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Cold field emission from hydrogen exfoliated graphene composites

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In the present letter, field emission property of highly wrinkled hydrogen exfoliated graphene (HEG) was studied using an indigenously fabricated setup under $\sim 10^{-6}$ mbar pressure. Graphene was coated on a flexible carbon cloth by spin coating for the field emission study. The turn on voltage obtained for a HEG field emitter is around 1.18 $V/\mu m$. Further, the field emission property of HEG was improved by decorating metal oxide over HEG. The stability of the field emitter was tested and field enhancement factor was calculated using Fowler–Nordheim plot. © *2011 American Institute of Physics*. [doi:10.1063/1.3587639]

Field emission is a quantum mechanical tunneling phenomenon wherein the emission of electrons occurs from the surface of the material to vacuum by an external applied electric field. This phenomenon occurs in high electric fields of the order 10^7-10^8 V/cm. The high electric field narrows the potential barrier at the emitter-vacuum interface sufficiently for the electrons to have a significant probability of tunneling from the emitter surface to vacuum. The efficiency of this emission process is tens of millions of times higher than in other known emission processes. The quantitative description of the process was first suggested by the Fowler–Nordheim (F–N) theory.[1] This theory relates current density to field strength (E) and work function (φ) with the following formula:

$$I = \frac{(aA\beta^2E^2)}{\varphi}\exp(-B\varphi^{3/2}/\beta E), \quad (1)$$

where $a = 1.54\times10^{-6}$ A eV V^{-2} and $B = 6.83\times10^7$ $eV^{3/2}$ V cm^{-1}, respectively. A is emission area and β is the field enhancement factor given by,

$$\beta = \frac{B\varphi^{3/2}d}{\text{slope}}. \quad (2)$$

One of the most remarkable results of field emission theory is prediction of very high current density. Very high current densities are possible due to following two factors: (1) no energy is required for maintaining the emission process if electrons exit the solid by a tunneling mechanism, that is, the emitter need not to be heated, irradiated, or otherwise exited by some external energy source and (2) there is a very large reservoir of electrons near the Fermi level of emitter. Field emission cathodes find applications in electron microscopy, Auger spectroscopy, flat panel displays, etc. One of the major problems of the modern vacuum microelectronics is fabrication of high efficiency, low-voltage field electron emitters with large surface area.

Carbon based materials are the commonly used nanomaterials for field emission applications because of their high aspect ratio, high field enhancement factor, and good electrical conductivity.[2–4] Graphene is a zero-gap two-dimensional carbon based nanosemiconductor with the energy bands of the π-electrons crossing the Fermi level at the edges of the Brillouin zone, leading to a Fermi surface made of six points.[5] It is having larger surface area, high electrical conductivity, and good mechanical strength, which made them useful for field emission applications. Previous report on free-standing graphite sheets with thickness less than 1 nm showed a low turn-on field of 4.7 $V/\mu m$ for electron field emission suggesting that the carbon nanosheets could be used as a potential edge emitter.[6]

The synthesis and characterization of powder hydrogen exfoliated graphene (HEG) are given in our previous report.[7] The field emission property was studied using an indigenously fabricated setup.[3] The field emitter (film) was made by the following procedure. 10 mg of 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 and 2000 rpm in the second stage. The film was heated under vacuum for 12 h to remove solvent. The field emission property of film was studied after loading in the setup, which contains a stainless steel cathode and gold coated copper anode.

The charge accumulation at the edges and foldings of graphene affects the potential barrier, which enhance the electron emission. The surface morphology and defects on HEG were studied using field emission scanning electron microscopy (FESEM) (Ref. 7) and transmission electron microscopy (TEM) shown in Fig. 1(a). The low magnification FESEM image in Fig. 1(b) shows the nearly uniform coating of HEG on carbon cloth.

The current density-electric field (J-E) plot for fabricated HEG field emitter is shown in Fig. 1(c). The turn on field for a current density of 10 $\mu A/cm^2$ and threshold field for a current density of 0.2 mA/cm^2 are about 1.18 $V/\mu m$ and 1.43 $V/\mu m$, respectively. The field enhancement factor (β) has been calculated from the F–N plot [inset Fig. 1(b)] and is about 4907. These values are better than that of planar graphene reported by Lee *et al.*[8] This significantly good performance of HEG can be due to the following reasons: the foldings and wrinkles on the graphene helped it to be a good field emitter. The defects on the graphene sheet lowered electron affinity that provided a low-energy barrier and enhanced electron emission. The electrical conductivity of HEG has been measured using a four probe method and is around 1.6×10^3 S/m. The large surface area of HEG, which is

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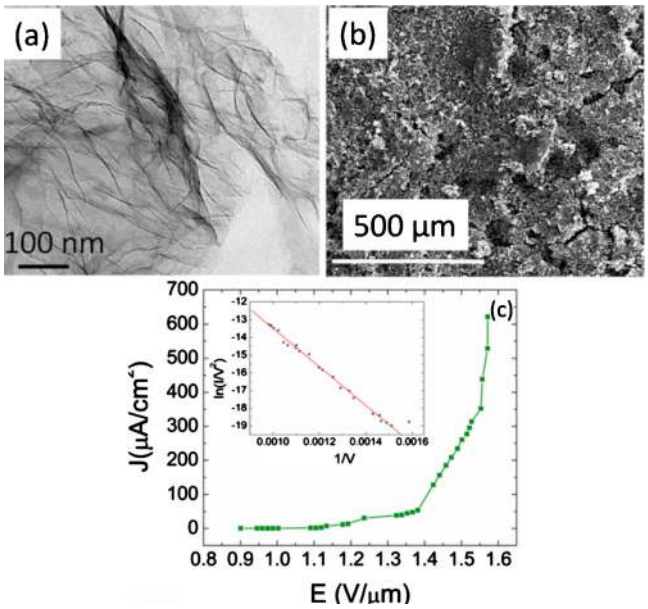

FIG. 1. (Color online) (a) TEM image of HEG (b) FESEM image of HEG coated on a carbon cloth and its (c) J-E and F–N (inset) plot.

around 442.9 m^2/g may also have a significant effect on field emission. The considerably good turn on voltage and threshold voltage of HEG can also be due to the residual hydrogen atoms present in the graphene. According to Lu *et al.*[9] the hydrogen atoms adsorbed on the surface and edges of graphene aggregate to form the localized states near the Fermi level, which is responsible for the emission. It is reported earlier that hydrogen plasma treatment improves the field emission of carbon nanotubes (CNTs). The theoretical studies by Maiti *et al.*[10] and Chen *et al.*[11] showed that under an electric field hydrogen molecule can reduce the ionization potential of CNT. Similar reason can be valid for graphene also considering the fact that CNT is rolled graphene sheet. Since the present graphene was synthesized in hydrogen atmosphere, there is a possibility of residual hydrogen atoms. The enhancement of electric current at low electric field is due to the charge distribution on carbon and hydrogen atoms and the resulting surface dipoles, which are expected due to the difference in electronegativity of carbon and hydrogen. At low fields, a large dipole moment is created between hydrogen (+ve) and carbon (−ve). The direction of the field is such that it assists in the extraction of electrons from graphene sheets, effectively by reducing the work function.

The field emission property of HEG was improved by decorating its surface with metal oxide (CuO and RuO_2) nanoparticles. The decoration was done by simple chemical reduction method. The decoration of CuO and RuO_2 on HEG reduces the work function of HEG effectively and increased the surface roughness, which helps in field emission. Figure 2 shows the FESEM images of (a) CuO/HEG and (b) RuO_2/HEG. Even though the particle distribution is more or less uniform in each case, the FESEM image CuO/HEG suggests that the particle size is not uniform. Though the overall particle size is low still there are some big CuO particles in CuO/HEG. In the case of RuO_2/HEG the particle size is more or less uniform. The TEM images of (c) CuO/HEG and (d) RuO_2/HEG shown in Fig. 2 confirms the uniform distribution of particles on graphene sheet. Figure 3 shows the J-E and F–N plot (inset) of CuO/HEG and RuO_2/HEG. The results are summarized in Table I. The turn on voltage and threshold voltage of CuO/HEG is better than that reported by Zhu *et al.*[12] for CuO nanowire film and Shang *et al.*[13] for strawlike CuO nanostructure. Similarly the field emission property of RuO_2/HEG is better than that reported by Knibbe *et al.*[14] for CNTs with nanosized RuO_2 particles deposition. The turn on field and threshold field of metal oxide coated HEG is lesser than that of pure HEG. This is due to the low work function and rough surface formed after the coating of these metal oxides on HEG. Though the work function of CuO is low compared to RuO_2, the turn on voltage of CuO/HEG is slightly higher than that of RuO_2/HEG.

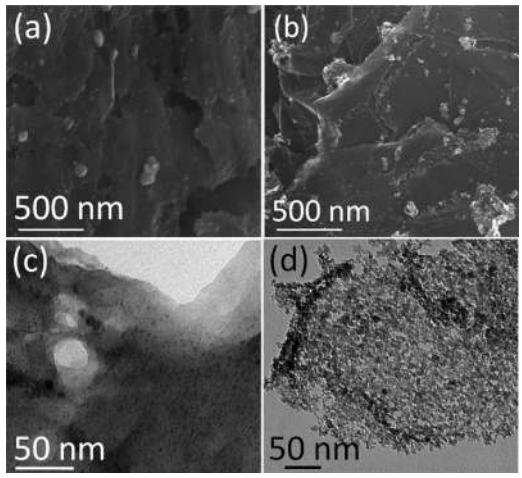

FIG. 2. [(a) and (b)] FESEM images of CuO/HEG and RuO_2/HEG. [(c) and (d)] TEM images of CuO/HEG and RuO_2/HEG.

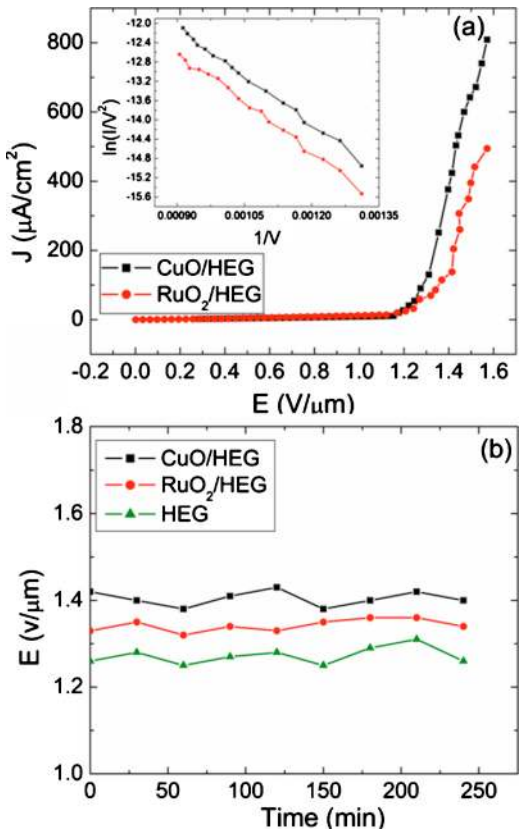

FIG. 3. (Color online) (a) J-E plot and F–N (inset) plot of CuO/HEG and RuO_2/HEG. (b) Stability study of HEG, RuO_2/HEG and CuO/HEG field emitters.

TABLE I. Summary of the experimental results.

Sample code	Turn on voltage for current density 10 $\mu A/cm^2$ ($V/\mu m$)	Threshold voltage for current 0.2 mA/cm^2 ($V/\mu m$)	Field enhancement factor
HEG	1.18	1.43	4907
CuO/HEG	1.1	1.32	7099
RuO_2/HEG	0.91	1.41	7621

The high field enhancement factor of RuO_2/HEG may be the reason for this high performance. The high field enhancement of RuO_2/HEG can be due to the uniform RuO_2 distribution on HEG. The FESEM and TEM images of CuO/HEG and RuO_2/HEG supports this. In addition to the F–N equation, the high field emission current of graphene and graphene nanocomposites is due to the shift in Fermi level toward the vacuum level by the application of electric field, which lowers the effective height of the potential barrier, cause the electrons to be emitted easily.[15]

The stability of each field emitter was studied for a current density of 0.1 mA/cm^2 for 4 h. The stability curve for each sample is shown in Fig. 3(b). The repeatability of field emitter was checked by testing each field emitter a minimum of four times. In each case the error in the measurement was less than 4%.

The field emission property of HEG and its composites has been studied after spin coating over a flexible carbon cloth. The surface wrinkles, presence of residual hydrogen, and shift in Fermi level gives a low turn on voltage and threshold voltage for HEG and its metal oxide composites. The low turn on voltage and threshold voltage and the stability measurements suggest that this material can be used for flexible filed emitters.

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