Chapter 7

Surfactant Assisted Synthesis of ZnO Coated Reduced Graphene Oxide Sheets and Their Electrical Properties

7.1 Introduction

Graphene is an allotrope of carbon whose structure is a single planar sheet of $sp_2$ bonded carbon atoms, which are densely packed in a honeycomb crystal lattice. It is a basic building block for graphitic materials of all other dimensionalities ([Geim & Novoselov 2007]). Due to its fascinating properties such as high optical transmittance over the visible and UV region, high thermal conductivity of about 5000 W/m.K and high intrinsic carrier mobility at room temperature, graphene has been applied in novel significant scientific and technological research ([Bonaccorso et al. 2010], [Novoselov et al. 2004]). Graphene can be modified for diverse applications such as scalability ([Li et al. 2009]), geometrical confinement to tune the band gap ([Nakada et al. 1996]), introducing chemical dopant to alter transport properties ([?]), and the addition of nanoscale metals to the surface for modifying optical properties ([Zaniewski et al. 2013], [Xu et al. 2012]).

On other hand, Zinc Oxide (ZnO) is a wide band gap n-type semiconducting oxide, which has numerous applications and can be effortlessly manoeuvred into different morphologies [Singh et al. (2008), Singh et al. (2012), Wahab et al.]
In order to realize ZnO into desired morphological shapes, many synthesis techniques are reported in the literature [Al-Hardan et al. (2010), Johnson et al. (2003)]. Each of the two materials, graphene and zinc Oxide individually, has versatile and diverse applications. Obviously, a blend of these can also exhibit novel properties than that of individual materials. In literature, we found many papers on different techniques adopted to synthesize Graphene-ZnO nanocomposites; such as Spray Pyrolysis (Lu et al. (2010)), chemical deposition route (Li & Cao (2011), Kamat (2010)), CVD (Yang et al. (2012b), Dong et al. (2012)), in situ hydrothermal route (Song et al. (2012)), R.F. Magnetron Sputtering of ZnO and mechanical exfoliation of highly oriented-paralytic-graphite (HOPG) (Hwang et al. (2010)), etc. Of course, these composite materials displayed a diverse range of applications with enhanced performance such as super capacitors (Zhang et al. (2009)), photo catalysis and photoluminescence, electrochemical sensors and photo detectors (Fu et al. (2012)), etc.

In the last few years, Graphene-ZnO nanocomposite materials have also emerged as promising materials for smart devices. Although, 2-D reduced graphene oxide templates provide a very good functionalized surface over which nanoparticles can be distributed widely but graphene based composites remain randomly stacked resulting in particle-particle aggregation which is limitation in device functioning (Huang et al. (2012)). To fabricate a device out of any material it is imperative to understand the materials electrical properties and these properties must be correlated with morphology, since it is well-known fact that electronic properties of any material strongly depend its morphology and structure. Many authors have studied I-V characteristics for graphene and graphite oxide (GO). They observed linear relationship between current and voltage (Xu et al. (2012), Punckt et al. (2013)). Whereas, for heterojunction graphene-ZnO I-V relationships were non-linear, demonstrating typical diode characteristics (Zhang et al. (2012)).

In this manuscript, we are reporting the study of electronic properties of graphene-ZnO nanocomposites, synthesized by using PVA as a surfactant. We are correlating electronic properties for the synthesized materials with their morphology and microstructure. We were successful in developing the microscopic heterostructure between p-type graphene and n-type ZnO. Such investigations based upon electronic properties of graphene-ZnO hetero-structures are very rare (Singh & Singh (2012)). Moreover, this study is novel and it is a step towards the goal of utilizing composites of chemically reduced graphene with metal-oxides for
band gap tuning in electronic device applications such as LED, solar cells etc.

7.2 Experimental Details

7.2.1 Synthesis of Composite

Graphite oxide (GO) was prepared from fine graphite powder following the method previously mentioned. In a typical synthesis of the composite, 200 mg of GO was dispersed in 50 ml of deionised water (DI) at room temperature by ultrasonication for 1 hour to form graphene oxide dispersion. Then other 50 ml of DI water containing 1.2 g polyvinyl alcohol (PVA) and 0.18 M solution of zinc acetate \((\text{CH}_3\text{COO})_2\text{Zn}.2\text{H}_2\text{O}\) were added to graphene oxide suspension with constant stirring and then this mixture was ultrasonicated again for 1 hour. Following this, the hybrid solution was gradually heated to 90°C from room temperature in a water bath by reflux condensation mode. Afterwards, 8 ml of hydrazine monohydrate liquid \((\text{N}_2\text{H}_4.\text{H}_2\text{O})\) was added to the mixture drop wise. The reaction was continued for 6 h at 90°C. Finally, the black mixture was collected by centrifugation. After washing with adequate deionized water and ethanol to remove the PVA and residual \(\text{N}_2\text{H}_4.\text{H}_2\text{O}\), the reduced graphene oxide/ZnO composite was obtained by drying at 80°C for 24 hour. The obtained sample was named as GZO. Similar procedure was applied to synthesize reduced graphene oxide (RGO) from graphene oxide solution.

7.2.2 Material Characterization

All chemicals used in our experiments were of analytical grade and obtained from Loba Chemie, Mumbai, India. The obtained powders were characterized using XRD and FESEM for their structural analysis. X-Ray diffraction (XRD) was carried out using Cu-Kα radiation with Shimadzu 7000 Diffractometer system. Morphologies of synthesized products were analysed by field emission scanning electron microscope (FESEM) of Carl Zeiss SUPRA 55 make. Electrical properties were studied with the help of a Keithley 616 Digital Electrometer and an Agilent LCR meter model no. E4980A. We employed Kelvin probe microscopy to map the surface potentials of the synthesized samples, these measurements were carried out by Trek model Type 320 C.
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7.3 Results and Discussion

7.3.1 Structural Analysis

The fabrication process of GZO composite is schematically illustrated in Fig. 7.1. Firstly an aqueous solution of certain amount of \((\text{CH}_3\text{COO})_2\text{Zn}.2\text{H}_2\text{O})\) and PVA was mixed with graphene oxide dispersion. Hydrazine was added to this solution while heating it gradually. Hydrazine can not only reduce graphene oxide sheets but also promotes the hydrolysis of zinc acetate. Wang et al. (Wang et al. (2011a)) has demonstrated that when GO is reduced to graphene by hydrazine in PVA solution, no precipitates are observed for three weeks. However when added directly, graphene does not disperse in PVA even on ultrasonication. Thus PVA improves the dispersion of GO/RGO. On the other hand it shows hydrophilic interaction with metal salts and leads to controlled nucleation and growth of metal oxide particles on graphene sheets (Zheng et al. (2006)).
In Fig. 7.2, XRD pattern of RGO exhibits a broadened and small peak around 26.4° which is ascribed due to the (002) plane of hexagonal graphite. The curve of synthesized graphite oxide shows a sharp peak (002) at 9.6°, corresponding to an interlayer spacing of 9.1 Å (Li et al. (2012b)). The enlarged interlayer distance compared with pristine graphite (3.37 Å) (Song et al. (2012)) is attributed to the introduction of oxygen-containing functional groups on the surface of graphite after oxidation. This interlayer distance is known to vary between 6.5 and 9.0 Å depending on the degree of oxidation (Yang et al. (2012a)). The XRD pattern of GZO composite was compared with the standard available data, and results indicate that the ZnO nanoparticles on the graphene sheets have wurtzite hexagonal structure. The intensity and sharpness of XRD peaks suggest that the ZnO particles present in the composite materials are highly crystalline (Saravanakumar et al. (2013)). In addition to ZnO peaks, a diffraction hump appears between 20° and 30° in the powder XRD pattern of the composite, which may have been originated due to exfoliated graphene sheets (Chen et al. (2012b), Anand et al. (2013)).
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Figure 7.2: X-ray diffraction patterns of synthesized samples.
In order to understand the morphology of the synthesized samples we carried out FESEM of all the samples. Figures 7.3 and 7.4 shows the FESEM images of reduced GO and GZO composite. In Fig. 7.3 we observe the interlinked porous 3-D network of reduced graphene oxide sheets. In Fig. 7.4 we see graphene sheets are embellished with ZnO nanorods. Owing to the sheet morphology graphene sheets in the composite are prone to stack each other. Surfactant used in this case not only assists formation of 3-D layer by layer architecture but also alleviates ZnO particle aggregation and thus helps in random distribution of ZnO nanorods throughout GZO. Clearly PVA has played a significant role to control interfacial interactions between graphene and metal oxide particles.
Figure 7.3: FESEM image of reduced graphene oxide.

Figure 7.4: FESEM image of reduced graphene oxide/ZnO composite.
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7.3.2 Electrical Properties

We recorded current-voltage (I-V) characteristics of all the synthesized samples by the Keithley Electrometer in 2-probe configuration. Figure 7.5 represents the I-V characteristics of reduced graphene oxide and GZO composites. In this figure, we observed linear I-V curves for RGO sample and non linear curve for GZO. RGO shows linear response of voltage with the current as they are exhibiting ohmic behaviour.

Almost similar results have also been reported by Xu et al. (Xu et al. (2012)) and Punckt et al. (Punckt et al. (2013)). Zhang et al. (Zhang et al. (2009)) has studied the heterostructures of graphene and ZnO and they obtained typical diode characteristics. In the present study since we have synthesized the composites of n-type ZnO and p-type graphene. We find that in PVA assisted composite, ZnO nanostructures are thoroughly distributed over and into the graphene sheets without any aggregation. Thorough distribution of ZnO over graphene sheet has made the microstructure of the material to behave as randomly distributed junctions between p-type graphene and n-type ZnO. I-V characteristics displayed by this composite material were non-linear; it can be explained on the basis of the microstructure inherited by the material due to incorporation of PVA. These randomly distributed p-n junctions between graphene and ZnO, are acting as random potential barrier networks. The DC conductivity of a random barrier network has been explained on the basis of effective medium theory developed by Sinkkonen (Sinkkonen (1980)). Another model based on the conduction theory has been proposed by Varpula et al. in which they have explained non-linearity in grain-structured metal oxides (Varpula et al. (2008)). Electronic properties of randomly distributed graphene/ZnO junctions can also be explained on the lines of Sinkkonen (Sinkkonen (1980)).
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Figure 7.5: I-V characteristics of RGO and RGO/ZnO composite.
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The electric potential $V_B$ and the electric field in the grain-boundary or the barrier region can be solved from 1-Dimensional Poissons equation using the depletion region approximation. According to Poissons equation we have:

$$\nabla^2 V_B = \frac{qN_d}{\varepsilon}$$  \hspace{1cm} (7.1)

Where $N_d$ is the donor density (per unit volume), $q$ is the charge and $\varepsilon$ is the permittivity. Usually, grain structured metal-oxide materials are n-type semiconductors, the electron density inside the grains is constant and is equal to the donor density $N_d$ (per unit volume). Electric charge on the surfaces of the grains has been induced due to the presence of surface states. This in turn, generates the surface and grain-boundary potentials, and also leads to the bending of energy bands near the surface of the grains and the grain boundaries. Movement of conduction electrons across the grain-boundary potential barrier $V_B$ has been limited substantially. Due to band bending there is depletion of conduction electrons near the surfaces of grains and the grain boundary. The band bending is also creates double Schottky barrier structure. These surface states are acting as localized energy levels in the forbidden energy gap. Free electrons of the grain structured film can be trapped on either of two types of surface states; extrinsic and intrinsic states \cite{Varpula2008, Ding2001}. The intrinsic states are localized energy levels created by the semiconductor itself or created by impurities, doping, dislocation and defects \cite{Varpula2008, Rozhkov2011}. Whereas, extrinsic surface states are generally created by the adsorption of gas or molecules at the surface \cite{Varpula2008, Ding2001}. On the basis of the above discussion, it can be concluded that the intrinsic surface states have been created by p-type graphene in n-type ZnO, which lead to creation of p-n junctions or a depletion layer in thus synthesized composite material \cite{Rozhkov2011}. Poissons equation can be solved by using depletion region approximation \cite{Varpula2008}. This suggests that charge density at grain-boundary $N_B$ is equal to the donor density $N_d$ times the depletion width, $x_d$, that is:-

$$N_B = 2N_dx_d$$  \hspace{1cm} (7.2)

When there is no voltage applied, the depletion widths on both sides of grain boundary are equal and solution of Eqn.(7.1) gives the grain-boundary potential. After solving the 1-D second order differential equation we obtain grain-boundary potential as:

$$V_{B_o} = \frac{qN_d x_d^2}{2\varepsilon}$$  \hspace{1cm} (7.3)
This grain-boundary potential can also be modified in the terms of grain-boundary charge density, hence

$$V_{B_o} = \frac{qN_B^2}{8\varepsilon N_d} \quad (7.4)$$

The maximum electric field at the grain boundary can be calculated from Eqn. 7.4, therefore

$$E_{o}^{max} = \frac{q\varepsilon d N_d}{\varepsilon} = \frac{qN_B}{2\varepsilon} \quad (7.5)$$

When the voltage $U_{barr}$ is applied across the grain boundary, there is shift in the depletion widths on either side of the boundary and now they are no longer equal. Moreover, the potential barrier depends on the voltage and it gives nonlinear current characteristics when applied voltage $U_{barr}$ is high (Varpula et al. (2008)).

For single potential barrier between p-n junction, current density is given by the well known equation [Sinkkonen (1980), Varpula et al. (2008)]:

$$J = q\mu N_d E_{o}^{max} e^{-\frac{qV_{B_o}}{k_BT N_{barr}}} Sinh\left(\frac{qU_{barr}}{2k_BT N_{barr}}\right) \quad (7.6)$$

where $q$ is the unit charge, $\mu$ the mobility of holes, $N_d$ the donor concentration, $E_{o}^{max}$ the maximum electric field in the barrier region, $U_{barr}$ the applied voltage and $V_{B_o}$ is the barrier height. We have to consider a condition that $U_{barr} \leq V_{B_o}$, if in the whole film there are $N_{barr}$ potential barriers then the voltage across a single barrier is given by $U_{barr} = \frac{U}{N_{barr}}$, where the voltage across the whole film is $U$. Using Eqns. 7.4, 7.5 and 7.6, the electric current flowing through the whole film of cross-sectional area $A$ can be easily solved:

$$I = A\mu \sqrt{\frac{2q^4 N_d^3 V_{B_o}}{\varepsilon} e^{-\frac{qV_{B_o}}{k_BT N_{barr}}} Sinh\left(\frac{qU}{2k_BT N_{barr}}\right)} \quad (7.7)$$

This equation has two regimes: a linear regime at low voltage and a non-linear regime at high voltages. The non-linearity at high voltages can be explained by the decrease in the height of the potential barrier (Varpula et al. (2008)). I-V characteristics of graphene/ZnO composite material follow almost similar trend as dictated by Eqn. 7.7.

Figures 7.6 and 7.7 represents the CPD maps of graphene and GZO composite respectively. It is clear from potential maps that the synthesized materials have different work functions. If we observe more closely we will find that graphene/ZnO composite assisted by PVA exhibits a higher surface potential, i.e. lower work function. Lower work function corresponds with higher fermi level position and lower free charge carrier concentration. This suggests that the
interactions between $ZnO$ and reduced graphene oxide sheets provides additional pathways for charge carriers. Interfacial charge transfer may have taken place from $ZnO$ to graphene. The increase in surface voltage can be envisaged as a significant step towards band gap tuning of graphene based heterostructures for future applications involving smart electronics.

Figure 7.6: Contact potential image of graphene.

![Contact potential image of graphene](image1)

Figure 7.7: Contact potential image of graphene.

![Contact potential image of graphene](image2)

7.4 Conclusion

In the concluding remarks, we can summarize the present study; in this work synthesis of Graphene/$ZnO$ composites was carried out by one step reduction
of precursors in presence of a surfactant. The structural and morphological results suggested a uniform graphene-metal oxide heterostructure where reduced graphene oxide sheets are anchored by ZnO nanorods. Electrical properties of these composites are correlated with their morphology. I-V characteristics of these samples were studied and it was found that PVA assisted Graphene/ZnO exhibited diode characteristics. This non-linearity in the I-V measurements may be attributed to the formation of random potential barriers between p-type graphene and n-type ZnO.