Synthesis of porphyrin- graphene oxide nanocomposite for an optical chemical sensor application

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Abstract

A specific and sensitive optical chemical sensor (optode) was fabricated for the determination of mercury ions. The optode was prepared by graphene oxide–porphyrin composite. The graphene oxide–porphyrin composite was synthesized and characterized by field emission scanning electron microscopy (FE-SEM), UV-Vis and Fourier transform infrared (FT-IR) spectroscopic techniques. The various experimental parameters such as pH of aqueous solution of Hg (II) and content of the THPP as well as the grapheme oxide have been optimized. This optode exhibited a linear range of 6.0×10^{-5} to 6.0×10^{-9} mol.L^{-1} Hg (II) with a detection limit of 3.2×10^{-9} mol.L^{-1} and a response time of ∼210 s.

Keywords:

Optical sensor, Graphene oxide nanosheets, Porphyrin, Mercury ions, Spectrophotometry UV-Vis.

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1. Introduction

Heavy metal pollution due to the indiscriminate disposal of wastewater is a worldwide environment concern. Wastewaters from many industries such as metallurgical, mining, chemical manufacturing, and battery manufacturing industries contain many kinds of toxic heavy metal ions. Mercury is a highly toxic heavy metal that causes human health problems and environmental contamination, and is also more toxic even from lead and arsenic. This metal represents a major toxicity to microorganisms and environment even in low concentrations. Mercury triggers several serious disorders for humans including allergic reactions and brain and neurological damage. If ingested by a pregnant woman, it can cause developmental delays in children. Therefore, the detection of very little amounts of mercury is extraordinarily important [1-4].

Design of control systems such as optical chemical sensors for determination of mercury in very low concentrations in water samples and rivers can be very useful and effective in the control and remove pollutants from the environment [1, 5]. In recent years, extensive research is allocated into optical chemical sensors. Optical chemical sensors used in different contexts such as environmental, clinical and industrial analysis. The use of optical chemical sensors, nutrients is very important particularly for the measurement of trace amounts of heavy metal ions in environmental samples. The application of optical chemical sensors is highly regarded especially for the determination of trace amounts of heavy metal ions in environmental samples, a variety of water and food [6-7].

Porphyrins have been studied as probe molecules in different materials and their application has been examined as detector for chemical sensors. Porphyrins are sensitive to metal ions. Nitrogen atoms in the structure of porphyrin ring is located inward, and with their only electron pairs can act as a strong ligand, and they keep the metal ions in the center and the formation a complexes [8-14]. Choosing a proper substrate and detector stabilizer, are a very important issue as another part of the membrane components in optical sensors. A proper grounds should be suitable functional groups to bind and detector stabilize on the plastic or glass fulcrum. Graphene Oxide with carboxyl functional groups, hydroxyl and epoxy on itself carbon surface, has been studied as a substrate and important factor to bind and stabilize detector on the Fulcrum [15-17]. Therefore, in this work, a specific and sensitive optical chemical sensor based graphene oxide–porphyrin composite was fabricated for the determination of mercury ions.

2. Experimental

2.1 . Chemicals

All reagents were prepared from analytical reagent grade chemicals supplied from Merck (Darmstadt, Germany), except $HgCl_2$ which was obtained from Aldrich. The 10^{-3} M mercury standard stock solution was prepared by dissolving 0.0811 g of $HgCl_2$ in a 250 mL volumetric flask and diluting to the mark with distilled water. Lower concentrations were prepared by serial dilution of the stock solution with phosphate buffer, pH 7.5 Universal buffer solutions (0.1 M) were prepared from phosphoric acid solutions and sodium hydroxide solutions and adjusting pH to the desired value (0.08 M). The final pH was adjusted with the addition of a sodium hydroxide.

2.2 . Synthesis of GO-THPP

2.2.1. Synthesis of THPP

Tetrakis (4-hydroxyphenyl) porphyrin (THPP) was prepared using a modification of A. D. Adler-f. R. Longo method [18]. Briefly in a typical reaction, 80 mL of propionic acid was loaded in a 250 mL round-bottomed flask and refluxed for 0.5 h. Then 1.146 g 4-Hydroxybenzaldehyde dissolved in 10 mL of propionic acid are added. After about 15 minutes the amount of 6.0 g of fresh distilled pyrrole was slowly added into the solution. After 45 min the mixture was placed at room temperature to precipitate formed. The dark purple product was filtered and washed thoroughly with ethanol until the filtrate became clear.

2.2.2. Synthesis of graphene oxide nanosheets (GO)

Graphene oxide was prepared using a modification of Hummers and Offeman's method [19, 20]. Briefly in a typical reaction, 1 g graphite, 1 g $NaNO_3$, and 46 mL H_2SO_4 were stirred together in an ice bath. $KMnO_4$ (8 g) was slowly added while stirring, and the rate of addition was controlled to prevent the mixture temperature from exceeding 20 °C. The mixture was then transferred to a 35 °C water bath and stirred for about 1 h, forming a thick paste. Subsequently, 80 mL de-ionized water was added gradually and the temperature was raised to 90 °C. The mixture was further treated with 10 mL 30% H_2O_2 solution. The solution was then filtered and washed with de-ionized water until the pH was 6 and dried at 65 °C under vacuum.

2.2.3. Synthesis of GO–COCl

Briefly in a typical reaction, 0.5 g GO–COOH was suspended in 30 mL $SOCl_2$ and 5 mL of DMF. The mixture was refluxed for 24 h at 70°C under nitrogen atmosphere. The resultant solution was filtered and washed with anhydrous tetrahydrofuran (THF) and dried under vacuum.

2.2.4. Synthesis of covalently attached porphyrin graphene oxide hybrids (GO-THPP)

Briefly in a typical reaction, a mixture of 30 mg GO–COCl and 60 mg THPP were taken in a 100 mL round bottom flask and 3 mL of triethylamine and 15 mL of DMF were added and heated to 80 ° C for 72 h under a nitrogen atmosphere. After the reaction, the solution was cooled to room temperature, and then poured into 250 mL diethyl ether to precipitate the product. The precipitate was collected by centrifuging at 8000 rpm for 30 min. The supernatant which contained dissolved THPP was discarded and the precipitate was washed thoroughly. After adding another 100 mL of diethyl ether, the mixture was sonicated for 5 min and then centrifuged at 8000 rpm for 30 min to collect the GO-THPP. Finally, the precipitate was washed with $CHCl_3$ five times following the above procedure.

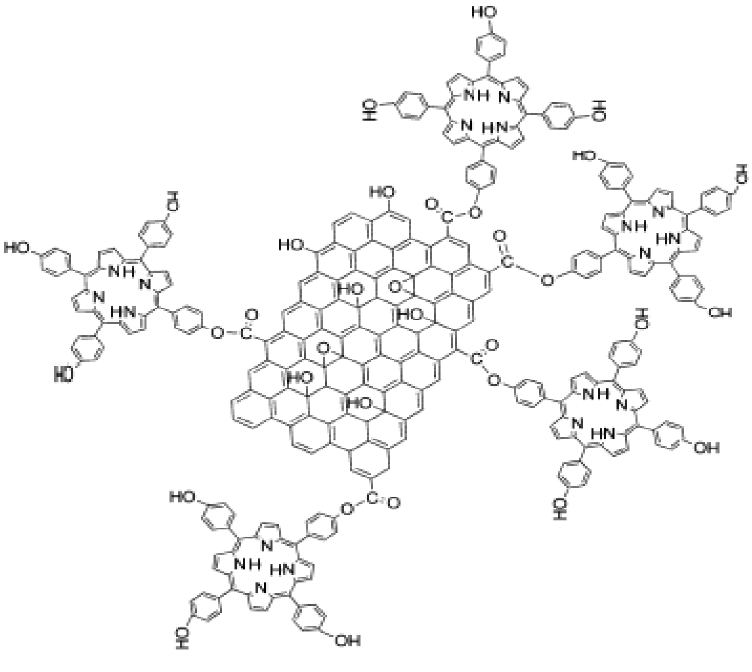

Fig. 1. The schematic illustration of GO-THPP

2.3. Structural and spectroscopic characterization of GO-THPP

The FTIR spectra were recorded using KBr plates in the range 500–4000 cm using a Nicolet 6700 FT-IR spectrometer. Fig. 2 shows the typical FTIR spectrum obtained for our graphite oxide material. The most characteristic features are the broad, intense band at 3430 cm^{-1} (O–H stretching vibrations) and the bands at 1725 cm^{-1} (C=O stretching vibrations from carbonyl and carboxylic groups), 1639 cm^{-1} (skeletal vibrations from unoxidized graphitic domains), 1380 cm^{-1} (C–OH stretching vibrations), and 1027 cm^{-1} (C–O stretching vibrations). The appearance of the peaks at around 2900 cm^{-1} is ascribed to the aromatic stretching vibrations of C–H bonds of GO. After covalent functionalization with porphyrins, a new peak appears at ~ 1582 cm^{-1} corresponding to the C=C vibrations of porphyrins and the peak of the C–O stretching vibration shifts to 1108 cm^{-1} ,and broadens. The peak present at ~1707 cm^{-1} is assigned to the bending vibration of the C=N of the porphyrin ring. The disappearance of the peak at 1380 cm^{-1} clearly indicates that in graphene oxide–porphyrin composites, the porphyrin molecules are covalently bonded to the graphene oxide via carboxylic acid linkage.

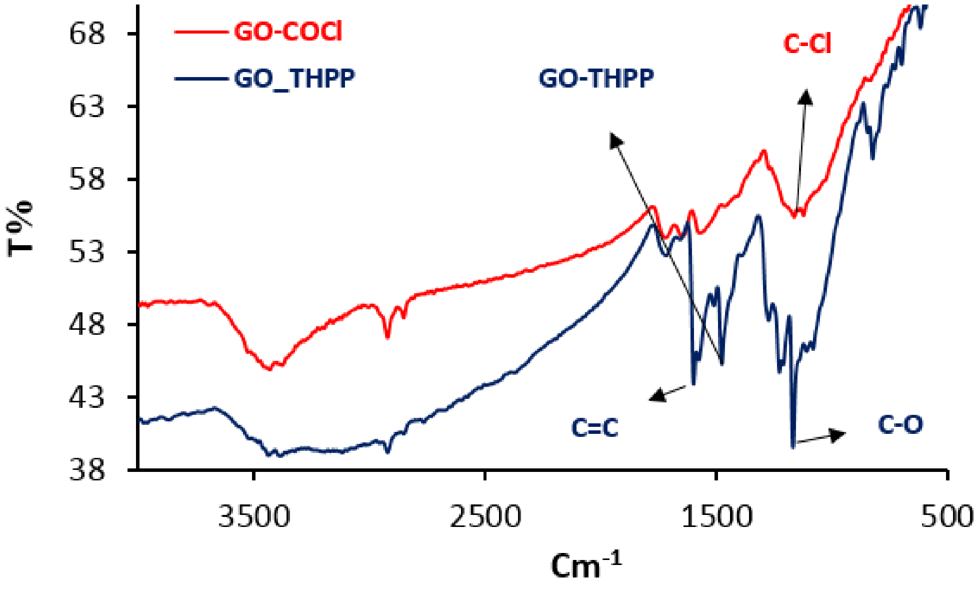

Fig. 2. FT-IR spectrum of graphene oxide and porphyrin–GO composites

The SEM image (Figure 3) shows that few layered graphene oxides are formed, although the SEM image does not estimate the layer numbers of the graphene oxide nanosheets exactly. Pure graphite exhibits ordered flakes of a 4–5µm range. The scanning electron micrograph for the GO–porphyrin hybrid materials (Fig. 3 B) demonstrates that a homogeneous system with a micrometer order of magnitude was obtained. On functionalization, GO exhibits a three-dimensional network of randomly oriented sheet-like structures with a wrinkled texture and hierarchical pores with a wide size distribution

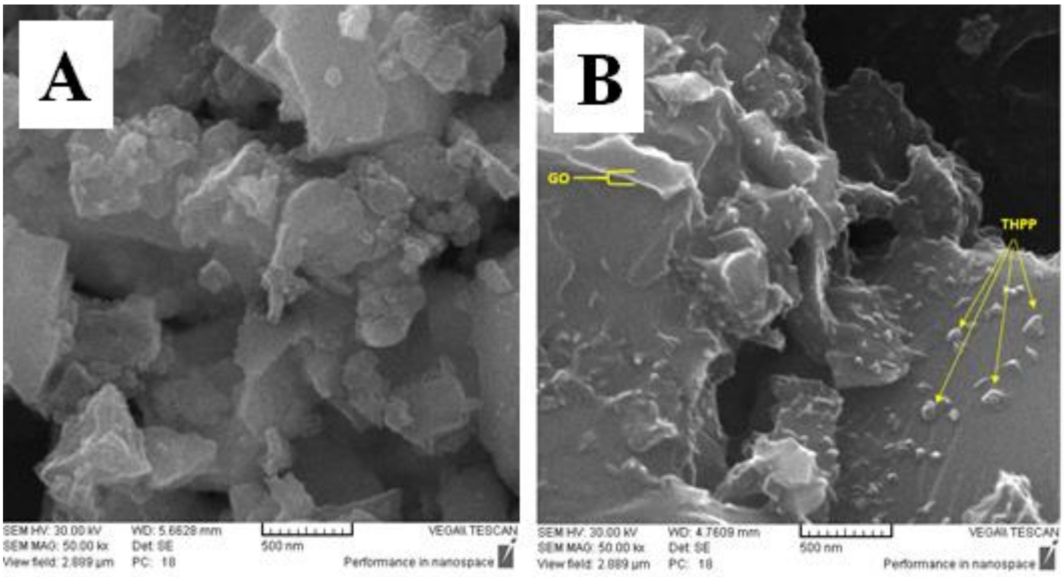

Fig. 3. SEM images of A) graphene oxide nanosheets and B) graphene oxide-porphyrin composites.

The optical absorption measurements were carried out by UV-Visible spectrometry. Fig. 4 shows optical absorption spectra of graphene oxide–porphyrin composites which agrees with the literature value.

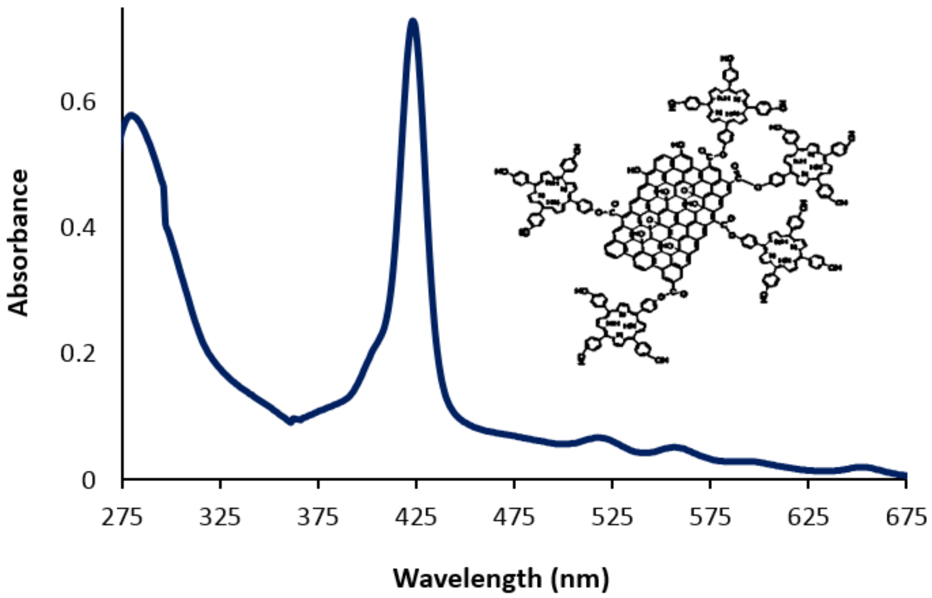

Fig. 4. UV/Vis spectrum of graphene oxide–porphyrin composites in DMF**.**

2.4. Membrane preparation

A mixture of 0.6 mg graphene oxide–porphyrin composites, was dissolved in 1.0mL of DMF. The membrane solution was homogenized with a magnetic stirrer for 15 min. A Plexiglas slides with 9 mm × 40 mm dimensions were cut to fit into standard spectrophotometer cells. The slides were cleaned with ethanol, then water and finally dried in an oven at 70 °C. The membranes were cost by pipetting 10 µL of the membrane solution onto a Plexiglas slide and spread it by a spin coater was deposit uniform thin films to flat substrates.

2.5. Measurement procedure

The membrane was conditioned by inserting it into a cell including 3 mL of phosphate buffer (pH 7.5). After 5 min the membrane absorbance was measured at 426 nm. Then, the cell was filled with the Hg (II) standard solution and after 210 s its absorbance was measured in the same wavelength

3. Results and discussion

3.2. Principle of the operation

Tetrakis (4-hydroxyphenyl) porphyrin (THPP) contains a nitrogen donor atom which could form internal bonds with soft metal ions such as mercury (II). THPP has high affinity to make a complex with mercury (II) ions. Mercury (II) ions form a complex with the ligand when the organic membrane contacts with the aqueous solution; therefore, the following ion-exchange reaction takes place:

$$H_2\,(L)_{(m)} + Hg^{2+}{}_{(aq)} \leftrightarrow (L)Hg_{(m)} + 2H^{+}{}_{(aq)} \qquad (1)$$

In this equation, ‘L’ is the Ligand. It can be seen that by the addition of mercury ions into the aqueous solution, the chromoionophore in the organic membrane is more deprotonated. Fig. 5 shows the absorption spectra of the optode with different concentrations of Hg (II) in the range 1.0×10^{-14} to 1.0×10^{-3} mol L^{-1} .

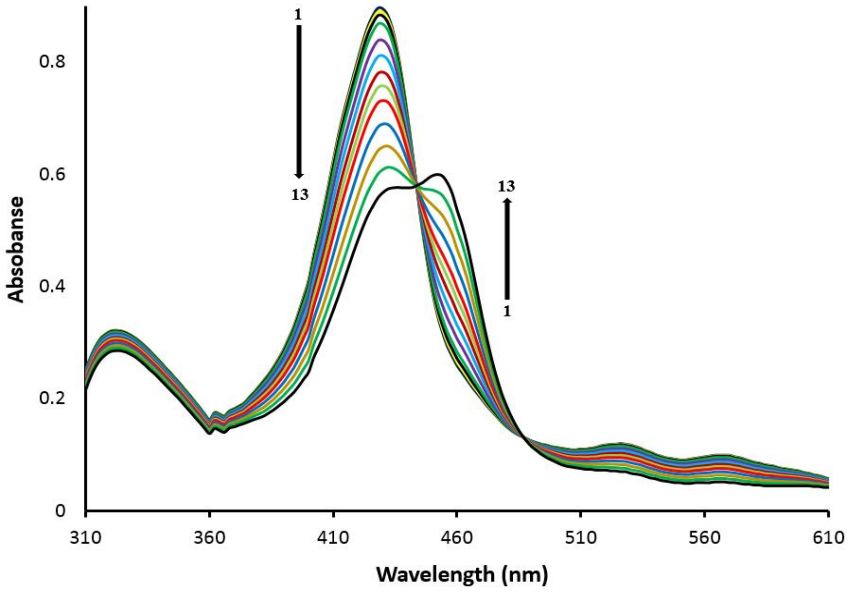

Fig. 5. Absorption spectra of the optical sensor in phosphate buffer solution (pH 7.5)containing different concentrations of Hg(II) as: 1) Blank solution (buffer); 2) 1.0×10^{-14}; 3) 1.0×10^{-13}; 4) 1.0×10^{-12}; 5) 1.0×10^{-11}; 6) 1.0×10^{-10}; 7) 1.0×10^{-9}; 8) 1.0×10^{-8}; 9) 1.0×10^{-7}; 10) 1.0×10^{-6}; 11) 1.0×10^{-5}; 12) 1.0×10^{-4}; 13) 1.0×10^{-3} mol.L^{-1} Hg(II).

4. Conclusion

In this work a new composites was synthesized based on the tetrakis (4-hydroxyphenyl) porphyrin (THPP) stabilized with graphene oxide as compound for the designs optical chemical sensor. The optode described in this work is easily prepared and provides a simple and inexpensive means for the determination of ultra-trace amounts of Hg (II) ions. Based on the results, it is clear that the determination of Hg (II) ions with optode prepared from graphene oxide–porphyrin composites were a selective and sensitive methods. The amount of mercury was measured in different water samples by the optode and also by ICP method. The results confirm that there was not any significant difference between the results.

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