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EDITORIAL

Sustainable and economical platforms for electrochemical (bio)chemical sensing based on micro- and nanotechnologies

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The sustainable development goals are a universal call aiming at balanced social, economic, and environmental sustainability. Within these goals, the responsible consumption and production of innovative devices that improve quality of life are chased. Electrochemical sensors can provide fast in situ monitoring of target species in samples of clinical, environmental, food, forensic, and industrial interests. Micro- and nanomaterials have demonstrated to be essential in the development of selective and sensitive sensing devices able to operate in real-world scenarios. Nevertheless, the sustainable production of sensing devices requires novel strategies and materials in the framework of a circular economy. Economical platforms that ally sustainability and accessibility play a key role in the evolution of innovative sensing devices for developing countries. In this context, some successful examples have been demonstrated, e.g., paper-based analytical devices, which open up new directions in this field.

The Topical Collection "Sustainable and economical platforms for electrochemical (bio)chemical sensing based on micro and nanotechnologies" shows the latest advances regarding the development of economical and sustainable sensing devices employing novel materials and fabrication strategies. Moreover, a wide range of applications are demonstrated which confirms the potential of electrochemical sensors in the real-world scenario, with the aid of micro- and/or nanomaterials. All the articles can be accessed via this link: https://link.springer.com/collections/aebhdffffi.

Two review articles were published in this Topical Collection. The first one by Pradela-Filho and coauthors is entitled "Paper-based analytical devices for point-of-need applications" which focuses on fundamental parameters to engineer paper-based analytical sensors employing colorimetric, fluorescence, and electrochemical detection systems. The combination of optical and electrochemical detection systems on paper devices is highlighted. Moreover, instrument-free distance-based detection using paper devices is presented as an alternative for resource-limited regions. The second review article by Ataíde and collaborators is also related to paper-based analytical devices; however, it outlines the recent advances on electrochemical paper-based biosensors for the diagnosis of viral diseases. The COVID-19 pandemic has demonstrated the need for portable, reliable, low-cost, and decentralized diagnostic assays for virus detection and electrochemical paper-based biosensors can fulfill this task successfully. This review is not only focused on COVID-19 virus but also on Dengue, Zika, Hepatitis, Ebola, AIDS, and Influenza viruses, that can be found in developing countries.

In the context of paper-based analytical devices, Oliveira and co-authors reported a simple strategy to produce an electrochemical paper-based sensor using graphite powder, polyester resin, and acetone. The fabricated conductive ink is deposited over vegetal paper by stencil printing. This disposable sensor was applied for paracetamol sensing in pharmaceutical tablets and blood collected from a healthy volunteer in order to perform a pharmacokinetic analysis. The greenness profile of the proposed paper-based sensor was 0.85, which was much improved in comparison with the HPLC method (0.59). Values close to 1.0 are the ideal considering the 12 principles of green analytical chemistry. This protocol of greenness evaluation of analytical methods is a suitable tool to compare methods regarding sustainability.

Another protocol to produce electrochemical paper-based sensors is based on pencil drawing. The hand pencil-drawing process to transfer graphite layers to a paper substrate is likely less reproducible than screen or stencil printing of conductive inks; however, it is much cheaper and does not require conductive inks that can be expensive. Moraes and co-authors proposed the use of a biodegradable 3D-printable resin to replace paper as substrate for pencil-drawn electrodes. Stereolithography masks were placed over

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3D-printed substrates to enable pencil drawing and the fabrication reproducibility was improved as verified by measuring the conductivity of the electrodes. Additional advantages compared to paper devices include higher mechanical stability and hydrophobicity that increases electrode lifetime.

Although less explored, graphite sheets are also a low-cost, flexible, and sustainable source of conductive substrates to develop electrochemical sensors. Pereira and collaborators reported an electrochemical sensor for antibiotic detection using graphite sheets that were treated by a plasma of CO_2. The plasma surface treatment improved the electrochemical activity of the electrodes by inserting oxygenated functional groups. The treated electrodes were applied for the voltammetric determination of chloramphenicol, ciprofloxacin, and sulfanilamide in water and urine samples, reaching sub-micromolar detection limits.

The reuse of recycled materials to develop new devices is a relevant contribution to the circular economy and sustainability. Silva and co-authors proposed the obtaining of reduced graphene oxide films from Zn–C battery waste and their application for the detection of paracetamol and hydroquinone in urine and tap water samples. The graphite electrodes found in discharged batteries were submitted to an adapted version of Hummer's method to provide reduced graphene oxide layers. The obtained electrochemical performance toward the detection of paracetamol and hydroquinone was like previous works using commercially available graphite or graphene materials.

Some articles of this Topical Collection reported on the use of commercial screen-printed electrodes to develop new biosensors and others described new conductive inks for screen-printed electrodes.

For instance, Ficek and co-authors reported a novel conductive ink for screen printing which contains boron-doped diamond (BDD) nanosheets. The authors demonstrated that the screen-printed BDD electrodes can be used for impedimetric sensing applications. Another innovative approach was reported by Khanaaekwichaporn and coauthors who screen printed carbon electrodes on a glove which was next modified by copper nanoparticles and then applied for the wearable sensing of paraquat residues in fruit, vegetables, and milk. Fast square-wave voltammetry revealed two unequivocal reduction peaks for paraquat identification and quantification.

A more recent strategy to produce bespoke electrodes for sensing is based on the 3D printing technology, especially using the fused deposition modeling (FDM) technique that employs molten polymeric filaments. Biopolymers, such as polylactic acid (PLA), are available for FDM 3D printing that brings sustainability to the fabrication process. Moreover, 3D printing is an additive manufacturing process that generates minimal waste (close to "zero waste"). Affordability, scalability, and reproducibility are some extra advantages. The development of novel conductive filaments is demanded in the field, and this Topical Collection shows the work by Stefano and co-authors which describes a protocol to fabricate conductive filaments based on PLA containing 28.5% wt. of carbon black microparticles. The 3D-printed electrodes were applied for sensing catechol and hydroquinone in waters and for H_2O_2 detection after surface modification with Prussian blue microparticles (catalyst) by electrodeposition. Similarly, Lisboa and co-authors reported the fabrication of electrodes using a labmade conductive filament made of PLA and 40% wt. graphite for ciprofloxacin sensing. Instead of a 3D printer, a 3D pen was used to transfer the molten filament to customized tubes to work as electrodes. Cieslik and collaborators presented a novel conductive filament based on PLA containing 5% wt. of boron-doped carbon nanowalls. The authors also reported a fabrication protocol using a 3D pen to obtain electrode with improved electrochemical performance in comparison to previous filaments based on carbon black and PLA. Dopamine sensing was presented as a proof of concept.

The use of commercially available conductive filaments to fabricate 3D-printed electrodes is certainly the most popular strategy reported in the literature. This Topical Collection also presents some examples of recent contributions using commercial conductive PLA-based filaments as follows. Koukouviti and co-authors reported a 3D-printed electrochemical device containing the nanoenzyme Fe(II)-MOF modifier that enables the glucose sensing in neutral pH conditions, the ideal condition for the direct sweat sensing by wearable devices. The 3D-printed electrode was fabricated with a carbon-black PLA filament. The nanoenzyme modifier was drop casted over the 3D-printed electrode and stabilized by a Nafion coating. The results are promising for wearable sensing applications. Another strategy to generate nanostructures over 3D-printed electrodes in a single step was demonstrated by Veloso and co-authors. Subminute laser ablation using a CO_2 infrared source of a 3D-printed carbon-black PLA surface improves the electrochemical performance of these electrodes. Flower-like Na_2O nanostructures are formed at the treated surface and the improved tyrosine detection in human urine was reported.

Another affordable and sustainable strategy to generate metallic nanoparticles without using any chemicals is based on spark discharge as reported by Karapa and collaborators. Plastic conductive electrodes made of polystyrene loaded with 40% wt. carbon fiber were manufactured by injection molding. A high voltage is applied between the plastic conductive electrode and a bismuth rod, from which Bi nanoparticles are released and deposited over the plastic electrode. The sparked bismuth-modified plastic electrode was able to detect cadmium and lead in sub-ppb levels in water and food samples.

The use of reagentless protocols to generate conductive substrates is a new trend in the development of sustainable electrochemical sensors. Laser sources can generate 3D porous disordered graphitic structures through the pyrolysis of polyimide and other materials. Such materials have been named as laser-induced graphene (LIG) and this term has been widely used in the literature. Herein in this Topical Collection we have a few examples of LIG electrodes, which is a sustainable and scalable approach to generate electrochemical platforms. Soares and coauthors reported the use of LIG as ion-selective electrodes for nitrite monitoring in food samples.

Matias and coauthors developed 3D-printed electrochemical cells that assemble LIG electrodes for forensic applications. The authors combined two scalable manufacturing protocols to generate electroanalytical devices that enable the analysis of microliter samples. The quantification of atropine, a substance used in criminal acts, in beverages was demonstrated. A new polymeric platform, polyetherimide, was proposed to generate LIG electrodes by Lima and Araújo. The obtained LIG electrodes were evaluated as portable sensors for xylazine detection in beverages considering a forensic scenario. This substance has been used in robbery and rape cases. Both examples show the potential application of LIG electrodes for portable forensic analyses.

The obtaining of metallic catalysts within graphene to generate novel material with electrocatalytic properties toward sensing has been reported by Yang and collaborators. A simple pyrolysis process of a solution containing Ni(II) and Pt(II) acetylacetonate salts and nitrogen-rich dicyandiamide can produce graphene-wrapped PtNi nanoparticles that provided the electrocatalytic oxidation of carbendazim, a widely used fungicide. The modified electrode was able to analyze carbendazim residues in fruit and vegetables. Qu and collaborators reported the one-step fabrication of WO_3-Fe_2O_3 nanocomposite by the hydrothermal method for gas sensing applications. The authors verified an optimal Fe–W ratio of 0.4 to obtain the best selectivity and sensitivity toward triethylamine detection. Both works report simple, one-pot, and low-cost procedures to synthesize metallic nanocomposites with electrocatalytic activity for improved sensing performance.

A protocol to fabricate multi-walled carbon nanotubes on a gold microelectrode array (CNTs@Au MEA) photolithographically designed on a glass substrate was presented by Singh and coauthors. The CNTs@Au MEA served as platform to generate glucose biosensors by immobilizing glucose oxidase directly over the CNT surface. Each glass chip (1 cm^2) enabled the analysis of 64 blood serum samples. Although photolithography is not so affordable in comparison with other fabrication technologies, the replacement of silicon by glass and the in situ CNT growth are relevant features aiming at the cost-reduction process.

Negahdary and coauthors explored a different approach to obtain an array of gold nanostructures that was based on electrodeposition. Jagged gold nanostructures anchored at a glassy carbon electrode served as assembling sites of graphene oxide-carboxylic acid functionalized CNTs and next for immobilizing aptamers for the diagnosis of Alzheimer's disease. This aptasensor presented a detection limit of 0.088 pg mL^{-1} toward the antibody detection. The direct immobilization of synthetic peptides on carbon nanostructures such as graphene oxide or graphene quantum dots was reported by Braz and collaborators for the development of an electrochemical immunosensor for leishmaniasis detection. These carbon nanostructures were first assembled on commercial screen-printed carbon electrodes. The obtained biosensor provided great selectivity for the analysis of human sera. The dual function of the synthetic peptides, for anchoring and detection, is an interesting approach for future applications toward the detection of other diseases. Another aptasensor was reported by Yang and collaborators which was based on gold nanoparticle decorated with 2D $Ti_3C_2T_x$. The nanocomposite acted as the binding sites for aptamers applied for chloramphenicol detection in milk samples.

The use of molecularly imprinted polymers (MIPs) is another potential and low-cost strategy to enhance selectivity and sensitivity of electrochemical sensors. The attachment of MIPs to magnetic nanoparticles can provide additional advantages such as for extraction procedures. Magnetic nanoparticles modified with MIP for homocysteine detection in biological fluids were presented by Conceição and coauthors. This approach enabled homocysteine quantification in the presence of very similar molecules, such as cysteine, N-acetylcysteine, oxidized and reduced glutathione, and cystine, as well as other constituents present in the biological matrices, such as uric acid. The analysis of synthetic plasma and urine samples as well as human urine was accomplished successfully.

Overall, the 24 articles compiled within this Topical Collection present a glimpse of recent contributions toward the development of sustainable and economical analytical platforms based on electrochemical detection. Contributing directly to the 3rd United Nations goal "Good health and well-being," I can highlight the works focused on high-throughput glucose sensing, aptamer-based biosensing of Parkinson disease, and especially the neglected disease leishmaniasis sensor. Importantly, paper-based analytical devices presented in reviews and full articles are probably the best platform to reach developing countries. Other works also presented important contributions in human health in which sensors were applied for target species of biological and pharmaceutical interests; however, the special focus of these works was on the 12th United Nations goal "Responsible consumption and production" by contributing to circular economy and sustainability. For instance, paper-based and biopolymer-based 3D-printed electroanalytical devices were utilized; the reuse of recycled battery waste; additive manufacturing procedures to fabricate sensors with “zero waste” generation; elimination of chemical and reagents by using laser-assisted procedures to produce graphene and other nanostructures at the sensor surface; and one-step synthesis protocols to reduce chemical waste generation. The application of portable electrochemical (bio)sensors for water quality monitoring, herein presented in some articles, contributes to “Clean water and sanitation” (6th United Nations goal) and “Life below water” (14th United Nations goal). Other papers devoted for forensic applications is directly related to “Peace, justice and strong institutions” (16th United Nations goal) as a fast, in field and reliable information given by a portable analytical method is mandatory for judicial decisions in court. In summary, this Topical Collection brings important contributions that are closely connected with the United Nations sustainable development goals proposed for a better world.

Declarations

Conflict of interest The author declares no competing interests.