



Effect of thermal treatment on conductometric response of hydrogen gas sensors integrated with HCl-doped polyaniline nanofibers



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HIGHLIGHTS

- Observation of the effect of annealing on H₂ sensors based on HCl-doped PANI.
- Revelation of crosslinking and partial carbonization of HCl-doped PANI upon annealing.
- Analysis of the influence of water and PANI's dopant on H₂ sorption kinetics.

ARTICLE INFO

Article history:

Received 3 May 2013

Received in revised form

27 November 2013

Accepted 29 December 2013

Keywords:

Polymers
Nanostructures
Heat treatment
Electrical properties

ABSTRACT

In this work, we investigated the effect of thermal treatments on the transduction of HCl-doped polyaniline (PANI) nanofibers integrated in conductometric devices upon exposure to 1% H₂ (carried by N₂). After drying in N₂ at ~25 °C for 12 h, our devices showed a ~10% decrease in electrical resistance upon exposure to 1% H₂. However, devices subject to 12-h drying in N₂ at ~25 °C followed by further thermal treatments in N₂ at 100 °C, 164 °C or 200 °C for 30 min showed different transduction behaviors. The devices subject to thermal treatments at 100 °C and 164 °C showed a ~7% decrease and <0.5% variation in electrical resistance, respectively. More interestingly, the device subject to the thermal treatment at 200 °C showed a transduction behavior with obvious opposite polarity, i.e. a ~5% increase in electrical resistance upon exposure to 1% H₂. Further analysis indicated that the observed results were related to the thermal treatments which caused HCl-doped PANI nanofibers to undergo (i) water desorption, (ii) crosslinking and/or (iii) partial carbonization.

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1. Introduction

Conducting polymers are a class of organic materials which possess the optical, electrical, electronic and magnetic properties of metals, while the processability and mechanical properties of conventional polymers [1–12]. Conducting polymers can be synthesized by electrochemical polymerization or oxidative chemical polymerization methods [1]. With the adjustment in preparative conditions, conducting polymers with different morphological features can be produced [13–19]. Conducting polymers have been widely used for many electrical and optoelectronic applications, such as polymeric electrodes [20–24], displays [17,25–27], fuel cells [28–31], light-emitting diodes [32–36] and organic solar cells [37–40]. As electrical properties of conducting polymers can vary with chemical contexts, conducting polymers can also be used for gas sensing [41–45]. To increase the sensitivity of gas sensors based

on conducting polymers, the active sensing component with a greater surface area (such as a porous network made up of nanofibers of a conducting polymer) can be used, instead of the same conducting polymer's bulk solid thin film [46,47].

Due to its ease of synthesis, polyaniline (PANI) becomes one of the most studied nitrogen-containing conducting polymers [41]. PANI can undergo reversible protonic doping to change conductivity by up to 10 orders of magnitude [1]. However, as the polymerization of aniline is pH-sensitive, caution should be taken to maintain appropriate low pH in the reaction media when the synthesis of the "classical" conductive PANI is desired [48]. Without secondary growth, PANI synthesized by oxidative chemical polymerization under sufficiently low pH conditions basically adopts the nanofiber structure as its intrinsic morphology [19].

Recently, some PANI-based polymers have been investigated for hydrogen sensing and hydrogen storage applications [49,50]. In general, the studies on hydrogen sensing show that conductometric sensors based on doped PANI can respond to hydrogen gas [47,51,52], while the studies on hydrogen storage show that the uptake of hydrogen by PANI varies from 0 to 10 wt% [53–59]. It is

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believed that the discrepancy in hydrogen storage could be related to the ambiguous and somewhat inconsistent materials processing procedures used, as the properties of PANI-based polymers (e.g. oxidation states, doping levels etc) can be affected by many subtle processing variables [1]. Thus, it is of particular interest to further investigate the effects of those processing variables on the interactions between H_2 and PANI-based polymers.

Since the discrepancy in hydrogen storage using PANI-based polymers might be caused by the different thermal treatments on HCl-treated PANI [53,57], a study intended to further investigate the interactions between H_2 and HCl-doped PANI subject to thermal treatment conditions at $\sim 25^\circ C$, $100^\circ C$, $164^\circ C$ or $200^\circ C$ was performed using conductometric devices integrated with HCl-doped PANI nanofibers. The above four thermal treatment conditions were chosen because (i) studies on hydrogen sensing experiments were usually performed at room temperature [47,60], (ii) extensive desorption of adsorbed water from PANI can occur at $100^\circ C$ [61] and adsorption of water on PANI can suppress the function of hydrogen gas sensors based on PANI [47], (iii) Panella et al. thermally treated HCl-doped PANI samples at $164^\circ C$ and showed 0% hydrogen uptake by HCl-doped PANI [57], and (iv) Cho et al. thermally treated HCl-doped PANI samples at $200^\circ C$ and showed 6% hydrogen uptake by HCl-doped PANI [53]. In addition to conductometric measurement, scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and Fourier-transform infrared (FTIR) spectroscopy were also used to study the morphology and chemical characteristics of HCl-doped PANI subject to thermal treatments.

2. Experimental

HCl-doped PANI nanofibers were synthesized by template-free oxidative chemical polymerization in a low-pH acidic aqueous medium [19,48,62]. Briefly, 10 ml of 0.02 M $(NH_4)_2S_2O_8$ in 1.0 M

$HCl_{(aq)}$ was quickly poured into a beaker containing 10 ml of 0.02 M aniline in 1.0 M $HCl_{(aq)}$ under magnetic stirring. The mixed solution in the beaker was magnetically stirred for 5 min, after which the magnetic stirring was stopped and the polymerization was allowed to proceed in the beaker for 2 h. After the 2-h reaction, the reaction mixture was transferred to a dialysis tubing (Spectra/Por, 12–14,000 MW cutoff). The reaction mixture was dialyzed against 4-L deionized water for 20 h. The dialysis bath was changed six times during the course of the 20-h dialysis. The dialyzed aqueous dispersion of PANI nanofibers ($\sim 1 \text{ mg mL}^{-1}$) was then transferred to a storage vial for future use.

The home-built apparatus used to thermally treat HCl-doped PANI nanofiber samples and/or perform hydrogen sensing experiments in a controlled atmosphere of flowing nitrogen gas (99.99%) is shown in Fig. 1. For computer-controlled conductometric measurement (accuracy of current measurements: $\pm 100 \text{ pA}$), the PANI sample was deposited on a glass slide with addressable gold electrode lines ($\sim 2 \text{ cm} \times 5 \mu\text{m}$; gap between the electrode lines: $500 \mu\text{m}$). After deposition, the device with the PANI sample was kept in a Petri dish. With the cover lid slightly left open, the sample was then dried in a fume hood. When the devices were not in use, they were stored in a desiccator to prevent excessive adsorption of water, which can suppress the function of PANI-based hydrogen gas sensors [47]. By modulating the gas-flow parameters, N_2 or 1% H_2 carried by N_2 was controllably delivered into the sealed gas-flow system to investigate the electrical response of HCl-doped PANI nanofibers subject to various thermal treatments [63–65]. For the preparation of various thermally treated PANI samples for material characterization, plain glass slides without electrode lines were used.

In this study, the SEM images were taken using a JEOL 6300FV field emission scanning electron microscope, the TGA profiles were taken using a TA Instruments 4100 thermal analyzer, and the FTIR spectra were recorded using a Perkin Elmer 2000 FTIR spectrometer.

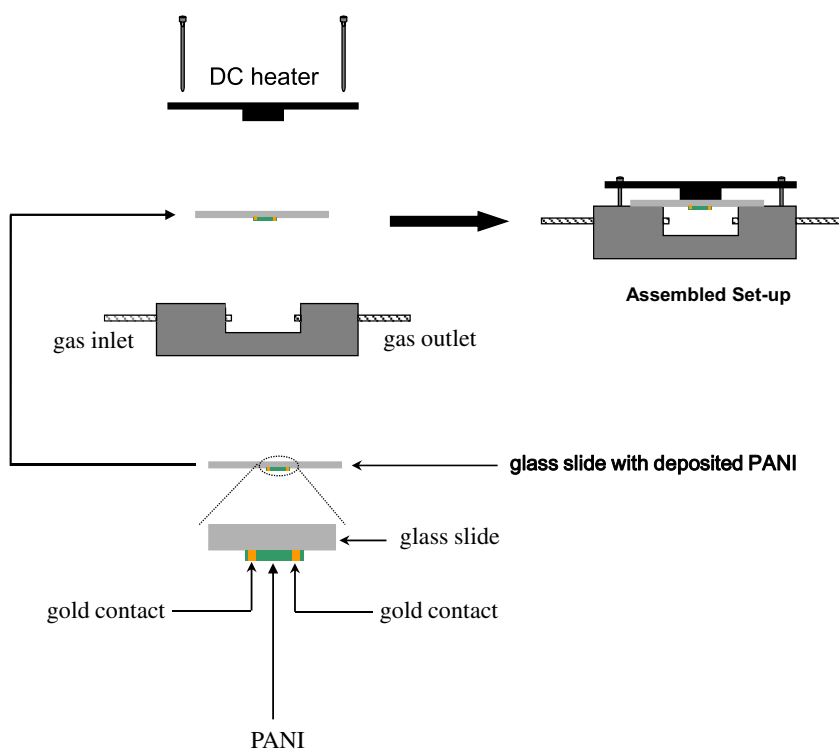


Fig. 1. Schematic illustration of the home-built apparatus used for performing thermal treatments or conductometric measurements on PANI samples deposited on glass slides (not drawn to scale).

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