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Distinctive polypyrrole nanobelts as prospective electrode for the direct detection of aliphatic alcohols: Electrocatalytic properties

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ABSTRACT

The effective working electrode based on polypyrrole (PPy) nanobelts was employed for the fabrication of highly sensitive and reproducible aliphatic alcohols chemical sensor. The unique PPy nanobelts were simply synthesized by in situ chemical polymerization of pyrrole monomer in the presence of ferric chloride as oxidant and methylene blue as reactive self-degraded template. The morphological properties and elemental mapping revealed that the synthesized PPy nanobelts possessed the uniform dimension with high aspect of chemical compositions. The PPy nanobelts electrode showed reasonably high electrical conductivity of ~1.80×10^{-4} Ω^{-1} cm^{-1}. The electrochemical and electrocatalytic behavior of PPy nanobelts based electrode toward the detection of aliphatic alcohols were elucidated by measuring the electrochemical impedance spectroscopy (EIS) measurements. Furthermore, the current (I)–voltage (V) characteristics were performed to evaluate the sensing performance of PPy nanobelts electrode toward the detection of aliphatic alcohols. Among different aliphatic alcohols, the methanol chemical sensor based on PPy nanobelts electrode displayed the highest sensitivity of ~205.64 μA mM^{-1} cm^{-2}, good detection limit of ~6.92 μM with correlation coefficient (R) of ~0.98271 and short response time (10 s).

1. Introduction

The major environment pollutants like CO_2, CO, SO_2 and volatile organic compounds (VOCs) are usually produced by the consumption of commonly used chemicals such as ammonia (NH_3), ethanol (C_2H_5OH), methanol (CH_3OH) and other aliphatic alcohols [1]. Moreover, the excessive use of VOCs such as aliphatic alcohols and ketones are continuously polluting the environment and causes the health problems [2]. Methanol is highly used as automotive fuel in motor vehicles and in making dyes and perfumes [3]. The surplus exposure of methanol to human could cause blindness, metabolic acidosis and might lead to death [4]. The combustion of other alcohol like propanol releases the toxic materials which are harmful to human beings [5]. The sensor technology is well known tool for the detection of VOCs such as, alcohols, ethers, esters, halocarbons, ammonia, NO_2 and warfare agent stimulants [6] and is highly demanding in industries, medicines and for domestic applications to detect the pollutants, toxic and harmful chemicals [7]. The electrochemical sensors have received much attention as promising chemical sensing tool to detect the harmful chemicals [8]. In this regards, the designing of effective working electrode with high electron transfer rate is still a challenge. The chemical sensor based on working electrodes of different nanomaterials such as polymers and metal oxide semiconductors are promising for the reliable detection of harmful chemicals owing to their reliability, high surface-to-bulk ratio, good adsorption characteristics and high selectivity [9].

Conjugated polymers are known as p-type semiconductors with unique electronic properties due to their reasonable electrical conductivity, low energy optical transitions, low ionization potential and high electron affinity [10]. These polymers could be easily synthesized through simple chemical or electrochemical processes and their conductivities could be altered by modifying the electronic structures through doping or de-doping procedures [11]. Therefore, conducting polymers could suitably work as an effective working electrode and might offer the fast response toward the detection of various harmful chemicals [7]. In general, the good selectivity, wide linear range, rapid response, portability and the room temperature working abilities are the basic requirements for the efficient working of chemical sensors [12]. Polypyrrole (PPy), a conducting polymer, is much explored material because it shows high electrical conductivity, high stability in air and aqueous media and thus, an extremely useful material for actuators, electric devices and for the efficient detection of the harmful chemicals [13,14]. Few literatures are reported on the sensor performances of

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PPy nanostructure based electrodes for the detection of aliphatic alcohols S. J. Hong et al. studied nitro vinyl substituted PPy as a unique reaction-based chemosensor for cyanide anion [15]. Lin et al. prepared the composite electrode of PPy-poly vinyl alcohol (PVA) by electrochemical method for the detection of methanol and ethanol vapor [16,17]. Jiang et al. prepared the composite films of PPy–PVA by in situ vapor state polymerization method and demonstrated the methanol sensing behavior based on the thickness of PPy–PVA film electrodes [18]. Recently, Babaei et al. determined the residual methanol content in the biodiesel samples by developing new PPy–ClO_4 electrodes via electrodeposition on interdigital electrodes [19]. The roughness and morphology of the PPy greatly influence the responses for the detection of harmful chemicals [20]. In this context, the unique and effective working electrode based on PPy nanobelts has been utilized for the fabrication of highly sensitive and reproducible aliphatic alcohols chemical sensor. The unique PPy nanobelts are simply synthesized by the in situ chemical polymerization of pyrrole monomer in presence of ferric chloride as oxidant and methylene blue as reactive self-degraded template. To the best of our knowledge, for the first time, PPy nanobelts have been directly applied as working electrode for the efficient detection of aliphatic alcohols using simple current (I)–voltage (V) characteristics.

2. Experimental

2.1. Synthesis of PPy nanobelts

In a typical synthesis of PPy nanobelts, 20.0 mmol of PPy monomer (1.4 ml, Sigma–Aldrich, ≥99.5%) and 4.0 mmol of methylene blue (1.27 g) were mixed in 30 ml DI (deionized) water under vigorous stirring for 30 min. Thereafter, 1 M (33.4 ml) dopant solution of ferric chloride ($FeCl_3$, Daejung, ≥99.5%) was added dropwise into the reactant mixture and the reaction was kept for 20 h under static condition at 5 °C. The obtained precipitates were centrifuged at ~4500 rpm for 10 min and the products were washed with copious amount of DI water, methanol and dried in vacuum oven. Herein, methylene blue played a significant role to obtain the morphology of nanobelts. The methylene blue generally has a planar hydrophobic section and hydrophilic end group and thus, acts as anionic template in aqueous solution. However, the methylene blue in aqueous acidic solution could dimerize and produce the oligomers which finally degrade during the polymerization, resulting to the formation of PPy nanobelts with the high surface area of ~46.6 m^2/g [21,22].

2.2. Characterization of PPy nanobelts

The morphological observations were studied by using field emission scanning electron microscopy (FESEM, Hitachi S-4700, Japan), 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-ray spectroscopy with the mapping mode. Raman spectra (Raman microscope, Renishaw) and Fourier transform infrared spectra (FTIR, Nicolet, IR300) were used for the structural characterizations. The ^{1}H NMR spectra of PPy nanobelts electrode in DMSO solvent were recorded by 600 MHz FT-NMR spectrometer (JNM-ECA600). The optical properties were characterized by the photoluminescence studies (JASCO, FP-6500) and UV–visible absorbance (2550 Shimadzu, Japan). The electrochemical impedance spectroscopy (EIS) measurements were carried out by VersaSTAT4 by using the two probes electrochemical system. PPy nanobelts electrode was used as working and Pt wire electrode as cathode in PBS solution of different concentrations of aliphatic alcohols under the ac signal of 5 mV over the frequency range of 100 kHz–1 Hz.

2.3. Fabrication and characterization of PPy nanobelts based aliphatic alcohol chemical sensor

Bulk samples in the form of pellets were prepared by compressing the finely grounded PPy nanobelts powder under a pressure of ~6.6 Ton. The prepared PPy electrode shows the surface area of ~39.8 m^2/g. The contacts were made by attaching the thin Cu wire on the pellet through the silver paste. Thereafter, the electrode was subjected to drying at 60 ± 5 °C for 2 h in an electric oven. The sensing performances of aliphatic alcohols were studied by a simple two electrode I–V characteristics using PPy nanobelts electrode as working and Pt wire as a cathode. The I–V characteristics were measured by the electrometer (Keithley, 6517A, USA). A fixed amount of 0.1 M phosphate buffer solution (PBS, 10.0 ml) of pH 7 and the wide concentration range of aliphatic alcohols (methanol, propanol and butanol) from 20 μM–1 mM were used for the experiments. The sensitivity of the fabricated alcohol chemical sensor was estimated by the slope of the current vs. concentration from the calibration plot, divided by the value of active area of sensor/electrode. The current response was measured from 0–2.5 V and the response time was measured as 10 s.

3. Results and discussion

3.1. Morphological characterizations of PPy nanobelts

The morphology of the synthesized PPy nanomaterials is analyzed by FESEM and TEM images, as shown in Fig. 1. From FESEM images (Fig. 1(a) and (b)), the synthesized PPy nanomaterials possess smooth and the uniform belt like morphology. Each PPy nanobelt presents the average thickness of ~100 nm and width of ~400 nm, as shown in Fig. 1(b). The morphology of the synthesized PPy has been further characterized by the TEM analysis (Fig. 1(c)). Similar morphology and the dimensions are observed in TEM image, which is consistent with the FESEM results. Interestingly, the morphology of PPy nanobelts has not changed under high energy electron beam, indicating the stability of PPy nanobelts.

Fig. 2 shows the topographic and three dimensional (3D) AFM images of synthesized PPy nanobelts. As observed in FESEM and TEM analysis, the nanobelts morphology is visibly seen in the AFM images. The synthesized PPy nanobelts show the reasonable root mean roughness (R_{ms}) of ~18.1 nm. It is reported that the high electrochemical behavior and electrocatalytic activity of electrode are related to the large roughness factor of the electrode materials [23]. In our case, the PPy nanobelts with reasonable R_{ms} value might deliver the electrochemical behavior toward the detection of aliphatic alcohols.

The elemental compositions of the synthesized PPy nanobelts are estimated by the element line scan image through EDS, as depicted in Fig. 3. The line scan image and pie profile (Fig. 3(a) and (b)) display that the synthesized PPy nanobelts are largely composed of carbon and nitrogen elements. Few traces of oxygen elements are also recorded which might due to surface moisture or atmospheric oxygen on the surface of nanobelts. Fig. 3(c) summarizes the existing elements of PPy nanobelts in weight percentage (wt%) and atomic percentage (at%). The synthesized PPy nanobelts are consisted of uniformly distributed carbon and nitrogen with at% of ~60.09 and ~39.41 respectively. The detection of C, N and O elements confirm the formation of synthesized PPy nanobelts.