Layered, Tunable Graphene Oxide Heterostructures for Wearable Electrocardiogram Sensors

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Abstract Smart, nanoscale engineered materials combined with wireless technologies within Internet of Things (IoT) are capable of delivering new level of health diagnostics. A reduced graphene oxide-nylon composite material is developed and tested, demonstrating its usefulness as a materials for sensors in a wearable, long term electrocardiogram (ECG) monitoring system. The heterostructure material is analyzed structurally, chemically and electrically by scanning electron microscope (SEM), atomic force microscopy (AFM), Fourier Transform Infrared (FTIR) spectroscopy, and resistivity analysis. Analysis points towards interesting tunability of electrical and optical properties, while live ECG data demonstrate its signal transduction capability and overall suitability as an ECG sensor.
Electrocardiogram (ECG) systems measure the electrical current produced by depolarization of the cardiac tissue during a heartbeat.\(^\text{[1]}\) Accurate ECG measurement therefore relies on the quality of the electrode, as the majority of signal degradation will occur at the skin-electrode interface.\(^\text{[1,2]}\) Currently, one of frequently used clinical electrodes is the wet, gel type Ag/AgCl adhesive electrode, owing to its very low impedance and excellent signal transduction.\(^\text{[3]}\) These electrodes however, are only practical in a clinical environment with a patient confined to a bed. Both the adhesive pads and the gel electrolyte have a short lifespan, needing frequent replacement if long periods of observation are required.

With increasing global prevalence of various chronic conditions, such as Type II Diabetes\(^\text{[4]}\) (also, see Supporting Online Materials) and associated cardiovascular disease (CVD),\(^\text{[5,6,7,8]}\) there is growing interest in the development of wearable, long-term constant monitoring systems for health parameters.\(^\text{[9,10]}\) The need for regular replacement of wet electrodes is impractical for a long-term monitoring system, and mostly incompatible with a wearable device. Alternatively, dry electrodes offer better long-term usability, but lower signal quality without undesirable preparation steps e.g. abrading, wetting or puncturing of the skin.\(^\text{[11,12]}\) The key task is therefore to find a suitable alternate electrode material that will be long lasting, biocompatible and resistant to biological fouling after long periods of skin contact, while also having good conducting properties.

Achieving these needs is possible with graphene, graphene oxide and their derivatives, classes of materials garnering massive attention for their remarkable physical properties\(^\text{[13]}\) in the past two decades. Consisting of atomically thin layers of carbon, graphene displays high mechanical strength, electrical conductivity, long term stability and low toxicity.\(^\text{[14,15]}\) While many pure graphene production methods involve high temperature gas-phase deposition techniques,\(^\text{[16,17,18,19]}\) this work relies on an alternative method of production practical for large scale production, and is one compatible with Nylon fiber-based material, as a support. An aqueous dispersion of graphene oxide is applied to Nylon fabric in a uniform coating, which is then chemically converted to reduced graphene oxide (rGO\(_x\)).\(^\text{[20]}\) The rGO\(_x\) coating is then characterized via a number of microscopic, spectroscopic and electrical measurement techniques,
elucidating the parameters behind the usefulness and opening the path for its improvement and large scale development of ECG electrodes.

Fabrication of the electrode begins with producing an aqueous suspension of graphene oxide (GO), according to a modified Hummer’s method, a detailed account of which can be found in the work of Dikin and Li. To begin, a precursor sample of graphite powder is chemically oxidized, then partially exfoliated by various chemical and thermal steps, yielding loosely packed atomic layers of graphite oxide. Ultrasonication is then used to fully exfoliate the graphite oxide stacks, producing a dispersion of single layer GO. The resulting dispersion is then purified through several cycles of centrifugation and washing with deionized water to remove unwanted residual metallic or acidic traces. After purification, we obtain an aqueous dispersion of GO. For a fabric substrate, Nylon is selected as a suitable candidate material for its strength, durability under varied chemical conditions, smoothness, absorbency. A portion of fabric is cut from a roll, washed, dried, and placed into a volume of a liquid GO dispersion. The fabric is left to soak overnight, insuring even distribution of liquid over and throughout the entire fabric surface. Next, the fabric is removed, placed on a hydrophobic sheet to prevent excessive runoff of the absorbed dispersion, and left to dry in a convection oven at 90 °C for 2 hours. This simple process results in a piece of fabric with a single coating of GO, while repeating the process will result in additional coatings of GO. In a single coating state, the fabric is not yet usable as an electrode since GO is not sufficiently conductive. Therefore, multiple deposition followed by a chemical reduction with hydrogen iodide (HI) steps are performed, since thermal reduction is not feasible. Once the desired thickness of GO has been achieved, a bath of HI is prepared and the coated and dried fabric is placed in the bath and left for 1 hour at room temperature. 1 hour is sufficient time to ensure that a substantial fraction of GO is chemically reduced, and the resulting rGO will be quantifiably conductive. Removing the fabric too early will result in an incomplete chemical reduction and lower electrical conductivity of the sensor. Once removed from the HI bath, the fabric is washed several times in deionized water to remove all traces of acid, then dried in a convection oven. The resulting fabric is highly electrically conductive, strong and durable, and ready to be implemented as an ECG sensor.
The ECG sensor is primarily a voltage sensor, and therefore its electrical properties are key to its functionality. Samples with successive coatings of rGOx were produced and cut into squares and rectangles of various sizes for electrical characterization. Bare Nylon is assumed to have nearly infinite resistance as it is highly insulating. In-plane transport measurements were performed with National Instruments© NI ELVIS II system and LabVIEW© software, and I-V characteristic curves were measured on a Semiprobe© probing station and with a Keithley© 4200 SCS characterization platform. Measurements were taken at various positions on the samples, then averaged. This was repeated for 10 mm, 15 mm and 20 mm squares, and 5x10 mm, 5x20 mm, and 5x30 mm rectangles. These dimensions were chosen in part because of relevant dimensions of wearable ECG electrodes. An effort was made to also measure out of plane resistance, but the geometry of the contact between probes and samples was prohibitive.

Scanning electron microscope (SEM) images were captured on a JOEL JSM-7610F Schottky Field Emission Scanning Electron Microscope under high vacuum. Samples were fixed to a sample holder with carbon tape and needed no additional preparation for imaging.

Atomic force microscope images (AFM) were taken on an Asylum Research MFP-3D AFM (Oxford Instruments, Abindgon, England) in tapping mode.

Fourier transform infra-red (FTIR) measurements were taken on a Perkin-Elmer© Spectrum Spotlight 200 FTIR microscope.

Electrocardiogram (ECG) data with the the rGOx fabric electrode (AD Instruments PowerLab ECG acquisition system) were taken from a volunteer. A healthy adult volunteer had electrodes attached to his skin, and remained stationary during signal measurement. Data were taken using rGOx fabric electrodes at the wrists and neck, and simultaneously at the same locations with Ag/AgCl wet electrodes for comparison.

Figure 1 shows the results of the resistance vs rGOx measurements for the amterial samples fabricated.
Figure 1. (a) Dependence of the resistance of the multilayered rGOx films, together with the two models. The first model (1a and 1b) is based on resistor network, whose parameters change as the number of layers and therefore thickness increases. The model 2 relies on the domain structure of rGOx. (b) graphical representation of the resistor network model for graphene oxide multilayers, with rGOx planes running left-to-right.

Given the unusually large drop-off shown in Fig. 1 (more than a factor of x20) in the value of the resistance as a function of increasing thickness, we have modeled our layered rGOx samples in two different ways to gain a better insight into processes leading to such a large change. One model (Model 1) is motivated by circuit model of the layered materials, where one relies on the simple resistor network shown on Fig. 1.b, with $r_\parallel$ representing the in-plane resistance of a rGOx monolayer, $r_\perp$ representing the resistance due to out-of-plane (that is between the layers) conduction, and $R_n$ being the equivalent resistance of the network corresponding to a rGOx sample composed of $n$ monolayers. We estimated $n$ for each of our samples as $n = t/\tau + 1 \approx t/\tau$, where $t$ is the measured sample thickness, and $\tau \approx 0.3 \text{ nm}$ is taken as the average distance between adjacent rGOx monolayers. By implementing the recursive relation
\[
R_{n+1} = \frac{(R_n + 2r_\perp)r_\parallel}{R_n + 2r_\perp + r_\parallel}
\]

we found that \(R_k\) models the measured resistances at lower thicknesses best when \(r_\parallel = 1.6 \times 10^3 \, \Omega\), \(r_\perp = 2.8 \times 10^7 \, \Omega\); and models the resistance at higher thicknesses (that is, as the drop in \(R\) occurs in Fig. 1) when \(r_\parallel = 70 \, \Omega\), \(r_\perp = 3.0 \times 10^6 \, \Omega\). The fact that the transition between these regimes is brought on by a 2 orders of magnitude decrease in \(r_\perp\), and one order of magnitude drop in \(r_\parallel\) suggests that the resistance drop might be attributable to a combined in-plane and out-of-plane changes of the transport properties, which in turn is caused by the changes in the in-/out-of-plane bonding as the thickness increases.

The second model we borrows from a similar model of changes in the resistance of multilayered graphene on thickness \[^{29}\]. Considerations leading to this model could be found in the previous high-resolution transmission electron microscopy (TEM) studies which show that in rGO\(_x\) layers the defect-free crystalline graphene oxide areas are continuous, i.e. can be viewed as continuous arrays of slightly overlapping micrometer scale defect-free grains \[^{28}\]. Due to this, and the defect-free areas being more conductive than the defect regions by several orders of magnitude, we viewed the structure of rGO\(_x\) as being roughly analogous to the grain-structure of CVD graphene - with the defect regions in rGO\(_x\) acting similar to the grain boundaries in CVD graphene. Duong \textit{et al.}\[^{29}\] give the following empirical relation between the resistance \(R\) and the average grain size \(A\) of CVD graphene layers:

\[
R = R_0 \left(1 + \left(\frac{A}{A_c}\right)^n\right), \text{ where } R_0, A_c \text{ and } n \text{ are fitting parameters.}
\]

At significant reduction the low defect regions in rGO\(_x\) provide a channel for percolation-like transport \[^{30}\], and are therefore the major contributors to a rGO\(_x\) layers’ conductivity. Therefore, we modeled the resistance drop by an increasing thickness-dependent effective percolation area related to both in-plane and out of plane conduction, as shown in the formula above, resulting in the Model 2 in Fig. 1a. We replaced the \(A/A_c\) term in the above equation with \(kt\), where \(k\) is a proportionality constant, and \(t\) is the
thickness. The relation \( R = R_0 (1 + (kt)^{-n}) \) is then fit for 50 nm and higher. The resulting fit is shown on Figure 1a (green curve), and corresponds to the values of \( R_0 = 2.09 \cdot 10^4 \, \Omega, k = 0.0155 \, nm^{-1} \) and \( n = 12 \). Clearly, this second model applies only to the sufficiently large thickness values.

The rGO\(_x\) coating serves as the electrical conductor in our sensor, and its physical characteristics will play a major role in determining its conductivity. Elucidating correlations between elementary electronic performance and the structural and morphological details is critical to understanding the pathways for the improvement of the current material and device level of functionality and integration. Therefore, an examination of physical and conformational characteristics of the rGO\(_x\) coated fabric.

Scanning Electron Microscope (SEM) images give us a clear picture of the surface structure of the composite heterostructure, as well as some insight into the process of surface restructuring as the film thickness increases, which is relevant to the control of the resistivity of the probes as ECG sensors. Figure 2 shows three fabric samples after varying levels of rGO\(_x\) thickness (columns left to right: 0 nm (bare Nylon fabric), 22 and 79 nm) and at increasing magnification. A zoomed out image (Fig. 2.a) shows a fabric which appears uniform and free of defects. At a rGO\(_x\) thickness of 22nm, the overall microscopic appearance of the fabric seems to be largely unchanged (Fig. 2.b). Closer examination at high magnification of the bare nylon fiber (Fig. 2.g) shows a series of a meso- and nanoscale defects. Examination at high magnification (Fig. 2.h) of 22nm film reveals a drastic reduction of the nanoscale defects, which have likely been uniformly covered by the rGO\(_x\) coating.
Figure 2. SEM images: of 0nm, 22nm, and 79nm rGO$_x$ heterostructures (panels (a) through (c)). These images show some minor textural changes, but maintain the overall appearance and structure of the fabric. At higher magnification, fibers are observed to be coated individually, but as thicker coatings are applied, some fibers become stuck together and increasingly large defects appear (panels d, e, f). Macro defects (~1μm, lateral size) become visible at high magnification (panels g, h, i), circled.

At a slightly lower magnification however, there appear to be visible discontinuities of the coating (Fig. 2.e). As a result of these discontinuities, the conductivity and signal transduction capability of 22nm rGO$_x$ film both remain relatively low. Examining 79 nm film composite (Figs. 2.c, f, and i), we see that while the nanoscale defects from the bare nylon are completely covered, new and larger defects begin to emerge as a result of the relative excess rGO$_x$ on the fabric surface. The appearance of the large defects may partially come from poorly controlled rate of deposition, as the substrate is kept in the solution, and there is no vacuum to assist in the control of the deposition rate [31]. Additionally, the regions of poor fiber coverage observed after a single coating are no longer observable, and electrical conductivity has risen significantly, likely as a result of the absence of observable voids. Up until a film thickness of 43nm, individual fibers remain clearly separate and able to move independently. However, with subsequent thickness of rGO$_x$ coating, the larger defects become significant, and excess rGO$_x$ can be
observed physically connecting adjacent fibers (Fig. 2.i). While the electrical conductivity has drastically increased with six-coated fabric, the larger defects become a concern as they may become nucleation points from which the structure grows in an un-intended manner (i.e. not surrounding the core nylon matrix and/or not coating it uniformly), and therefore may lead to less stable material and less reliable ECG probe. In short, frayed edges (Figs. 2.f,i) may lead to loss of coverage, and eventual loss of functionality for regions of fabric.

Available literature on the relationship between surface morphology of so deposited GOx and sensor design requirements and performance is mostly directed towards optical [32] and biochemical biosensors [33]. However, a relative large scale robustness of the ECG sensors proposed here despite presence of some defects points towards: (a) a pathway for future improvement through defects' engineering, and (b) current level of applicability of rGOx in ECG and related sensors.

Atomic force microscope (AFM) images were obtained to provide detailed micro–and nano–characteristics at the composite fabric surface. As in the SEM images, nanoscale defects are noticeable in the bare fabric (Fig. 3.a). These defects start to become smoothed over by a thin film of rGOx (Fig. 3.b) and are subsequently replaced by larger microscale defects in the rGOx film (Fig. 3.c,d) as additional rGOx deposition occurs. Figs. 3a-d represent 6x6 μm² scans over single fibers. Due to the curvature of the individual fibers, the actual height of the defects is difficult to measure and calculate, but the broad range of changes in relative variation of heights appears to be 1.5 to 3.5 nm. This finding builds on the past work, [34] where GO nanosheets are found to have a thickness of the order of 1.0 nm and
Figure 3. (panels (a) through (d)) show AFM images of 0, 22, 43 and 79 nm rGO film respectively, on nylon fibers. Nanoscale defects are shown in the bare nylon (a), covered up with the initial rGO coating (b). Additional rGO coatings may slowly produce larger defects (c-d). Topographical linear scans extracted from AFM data (e) show surface defect height is limited to below 3.5 nm regardless of coating thickness, and defects’ lateral size limited to approximately 300 nm.

reduced GO nanosheets are typically 0.3 - 0.6 nm. These values can be obtained by AFM, and the change in thickness can likely be attributed to the removal of the various out-of-plane oxide groups. Measurements with scanning tunneling microscopy (STM) support these findings.\[34\] From our observations of defects in the 1-3 nm range, we have good reason to believe that these defects arise from a small number of rGO sheets (likely fewer than 5) either folding back on themselves or randomly overlapping.\[35\] Alternatively, these defects could be the result of unreduced (or, more precisely, less than
“average reduced”) sheets remaining randomly dispersed within the film.[36] Understanding of the structure of rGOx films that goes beyond morphological studies (such as AFM and SEM) is needed, and we offer the results of Fourier Transform Infrared (FTIR) spectroscopy, in the next section.

In addition to the correlation between morphology and structure, performing FTIR is important as we look to elucidate the role of different functional groups in the process of stepwise increase of film thickness, which itself is necessary to obtain proper electrical (and, in future applications, optical) characteristics of rGOx ECG sensors. FTIR measurements were performed on a Perkin-Elmer® Spectrum Spotlight 200 FTIR microscope. The FTIR spectra of samples discussed here showed many of the typical vibrational peaks of graphene oxide and its derivatives, such as 980 cm\(^{-1}\), (sp\(^2\) C-H stretching mode), 1017 cm\(^{-1}\) (alkoxy stretch at C-O moiety), \(~1350\) cm\(^{-1}\) (D-feature, associated with the C-O-C (epoxide) group, involving a phonon-defect interaction in the sp\(^2\) graphitic structure), 1504 cm\(^{-1}\) (sp\(^2\) hybridized C=C bond), 1577 cm\(^{-1}\) (G-feature, first order Raman scattering as a single E\(_{2g}\) phonon optical vibration in the graphitic structure,), and 1712 cm\(^{-1}\) (carboxyl stretching mode, likely picking up contributions from both COOH and C=O) and several others, as shown in Fig. 4 (top panel).[37,38,39] As the atomic content in the film varies with the increasing thickness, relevant changes in the FTIR spectral width and centerline position are expected.

Most features have small change in the peak position \(\Delta\omega_C\), about 1-3 cm\(^{-1}\), as shown in various panels of Fig. 5. One can identify two types of spectral features; those where the FTIR absorbance changes monotonously with the increasing film thickness, and those where the change is non-monotonous. This indicates that different bonding mechanisms contribute differently to structural properties of rGOx, with the increasing thickness. Overall, the change in absorbance is smaller with the increasing thickness, as one would expect for the thickness-limited process. We note the small scale of the changes and the near-linear behavior, in contrast to the electrical properties.
Figure 4. (a), ATR FTIR data in a broad mid-infrared range showing a number of structurally relevant features of rGO, discussed in the main text. (b) shows change in absorbance as a function of film thickness for the selected set of the most relevant rGO features. Data imply that despite the drastic (albeit favorable) influence of film thickness on the electrical properties, the optical (and likely chemical) behavior of the film remains fairly stable.

A more significant change is seen in two relevant features: \( sp^2 \) C-H bend at 980 cm\(^{-1} \) (\( \Delta \omega_C = 24 \) cm\(^{-1} \)) and epoxide C-O-C asymmetric stretch near 1240 cm\(^{-1} \) (\( \Delta \omega_C = 10 \) cm\(^{-1} \)). Based on available GO\(_x\) literature, and our study here, we propose that these two features, together with the carboxylic moieties at 1712 cm\(^{-1} \) discussed above, are most responsible for the defect creation discussed in SEM and AFM sections, and
therefore point towards likely development path of further improvement of this material for sensor
through the tuning of the wet chemistry process.

**Figure 5.** (a-f) Changes in FWHM and the center peak position for six of the spectral features from Figure 5. The overall quality of the heterostructure is clear from small changes to both quantities across a number of features. (g) A measure of the disorder change with film thickness, shown through relative intensity of D and G features, based on Raman spectroscopy of these films. Uncertainties in (g) are the size of the symbol or smaller.

To this end, an analysis of the ratio of the D- and G- spectral features ($I_D/I_G$), as a function of the film thickness is performed. These data are shown in the bottom panel of Fig. 5 and demonstrate several interesting effects. First, the overall scale of change in $I_D/I_G$ is comparable to most nanoscale (1-10 nm) thick GO$_x$ sheets, and it is relatively small (between factor of 1 and less than 3). Second, our fitting analysis has shown that the spread of FWHM values is larger for the G feature than for the D-feature, which confirms the specific role of the C-O-C bond in the multilayered growth of GO$_x$ \cite{38,39,40}, and
suggests that the path towards improving the homogeneity of the film is through more careful annealing of defects and different variants of Hummer’s method \[^{[41]}\].

Somewhat surprisingly, rGO, dry electrodes outperformed the standard wet electrodes at each of the measurement sites. The composite fabric electrode returned an ECG signal with clearly identifiable PQRST peaks (Fig. 6a, inset) as well as displaying higher ECG signal amplitude and lower noise compared to the wet electrode (Fig. 6a,c). Both of these results (higher amplitude and lower noise) are encouraging and warrant both development of sophisticated wearable electronics and clinical trials.

Fig. 6.a shows an overlay of two simultaneously recorded ECG signals, measured at the same location on the body. The rGO, electrode displays a signal amplitude nearly double that of the Ag/AgCl electrode. This is highly advantageous, as a low power CMS will have limited signal boosting capability and will be operationally limited to a certain minimum signal amplitude.

In addition to the signal amplitude, the level of noise is another key measure of the signal quality.\[^{[40]}\] During the ECG cycle, there is a period between the T and P waves with essentially no muscle activity, and therefore a zero voltage. This is referred to as the isoelectric region. Since there is no cardiac activity in the isoelectric region, noise is easily noticeable. It can be used as a strong indicator of the overall noise in, and therefore quality of, the ECG signal.\[^{[42]}\] Figure 6(d) shows the isoelectric noise vs. activity for ECG data recorded simultaneously on gel-type electrodes and rGO, fabric electrodes and shows a distinct difference in the behavior of the two electrodes, where the wet electrodes display more widely scattered 2-dimensional behavior, while the rGO, electrode behavior is less scattered, indicating better noise coherence, which in turn implies less of a problem for the signal extraction and amplification.
Figure 6. (a) Overlay of live ECG data collected simultaneously with Ag/AgCl gel-type electrodes and dry rGO$_x$ electrodes. The two traces show similar behavior, but the rGO$_x$ electrode displays an amplitude nearly double the Ag/AgCl electrode. Additionally, characteristic ECG features (PQRST waveform) are clearly identifiable in signal collected from rGO$_x$ electrodes (inset); (b) and (c) ECG signal recorded with two different size rGO$_x$ electrodes, 1cm$^2$ ans 4 cm$^2$, respectively. (d) Scatter plot of activity vs isoelectric noise for conventional gel-type and dry rGO$_x$ electrodes extracted from live ECG signal. Isoelectric noise is measured during the T-P interval of the ECG cycle, and is considered a good measure of noise in the ECG signal.

We see that the rGO$_x$ fabric electrodes display comparable overall activity (vertical axis) as well as lower isoelectric noise (horizontal axis). These observations imply rGO$_x$ based sensors are capable of low-noise ECG data collection in a few kΩ resistance range (with the range itself modifiable through tweaking of the rGO$_x$ growth process), close to the typical value of human skin resistance. Potentially equally relevant for the applications, the signal increases with the area of the contact between the rGO$_x$ electrode and human skin, as shown in Fig. 6 b, c.
A heterostructure was produced by coating plain nylon in reduced graphene oxide. The highly conductive and sturdy composite heterostructure was fashioned into an ECG electrode and successfully used to gather live ECG data. The rGOx electrode outperformed the industry standard gel-type Ag/AgCl electrode in terms of signal amplitude and noise level for ECG data collected from the wrist and neck. The equivalent circuit model of electrode-skin electrical system would indicate that one possible explanation for the significantly lower noise in the rGOx electrode is the removal of extraneous voltage sources found in the Ag/AgCl electrode at the skin-electrode interface. AFM images were collected to better understand the structure of the rGOx coating and identify possible pathways for the future optimization needed for the buildup of on-chip, integrated wearable electronics for Internet of Things (IoT) healthcare and related applications. Surface imaging techniques show that deposited graphene oxide layers initially smooth over natural defects in the Nylon, but progressively thicker films begin to develop defects at the surface, indicating that wet and solid state chemistry methods are needed for the future improved production of defect free version of such films. These defects are likely the result of the amalgamation of 1-5 layers of GO flakes, or alternatively, the result of oxygen atoms left behind in out-of-plane dangling bond scenario, after incomplete chemical reduction. Larger defects are more likely caused by the amalgamation of a number of such flakes. These defects do not cause any noticeable impact on the electrical performance of the composite heterostructure. Ideally, we would have correlated electrical and optical properties discussed here even more thoroughly. However, we note that electrical properties measurements were significantly easier to conduct in the in-plane configuration, while optical properties are significantly easier to measure in the out-of-plane configuration. It is therefore not completely surprising to see qualitatively different behavior of these two types of properties as a function of the film thickness, namely highly non-linear changes in electrical properties and, with a few exceptions, approximately linear and weakly changing optical properties. The findings presented strongly indicate that the use of multi-layer GO heterostructures supports the use of multilayer rGOx for two types of sensors simultaneously: a. sensors with non-linear response (based on in-plane transport), b. approximately or nearly linear sensors (based on out-of-plane
optical properties). In addition to this, we also note that multilayer rGOx heterostructures are highly tolerant towards presence of defects, as seen in AFM and SEM studies.

Future study of this material will involve more sophisticated fabrication techniques to achieve full in-plane and out-of-plane characterization of transport and bonding properties. Additionally, biocompatibility and fouling studies will be important to the applicability of the material as an ECG sensor for long-term use. Based on current state of rGO research, we don’t expect biocompatibility and fouling studies will prevent use of these electrodes in collection of ECG signal.

Based on the overall electrical, structural and spectroscopic data, it is clear that one can design a multiprobe rGO, ECG sensor where the range of physical properties of the component probes spans the relevant conditions of the skin, such as in warm weather vs cold weather, dry vs humid conditions, sick vs healthy person. These environmental and patient condition variations can contribute to changes of the overall impedance of the skin by as much as two orders of magnitude, and yet this material remains a viable ECG sensor candidate.

**Acknowledgments:** We acknowledge assistance of Dr. Y. A. Samad in early stages of rGOx growth, and Dr. Ahsan Khandoker for use of the Electrophysiology Laboratory at KU.

**Funding:** This work was supported by the Mubadala-SRC through 2013-HJ-2440 grant and, in the early stages, in part through the SRC 2011-KJ-2190. NGH acknowledges the support of the Graduate Studies Office at KUST, and KL and AFI acknowledge 2013-KUIRF-L2 support in the early stages of the project. A part of this work was conducted in the KU Core Nanocharacterization Facilities, and a part in KU KSRC. We thank A. R. Devarajan for technical assistance. DM and AFI acknowledges Colgate University support and AFI acknowledges support and hospitality of Cornell University Cornell CNF, funded through NSF.

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**Conflicts of Interest:** The authors declare no conflict of interest.

**Data Availability:** Data are available upon reasonable request.

**Supplementary Materials:** Accompanying file contains figures that offer additional information about this work.
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N. G. Hallfors, D. Maksimovski, I. A. H. Farhat et al., Supporting Online Materials for Layered, Tunable Graphene Oxide Heterostructures for Wearable ECG Sensors manuscript

SUPPORTING ONLINE MATERIALS FOR
Layered, Tunable Graphene Oxide Heterostructures
for Wearable Electrocardiogram Sensors

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Figure SOM 1. Prevalence of Type II Diabetes among various socioeconomic groups (based on WHO annual report [4]). Type II Diabetes is strongly correlated to cardiac health issues and is among major leading causes of mortality worldwide [4].
Figure SOM 2. Main procedural steps in preparation of the nylon – rGO\textsubscript{x} heterostructures in this report.

Figure SOM 3. Resistance of the rGO\textsubscript{x} films scaled by the length (main) and area of electrodes (inset). The uncertainties are omitted for clarity, but are comparable to the ones reported in the main text.
Figure SOM 4. A version of Fig. 2 from the main text with additional SEM scans, added for scale and comparison.