Green and Solid State Reduction of GO Monolayers Sandwiched between Arachidic Acid LB Layers

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Abstract

A novel, single step and environment friendly solid state approach for reduction of graphene oxide (GO) monolayers has been demonstrated, in which, arachidic acid/GO/arachidic acid (AA/GO/AA) sandwich structure obtained by Langmuir-Blodgett (LB) technique was heat treated at moderate temperatures to obtain RGO sheets. Heat treatment of AA/GO/AA sandwich structure at 200 °C results in substantial reduction of GO, with concurrent removal of AA molecules. Such developed RGO sheets possess sp^2 -C content of ~69%, O/C ratio of ~0.17 and significantly reduced I(D)/I(G) ratio of ~1.1. Ultraviolet photoelectron spectroscopy (UPS) studies on RGO sheets evidenced significant increase in density of states in immediate vicinity of Fermi level and decrease in work function after reduction. Bottom gated field effect transistors fabricated with isolated RGO sheets displayed charge neutrality point at a positive gate voltage, indicating p-type nature, consistent with UPS and electrostatic force microscopy (EFM) measurement results. The RGO sheets obtained by heat treatment of AA/GO/AA sandwich structure exhibited conductivity in the range of 2-7 S/cm and field effect mobility of 0.03-2cm²/Vs, which are consistent with values reported for RGO sheets obtained by various chemical/ thermal reduction procedures. The extent of GO reduction is determined primarily by proximity of AA molecules and found to be unaltered with either escalation of heat treatment temperature or increase of AA content in sandwich structure. The single-step GO reduction approach demonstrated in this work is an effective way for development of RGO monolayers with high structural quality towards graphene-based electronic device applications.

Keywords: Graphene oxide, reduced graphene oxide, green solid state reduction, arachidic acid, sandwich structure, Langmuir-Blodgett

1. Introduction

Among diverse graphene-based materials, reduced graphene oxide (RGO) has been extensively explored, in view of its tunable bandgap, semiconductor characteristics, controllable de-oxygenation and attractive applications as an alternative to graphene [1–3]. RGO layers typically consist of a mixture of sp^2 -C and sp^3 -C domains, where the relative ratios of sp^3 -C and oxygen functional groups are substantially lower than those of GO precursors [4]. RGO, usually obtained by de-oxygenation of GO, was shown to be either semiconducting or conducting, with a range of conductivities depending on the adopted reduction process [1,4–6]. In addition to tunable conductivity, RGO also has several attractive properties, including large specific surface area, high thermal stability, excellent electrical and thermal conductivity, high carrier mobility and superior mechanical properties required for a variety of promising applications in nanoelectronics [1,7,8]. Considering these attractive characteristics, utility of RGO monolayers have been widely explored during the past two decades in the field of optoelectronics, photovoltaic devices and sensor applications, as well [1,7–9].

Several reduction approaches have been explored so far to obtain RGO from a variety of GO structures. These procedures can be mainly classified as 'reduction of GO in solution phase' and 'reduction in the solid state'. In solution phase approaches, as-synthesized GO dispersions are reduced in liquid ambience to form RGO dispersions and the obtained sheets are subsequently transferred onto a variety of solid substrates by suitable deposition methods [10–13]. On the other hand, various solid state reduction approaches were also explored to produce RGO, such as, thermal reduction, exposure to reducing agents/chemical vapors followed by heat treatment [14,15]. Most of these solid state approaches involve heat treatment in the temperature range of 400–1000 °C, either directly or after chemical reduction with reagents such as, hydrazine (N₂H₄) derivatives [16], sodium borohydride (NaBH₄) [17], alkali (NaOH, KOH) [18], hydrohalic acids (HI) [19], sulfur containing compounds [20] and alcohols [21]. Most of these reducing reagents are toxic and known to be harmful to the environment as well as human beings [22]. Further, usage of these chemicals may lead to generation of by-products and residues along with RGO, which are not suitable for water, biomedical, agricultural and energy applications [7,9,23,24]. There are other approaches such as microwave, photo-assisted, plasma and

electrochemical reductions [19,25–27], which have certain practical concerns and limitations. For example, in the case of electrochemical reduction, the process is largely limited to conductive substrates (electrodes) and cannot facilitate complete elimination of the defects and vacancies inherited from the precursor GO [4,27].

Apart from widely explored chemical and thermal reduction procedures, a few alternative and green reduction methods have also been proposed by various researchers. Pioneering the green reduction approaches, Zhang et al. proposed reduction of GO using ascorbic acid (vitamin C) and demonstrated the efficiency and scalability of the process without any hazardous final products [28]. Along these lines, various biological reductants including lemon juice, guava leaf, palm oil leaf, green tea extract, barberry fruit etc. were explored for efficient reduction of GO structures [28–32]. Table 1 shows a comparative summary of various green GO reduction methods and their effect on degree of reduction in terms of C/O ratio, I_D/I_G ratio, conductivity values as well as nature/thickness of RGO sheets. Most of these green reduction methods are practiced in the solution phase considering the ease of execution in single step while, adoption of solution phase processes may induce formation of agglomerates, crumpled or foam structures, multilayers and such morphologies are not suitable for fabrication of electronic devices.

Current manuscript demonstrates a novel, single-step and environment-friendly solid state GO monolayer reduction approach, in which, arachidic acid/GO/arachidic acid (referred as AA/GO/AA, hereafter) sandwich structures developed using Langmuir-Blodgett (LB) technique were heat treated to obtain RGO layers. The LB transferred AA/GO/AA sandwich structure on SiO₂/Si substrates consists of a monolayer of AA on either side of GO and was heat treated at a moderate temperature of 200 °C for AA supported reduction of GO monolayers. In order to establish the effectiveness of this novel reduction approach, surface morphology, chemical composition, electronic structures and electrical transport properties of obtained RGO sheets have been investigated. To the best of our knowledge, this is the first green solid state reduction method to obtain RGO monolayer sheets. The RGO sheets obtained via this procedure are uniformly thick monolayers (~1 nm) with flat morphology, devoid of any wrinkles and suitable for electronic device fabrication. Most importantly, the demonstrated approach doesn't involve/generate any toxic chemicals and the final product (RGO monolayers) are suitable for

biomedical, agricultural and energy applications. The current single-step reduction approach is considered as a practical way for development of RGO monolayers with high structural quality, aiming towards graphene-based electronic device applications.

2. Experimental details

2.1. Development of AA/GO/AA Layered Structures

Langmuir-Blodgett (LB) technique is well known for deposition of organic monolayers and multilayer films of amphiphilic molecules on solid substrates, with an ordered arrangement [41]. Arachidic acid (AA) is an amphiphilic fatty acid molecule that possesses a hydrophilic – COOH group at one end and the hydrophobic hydrocarbon chain at the other end. At the airwater interface, the hydrophilic (polar, –COOH) end is immersed in water, while the hydrophobic chains orient themselves at the air-water interface, as shown in Fig. S1.

For the LB deposition of arachidic acid molecules, ultra-filtered and de-ionized water (Millipore, 18.2 M Ω -cm) was used as subphase. The pH of subphase was maintained at 5.5±0.1 using dilute HCl/NaHCO₃. Typically, 150 µl solution of arachidic acid in chloroform (~1 mg/ml) was spread on the subphase and the subphase temperature was maintained at 10±1 °C. A typical surface pressure–mean molecular area (π -A) isotherm of arachidic acid on water surface obtained at a compression speed of 3 mm/min is shown in Fig. S2(a), which clearly shows the phase transitions during the compression of AA molecules. At a typical target pressure of ~30 mN/m, the stable monolayer formed on the surface of the subphase was transferred onto solid substrates, as shown in the inset of Fig. S2(a). Alternate lifting and dipping of a hydrophilic substrate (at 3 mm/min speed) result in formation of head-to-head and tail-to-tail layered structures, a schematic of which is shown in Figs. S2(b) and S2(c).

In the present work, the synthesis of GO was accomplished by using a modified Hummers-Offeman's method, as described earlier [14] and graphite powder (Bay carbon, SP-1) as a starting material. AA monolayer was transferred initially onto RCA-1 treated SiO₂/Si substrates under the above-mentioned conditions. Subsequently, GO monolayers were transferred over the AA film to obtain 'AA-GO' structure, under optimized GO transfer conditions described in previous work [42]. Finally, another AA monolayer was transferred over

the AA-GO structure to develop a 'AA-GO-AA' layer structure, which will be referred to as AA/GO/AA structure. Along with this, LB deposition of GO layers on a bare SiO₂/Si substrate was carried out for the purpose of comparison. In addition, a 3AA/GO/3AA sandwich structure has also been obtained by sequential LB deposition of 3AA layer, GO monolayer and another 3AA layers using similar procedure, for the purpose of comparison studies.

2.2. Reduction of GO in AA/GO/AA Layered Structures and characterization

The as-transferred AA/GO/AA layered structure was subjected to heat treatment in vacuum (~10⁻⁵ mbar) in the temperature in the range of 200–400 °C for 1 hr. For the purpose of comparison, GO monolayers deposited on SiO₂/Si (without AA layers) were also subjected to similar heat treatment in vacuum. The morphology, chemical composition, structural properties of as transferred and heat treated sheets were investigated by various techniques and the details are as follows. The surface morphology of the sheets was studied by Raith-150-Two scanning electron microscope (SEM) at 10 kV and, atomic force microscopy (AFM) images were recorded using Digital Instrument Veeco-Nanoscope IV Multimode scanning probe microscope in tapping mode. The surface electrical characterization of GO and RGO sheets on SiO₂/Si substrate was carried out by a Digital Instrument Veeco-Nanoscope IV Multimode scanning probe microscope in dual pass tapping mode. A Pt-Ir coated tip having a resonance frequency of ~ 75 kHz and quality factor (k) ~ 235 was used. Topographical information was obtained in the first scan, after which the second scan was performed by lifting the tip to a height in the range of 15 to 140 nm, above the sample surface. During the second scan, a DC voltage was applied to the tip for electrostatic force microscopy (EFM) measurements. Chemical composition of the sheets before and after the heat treatment was studied by X-ray photoelectron (XPS) spectroscopy, with Phi500 Versa Probe-II XPS system equipped with monochromatic Al K_{α} X-ray source. XPS peak fitting was performed using XPS Peak 4.1 software. For Ultraviolet photoelectron spectroscopy (UPS) measurements, a He discharge lamp operated to emit He-I (21.2 eV) and He-II (40.8 eV) flux was used. For UPS data analysis, Avantage V3.9 software was used with Shirley type background fitting and by considering each component peak as Gaussian. The overall energy resolution was 0.7 eV for XPS and 0.1 eV for UPS measurements. For work function measurements by He-I UPS, the sample was biased to - 3 V to accelerate low energy

secondary electrons. Fourier transform infrared (FT-IR) spectra of these samples on CaF_2 substrate were recorded using Perkin Elmer Spectrum One instrument in wavenumber range of 1300–3000 cm⁻¹. Micro-Raman spectroscopy was performed using Horiba Jobin Yvon HR800 confocal Raman microprobe equipped with 514 nm Ar+ laser.

Electrical characterization of as-transferred GO and obtained RGO sheets was carried out using a two-probe arrangement, and bottom-gated field effect transistor (FET) geometry was employed to measure the field effect mobility. The device structures were fabricated by transferring isolated RGO monolayer sheets on to the SiO₂(100 nm)/Si substrate, over which, Cr/Au (5 nm/100 nm) source and drain electrodes were patterned by e-beam lithography (Raith-150-Two) and deposited by sputtering. A 150 nm thick aluminium back gate contact was deposited by thermal evaporation. The channel length and width were in the range of 10–20 μ m and 10–30 μ m, respectively. The device characterization was carried out using a Keithley4200-SCS semiconductor characterization system.

3. Results and Discussion

Fig. 1(a) shows a typical SEM image of AA layer deposited on SiO₂/Si substrate, which exhibits a uniform coat with rough morphology formed by AA molecules. The SEM image recorded after transfer of GO sheets over the AA layer (Fig. 1(b)) shows uniformly distributed, isolated and clearly visible GO sheets over the rough AA molecule coating. Further, Fig. 1(c) shows the SEM image of AA layer transferred over the AA/GO structure, in which the GO sheets are not clearly visible due to formation of uniform AA layer overcoat. The AA/GO/AA structure deposited on SiO₂/Si substrate was heat treated in vacuum at 200 °C for 1 hr and the subsequently recorded SEM image is shown Fig. 1(d). After heat treatment, the GO sheets are again clearly visible throughout the substrate, which indirectly suggests the removal of AA molecules during heat treatment and nearly unaffected morphological stability and surface density of GO sheets.

The changes in morphological features of AA/GO/AA structure, before and after heat treatment at 200 °C were also examined by recording corresponding AFM images. The typical AFM image of AA/GO/AA layered structure on SiO₂/Si substrate is shown in Fig. 2(a), where

the GO sheets appear to be completely encased by AA molecule coat. After heat treatment of the AA/GO/AA structure (Fig. 2(b)), clearly visible GO sheets with good contrast were observed and practically no residual AA was seen at the GO layer surface. However, these sheets exhibited a slightly uneven surface with typical surface roughness ~0.2 nm, which is marginally higher than that of GO/RGO sheets (~0.1 nm) [42]. From both these SEM and AFM studies, it is inferred that the morphology of GO sheets remains nearly unaffected even after heat treatment of AA/GO/AA layered structures at 200 °C, similar to features of GO layers subjected to direct heat treatment at 200 °C (results are not shown here).

The changes in chemical composition of AA/GO/AA layered structures before and after heat treatment at 200 °C were analyzed by recording the FT-IR spectra in the wavenumber range of 1300–3000 cm⁻¹. Fig. 3 shows the FT-IR transmittance spectra of as-transferred AA/GO/AA layered structures on CaF₂ substrate and those recorded after subsequent heat treatment. The astransferred AA/GO/AA layered structure primarily shows dominant AA molecule characteristics where, the intense vibrational bands at ~2918 cm⁻¹ and ~2850 cm⁻¹ are due to CH₂ asymmetric and symmetric stretching modes of hydrocarbon chains of AA molecules, respectively. The intense vibrational band observed at ~ 1700 cm⁻¹ is attributed to carbonyl stretching vibration of carboxylic acid groups of AA. The weak doublet seen ~1473 cm⁻¹ and ~1463 cm⁻¹ is due to CH₂ scissoring vibrations while, the weak vibrational band at ~2955 cm⁻¹ due to CH₃ asymmetric stretching vibrations of AA molecules [43]. The spectrum recorded after heat treatment at 200 °C shows a substantial decrease in the intensities of both the CH₂ vibrational bands (~2918 cm⁻¹ and ~2850 cm⁻¹) as well as carbonyl stretching band of the carboxylic acid group (~1700 cm⁻¹). While the CH₂ and –COOH vibrational peaks practically disappear after heat treatment, interestingly a new broad vibrational peak has been found to emerge in the wavenumber range of 1550–1575 cm⁻¹. Absence of characteristic vibrational bands of AA molecules after heat treatment at 200 °C indicates nearly complete removal of AA and the fresh peak evolved in the range of 1550–1575 cm⁻¹ is attributed to the skeletal in-plane vibrations of sp^2 hybridized C=C bonds in GO sheets [44]. Appearance of prominent vibrational peak allied with sp^2 hybridized C=C is a clear indication of the recovery of graphitic carbon content, during heat treatment of GO sheets in close proximity of AA molecules.

Raman spectra of AA/GO/AA structures transferred on SiO₂/Si substrate were recorded before and after heat treatment at 200 °C and the typical spectra are shown in Fig. 4. For the purpose of comparison, Raman spectra of GO sheets on SiO₂/Si substrate (without AA layers) and subsequently heat treated at 400 °C were also included in Fig. 4. The Raman spectra of astransferred GO sheets (Fig. 4(a)) as well as AA/GO/AA layered structure (Fig. 4(c)) typically show the presence of D- and G-bands of GO at ~1340 cm⁻¹ and ~1602 cm⁻¹, respectively [15,45]. After heat treatment at 200 °C, the GO sheets on SiO₂/Si displayed a small red-shift of G-band to ~1598 cm⁻¹ (Fig. 4(b)). In contrast, a much larger red-shift of G-band to ~1592 cm⁻¹ was observed in the case of heat-treated AA/GO/AA structures (Fig. 4(d)). Significant red shift of Gband is an indicative of substantial reduction of GO sheets and restoration of the graphitic network, which is clearly more effective in the case of AA/GO/AA sandwich structure, having AA layers in close proximity of GO sheets. The I(D)/I(G) ratio of as-transferred AA/GO/AA structure was found to be ~1.6, similar to that of GO sheets on SiO₂/Si substrate [14,15,46]. However, the I(D)/I(G) ratio of AA/GO/AA sandwich structure was found to reduce to a value of ~1.1, after heat treatment at 200 °C. The decrease in I(D)/I(G) ratio is again an indicative of a substantial reduction of GO and recovery of the graphitic carbon network [8,15]. These results show that substantial reduction and restoration of graphitic network take place in AA/GO/AA sandwich structure after heat treatment at 200 °C.

The extent of de-oxygenation and the nature of chemical bonding in RGO sheets formed after heat treatment of AA/GO/AA sandwich structure have been studied by recording the XPS spectrum (Fig. 5). For the purpose of comparison, the de-convoluted C 1s spectra of GO sheets on SiO₂/Si substrate (without the AA layer) before and after heat treatment at 400 °C in vacuum are also shown in Fig. 5(a) and 5(b), respectively. The C 1s spectrum of GO in sandwich structure showed considerably different features from that of as-transferred GO sheets (Fig. 5 (a)) due to the presence of AA layer coat, hence is not shown here. Fig. 5(c) shows the deconvoluted C 1s core level XPS spectra of RGO sheets obtained by heat treatment of AA/GO/AA structure at 200 °C. The corresponding peak positions along with the relative integrated intensities of the de-convoluted components are listed in Table 2, along with those of as-transferred and heat treated GO samples. Both the heat treated GO sheets (Fig. 5(b)) and AA/GO/AA structures (Fig. 5(c)) displayed dominant sp^2 -C content, along with the reduced sp^3 - C/damaged alternant hydrocarbon and oxygen functional group contributions on the higher binding energy side (> 285.5 eV). From Fig. 5(b) and Table 2, it may be observed that the sp^2 -C content of RGO sheets obtained by heat treatment at 400 °C (without the AA layers) is ~63 % and the O/C ratio is ~0.24. On the other hand, for the AA/GO/AA structure heat treated at 200 °C, the sp^2 -C content was found to be ~69% and the O/C ratio is seen at ~0.17. Table 2 also shows that the ratio of non-graphitic to graphitic carbon content 'X' for the heat treated AA/GO/AA structure is significantly lower (~0.41) than those of precursor GO (~1.16) and GO-400 °C (~0.52) samples.

Significant increase of sp^2 -C content, decrease of O/C ratio and X value after the heat treatment (200 °C) of AA/GO/AA structures indicates a substantial reduction of GO in single step reduction process, which is consistent with the corresponding Raman results. The substantial reduction of oxygen content is associated with disappearance/decrease of contributions of oxygen functional groups and, recovery of graphitic network is attributed to the presence carbonaceous products formed by the decomposition of AA molecules. It may also be noted that the extent of GO reduction obtained by heat treatment of sandwich structure at low temperature of 200 °C is significantly superior to the case of GO sheets (without the AA layer) heat treated at 400 °C. These results, along with Raman and FT-IR studies reveal that, GO sheets can be effectively reduced by heat treatment at moderate temperature of 200 °C in close proximity of AA layers and, the extent reduction is similar to those reported via chemical reduction with hydrazine, followed by heat treatment at temperatures in the range of 400–1000 °C [14,15,47].

Figs. 6(a-c) show the valence band (VB) spectra of RGO sheets on Si substrate obtained by heat treatment of AA/GO/AA sandwich structure at 200 °C among which, Fig. 6(a) shows the He-II photoelectron spectrum of RGO sheets. The corresponding de-convoluted spectrum is shown in Fig. 6(b) and, Table 3 lists the peak positions of de-convoluted components of He-II VB spectrum of RGO sheets obtained through this procedure. The de-convoluted spectrum shows C 2p- π peak (3.7-4.0 eV) with considerable intensity, accompanied by the presence of a prominent C 2p-(π - σ) band at 5.7-6.0 eV. Apart from these, the C 2p- σ band (~6.9 eV), C 2s-2pmixed band (~9.1 eV) and C 2s band (~13.7 eV) were found to be shifted to higher binding energies, as compared to the values reported for GO sheets [48]. Further, an additional peak has been observed at ~11.5 eV, which may be attributed to the C–H 2p- σ states [49]. Appearance of C–H 2p- σ states is due to the presence of residual AA molecules along with RGO sheets, as indicated by AFM studies. Fig. 6(c) shows the magnified regions near the Fermi level for RGO sheets, where a noticeable increase in density of states (DOS) near the Fermi level has been observed. These features are attributed to increase in intensity of C 2p- π states and, proximity of the Fermi level with the valence band edge (VBE) is an indicative of p-type nature of formed RGO [26,48]. In continuation to these studies, Fig. 6(d) shows the secondary electron threshold region of the He-I spectra of RGO sheets obtained after heat treatment of AA sandwich structure. The work function is found to be ~4.0 eV, similar to that observed for chemically reduced GO sheets [48]. The decrease in work function after reduction is attributed to the removal of oxygen functional groups and increase in the graphitic carbon content, consistent with XPS, FT-IR and Raman results.

EFM measurements have been performed to investigate the surface electrical properties of RGO sheets obtained by heat treatment of AA/GO/AA sandwich structure at 200 °C and Fig. 7 shows the AFM and EFM images of obtained RGO sheets. The EFM images correspond to a tip-sample surface separation (*h*) of 20 nm and tip bias voltage (V_{tip}) of 2 V. For the purpose of comparison, AFM and EFM images of GO sheets (without the AA layer) on SiO₂/Si (Fig. 7(a) and 7(d)) and those obtained after heat treatment at 400 °C in vacuum (Fig. 7(b) and 7(e)) are shown as Fig. 7. The phase image of RGO sheets obtained by heat treatment at 400 °C without the AA layer (Fig. 7(e)) shows a relatively small contrast $\Delta \Phi$ (~ 1.2°). In comparison, the RGO sheets obtained from AA/GO/AA sandwich structure after heat treatment at 200 °C (Fig. 7(f)) showed much larger values of phase contrast for which, $\Delta \Phi$ is in the range of 2.5-2.7 ° at the edges of the sheets. The dependence of $\Delta \Phi$ on V_{tip} in the range of -2 V to +2 V was studied at a constant value of *h*=20 nm and these results are shown in Fig. 8. The data exhibits characteristic parabolic dependence of the phase shift on tip bias voltage, represented by equation (1) in all the cases and are fitted accordingly [50–52].

$$\Delta \Phi = (-Q/2k) \Delta C^{ll}(h)(V_{tip} - V_s)^2$$
(1)

where, $\Delta C^{ll}(h)$ is the difference between the second derivatives of the tip-sample capacitance and the tip-bare substrate capacitance, Q and k are respectively, the quality factor and the force constant of the cantilever, V_{tip} is the tip bias voltage and V_s is the local surface potential.

Parabolic dependence is seen at relatively smaller curvature for RGO sheets obtained by heat treatment at 400 °C, without the AA layer. The curvature is substantially larger for the RGO sheets obtained by heat treatment of AA/GO/AA structure at 200 °C. It may be pointed out that for these RGO sheets, the vertex point (the maximum of the parabolic fitting which represents the surface potential of the samples) is in the range of 25–35 mV, indicating their p-type nature. The larger curvature of the parabola is an indicative of the higher conductivity of RGO sheets, which are consisting with the corresponding XPS and Raman results. Increase in curvature of parabola with the extent of reduction of GO sheets (Fig. 8) is thus attributed to increase in their dielectric constant, which accompanies the increase in free charge carrier density and conductivity owing to the reduction process, as reported earlier [53,54]. The positive value of vertex point of the parabolic dependence in this case is also indicative of the p-type nature of RGO sheets, consistent with the UPS studies. Further, the phase contrasts (Fig. 8) seen for RGO sheets obtained by heat treatment of AA/GO/AA structures are comparable to those of RGO sheets obtained by chemical reduction with hydrazine, followed by heat treatment in argon at 400 °C for different durations (3 hr (RGO-1) and 6 hr (RGO-2), Fig. S4). It is also noteworthy that the non-destructive EFM technique can be effectively utilized for a qualitative comparison of RGO sheets of varying conductivities.

In order to investigate the effect of de-oxygenation and restoration of graphitic network on the electrical transport properties of RGO sheets, bottom gated field effect transistors (FETs) have been fabricated on isolated RGO monolayer sheets on SiO₂/Si substrates obtained by heat treatment of AA/GO/AA sandwich structure. The channel length and width were in the range of 12–25 μ m and 10–30 μ m, respectively. Fig. 9 shows the typical I_{DS}-V_{DS} characteristics of RGO sheets measured in bottom gated-FET geometry. I_{DS}-V_{DS} characteristics RGO sheets obtained by heat treatment of GO sheets (without AA layers) in vacuum at 400 °C were also examined along with those obtained by heat treatment of AA/GO/AA structure at 200 °C. The RGO sheets obtained by heat treatment at 400 °C exhibit non-linear I-V curves and their conductivities are in the range of $(10^{-2} - 10^{-1})$ S/cm, which are much larger than those of typical GO sheets [15]. In contrast, the RGO sheets obtained by heat treatment of AA/GO/AA structures exhibited linear I-V curves and displayed substantially higher conductivities in the range of 2–7 S/cm. A typical top view SEM image of an RGO monolayer-based FET geometry is shown in the inset of Fig. 9(b).

Typical transfer characteristics (I_{DS} - V_{GS} curve at $V_{DS} = 1$ V) of back gated FETs based on RGO sheets obtained by heat treatment at 400 °C (without AA layer) as well as RGO sheets obtained by heat treatment of AA/GO/AA structures at 200 °C were measured in the gate voltage range of -20 V to +20 V and are shown in Fig. 9. For the FETs fabricated with RGO sheets obtained by heat treatment at 400 °C, I_{DS} decreases with decrease of negative gate voltage and continues to decrease as the positive gate voltage is increased to +20 V, thus displaying a p-type behaviour. On the other hand, the FETs fabricated with RGO sheets obtained via heat treatment of AA/GO/AA structure displayed larger currents of 1-2 order higher magnitude, also showing a p-type behavior. This may be attributed to the influence of surface adsorbed of oxygen molecules or residual hydroxyl groups on RGO sheets, which can serve as deep electron traps and suppress n-type conductivity [15,55]. For the RGO sheets heat treated at 400 °C (without the AA layer), the hole mobility is found to be in the range of 0.001–0.04 cm²/V-s. In comparison, for RGO sheets obtained by the heat treatment of AA/GO/AA structure, the hole mobilities are found to be in the range of 0.03-2 cm²/V-s. The conductivity and field effect mobility of RGO sheets obtained by reduction of AA/GO/AA sandwich structures are thus comparable to those obtained by hydrazine vapour exposure followed by a heat treatment as well as the range of values usually reported in the literature for RGO sheets obtained by various chemical/thermal reduction methods [15,56].

Further, to examine the effects of (a) escalation of heat treatment temperature and (b) multiplying AA layers in sandwich structure on extent of GO reduction, two entirely different reduction procedures were adopted. In the first case, typical as-transferred AA/GO/AA structure was subjected to heat treatment in vacuum ($\sim 10^{-5}$ mbar) at 400 °C for 1 hr. In the second case, a set of three layers of AA have been used instead of AA monolayer in the sandwich structure (3AA/GO/3AA) and subjected to heat treatment in a vacuum ($\sim 10^{-5}$ mbar) at 200 °C for 1 hr.

The XPS data for both these types of samples are shown in table S1. As compared to the optimized samples (AA/GO/AA heat treated at 200 °C), no further or significant changes in reduction have been observed with either escalation of heat treatment temperature or increase of AA layers Table S1). Interestingly, GO sheets were clearly seen after heat treatment of 3AA/GO/3AA structure at 200 °C, despite the availability of larger quantity AA in precursor structure (Fig. S3). However, the height profile measurements carried out on these samples showed a largely uneven surface with high surface roughness (0.6–0.8 nm), in comparison with the limited roughness seen for the case of AA/GO/AA structure (~ 0.2 nm, Fig. 2(b)). These features are attributed to incomplete removal of AA molecules from the GO sheet surface.

4. Conclusions

The present work introduces a novel, single-step and environment friendly reduction method via heat treatment of AA/GO/AA sandwich structure developed by sequential LB processing at moderate temperature of 200 °C. Heat treatment of AA/GO/AA sandwich structure does not lead to significant change in the thickness, surface density and overall morphology of the GO sheets, except the presence of residual AA molecules. Further, heat treatment of AA/GO/AA sandwich structure at 200 °C causes substantial reduction of GO, resulting in RGO layers with sp^2 -C content of ~69%, O/C ratio of ~0.17, non-graphitic/graphitic carbon ratio of ~0.4 and I(D)/I(G) ratio of ~1.1. Valence band electronic structure studies using UPS, nondestructive assessment of conductivity by EFM measurements and electrical characterization studies with bottom gated FETs have been used to compare the extent of reduction and electrical properties of RGO sheets obtained by heat treatment of AA/GO/AA sandwich structures at low temperatures (200 °C). Precisely, the RGO sheets obtained by heat treatment of AA/GO/AA sandwich structure exhibit a dominantly p-type conductivity in the range of 2–7 S/cm and hole mobility in the range of (0.03-2) cm²/V-s. These electrical parameters are comparable with those reported for RGO sheets usually obtained by hydrazine vapour treatment, followed by heat treatment in the range of 400–1000 °C. Thus, GO sheets can be effectively reduced by heat treatment of LB-transferred AA/GO/AA sandwich structures having AA molecules in close proximity with GO sheets, which play a significant role in reduction of GO sheets and substantial recovery of graphitic network. The solid state reduction procedure proposed in the present work

not only offers a simple, easily adoptable and environment friendly route for the reduction of GO sheets, but also facilitates their applications in development of solid state device structures.

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Figure 1. SEM images of as-transferred (a) AA layer, (b) AA/GO and (c) AA/GO/AA layer structure and (d) after heat treatment of AA/GO/AA sandwich structure at 200 °C in vacuum for 1 hr.



Figure 2. Typical AFM images of as-transferred (a) AA/GO/AA structure on SiO₂/Si and (b) after heat treatment at 200 °C in vacuum for 1hr. Inset of (b) shows the height profile of RGO sheet.



Figure 3. FT-IR spectra of (a) as-transferred AA/GO/AA structures and (b) after heat treatment at 200 °C.



Figure 4. Raman spectra of (a) as-transferred GO/SiO₂/Si and (b) after heat treatment at 200 °C, (c) as-transferred AA/GO/AA structure and (d) after heat treatment at 200 °C.



Figure 5. De-convoluted C-1s core level XPS spectra of (a) as-transferred GO sheets and (b) after heat treatment at 400 $^{\circ}$ C, (c) after heat treatment of AA/GO/AA structure at 200 $^{\circ}$ C.



Figure 6. (a) He-II valence band spectrum of AA/GO/AA structures after heat treatment at 200 °C. (b) shows the de-convoluted He-II VB spectra, after background correction and, the magnified regions near Fermi level region are shown in (c). (d) Secondary electron threshold region of He-I spectra of AA/GO/AA structure after heat treatment at 200 °C.



Figure 7. Typical AFM and EFM images of (a,d) GO sheets on SiO₂ substrate, (b,e) GO sheets heat treated at 400 °C in vacuum, (c,f) after heat treatment of AA/GO/AA structure at 200 °C. The phase contrast profiles are shown in the EFM images (d-f).



Figure 8. Typical parabolic dependence of $\Delta \Phi$ on tip bias voltage for h = 20 nm at a typical location near the edges of GO (- \blacktriangle -), RGO obtained by heat treatment at 400 °C in vacuum without AA layer (- \bullet -) and heat treatment of AA/GO/AA structure at 200 °C (- \blacksquare -) sheets.



Figure 9. I_{DS} - V_{DS} plots of (a) RGO sheets obtained by heat treatment at 400 °C in vacuum without AA layer, and (b) AA/GO/AA structure after heat treatment at 200 °C, along with SEM image of a typical RGO monolayer sheet in two probe contact geometry as inset. Transfer characteristics of the bottom-gated FET employing (c) RGO sheets obtained by heat treatment at 400 °C in vacuum without AA layer, (d) AA/GO/AA structure after heat treatment at 200 °C.

Reducing agent & Process C/O ID/IG σ (S/cm) or Type of layers or References method of of Rs (k Ω / \Box) thickness of RGO fabrication reductio (nm) n Ficus carica and Solution 3.57 5-7 layers [23] _ _ Phragmites australis Vitamin C Solution 5.17 multilayers [33] _ _ Brassica oleracea Solution 3.63 40nm [34] _ _ var. gongylodes Ziziphus spina-Multilayers Solution 1.85-[35] christi 1.92 ascorbic acid, 4.98 1.93 755.70 S/m Multilayers Solution [36] gallic acid, and 3.23 1.91 sodium citrate 3.53 1.91 3 Palm oil leaves Solution 1 Multilayers [37] _ extract Vernonia Solution 3.88 Multilayers [38] _ amygdalina plant (locally called "dhebicha") 1.28 Multilayers wood sheets Solution _ -[39] L-ascorbic acid, 50 Multilayers [40] Solid-1.10 _ _ °C, 48 hr state (~ 50 µm) Arachidic acid @ Solid-5.88 1.1 ~ 2-7 S/cm or Monolayer (1 nm) This work 1hr at 200 °C ~1000 k Ω sq⁻¹ state

Table 1. A comparative summary of green reduction methods and their effect on the degree of reduction in terms of C/O ratio, I_D/I_G ratio, conductivity values, as well as the nature/thickness of the RGO sheets

Table 2. Peak positions (in eV) of various de-convoluted components of C-1*s* core level XPS spectra of GO, AA/GO/AA structure after heat treatment, as indicated. The integrated intensity values (%) are given in parenthesis. The last column gives the values of O/C ratio and X (ratio of non-graphitic carbon to graphitic carbon).

	Sample							O/C	
	(heat treatment	sp^2 -C	<i>sp</i> ³ -C	C-O	C=O	COOH	π - π^*	ratio	Х
	Temperature)							Tatio	
	G 0	284.4	285.3	286.6	287.2	288.6	289.9	0.46	1 1 6
	GO	(42)	(15)	(17)	(17)	(6)	(3)	0.46	1.16
	GO	284.5	285.4	286.2	287.1	288.4	289.5		
	(400 °C)	(63)	(15)	(10)	(4)	(5)	(3)	0.24	0.52
_	AA/GO/AA	284.4	285.4	286.2	287.2	288.5	289.5	0 4 -	0.44
	(200 °C)	(69)	(14)	(9)	(4)	(2)	(2)	0.17	0.41

Table 3. De-convoluted peak positions (in eV) of He-II UPS valence band spectra of AA/GO/AA structures after a heat treatment (as indicated).

Sample (Heat treatment temperature)	С 2 <i>р-</i> π	С 2 <i>р-</i> (π-σ)	С 2р-б	C 2 <i>s</i> -2 <i>p</i> mix	С-Н 2 <i>р-</i> σ	C 2s
AA/GO/AA (200 °C)	3.7	5.7	6.9	9.1	11.2	13.7

Electronic Supplementary Information

Green and Solid State Reduction of GO Monolayers Sandwiched between Arachidic Acid LB Layers

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Figure S1. Schematic diagram of an arachidic acid (AA) molecule at the air-water interface.



Figure S2. (a) Typical π -A isotherm for an AA monolayer at subphase pH of 5.5 and the schematics of (b) one monolayer of AA and (c) three monolayers of AA.



Figure S3. Typical AFM images of 3AA/GO/3AA structure after heat treatment at 200 °C.



Figure S4. Typical parabolic dependence of $\Delta \Phi$ on tip bias voltage for h = 20 nm at a typical location near the edges of GO (-•-) RGO-1 (-▲-) and RGO-2 (-■-) sheets.

Table S1. Peak positions (in eV) of de-convoluted components of C-1*s* core level XPS spectra of AA/GO/AA and 3AA/GO/3AA structures after heat treatment, as indicated. The integrated intensity values (%) are given in parenthesis. The last column gives the values of O/C ratio and X (ratio of non-graphitic carbon to graphitic carbon).

Sample (Heat treatment Temperature)	sp ² -C	sp ³ -C	C-0	C=O	СООН	π-π*	O/C ratio	X
AA/GO/AA	284.4	285.4	286.2	287.2	288.5	289.5	0.16	0.38
(400 °C)	(70)	(14)	(8)	(4)	(2)	(2)		
3AA/GO/3AA	284.4	285.4	286.2	287.2	288.5	289.5	0.10	0.44
(200 °C)	(66)	(16)	(8)	(4)	(3)	(3)	0.18	0.44