticles.

In this work, CoPc has been effectively supported onto CB by producing a stable dispersion through a single step approach. The optimized DMF:water mixture allowed to modify printed electrodes without any negative effect on electrochemical response due to the partial conductive-ink dissolution. The resulting SPE modified with hybrid nanocomposite CB/CoPc was tested towards thiocholine, the enzymatic product of butyrylcholinesterase (BChE), using butyrylthiocholine as substrate. Successively, the relevant electrochemical properties obtained in the thiocholine detection were exploited for BChE biosensor construction. Hence, BChE was immobilised onto CB/CoPc-SPE, and this inhibitive biosensor was challenged towards the organophosphorus pesticide paraoxon.

2. Experimental

2.1. Equipments

Cyclic voltammetry (CV) was performed using an Autolab electrochemical system (Eco Chemie, The Netherlands) equipped with PGSTAT-12 and GPES software (Eco Chemie, The Netherlands). Amperometric measurements were carried out using a portable potentiostat PalmSens (Palm Instruments, The Netherlands). In order to reduce electrical noise during measurements, sometimes due to poorly diligent connection, i.e crocodile clips [26], SPEs were connected to potentiostat by using in-house edge connector (Fig. S1, Supporting Information). UV–vis measurements were obtained using a spectrophotometer UV 1800 (Shimadzu, Japan). The FTIR absorption spectra were recorded on a Shimadzu Prestige 21 spectrophotometer using KBr pellets. The UV–vis reflectance spectra were recorded on a Perkin-Elmer 950 spectrophotometer.

2.2. Reagents

All chemicals from commercial sources were of analytical grade. Butyrylcholinesterase (BChE) from equine serum, butyrylthiocholine chloride, glutaraldehyde (GA), bovine serum albumin (BSA), paraoxon ethyl, Nafion 5% (v/v) were purchased from Sigma Chemical Company (USA). Carbon Black (CB) N220 was obtained from Cabot Corporation (Italy) and cobalt phthalocyanine was purchased from Fluka (USA). CB N220 showed carbon nanoparticle aggregates having diameters comprised between 17.95 and 32.5 nm, in accordance with the manufacturer's diameter (19–29 nm) [10].