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Fabrication of a flexible H_2 sensor based on Pd nanoparticles modified polypyrrole films

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HIGHLIGHTS

- Flexible H_2 sensor made of Pd NPs-PPy film by layer-by-layer *in situ* self-assembly.
- Introducing Pd NPs effectively improved the response of Pd NPs-PPy.
- Flexible H_2 sensor made of Pd NPs-PPy had stronger response than that made of Pt-PPy.

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ABSTRACT

Novel flexible H_2 gas sensors were fabricated by self-assembling the Pd-based complex and polypyrrole (PPy) thin films layer-by-layer on a plastic substrate and then reducing *in-situ* Pd-based complex thin film to a Pd-PPy thin film. Microstructural observations revealed that Pd nanoparticles (Pd NPs) formed on the surface of the PPy film. The effect of the amount of decorated Pd NPs on the response and stability of the Pd NPs-PPy thin film was investigated. The response of the PPy thin film was improved by the Pd NPs, supplying catalytically active sites for H_2 gas molecules. The flexible H_2 sensor that was made of Pd NPs-PPy thin film had a high performance with strongest response, good stability and high flexibility at room temperature. The flexible H_2 gas sensor exhibited a strong response that was greater than that of sensor that was made of Pt-PPy at room temperature.

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1. Introduction

Hydrogen (H_2) sensing has recently attracted considerable interest, because H_2 is applied to many fields, such as fuel cells, cars with H_2 engine, industrial processing and others [1,2]. However, H_2 is an odorless and flammable gas. The flexible sensors had the lightweight property so that they have been laminated over the entire surface of a tube to detect any leakage of hydrogen [3]. Therefore, it is important to fabricate flexible hydrogen sensors with high mechanical durability and strong gas response for developing of hydrogen-based technology.

Conventional H_2 gas sensors are primarily deposited on rigid inorganic substrates such as glass or silicon wafers based on metal oxide materials and typically must usually be used at temperatures from 300 to 500 °C to maintain proper operation [4,5]. However, the long-term stability of the metal oxide gas sensors drifts at higher operating temperatures because oxygen vacancies in the metal oxides diffuse [6]. Noble metals such as Pt, Pd and Au have been used as a good catalyst for detection of H_2 at room temperature [7–11]. Moreover, Pd has been commonly used as a catalyst to enhance H_2-sensing at room temperature because of its low hydrogen-binding energy, compared to Pt catalyst [12]. Recently, Y. Sun et al. [3,13,14] fabricated flexible hydrogen sensors those were made of Pd nanoparticles (Pd NPs) decorated single-walled carbon nanotubes (SWCNTs) using the dry-transfer printing method. Y. H. Kim et al. [15] fabricated a flexible hydrogen sensor based on chemical vapor deposition (CVD) graphene decorated with thermally evaporated Pd NPs on copper foil. These methods require quite critical and complex processes. G. S. Chung et al. [16] fabricated a flexible hydrogen sensor based on ZnO nanorods (NRs) incorporated with a Pd catalyst on polyimide (PI) substrate using an aqueous solution method. Our previous work [17], described the fabrication of flexible H_2 gas sensors by the layer-by-layer (LBL) *in situ* self-assembly of multi-walled carbon nanotubes (MWCNTs) thin films on polyethylene terephthalate (PET) substrates, followed by modification *in situ* with Pd NPs.

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Conducting polymers such as polythiophene, polypyrrole (PPy) and polyaniline had remarkable mechanical and electrical properties, which can be used in actuators, sensors and electrochromic devices [18,19]. Among conducting polymers, PPy has attracted much interest because it is easily synthesized and its surface charge characteristics can easily be modified by changing the dopant species in the material during synthesis. Recently, Torsi et al. [20] fabricated a H_2 sensor that was made of Pd-doped metallic inclusions in a PPy film. L. Al-Mashat et al. [21] fabricated a H_2 sensor that was made of PPy nanofiber. All of the above sensor systems are based on the use of rigid substrates (Al_2O_3). Our previous work [22], described the fabrication of flexible H_2 gas sensors that was based on PPy thin film decorated with Pt nanoparticles (Pt NPs). However, no attempt has been made to form a flexible H_2 gas sensor that was made of a PPy thin film decorated with Pd NPs using LBL self-assembly. In this study, a flexible H_2 gas sensor based on a thin film of PPy that is decorated with Pd NPs (Pd NPs-PPy) on a PET substrate was fabricated by LBL *in situ* self-assembly. The thin films were observed by scanning electron microscopy (SEM) coupled with energy dispersive spectrometry (EDS). The effect of the decorated Pd NPs concentration on the H_2 sensing properties of the sensors was investigated. The flexibility and gas sensing properties, including strength of the response, sensing linearity, reproducibility, interfering effect and stability of the sensor were also investigated. The H_2 sensing mechanism of PPy decorated with Pd NPs thin film was investigated.

2. Experimental

2.1. Materials

3-Mercapto-1-propanesulfonic acid sodium salt (MPS), poly(-allylamine hydrochloride) (PAH; Mw = 15,000), poly(-styrenesulfonic acid) sodium salt (PSS; Mw = 70,000), pyrrole monomer (98%), *p*-toluene sulfonic acid (*p*-TSA) and ferric chloride ($FeCl_3$), $PdCl_2$ and $NaBH_4$ were obtained from Aldrich. All used deionized water (DIW) was prepared using a Milli-Q Millipore (Bedford, MA, USA) purification system, and the resistivity of water was above 18.0 MΩ/cm.

2.2. Fabrication of flexible substrates

The structure of the flexible H_2 gas sensor was the identical to that in our earlier study [23]. The interdigitated gold electrodes (IDE) were made by sputtering first Cr (50 nm thick) and then Au (250 nm thick) at temperature from 120 to 160 °C. The gap between electrodes was 0.2 mm. The substrates were first immersed in a bath that contained a solution of H_2O_2/H_2SO_4 (1:2 volume) for 3 min and then rinsed with DIW to get hydrophilic Au/Cr/PET substrates. Fig. 1(a) schematically depicts the structure of the flexible substrate. Fig. 1(b) shows the flexibility of the flexible substrates.

2.3. Fabrication of flexible H_2 sensor based on Pd NPs-PPy film

The fabrication of the Pd NPs-PPy thin film on the PET substrate using LBL *in situ* self-assembly was similar to our earlier studies [17,22]. In a typical fabrication, the negatively charged MPS/Au surface was produced by immersing the hydrophilic Au/Cr/PET substrate in 2.0 mM aqueous MPS for 24 h; rinsing it with DIW, and then drying it at 80 °C. A negatively charged $(PSS/PAH)_2$/MPS/Au/Cr/PET substrate was fabricated by alternately depositing PAH (pH 4) and PSS (pH 1) aqueous solutions onto the negatively charged MPS-modified substrate for 10 min followed by rinsing and drying. The active solution for optimal PPy film was prepared using a solution of 0.006 M $FeCl_3$, 0.026 M *p*-TSA and 0.02 M pyrrole, as described in the literature [24,25]. A monolayer PPy thin film was produced by immersing the $(PSS/PAH)_2$/MPS/Au/Cr/PET substrate in active solution for 5 min. Then, the PPy/$(PSS/PAH)_2$/MPS/Au/Cr/PET substrate was immersed in aqueous $PdCl_2$ (0.25%) for 10 min; rinsed with DIW and then dried at 80 °C. Subsequently, the as-prepared Pd-based complex was reduced by immersing the Pd(II)-PPy/$(PSS/PAH)_2$/MPS/Au/Cr/PET substrate in aqueous $NaBH_4$ (0.04%) for 10 min, rinsing it with DIW and then drying it at 80 °C. The flexible H_2 sensor based on Pd NPs-PPy film was obtained.

2.4. Instruments and analysis

The surface microstructure of the thin film that was coated on a PET substrate was investigated using a field emission scanning electron microscope (FEI company, Nova NanoSEM™ 230) equipped with an energy dispersive spectrometer (EDS). The electrical and sensing properties were measured using a bench system at room temperature, as shown in Fig. 2(a). The volume of the bench system is 18 L Fig. 2(b) depicts the measuring electric circuit used here, in which V is the supply voltage, R_s is the resistance of the sensor, R_l is the resistance of the load resistor, and V_m is the measured voltage. Each flexible H_2 sensor was connected in series with a load resistor and a fixed 5 V was continuously supplied to the sensor circuit from a power supply (GW, PST-3202). The resistance (R_s) of the flexible H_2 sensor was determined from the voltage (V_m) at the ends of the load resistor (R_l) using a DAQ device (NI, USB-6218) which the resolution is 12 bits in various concentrations of gas. The desired H_2 gas concentrations, obtained by mixing a known volume of standard H_2 gas (99.999%) and dry air, were injected into the chamber. The interfering experiment was performed by measuring the resistance of the sensor upon controlled concentration of 20, 200 and 5 ppm for NH_3, CO and NO_2 gases, respectively. The gas inside the chamber was uniformly distributed using a fan. After the testing time, the chamber was purged with dry air and the experiment was repeated for another cycles. All experiments were performed at room temperature, and the relative humidity was 40 ± 3% RH. Flexibility experiment was performed in which the flexible H_2 sensors were bent to various degrees as their responses were monitored as a function of the period of exposure to H_2 gas. The bending angle was measured using a goniometer. The sensor response (S) was calculated by $S = (R_{air} - R_{gas})/R_{air} = (\Delta R/R_{air})$, where R_{air} and R_{gas} are the electrical resistances of the sensor in the air and tested gas, respectively.

3. Results and discussion

3.1. Microstructure of surface

Fig. 3 shows the SEM image of the *in situ* self-assembled of manolayer of PPy and Pd NPs-PPy thin films on a modified PET substrate. Fig. 3(a) shows the formation of the cauliflower like structure interconnected with each other of PPy, which is highly porous. Fig. 3(b) shows the PPy film that was decorated with 35,000 ppm Pd NPs. The thin film was compact, and, included some voids; many bright Pd granular nanoparticles were observed on its outer surface. Therefore, the sensor surface, modified by the deposition of a Pd thin overlayer, was porous. The particulate agglomerates of various sizes from 15 to 130 nm and the average size of Pd NPs on the Pd NPs-PPy thin film was 63 nm by SEM image analysis. The as prepared Pd NPs-PPy thin film was also analyzed by EDS (Fig. 3(c)), which showed the existence of C, O, Na, S and Pd, which further confirm that the Pd NPs were surely self-assembled on the surface of PPy film.

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