Editorial Corner

Progressions in Modified Graphite Electrodes with Green Nanostructured Materials for Low Cost and Sustainable Electrochemical Detection of Environmental Contaminants

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In recent decades, several established analytical techniques such as inductively coupled plasma mass spectrometry, atomic absorption spectroscopy, and atomic fluorescence spectrometry have been employed for the effective detection of environmental contaminants in different matrices [1]. Nevertheless, these analytical methods are laborious, expensive, demand extensive knowledge to execute, and are troublesome to enforce in practice because of their cumbersome equipment. Electrochemical techniques have been created based on their simplicity, speed, cost-effectiveness, enhanced sensitivity, and precise analytical capabilities [2]. Typically employed materials for electrochemical electrodes include mercury, copper, nickel, and noble metals (gold, platinum, and silver), as well as carbon-based materials such as graphite, glassy carbon, and carbon fiber. Several concerns including the toxicity of mercury, vulnerability to corrosion of copper, and the more expensive nature of noble metals and glassy carbon have restricted the applications of these electrodes. Conversely, graphite electrodes (GE) are cost-effective yet very efficient in electrochemical applications, making them a viable choice for the development of affordable electrochemical sensors. Graphite demonstrates exceptional electrical conductivity, which enables effective electron transfer during reactions. Additionally, it has great chemical stability, enabling it to operate in different electrolytic conditions without substantial impairment owing to its resistance to corrosion. Their broad ranges of potential values (e.g., –0.8 to 0.8, –1.0 to 0.8, and –0.8 to 0.6 V vs saturated calomel electrode in H_2SO_4, KCl, and NaOH solutions) allow for the investigation of various redox processes, while little background currents improve the sensitivity and accuracy of measurements [3].

Three types of sensors based on GE are widely recognized, namely 1) pencil graphite electrode (PGE), 2) carbon paste electrode (CPE), and 3) screen printed electrode (SPE). A PGE is often employed in the electrochemical detection of heavy metals and other analytes, such as insecticides, fungicides, herbicides, and pharmaceutical residues [3]. The use of PGE as working electrodes is justified by their affordability, user-friendly nature, and disposable nature, which eliminates the need for time-consuming electrode surface cleaning or polishing. In general, pencil leads, regardless of the manufacturer or hardness, have a resistance below 5 Ω, making them very conductive and therefore appropriate as electrode material. The predominant configuration of a PGE involves a pencil lead that is inserted into a commercially available mechanical pencil, serving as a holder. Pencil graphite leads are composite materials composed of essentially 65% graphite, 30% clay, and a binder such as wax, resins, or high polymer. To preserve a consistent electroactive surface area, the pencil holder is positioned vertically and a constant length of the pencil rod is consistently added and immersed into the solution under analysis [3]. As for CPE, it has garnered interest as electrodes mostly because of its beneficial properties including chemical inertness, durability, renewability, consistent response, low ohmic resistance, and absence of internal solution requirement. Specifically, issues related to passivation can be effectively resolved by a straightforward and rapid process of surface regeneration [4]. CPE is suitable for various sensing and detection applications including pharmaceuticals, pesticide residues, and heavy metals [4]. The fabrication of a CPE involves the traditional packing of soft carbon pastes into suitable electrode bodies. A carbon paste holder can be effectively implemented by drilling a well into a short Teflon rod, glass tube, or polyethylene syringe filled with a paste. This paste is then electrically connected to the holder through a conducting wire. The end hole diameter designed to shape the appropriate carbon paste surface is chosen within the range of 2–10 mm for standard CPEs, which is sufficient for the majority of electrochemical experiments [5]. Finally, a screen-printed electrode (SPE) is a fascinating electrode design that integrates a working electrode made of carbon material, a reference electrode, and a counter electrode within a single-printed substrate. This electrode variant offers straightforward, easily transportable, and disposable sensing applications. Furthermore, as all the necessary electrodes for electrochemical measurement are present in a single SPE, it is appropriate for in situ measurement or point-of-care testing. The excellent properties of graphite make it one of the most commonly utilized materials for the fabrication of SPE [6]. SPE has been reported as the widest technique for the detection of various environmental contaminants in including heavy metals, pesticide residues.

Traditional GEs have several limitations for electrochemical detection, such as reduced sensitivity and repeatability, slower electron transfer kinetics, compromised durability, and the requirement for higher over-potential in electrocatalytic processes. One possible approach to address these issues is to modify the electrodes [7]. Electrode modification using nanomaterials (NMs) has gained significant attention due to their enhanced sensitivity, magnified response signals, and improved repeatability. NMs exhibit distinct physicochemical properties compared to bulk materials, which are primarily influenced by their size and shape [8]. Metallic nanoparticles (NPs), metal oxides, graphene, carbon nanotubes (CNT), metal-organic frameworks, and other types of NMs are highly promising materials employed for electrode modifications [9]. Graphite electrodes can be modified with NMs using several methods such as drop casting [10], dip coating [11], spin coating [12], screen-printing [13], inkjet printing [14], paste electrodes [4], growth processes [15], and electrochemical deposition [16]. NMs provide enhanced sensitivity, selectivity, and stability compared to unmodified electrodes. This is achieved by introducing additional active sites for analyte adsorption, expanding the electrochemical surface area, and enhancing electron transport between the analyte and the electrode [17]. Nevertheless, the synthesis of these NMs by traditional methods entails the use of numerous dangerous chemicals such as hydrazine, sulphuric acids, hydrofluoric acid, hydrochloric acids, etc., which are not ideal for routine laboratory procedures. In addition, a diverse variety of organic solvents including methanol, acetone, ether, benzene, toluene, esters, halogenated, and nitrated hydrocarbons are widely employed in chemical synthesis. These solvents have a high level of volatility, toxicity, and danger, leading to significant concern for both human health and the environment [18]. Hence, it is strongly imperative to guarantee the environmentally friendly manufacturing of NMs to prevent any adverse impacts on human health and the environment. The synthesis of NMs via environmentally friendly methods enhances the advancement of green electrochemical sensing platforms. This involves the use of non-hazardous solvents and reagents for green synthesis, as well as the production of NMs from waste resources [19].

Efficient fabrication of NMs from different types of waste has become increasingly important. The fabrication of numerous important metal NPs including Pb, Pd, Zn, and Cu, as well as metal oxide

NPs such as Cu_2O, CuO, Mn oxide, and Zn oxide, can be extracted from industrial and electronic wastes such as printed circuit boards, used batteries, vehicle shredder residue, and aluminum cans [20]. Within the mining industry, waste materials such as mine tailing, metallurgical slag and acid mine drainage serve as valuable sources for NPs containing magnetite, iron oxide, cobalt ferrite, silver (Ag), gold (Au), zinc (Zn), and copper (Cu). Natural waste materials, including agricultural, forestry, fruits and vegetables, and other biomass waste such as banana peel, rice husk, corn cob, egg shells, coconut husk, fish/shrimps, etc., are valuable resources for the synthesis of cellulose CNT, graphene, graphene oxide, and fullerenes [21]. Organic synthesis by biological methods, known as biosynthesis, utilizes living organisms including bacteria, fungi, yeast, algae, enzymes, and plant extracts to generate metal NPs [20]. Most biological entities function as templates that facilitate the stability of nanostructures by natural polymers. The biopolymers improve the biocompatibility of these NPs and inhibit their tendency to aggregate into clusters [22].

Production of graphite-based sensors augmented by environmentally friendly nanomaterials obtained from various sources of waste offers several advantages, as these wastes are nearly cost-free and ubiquitously available. Furthermore, the utilization of trash as raw materials might yield environmental benefits by advancing the notion of the circular economy [23]. The green synthesis of NMs utilizing living microorganisms is a straightforward, ecologically friendly, and pure process. Hence, the incorporation of eco-nanomaterials into graphite-based electrodes shows potential for the advancement of an affordable and environmentally friendly sensing platform for heavy metal pollutants. Not to mention, there are also other green options accessible, i.e. the use of green solvents such as ionic liquids (ILs) and deep eutectic solvents (DESs) [24], [25]. ILs consist of organic compounds or a combination of salts that exhibit high ionic conductivity, intriguing solvent characteristics, broad potential ranges, exceptional chemical and thermal stability, intrinsic catalytic properties, minimal volatility, and favorable biocompatibility [26]. DESs are a new category of environmentally friendly solvents that are produced by combining hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs). Quaternary ammonium salts are commonly known as HBAs, whereas HBDs encompass a range of compounds such as alcohols, amines, polysaccharides [27]. DESs are a sustainable alternative to traditional solvents due to their non-toxic nature, environmental friendliness, biodegradability, and cost-effective production without the need for purifying procedures [18]. DESs often exhibit comparable physicochemical characteristics to ILs, but they are the superior choice for the development of cost-effective and eco-friendly sensors due to their substantially lower cost compared to ILs [28], [29]. In addition, the tunable properties of both ILs and DESs make them highly versatile in designing sensors for a wide range of applications, including the detection of various pollutants and toxins. These sustainable solvents not only enhance sensor performance but also contribute to reducing the environmental footprint of sensor production. As the demand for eco-friendly technologies grows, the integration of green solvents into sensor development will likely play a crucial role in fostering more sustainable industrial practices.

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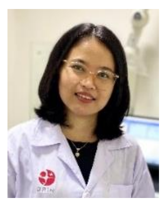

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