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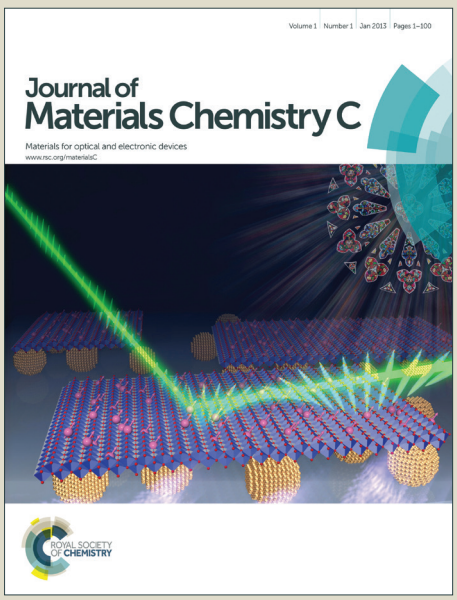

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Unique quasi-vertical alignment of RGO sheets under applied non-uniform DC electric field for enhanced field emission

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Abstract:

In this paper, we report unique quasi-vertical alignment of reduced graphene oxide (RGO) sheets under applied non-uniform high DC electric field deposited on carbon cloth (CC) substrate, which eventually resulted in enhanced field emission characteristics. Significant improvement in enhancement factor was achieved with major increment in current due to alignment of thin RGO edges under applied non-uniform electric field. The non-uniform field was generated by conical shape of the top electrode (anode). Moreover, the experimental findings have been validated through simulated modeling of electric field over RGO sheet using finite element method for both planar and conical top electrode geometrical configurations. This observed phenomenon could have a potential fundamental impact on field emission applications with vertically aligned graphene and RGO based materials in the coming years.

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Introduction:

In recent years the exponential rise of graphene and reduced graphene oxide (RGO) based research can be attributed to its diverse range of electronic properties favorable for many device applications. The fact that this 2-D analogue of graphite provides immense flexibility to tune its electronic properties at the atomic scale ushered a new era for material research[1-3]. Among the many distinct features of graphene and RGO, changes in the peripheral edge site geometry bear a significant effect in the attenuation of the electronic properties. This is well established in carbon nanotubes where Zhou *et al*. reported that geometrical effects influence the work function, amplification factor in single walled carbon nanotubes and adjustment of the localized electronic states of the emitting regions can affect the field emission characteristics[4]. Recently it has been reported, that graphene and RGO leads to better field emission due to its protruding edge effect of the sheet boundary peripheral region[5]. The presence of rich edges influences the electronic transport enabling easier tunneling of electrons producing a lower barrier potential to eject electrons into vacuum[4]. Evidence of exceptional field emission has been found in case of freestanding RGO edges by virtue of its lower work function attribute. The results are even better than freestanding pure graphene edges on a substrate[6, 7]. The additional presence of edge functional groups only assists further leading to a more distorted sp^3 configuration from a planar sp^2 in RGO [5, 8].With their large lateral surface dimension, atomic thickness, high conductivity and good flexibility, graphene and reduced graphene oxide are expected to randomly align themselves to the electric field direction under an applied field, which eventually should result in enhanced local field emission[5].Currently, a lot of techniques are being employed for the enhancement of field emission in RGO. For example, edge enhancement of RGO through plasma etching, and capping of free standing RGO edges over silicon and copper grid substrates have been the most significant. [6, 7, 9-15]It is interesting to note

that aligned edges of RGO and graphene proved to be a much improved field emitter in these cases due to their increased aspect ratio. However in this work, part our motivation was to observe the changes in structural attributes in two-dimensional materials like graphene and RGO when high field was applied through a planar and conical top electrode configuration and then study its field emission characteristics.

In this paper we report a fascinating observation where RGO sheets get quasi-vertically oriented under the applied high non-uniform DC electric field generated by conical (non-planar) shape of the anode. The RGO sheets were assembled over flexible carbon cloth (CC) substrates by using a simple EPD (electrophoretic deposition) process. Henceforth, we also simulated our experimental results using finite element modeling (FEM) method under high field. We mimicked the non-planar geometry of the top electrode and then compared with the planar electrode configuration to map the variation of electric field dispersion on interaction with RGO sheet to validate our hypothesis.

Experimental details:

RGO Synthesis:

Hydrophilic suspension of graphite oxide was synthesized following a modified Hummer's and Offeman's method from graphite powders. The synthesized GO with a loading of (1mg/ml) was further dissolved in DI water and exfoliated for 30 minutes in a high power sonicator and the supertanant was collected to obtain a yellow colored stable hydrophilic suspension of single layer graphite oxide layers (GOSL). This obtained GOSL solution was reduced by drop wise addition of appropriate amounts hydrazine hydrate (35 wt% in water) and ammonium hydroxide (25 wt%. in water) in a water bath at constant 90°C for ~1h till the solution turned into a black stable suspension of hydrophilic RGO [16-18].

Electrophoretic deposition of RGO:

For the electrophoretic deposition (EPD) of RGO, a 50 ml solution of RGO at loading (1mg/ml) was taken in a beaker and the deposition was carried out over carbon cloth fabric at constant current density ~2.5 mA/cm^2 for 10 minutes. The inter electrode distance for the depositions was kept constant at ~4 cm [5].

Condition for alignment of RGO flakes:

The non-uniform field over thin RGO layers deposited on carbon cloth substrate was generated using a conical tip anode with tip diameter ~ 0.5 mm. This sample is designated as *n*-RGO. The uniform field on a similar sample was generated through a flat tip anode with tip diameter 1.2 cm and designated as *u*-RGO. The flat tip anode area was taken to be greater than the actual sample area. In each case the sample was kept inside a high vacuum chamber and the amount of field applied was ~2000 V/mm for ~5 min. Both configurations have been shown schematically in figure 1.

Characterizations:

The thin films have been characterized using XPS (monochromatic Al Kα (hν = 1486.6 eV) X-ray source and a hemispherical analyzer by SPECS, HSA 3500. The recorded spectra were charge corrected using the C1s line of the adventitious carbon at 284.4 eV as a reference was done to determine the nature of bonding and the different functional groups being present in the structure and for elemental compositional analysis. RAMAN spectroscopy was conducted using (WITEC alpha, 300R) to confirm the successful synthesis of the carbon materials. High-

resolution transmission electron microscopy (HRTEM, JOEL - JEM 2100) was done to confirm the successful synthesis of the fabricated materials. The field emission scanning electron microscopy (FESEM, Hitachi S-4800) analysis was carried out to study surface morphology of the thin films and finally Field Emission (FE) was carried out by using a standard high vacuum FE set up.

Results and discussion:

Figure 2(a) shows the high resolution C1s XPS spectrum corresponding to the RGO sample that it is dominated by (284.7 eV) peak due to the presence of C=C/C-C bonds as expected. It was further observed that the contributions of oxygen functional groups namely C-O (epoxy or alkoxy) (286.6 eV) and C=O (288.5 eV) is very less which is consistent for RGO like materials[11]. Sufficiently low contribution of the oxygenated functional groups signifies successful formation of RGO through the reduction of graphite oxide (GO). Figure 2(b) shows the Raman spectra for RGO. The Raman bands (D, G, 2D) represent all the distinctive features that is encountered in case of the sp^2 carbon nanostructures. The HRTEM micrographs and selected area electron diffraction (SAED) pattern of RGO flakes are shown in the inset of figure 2(b). Inset shows the signature characteristics of very thin and flaky layered distribution of few RGO sheets along with the corresponding SAED pattern possessing hexagonal symmetry[19].

In figure 3 the FESEM micrographs of EPD deposited RGO thin films on carbon cloth in before and after the application of high uniform (*u*-RGO) and non-uniform (*n*-RGO) electric field are shown. Morphology of as synthesized RGO film deposited over carbon cloth substrate is shown in figure 3(a). We observed that no significant edge alignment could be achieved for RGO thin film under uniform electric field (*u*-RGO) as depicted in figure 3(b). However after the application of the high non-uniform DC electric field, significant changes to the RGO

morphology can be seen (*n*-RGO), as shown in figure 3(c, d). Furthermore, it is evident that the aspect ratio has changed drastically in *n*-RGO and the observed aspect ratio has been increased to micrometer order in the direction of applied field.

From a generalized perspective this phenomenon can be explained by the interaction of non-uniform electric lines of force coming from the top conical anode over RGO sheets. Now because of the conical shape of the top electrode the density of the lines of forces will be strongest at the tip center and then gradually becoming divergent and weaker as it moves away. This implies that non-uniform field dispersion can act over the RGO sheets depending on the anode geometry. The ramifications of which subsequently led to the quasi vertical alignment of the RGO edges. Now when this high field interacted with RGO which is peripherally surrounded by negative charges in the form of carboxylic and epoxy ions at the edges generates an attractive Coulombic force that successfully leads to the quasi alignment of the edge sites in the direction of the applied field.

To verify this intuitive notion simulative analysis were conducted. For 3D simulation of the electric field dispersion under uniform and non-uniform field for RGO sheets, we have employed FEM method using ANSYS Maxwell software package. While the experimental system consisted of innumerable RGO sheets, the representative theoretical models discussed here were designed only for a single RGO flake to simulate the local electric field dispersion using a flat (uniform field) and conical top electrode (non-uniform field). Henceforth, the obtained results were found to be consistent with the experimental findings.

To model the RGO sheets, a three-dimensional structure assigned as graphite with thickness ~3 nm and periodic structural rippling was used. 2 kV potential difference was applied in between the top and bottom electrodes and the whole system was placed in vacuum for all

calculations. For simulation, we have chosen two configurations of the top electrode. To simulate the effect of high uniform DC field, a planar top electrode with much larger dimension compared to the RGO sheet was chosen. However to simulate the effects of non-uniform field, we have chosen a conical shaped top electrode geometry for which the left edge of the modeled RGO sheet aligns approximately parallel to the axis of the conical top electrode i.e. along z direction (Fig. 1).

From figure 4, we observe the obtained solutions of the electric field dispersion over the RGO sheet under the influence of applied high DC voltage for both planar and conical top electrode geometrical configurations. Figure 4(a) and 4(b) depict the field magnitude distribution over RGO sheet due to planar top electrode geometry from top and side views respectively while Fig. 4(c) and 4(d) show the same for conical top electrode geometry. The simulated results readily suggest that when top electrode geometry is planar, uniform field dispersion is obtained throughout the edges of the RGO sheet. However when the top electrode geometry is changed in favor of a conical one, one can observe that the maximum field density has shifted towards the left edge boundary of RGO indicated by the density of the red/orange color dispersion (figure 4d). As the left edge was modeled to remain below approximately near and parallel to the tip of the conical anode in the vertical axis (z) for all calculations, this successfully generated non-uniform high field density dispersion. Hence, these observations validate our hypothesis and tallies with our experimental findings to a good extent.

Next we conducted the field emission (FE) analysis *u*-RGO and *n*-RGO thin films over carbon cloth. It is expected that the enhanced edge geometry of RGO sheets under applied non-uniform field will directly reflect in the FE characteristics and hence forms an integral part of the analysis. To carry out the field emission measurements, a standard custom-made diode

configuration set up was used. The whole arrangement was mounted in a liquid nitrogen trapped rotary-diffusion high vacuum chamber (~2 x 10^{-6} mbar). The inter electrode distance was adjusted using a micrometer screw and kept at a constant distance of 2.5 mm for both samples. The corresponding current (I) vs electric field (E) curves were obtained for both samples. Henceforth these results were further analyzed using the Fowler–Nordheim (F–N) relation[20]

$$I = Aat_F^{-2}\varphi^{-1}(\beta E)^2 \exp\left\{-\frac{b\upsilon_F\varphi^{\frac{3}{2}}}{\beta E}\right\} \quad (1)$$

Where A is the effective emission area, β is the enhancement factor, t_F and υ_F are the values of special field emission elliptic functions for a particular barrier height φ. Again, a = 1.54×10^{-6} (A V^{-2}eV) & b = 6.83×10^{3}(V $eV^{-3/2}$ μm^{-1}) are the 1st and the 2nd F-N constants respectively. φ is called the work function of the material and related to β by the following equation:

$$\beta = -b\varphi^{3/2}/S \quad (2)$$

where S is the slope of the F-N plot, i.e. a plot of $ln(I/E^2)$ versus $1/E$ obtained from the modified F-N equation (1). Previous reports[12, 21] suggest that the same equation can be used for vertically aligned graphene and RGO flakes also. The corresponding field emission characteristics for the thin film sample have been shown in the figure 5(a, b) followed by their corresponding F-N plots in each of the insets.

From the I-E curves, it is evident that good field emission characteristics could be achieved in case of *n*-RGO film. Very low turn-on field (E_{to}~ 0.55V μm^{-1}) was observed for both samples (taking the turn-on field to be defined at I = 1μA for all the samples). However maximum emission current (~105 μA) achieved in *n*-RGO film is very large compared to emission current (~6 μA) from *u*-RGO [figure 5a]. The field enhancement factors (β) were calculated from the linear regions of FN plots of both samples, assuming the work function (Φ) of both the materials to be as same as graphite ~ 5 eV[22, 23]. It is found that the β value (~19430)

for *n*-RGO film is much higher compared to *u*-RGO (β~11019) in which sufficient edge alignment wasn't observed under the action of applied uniform electric field (figure 5b).The significant increase in the enhancement factor in case of *n*-RGO film firmly suggests that better aspect ratio was attained under the action of non-uniform field and carbon cloth substrate provided a good conducting platform, which in turn contributed to a much higher number of emitter sites and generated immense emission current for improved FE properties[7]. On the other hand, it is worth mentioning in this context that there are few previous reports where a modified F-N relation has been suggested considering a non-planar cathode emitter geometry [24, 25].This is related to our work as emitter geometry changes in *n*-RGO film, i.e, emitter (RGO) geometry transforms from planner to vertically aligned under applied non-uniform electric field. Yuasa *et al*.[25] developed a model and modified the F-N relation considering a non-planar (hyberboloidal) surface emitter to account for additional enhancement factor depending on emitter geometry. It is stated that instead of the $I/V^2 \propto \exp(-A/V)$ current–voltage characteristics in the F–N model, it is replaced with $I/V^3 \propto \exp(-A/V)$ taking non-planar (hyperboloidal) emitter geometry into consideration. However the authors[25] concluded that the right hand side of the modified F-N formalism follows the same exponential factor of the conventional F-N equation. This justifies the validity of planar model as current voltage characteristics are mainly governed by the exponential term while the power on the left side of the equation is of trivial importance. Hence conventional F-N relation works well here and have been used in the past to compute β for vertically aligned graphene and RGO flakes[12, 21]as mentioned earlier. In figure 3(c), the time stability curve is shown for the quasi vertical edge enhanced *n*-RGO thin film. It is found that the current emission for the film demonstrates very good stability corresponding to applied field 480

V/mm for a long period of time (~10 mins) and reflects its robustness for usage in FE applications.

Conclusions:

In summary, non-uniform high field dispersion assisted quasi-vertical orientation of RGO sheets (*n*-RGO) over carbon cloth was achieved for enhanced field emission characteristics. Non-uniform field generation depended majorly on the top electrode geometry to align the free RGO edges. Simulated results further corroborated the same analogy when modeled using different top electrode geometrical configurations. Finally, due to this quasi alignment of the RGO sheets under non-uniform field led to significant improvement of RGO's enhancement factor (β) with substantial increment of emission current. Hence this could have a potential impact on fundamental understanding of field emission with enhanced edges of RGO and graphene based materials.

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Figures:

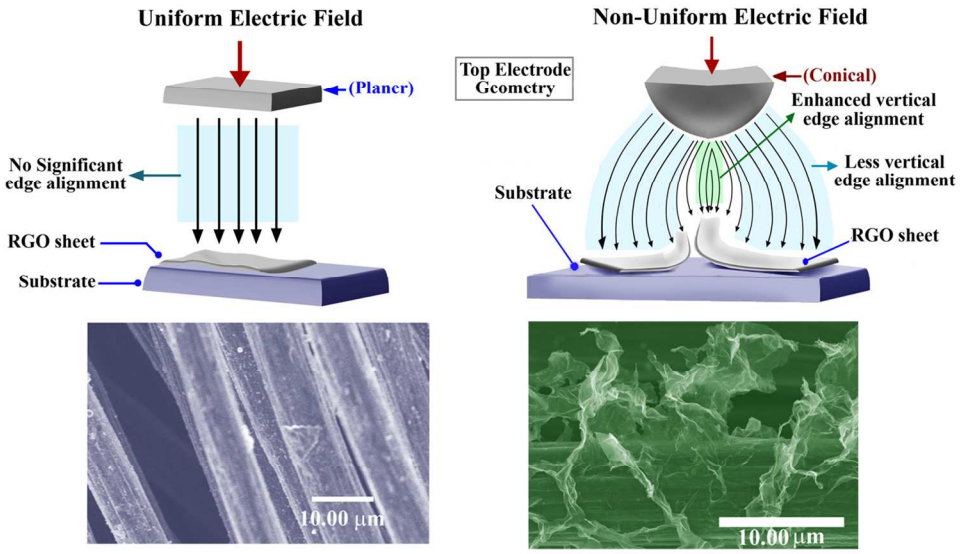

Figure1: Schematic illustration representing planar and non-planar top electrode configurations for generation of uniform and non-uniform electric field generation over RGO sheet under applied high DC electric field

Fig 1: Roy *et al.*

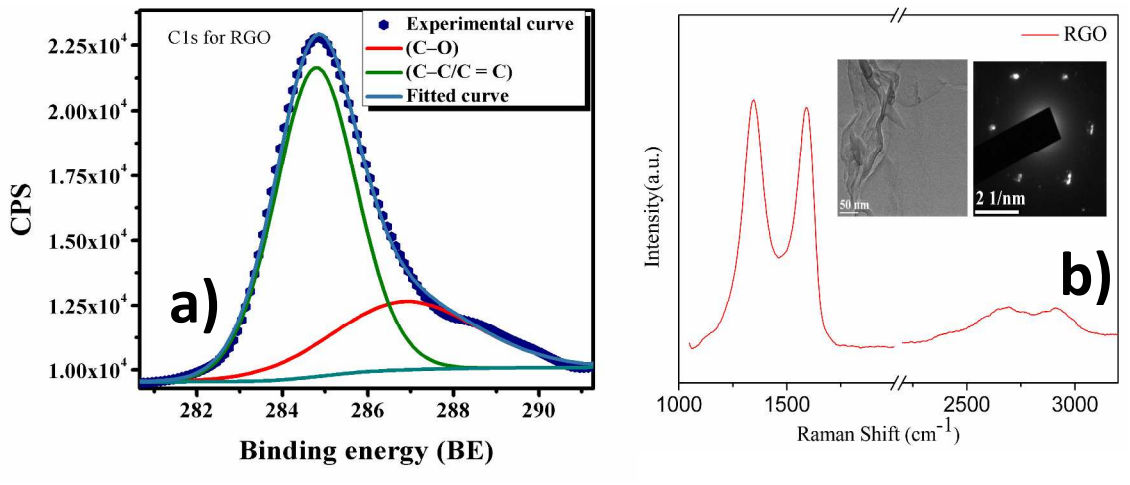

Figure 2(a) XPS C1s spectra corresponding to the synthesized RGO sample (b) Raman spectrum of RGO. The Inset corresponds to a low magnification HRTEM image and SAED image of RGO flake

Fig 2: Roy *et al.*

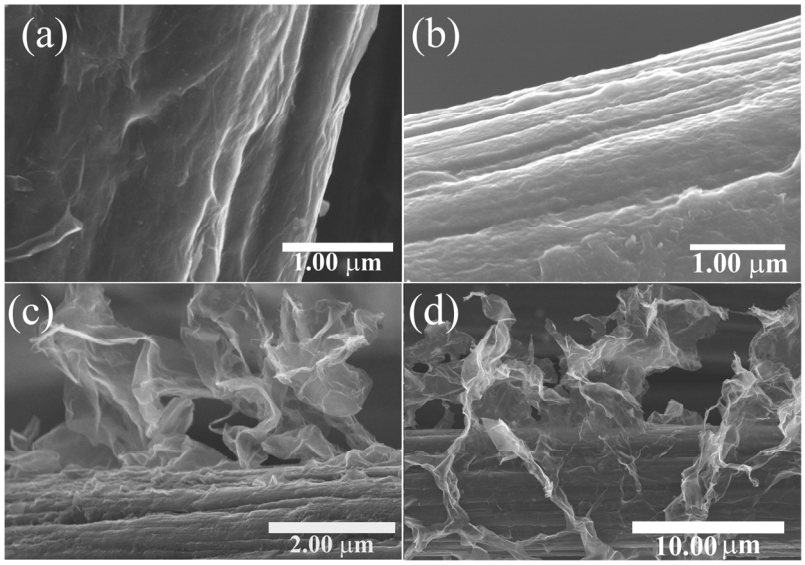

Figure 3(a, b) morphology of RGO flakes deposited on carbon cloth before and after application of electric uniform field (c, d) morphology of RGO flakes deposited on carbon cloth after application of non-uniform electric field

Fig 3: Roy *et al.*

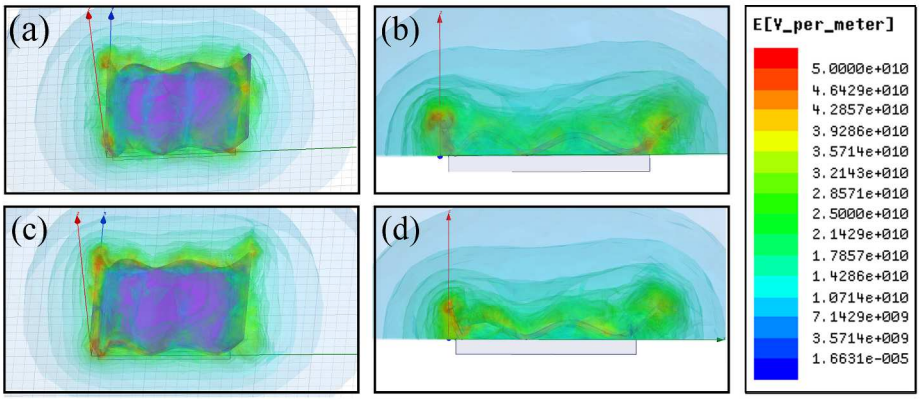

Figure 4(a, b) depicts the field gradient distribution over RGO sheet due to planar top electrode geometry in top and side view respectively (c, d) shows the field gradient distribution over RGO sheet in top and side view due to conical shaped top electrode geometry

Fig 4: Roy *et al.*

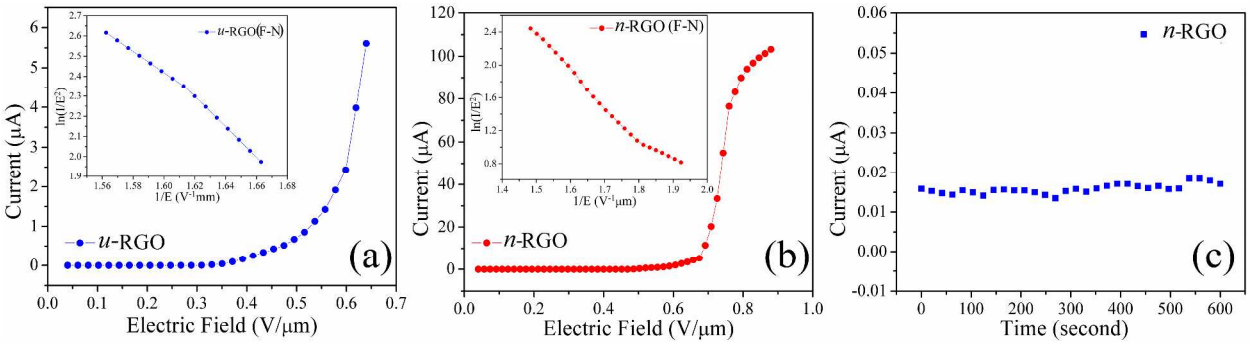

Figure 5(a, b) Current (I) *vs* (E) electric field curves of *u*-RGO and *n*-RGO films deposited on carbon cloth with their corresponding F-N plots in their insets (c)Time stability of the emission current of *n*-RGO film after quasi vertical alignment of the edges

Fig 5: Roy *et al.*

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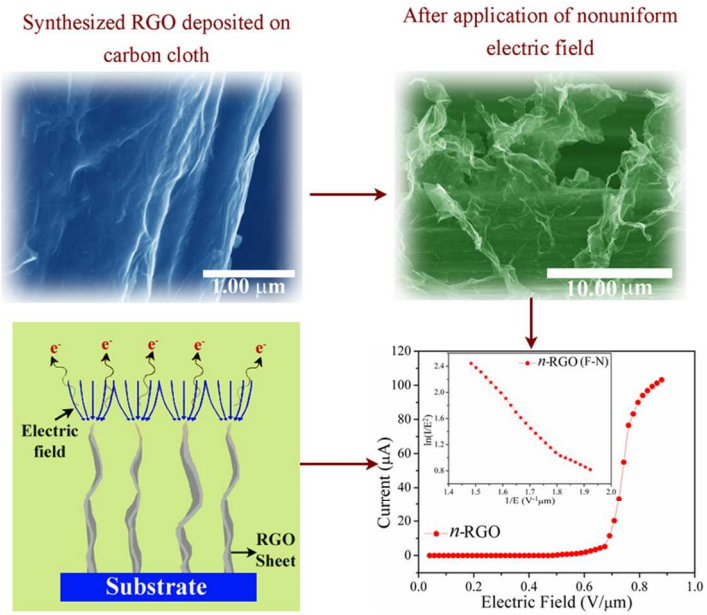

Quasi-vertical alignment of as-synthesized RGO sheets under non-uniform electric field deposited over carbon cloth substrate and its field emission characteristics

Roy *et al.*