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Impedometric phenol sensing using graphenated electrochip

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ABSTRACT

The manuscript reports impedance based sensing of phenol using electrochemically reduced graphene oxide (E-rGO) modified screen printed electrode (SPE). The chemically synthesized graphene oxide (GO) was reduced electrochemically directly on the electrode surface. The E-rGO was characterized using various analytical techniques like UV–vis spectroscopy, Transmission electron microscopy (TEM), Atomic force microscopy (AFM), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR) and contact angle measurement, to get insight to its properties. The SPE/E-rGO was then used for the detection of phenol using impedance spectroscopy. Prior to impedance based phenol sensing, the mechanism of phenol oxidation was examined using differential pulse voltammetry (DPV), which showed presence of three well defined peaks at 0.62 V, 0.24 V & 0.004 V, corresponding to the oxidation of phenol, and its oxidation products. As a function of phenol concentration, the increase in oxidation current followed the linear equation having slope of -1.76×10^{-9} A/μM and intercept of -4.69×10^{-7}, with regression coefficient of 0.996. For impedometric sensing, change in polarization resistance with change in phenol concentration was used as a signal and the dynamic linearity range was obtained from 1 μM to 40 μM. The linearity curve exhibited slope of $-7.6\ \Omega\text{cm}^{-2}\ \mu\text{M}^{-1}$, intercept of 986.67 and regression coefficient (R^2) of 0.989 respectively. The effect of solution pH on impedometric response of graphenated electrochip was also evaluated. The impedometric results of phenol sensing were further validated using amperometery using same concentration range (1 μM to 40 μM) of phenol. The amperometry results obeyed the linear equation with slope of −0.06 A/M (ampere/molar), intercept of −13.98, and regression coefficient (R^2) of 0.99. The graphenated electrochip exhibited good reproducibility and selectivity towards the analyte and offers greater ease of use.

1. Introduction

Phenol is a protoplasmic poison that has a virulent impact on all living organisms like plants, animals and humans [1]. Its existence in the environment is mostly from industrial wastes like from coal and petroleum industry, resins and plastics industry, dye and chemical industry, to name a few and sometimes from natural activities also [2]. If it enters drinking water and is present in exuberance, it gives unpleasant taste to the drinking water even at minute concentration and can enter the body by ingestion or through contact with the skin [3]. Phenol shows incredible affinity for nervous system and high concentration of phenol can likewise bring about nervous system injuries [4,5]. As a result, it has been incorporated into the list of priority pollutant by numerous nations. The permissible limit of phenol in natural water is 0.001 ppm [6].

Conventional techniques like spectrophotometry [7], capillary electrophoresis [8], chromatography [9] and electrochemical technique [10] are being used for evaluation of phenol concentration in water. But majority of these techniques are laboratory oriented, and require complex instrumentation. As a result, such techniques remain in limited accessibility and can not be used at houses for quality assurance of drinking water.

The electrochemical impedance spectroscopy (EIS) though not very frequently employed for chemical sensing, but it is inherently capable of facilitating more precise data as compared to conventional electrochemical techniques like voltammetry, etc. However, for any sensor/transducer, the electrode modifying material is of the outmost importance for ensuring the sensitivity. Among numerous materials employed for sensing applications, the graphene oxide has gained massive interest in scientific community [11,12]. Its honeycomb like structure having closely packed sp^2-bonded carbon atoms makes it a potential material for applications like field-effect transistors [13], batteries [14], nano-electronics [15], ultrasensitive sensors [16], electromechanical resonators

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[17], fuel cells [18] and supercapacitors [19]. For electrochemical prospective, the graphene and its derivatives like reduced graphene oxide, have been shown to effectively increase the redox currents by contributing to the charge transfer and mass transfer processes. This is feasible due to its high porosity and interface surface area.

Among various methods opted for synthesis of graphene or reduced graphene oxide, researchers are now paying enormous interest towards electrochemical reduction of graphene oxide to form reduced graphene oxide (rGO) [10]. The rGO can be defined as a derivative of graphene that has been partially reduced. The carboxyl and alcohol groups likely to be present on its surface act as binding sites for chemical sensing. In this work, impedometric sensor has been fabricated using electrochemically reduced graphene oxide (E-rGO), which has been used for phenol detection. The chemically synthesized graphene oxide was reduced electrochemically, directly on the surface of screen printed electrode (SPE), the advantage of which is fast reaction, minimal usage of toxic chemicals and direct deposition on electrode surface. Therefore, the resulting material do not get contaminated [20]. The E-rGO modified SPE has been referred to 'graphenated electrochip' in the manuscript. The graphenated electrochip presented significant response towards phenol sensing both in standard solutions as well as in real samples. The change in the electrical impedance is observed to be dependent on the phenol concentration from 1.0 μM to 40 μM. The electrochip is easy to use and fabricate.

2. Experimental details

2.1. Materials

Graphite powder, potassium permanganate ($KMnO_4$), potassium ferricyanide ($K_3[Fe(CN)_6]$) and potassium ferrocyanide ($K_4[Fe(CN)_6]$) were obtained from Loba Chemie Pvt. Ltd., Mumbai, India. Sulfuric acid (H_2SO_4), hydrochloric acid (HCl), phosphoric acid (H_3PO_4) and hydrogen peroxide (H_2O_2) were procured from Merck Millipore, Mumbai, India. Sodium nitrate ($NaNO_3$) was obtained from S.D. Fine-Chem Ltd, Mumbai, India. Phenol, cresol, benzene, toluene, nitro-phenol were procured from Himedia, Mumbai, India. All chemicals were used as received.

2.2. Instrumentation

The electrochemical synthesis of E-rGO and its electrochemical characterization was done on electrochemical analyzer from CH Instruments, Model CHI-1100, USA (http://www.chinstruments.com) using carbon coated screen printed electrodes (SPE) from Zensor, Taiwan. The electrochemical impedance spectroscopy (EIS) studies were done on CHI 660C impedance analyzer (CHI Instruments Inc., USA). For TEM, absorbance and FTIR studies, the electrochemical reduction was done on indium tin oxide (ITO) coated glass plates (1 cm × 1.5 cm). The ITO was used as a working electrode, Ag/AgCl as reference electrode and platinum wire as an auxiliary electrode. The E-rGO got deposited on conductive ITO surface in the form of black film. Before using, ITO glass plates were sequentially cleaned by ultrasonic cleaning in ethanol, isopropyl alcohol and DI water for 10 min each, followed by drying in vacuum. The absorbance was measured on UV–vis spectrophotometer (Hitachi, U 3900 H, Japan) in transmittance mode. For FTIR studies, the film was scraped off from the ITO surface, and was crushed to make its fine powder. This fine powder was mixed with moisture free KBr to make pellets. The spectra were recorded on Varian FTIR system (600 series, USA). For TEM imaging, the sample was dissolved in chloroform and was sonicated for 10 min. The drop of this solution was put on copper grid for TEM imaging and the solvent was allowed to dry. The Energy Dispersive X-ray Spectroscopy (EDAX) was done on the instrument from Oxford, model-Incax-act, 51-ADD0013. The contact angle measurements were performed on DSA 100, (Kruss, Germany), using sessile-drop technique and used water droplet as test liquid. A drop of de-ionized water was placed on the surface of GO and E-rGO modified electrodes and measured its angle of contact with electrode surface. The analysis was performed using 'ADVANCED' software and the snapshots of droplet formation on electrode surface were taken by in-built camera. The Raman spectra of GO and E-rGO were attained using Raman analyzer from Renishaw (UK). The atomic force microscopic (AFM) images of GO, and E-rGO were recorded on Parks Systems XE-AFM, Korea. The pH measurements were performed on a digital pH meter (PICO pH Meter, LabIndia Analytical Instruments Pvt. Ltd., India).

2.3. Synthesis of graphene oxide

The graphene oxide (GO) was prepared using modified Hummer method [21,22]. Briefly, 5.0 g of graphite powder and 2.5 g of sodium nitrate ($NaNO_3$) were mixed in 108.0 mL of sulfuric acid (H_2SO_4) and 12.0 mL of phosphoric acid (H_3PO_4), followed by stirring in an ice bath for 10 min. Subsequently, 15.0 g of potassium permanganate ($KMnO_4$) was slowly added maintaining the temperature of the mixture below 5 °C. The suspension was then left in an ice bath for 2 h to react, followed by stirring for 60 min in water bath at 40 °C. The temperature of the mixture was maintained at 98 °C for 60 min while water was added continuously with stirring. The final volume was made 400 mL by adding de-ionized water. After 5 min, 15.0 mL of hydrogen peroxide (H_2O_2) was added with constant stirring. The reaction mixture was centrifuged and washed with deionized water and 5% HCl solution repeatedly. Later, the reaction product was dried at 60 °C for overnight in a heating oven.

2.4. Synthesis of electrochemically reduced graphene oxide (E-rGO)

The electrochemical reduction of graphene oxide was performed on screen printed electrode (SPE). Before electrochemical experimentation, the electrode was washed several times with deionized water and was air dried. Simultaneously, graphene oxide powder was dispersed in deionized water having concentration of 1 mg/mL. The SPE was connected to potentiostat and reduction parameters were set. Subsequently, 5.0 μL of graphene oxide suspension was dropped on SPE surface using micropipette and run the reduction using cyclic voltammetry. The potential was cycled from 0.0 V to −1.2 V (vs Ag/AgCl) at scan rate of 100 mV s^{-1} for 20 cycles. For E-rGO synthesis on indium tin oxide (ITO) coated glass plate, the ITO was used as working, Ag/AgCl as reference electrode and platinum wire as an auxiliary electrode. The electrode set up was dipped in colloidal solution of graphene oxide and experiment was run. The SPE after E-rGO deposition is termed as graphenated electrochip for reference in the manuscript.

2.5. Electrochemical sensing of phenol

The electrochemical sensing of phenol was accomplished using electrochemical impedance spectroscopy (EIS). The stock solution of phenol (10 mM) was prepared in phosphate buffer (pH-7.0). The dilute aliquots were also prepared in buffer. The electrochemistry of phenol was studied using differential pulse voltammetry (DPV) before quantitative estimation using impedance. For DPV measurements, 10 μL of the phenol solution (40 μM) was dropped on the surface of graphenated electrochip. The potential was run from 0.9 V to −0.2 V at scan rate of 50 mV s^{-1}. For impedance experiments, the frequency range was from 1.0 Hz to 10^5 Hz and amplitude was 10 mV. On the basis of DPV results, the impedance detection of phenol was performed at constant potential of 0.62 V