Sensors and Actuators B 157 (2011) 275–281

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Flexible H_2 sensor fabricated by layer-by-layer self-assembly of thin films of polypyrrole and modified *in situ* with Pt nanoparticles

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ARTICLE INFO

Article history:
Received 10 September 2010
Received in revised form 18 February 2011
Accepted 28 March 2011
Available online 6 April 2011

Keywords:
Flexible H_2 sensor
Layer-by-layer (LBL)
In situ self-assembly
Polypyrrole (PPy)
Pt nanoparticles

ABSTRACT

A novel flexible H_2 gas sensor was fabricated by the layer-by-layer (LBL) self-assembly of a polypyrrole (PPy) thin film on a polyester (PET) substrate. A Pt-based complex was self-assembled *in situ* on the as-prepared PPy thin film, which was reduced to form a Pt-PPy thin film. Microstructural observations revealed that Pt nanoparticles formed on the surface of the PPy film. The sensitivity of the PPy thin film was improved by the Pt nanoparticles, providing catalytically active sites for H_2 gas molecules. The interfering gas NH_3 affected the limit of detection (LOD) of a targeted H_2 gas in a real-world binary gas mixture. A plausible H_2 gas sensing mechanism involves catalytic effects of Pt particles and the formation of charge carriers in the PPy thin film. The flexible H_2 gas sensor exhibited a strong sensitivity that was greater than that of sensors that were made of Pd-MWCNTs at room temperature.

1. Introduction

Hydrogen (H_2) sensing has recently attracted considerable interest, since H_2 is important in a wide range of fields, such as fuel cells, cars with H_2 engine, industrial processing and others [1,2]. H_2 is a hazardous, odorless and flammable gas. The fabrication of sensitive sensors to detect and monitor hydrogen is therefore a key to the development of a new hydrogen-based technology.

The fabrication of organic electronic devices on plastic substrates has attracted much interest recently. A new trend towards the direct integration of sensors on flexible substrates has become evident. Flexible multisensor platforms that support temperature, humidity and gas detection will be manufactured at very low cost and integrated into smart textiles or radio frequency identification (RFID) tags for logistics applications [3,4]. The development of sensors should be consistent with the future goal of the development of the completely plastic RFID tag, and extensible to the sensing of various gases. The main challenge is not only their manufacture, but also the stability of their mechanical, electrical and gas-sensing properties.

Recently, Sun et al. [5–7] fabricated SWCNTs on polyester (PET) substrates by using the dry-transfer printing method and, then, decorated the SWCNTs with Pd nanoparticles by evaporating thin layers of Pd by electron-beam evaporation. The SWCNTs thus decorated were used to sense H_2. This fabrication technique is complex and expensive. Our previous work [8], described the fabrication of flexible H_2 gas sensors by the layer-by-layer (LBL) *in situ* self-assembly of MWCNT thin films on PET substrates, followed by modification *in situ* with Pd nanoparticles. The LBL self-assembly that is based on the sequential adsorptions of ionized polyelectrolytes and oppositely charged materials in aqueous solutions has many advantages, as a means of fabricating flexible H_2 gas sensors, including simplicity, inexpensiveness, low temperature of deposition, controllability of the thickness in the nanometer and to micrometer scales, and the lack of a need for any complex equipment [9,10].

Conducting polymers such as polythiophene, polypyrrole (PPy) and polyaniline have been intensively studied because of their remarkable mechanical and electrical properties, which can be exploited in actuators, sensors and electrochromic devices [11,12]. Among conducting polymers, PPy has attracted much interest because it is easily synthesized; it has relatively good environmental stability, and its surface charge characteristics can easily be modified by changing the dopant species in the material during synthesis. Torsi et al. [13] proposed a reversible and reproducible H_2 sensor that was based on Pd-doped metallic inclusions in a PPy film. Al-Mashat et al. [14] reported that forming PPy into nanofiber improved its sensitivity as an H_2 sensor. All of the above sensor systems are based on the use of rigid substrates (Al_2O_3). However, no attempt has been made to form a flexible H_2 gas sensor that is based on a PPy thin film by LBL self assembly. Additionally, platinum (Pt) thin films and fine particles have been extensively used to improve the H_2 sensing properties of sensors that are made of metal oxide films because of their catalytic properties [15]. There-

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doi:10.1016/j.snb.2011.03.062

fore, in this study, a flexible H_2 gas sensor based on a thin film of PPy that is decorated with Pt nanoparticles (Pt-PPy) on a polyester (PET) substrate was fabricated by LBL *in situ* self-assembly. The thin films were observed by scanning electron microscopy (SEM). The effect of the Pt concentration on the H_2 sensing properties of the sensors was investigated. The flexibility and gas sensing properties, such as strength of the sensitivity, sensing linearity, reproducibility and stability of the sensor were also investigated. Chemical analysis of real-world binary gas mixtures of interfering NH_3 gas and targeted H_2 gas was investigated. The H_2 sensing mechanisms of Pt-modified PPy thin film were 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 ($FeCl_3$), H_2PtCl_6 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 H_2 sensor

The structure of the flexible H_2 gas sensor was the identical to that in our earlier study [16]. The interdigited 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 ratio) for 3 min. The substrates were thoroughly rinsed with DIW after each step. This process made the substrates hydrophilic. The negatively charged MPS/Au surface was prepared 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 cyclic PSS/PAH bilayer film architecture was produced by alternately depositing PAH (pH 4) and PSS (pH 1) aqueous solutions onto the negatively charged MPS-modified substrate. The immersion time of each layer thus produced was about 10 min, and immersion was followed by rinsing and drying. A two-cycle PSS/PAH bilayered film was fabricated by repeating the above process, yielding a negatively charged $(PSS/PAH)_2$/MPS/Au/Cr/PET substrate.

The active solution for use in forming the PPy contained the oxidizing agent ($FeCl_3$) and *p*-TSA, and its pH was adjusted to pH 1 by adding HCl; then the pyrrole monomer was added. The optimal PPy film was produced using a solution of 0.006 M $FeCl_3$, 0.026 M *p*-TSA and 0.02 M pyrrole, as described in the literature [17,18]. The active solution was stirred for 15 min. The optimal deposition times in PPy active solution and PSS solution were for 5 and 10 min, respectively. A monolayer PPy was self-assembled *in situ* as a thin film on the $(PSS/PAH)_2$/MPS/Au/Cr/PET substrate. Then, the PPy/$(PSS/PAH)_2$/MPS/Au/Cr/PET substrate was immersed in aqueous $PtCl_6^{2-}$ (0.25%), an anionic metal complex, for 10 min; rinsed with DIW and then dried at 80 °C. The as-prepared Pt-based complex was reduced by immersing the Pt(IV)-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. Fig. 1 schematically depicts the fabrication of a flexible H_2 sensor by the LBL *in situ* self-assembly of an Pt-PPy thin film on a PET substrate. Fig. 2(a) schematically depicts the structure of the flexible gas sensor. Fig. 2(b) shows the flexibility of the Pt-PPy thin film assembled *in situ* on a PET substrate.

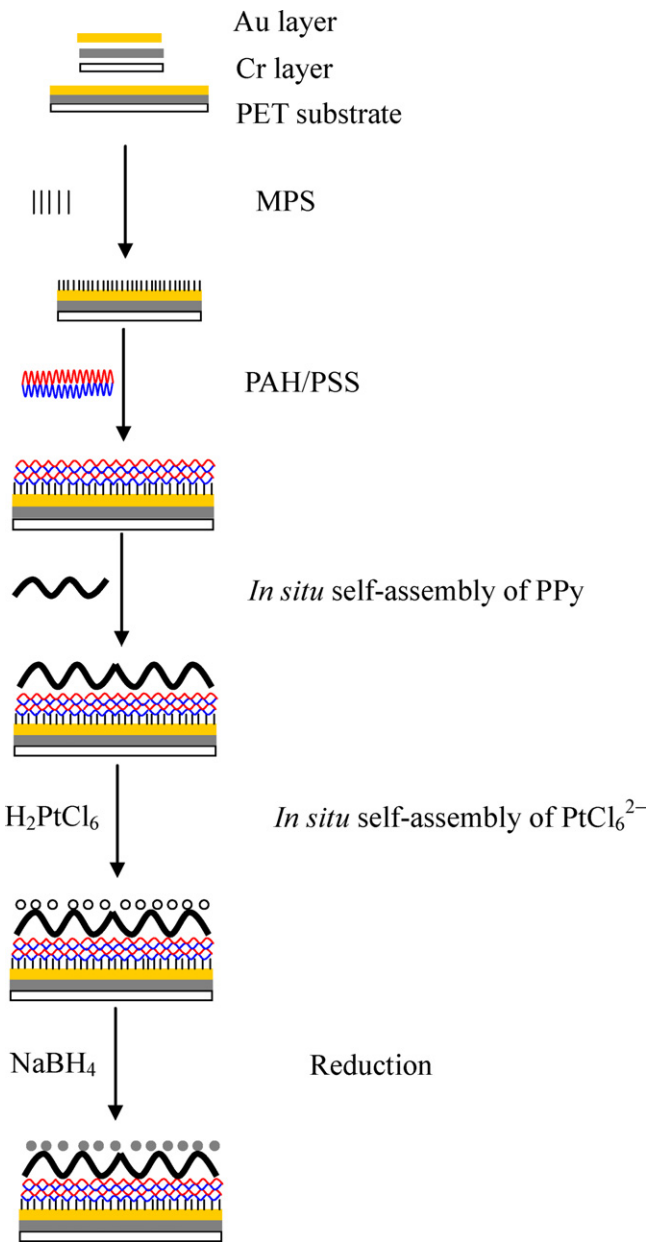

Fig. 1. Fabrication of flexible H_2 sensor by LBL *in situ* self-assembly.

2.3. 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 (FE-SEM, Hitachi, S-4100). The electrical and sensing characteristeristics were measured using a bench system at room temperature, as shown in Fig. 3. Each 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 of the sensor was determined from the voltage at the ends of the load resistor using a DAQ device (NI, USB-6218) in various concentrations of gas. The desired H_2 gas concentrations, obtained by mixing a known volume of standard H_2 gas (99.999%), were injected into the chamber. The volume of the chamber is 18 l. The cross-sensitivity experiment was performed by measuring the resistance of the sensor upon controlled various concentration of NH_3. The gas inside the chamber was uniformly distributed using a fan. After some time, the chamber was purged with air and the