Structural, morphological and sensing properties of layered polyaniline nanosheets towards hazardous phenol chemical

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ABSTRACT

Reliable sensing properties towards hazardous phenol chemical were detected by the novel working electrode of layered polyaniline (PANI) nanosheets. The layered PANI nanosheets were synthesized by the chemical polymerization of aniline monomer in the presence of hydrochloric acid and ammonium persulphate at 5 °C. The morphological, structural, optical, electrical and electrochemical properties of layered PANI nanosheets were extensively studied. The electrochemical behavior of layered PANI nanosheets based electrode was demonstrated by the electrochemical impedance spectroscopy (EIS) and cyclovoltametry (CV) measurements. The layered PANI nanosheets electrode showed reasonably good electrocatalytic activity towards the detection of phenol chemical, which resulted from the high redox current and low R_{CT}. The current–voltage (I–V) characteristics were used to elucidate the sensing parameters of the fabricated phenol chemical sensor with layered PANI nanosheets electrode. The fabricated phenol chemical sensor with layered PANI nanosheets electrode significantly attained the high sensitivity of $\sim$1485.3 μA mM^{-1} cm^{-2} and the detection limit of $\sim$4.43 μM with correlation coefficient (R) of $\sim$0.9981 and short response time (10 s).

1. Introduction

Phenol and phenolic compound are widely used chemicals in plastics, fertilizers, paints, rubber, adhesives, paper and soap industries [1]. It is also used as an antiseptic, a topical anesthetic for sore throat lozenges and sprays as a skin exfoliant [2]. The excess concentration of phenol and phenolic compounds is an issue of environmental concern due to their toxicity and persistence or high adsorptive nature in the environment [3]. Phenol if ingested in excess by human body could cause nausea, vomiting, sweating, diarrhea, excessive salivation and headache [4]. The acute exposure to phenol and its derivatives might also cause gastrointestinal irritation, cardiovascular, central nervous system and respiratory effects [2,5]. The detection, identification and the quantification of phenol and its compounds are very important for clean environment. For the detection of phenol, several analytical techniques like gas chromatography [6], high performance liquid chromatography [7], capillary electrophoresis [8] and spectrophotometry [9] are used so far. The major drawbacks of these analysis methods are time-consuming, complex to perform and not easy to operate under in-situ monitoring which limits the practical applications.

Electrochemical methods are the most adopted technique due to the advantages associated with its high sensitivity, greater selectivity, time efficiency, and reproducibility [10].

A unique organic p-type semiconductor polymer, polyaniline (PANI) is highly searched polymer due to its unique acid–base chemistry, stable electrical conduction, high-environmental stability and ease of fabrication [11–13]. Importantly, PANI possesses the typical conjugated bonds in the polymer skeleton which could be responsible for the charge conduction due to the generation of polarons or bipolarons [14]. The variable conductivity makes PANI as promising material for the specific application of electronics, optoelectronic, electrochemical, electrochromic, photovoltaic and sensing devices [15]. Moreover, the presence of the reactive –NH-groups in the polymer chain (PANI), positioned on either side by phenylene rings imparts the chemical flexibility to the system and improves the processibility to a large extent. PANI nanomaterial shows the versatility of nanostructures in the form of nanofibers, nanorods, nanowires and nanoflakes with high surface/volume ratio and low diffusional resistance [16]. Various PANI nanostructures display the improved optical, structural, electronic and electrical properties which might act as useful candidate for the application in electrochemical, electrochromic, biosensors and chemical sensors devices [17–18]. Recently, PANI nanomaterials have gained a great attention in the field of sensors including gas sensor, biosensor and chemical sensors [19]. In context of PANI based sensors, Kukla et al. prepared PANI thin films for detecting ammonia [20].

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Bo et al. explained the electrochemical DNA biosensor by PANI nanowires modified graphene electrode [21]. Recently, Kunzo et al. fabricated the hydrogen sensor based on unique oxygen plasma treated PANI thin film [22]. Till date, very few reports are available on phenol sensor using PANI nanomaterials. An amperometric phenol biosensor based on PANI electrode was studied in the aspects of optical and electrochemical properties [23]. Zhang et al. designed the composite electrode of PANI-ionic liquid-carbon nanofiber for the fabrication of highly sensitive amperometric biosensors towards phenols [24]. To the best of our knowledge, for the first time the layered PANI nanosheets based electrodes are used as an effective chemical sensor towards the efficient detection of phenol. In this paper, the layered PANI nanosheets have been synthesized through the chemical polymerization and applied directly for the fabrication of phenol chemical sensor. The fabricated phenol sensor based on layered PANI nanosheets exhibit a high sensitivity of $\sim 1485.3 \mu A \; mM^{-1} \; cm^{-2}$ and very low detection limit of $\sim 4.43 \mu M$ with correlation coefficient (R) of ~ 0.9981 and short response time (10 s).

2. Experimental

2.1. Synthesis of layered PANI nanosheets

For the layered PANI nanosheets, the mixture of 0.1 mol of aniline monomer (Sigma-Aldrich, $\geq 99.5\%$) and 0.5 mol hydrochloric acid (HCl, Daejung Chemicals, Assay 35–37%) was dissolved in 150 ml deionized (DI) water and stirred for 15 min. The mixture was heated to 60 °C under constant stirring and later, 0.1 mol ammonium persulphate (APS, Sigma-Aldrich, $\geq 98\%$) was quickly added. Thereafter, the entire reaction mixture was immediately placed on an ice bath and maintained at the temperature of ~ 5 °C for 6–8 h under static condition. After completion of the reaction, the greenish blue color precipitate was obtained. The precipitate was filtered and washed with copious amount of DI water and dried under vacuum for 24 h to obtain greenish-blue layered PANI nanosheets.

2.2. Characterization of layered PANI nanosheets

The morphological observations were studied by using field emission scanning electron microscopy (FESEM, Hitachi S-4700, Japan), the transmission electron microscopy (TEM, JEM-2010-JEOL, Japan) and the atomic force spectroscopy (AFM, Nanoscope IV, Digital Instruments, Santa Barbara, USA). The line scan element mapping was analyzed by the FESEM coupled Energy dispersive X-rays spectroscopy with the mapping mode. The structural modifications of the layered PANI nanosheets were studied by the Fourier transform infrared (FTIR; Nicolet, IR300), Raman scattering (Raman microscope, Renishaw) and X-rays diffraction (XRD, Rigaku, Cu Kα, $\lambda = 1.54178$ Å) spectroscopy. The optical properties were measured by UV–vis spectrophotometer (JASCO, V-670, Japan) and the photoluminescence (PL) spectrum of layered PANI nanosheets was obtained with FluoroMax-2 Jobin-Yvon Spex Fluorometer (S.A. Inc.) with the excitation at ~ 320 nm. The electrochemical behavior of layered PANI nanosheets based electrode was studied by the cyclic voltammetry (CV), using the WPG100 electrochemical measurement system. The CV was performed in a three-electrode one compartment cell using layered PANI nanosheets as working electrode, Pt wire as counter electrode and an Ag/AgCl reference electrode. Electrochemical impedance (EIS) measurements were carried out by two probes electrochemical system using layered PANI nanosheets electrode as working and Pt wire electrode as cathode in PBS solution with different concentration of phenol by applying 10 mV ac signal over the frequency range of 100 kHz–1 Hz using VersaSTAT4.

2.3. Fabrication and characterization of phenol chemical sensor using layered PANI nanosheets electrode

The electrode was prepared by compressing the finely grounded layered PANI nanosheets powder under a pressure of ~ 6.6 t to form the pellets. The contacts were made by attaching the thin Cu wire on the pellet with the silver paste. Afterward, PANI electrode was subjected to drying at 60 ± 5 °C for 5–6 h in an oven under N_2. The phenol sensing performance was determined by simple two electrode current–voltage (I–V) characteristics (Electrometer, Keithley, 6517 A, USA), in which the layered PANI nanosheets pellet based electrode was used as working electrode and Pt wire as a counter electrode. A fixed amount of 0.1 M phosphate buffer solution (PBS, 10.0 ml) and the wide range of phenol concentrations from 20 μM–0.32 mM were used for the determination of sensitivity. The sensitivity of the fabricated phenol chemical sensor was estimated from the slope of the current versus concentrations from the calibration plot divided by the value of active area of sensor/electrode. The current response was measured from 0 V–2 V while the response time was measured as 10 s.

3. Results and discussion

3.1. Morphological characterizations of layered PANI nanosheets

Fig. 1 shows the FESEM and TEM images of layered PANI nanosheets. At low resolution (Fig. 1(a,b)), the synthesized PANI displays the uniform and compact layered sheets like morphology. The layered PANI nanosheets exhibit the average thickness of several hundred nanometers, as shown in Fig. 1(c). The morphology of the synthesized PANI is further characterized by TEM analysis, as depicted in Fig. 1(d). The layered morphology of PANI nanosheets is clearly visible which is similar to the FESEM results. There is no deformation of the morphology of layered PANI nanosheets under the high electron beam of TEM, suggesting the stability of the synthesized layered PANI nanosheets.

Fig. 2 shows the topographic and three dimensional (3D) AFM images of layered PANI nanosheets. The layered morphology of the synthesized PANI is visibly recorded in the topographic mode, as shown in Fig. 2(a). The 3D AFM image (Fig. 2(b)) has confirmed the same layered morphology, as detected in the topographic mode. The roughness of layered PANI nanosheets is estimated from AFM images by taking the value of the root mean roughness (R_{rms}). The layered PANI nanosheets exhibit relatively the high roughness of ~ 52.3 nm. It is known that the electrode materials with large roughness factor display higher electrochemical behavior or the electrocatalytic activity [25]. The high roughness of layered PANI nanosheets might improve the electrochemical behavior towards the detection of phenol.

Fig. 3(a) shows the X-rays diffraction (XRD) patterns of layered PANI nanosheets. Typically, two diffraction peaks at 19.3° and 25.1° are recorded, corresponding to the periodicity parallel and perpendicular to the polymer chain, respectively. These peaks are also assigned to emeraldine structure of PANI. The recorded XRD patterns are similar to PANI sheets or matrix [25]. The element composition of the layered PANI nanosheets is analyzed by taking the line scan element mapping through EDS. Fig. 3(b, c) shows the line scan element mapping image and pie profile of the elements. The C and N elements are majorly distributed in the line scan mapping however, the traces of Cl and S elements are also detected, as seen in the corresponding pie bar graph as shown in Fig. 3(c). The uniform distribution of C and N elements confirm the formation of layered PANI nanosheets.