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# Sensitive methanol sensor based on PMMA-G-CNTs nanocomposites deposited onto glassy carbon electrodes

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ABSTRACT

A new series of polymethyl methacrylate–graphene–carbon nanotubes crossbred nanocomposites in the form of PMMA-G-CNTs has been synthesized using simple dissolution procedure in organic media. The desired nanocomposites have been prepared using different loading (2∼30%) from consequently mixed GNPs/CNTs ratio and confirmed by various characterization techniques utilized to corroborate the assembly of these new hybrid series including X-ray diffraction analysis, Fourier transform infrared spectroscopy and scanning electron microscopy. The PMMA-G-CNTs nanocomposites were deposited on flat glassy carbon electrodes (GCE) to result in a sensor that has a fast response toward methanol in the phosphate buffer phase. Features including high sensitivity, low-sample volume, reliability, reproducibility, ease of integration, long-term stability, and enhanced electrochemical responses are investigated. The calibration plot is linear ($r^2$=0.9895) over the 1.0 nmol $L^{-1}$ to 10.0 mmol $L^{-1}$ methanol concentration ranges. The sensitivity and detection limit is 13.491 μA $cm^{-2}$mmol $L^{-2}$ and 0.39 ± 0.1 nmol $L^{-1}$ (at a signal-to-noise-ratio, SNR of 3), respectively. With such excellent features of analytical parameters, the developed sensor provides a new strategy for determination of methanol in biomedical and environmental analytes with satisfactory results.



## 1. Introduction

Poly(methyl methacrylate) (PMMA) is an interesting amorphous thermoplastic synthetic polymer. PMMA is known as acrylic-glass owing to the transparency and chemical stable properties. PMMA is a brittle and easily scratched polymer compared with conventional inorganic glass, which properties were improved by physical or chemical modification of PMMA. The easy and low-cost fabrication of PMMA makes it suitable for many bioengineering applications including the fabrication of artificial cornea [1], micro-patterning for culture of cortical astrocytes [2], and stents for growing tissues of osteoblast [3] so on. Among different fabrication processes of PMMA such as gelation, injection and casting, plasma polymerization is one capable of rapidly depositing uniform nano-scale films on almost any substrates of various geometry [4–6]. Furthermore, modified PMMA with enhanced mechanical performance has been attempted through the formation of strong and transparent polymer composite materials [7–9].

Recently, there has been growing attention in toxic investigation, especially for hazardous chemicals, due to concerns regarding environmental safety and human health. Methanol is an organic solvent, which is broadly applied in many industries and research laboratories for R&D purposes. Long-term exposure to MeOH vapor can result in diseases such as eye-sight trouble, nerve disease and possibly even death. Hence the determination of methanol in liquid phase is an important by simple and reliable methods. Generally, methanol uses as organic solvent with extensive utilizations in automotive fuels as well as developing of colored materials, dyes and pigments, drugs and medicines, aromas and perfumes, formaldehyde and other chemicals etc, which is highly toxic, carcinogenic, and often serious to human health and environments [10–12]. Owing to its large-scale of applications, toxicity and clinical applications, the improvement of a simple and reliable methanol sensor has become essential. The conducting polymer nanocomposite with grapheme and carbon nanotubes has attractive properties such as large-surface area, non-toxicity, chemical-stability, chemical activities, and high-conductivity, which provided high-electron communication features that promoted direct electron transfer towards the

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target chemicals. Generally, it was also demonstrated that nanocomposite materials such as porous-frameworks of grapheme or CNTs can offer large surface-area, permanent-porosity, high thermal-stability, and potential improvement of selective and sensitive chemical sensor performances. As methanol is highly toxic and generally critical to human-health as well as environment, it is urgently required the development of a simple and reliable methanol sensor using PMMA-G-CNTs nanocomposites. Mainly, nanocomposites based sensors owing to their many particular advantages over the conventional methods, such as high response, low charge, and portability, are widely employed for the detection of contaminated or toxic pollutants, chemical process control, and monitoring of air/water contamination in the environment [13–15]. Removal of methanol from industrial wastewater or effluents is one of the most important issues in environmental and health fields. Various methods were developed for the removal of carcinogenic compounds from industrial water effluents. There are some issues still remaining unsolved such as facile and low-cost green preparation of the nanocomposites material, removal efficiency in hazardous methanol compounds, and facile reusability of the stable nanocomposite materials. In addition, the mesoporous nature of the nanocomposites material allows its facile recycling without significant loss of sensor efficiency. The excellent adsorption/absorption capacity of the nanocomposites, together with other advantages such as its reusability, easy separation, and environmentally friendly composition, makes it a suitable sensor for removal of target methanol from environmental and industrial wastes. In this approach, it was employed a simple technique to prepare PMMA-G-CNTs nanocomposites aggregation with virtually controlled morphology, which revealed a steady growth assembly in composites and their prospective applications. For PMMA-G-CNTs nanocomposites, it was an excellent chemical sensing application to confirm the electrical properties as well as improve the development of frequent electronic and optoelectronic materials [16–19]. PMMA-G-CNTs nanocomposites permit very sensitive transduction of the liquid/surface interactions to modify in the structural, optical and chemical properties. The significant feature is to accomplish a variety of morphological arrangements offer different methods of modification of the toxic chemical sensing property. A low-cost, portable and reliable methanol sensor with high sensitivity, selective and fast response features is required for the current materials of sensor monitoring, especially the water or environmental pollution control in liquid phase and timely detecting of ultra concentrations. In this approach, PMMA-G-CNTs nanocomposites were used to fabricate a simple and efficient chemical sensor and assessed the selective chemical sensing performances considering the target methanol analyte at room conditions. To the best of our knowledge, this is the first report for detection of target methanol with prepared mesoporous PMMA-G-CNTs nanocomposites using simple, convenient, and reliable *I–V* technique in short response time.

## 2. Experimental section

### 2.1. Materials and methods

Graphene nanoplatelets (GNPs) and multi-wall carbon nanotubes (MWCNTs), with an average diameter of (110–170) nm, both were purchased from Sigma-Aldrich Company and were used as extradited without any further purification. White polymethyl methacrylate (PMMA) was purchased from PDH company and also used as received. Ethyl acetate reagent ACS, spectroscopic grad (99.5%) was purchased from ACROS organics and used as solvent for different synthesized formulations. Monosodium phosphate, methanol, butyl carbitol acetate, disodium phosphate, ethyl acetate, dichloromethane, acetone, chloroform, ethanol, ammonium hydroxide, formaldehyde, and all other chemicals were in analytical grade and purchased from Sigma-Aldrich Company. The X-ray diffraction analysis (XRD) with powder X-ray diffractograms were determined in $2\theta$ range from 10–80° with the support of Philips diffractometer (type PW 103/00) using the Ni-filtered CuKα radiation. Fourier transforms infrared spectroscopy (FT-IR), FT-IR spectra were examined by using ATR smart part technique in the wave-number range 4000–400 $cm^{-1}$ using Thermo-Nicolet-6700 FT-IR spectrophotometer. The Field-emission scanning electron microscopy (FESEM) for the morphological features was characterized by FESEM (JEOL JSM-7600F, Japan). The FESEM samples were prepared by evaporating a dilute solution of each nanocomposite on a smooth surface of aluminum foil, and subsequently coating it with gold–palladium alloy. The microscope was operated at an accelerating voltage of 2.0 kV and 10.0 mm work distance carbon film. *I–V* technique (two electrodes; GCE and Pd-wire) is measured by using Keithley-Electrometer from USA.

### 2.2. Synthesis of PMMA-G-CNTs nanocomposites

A new series of PMMA-G-CNTs hybrid nanocomposites was synthesized using simple dissolution process in organic solvent as the following: for each formulation 1.0 g of pure PMMA was poured onto nearly about 50.0 mL of ethyl acetate and stirred under magnetic stirrer for 15 min. Mixed GNPs/CNTs ratio of (40/60%) was used as fixed ratio and prepared by mixing GNPs and CNTs in the ratio of 40–60%, respectively. Different loading (2–30%) of the previously mixed GNPs/CNTs was added one portion to the previous solution at the stirring speed of 800 rpm at 60.0 °C. this process was allowed for 6 h and followed by solvent evaporation in Petri dishes for at least 24 h at room temperature. The obtained products were dried under vacuum (5 and 10 Torr) for 10–12 h at 50.0 °C. The suggested symbols for the different mixed loading for PMMA-G-CNTs nanocomposites were clarified in Table 1.

### 2.3. Fabrication and detection technique of methanol with PMMA-G-CNTs nanocomposites

Rod-type GCE (Diameter: 0.2006 cm; Surface area, 0.0316 $cm^2$) was fabricated with PMMA-G-CNTs nanocomposites (2.0 μg) using butyl carbitol acetate (BCA; 2.0 μg) and ethyl acetate (EA, 10.0 μL) as a conducting coating agent. Then PMMA-G-CNTs/GCE film (thickness is 1.0 μm) is kept in the oven at 40.0 °C for three hours until the film is completely dry and uniform. 0.1 mol $L^{-1}$ phosphate buffer solution (PBS) at pH 7.0 is made by mixing of unimolar concentration of 0.2 mol $L^{-1}$ $Na_2HPO_4$ and 0.2 mol $L^{-1}$ $NaH_2PO_4$ solution in 100.0 mL de-ionize water. PMMA-G-CNTs/GCE as a working and Pd-wire were worked a counter electrode respectively. As received methanol (99.9%) is diluted to make various concentrations (0.1 nmol $L^{-1}$ to 1.0 mol $L^{-1}$) in DI water and used as a target analyte. 25.0 μL of target analyte solution is dropped into the 5.0 ml PBS during each sample measurements. The ratio of voltage versus current (slope of calibration curve) was used to measure of methanol sensitivity. Detection limit is

**Table 1**
Loading and symbols for PMMA-G-CNTs nanocomposites.

| Symbol | (GNPs/CNTs) loading (weight), % |
|---|---|
| **PMMA (pure)** | – |
| **PMMA-G-CNT$_a$** | (0.02 g), 2% |
| **PMMA-G-CNT$_b$** | (0.05 g), 5% |
| **PMMA-G-CNT$_c$** | (0.10 g), 10% |
| **PMMA-G-CNT$_d$** | (0.20 g), 20% |
| **PMMA-G-CNT$_e$** | (0.30 g), 30% |