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Synergy between Printex nano-carbons and silver nanoparticles for sensitive estimation of antioxidant activity

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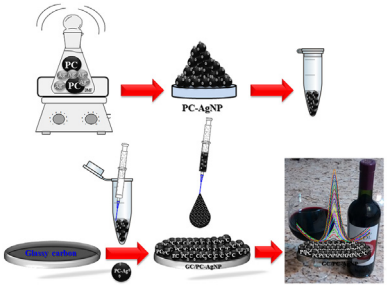
HIGHLIGHTS

- We highlight the use of Printex L6 nano-carbon as a much cheaper alternative to carbon nanotubes and graphene.
- The hybrid nanomaterial was completely characterized by MET, EDX, SAED, DRX, RAMAN and cyclic voltammetry.
- The silver nanoparticles (size range 1-2 nm) were prepared directly onto the surface of the Printex 6L Carbon "nanocarbon".
- An ultrathin film PC-AgNP nano-structured showed a synergetic effect between PC nanocarbons and AgNP.
- Sensitive estimation of antioxidants at a low applied potential (91 mV vs. Ag/AgCl) and low detection limit (63.3 nmol L^{-1}).

GRAPHICAL ABSTRACT



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ABSTRACT

We report on the synthesis, characterization and applications of a Printex L6 carbon-silver hybrid nanomaterial (PC-Ag), which was obtained using a polyol method. In addition, we also highlight the use of Printex L6 nano-carbon as a much cheaper alternative to the use of carbon nanotubes and graphene. The silver nanoparticles (AgNP) were prepared directly on the surface of the Printex 6L carbon "nano-carbon" material using ethylene glycol as the reducing agent. The hybrid nanomaterial was characterized by High-angle annular dark-field transmission electron microscopy (HAADF-TEM), energy−dispersive X-ray spectroscopy (EDX), selected area electron diffraction (SAED), Raman spectroscopy and cyclic voltammetry. Optimized electrocatalytic activity on glassy carbon electrode was reached for the architecture GC/PC-Ag, the silver nanoparticles with size ranging between 1 and 2 nm were well −distributed throughout the hybrid material. The synergy between PC nano-carbons and AgNPs was verified by detection of gallic acid (GA) at a low applied potential (0.091 V vs. Ag/AgCl). GA detection was performed in a concentration range between 5.0×10^{-7} and 8.5×10^{-6} mol L^{-1}, with a detection limit of 6.63×10^{-8} mol L^{-1} (66.3 nmol L^{-1}), which is considerably lower than similar devices. The approach for

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fabricating the reproducible GC/PC-Ag electrodes is entirely generic and may be explored for other types of (bio)sensors and devices.

1. Introduction

The development of analytical methodologies for the detection and quantification of polyphenolic compounds, especially those naturally present in foods, has become a subject of great interest because such organic molecules have biological properties associated with human health, including antiinflammatory, antihistaminic, and antitumor activities, together with the ability to scavenge free radicals [1]. These antioxidant polyphenolic compounds are able to alleviate several diseases associated with oxidative stress, including cardiovascular and neurodegenerative disorders [1,2]. Gallic acid (GA), or 3,4,5-tri-hydroxybenzoic acid, is a major source of dietary antioxidants and is one of the main phenolic compounds found in grapes, black tea, several plants and humic substances [1]. The presence of one or several phenolic groups is responsible for the antioxidant activity of GA, which is capable of reducing the toxic effects of reactive oxygen species and radical compounds [2].

The development of sensitive and robust methods for GA determination is important due to the positive effects of phenolic antioxidants on human health [1]. The "determination of total phenols" is complicated because of their chemical complexity and difficulties in the extraction process, as well as in dealing with food sample matrices [1]. A good indication of the level of antioxidants present in any sample [3] can be obtained in an indirect manner by the estimation of "total polyphenols" using spectrophotometric protocols (Folin-Ciocalteu method) based on the reaction of phenolics with a colorimetric reactant, thereby allowing their measurement in the visible region of the spectrum [4].

The analytical performance for GA determination, including sensitivity and selectivity, can be obtained using methodologies such as liquid and gas chromatography; however, these analyses cannot be easily performed on a routine basis due to constraints and cost [2]. Alternatively, electrochemical sensors can be a suitable alternative for rapid, reliable and cost–effective in-situ analysis. A wide variety of electrode materials, including nanostructured materials, can be used to improve the sensitivity, selectivity, stability of GA detection [5–7] and allow for the possibility of discrimination between different compounds or polyphenol classes [2]. Among them, carbon nanotubes (CNT) and graphene (GO) have paved the way for new and improved sensing devices, owing to their good mechanical, chemical and electrical properties, [6–9]. In contrast, the bright prospects for the use of CNT, GO and fullerenes are overshadowed by their prohibitively high production costs and issues with purity [10].

As an alternative to the nanostructured carbon materials previously mentioned, the Arduini and Compton groups [2,11,12] have demonstrated the successful use of carbon black (CB) for several electrochemical sensors. In order to identify carbon materials with improved electroanalytical performance, the Compton group reported the advantageous use of carbon black as a much cheaper alternative to carbon nanotubes as a sensor for nicotine determination [12]. In this regard, Santos and co-workers [15] recently reported a comparative study between carbon black and Printex L6 carbon (PC) for the electrogeneration of hydrogen peroxide, with the better results being obtained for PC. In the same study, the authors summarized the main properties of the PC. As they related, PC is a commercial carbon material and can be defined as an alkaline pigment of furnace type with excellent physical, chemical and electrochemical properties [15]. It presents the Brunauer-Emmett-Teller (BET) surface of 265 $m^2\ g^{-1}$, a density of 1.8 g cm^{-3} and primary use in organic degradation, where PC was used for the degradation of phenols [16] and hexane [17], for catechol oxidation and for removing organic pollutants from secondary effluents [18,19]. PC has been extensively investigated by the Lanza group for the electrochemical generation of hydrogen peroxide in alkaline aqueous solution, oxygen reduction to hydrogen peroxide, electro-fenton degradation of the food dye amaranth and electrogeneration of hydrogen peroxide in acid medium using PCs with Fe_3O_4 nanoparticles, cobalt(II) and manganese(II) phthalocyanines [20–24]. The main differences between PC and other carbonaceous materials (carbon nanotubes and graphene) include: i) a better heterogeneous electron transfer constant in the presence of a ferricyanide redox mediator; ii) an improvement in terms of reduced overpotential and/or low background current for several analytes; iii) more uniform coverage of the working electrode than CNT and GO, which display cluster structures, influencing direct under sensitivity [13,14].

A wide variety of nanomaterials, especially metal nanostructures with different properties, have found broad application in several analytical methods [25]. Carbonaceous materials decorated with transition metal nanoparticles including gold, nickel, antimony, copper, platinum, bismuth and silver [7,10,26–32] have been used to increase the activity of sensors electrochemicals. In the case of electrochemical sensors, the modification of electrode surfaces using AgNPs has received wide-spread attention mainly due to their interesting electrocatalytic properties [2,7,9]. In this work, we report a study focusing on the synthesis, characterization and application of a novel nanocomposite based on AgNPs supported directly on PC. This novel hybrid nanomaterial yielded excellent sensitivity for GA electro-oxidation, as well as a high synergetic effect, good analytical performance and a low detection limit. The sensor developed with the hybrid PC-Ag nanomaterial is shown to be promising for fast, simple and sensitive determination of GA and can be used for the estimation of total polyphenols in wine samples.

2. Experimental section

2.1. Reagents and solutions

All chemicals were of analytical grade and were used without further purification. Silver nitrate (99% purity) was obtained from Merck (Darmstadt, Germany). Gallic acid and dimethylformamide (DMF) were obtained from Sigma–Aldrich (St. Louis, MO, USA) and ethylene glycol was obtained from Carlo Erba (France). 4-aminoantipyrine (AAP) was purchased from Sigma–Aldrich (St. Louis, MO, USA); potassium hexacyanoferrate(III) ($K_3[Fe(CN)_6]$) was purchased from J. T. Baker (Center Valley, PA, USA); anhydrous sodium tetraborate was purchased from Nuclear (Brazil); boric acid was purchased from Synth (Brazil); sodium hydroxide was purchased from Merck (Brazil). The PC was purchased from Degussa (Essen, North Rhine-Westphalia, Germany). High purity nanopure water (resistance, 18 >MΩ cm^{-1}) was obtained from a Nanopure Ultrapurification System (Barnstead Inc., Waltham, MA, USA). The 0.1 mol L^{-1} phosphate buffer solution (pH 7.0) was home prepared