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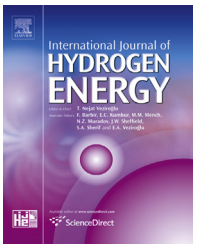

Platinum and platinum–iron alloy nanoparticles dispersed nitrogen-doped graphene as high performance room temperature hydrogen sensor

Raghu Sripada [a,c], *Vinayan Bhagavathi Parambath* [b], *Mridula Baro* [a], *Santhosh P Nagappan Nair* [c], *Ramaprabhu Sundara* [a,*]

[a] *Alternative Energy and Nanotechnology Laboratory (AENL), Nano-Functional Materials Technology Centre (NFMTC), Department of Physics, Indian Institute of Technology Madras (IITM), Chennai 600036, India*
[b] *Helmholtz Institute Ulm for Electrochemical Storage (HIU), Helmholtzstr. 11, Ulm D-89081, Germany*
[c] *Low Temperature Physics Laboratory, Department of Physics, Indian Institute of Technology Madras (IITM), Chennai 600036, India*

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ABSTRACT

In the present work, room temperature hydrogen sensing properties of platinum (Pt) and platinum–iron (Pt_3Fe) alloy nanoparticle (NP) decorated nitrogen doped graphene were investigated. In order to incorporate the nitrogen functional groups within the graphene matrix, first graphene was coated with the nitrogen anionic polyelectrolyte followed by the pyrolysis in inert atmosphere. Further Pt and Pt_3Fe nanoparticles were decorated on nitrogen-doped graphene (NG) by modified polyol reduction technique. The systemic investigation of hydrogen sensing properties of Pt/NG and Pt_3Fe/NG NPs at 4 vol% of hydrogen reveals the excellent sensitivity of these composites. The present study shows that Pt_3Fe/NG NPs composite can be believed as a high performance room temperature sensing material.

Introduction

In the quest for green energy resources, hydrogen has its own importance because it is renewable as well as having almost zero emission. Also it is the smallest molecule in size, light in weight and having high buoyancy and diffusivity. Due to these characteristics its burning velocity is very high and is very difficult to contain it. It has low ignition energy of 0.017 mJ and high combustion energy of 142 kJ/mol with a wide flammable range of 4 vol% to 75 vol% [1–3]. All these pose number of difficulties in storage and transportation of hydrogen. So it is clear that even though hydrogen is a potential source of clean energy, it poses a challenge with safety issues. Auto ignition temperature of hydrogen in air is between 500 °C to 577 °C [4]. Being colorless, odorless and tasteless human beings cannot detect hydrogen. Therefore fast response sensors are necessary for detection of leakages of flammable H_2 before it leads to explosion. Sensors are necessary for concentration monitoring as well.

* Corresponding author.
E-mail address: ramp@iitm.ac.in (R. Sundara).

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Platinum, due to its catalytic activity towards hydrogen is widely used in many of the hydrogen related applications like fuel cells, manufacturing industries, gas sensors hydride batteries and switchable optical devices [5–12]. Since this noble metal is very expensive and less abundant in the nature it is necessary to reduce its consumption. H_2 initially interacts with the surface of Pt before it diffuses into the metal. So by enhancing the physical surface area of Pt we can increase the interaction of H_2 with the metal there by making maximum utilization of Pt. This can be achieved through reducing the particle size of Pt and subsequent decoration on inexpensive support material having high surface area and high electrical conductivity. Another approach to reduce the Pt consumption is alloying of Pt with inexpensive 3*d* transition metals.

Graphene and carbon nanotubes are suitable support materials for the dispersion of metal nanoparticles due to their excellent properties such as large surface area, good thermal and chemical stability, and also high electrical conductivity and have been explored in various applications such as gas sensors, fuel cells and hydrogen storage [6,13–20]. These support materials do not need any preheating for operation unlike metal oxide based sensors which operate at elevated temperatures [21,22]. Recent reports reveal that doping of carbon supports with nitrogen, boron and sulfur can enhance the uniform dispersion and strong binding of metal NPs on the support [23,24]. These dopants can create uniform defect sites on graphene layers, which can act as nucleating sites for NPs growth. Nitrogen doped graphene was synthesized by researchers in various ways such as chemical vapor deposition of graphene using methane as carbon source in presence of ammonia or propane, heat treating graphene at 900 °C in presence of ammonia and argon and using nitrogen plasma [25–34]. These methods are difficult to scale up, time consuming and not cost effective. So it is required to develop a simple nitrogen doping approach for carbon supports in a cost effective approach.

In the present work nitrogen doping of graphene support were carried out using an anionic polyelectrolyte and nitrogen-containing polymer. Pt NPs and platinum–iron alloy (Pt_3Fe) NPs were impregnated on nitrogen doped graphene. The smaller particle size enhances the amount of hydrogen adsorbed as it increases the number of active sites [35,36]. Films of as-prepared materials were developed by drop casting technique on alumina substrate with two gold-coated electrodes. A resistive H_2 sensor response study was carried out at room temperature.

Experimental section

Material synthesis

Graphite oxide (GO) was prepared by Hummer's method from graphite powder [37]. Graphene was prepared by hydrogen exfoliation technique [38]. Briefly, graphite oxide was taken in a quartz boat placed in a tubular furnace whose both ends are closed by end couplings and has provision of inlet and outlet for gas. At first it was purged with argon for 15 min then hydrogen is allowed and temperature is raised to 300 °C. Within minutes when temperature reached 200 °C reduction and exfoliation occurred. This material is labeled as G.

Graphene was coated with anionic electrolyte Poly (sodium 4-styrenesulfonate) (average M_w ~70,000) (PSS) as reported by Yang et al. [39]. Graphene is added to 1 wt% aqueous solution of PSS with concentration of 0.15 mg mL^{-1} followed by strong stirring followed by sonication. Obtained dispersion was maintained at 50 °C for 12 h. Then the solution was washed with DI water several times to remove excess PSS and dried in vacuum oven at 70 °C for 24 h. Pyrrole monomer was used as the nitrogen source. In 100 mL of 0.1 M solution of HCl 200 mg of PSS coated graphene was dispersed by ultrasonication for 30 min. 1 mL of pyrrole and 2.4 g of $FeCl_3$ was added to this solution and kept for 24 h at 50 °C for polymerization. Later it was washed with copious amount of water. The obtained material was placed in a quartz boat, which is placed in tubular furnace with closed end couplings and provision for gas flow. It was purged with argon for 15 min and heated to 800 °C in argon flow for 3 h. It is allowed to cool in argon flow. Obtained material was washed with acetone and followed by copious amount of water. This sample is labeled as NG.

100 mg of NG was added to 200 mL of solution of ethylene glycol (EG) and water in the ratio 3:1 and kept for stirring for 7 h while adding suitable amount of H_2PtCl_6 drop wise for 35 wt.% loading. 2.5 M NaOH solution is added slowly till pH of the solution reaches 11. This solution was refluxed for the further reduction for 7 h at 130 °C. Later it is washed with copious amount of water and dried in vacuum oven at 60° C. It was labeled as Pt/NG. For platinum–iron alloy decoration similar method is followed. In the present case, suitable amount of H_2PtCl_6 and $FeCl_3$ solutions were added drop wise for 35 wt.% loading. It was labeled as Pt_3Fe/NG. Fig. 1 illustrates the schematic of the synthesis procedure.

Characterization techniques

X-ray Diffraction studies were carried out in PANalytical X'pert PRO X-ray diffractometer with Copper Kα as source with nickel filter. The step size used was 0.016° and data was acquired from 5° to 90° (2θ). Raman spectroscopy studies were carried out using Horiba Jobin Yvon HR800UV with 632 nm excitation sources. The morphology of the samples were studies by field emission scanning electron microscope FEI QUANTA 3D and transmission electron microscopy FEI Tecni G2 20 S-TWIN (200 eV) and X-ray photoelectron spectroscopy was carried out using Specs X-ray photoelectron spectrometer with Mg Kα x-ray source, PHOIBOS 100MCD energy analyzer was used.

Film fabrication

An alumina substrate of 15 mm × 15 mm × 1 mm is coated with two parallel gold electrodes of 10 mm long and 2 mm wide by electron beam evaporation. In 1 mL of ethanol, 40 μL of 1 wt.% Nafion solution and 5 mg of sample was added and ultrasonicated to disperse the sample. This slurry was drop casted on the substrate. On end of the electrodes a 3 mm space was left out to furnish two wire contacts as shown in Fig. 2(b and c).

Sensor response studies

Hydrogen sensor studies were carried out in homemade hydrogen sensor test station as shown Fig. 2(a). It consists of a

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