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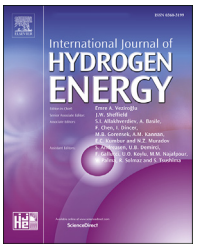

Room temperature hydrogen gas sensing properties of mono dispersed platinum nanoparticles on graphene-like carbon-wrapped carbon nanotubes

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ABSTRACT

We present platinum nanoparticles dispersed wrinkled graphene-like carbon-wrapped carbon nanotubes (Pt/GCNTs) as a room temperature chemiresistive hydrogen gas sensor. Pt nanoparticles are decorated over GCNTs surface using poly (sodium 4-styrene sulfonate) (PSS) functionalization, followed by ethylene glycol reduction method. The highly defective wrinkled graphene-like surface of GCNTs provides large surface area and PSS functionalization provides stable immobilization of mono dispersed Pt nanoparticles on the carbon surface. A simple and inexpensive drop cast technique is used to fabricate the thick film sensor of the material. Hydrogen resistive gas sensing properties of Pt/GCNTs are studied at different gas concentrations, temperatures and Pt wt. % loadings. Pt/GCNTs sensor shows optimal sensitivity at room temperature with stable and reproducible response towards hydrogen. The sensor with 2 wt. % of Pt showed maximum sensitivity that is three fold higher than Pt decorated carbon nanotubes (Pt/CNTs) with the same Pt wt. % loading. The present study shows potential to explore novel H2 sensors.

Introduction

Hydrogen (H_2), being a high efficiency, renewability, versatility and environmentally clean energy carrier, is finding significant interest in applications ranging from fuel cell based transportation systems, cryogenic fuels, power generation and in many industries [1–5]. However, safety continues to be major concern during H_2 production, storage and transportation and hence need to be adequately addressed for future H_2 economy. H_2 is a colourless, odourless and highly flammable gas at concentrations 4–75% by volume in air [5,6]. Hence, development of highly efficient H_2 sensor is necessary to monitor the leaks and measure the concentration of H_2. In this regards, a lot of intense research is going on towards improvement of sensitivity, selectivity, reliability and response time of H_2 sensors as well as for reduction of cost, sensor size and power consumption [6]. Chemiresistive

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sensors undergo a change in their resistance upon exposure to a test gas. Chemiresistive sensors are most attractive due to their cost effective simple structure and very precise readings may be achieved with minimal electronics [6]. Most of commercially available chemiresistive H_2 sensors are composed of metal oxides (*e.g.*, tin oxide) films which are operated at elevated temperatures (200–500 °C) [6–10]. Room temperature H_2 sensors are preferred due to their safe operation, low power consumption and long life time [11–13].

Carbon nanotubes (CNTs) and graphene have attracted great interest in gas sensing applications due to their high surface area, good electrical conductivity, room temperature operation and low level detection limits [14–18]. The gas sensing mechanism of these materials is based on their conductance change upon the adsorption/desorption of gaseous molecules [7,14,19]. However, pristine carbon nanotubes and graphene are almost insensitive towards some gases for which they have low adsorption energy such as H_2 [20–24]. Pt (platinum) and Pd (palladium) are known for their high catalytic activity towards H_2 and widely studied for fuel cell, hydride batteries and gas sensing applications [11,20,25]. Dispersion of metal nanoparticles (NPs) on high surface area carbon nanostructures improves the sensitivity, selectivity and response of carbon materials toward H_2 as well as increases surface to volume ration of Pt for better interaction with H_2 and hence enhances the overall sensing performance. In this regard, Pt and Pd NPs decorated multi-walled carbon nanotubes (MWCNT) have been studied as H_2 sensors [20–22]. Comparison to MWCNT, Pd NPs decorated single-walled carbon nanotubes (SWCNT) have reported with better sensitivity and shorter response time [26,27]. But, from application point of view MWCNT have advantage over SWCNT due to their ease in production and lower cost [20]. Recently, Pt decorated MWCNT forest was tested and 2% sensitivity for 3% H_2 in air was reported [28]. Randeniya et al. [29] investigated the H_2 sensing properties of MWCNT yarn coated with Pd–Pt particles and reported a sensitivity of 4% for 4% H_2 in air. Very recently, Yaqoob et al. [30] fabricated H_2 sensor by dispersing Pd nanocubes into MWCNT-reduced graphene oxide (RGO) mixture and achieved sensitivity of 35% at 1% H_2. In this present work, we utilized wrinkled graphene-like carbon-wrapped carbon nanotubes (GCNTs) as base materials for decoration of Pt nanoparticles. GCNTs can be synthesized by using facile chemical vapor deposition) (CVD) technique like MWCNTs [31]. The wrinkled graphene like surface structure provides a highly defective and large surface area and, the one-dimensional structure of multi-walled carbon nanotubes offers efficient conducting paths to this system [31–33]. So, in comparison to MWCNT/graphene mixture, GCNTs is expected to provide better charge transfer for improvement of sensitivity of the sensor.

It is revealed that small size and uniform deposition of metal NPs is important for high performance H_2 sensor [20,34]. Generally, metal NPs are deposited on CNTs by attaching functional groups (*e.g.*, hydroxyl, carboxyl and carbonyl groups) to the CNTs surface using harsh acid oxidization [20–22]. Unfortunately, the strong acid treatment damages the structure of by introducing large amount of defect that affects the conductivity of CNTs [13,33]. It is reported that, acid functionalization imparts some 'stacking' of the graphene sheets and hence reduces the surface area of graphene [35]. In addition, this approach deposits NPs mostly at defect sites and at edges and hence may results non-uniform dispersion and agglomeration. Functionalization using poly (sodium 4-styrenesulfonate) (PSS) provides stable and uniform nucleating sites for metal NPs as well as preserves intrinsic electronic and structural properties of the carbon material [35,36]. So, we used PSS functionalization to disperse Pt NPs on GCNTs which is also relatively fast and easy method.

The objective of the present work is to fabricate high sensitivity Pt/GCNTs H_2 sensor using effective and easy technique. The simple drop cast thick film sensor of Pt/GCNTs (with only 2 wt. % Pt loading) shows three fold higher sensitivity than Pt NPs decorated carbon nanotubes (Pt/CNTs). Pt/GCNTs sensor shows stable and reproducible response towards H_2 at room temperature.

Experimental

Material synthesis

GCNTs were prepared using single-furnace catalytic chemical vapor deposition (CCVD) technique [31]. Mish metal ($MmNi_3$) based alloy hydride and graphite oxide (GO) were used as the catalyst. GO was prepared by modified hummer method. The tubular furnace was heated up to 250 °C in argon atmosphere and hydrogen was allowed for 30 min. Then the temperature was increased up to 700 °C and acetylene (C_2H_2) was allowed. The furnace was cooled down to room temperature in argon atmosphere. The as-prepared sample was purified by air oxidation and acid treatment. Air oxidation was performed by heating the sample at 400 °C in air to remove the closed tips of carbon nanotubes and amorphous carbon. The air-oxidized sample was treated by refluxing in concentrated nitric acid at 60 °C to remove catalyst-metal impurities.

The syntheses of Pt/GCNTs samples were carried out by ethylene glycol reduction technique. Firstly, GCNTs were functionalized with poly (sodium 4-styrenesulfonate) (PSS). For PSS functionalization, 100 mg of GCNTs was ultrasonically treated for 1 h in NaCl solution (100 ml, 1 M) and PSS (200 mg) was added and stirred for another 1 h. Subsequently, the excess PSS was removed by repeated centrifugation/wash cycles. Finally, the sample was dried in vacuum at 60 °C. Then 100 mg of PSS functionalized GCNTs were dispersed in 100 ml of ethylene glycol solution. The pH of the solution was adjusted to 11 by adding NaOH. Then, different amount of H_2PtCl_6 was mixed to the solution to get the different weight fraction of Pt (2, 5, 10, 30 wt. %) in the final composite. The mixed solution was refluxed at 160 °C for 3 h.

Characterization technique

The Powder X-ray diffraction (XRD) studies were carried out with a PANalyticalX'Pert Pro X-ray diffractometer with nickel-filtered Cu Kα (1.54 Å) radiation as the X-ray source. The pattern was recorded with a step size of 0.016°. Thermo gravimetric analysis of the materials was performed with thermogravimetric analyzer (TGA) & differential scanning calorimeter (DSC) (DSC SDT Q600). The morphologies of the

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