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M A Mustapa[1], Sumiaty Ambran[3], Ali Yuzir*[1,2]

[1]Disaster Preparedness & Prevention Centre, Malaysia-Japan International Institute of Technology (MJIIT), Universiti Teknologi Malaysia (UTM), 54100 Kuala Lumpur, Malaysia
[2]Department of Environmental Engineering and Green Technology (EGT), Malaysia-Japan International Institute of Technology (MJIIT), Universiti Teknologi Malaysia (UTM), 54100 Kuala Lumpur, Malaysia
[3] Department of Electronic Systems Engineering, Malaysia-Japan International Institute (MJIIT), Universiti Teknologi Malaysia (UTM), 54100 Kuala Lumpur, Malaysia

*Corresponding author e-mail: muhdaliyuzir@utm.my

Abstract. Carbon nanotubes (CNTs) and graphene are carbon-based materials with great potential for electrochemical sensing in various applications such as for the environmental, biological, and physical sensors. For environmental applications, the sensor used to detect heavy metals such as cadmium (Cd), lead (Pb), mercury (Hg), iron (Fe), and other heavy metals that present in the water qualitatively and at the lowest limit of detection value. The uniqueness of their structures and chemical properties has attracted many researchers to develop carbon-based electrochemical sensors for environmental applications. These carbon materials are low-dimensional, thus providing the elevated aspect ratios and subsequently able to increase the sensitivity of the sensor probe. In the meantime, the graphene has its advantages in terms of its large surface area per unit volume to absorb and trap the molecules on the surface. In theory, the carbon atom is in the mid-range of electronegativity and can thus form a stable covalent bond with other molecules. These two materials are therefore consistent to bond with other functional groups such as amine, aldehyde, carboxyl, and thiol groups. All these functional groups can be functionalized with specific ligands or receptors for that particular heavy metal to provide specific and sensitive detection. Convenience in terms of their functionality, making them the center of attention as versatile platforms for functionalizing and designing an electrochemical sensor probe based on applications of concern. This paper focuses on reviewing carbon-based electrochemical sensors development to detect heavy metal in water for real-time monitoring of water quality, thus providing a brief overview of the sensor design reported previously.

1. Introduction

Carbon-based materials such as carbon nanotube (CNT) and graphene have a high potential to develop as probe sensors [1-3]. These carbon materials have a unique, distinctive, and potentially to be developed as a carbon-based electrochemical sensor, especially for detecting the presence of heavy metal in the water source [4, 5]. Historically, carbon material, like CNT, has been studied for more than 20 years [5]. It has been used for various applications such as in microelectronics, computing, medicinal therapy, electrochemical biosensors, and chemical sensors [6-12]. Nowadays, the use of a carbon-based electrochemical sensor to detect heavy metals in water sources has become great attention by researchers [13]. Although studies have been conducted for a long time on the electrochemistry of carbon-based sensors for heavy metal detection, they are still a concern for researchers today. It has motivated scientists to enhance the efficiency of detector capacities to detect heavy metal presence in water by advancing science and technology in interdisciplinary studies. It can be demonstrated by the increase in

research output for this field, which has been successfully published in scientific journals such as integrated MOF with carbon-based material to enhance heavy metal detector sensitivity [14, 15] and carbon-based material functionality to detect various heavy metals in water simultaneously [16-18]. This article presents the type of carbon-based material used for heavy metals detection, briefly characteristic and chemical properties of graphene and carbon nanotube (CNT), and lastly, applications of graphene and CNT in heavy metals detection.

1.1. Graphene

Graphene is a two-dimensional (2D) sheet of carbon atoms that has a large surface area and more significant than single-wall carbon nanotubes (SWCNTs) [19]. The carbon atoms are bonded by sp^2 bonds and in the form of hexagonal configuration. These bond and electron configuration has made it own a large surface area. Additionally, the mechanical strength of graphene is 200 times greater than steel, owing high in elasticity and also thermal conductivity[20]. It is inexpensive to make graphene using graphite. The use of graphene is, therefore, more cost-effective and worth it. There are several ways to produce graphenes, such as through chemical vapor deposition (CVD) [21], ultrasonication [22], and plasma etching [23].

1.2. Carbon nanotube (CNT)

CNT was discovered by Iijima in 1991 and was revolutionized in the field of polymer nanocomposites [24]. CNT derives from graphene sheets and appears as cylinders resulting from graphene sheet rolls [25]. Typically, CNTs are referred to as single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). The CNT is an excellent adsorbate due to its unique characteristics such as hollow and layered structure, high surface area, and in the form of nanosize [26].

2. Application of graphene and CNT in an electrochemical sensor for heavy metal detection.

2.1. SnO_2/rGO electrochemical sensor for the detection of various heavy metals simultaneously.

Wei et al. [27] have developed an electrochemical-based sensor by using a base glassy carbon electrode (GCE) to detect the various heavy metals ions (HMIs) presence in drinking water simultaneously. The targeted heavy metal ions were Cd (II), Pb (II), Cu (II), and Hg (II). In this experiment, the surface of the electrode was modified with Tin oxide (SnO_2) integrated with reduced graphene oxide (rGO) to allow the binding interaction between the electrode surface and HMIs. Before the electrode surface modification, the GCE was thoroughly polished with alumina powder and rinsed with DI water. Subsequently, being sonicated with the mixture of alcohol and DI water before dried under nitrogen condition. The heterogeneous mixture of SnO_2/rGO was prepared in alcohol and agitated with a sonicator. The mixture was then coated on the electrode, and the solvent evaporated at room temperature to obtain the modified electrode SnO2/rGO nanocomposite film. Figure 1 shows the surface morphology of SnO_2/rGO coated on the GCE observed under transmission electron microscopy (TEM). Figure 1(a) shows the sheet of graphene layer was well coated with SnO_2 nanoparticles and profoundly formed a uniform size on the GCE surface. The average diameter size of SnO_2 nanoparticles coated on the surface was about 4-5 nm, as shown in figure 1(b).

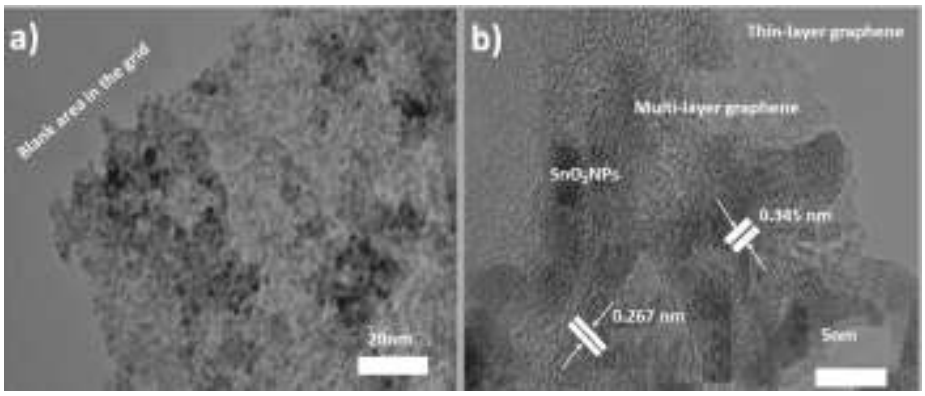

Figure 1: (a) TEM image of SnO_2/rGO modified electrode (b) image of the well-crystallized polycrystalline structure of SnO2 nanoparticles [27].

The research group characterized the SnO_2/rGO coated on the GCE surface by using a square wave anodic stripping voltammetry (SWASV) method and the result obtained as shown in figure 2 (a) and (b). Each step of the modification process would change the current during the process of GCE surface modification as shown in figure 2(a). Based on their result obtained, the specific HMIs would provide the current at a specific electrical potential, as shown in figure 2(a). Thus, facilitate to detect the various HMIs simultaneously as shown in figure 2(b)

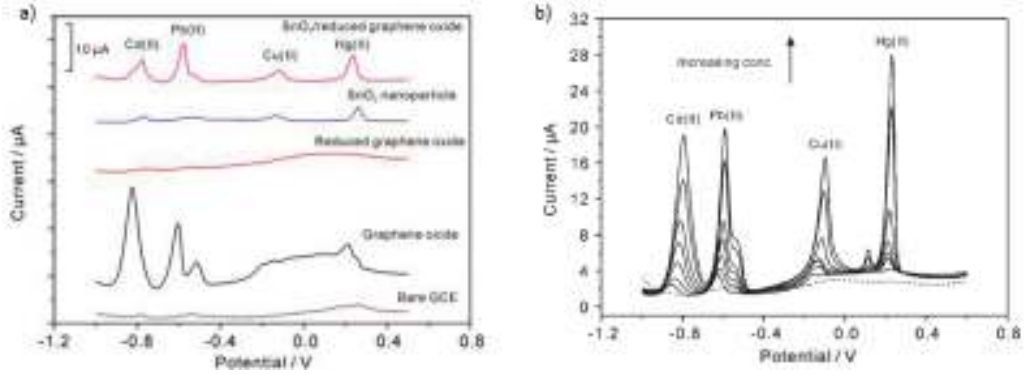

Figure 2: (a) characterization and optimization of SnO_2/rGO (b) detection of different HMIs [27].

The square wave anodic stripping voltammetry technique was applied to perform and measure the detection of HMIs in water samples. The result obtained showed the limit of detection of Cd (II), Pb (II), Cu (II), and Hg (II) were 1.015 X 10^{-10} M, 1.839 X 10^{-10} M, 2.269 X 10^{-10} M, and 2.789 X 10^{-10} M, respectively.

2.2. Modified glassy carbon electrode (GCE) coated with integrated graphene aerogel-metal-organic framework (MOF) for simultaneous detection of multiple HMIs

In 2019, Lu et al. [28] invented a new method for electrochemical sensors based on GA and MOF to simultaneously detect the presence of different types of HMIs in aqueous solution. They had modified the GCE surface by coating with the GA-UiO-66-NH_2 (MOF). The hybridization method of GA-UiO-66-NH2 was conducted on the GA matrix by the in-situ growth of UiO-66-NH2 crystal. Using GA can further accelerate the electron transfer within the GA matrix and thus improve the composite's conductivity. The UiO-66-NH2 has been used as a receptor with a specific binding site to permit binding interaction between the HMIs and UiO-66-NH2. This sensor probe was capable of identification of HMIs such as Cd^{2+}, Pb^{2+}, Cu^{2+}, and Hg^{2+} in aqueous solution individually or simultaneously with the high specificity and sensitivity. HMIs detection was evaluated by using differential pulse stripping voltammetry (DPSV) operated at room temperature. The modified GCE was immersed in different concentrations of HMIs diluted in the acetate buffer to detect the HMIs.

The characterization of surface morphology formed on the modified GCE was observed under SEM and TEM, as shown in figure 3. Figure 3(A) shows the unique properties of GA that are porous structure have led to the formation of porous surfaces on the GCE. This porous structure, therefore, increases the surface area and the active binding site where binding interaction with functional group material was facilitated. The UiO-66-NH2 coated on the surface was then confirmed by observing under transmission electron microscopy (TEM), as shown in figure 1 B and D.

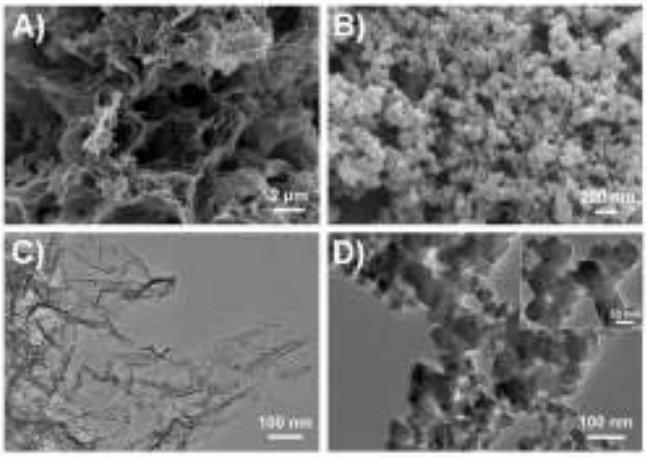

Figure 3: SEM images of (A) GAs, (B) UiO-66-NH2, and TEM images of (C) GAs, (D) UiO-66-NH2 [28].

In this experiment, they had tested the performance of this sensor probe to detect the HMIs individually. Based on the result obtained, for each HMIs resulted in different and specific potential value. The limit of detection for each HMIs were 0.02 µM for Cd^{+2}, 1.5 nM for Pb^{+2}, 7 nM for Cu^{+2}, and 2 nM for Hg^{+2}. This amount of detection was lower than the amount recommended by the World Health Organization (WHO) for drinking water [28].

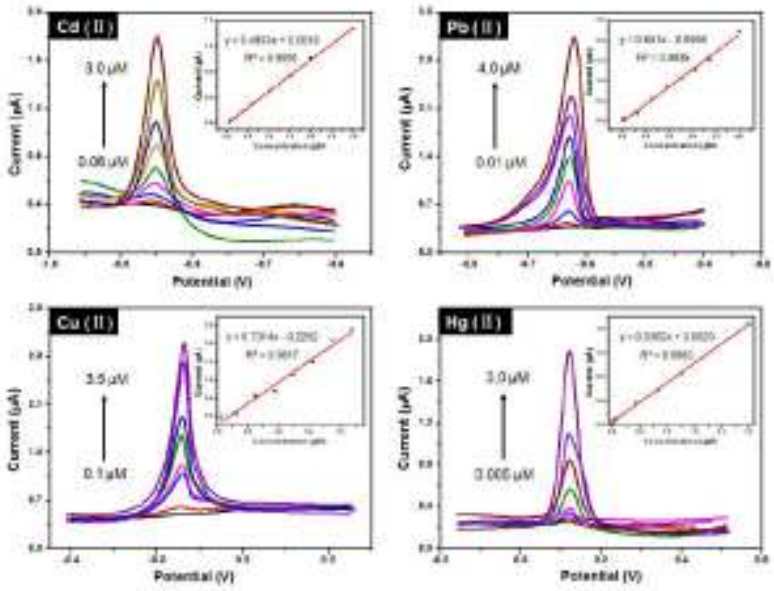

Figure 4: Detection of different HMIs individually [28].

This sensor probe was tested with various HMIs samples in aqueous solution. The potential value detected in simultaneous and individual performance was showed a similar result, as shown in figures 5 and 6.

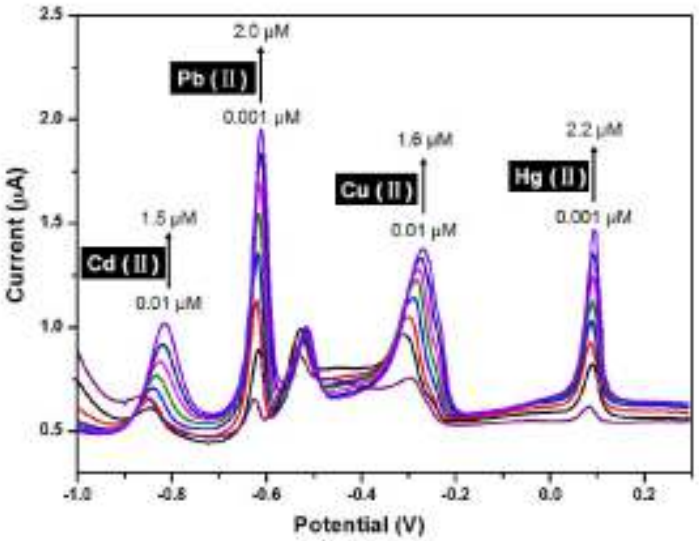

Figure 5: Detection of different HMIs simultaneously [28].

The limit of detection was 9 nM for Cd^{+2}, 1.0 nM for Pb^{+2}, 8 nM for Cu^{+2}, and 0.9 nM for Hg^{+2}. This experiment indicated that the potential of a MOF-electrochemical based sensor as a new platform for the detection of various HMIs simultaneously and applicable for onsite HMIs monitoring.

3. Conclusion

To understand their characteristics before implementing them in chemical sensing applications, the study of their chemical properties is vital. There is still great potential in the use of carbon-based material as a platform for electrochemical sensor probes at the moment. Nevertheless, the use of carbon-based material alone is insufficient for use in a matrix solution. The integration of carbon material with other biomolecules such as aptamers, deoxyribonucleic acid (DNA), enzyme, and antibody would specifically functionalize the carbon-based material and, therefore, increase the selectivity and sensitivity of the electrochemical sensor based on carbon in the detection of heavy metal ions.

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