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# Selective growth of inorganic nanomaterials on an oxidized graphene scaffold





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#### ABSTRACT

A low-temperature solution method was proposed for the site-selective growth of ZnO nanorods (NRs) and Au nanoparticles by making use of the wettability contrast of a graphene/graphene oxide (G/GO) template. Au nanoparticles were found to nucleate and grow selectively over a GO area of the G/GO template. ZnO NRs selectively grew on graphene regions of the template without growing the seeds required for selective growth. We demonstrated diode-like and field emission behaviors of the ZnO NRs selectively grown on a G/GO template, which showed good optical, electrical, and mechanical properties. These materials are potential candidates for the large-scale fabrication of flexible electrical and optical nano-devices.

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### 1. Introduction

The low-temperature solution process growth of inorganic materials, such as metals and metal oxides, in the nanometer regime has attracted attention because the process is easily conducted, the particle shapes and sizes may be controllably tuned, and the materials are potentially useful for the development of future optical and electronic devices [1–6]. The selective deposition of nanostructures is in demand for the fabrication of arrays of micro- and nano-devices on large-area substrates. Graphene, which comprises a two-dimensional (2D) sheet of sp<sup>2</sup>-hybridized carbon, has aroused tremendous interest as a transparent electronic material with unique mechanical properties [7–12]. The properties of oxide semi-

conductors in the nanoscale form are markedly different from their bulk counterparts as a result of quantum confinement effects [13–16]. The synthesis of a hybrid structure consisting of semiconducting one-dimensional (1D) oxide nanomaterials over a 2D graphene layer could potentially provide excellent functionalities for nano-device applications provided that the material properties could be harnessed effectively. Combinations of these two materials can yield three-dimensional (3D) heterostructures that display good optical and electrical properties [17–19].

Zinc oxide (ZnO) is a semiconductor material with a direct band gap of 3.37 eV [20]. The semiconducting properties of ZnO are useful in a range of electronic, photovoltaic, electrochemical, and electromechanical applications, including

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sensors, transistors, UV light-emitting diodes (LEDs), electroluminescent displays, solar cells, and piezoelectric nano-generators [21-23]. The fabrication of micro- and nano-devices requires the site-selective deposition of nanomaterials with a particular morphology onto a substrate via micro-patterning techniques [24-27]. Recently few attempts have been taken towards the growth of hybrid system of aligned semiconducting nanorods (NRs) and graphene layers [28-30]. Choi et al. [28] reported the aligned ZnO NRs on graphene layer by employing the seed deposition and creating the graphene dot pattern array on SiO<sub>2</sub>/Si substrate using photolithographic method. Further, they removed the ZnO NRs from unwanted regions (SiO<sub>2</sub>) using the ultrasonically assisted mechanical treatment. Therefore, in their study, alignment of NRs was controlled by seeds which act as nucleation sites and selectivity by the difference in adherence energies of ZnO NRs on graphene layer and SiO<sub>2</sub>/Si regions. Hong et al. [29] reported the aligned growth of InAs NRs in periodic array on a graphitic film by combining the substrate patterning and the formation of van der Waal heteroepitaxy employing the metal-organic vapor-phase epitaxy method.

The present study describes a low-temperature, wetchemical route to the seed-free growth of 1D ZnO NRs utilizing the wettability contrast (hydrophobic and hydrophilic regions) on a patterned graphene/graphene oxide (G/GO) template wherein graphene oxide regions are hydrophilic and graphene regions are hydrophobic. L-Arginine  $(C_6H_{14}N_4O_2)$ was coated onto the graphene oxide regions to increase the wettability contrast of the template and support the selective growth of ZnO NRs over the graphene regions. The as-grown ZnO NRs displayed rectifying and field emission properties. The hybrid ZnO NR/graphene structure displayed a stable rectifying performance under bending conditions, thereby supporting the material's potential use in flexible electronics. We also demonstrated a very simple solution-based method [31-33] for selectively growing Au nanoparticles on a patterned G/GO template. Unlike the ZnO NRs, the Au nanoparticles were found to grow over the GO region.

### 2. Experimental section

# 2.1. Synthesis and transfer of the graphene to the target substrates

Graphene films were synthesized on Cu foil (25  $\mu$ m) using CVD methods. First, the Cu foil was inserted into a quartz tube that was further loaded in a larger-diameter quartz tube attached to the thermal CVD instrument. A H<sub>2</sub> gas stream (~8 SCCM) was introduced into the tube, the temperature was increased to 1000 °C, and the temperature was maintained for 25 min to anneal the Cu foil. A CH<sub>4</sub> gas stream (~20 SCCM) was introduced into the chamber over 30 min, and then the chamber was cooled to room temperature under the flow of H<sub>2</sub> gas (~8 SCCM). The graphene film that had grown on the Cu foil was coated with a thin layer of polymer, poly(methyl methacrylate) (PMMA) on one side, and the other side of the graphene was etched away by applying O<sub>2</sub> plasma (20 SCCM) at 100 W for 5 s to enable reactive ion etching (RIE). The Cu foil having a graphene layer on the upper side was

placed in an aqueous 0.1 M ammonium persulfate ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>  $O_8$ ) solution until all of the Cu had dissolved to form hydrated CuSO<sub>4</sub>. The resulting film was transparent, after the Cu foil had been etched away. The film was rinsed with deionized water to remove residual etchant and was transferred to the desired substrate (SiO<sub>2</sub>/Si or PET). The transferred film was dried for 5 h to adhere the film to the target substrate. The PMMA layer was removed by soaking the film in acetone for a few minutes, which resulted in the complete transfer of the graphene layer onto the target substrates.

#### 2.2. Preparation of the graphene/graphene oxide template

The graphene layer transferred to the desired substrate was patterned using photolithography methods. The graphene on the substrate was coated with a photoresist (AZ1512), and UV light was directed onto the photoresist through a Ni/Cr mask, which crosslinked the photoresist in the desired pattern. The graphene/graphene oxide patterns were then created by exposing the sample to  $O_2$  plasma. The conditions of the  $O_2$  plasma power, the flux of the  $O_2$  plasma, and the time of exposure were optimized. The GO produced under each set of conditions was characterized and analyzed by Raman spectroscopy (WITec focus innovations, Alpha 300R with 532 nm laser Raman microscope), contact angle measurement (KRUSS GmbH, Germany, FM40 Easy Drop), and XPS (K-alpha, Thermo VG, U.K. using a monochromatic Al X-ray source (Al Ka line: 1486.6 eV), appropriate charge shifting corrections were performed based on the C1s peak at 284.8 eV). The optimized condition for the formation of selective patterns of GO on the graphene substrate were found to be 10 SCCM  $O_2$  plasma treatment at 20 W power for 2 s. Finally, the photoresist was removed by dissolving in acetone to obtain patterned GO on the graphene substrate. SEM images were recorded using a JEOL, JSM-6701F field emission scanning electron microscope.

# 2.3. Functionalization of the graphene/graphene oxide template with L-arginine

The patterned graphene/graphene oxide template was treated with an aqueous solution of L-arginine. The substrate was floated face-down on top of a volume of the  $2 \times 10^{-3}$  M aqueous L-arginine solution (20 mL), and then heated at 60 °C for 2 h. The substrate was washed and then used to grow (separately) ZnO NRs and Au nanoparticles.

# 2.4. Low-temperature deposition of the Au nanoparticles and ZnO NRs

Au nanoparticles were deposited onto the graphene/graphene oxide template by placing the template face-down in a  $5 \times 10^{-3}$  M aqueous HAuCl<sub>4</sub>·3H<sub>2</sub>O solution (2 mL) containing  $2 \times 10^{-3}$  M L-arginine (5 mL). After deposition, the template was washed with water and dried. ZnO NRs were grown in a solution containing equimolar ( $25 \times 10^{-3}$  M) Zn(NO<sub>3</sub>)<sub>2</sub> and hexamethylenetetramine (HMT), prepared in a 250 mL volume of deionized water. The solution was stirred vigorously at 300 °C for 3 min. The substrate was then dipped into the solution vertically, and the solution was covered and heated

at 95 °C for 6 h. The solution was cooled, and the substrate was washed with water under sonication to remove the ZnO crystallites that had attached by physical adsorption to the substrate. The substrate was then dried at 100 °C for 10 min to completely dry the sample.

## 3. Results and discussion

Fig. 1(a) shows a schematic representation of the fabrication steps involved in the preparation the G/GO template. Initially, graphene films were synthesized on copper foils by chemical vapor deposition (CVD) methods, as reported elsewhere [34]. After growth, the graphene films were transferred onto the target substrates (SiO<sub>2</sub>/Si) using a poly(methyl methacrylate) (PMMA) supporting layer. The transferred films were dried, and the PMMA was removed by soaking the films in acetone. The dot patterns were created on transferred graphene (dots were covered by photo-resist material) on SiO<sub>2</sub>/Si substrate using a conventional photolithography method subsequently followed by O<sub>2</sub> plasma treatment. Finally, the photo-resist was removed by acetone to obtain the patterned G/GO template. The right side of Fig. 1(a) shows a scanning electron microscopy (SEM) image of the G/GO template showing the graphene dots surrounded by graphene oxide. In this way, we can create G/GO template of any desired shape and size depending on the photolithographic mask. In addition to dot patterns, curved lines were also formed. Fig. S1(a and b) shows the optical images of dot patterns (here, dots are ones of GO, reverse pattern) and curved lines of G/GO templates, respectively. Further, hydrophobic and hydrophilic contrast level between graphene and converted GO was tested by water adherence level. Few drops of water were dropped over both kinds (dots as well as curved lines) of G/GO templates. It was noted that the water adheres only on the converted GO regions showing the good hydrophobic and hydrophilic contrast level between graphene and converted GO regions. Fig. S1(c and d) shows the photographs of the water adhered dots and curved lines patterned G/GO templates, respectively. Further, the atomic force microscopic (AFM) image of curved lines on G/GO template was recorded to see the differences between graphene and converted GO regions as shown in Fig. S1(e). Here, all, SEM, optical, photographic and AFM images are shown under the best optimized O<sub>2</sub> plasma treatment conditions for converting the graphene into GO. The complete conversion of graphene to GO by O<sub>2</sub> plasma treatment depends mainly on three parameters: the power, flux, and the time of the O2 plasma exposure process. These parameters were optimized by varying one parameter while holding the other two parameters fixed. The most suitable treatment time and flux were found to be 2 s and 10 SCCM. The oxidation of graphene depends strongly on the power of the  $O_2$  plasma. The  $O_2$  plasma power was varied from 10 to 40 W, and the resulting GO in each case was analyzed for the formation of defects and the ratio of the C–C  $(sp^2)$  to C– O bonds using Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) techniques. Fig. 1(b) shows the Raman spectra of the O<sub>2</sub> plasma-treated graphene at different plasma powers (0, 10, 20, 30 and 40 W). Graphene displayed three main Raman bands: the D band at 1345  $cm^{-1}$ , the G band at

1594  $\text{cm}^{-1}$ , and the 2D band at 2676  $\text{cm}^{-1}$  under 532 nm laser excitation. The D band was indicative of the presence of defects [35,36]. The Raman spectra in Fig. 1(b) clearly revealed that the intensity of the D band increased as the power of the plasma increased. The D band intensity exceeded the G band intensity at 10 W, confirming the formation of GO by the presence of oxygen bonds on the surface of the graphene. The inset of Fig. 1(b) shows a plot of the ratio of the intensities of D band to G band  $(I_D/I_G)$  as a function of the plasma power, which permitted estimation of the level of defects in the carbon materials. The  $I_D/I_G$  ratio increased as the plasma power increased, remained nearly constant between 10 and 20 W, and then further increased above 20 W to a value that indicated a high degree of disorder. Fig. 1(c) shows the original XPS spectra of graphene treated with different O<sub>2</sub> plasma powers (0, 10, 20, 30 and 40 W). A peak at  $\sim$ 284.5 eV having slight asymmetry towards higher binding energy has been observed. The intensity of the peak was found to decrease as O<sub>2</sub> plasma power increase with slight shifting of center of peak towards higher binding energy. To extract the more information the peak has been deconvoluted in its constituents peaks. After deconvolution three peaks were observed at 284.8 eV, 285.3 eV and 289.1 eV corresponding to C-C (Fig. 1(d), left), C-O (Fig. 1(d), right) and C=O (Fig. S2(a)) bonds, respectively [37,38]. The intensity of C-C peak shows the purity of graphene sample whereas contribution of peaks C-O and C=O indicate the oxidation of graphene. The intensity of the peak at 284.8 eV decreased as the  $O_2$  plasma power increased beyond 10 W, as shown in left of Fig. 1(d), indicating that fewer C–C sp<sup>2</sup> bonds were present in the material.  $O_2$ plasma treatment above 10 W created defects in the C-C chains. The peak at 285.3 eV shifted to higher binding energies at a 20 W plasma power, and it continued to shift toward higher binding energies as the power increased, as shown in the right of Fig. 1(d). The overall intensities of the peaks at 285.3 eV, which corresponded to C-O bonds, also decreased as the  $O_2$  plasma power increased whereas their relative intensities with respect to C-C sp<sup>2</sup> bonds increases. Fig. 1(e) shows a plot of the ratio of the intensities of the C-C and C–O  $(I_{C-C}/I_{C-O})$  peaks. The plot decreased and stabilized at 20 W, indicating that the graphene underwent oxidation [39]. The intensity of the peak at 289.1 eV (Fig. S2(a)) initially increases for 10 W and then decreases as the O<sub>2</sub> plasma power increases beyond 10 W. The ratio of intensities of C-C and C=O  $(I_{C-C}/I_{C=O})$  peaks is shown in Fig. S2(b) which also decreases showing the similar behavior as for  $I_{C-C}/I_{C-O}$ (Fig. 1(e)) indicating that the oxidation of graphene. The peak corresponding to C-O contains hydroxyl group and C=O contains carbonyl and carboxyl groups. The Raman and XPS data obtained from the as-prepared GO under different plasma treatment conditions revealed that the most suitable optimized parameters for achieving complete conversion of graphene to graphene oxide were an O<sub>2</sub> plasma power of 20 W, operated at 10 SCCM, for a duration of 2 s.

The G/GO template surface properties were characterized by obtaining contact angle measurements. Fig. 2(a) shows the contact angle as a function of the  $O_2$  plasma treatment power. Images of the liquid droplets obtained in real time are shown in the inset of Fig. 2(a). The contact angle obtained on the pristine graphene decreased as the  $O_2$  plasma power



Fig. 1 – (a) Schematic illustration of the steps involved in fabricating the graphene/graphene oxide template. The right-hand side shows an SEM image of the dot (graphene) pattern on the graphene/graphene oxide template. (b) Raman spectrum of the graphene treated under different O<sub>2</sub> plasma powers, at 10 SCCM, for 2 s. The inset shows the intensity ratio of the D and G peaks ( $I_D/I_G$ ). (c) Original XPS spectra of the graphene treated under different O<sub>2</sub> plasma powers, at 10 SCCM, for 2 s. (d) The peaks at 284.8 eV (left) and 285.3 eV (right), corresponding to C-C (sp<sup>2</sup>) and C-O bonds, respectively, are shown after deconvolution the original XPS spectra to reveal the intensity changes at different plasma powers. (e) Plot of the ratio of the intensities of the C-C (sp<sup>2</sup>) and C-O bonds in the graphene and GO, prepared at different plasma powers. (A colour version of this figure can be viewed online.)



Fig. 2 – (a) The contact angles measured at each  $O_2$  plasma power. The inset shows the corresponding images of the liquid droplets obtained in real time. (b) Optical transmittance spectra of graphene and GO prepared at different plasma powers. (A colour version of this figure can be viewed online.)

increased. The contact angle obtained after applying  $O_2$  plasma treatment at 20 W was measured to be 35°. Above this power, the contact angle further decreased and remained nearly constant, 15°. These results indicated that the hydrophobic graphene was converted into the hydrophilic GO form

due to an increase in the polarity of the graphene surface due to the formation of oxygen bonds with the carbon atoms. The ratio of the hydrophobic (graphene)/hydrophilic (GO) surface areas was adjusted by treating the patterned G/GO template with an aqueous solution of L-arginine. L-Arginine is an amino acid that contains an amine group on one end and a carboxyl group on the other end. GO contains a large amount of hydroxyl and epoxy groups on its basal plane, as well as few other O-containing groups such as carbonyl and carboxyl groups at the edge [40]. Arginine has carboxylate (COO<sup>-</sup>) and guanidinium (CN<sub>3</sub>H<sup>±</sup>) groups, both of which can form hydrogen bonds with OH on GO. Accordingly, arginine has a stronger interaction with GO than with pristine graphene. A recent study based on density functional theory calculation has also shown that the adsorption energy of arginine-containing tripeptide on GO is almost four times larger than that on pristine graphene [41]. Therefore, 1-arginine was found to grow selectively on the GO regions presumably due to the formation of amide bonding between the amine group of L-arginine and the carboxyl group present on the GO surface. Fig. 2(b) shows the optical transmittance pattern obtained from the graphene and GO surface. The optical transmittance increased as the extent of graphene oxidation increased due to the formation of C–C sp<sup>3</sup> bonds.

The hydrophobic/hydrophilic contrast of the G/GO template was exploited for the selective growth of inorganic materials (Au and ZnO). Fig. 3(a) shows a schematic diagram of the process by which inorganic materials (Au and ZnO) were selectively deposited. Two separate G/GO templates with opposite dot patterns were prepared. In one case, the dots were composed of GO regions that induced the deposition of Au nanoparticles (NPs), and in the other case, the dots were graphene regions that induced ZnO NR deposition. Au NPs deposition was achieved by floating the G/GO template facedown on 5 mM aqueous HAuCl<sub>4</sub> solution and 2 mM aqueous L-arginine solution, wherein the amino acid acts as the reducing agent for the formation of Au NPs from HAuCl<sub>4</sub>. The Au NPs were seen to deposit on the GO surface which is also covered with L-arginine molecules due to electrostatic forces. Au NPs having a positive surface charge could conveniently sit on the negatively charged carboxylic acid group of the amino acid, resulting in a selective deposition on the GO surfaces. ZnO NR were grown in an equimolar (25 mM) solution containing Zn(NO<sub>3</sub>)<sub>2</sub> and HMT, prepared in 250 mL deionized water. ZnO is hydrophobic and thus preferentially deposited onto the hydrophobic graphene surface. The X-ray diffraction (XRD) and photoluminescence (PL) spectra of as grown ZnO NRs are shown in Figs. S3(a) and (b), respectively. The dominant peak along (002) direction in XRD indicates that the as grown ZnO NRs are almost vertically aligned (c-axis oriented) and broad fall in visible region of PL intensity indicates that the presence of defects [42] in as grown ZnO NRs that may possibly occur due to the stress adoption in vertically aligned ZnO NRs [43]. Figs. 3(b) and (c) show the scanning electron microscopy images of the deposited Au nanoparticles and ZnO NRs, respectively. Here, ZnO NRs are not perfectly vertically aligned. The alignment of NRs can be improved by making the growth process slow through very low concentration (Molarity) of zinc nitrate solution and increasing the deposition time. In this way, the zinc ions will start to deposit on the graphene region very slowly and alignment will be relatively better. We tried to do this but we observed that if we keep very slow deposition time and low concentration, the density of NRs is very less. So, one has to optimize between time and concentration by compromising the alignment



Fig. 3 – (a) Schematic illustration of the selective deposition of the inorganic materials, ZnO and Au, on the graphene and GO surfaces, respectively. SEM images of the selective (b) Au nanoparticle deposition, and (c) ZnO NR growth. (d) Schematic diagram showing the attachment of *i*-arginine molecules onto the GO regions, and the subsequent attachment of Au nanoparticles over these regions. The ZnO NRs attached to the graphene regions. (A colour version of this figure can be viewed online.)

depending on the applications. There is some limit below which it is difficult to grow the nanostructures selectively. In the present study we were successfully able to convert the 2  $\mu$ m size of graphene into graphene oxide dots by oxygen plasma but we realized that the deposition of nanostructures on such small dots is difficult. We speculate, probably it is due to that such small hydrophobic or philic region is not sufficient to provide the driving force for favorable ions or groups present in the desired starting solution. Fig. 3(d) shows a schematic representation of the process by which the Au nanoparticles were attached to GO regions whereas the ZnO NRs were grown on the graphene regions.

The potential utility of the selectively grown ZnO NRs on a flexible G/GO template was demonstrated by measuring the sample's diode-like behavior and field emission properties. The double layer stacked graphene films were transferred onto a polyethylene terephthalate (PET) substrate. In addition, the third layer of graphene was also transferred on the double layer stacked graphene films/PET substrate which is used to make G/GO template. The G/GO template was prepared in a dot pattern (the dots were graphene) using photolithography technique and the optimized O2 plasma treatment parameters (20 W, 10 SCCM, 2 s). The regions surrounding the graphene dots presented a GO upper layer on a lower pristine double layer graphene. G/GO template/double-layer graphene/PET substrate was dipped in the ZnO precursor solution, and ZnO NRs grew on the hydrophobic graphene dots. Aluminum metal electrodes were deposited using shadow mask on top of the ZnO NRs grown on the array of graphene dots on the G/GO template. Here, Al and bottom double layer graphene acted as top and bottom electrodes, respectively. A schematic diagram of the Al/ZnO NRs/graphene dot/double-layer graphene on substrate (PET or SiO<sub>2</sub>/Si) is shown in the inset of Fig. 4(a). The current-voltage (I-V) characteristics of the Al/ZnO NRs/graphene dot/double-layer graphene on the PET substrate were measured. For comparison, a similar structure was prepared on SiO<sub>2</sub>/Si template and I-V characteristics were measured. A Non-linear diode-like behavior was observed in the Al/ZnO NRs/graphene dot/double-layer graphene structure. The diode like behavior was attributed to the barrier formation between the ZnO NRs and the graphene dots as Al metal makes ohmic contact to the ZnO NRs due to their almost similar work function and confirmed by observed linear I-V curve from Al/ZnO NRs/Al structure. A semi-logarithmic plot of the diode-like I-V characteristics is shown in Fig. 4(a). The I-V characteristics on the flexible PET substrate were compared with those of a similar structure on a rigid  $SiO_2$  substrate, as shown in Fig. 4(a). The I-V characteristics of the sample mounted on the PET substrate were relatively poorer than those obtained from the sample mounted on the SiO<sub>2</sub> substrate because the PET surface was rough and, thus, the graphene layers transferred onto the PET were relatively disordered. The diode characteristics were modeled using the thermionic emission framework. According to this model, the current as a function of the voltage may be expressed by the following equation [44,45]:



Fig. 4 – (a) Semi-logarithmic plot of the diode-like I–V characteristic of the structure prepared on a flexible PET or rigid SiO<sub>2</sub> substrate. The inset shows a schematic diagram of the Al/ZnO NRs/graphene dot/double-layer graphene on a PET substrate. (b) Semi-logarithmic plots of the diode characteristics obtained in the flat configuration or in the in-plane and out-of-plane bending configurations, as well as after recovery from bending. (c) The values of *n* and  $\Phi_b$  under these conditions and their corresponding strains. (d) Schematic diagram of the bending of bands at the interface between the ZnO NRs and the graphene dots due to the mismatch between the work functions. (A colour version of this figure can be viewed online.)

$$I = I_{s} \left[ \exp \frac{qV}{nKT} - 1 \right]$$
<sup>(1)</sup>

where V is the applied forward voltage, q is the electronic charge, n is the ideality factor, T is the absolute temperature, K is the Boltzmann constant, and  $I_s$  is the saturation current.  $I_s$  may be expressed as:

$$I_{s} = AA^{*}T^{2} \exp\left(\frac{-q\Phi_{b}}{KT}\right)$$
(2)

where  $\Phi_b$  is the barrier height formed at the interface between the ZnO NRs and the graphene dots, A is the junction area, and  $A^*$  is the effective Richardson constant. The values of nand  $\Phi_b$  were calculated using the value 36 A  $cm^{-2}\,K^{-2}$  for A' for ZnO [45,46], and the total area of overlap between the ZnO NRs and the graphene dots was calculated to be  $7849.9 \times 10^{-2} \,\mu\text{m}^2$ . This area actively contributed to the formation of junctions. The values of *n* and  $\Phi_b$  were calculated from the slope and intercept of a linear fit to the semi-log plot. The values of n and  $\Phi_b$  for the flexible PET substrate were calculated to be 3.46 and 0.55 eV, respectively, and these values for the SiO<sub>2</sub> substrate were calculated to be 2.0 and 0.7 eV, respectively. The high value of *n* can be attributed to the multiple current path ways due to the occurrence of defects in ZnO NRs as revealed in PL spectra (Fig. S2(b)) [45]. The differences were understood in terms of the PET surface roughness relative to the smooth SiO<sub>2</sub> surface. The PET surface yielded rough junction contact at the interface between the ZnO NRs and the graphene dots. The performance of the device on the flexible PET substrate was tested under in-plane and out-of-plane bending conditions. Fig. 4(b) shows semi-logarithmic plots of the diode characteristics obtained from flat, in-plane bent, and out-of-plane bent substrates, and from a substrate that had recovered from bending. The values of nand  $\Phi_b$  under all these conditions and their corresponding strains are plotted in Fig. 4(c). The diode parameter n varied symmetrically with respect to the in-plane and out-of-plane bending, and it recovered its original value (flat) after being returned to a flat configuration. The value of n changed from 3.5 (flat) to 4.5, corresponding to a maximum strain of 1.9% (a 5 mm bending radius). Moreover, the value of  $\Phi_b$  did not change significantly over all in-plane bending, out-of-plane bending, or recovery conditions, relative to the original value in the flat configuration. Small variations in the diode parameters *n* and  $\Phi_b$  under the bending test suggested that the Al/ ZnO NRs/graphene dot/double-layer graphene structure was reliable and could potentially be used in a variety of electronic devices in which diode characteristics are required. The diode characteristics in the present case were attributed to the barrier formed at the interface between the ZnO NRs and the graphene dots. The properties of this barrier have been reported elsewhere in the context of nanogenerator applications [47]. The bending of the bands at the interface between ZnO NRs and graphene dots due to mismatch between the work functions is schematically illustrated in Fig. 4(d). Under forward bias conditions, a positive voltage was applied to the double-layer bottom electrode and a negative voltage was applied to the top Al electrode. An increase in the applied voltage induced the bands to flatten, and the current gradually increased. After a certain threshold voltage, a small

323

increase in the applied voltage produced a large current flow. On the other hand, application of a positive voltage to the top Al electrode and a negative voltage to the bottom double-layer graphene electrode increased the band bending, which prohibited the electrons from crossing the interface, resulting in a current of zero.

In addition to measuring the rectifying properties of the selectively grown ZnO NRs on a graphene dot/double-layer graphene/PET substrate, the field emission properties were also measured. Field emission is a quantum mechanical effect that has attracted significant interest for its potential use in display and other electronic applications. Onedimensional ZnO nanostructures are reported to act as good field emission cathodes [48]. The field emission measurement was conducted by preparing a structure similar to that used to prepare the diode except that the top electrode was formed by the deposition of Al. Only one large dot was patterned on the top layer of the graphene, rather than an array of dots. A fluorescent material was deposited on an indium tin oxide-coated glass plate, which was used as the anode. The bottom doublelayer graphene layer was connected to the cathode, and the distance between the anode and the emissive material (the ZnO NRs) was 820  $\mu m.$  Fig. 5(a) shows a plot of the emissive current density (J) as a function of the macroscopic electric field. The macroscopic field (E) was calculated by dividing the external applied voltage by the distance between the anode and the emissive material (820 µm). The variation of J with respect to E (Fig. 5(a)) indicated that the current was dramatically enhanced by the application of a  $3 V/\mu m$  electric field, as has been reported previously [44]. The turn-on electric field, defined as the value of the electric field at which the current density reached  $10 \,\mu\text{A/cm}^2$ , was found to be  $3.5 V/\mu m$ . The field emission characteristics were fit to the Fowler-Nordheim (F-N) model. According to this model, the relationship between J and E may be expressed as

$$J = A\left(\frac{\beta^2 E^2}{\phi}\right) \exp\left(\frac{-B\phi^{3/2}}{\beta E}\right)$$
(3)

where A =  $1.56 \times 10^{-6}$  AV<sup>-2</sup> eV, B =  $6.83 \times 10^{7}$  V cm<sup>-1</sup> eV<sup>-3/2</sup>,  $\beta$  is the field enhancement factor,  $\phi$  is the work function, and *E* is the applied electric field in V/µm. The above equation, in F–N coordinates, may be represented as

$$\ln\left(\frac{J}{E^2}\right) = \ln\left(A\frac{\beta^2}{\phi}\right) - \frac{-B\phi^{3/2}}{\beta E}$$
(4)

The F–N plot of  $\ln(J/E^2)$  as a function of 1/E yielded a straight line, as shown in Fig. 5(b), confirming that the measured current arose from the quantum tunneling effects of the carriers and resulted in the field emission properties of the ZnO NRs. The value of  $\beta$  could be calculated by substituting the value of  $\phi$  into the slope of the straight line.  $\beta$  was found to be on the order of ~10<sup>3</sup> which was comparable to the value reported previously [42]. Fig. 5(c) shows an SEM image of the selectively grown ZnO NRs on the graphene dot/double-layer graphene/PET substrate prior to conducting the field emission measurements. Fig. 5(d) shows a photograph of the uniform fluorescence from the ZnO NRs selectively grown on a large graphene dot, obtained during the field emission measurements.



Fig. 5 – (a) Plot showing the emissive current density (J) as a function of the macroscopic electric field. (b) The F–N plot, ln(J/E<sup>2</sup>) as a function of 1/E, yielded a straight line. (c) SEM image of the ZnO NRs selectively grown on the graphene dot/double-layer graphene/PET substrate prior to conducting the field emission measurements. (d) Photograph of the uniform fluorescence obtained during the field emission measurements of the selectively grown ZnO NRs on a large graphene dot. (A colour version of this figure can be viewed online.)

# 4. Conclusions

In summary, a G/GO template was prepared under the optimized O<sub>2</sub> plasma conditions and was used to promote the selective deposition of inorganic (ZnO and Au) nanomaterials based on the hydrophobic/hydrophilic contrast using a low-temperature solution method. The selective growth of ZnO NRs on the G/GO template displayed rectifying and field emission properties that may be useful in flexible electronic applications. The rectifying behavior of the diode, which was attributed to the formation of a barrier between the ZnO NRs and the graphene interface, performed reliably under bending and recovery tests, demonstrating excellent mechanical properties. Good field emission properties were observed from the ZnO NRs grown on graphene dots. The present work provides a method for fabricating large-area patterned microdevices consisting of ZnO NRs on graphene surfaces for use in photodetectors, nanogenerators, and light emitting devices. The selective deposition of Au nanoparticles over the GO surface improves the potential applicability of this patterned template to catalysis and detection sensor applications.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon. 2014.07.008.

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