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Recent Trends and Application of Nanomaterial Based on Carbon Paste Electrodes: A Short Review

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Abstract: Carbon paste electrodes (CPEs) are a type of electrochemical sensor that have been widely used for sensing and monitoring various analytes. Recently, there has been a growing interest in incorporating nanomaterials into CPEs to improve their performance and sensitivity. Here are some recent trends and applications of modified CPEs based on nanomaterials, which have been shown to have enhanced sensitivity and selectivity for the detection of various analytes such as those in food and drug samples. The high surface area and electrical conductivity of CPEs make them ideal for use in electrochemical sensing applications. Nanomaterial-based CPEs have also been widely studied for their high sensitivity and selectivity in sensing various analytes. Nanomaterials such as Multi-Walled Carbon Nanotube (MWCNT), Single-Walled carbon Nanotube (SWNCT), Graphene, or other naomaterial have excellent electrical conductivity, large surface area, and high mechanical strength, making it an attractive nanomaterial for use in CPEs. A CPEs-based nanomaterial has been used in electrochemical detection, demonstrating improved sensitivity compared to traditional CPEs. In general, the incorporation of nanomaterials into CPEs has opened up new opportunities for the development of highly sensitive and selective electrochemical sensors for a wide range of applications including environmental monitoring, drug diagnosis, and food safety.

Keywords: Nanomaterial; carbon paste electrode; sensor; food and drug

1. Introduction

The voltametric method is an electroanalytic method that employs a system of working electrodes, counter electrodes, and reference electrodes. The voltametric method offers the advantages of becoming suitable for organic and inorganic electroactive molecules, having a lower limit of detection and good selectivity and sensitivity, and the surface of the working electrode being specifically designed[1-3]. The types of working electrodes that are often used are carbon[4], graphite[5], platinum[6], and gold[7]. Carbon is an excellent electrode material due to its low cost, wide potential range, high current densities, and long-term stability[8-10]. Carbon and its derivatives, which are known as high-performance materials, play an important role in the field of electrochemistry[11-13].

Carbon paste electrodes (CPEs) are carbon-based material that is produced from pasting liquid and carbon powder shows good mechanical resistance and stability, easy preparation, and renewal of the surface in the electrochemical sensor application[14-15]. The working electrode in the voltametric method is generally a carbon paste electrode. Ralph Norman Adams' invention of CPEs in 1959 introduced a novel kind of CPEs as an alternative to mercury electrodes[16]. The disadvantages of the use of traditional CPEs are less optimal sensitivity and reproducibility, slower electron transfer kinetics, lower stability in different solution compositions, and the need to increase the electro-catalytic overpotential [17-18]. After that, many researchers studied the CPEs and their modification such as using nanomaterial to improve their properties including increasing the mechanical stability, sensitivity, and selectivity[19-21]. Graphene[22], carbon nanotubes (CNTS)[23], metal nanoparticles[24], carbon quantum dot[25], and ioniq liquids[26] have been widely used as a modifier to improve the properties of CPEs due to their biocompatibility and good electrocatalytic activity.

Multi-Walled Carbon Nanoparticles (MWCNTs) as a modifier to CPEs (MWCNTs/CPE) in the voltammetric determination of zinc ions (Zn(II)) has been reported by Tesfaye et al.[27]. The performance of CPEs was increased with the presence of MWCNTs, which have a large surface area and good conductivity. The modified CPEs with MWCNTs show a higher anodic peak of -1.190 V, while the unmodified CPEs were not observed. In addition, the MWCNTs/CPE show a good limit of detection of 2.48 nm, a linear dynamic response of 0.02-10.00 µm, and a high accuracy of 100% in detecting zinc ions, making them potentially useful in electrochemical detection.

Nitrile detection in soil solution using electrochemical sensor CPEs modified with a mixture of MWCNTs, silver nanoparticles (AgNPs), and chitosan has been studied by Gurban et al.[28]. This material was prepared to increase the electrocatalytic behavior, sensitivity, and selectivity of CPEs in nitrite detection. The result shows that this material has a stable sensor surface and successfully increases the roughness and electroactive surface area of the sensor. Furthermore, the decrease in oxidation potential value (0.725 to 0.51 V) and higher anodic peak (113 µA) make the sensor have good electrocatalytic behavior with a selectivity of 204.4 $mA.M^{-1}.cm^{-2}$, a limit of detection of 2.3 µM, and a linear range of 1.7 mM.

Modification of CPEs have been applied in the fabrication of electrochemical sensors and biosensors for the electrochemical sensing[29-30]. CPEs have been referred to as ion-selective electrodes because of their excellent resistance, low ohmic resistance, stable response, and suitability for a wide range of sensing and detection applications compared to other electrodes[31-32]. In addition, CPEs modified with nanomaterials or nanoparticles have received a lot of attention due to their properties that increase the rate of electron transfer by lowering excess voltage, large response signal, and more acceptable repeatability[33-35].

Fatoni et al.[36] studied the performance of carbon active-$NiFe_2O_4$ nanoparticles to enhance the electron transfer and redox potential behavior of carbon paste electrodes in the application of glucose biosensors. Carbon active acts as the main building material, whereas $NiFe_2O_4$ nanoparticles improve conductivity. The addition of $NiFe_2O_4$ nanoparticles successfully enhances the conductivity and electron transfer rate of the CPEs. A good linear response with an oxidation peak at 0.12 V and reduction peaks at -0.4 V concluded that the carbon active-$NiFe_2O_4$ nanoparticles can be used as a modifier of CPEs in glucose biosensors.

The modification of CPEs based on nanomaterial particles has been reported by many researchers to increase their performance in electrochemical detection. This section will examine research results about CPEs and their modification using nanomaterials. The properties, the influence of the addition modifier, and their application for electrochemical detection as food or drug sensors.

2. Preparation of CPEs

The electrochemical sensor manufacture is usually done using a single three-electrode system (electrode counter, working, and reference) or printing methods (printing circuits, 3D printing, and screen printing) as an advanced technology in the sensor manufacture. Printing methods that are more practical depend on the production of sensors with flexible substrates and rigid in geometry and thickness. Abdallah et al.[37] has designed the sensor based on the three-electrode system using the printing process (Figure 2). The working electrode using gold nanoparticles (Fig. 2a), the electrode reference using Ag/AgCl (Fig. 2b), and carbon as the electrode counter. The purpose of the use of carbon is due to its properties of having a higher surface area, which can reduce the current density of this electrode compared to the working (Au) and reference electrodes (Ag/AgCl).

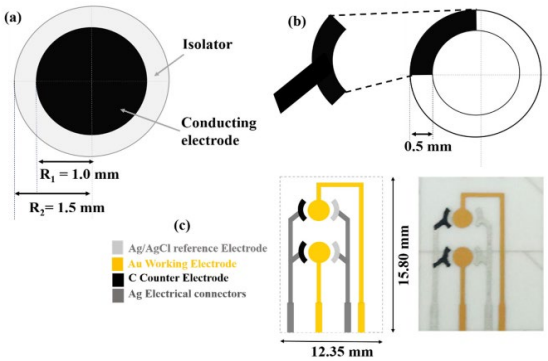

Fig. 2: The design of working electrode (a), reference electrode (b), and multi-integrated microelectrode (c)[37]

The electrochemical sensor design in the form of multi-integrated microelectrodes is shown in Fig. 2c.

Microelectrodes were combined on the same chip to prevent noise, which can reduce sensitivity and increase the detection limit in the electrochemical analysis process. Furthermore, the microelectrodes can improve mass transport, shorten response times, and lower resistance.

Many research has provided another methods for preparing CPEs using carbon material. Carbon paste is frequently preparing by mixing and grinding paraffin with carbonaceous material such as graphite, carbon microspheres, and multiwall carbon nanotubes powder using mortar until the paste was obtained, then packaged or pressed into a suitable electrode body (Teflon tube)[38-40]. The SEM images of CPEs that produced from graphite, carbon microspheres, and MWCNTs[41] can be seen in Figure 2. The characteristic of CPEs from graphite shows the distinct edges that correspond to the carbon surface; the carbon microspheres show the spherical carbon sphere with different sizes; and the sausage-like structure with light lumps confirmed the amorphous carbon from the MWCNTs. Based on the voltammetric behavior observed in the analysis, the performances decrease in following order: carbon microspheres > graphite > MWCNTs.

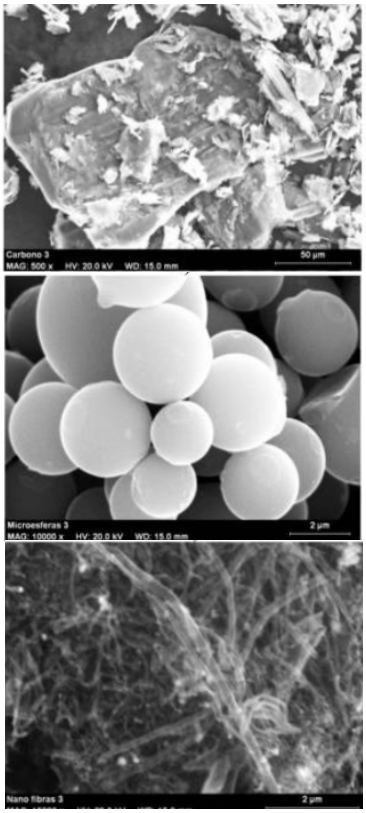

Fig. 2: The SEM images of CPEs synthesize from graphite (a); carbon microsphere (b); MWNTS (c)[26]

Fabrication or modification of CPEs also can be done using nanomaterial by inserting the nanomaterial, such as gold, platinum, or graphene into the tube, then pressing the electrode surface against a filter paper and turn the nanomaterial tube until the paste is compressed. Finally, the CPEs was already used after the smoothed with a clean paper (Fig. 3)[42-43]. The CPEs preparation are an important feature of carbon pastes because it can produce the good easy surface renewal as well as the removal of a significant portion of the paste if necessary. In practice, wet filter paper can be used to quickly renew the paste's surface[44-45].

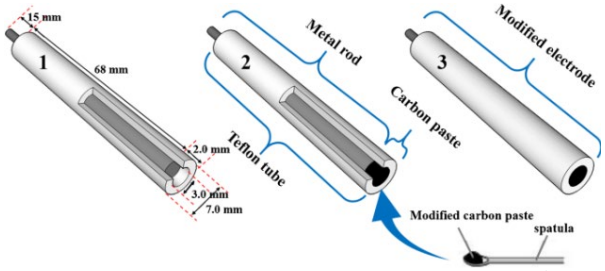

Fig. 3: The modified of carbon electrode paste [42]

3. Modification of CPEs with nanomaterial

The modified carbon pastes are generally composed of a non-electrolytic binder and graphite. A modifier is an additional component in the mixture. The modifying agent (conductive powder) is typically a substance, but additional components, such as enzymes. In addition, combination of modifiers in the case of carbon paste-based sensor or biosensors may be added to make the CPEs. The intended use of modifying agent is to obtain high-quality new sensors with preferable and pre-defined characteristics for selective and sensitive determination in electrochemical detection[46-47].

Nanomaterial is a material that has a larger surface area that widely used in many applications such as drug delivery to maximize drug efficiency, as a catalyst due to the higher surface area that can increase the catalytic activity in many chemical reactions including esterification, fuel cell, hydrocracking, and so on[48-50]. The use of nanomaterials as a modifier to CPEs has been done by many researchers. Nanomaterial can enhance the electrochemical performances, including improving the non-faradaic current of CPEs, sensitivity, and limit of detection of CPEs's electrode in the electrochemical detection of food, drug, so on[51-52].

The use of Multiwalled carbon nanotubes (MWCNTs) and chitosan as a modifier of CPEs for nitrile detection in soil solution has been reported by Gurban et al.[28]. The SEM images of the CPEs that were modified using chitosan (Fig. 4b) show a rough surface with a thin and homogeneous layer compared to the unmodified CPEs (Fig. 4a). The addition of MWCNTs to the CPEs causes the morphology of the CPEs to have a more uniform distribution of particles (Fig. 4c). Furthermore, when the CPEs are modified with a mixture of MWCNTs and chitosan (Fig. 4d), the morphology has a uniform coating and a stable surface. In addition, the increase in roughness indicated that the material has a good electroactive surface area.

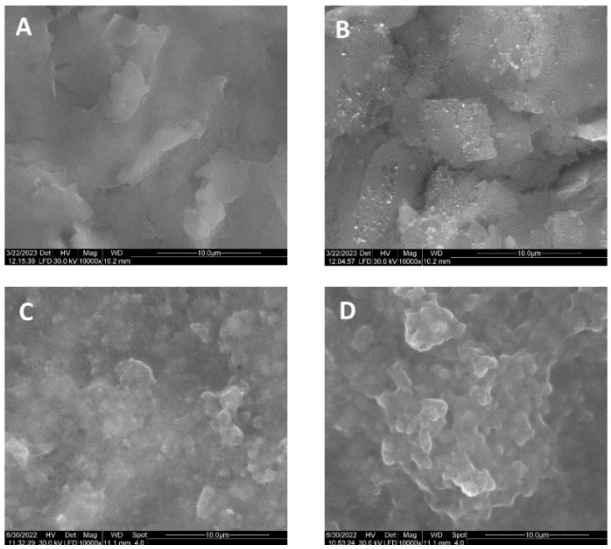

Fig. 4: The SEM images of unmodified CPEs (a), and modified CPEs with chitosan (b), MWCNTs (c), MWCNTs-chitosan (d)[28)]

The electrochemical oxidation of nitrite over the modified CPEs was performed using 1 mM of nitrite and sensors that contain 1 mg/mL of MWCNTs, 0.5% of chitosan, and 1,8-DAN of poly and sol-gel matrix. The cyclic voltammograms are shown in Figure 5. The oxidation nitrite peak of CPEs that were modified with MWCNTs occurred at 0.813 V and the anodic peak at 21.45 µA (Fig. 5a). The presence of chitosan (MWCNTs-chitosan) causes the oxidation nitrite peak to decrease in neutral medium (0.748 V), whereas producing a higher anodic peak of 27.3 µA (Fig. 5b). These findings showed that the modified CPEs with a mixture of MWCNTs and chitosan performed well in electrocatalytic activity. Furthermore, no electrocatalytic activity was identified in the modified with poly 1,8-DAN (Fig. 5c) and when MWCNTs were entrapped in the sol-gel matrix, their electrocatalytic activity increased (Fig. 5d).

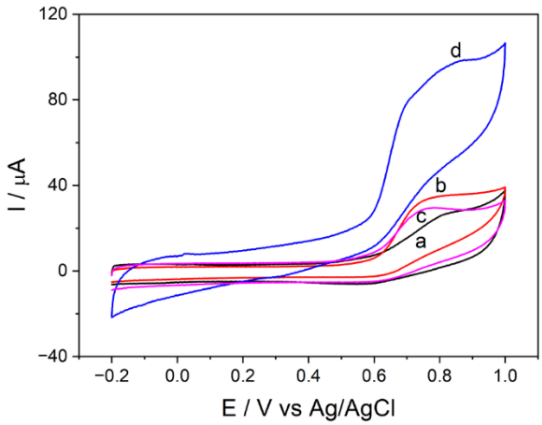

Fig. 5: Cyclic voltammogram of modified CPEs with MWCNTs (a), MWCNTs-chitosan (b), poly 1,8-DAN (c), and MWCNTs entrapped in the sol-gel matrix (d)[28)]

4. CPEs based on nanomaterial as a sensor

Modified CPEs with nanomaterials in many applications, especially as sensors or biosensors, have been reported in previous research. A sensor is used to detect the physical and chemical properties of a physical quantity based on the electrical or optical signal that is detected by an electronic instrument. A biosensor is one of the sensors that has advantages in high sensitivity, selectivity, and stability. The performance of a biosensor in electrochemical detection could be done in enzyme, antibody, or cell detection. A transducer converts a bioreceptor signal from enzyme, antibody, bacteria, or cell into a quantifiable signal that generates an electrical signal (Figure 5). Next, the electrochemical detection based on the electrical signal appears in the form of a potentiometric, amperometric, impediometric, or conductometric curve (Figure 6)[53)].

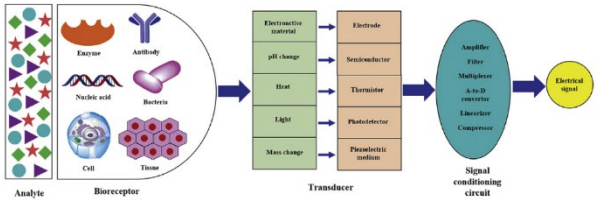

Fig. 5: Schematic diagram of biosensor[53)]

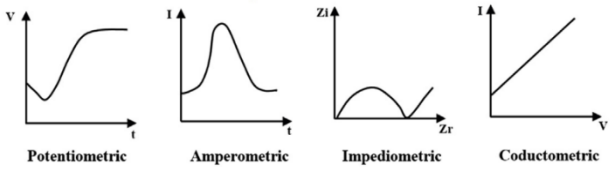

Fig. 6: An electrochemical signal of biosensor[53)]

In electrochemical detection, a sensor or biosensor is usually used in widely application. In medical field such as cancer or diabetic diagnostic, determination of sample in environment, soil, water, or drug discovery, and as a food quality control (Figure 5).

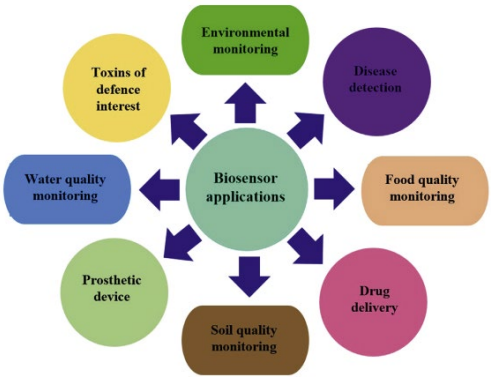

Fig. 5: The application field of biosensor [53)]

Nanomaterials can be used as a material to produce sensors. Sensors that can be applied to a wide range of applications, as well as the use of nanomaterials with

several advantages, have prompted researchers to perform comprehensive research in this area.

4.1 Modified CPEs with nanomaterial as food sensors

Synthetic dyes are widely used in food products such as carbonated drinks, jams, and others. Since many synthetic dyes lead to illness, it is critical to establish sensors that can identify the dyes in food products. Carbon paste electrodes through the voltametric method seem to be effective for these aims. Modification of CPEs to detect the synthetic dyes in real samples shows good limits of detection[54-56]. Readers interested in establishing electrodes with low cost for the efficient identification of dyes in food products such as carbonated drinks or jams will find this review useful.

A promising study demonstrated by Zhou et al.[57] that develops carbon paste electrode to identify curcumin (bright yellow coloring agent) in food samples. They are using molecularly imprinted polymer nanoparticles that synthesize through the polymerization by thermally induced precipitation polymerization. Polymer, graphite powder, and paraffin oil were combined to create the MI-CPE electrode. The results showed that the good electrode performances based on the oxidation peak at 0.434 V at pH 3.06. The optimum polymer addition ratio throughout the MI-CPE electrode was 20%. A good linear correlation with a concentration in the 0.1–50 µM range, with a detection limit of 10.1 nM was observed. The results of this study provide recovery rates ranging from 90.77 to 105.7%. This result shows that molecularly imprinted polymer-based CPE has good selectivity and sensitivity in the analysis of dyes in food products. Similar research by Cakir et al.[58] used palladium nanoparticles (PdNP)-coated with graphite electrodes as modifiers of CPEs to detect curcumin in turmeric powder and found linear calibration in the 0.03–0.6 µm range with a limit of detection of 2.2 x 10^{-9} nM. The palladium nanoparticle performs better than the molecularly imprinted polymer in curcumin detection due to its superior selectivity, dispersibility, and thermal stability[59,60].

Magnetic molecularly imprinted polymer (MMIPs) from magnetite nanoparticles iron (III) acetylacetonate as a modifier of CPEs for the detection of folic acid or folate (vitamin B_9) in different foodstuff samples has been investigated by Khan et al.[61]. Folate is an important nutrient for the human body, especially for pregnant or breastfeeding women, to avoid birth abnormalities. Furthermore, folate prevents heart and blood vessel illnesses, cancer, and Alzheimer's disease. MMIPs are classified as a biomimetic sensor that is potentially used as electrode for electrochemical analysis due to its high efficiency, low-cost production, good electron transfer mass, stability, selectivity, and sensitivity[62,63]. The results show that the electrode produce good linear dynamic range of 2-12 µM and limit of detection of 1 x 10^{-7} M. The MMIPs electrode outperformed the magnetic non-molecularly imprinted polymer (MNIPs) electrode to detect folate in several foodstuff samples, with recovery ranging from 92 (orange sample) to 103% (broccoli sample). The high surface area of MMIPs (165.76 m^2/g) influences its electrocatalytic activity in folate detection, whereas MNIPs' surface area is 34.82 m^2/g. Moreover, SEM images of the MMIPs (Fig. 6a) demonstrate that they are more porous and granular than the MNIPs electrode (Fig. 6b). The morphology of the MMIPs has well-distributed and uniform particle size that exhibits many cavities and sites for folate absorption. This result was confirmed by the HPLC-UV analysis, the MMIPs adsorbed the analyte (folate) up to 98%, while the MNIPs only adsorbed 9%. The reusability test of the MMIPs in the electrochemical folate detection exhibits good accuracy and can be used up to five times. Hasan et al.[64] used copper oxide nanoparticles generated from osmium basilicum leaves to modify CPEs. High stability of 98% and recovery of 108.8% make copper oxide nanoparticles perform effectively in the electroanalysis of folic acid, with a detection limit of 2x10^{-6} M and a linear range of 0.01 to 1.5 M. According to the results of the two studies, iron (III) acetylacetonate exhibited better electrochemical activity than copper oxide nanoparticles in detection of folate. The high transport mass and energy of iron (III) acetylacetonate demonstrate good activity and selectivity in electrochemical detection.

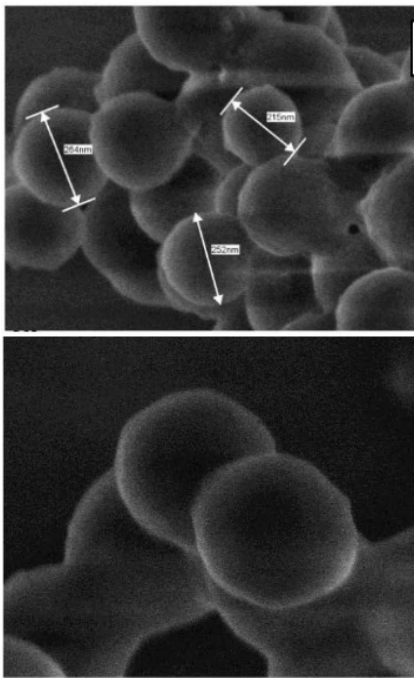

Fig. 6: The SEM images of MMPIs (up) and MNIPs (down) electrode[61]

Detection of toxic chemicals in food, such as pesticides, additives, poisons, and residues, is very important because they can affect human health and produce food that is not safe for health. The use of metal oxides, alloys, polymers, or nanomaterials as CPE modifiers shows that the nanomaterials have better selectivity, making them suitable for use as modifiers[65-66]. Single-wall carbon

nanotubes (SWCNTs) and Multi-wall carbon nanotubes (MWCNTs) are the nanomaterial that widely used as an electrode for food sensor due to their good electrical conductivity that can transform the CNT's conductivity to the large gap semiconductor from a conductor[67-70]. Analysis of vanillin (produce from vanilla beans) in food sample using MWCNTs as a sensor electrochemical by Hareeha et al.[71] show a good dynamic linear and low detection limit of 0.50–18.00 µM and 0.0199 µM, respectively. This CPEs resulted in a sufficient restoration of vanillin in various food samples and produced CPEs with good reliability and reproducibility for the vanillin found in food samples. The detection of vanillin in food samples with better performance has been investigated by Gupta et al[72]. using CPEs-based NiO decorated single wall carbon nanotubes (NiO-SWCNTs) nanocomposites. The presence of metal oxide NiO-SWCNTs enhanced the oxidation peak of vanillin 12 times and decreased the oxidation overpotential of vanillin up to 50 mV. Furthermore, a linear range of 0.01–350 µM and a detection limit of 0.007 µM indicate that the NiO-SWCNTs nanoparticle is an accurate vanillin sensor.

Indigo carmine (ICN) is a hydrophilic coloring agent that is widely used as a food coloring to produce blue color in food, beverages, or the formulation of pharmaceutical pills[73-74]. Higher ICN concentrations in the human body can cause a variety of problems, including hypertension, cancer, tumors, and genetic difficulties[75]. The detection of ICN using poly(dl-phenilalamine)-layered carbon nanotube paste electrode (PAN)LCNTPE) has been reported by Bhimaraya et al.[76]. The electrochemical activity of the (PAN)LCNTPE electrode in the Indigo carmine detection outperformed that of the bare carbon nanotube paste electrode. This finding is based on the increase in anodic peak current, and the higher the ICN concentration, the greater the increase in anodic peak, with a limit of detection about 0.0216 µM. The (PAN)LCNTPE electrode has good stability, repeatability up to 10 times cycles, and recovery reaches 100%. In addition, this electrode also provides high electron transfer, an electrochemical rate constant, and a large surface area. The (PAN)LCNTPE electrode show good performances in the indigo carmine detection compared to the other research. A poly(glutamic acid)-layered multi-walled carbon nanotube for the modification of CPEs in the electrochemical analysis of chocolate samples reported by Hareesha et al.[77] successfully produced a new electrode that decreased the oxidative peak current to 0.1308 V. Furthermore, good electroanalysis activity was observed due to the linear range of 5–50 M with limits of detection and quantitation of 0.36 and 1.20 M, respectively.

Aflatoxins (AF) in foodstuff analyses using biosensors based on nanomaterials have been studied by Abdallah[37]. Aflatoxin is one of the contaminants (fungi) in food products that is commonly found in peanut and maize products[78]. AF can cause chronic diseases in humans due to the carcinogen molecules that it contains[79]. The biosensor was produced by three screen-printed electrodes using gold nanoparticles, silver/silver chloride nanoparticles, and carbon paste. The detection of AF toxin in sample food (rice milk) using this new CPEs shows better electrocatalytic activity than using another nanomaterial that has been studied by other researchers in the same sample (rice milk). The AF toxin detection in a buffer shows a limit detection of 50 fg/mL and a sensitivity of 18 µA/ng.mL^{-1}. Electrochemical detection of AF toxin showed linearity in the range of 0.5 to 2.5 p/mL, which concluded that modified CPEs with nanoparticle gold and silver can be used in low concentrations and are appropriate for electrochemical detection. Shadjou et al.[80] developed a sensor based on silver nanoparticles and a glassy carbon electrode for the electrochemical detection of aflatoxin in milk samples. Silver nanoparticles produce an easy sensitive electrochemical sensor, with a linear range of 0.015 mM to 25 mM and a limit of quantification of 2M in the electrochemical monitoring of aflatoxin.

Graphene, as a nanomaterial that has good mechanical and thermal stability and electrical properties, has great potential for use in electrochemical detection for food analysis[81-83]. Because graphene has a large surface area and many active sites, it has a high potential for charge molecular interactions, which can improve CPE selectivity and sensitivity[84-85]. The detection of Rhodamin B (RhB) (a synthetic dye in food samples that can cause irritation to the skin or eye[86]) through electrochemical detection using carbon paste electrode-base graphene was reported by Kartika et al.[87]. The CPE-based graphene has a wide linear range and a low limit of detection of 2–10 µm and 1.94 µm, respectively, indicating that it is highly sensitive and selective in the detection of RhB dye. Zhou[88] reported a similar study in which graphene nanoparticles were used as a modifier of CPE for the detection of bisphenol A in milk samples, resulting in a sensor with a good linear range of 0.01–10 µm and a limit of detection of 5 nM. The summary of the use of nanomaterial as a modifier of carbon paste electrode in food analysis can be seen in Table 1.

4.2 Modified CPEs with nanomaterial as Drug Sensor

The use of carbon paste electrode as a sensor has been investigated by Salim et al.[89]. A simple and sensitive voltametric technique for identifying the veterinary drug nitroxinil (NTX). NTX is an anthelmintic drug that fights against parasitic worms in sheep and cattle[90]. The voltametric activity of CPEs in the NTX detection resulted in an anodic peak current that was a linear function of NTX concentration over the range of 3.9 x 10^{-6} – 1.0 x 10^{-4} µM, with detection of limit of 3.1 x 10^{-7} µM and a quantification limit of 9.4 x 10^{-7} µM. This electrode also was used to evaluate the drug's residual levels in bovine meat, kidney, fat, and milk samples. When compared to the reference method, this process obtained good results.

A modified carbon paste electrode (CPEs) using

multiwall carbon nanotubes (MWCNTs), single-walled carbon nanotubes (SWCNTs), glassy carbon, and graphene oxides for the naproxen detection has been carried out by Hendawy et al.[91]. Naproxen is a nonsteroidal anti-inflammatory drug that acts by reducing hormones that cause inflammation and pain[92]. The results revealed that glassy carbon powder-based electrodes performed better than graphite electrodes. The use of carbon nanotubes with MWCNTs or graphene results in a decrease of the oxidation peak, which could be due to carbon nanotube's high hydrophobicity. The modified CPEs with SWCNTs shows better performance than other nanomaterials. Therefore, the detection of Naproxen and its degradation was done using carbon paste electrodes combined with 10% SWCNTs. There are two peaks at 0.85 V and 1.18 V was observed. The peak at 1.18 V shows good reproducibility and sensitivity compared to the peak at 0.85 V. The analytical application proposed that the use of SWCNTs/CPEs for the measurement of naproxen was successfully conducted. The determination of naproxen using SWCNTs/CPE shows wide linear range of 4.35–65.5 µM and a limit of detection of 6.255 µM. Based on this result, the use of a nanomaterial SWCNTs based carbon paste electrode can be used to determine naproxen in biological samples without additional pretreatment. Another determination of naproxen through the electrochemical analysis using CPEs modified with activated carbon nanoparticle has been reported by Soltani et al.[93] and the result shows better electrochemical process compared to the use of SWCNTs/CPE. Activated carbon nanoparticles have good adsorption capacities due to their many pores in their internal structure, large surface area, and high porosity and conductivity. Activated carbon nanoparticles were used as CPE modifiers to improve accuracy, sensitivity, selectivity, and the surface electrode for naproxen oxidation detection. The use of activated carbon nanoparticles up to 4.5 times bigger than unmodified CPEs resulted in an increase in the oxidation peak of naproxen. In the electroanalysis of naproxen with 0.005 g activated carbon nanoparticles at pH 6, a linear curve in the range of 0.1–120 µm with a detection limit of 0.0234 µM was detected. The repeatability was achieved five times, with good stability lasting up to 4 weeks and a decrease of 5 percent in peak current. The recovery of naproxen in pharmaceutical and blood samples is up to 99.8% and 99.00%, respectively.

Acyclovir is a type of antiviral drug that assists the body in fighting illness as well as offering immunity. Acyclovir is commonly used as a herpes zoster infection medicine to reduce the symptoms and spread the infection of the herpes zoster virus[94-95]. Naghian et al.[96] utilized CPEs modified with cadmium oxide nanoparticles (CdONPs) and Fe_3O_4 for identifying acyclovir in tablets, blood serum, and urine samples. CdONPs are a metal oxide material with a high thermal stability, surface area, and isoelectric point, which results in greater electrochemical conductivity in electrochemical analysis. The presence of CdONPs on the surface of the CPEs generates cavernous and porous surface morphology (Fig. 7), resulting in an increase in surface area (from 0.14 cm^2 to 0.31 cm^2) and electroactive species. The electrochemical analysis of acyclovir over the CdO/Fe_3O_4/CPE shows that the oxidation peak current increases with increasing scan rate, with a linear range of 1-100 µM and a limit of detection of 0.3 µM. Furthermore, long-term stability was observed with a 5% decrease signal after 8 weeks. Acyclovir determination in different samples (tablet, urine, and plasma) demonstrates great performance and accuracy, with a recovery of 94 - 104.4%.

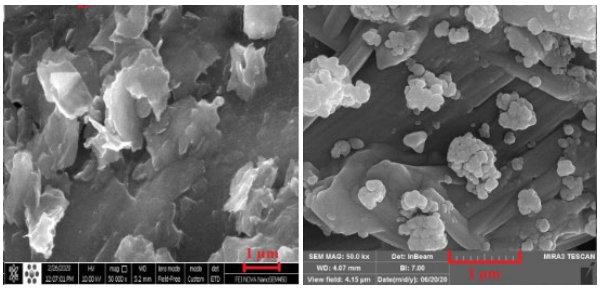

Fig. 7: morphology of carbon paste electrode (left) and carbon paste electrode modified with CdONPs (right)

Trimethoprim is an antimicrobial agent that can be used and meningitis systems. A higher concentration of levofloxacin in the human body (the maximum limit was 100 ppb) has the potential to harm the kidneys and liver[97-98]. The electrochemical analysis of Trimethoprim using a magnetic molecularly imprinted carbon paste electrode (MCPE) based on Fe_3O_4, MWCNTs, and graphene oxide in order to improve the stability, selectivity, and reusability of the MCPEs was studied by Liu et al.[99]. Modified CPEs using F_3O_4@MWCNTs increased the magnetic properties and electron conductivity of the MCPEs due to the increase in the redox peak. The modification of MCPEs with graphene oxide causes the redox peak to further increase, which enhances the conductivity of the MCPEs. The redox peak decreases after modification of MCPEs with molecularly imprinted polymers, MIP@Fe_3O_4@MWNTs, due to the low conductivity of MIP. Furthermore, the slice decreased in redox peaks and conductivity with the addition of graphene oxide (MIP@Fe_3O_4@MWCNTs/rGO/MCPE). The electrochemical analysis of Trimethoprim detection using MIP@Fe_3O_4@MWCNTs/rGO/MCPE electrodes shows good stability, sensitivity, and selectivity with a wide linear range from 4 x 10^{-9} to 5 x 10^{-4} M and a limit of detection of 1.2 x 10^{-9} M. In a similar study with greater electroactivity, Patil et al.[100] proposed electroanalysis of trimethoprim using a sensor modified with ZnO nanoparticles. In trimethoprim detection, ZnO has a larger surface area, a larger band gap area, and stronger optical electrical conductivity than unmodified CPEs. The voltammogram data demonstrate that the high peak current was identified even though the reduction peak was not observed, indicating an irreversible electrode

mechanism. Trimethoprim analysis processes using sensors based on ZnO nanoparticles show a linear range of 8 x 10^{-7} M to 1 x 10^{-5} M with a limit of detection of 2.58 x 10^{-8} M and a limit of quantification of 8.61 x 10^{-8} M. The remarkable catalytic ability, stability, and electrical conductivity of the ZnO nanoparticle are attributed to its high sensitivity because of the low LOD achieved. Trimethoprim detection in pharmaceutical and urine samples recovered up to 99.36% and 98.33%, respectively.

A carbon paste electrode based on a glassy carbon electrode that was modified using Ruthenium/Vulcan nanoparticles for Idarubicin anticancer drug detection was performed by Kaya et al.[101]. Ruthenium's characteristics, which promote the movement of electrons in redox processes, can increase the electronic conductivity, selectivity, and sensitivity of CPEs. The morphology of the new modified CPEs suggested that the addition of Ruthenium caused the morphology of the CPEs to be well dispersed on the glassy carbon. The electrochemical analysis in the oxidation and reduction processes indicated that the modified CPEs with Ruthenium/Vulcan enhanced the electronic conductivity and electron transfer kinetics with a low limit of detection of 9.25 x 10^{-9} and a low limit of quantification of 2.8 x 10^{-8} M, whereas the charge transfer resistance decreased. For another electrochemical detection of Idarubicin, Arkan et al.[102] constructed modified CPEs consisting of carbon nanofiber (CNF) and TiO_2 nanoparticles that had a high surface area, adsorption, and thermal stability. TiO_2 nanoparticles and CNF improve the effective electrode area and assist in the diffusion of idarubicin during the electrochemical process. Furthermore, great electrochemical performances, including an increase in peak current due to the large surface area and conductivity of TiO_2 and CNF were seen in the idarubicin detection. The quantitative analysis demonstrates good sensitivity, with a linear range of 0.012-10 µm and a detection limit of 3 nM. Furthermore, the TiO_2-CNF/CPE showed similar oxidation behavior and oxidation potential to the dunorubicin or dosorubicin detection. The summary of the use of nanomaterial as a modifier of carbon paste electrode in drug analysis can be seen in Table 2.

5. Computational insight in carbon nanotubes based sensors

Nanomaterials such as carbon nanotubes (CNTs) have been developed rapidly for sensor applications. They can be used for sensors of various chemical and biological substances, such as ethylene, glucose, various enzymes, etc[103]. Computational studies are needed to study the molecular sensor mechanism, for example, the type of interaction between the sensor and the analyte (covalent or non-covalent)[104-107], and the adsorption behavior of the analyte into the sensor material[108-109].

Li, et al.[108] have conducted a computational study of how selective sensing of ethylene and glucose on CNTs-based sensors. Through this computational study, electrical conductance, transmission coefficient, receptor density effect, the band gaps of the nanotubes, and the atomic modification of the receptor on detection sensitives are investigated. The stages in the computational method for studying this are the first to create a configuration of the CNTs molecule and its accompanying metal or functional groups. Then the configuration of this molecule needs to be optimized so that the system can be converged. An example of an optimized structure is shown in Figure 8. There are several types of computational methods that can be used, for example, "classical" methods, such as force fields or ab initio quantum mechanics methods, such as DFT, HF, MP2, etc. And yet the ab initio method will provide better accuracy than the classical method but requires more complex method features, such as attention to charge transfer calculations, quantum transport calculations, and charge density.

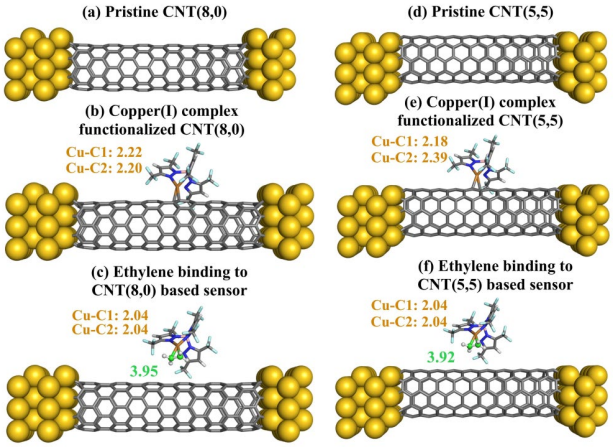

Fig. 8: The screenshot of optimized structures for ethylene detection in semiconducting CNT(8,0)-based systems (a, b, c) and metallic CNT(5,5)-based systems (d, e, f). The colors of C, N, O, H, B, F, Au, and Cu are grey, blue, red, white, pink, cyan, gold, and brown. The ethylene molecules are pictured in the ball-and-stick representation with their carbon atoms shown in green. The copper-carbon bond lengths (in Å) are labeled brown; the closest distances between the ethylene molecule and the nanotube surface are labeled green.

Conclusion

Carbon paste electrodes (CPEs) as ion-selective electrodes are widely used as a working electrode for the determination of electrochemically active compounds. The modification of CPEs to increase its responsive detection has been studied for many years. Modified CPEs based on nanomaterials have been used as a sensor for food or drug analysis in the term of carbon paste-based nanomaterial including graphene, MWCNT or SWCNT. Modified CPEs with nanomaterial as a food or drug sensor using Voltametric methods show the good linear range area and low detection limits of CPEs. Furthermore, it can increase the selectivity and sensitivity of CPEs in detecting of commercial dyes in food and drug.

Declaration of conflicting interest

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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