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Hydrogen gas sensing performance of polyaniline/titania/nickel oxide nanocomposite at room temperature

Shahruz Nasirian [a,*], Seyed Yaser Razavi [b]

[a] Department of Electrical Engineering, Mazandaran University of Science and Technology, Babol, Iran
[b] Department of Mechanical Engineering, Mazandaran University of Science and Technology, Babol, Iran

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ABSTRACT

Monitoring and control of hydrogen gas (H_2) as a green energy resource by smart sensors is necessary for the safe H_2 economy. In this work, we present a resistance-based H_2 sensor based on a polyaniline/titania/nickel oxide nanocomposite (PTNN) thin film. PTNNs were synthesized by an in-situ self-assembly chemical oxidative polymerization of aniline monomers and deposited onto an epoxy glass substrate with Cu-interdigited electrodes. Synthesized samples were structurally and surface morphologically characterized. H_2 sensing behavior of the fabricated sensors was investigated for different concentration of gas, and a significant response (22.1%) and response time (67 s) toward 0.6 vol% H_2 observed at room temperature (25 °C) and relative humidity (RH). PTNN sensor with Ti/Ni ratio of 1/3 was exhibited a good Long-term response up to 60 days.

1. Introduction

In near decade, the use of green energy is taken into consideration for a safe civilization. The reducing hydrogen gas (H_2) is a renewable energy resource with the largest energy content of any fuel due to low minimum ignition energy (0.017 mJ), high heat of combustion (142 kJ/g) and wide flammable range (4–75%) [1,2]. However, H_2 has physical features such as colorless, odorless and tasteless, and it has the smallest molecules that can leak easily during manufacturing, storage and consuming processes without detecting by human senses [3–7]. Therefore, detection and monitoring of H_2 concentration leakage have become important issues for the development of a safe hydrogen economy. The numerous efforts have been widely investigated and reported semiconducting metal oxides (MOXs) as H_2 sensors in various types such as resistor devices. These sensors generally have a high operating temperature (>100 °C) and low sensitivity toward H_2 at environmental conditions [1,4,5–12]. Benkara et al. [9] have developed the films of ZnO/TiO_2 nanocomposite for H_2 sensor at 0.8 vol% gas and working temperature of 100–160 °C. Their highest gas response was approximately 1.48 at 160 °C with the response time of about 200 s. Pascu et al. [10] have reported an H_2 gas sensor based on a Pd/SiO_2/4H-SiC MOS capacitor which had a response of 80% (20%) upon exposure to 10,000 ppm H_2 gas at the working temperature of 525 K (300 K), respectively. Moreover, the response/recovery times of about 5–6 s, respectively, were measured at 10,000 ppm H_2 in nitrogen.

The researches have proved that the increase of H_2 sensitivity and chemical stability with the decrease of operating temperature can be revealed by the addition of MOXs into the protective organic material matrix such as conducting polymer [4–6,13]. One of the conducting polymers with π-conjugated chain structure, rich redox properties, excellent electrical conductivity and ease of synthesis is polyaniline [2–6,13–17]. Srivastava et al. [14] have developed the thin films of polyaniline/TiO_2 composites for H_2 filled environment at room temperature with the response (response time) of 1.65 (230 and 210 s). Nasirian et al. [5,17] have investigated an H_2 sensing layer based on thin films of polyaniline/TiO_2 (polyaniline/TiO_2/SnO_2) nanocomposite which had a best response of 1.63 (1.25) and response/recovery time of 83/130 (75/117) sec toward 0.8 vol% gas at room temperature. In all of these reports, H_2 sensors of polyaniline-MOXs composites have low sensing properties and long response/recovery time that still need more improvement.

Accordingly, with the best of our knowledge, there are no reports on the use of n-type titania (TiO_2) and p-type nickel oxide (NiO) nanoparticles into protective protonated-polyaniline matrix for H_2 sensor. The present article focuses on the preparation,

* Corresponding author.
E-mail addresses: shahruznasirian@ustmb.ac.ir, shahruznasirian@gmail.com (S. Nasirian).

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characterization and H_2 sensing properties of polyaniline/titania/nickel oxide nanocomposite (PTNN) thin films at environmental conditions.

2. Experimental

2.1. Materials

Aniline monomer (99% purity),ethanol (99.8%), hydrochloric acid (HCl) (36% concentrated), titanium tetrachloride (99.5%), nickel(II) nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$) and 10-camphor sulfonic acid (CSA) were purchased from Merck Co. Ammonium peroxide sulfate (APS) (99%), chloroform (99.9%), and ammonia solution (25% concentrated) were purchased from Sigma-Aldrich Co.

2.2. Methods

2.2.1. Synthesis of polyaniline

In an in-situ chemical oxidative polymerization process, 1 M of double distillated aniline into 100 ml an aqueous HCl solution was dissolved. Then, APS solution, with an equal molar ratio of aniline, was added in aniline solution in drop wise manner under constant magnetic stirring for 3 h at 5 °C. The resultant product was appeared dark green color. The product was filtered and washed several times with 1 M HCl solution until the filtrate become colorless. The final solution dried at 60 °C in a vacuum oven for overnight.

The product was added to 0.1 M aqueous solution of ammonia under stirring for 12 h. Then the solution, washed with deionized water several times and finally dried at 60 °C in a vacuum oven until obtaining undoped emeraldine-base of polyaniline (UEP) [5].

2.2.2. Synthesis of TiO_2 nanoparticles

One milliliter (ml) of titanium tetrachloride was slowly added dropwise into 1 ml of ethanol under stirring at room temperature. Then the resulting yellowish solution stirred for 72 h under 80% humidity. The light yellowish sol was aged for half day and prepared under ultrasonic waves for 30 min (exposed with ultrasonic waves at a frequency of 40 kHz and a 60Wpower). The gel was heated at the 120 °C until a dry-gel was obtained. The dry-gel precursor was calcined for 2 h at 500 °C at a ramping rate of 5 °C/min, for the formation of anatase phase TiO_2 nanopowders.

2.2.3. Synthesis of PTNN

For the synthesis of PTNNs, (a) 20 wt% of TiO_2 nanoparticles than aniline monomers were dispersed and suspended in 0.1 M aniline solution and (b) $Ni(NO_3)_2{\cdot}6H_2O$ solution, were prepared. (b) -solution was added into (a) -solution with different Ti/Ni ratio (1/1, 1/2, 1/3 or 1/4) and the products were stirred for 3 h. Then APS solution added dropwise to suspension at 5 °C under quick mixing. After 3 h, a good degree of polymerization with dark green color was achieved. The solution after aging, filtered, washed frequently with 1 M HCl and dried in a vacuum oven for overnight. The product was added to 0.1 M aqueous solution of ammonia under stirring for 12 h. The product washed with deionized water several times and finally dried at 60 °C by a vacuum oven. PTNN with Ti/Ni ratio of 1/1, 1/2, 1/3 and 1/4 is named PTNN1, PTNN2, PTNN3 and PTNN4, respectively.

2.2.4. Sensor preparation

Finger type Cu-interdigited electrodes were patterned onto $20 \times 20\ mm^2$ area of an epoxy glass substrate for sensor preparation. The width of overlap electrode and the gap between two successive electrodes was 0.3 mm. 0.1 gr of UEP or PTNNs was separately mixed with CSA by grinding in a smooth agate mortar and any mixtures were separately added in 10 ml chloroform. The solutions stirred several days at 2 bar N_2 atmosphere to make a homogenous conducting solution.

The products were deposited on the cleaned substrate using the spin coating technique under a speed of 3000 rpm. The obtained thin film dried in a vacuum oven at 60 °C. CSA-doped polyaniline thin film was denoted as CDP.

The gas sensing experiment was carried out in an enclosed polyethylene chamber with a total volume of 4500 ml. Fig. 1 shows the schematic diagram of our handmade gas sensor setup. The

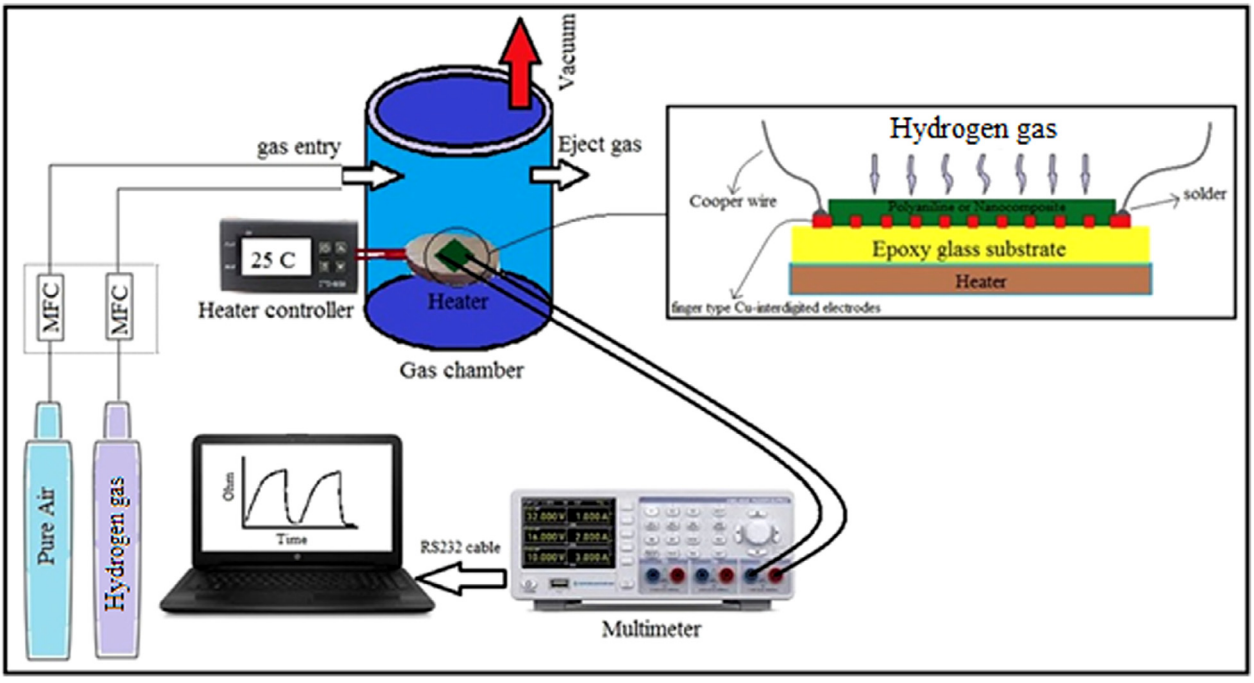

Fig. 1. The schematic block diagram of our handmade gas sensing setup.