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Methane sensor based on nanocomposite of palladium/multi-walled carbon nanotubes grafted with 1,6-hexanediamine

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ABSTRACT

Palladium nanoparticles (PdNPs) were electrolessly deposited on 1,6-hexanediamine grafted multi-walled carbon nanotubes (MWCNTs) to form nanocomposite which was then characterized by scanning electron microscopy, proton nuclear magnetic resonance spectroscopy, and infrared spectroscopy. First, the electrocatalytic activity of MWCNT/PdNPs for methane (CH_4) on a gold electrode in 0.50 M H_2SO_4 was studied by cyclic voltammetry and the results demonstrated that MWCNT/PdNPs could be employed to oxidize CH_4. A simple CH_4 sensor was then fabricated by depositing the MWCNT/PdNPs nanocomposite onto an indium tin oxide substrate. The effects of carrier gas, amount of nanocomposite and temperature on the response of the sensor were investigated in detail. The sensor exhibits good sensitivity and selectivity to CH_4 in dry air at ambient conditions. It showed linear response to CH_4 at 0–16% v/v with a detection limit of 0.167% v/v (signal/noise = 3). The response and recovery times were less than 35 and 12 s, respectively. Common gases such as N_2, CO and CO_2 showed no interference but H_2 and NH_3 displayed slight interference to the sensor.

1. Introduction

Coal gas leakage and explosion can cause serious damage and loss of human life. As such considerable efforts have been made to prevent coal gas explosion. Methane (CH_4), as a major component of coal gas, is one of the most important gases to be detected [1]. Various techniques for detecting CH_4 have been reported including microbial biosensor [2], metal oxides [3,4], infrared, and laser light-emitting diode sensors [5,6]. However, they are typically complicated, expensive to manufacture, and difficult to operate and maintain. Metal/carbon nanotube hybrid materials have recently attracted much attention because of their promising applications in nanoelectronics as well as high-sensitive gas sensors [7–13]. It has been proposed that nanocomposite of metal and multi-walled carbon nanotube (MWCNT) can be applied to inert gas detection when loaded appropriately, particularly with transition metals that interact with CH_4 or carbon dioxide. Lu et al. [14] coated single-walled carbon nanotubes with palladium (Pd) by sputtering to detect CH_4 at room temperature. Pal and co-workers [15] prepared carbon nanotubes and nanofibers by electrodeposition to investigate their sensitivity to CH_4. Casalbore-Miceli et al. [16] deposited a conducting polymer of substituted polythiophene and its impedance changed with the concentration of CH_4. Recently Li et al. [17] prepared Pd and MWCNT nanocomposite for detection of CH_4. Although these materials show response to CH_4 at room temperature, their fabrication methods involve more sophisticated and relatively expensive equipment and are complicated. Furthermore, this MWCNT/Pd sensor did not demonstrate the dynamic response behavior of CH_4 at different concentrations in detail.

In this work, we report a simple strategy of synthesizing nanocomposite of Pd and MWCNTs grafted with 1,6-hexanediamine using a chemical reduction method. This nanocomposite was employed to assemble a CH_4 sensor which could function well in ambient conditions. The resistance of the sensor was monitored at different carrier gases, i.e., N_2, dry and humid airs, and CH_4 concentrations of 0.50, 1.0, 1.5, 3.0, 5.0, 10.0, and 16.0 vol%. The proposed sensor exhibits a wide dynamic response range to CH_4 (0.0–16.0 vol%). It possesses the advantages of fast response and short recovery times of less than 35 and 12 s, respectively.

2. Experimental

2.1. Chemicals and reagents

N,*N*-dimethylformamide (DMF), ethanol, 1,6-hexanediamine, concentrated nitric acid (HNO_3), palladium(II) chloride ($PdCl_2$,

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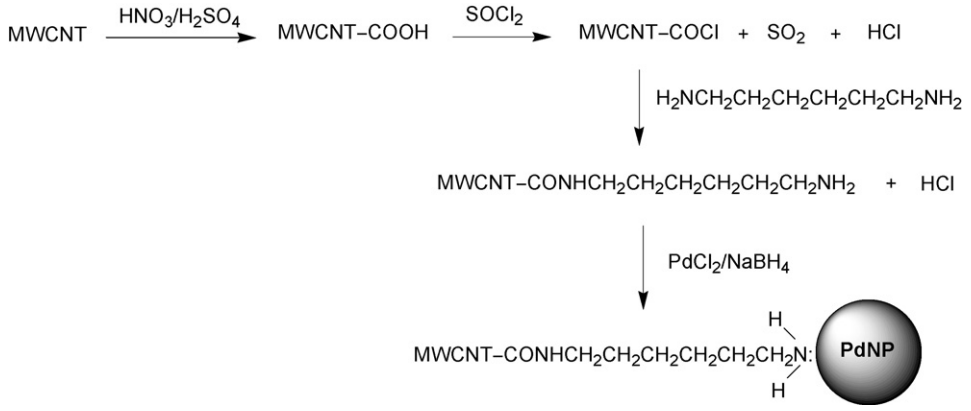

Scheme 1. Reaction scheme for the synthesis of MWCNT–NH_2/PdNPs.

99.9%), sodium borohydride ($NaBH_4$), concentrated sulfuric acid (H_2SO_4), thionyl chloride ($SOCl_2$), and toluene were obtained from Aldrich (Milwaukee, WI, USA). MWCNTs were purchased from Shenzhen Nanotech Port Co., Ltd. (Shenzhen, China). All chemicals were of analytical purity and used as received without further purification. Purified water from a triply distilled quartz apparatus was used to prepare all solutions. CH_4 (99.99 vol%) was obtained from Taigang Gas Mixing Co., Ltd. (Taiyuan, China) and N_2 (99.99 vol%) was from Fujiang Special Gas Company (Taiyuan, China).

2.2. Nanocomposite preparation

MWCNTs were pretreated with a selective oxidation step at 530 °C in air for 30 min to remove amorphous carbon. The MWCNTs were further oxidized in a mixture of HNO_3 (68%)/H_2SO_4 (98%) (1:3 v/v) at 60 °C for 4 h. The resulting carboxylated MWCNT (MWCNT–COOH) were filtered and washed with deionized water until pH 7 and then dried in vacuum [18]. The MWCNT–COOH was converted to MWCNT acyl chloride (MWNT–COCl) as an intermediate product for further chemical functionalization [19]. MWNT–COCl was prepared by stirring 150 mg of MWCNT–COOH in a 30 mL mixture of $SOCl_2$ and DMF (20:1 v/v) at 70 °C for 24 h. $SOCl_2$ and DMF were removed via vacuum distillation. 1,6-hexanediamine was added to the MWNT–COCl at 100 °C and left for 2 days until no HCl gas evolved. After cooling to room temperature, the amino-functionalized MWCNT (MWCNT–NH_2) was washed with ethanol five times to remove the excess 1,6-hexanediamine. 50.0 mg of MWCNT–NH_2 and 17.8 mg of palladium chloride were added into 50 mL of water and stirred. 5.0 mL aqueous solution of $NaBH_4$ (38.0 mg) was added dropwise to the mixture as reductant for $PdCl_2$ for 5 min to obtain the MWCNT–NH_2/PdNPs. All the reactions are summarized in Scheme 1. The solid nanocomposite product was washed with water and dried overnight under vacuum and kept for future use.

2.3. Nanocomposite characterization

Scanning electron microscopic (SEM) image was done on a JEOL JSM-6700F scanning electron microscope (Tokyo, Japan) operating at 10 kV. ^{1}H NMR spectra were obtained on a Bruker Avance DRX 300 MHz nuclear magnetic resonance spectrometer (Fallanden, Switzerland) in $CDCl_3$ solutions. Chemical shifts were reported relative to tetramethylsilane (TMS). Fourier transform infrared (IR) spectra were acquired on a Nicolet Magna-IR 750 spectrometer (Thermo Fisher, Waltham, MA, USA) in the wavenumber range 500–4000 cm^{-1} at a resolution of 4 cm^{-1}. The nanocomposite samples were mixed with KBr and pressed to form KBr plates.

2.4. Electrochemical measurement

Cyclic voltammetric measurements were performed on a Chenhua Instruments CHI660C (Shanghai, China) electrochemical system with a conventional three-electrode cell. The working electrode was a gold (Au) electrode with a diameter of 4 mm, the auxiliary electrode was a platinum wire, and the reference electrode was Ag/AgCl. All cyclic voltammograms were recorded in 0.50 M H_2SO_4 solutions at 25 °C.

2.5. Sensor fabrication

Since indium tin oxide (ITO) glass has good electrical conductivity (~10 Ωcm), it was employed as a solid substrate for the nanocomposite. The nanocomposite was added to toluene as it was a good solvent for dispersing the nanocomposite. 80 μL of 0.50 mM nanocomposite toluene solution of MWCNT–NH_2/PdNPs was coated on an ITO glass (1 × 2 cm) and left to dry. Scheme 2 displays the experimental setup for detection of CH_4. The sensing system is mainly consisted of a home-made gas chamber, an ITO-based sensor and a direct current power source (applied voltage = 1.25 V). The chamber volume is 100 mL. The gas flow was controlled by an Ecotech GasGal 1100 mass flow controller (Victoria, Australia) and the total gas flow through the chamber was 100 standard cubic centimeter per minute. Purified air (> 99.99%) was produced from a Model BML-9551 Zero Air Generator (Beijing Monitor Environment Technology Ltd., Beijing, China) which did not contain any impurity gases such as hydrocarbons, CO and CO_2. Various concentrations of CH_4 were generated by blending a stream of 99.99 vol% CH_4 with a stream of purified air using the mass flow controller. The sensor signal was monitored in terms of resistance by a 34410A digital multimeter (Agilent Technologies, Santa Clara, CA, USA). The data was input and kept in a personal computer. The response of the sensor (S) is defined as $S = (R_0 - R)/R_0$, where R_0 and R are the resistances of the sensor in the presence of carrier gas and CH_4, respectively. The resistance of the MWCNT–NH_2/PdNPs/ITO sensor decreased with the increase in CH_4 concentration.

3. Results and discussion

3.1. Characterization of MWCNT/Pd nanocomposite

The MWCNTs functionalized with–COOH,–NH_2 moieties and immobilized with PdNPs, respectively and were then characterized by IR, ^{1}H NMR and SEM. Fig. 1 displays the IR spectra of the MWCNT–COOH, MWCNT–NH_2 and MWCNT–NH_2/PdNPs. For the MWCNT–COOH, the peak at 1716 cm^{-1} corresponds to the C=O group stretching vibration. For the MWCNT–NH_2, the peak of