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Optimisation of the GCE electrode Architectures based on MWCNT and Silver nanoparticles for Electrochemical Sensing of BPA

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***Abstract*—A novel electrochemical sensor for bisphenol A (BPA) comprising a functionalized multiwalled carbon nanotube (MWCNT) and a low cost Silver nanoparticle (AgNP) modified glassy carbon electrode (GCE) has been developed. The MWCNT was functionalized with carboxylate groups by nitric acid and was characterized by FT-IR . The electrochemical characterization of the developed sensor was investigated by cyclic voltammetry. Modified electrode architectures with MWCNT and different amounts of deposited AgNP layers were tested. Under the best experimental conditions, the sensor exhibited a linear response to BPA from 70nM to 6000nM, with a limit of detection of 40 nM. Finally, real samples tests in drinking water were tested.**

Keywords—BisphenolA, Carbon nanotubes, Silver nanoparticles, Electrochemical sensor

I. INTRODUCTION

Bisphenol A (BPA) is a chemical that is used in polycarbonate plastics, a high performance transparent, rigid plastic. It is also used to produce epoxy resins used to make protective coatings and linings for food and beverage cans and vats. BPA can migrate in small amounts into food and beverages stored in materials containing the substance, and have adverse effects,including cancers, diabetes, hypertension, obesity. In this context, the development of electrochemical sensors for the detection of BPA is a very important subject of research. Different analytical techniques have been used to this aim including high-performance liquid chromatography[1], liquid chromatography–mass spectrometry [2],molecular imprinting [3]… Recently, the electrochemical methods have boomed in convenient and effective detection of BPA with high sensitivity, simple operation, low cost, good selectivity and portability.

MWCNT have excellent conductivity, chemical stability, and large specific area. Carbon nanotube was used in nanoelectronics devise [4], batteries and as nanomaterial modifiers of the surfaces of electrochemical sensors [5]

Silver nanoparticles (AgNPs), is cheaper than other nanomaterials and has opened up new horizons for the development of electrochemical sensors with low cost and excellent electroanalytical performances. In this work, electrochemical sensor for BPA detection consisting of a functionalized MWCNT plus AgNPs modified glassy carbon electrode has been developed. The architectures of the modified were optimized, including the pH of the buffer solution, and MWCNT and AgNPs loading.

II. Experiments

Electrode preparation

The MWCNT were functionalized with carboxylate groups by nitric acid . The bare glassy carbon electrode surface was polished before each experiment with a powder of alumina of 1.0.3, 0.05 µm and was then washed thoroughly with distilled water. To improve the sensitivity of the sensor, the amounts of AgNPs was optimised and the concentration of MWCNT(0.2%) is chosen as it is mentioned previsiouly [5] . The MWCNT(0.2%)/GCE was prepared by casting 2 µL of MWCNT(0.2%) dispersion on the surface of the cleaned GCE and then dry it in the oven . For fabricating AgNPs/MWCNT/GCE, AgNPs suspension was deposited on the surface of MWCNT(0.2%)/GCE. Different assemblies were prepared consisting of 3, 5 or 7 layers of AgNPs on a MWCNT (0.2%)/GCE.

Results and discussion

A. Fourier transform infrared spectroscopy study

Fig.1 shows the FTIR spectrum of functionalized carbon nanotubes (MWCNT-COOH). The carbon nanotube shows a major peak at about 3436 cm^{-1}, this can be attributed to the hydroxyl group –OH [6] . The presence of a peak at 2900 cm^{-1} correspond to the aliphatic group (C-H) [6] . The wave number at 1554 cm^{-1} is due to the aromatic and unsaturated structure of the C = C bonds [7].

A characteristic C=O band of carboxyl functional group was observed at 1635 cm^{-1} [7] indicates that functional surface modification by nitric acid is successful.

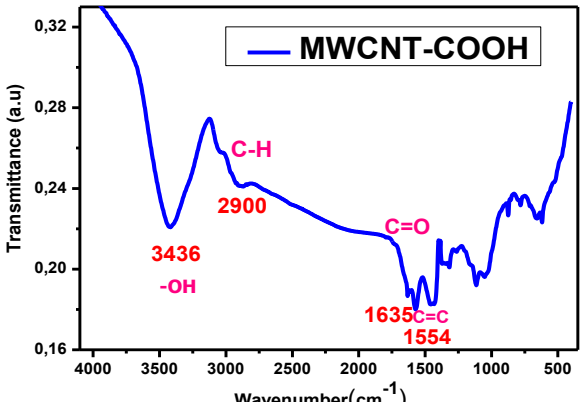

Fig.1. FTIR spectra of the functionalized MWCNT

B. Optimization of the modified electrode

In order to improve the sensitivity and to obtain a sensor with good performances with regard to BPA, we have studied different volumes of AgNPs and we have fixed a 0.2% MWCNT concentration as an optimal value found in our previous work [5]. In this context, we deposited on the surface of GCE (2µl) of the MWCNT suspension (0.2%). Subsequently, the number of layers of AgNPs deposited on the surface MWCNT (0.2) / GCE were optimized. In this context, 3, 5 and 7 layers of AgNPs were prepared on the surface of MWCNT(0.2)/GCE for each layer depositing 2µl of AgNPs. We notice that the best performance was obtained using the following structure AgNPs (3)/MWCNT(0.2)/GCE **(Table1)**.

Table 1.Optimisation of number of layer of AgNPs

Structure	Current (µA)
AgNPs (3) / MWCNT (0.2) / GCE	0.68
AgNPs (5) / MWCNT (0.2) / GCE	0.15
AgNPs (7) / MWCNT (0.2) / GCE	0.28

C. Characterization of the bare and modified electrodes

The GCE was characterized before and after each modification by CV in the presence of BPA.

Fig.2 shows the cyclic voltammetry measurements for Bare and modified electrode in the presence of BPA. At bare GCE electrode, the oxidation peak of BPA was the lowest.

For AgNPs (3)/MWCNT(0.2)/GCE, the property with respect to the electro-oxidation of BPA was further improved, which can be attributed to the excellent high conductivity and the high specific surface area of the AgNPs and MWCNT, which indicate that the AgNPs(3)/MWCNT nanocomposite greatly, facilitates the electron transfer between solution and electrode interface. This can be attributed to the synergetic effect of both nanomaterial modifiers.

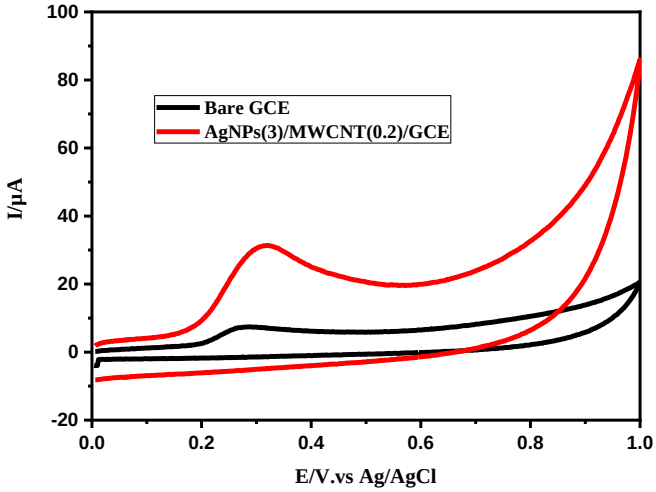

Fig.2. CV of bare GCE, and AgNPs (3)/MWCNT (0.2)/GCE.

D. Effect of the pH

The effect of pH on the electrochemical oxidation response of 20 µM BPA sensor was studied by cyclic voltammetry in the pH range from 5 to 9 **(Fig.3)**.

The current intensity increased gradually from pH 5.0 to 7.0, and then Decreases **(Fig.4)**, this behavior is also observed in [9]. In this work, pH 7.0 PBS was thus selected as the supporting electrolyte .

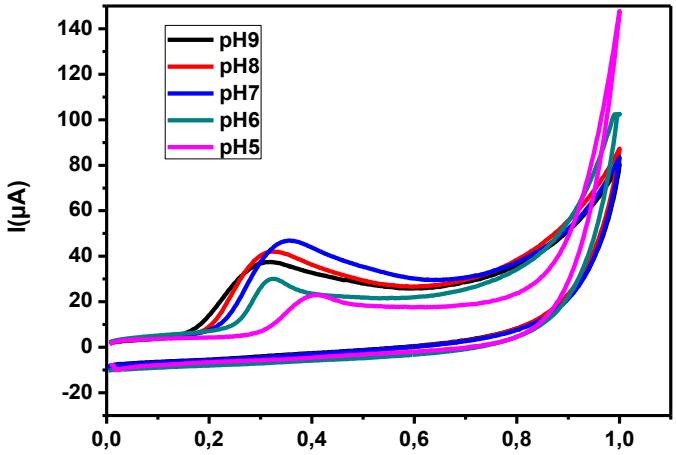

Fig.4. CV for AgNPs (3) / MWCNT (0.2) / GCE with different pH values: 5.6, 7, 8 and 9

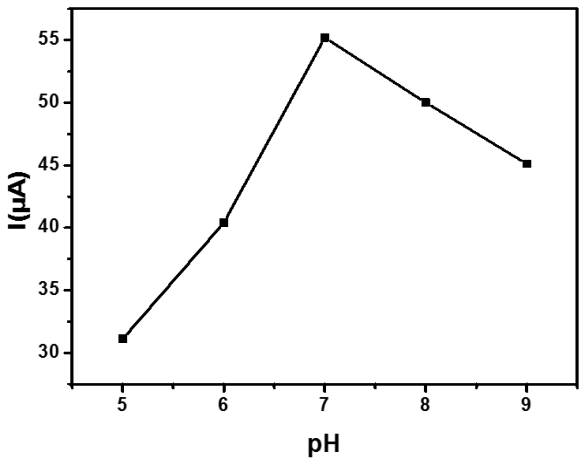

Fig.5. The plot of I (µA) vs pH

E. Cyclic voltammetry for different concentrations of BPA

The electroanalytical determination of different concentration of BPA using the configuration AgNPs (3)/MWCNT (0.2) / GCE, was performed by CV. The calibration curve constructed, exhibited a linear range from **70nM** to **6000 Nm** and a limit of detection of **40nM.**

F. Interferences and pratical application

Interferents tested were: ethanol, methanol, hydroquinone, phenol, Ca^{2+}, K^{+}, Na^{+} and Mg^{2+}, did not have significant influence, with deviation of less than ± 9% on BPA signals.

The present sensor was t ested to detect BPA in mineral and Tap water, The recovery was between 95 and 104% indicated that the sensor was adequate for real sample tests.

CONCLUSION

In this work, we are interested in the optimization of the modified eectrode architectures for electrochemical sensing of BPA for environmental application.

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