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Simultaneous determination of isoproterenol, acetaminophen, folic acid, propranolol and caffeine using a sensor platform based on carbon black, graphene oxide, copper nanoparticles and PEDOT:PSS

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ABSTRACT

We explored the use of carbon black (CB), graphene oxide (GO), copper nanoparticles (CuNPs) and poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) as electrode materials for the simultaneous determination of isoproterenol, acetaminophen, folic acid, propranolol and caffeine. The designed nanostructured surface was widely characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), contact angle measurements and electrochemistry. From electrochemical characterization assays carried out towards the potassium ferricyanide redox probe, fast electron transfer kinetics and a considerably higher electroactive surface area were observed for the modified electrodic surface based on CB, GO, CuNPs and PEDOT:PSS film. Using square-wave voltammetry (SWV), well defined and resolved anodic peaks were detected for isoproterenol, acetaminophen, folic acid, propranolol and caffeine, with peak-to-peak potential separation not less than 170 mV. Then, the SWV technique was explored for the simultaneous determination of quinary mixtures of these analytes, resulting in analytical curves with linear ranges and limits of detection at micromolar concentration levels. The practical viability of the proposed voltammetric sensor was illustrated in the analysis of human body fluid samples. The proposed sensor showed good repeatability and a successful application using urine and serum matrices, with recoveries close to 100%.

1. Introduction

The junction of electrochemical techniques and nanomaterials for the creation of novel electroanalytical methods is a combination that has previously worked in and still is a current trend in analytical chemistry. In particular, a significant number of scientific contributions have been reported on the use of carbon-based nanomaterials. Actually, the sprayed use of carbon nanomaterials for electrochemical and electroanalytical purposes is linked to the reality that carbon nanostructures are undoubtedly one of the most researched topics in materials science [1]. Major representatives of carbon nanomaterials are carbon nanotubes and graphene. The latter is a carbon nanomaterial composed of sp^2 hybridized carbon atoms in two-dimensional layers [2] and presents variable and excellent thermal, electrical and optical properties, in addition to its versatile chemistry, and it is suitable to chemical and biochemical functionalization [3].

Graphene electrochemistry is relatively well established, and uses of graphene cover different areas of electrochemistry, including development of (bio)fuel cells [4,5], supercapacitors [6], sensors and biosensors [7,8]. Graphene oxide comes from graphene sheets that were subjected to an oxidative functionalization process resulting in a hydrophilic nanomaterial. Some potentialities of graphene oxide as a sensitive electrodic surface, as well as a nanocarbon matrix for immobilization of biological recognition species in the design of biosensors, were recently divulged [9–11].

There are few works exploring the electrochemical features and electroanalytical performance of carbon electrodes based on the combination of different carbon allotropic forms. However, this is an interesting and exciting idea, as a synergistic effect may be achieved from the combination of physical and chemical features. Our research group has reported on the excellent electrochemical performance of vertically aligned carbon nanotubes and graphene oxide composites [12,13] as well as high surface area carbon nanotubes and diamond-like carbon hybrid electrodes [14,15]. In other works, it was demonstrated that a synergistic effect could be provided from the combined use of carbon nanotubes and graphene sheets for the electrochemical sensing of targets such as acetaminophen [16], tetracycline [17] and glucose [18]. Carbon black is another carbon nanomaterial with recent enthusiastically reported electrochemical capabilities, and it has become a relevant option for combination with different carbonaceous

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nanostructures in order to obtain high performance electroanalytical sensors.

Carbon black is a very low-cost carbon nanomaterial composed of amorphous and quasi-graphitic primary nanoparticles (average diameter between 3.0 and 100 nm), which form nanostructured aggregates [19]. Among its physical and chemical properties, highlights include its typically high surface area (up to 1000 m^2 g^{-1}) and good electrical conductivity [20,21]. In electrochemistry, this carbon nanomaterial is traditionally used as a carbon support for metallic nanocatalysts, for example, as an electrodic material for direct electrooxidation of alcohols [22,23] and oxygen reduction reactions [24,25]. Further, the use of carbon black as the working electrode itself has been shown to be an excellent strategy in the design of electrochemical sensors and biosensors [19,26]. The combined use of graphene and carbon black as electrode modifiers in the scenario of analytical electrochemistry has been reported by Lu et al. [27], for the determination of rutin.

As mentioned, graphene oxide and carbon black have been successfully explored as electrode modifiers and supports for metallic nanostructures. One kind of metallic nanostructure frequently explored for analytical purposes is copper nanoparticles (CuNPs). CuNPs can be chemically synthesized or electrochemically deposited on a carbon substrate, and their use for electrochemical sensing purposes has been classically addressed in the non-enzymatic sensing of biomolecules, mainly glucose [28]. However, the electroanalytical potentialities of CuNPs can be broader and should be explored, as CuNPs can provide a high conductivity surface and a high surface area nanostructured interface.

For effective immobilization of these materials on electrode surface, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) has been employed. This is a conducting polymer made up of a combination of two ionophore compounds, poly(3,4-ethylenedioxythiophene) (PEDOT) and poly(4-styrene sulfonate) (PSS). The PEDOT:PSS reagent has good compatibility with metallic nanoparticles, polymers and carbonaceous materials (graphene and carbon nanotubes), and has been used with success in the development of electrochemical sensors [29,30]. Among the advantages of PEDOT:PSS nanomaterials are good stability, homogeneity and high conductivity during electrochemical experiments. The synergistic effect of PEDOT:PSS with carbon material has been reported recently in the literature [29–32].

Isoproterenol is a medication used for the treatment of bradycardia, allergic emergencies, cardiac shock, and heart attack. An excess of the drug can cause heart failure and arrhythmias [33,34]. Acetaminophen (paracetamol) is a drug utilized to alleviate pain (muscular, headache, backache, and toothache) and coughing, and to reduce fevers. However, overdose and chronic use of acetaminophen can cause liver and kidney damage [35,36]. Folic acid (vitamin B9) is a water-soluble compound that can act as a coenzyme in the transfer and utilization of carbon groups and in the regeneration of methionine from homocysteine. Deficiency of the vitamin causes anemia and increases the likelihood of heart attack and stroke [37,38]. Propranolol is a β-adrenergic blocking drug indicated for the treatment of hypertension and the prevention of myocardial infarction, angina, and cardiac arrhythmias [39,40]. Overdose of this drug can cause bradycardia (decreased heart rate), hypotension (decreased blood pressure), bronchospasm (contraction of the lungs), and acute heart failure. Caffeine is a natural alkaloid widely used as a nervous stimulant and to increase alertness. However, in excess it can reduce fine motor coordination and cause dizziness, tremor, nausea, insomnia, headaches, nervousness, and seizures. It is used in analgesic formulations in combination with non-steroidal anti-inflammatory drugs [41,42]. The compounds considered in this work can be consumed simultaneously by a patient, since they belong to different drug classes. Their consumption depends on the type of treatment required, so one or more drugs may be administered together [43–45]. Therefore, for monitoring purposes, it is highly desirable to be able to simultaneously determine these analytes in different matrices.

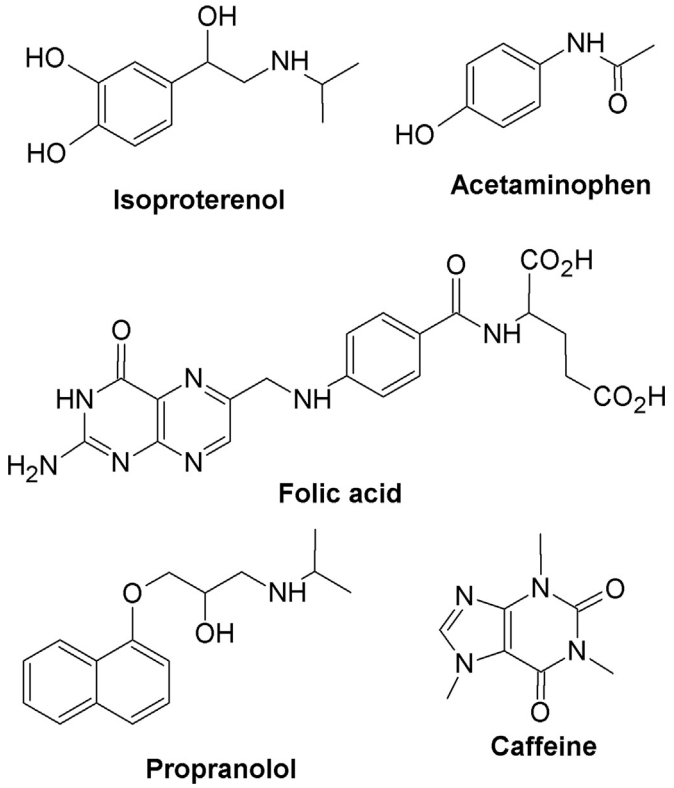

Fig. 1. Chemical structures of determined analytes.

In this work, we use carbon black, graphene oxide, copper nanoparticles and PEDOT:PSS as an electrode material for the simultaneous determination of isoproterenol, acetaminophen, folic acid, propranolol and caffeine (see chemical structures in Fig. 1). To the best of our knowledge, this is the first work reporting an electrochemical method dedicated to the simultaneous determination of these five analytes.

2. Experimental

2.1. Chemicals, solutions and samples

Standards of isoproterenol, acetaminophen, folic acid, propranolol and caffeine were purchased from Sigma-Aldrich. The conducting polymer PEDOT:PSS employed in the working electrode modification procedures was also obtained from Sigma-Aldrich. All additional reagents used in this work were of analytical grade. Graphene powder was acquired from Graphene Supermarket and carbon black (CB) VXC72R powder was kindly supplied by Cabot Corporation. The aqueous solutions were prepared using ultrapure water supplied by a Millipore Milli-Q Direct-0.3 purification system. All analyte stock solutions were prepared at a concentration level of 1.0×10^{-2} mol L^{-1}. The folic acid stock solution was prepared using 0.1 mol L^{-1} NaOH, and isoproterenol, propranolol, acetaminophen and caffeine stock solutions were prepared directly in ultrapure water.

Two synthetic human body fluid (urine and human serum) samples were analyzed. The synthetic urine sample was prepared in a 25 mL volumetric flask using the following reagents and concentrations: 2.0×10^{-2} mol L^{-1} KCl, 4.9×10^{-2} mol L^{-1} NaCl, 1.5×10^{-2} mol L^{-1} KH_2PO_4, 1.0×10^{-2} mol L^{-1} $CaCl_2$, 1.8×10^{-2} mol L^{-1} NH_4Cl and 1.8×10^{-2} mol L^{-1} urea. The flask volume was completed with ultrapure water [46,47]. The synthetic serum sample was also prepared in a 25 mL volumetric flask using the following reagents and concentrations: 4.0×10^{-6} mol L^{-1} methionine, 2.0×10^{-3} mol L^{-1} NaCl, 2.0×10^{-4} mol L^{-1} $NaHCO_3$, 1.3×10^{-6} mol L^{-1} cysteine, 3.5×10^{-6} mol L^{-1} glycine, 2.1×10^{-6} mol L^{-1} tryptophan,