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A facile synthesis and field emission property investigation of Co_3O_4 nanoparticles decorated graphene

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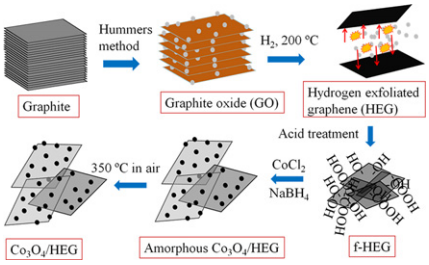
HIGHLIGHTS

- A facile technique for the synthesize of Co_3O_4/HEG.
- Developed a flexible field emitter.
- Low turn-on field and threshold field.
- Emitter shows better stability.

GRAPHICAL ABSTRACT



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ABSTRACT

The present work describes the synthesis of cobalt oxide nanoparticle decorated hydrogen exfoliated graphene (Co_3O_4/HEG) by exfoliating graphite oxide in hydrogen atmosphere followed by chemical reduction of cobalt salt using sodium borohydride. The synthesized material has been characterized by X-ray diffractometry, thermogravimetric analysis, field emission scanning electron microscopy and transmission electron microscopy. A flexible field emitter has been fabricated by spin coating this material on carbon cloth. Electron emission characteristics of Co_3O_4/HEG have been investigated using an in-house fabricated setup and analyzed using Fowler-Nordheim equation. Turn-on and threshold fields of 1.12 and 1.35 V μm^{-1}, respectively have been observed for this material. Moreover, the present field emitter shows a reasonably good stability and repeatability.

1. Introduction

Cobalt oxide (Co_3O_4) has large number of applications in its bulk as well as nano forms. Co_3O_4 particles of different size and shapes have been used in batteries [1–4], sensors [5,6], field emitters [7,8] and electro chromic devices [9] due to their unique structural and magnetic properties [10]. The different synthesis procedures for Co_3O_4 include solvothermal/hydrothermal technique [11–13], sol-gel technique [10,14] and electro deposition [9,15]. Though there are reports on the field emission property of Co_3O_4 [7,8] the poor electrical conductivity limits its usage in several electronic applications. Commonly used additive materials are graphite, conducting carbon and conducting polymers which give path for the electron flow. In some cases, however, the conducting material covers the Co_3O_4 particles fully and consequently, specific applications cannot completely utilize the Co_3O_4 material property. Hence, different approaches are followed in order to utilize the properties of Co_3O_4 such as growing Co_3O_4 nanoparticles on a conducting substrate, decoration of Co_3O_4 nanoparticles on conducting nanostructures etc [16].

After the successful extraction of single layer of graphene from the bulk graphite by micromechanical cleavage [17], it has become the most studied nanomaterial by the scientific community. The strange properties of graphene such as extraordinary high room

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temperature carrier mobility above 100,000 cm^2 V s^{-1} [17,18] conductance quantization [19] potential of inducing a band gap through the lateral quantum confinement [18] and prediction for epitaxial growth [20] make graphene a promising material for future electronic circuits. Recently, it has been reported that graphene is a promising material for field emission applications too. A maximum emitted current of 170 nA and turn-on voltage of 12.1 V are have been reported for planar graphene [21]. In the case of planar graphene, emission is mainly from the edges of graphene sheet. Lee et al. [21] have suggested that one can reduce the voltage for electron emission from graphene sheets by creating more emission sites on the surface of graphene sheet. In our previous study, field emission properties of wrinkled graphene with a turn-on field of 1.18 V μm^{-1} have been reported [22]. Similarly, Malesevic et al. [23] have reported an enhancement in field emission property with few layer graphene which gives a turn-on field as low as 1 V μm^{-1} and field amplification factor up to several thousands. Using single and few layer graphene flakes, a field emission current up to 1 μA has been achieved from the flat part of graphene flakes at applied fields of few hundred volts per micrometer [24]. In the present study, field emission properties of Co_3O_4 decorated HEG (Co_3O_4/HEG) have been investigated.

2. Materials and methods

2.1. Materials

Graphite (99.99%, 45 μm) was purchased from Bay Carbon, Inc USA. All other reagents like sulfuric acid, nitric acid, potassium permanganate ($KMnO_4$), sodium nitrate, sodium borohydride ($NaBH_4$), sodium hydroxide (NaOH) and cobalt chloride ($CoCl_2$) were analytical grade. Deionized (DI) water was used throughout the experiment.

2.2. Synthesis of Co_3O_4/HEG

HEG was synthesized as described elsewhere [25]. Briefly, HEG was synthesized by exfoliating graphite oxide (GO) in hydrogen atmosphere at 200 °C. As synthesized HEG was functionalized by treating with conc. H_2SO_4:HNO_3 (3:1 by vol.), prior to metal oxide decoration. Co_3O_4 nanoparticles were decorated on functionalized HEG (f-HEG), as follows. 160 mg of f-HEG was dispersed in DI water by ultrasonication followed by magnetic stirring for 5 h. Calculated quantity of cobalt chloride (119 mg) was added to the above solution under stirring to get a 20 wt. % loading of Co_3O_4 on HEG. After 24 h, 40 ml of reducing solution (mixture of $NaBH_4$ and NaOH) was added to the above solution drop wise. The sample was then washed with DI water, filtered and dried. Later, the powder was annealed at 350 °C in air atmosphere for 1 h.

The field emitter was prepared by spin coating Co_3O_4/HEG on a flexible carbon cloth. The spin coating solution was prepared as follows: 10 mg of Co_3O_4/HEG was dispersed in 1 ml of 0.5% Nafion solution by ultrasonication. This dispersion was later spin coated on a flexible carbon cloth using 500 rpm in the first stage for 20 s and 2000 rpm in the second stage for 30 s. The film was heated at 110 °C under vacuum for 12 h to remove solvent.

2.3. Experimental techniques

Powder X-ray diffraction studies were carried out using a PANalytical X'PERT Pro X-ray diffractometer with nickel-filtered Cu K_α radiation as the X-ray source. The pattern was recorded in the 2θ range of 5°–90° with a step size of 0.016°. Thermal stability of the materials was studied using thermogravimetric analysis (TGA) employing a Perkin-Elmer TGA 7 analyzer. TGA was done in air atmosphere in the temperature range room temperature to 750 °C with a heating rate of 20 °C min^{-1}. Morphology of the samples was characterized by field emission scanning electron microscopy (FESEM, FEI QUANTA). Elemental presence was investigated using the energy dispersive X-ray spectrum connected to FESEM. Transmission electron microscopy (TEM) was carried out using a JEOL JEM-2010F microscope. For TEM measurements, samples were dispersed in absolute ethanol using mild ultrasonication and casted onto carbon coated Cu grids (SPI supplies, 200 mesh). Field emission studies were done using an indigenously fabricated setup [26]. The setup consisted of a sample holder having stainless steel cathode and gold coated copper anode. This sample holder was connected to a high vacuum pump station to conduct the experiment under a pressure of 10^{-6} mbar (10^{-6} torr). Electrical contact was given between the substrate and cathode using silver paste. Voltage was applied between the cathode and anode using a Keithley 237 high voltage source.

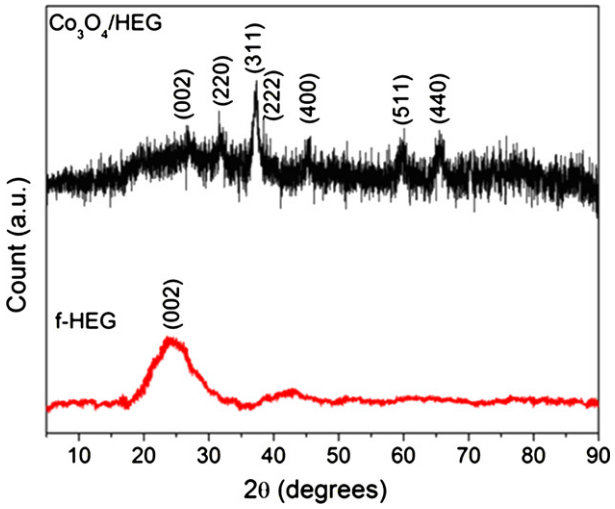

Fig. 1. X-ray diffraction pattern of f-HEG and Co_3O_4/HEG.

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) patterns of f-HEG and Co_3O_4/HEG. f-HEG exhibits a broad peak around 25°, corresponding to (002) plane of graphitic carbon. The broad and amorphous like

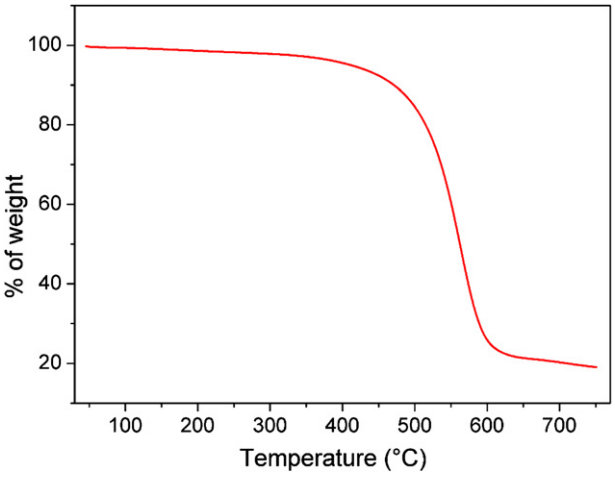

Fig. 2. Thermogravimetry analysis of Co_3O_4/HEG.