Low Noise Field Effect Biosensor with Electrochemically Reduced Graphene Oxide

J. Basu, A. Baral, N. Samanta, N. Mukherjee, and C. Roychaudhuri

Department of Electronics and Telecommunication Engineering, Indian Institute of Engineering Science and Technology (IEST), Shibpur, Howrah-711103, India
Centre of Excellence in Green Energy and Sensor Systems, Indian Institute of Engineering Science and Technology (IEST), Shibpur, Howrah-711103, India

Received February 9, 2018; revised manuscript received March 29, 2018. Published June 5, 2018. This paper is part of the JES Focus Issue on Ubiquitous Sensors and Systems for IoT.

Electronic detection of biomolecules by conductance, impedance or amperometric measurements have been extensively researched on various nanostructured substrates like nanowires, nanoribbons, ordered and random nanorods, nanotubes, nanorods and nanoparticles. The substrates commonly deployed for realizing these nanostructures include silicon and its oxide, indium oxide, graphene, carbon nanotubes, anodized alumina, zinc oxide and various polymers. Nanostructured substrate not only improves the binding efficiency of the analyte due to large surface area to volume ratio but also shows a possible catalytic effect in the diffusion of the analyte molecules within the nanomolecules. Further, it has been reported that the 3D configurations of the nanostructures are significantly more sensitive than their 2D counterparts, owing to larger surface area to volume ratio and increased diffusion flux. In particular, 3D graphene has been widely explored in the form of nanorods, nanowalls and nanogrids for ultrasensitive detection of various biomolecules like proteins, DNA, virus and others. For example, it has been reported that reduced graphene nanowalls, fabricated by electrophoretic deposition on graphite electrode from a suspension containing graphene oxide nanosheets, results in ultra-high resolution electrochemical biosensor for detection of four bases of DNA having zero bandgap material, its bandgap can be tailored significantly by applying external electric field or by surface adsorption of charged biomolecules, resulting in a significant modulation of the transconductance. Graphene biosensors have been used for detection of different biomolecules, like protein biomarkers, cholesterol, glucose, urea and others. However, due to poor signal to noise ratio, they have not been successfully deployed in serum.

For the fabrication of reduced graphene oxide on various substrates, direct electrochemical deposition of GO, drop-casting of graphene, drop-casting of GO followed by its electrochemical reduction and also reduction by hydrazine, spray-coating and spin-coating have been mostly used. The thickness and uniformity of graphene films are not well controlled by these methods which deteriorates the stability and reliability in FET biosensing and hence in 2D graphene, the lowest level of detection achieved is only in picomolar range. Compared to all the GO reduction methods mentioned above, electrochemical reduction has received little attention in terms of FET biosensing applications. The greatest advantages of electrochemical reduction over other methods are mild reaction conditions, control of the reduction process, achieving a complete reduction of GO and availability of a wide range of environmentally safe electrolytes to choose from.

Amongst the various techniques, some researchers modified the glassy carbon electrode (GCE) with self-assembly of GO and then reduced it electrochemically. Although this method has been successfully used for the preparation of graphene films by electrochemical method, they have several limitations. For example, in this reduction process, it is difficult to control the reduction of GO on the electrode with a limited area, leading to low-yield production. Moreover, the produced graphene may be limited to the surface of electrode because the underplayed parts, not in touch with the solution may not be easily reduced. Further, it has limited potential window and cannot be used for electrocatalytic applications. On the other hand, electrochemical method to prepare graphene directly in solution is green, high yield for electrocatalytic applications. On the other hand, electrochemical method to prepare graphene directly in solution is green, high yield and low cost, with potential for commercialization. As ERCO is expected to consist of multiple layers with some edge effects, the change in transconductance upon attachment of biomolecules may be lower than single or bilayer graphene sensors. But the intrinsic device noise decreases significantly for multilayer graphene which is expected to reduce the temporal fluctuations in the drain-source current and hence improve the signal to noise ratio. Moreover, these sensors might facilitate frequency domain detection of biomolecule binding events from the noise spectroscopy analysis, which is usually more precise and sensitive. Thus, it will be meaningful to develop ERCO based FET biosensors for point-of-care (POC) diagnostic applications due to their advantages of low cost, simple and clean fabrication coupled with the possibility of achieving sensitive and reliable performance.

For diagnostics, detection of viral infections like Hepatitis B, Hepatitis C, HIV and others are of utmost priority since they are fatal for mankind. Commercially existing virus detection techniques are based on enzyme linked immunosorbent assay (ELISA) which suffer from poor sensitivity, resulting in detection at higher viral loads. At this stage, the cost of treatment increases significantly. Thus, it is desirable to achieve low detection limit, down to few femtomolars. There have been recent attempts on lowering the limit of virus detection by using...
plasmonic gold nanoparticles and electronic ELISA using indium oxide nanoribbons. However, these technologies are not convenient for field testing as they require labels and extensive biochemical processing. Hence, numerous researches have been carried out on label free detection of viruses but most of them suffer from poor signal to noise ratio limit.

To address these challenges, in this paper, we report the fabrication of ERGO on FTO glass directly by electrochemical reduction of GO in solution, followed by their immobilization with specific antibodies. The sensor has been experimented with a field deployable sensing set-up using Hep-B surface antigen as the specific molecule and Hep-C antigen as the non-specific molecule, in buffer and serum. Both the transient and steady state characteristics have been observed to estimate the drain current sensitivity and the frequency shift in the noise spectra upon capture of biomolecules. The performance has been compared with state-of-the-art label free graphene sensors, reported previously.

**Experimental**

Fabrication of ERGO.—ERGO films have been electrodeposited on FTO coated glass substrate (Tech 10, Pilkington NSG) through three electrode system from GO, synthesized by modified Hummer's method using fine graphite powder. The chemicals used in this experiment are of analytical grade and purchased from Sigma Aldrich. In modified Hummer’s method, fine graphite powder has been exfoliated and oxidized to obtain brownish GO powder. The obtained GO has then been electrochemically reduced on FTO coated glass substrates by chrono-amperometric technique using potentiostat (CHI61456E) at an applied potential of −1.2 V for 400 seconds at room temperature (25 °C). To do so, 0.5 mg/ml GO powder has been uniformly dispersed into the aqueous solution of 0.25 M NaCl (Sigma Aldrich) by ultrasonication for 25 minutes and pH of the solution has been adjusted to 3 for good adherence of the films. Then the solution has been transferred into a three electrode cell where FTO coated glass substrate (1 cm × 1 cm), a platinum wire and Ag/AgCl (3 M) have been used as working, counter and reference electrodes respectively. Prior to deposition, the FTO coated glass substrates have been cleaned thoroughly by ultrasonication for 5 minutes in hot (70 °C) DI water with the addition of 1% Hellmanex III (bought from Sigma Aldrich, product code: Z805939). Then rinsed the substrate twice in boiling DI water and again ultrasonication has been done for 5 minutes in isopropyl alcohol followed by washing with DI water. After that, the substrate has been dried using filtered compressed gas and then the ERGO film has been deposited. The obtained black ERGO films on substrate has been dried using filtered compressed gas and then isopropyl alcohol followed by washing with DI water. After that, the DI water and again ultrasonication has been done for 5 minutes in hot (70 °C) DI water for both the cases corresponding to the redox reaction between the [Fe(CN)6]3−/4− redox couple. The higher peak after ERGO deposition may be attributed to the increase in the electrical conductivity after reduction, probably due to the restoration of the π-conjugated system induced by the deoxygenation and dehydration.

Functionalization of ERGO.—Before functionalization, metal electrodes have been deposited on ERGO on screen printing of high temperature silver paste, followed by annealing at 720 °C. The width and length of the electrodes are 100 μm each. For immobilization of anti Hep-B monoclonal antibody, purchased from Sigma Aldrich, St. Louis, MO, USA) the graphene coated sensor has been treated with 25% glutaraldehyde aqueous solutions (procured from Sigma Aldrich) for 4 h, which acts as the crosslinker between antibody and graphene sheets. After treatment, each sample has been rinsed thoroughly with de-ionized water. Then the sensor has been incubated with anti Hep-B antibody for 1 h followed by washing with phosphate buffer saline (PBS). This process activates the negatively charged carboxylic groups of graphene and improves the covalent binding of antibodies. The unoccupied sites of the functionalized sensor has been blocked by incubating with blocking solution bovine serum albumin (1wt% BSA) at room temperature for 1 hour followed by washing with PBS. These parameters have been optimized previously. To enclose the active region of the sensor, a well of approximately 2 mm by 2 mm dimension has been cut using a diamond scriber in a polydimethylsiloxane (PDMS) sheet of 2.5 mm thickness. Then the well has been placed on the substrate by observing under an optical microscope (Leica DM 2500). The width of the PDMS sheet is around 4 mm on all the sides. The PDMS sheets made from SYLGARD 184A and SYLGARD 184 B (Product code: 761036 and 761028 respectively) has been procured from Sigma-Aldrich. For proper sealing of the PDMS with substrate, oxygen plasma treatment has been done. During testing process, a PDMS cover has been placed on top of the well after filling it with electrolyte, to reduce any possible fluctuations in the drain current due to evaporation.

**FET measurement.—**Each sensor chip has been interfaced with the PC through a sensor holder set up. In the setup, the bond pads of the sensors have been placed below the probes of the sensor holder. The probes of the sensor holder which are in contact with the drain and source electrodes are spring loaded and an adjustment screw has been provided to align them with the bond pads. The gate electrode has been inserted through a small hole in the setup and soldered to a metal connector. The picture of the setup is shown in Fig. 2. The gate electrode has been connected to a power supply (Keysight technologies).

**Figure 1.** Cyclic voltammetry curves of GO and ERGO.

**Figure 2.** Picture of sensor measurement setup.
The steady state and transient drain-source current measurements have been recorded with the control solution PBS, both before and after antigen capture using a PC interfaced Keithley 6487 meter. Further, Hep-C has been used as the non-specific antigen and both Hep-B and Hep-C has been prepared in buffer and serum in the range of 1 fM to 20 pM for testing the sensitivity and selectivity of the sensors. Each measurement has been carried out on five sets of sensors.

The fluctuations of drain current with time for a constant drain to source voltage ($V_{DS}$) and gate to source voltage ($V_{GS}$) have been monitored for power spectral density (PSD) measurement by interfacing the Keithley unit with a PC through a serial port.

The PSD ($S(f)$) of the transient fluctuations has been computed in MATLAB using Equations 1 to 3:

$$
\Phi (0) = \Phi (f_0) = \frac{1}{N^2} |C_0|^2
$$

$$
\Phi (f_k) = \frac{1}{N^2} \left( |C_k|^2 + |C_{N-k}|^2 \right), \quad k = 1, 2, \ldots, \left( \frac{N}{2} - 1 \right)
$$

$$
\Phi (f_N) = \Phi \left( f_{\frac{N}{2}} \right) = \frac{1}{N^2} |C_{\frac{N}{2}}|^2
$$

where, $f_k = \frac{k}{\Delta t}$ and $\Delta t$ is the sampling interval. Finally according to Parseval’s theorem, $\Phi(f)$ has been multiplied by the sampling interval $\Delta t$ and $N$ to obtain power spectral density function, $S(f)$. Data with equidistant time scale has been recorded and subdivided into sets, containing multiples of $2n$ data points. For $S(f)$ calculation, spectra consisting of 800 Fast Fourier Transform (FFT) points in frequency have been averaged for 200 s.

Structural characterizations.—Scanning electron microscope of the ERGO film has been carried out using ZEISS FESEM with an operating voltage of 20 kV. The smoothness of the film has been assessed from SEM measurements. The surface chemistry of electrochemically reduced GO has been studied by X-ray diffraction (XRD). XRD data of the samples have been collected by a Bruker D8 ADVANCE diffractometer using CuKα radiation ($\lambda$=0.15406 nm). The 2θ angular regions between 5° and 70° have been explored at a scan rate of 5°/min. The thickness and presence of defects has been studied by Raman spectroscopy (LabRAM HR Evolution-HORIBA). Thickness has also been correlated with surface profilometer.

Results and Discussion

Structural.—The XRD patterns of GO powder and ERGO thin films are shown in Fig. 3a. The GO powder shows a prominent interlayer spacing with a major diffraction peak at 2θ value of 11.5°, indicating the interlayer spacing of 7.43 Å due to the oxygen functional groups and water molecules in the interlayer of hydrophilic GO. This suggests successful oxidation of pristine graphite powder. The diffraction peak at 2θ=11.5° corresponds to the (001) crystallographic plane of GO. After the electrochemical reduction of self assembled GO, the diffraction peak at 2θ=11.5° completely

![Figure 3.](image-url)
disappears. This suggests the regeneration of the crystalline nature of graphene by the removal of oxygen functional groups during electrochemical reduction. Compared with GO, the ERGO samples show the presence of a distinct broad diffraction peak at 20 = ∼25°, corresponding to the (002) crystallographic plane. These results confirm that the oxygen and hydrogen causing the basal spacing of GO has been effectively removed in ERGO.

Raman spectra of GO and ERGO is indicated in Fig. 3b. It depicts well derived D,G and 2D bands. The obtained D band at 1330 cm⁻¹, G band at 1599 cm⁻¹ and 2D band at 2690 cm⁻¹ indicates typical GO and ERGO structure. The D band indicates the presence of defects or edges. Higher disorder leads to a broader G band as well as D band with relatively higher intensity compared to that of G band. 2D peak is secondary D peak and it’s intensity reduces for multi-layered graphene. The intensity ratio of D to G peak (ID/IG) is approximately 0.98 for GO which decreases with reduction to ∼0.62 for ERGO. This reduced ratio of ID/IG along with a sharper G peak in ERGO suggests decrease in defects with reduction. The reduction of GO results in the crystalline order of sp² carbon atoms with an increasing π-electron conjugation sp² network. The broad attenuated 2D-band in ERGO is indicating dispersive character as a function of the excitation energy and a few layered structure of ERGO. Further, the 2D band of ERGO resembles almost a graphite structure, which indicates that multiple layers of ERGO have been fabricated. This can also be correlated with the surface profilometry of ERGO film, shown in Fig. 3c which indicates that the thickness of ERGO is around 40 nm. The surface morphology of ERGO thin film on FTO substrate is shown in Fig. 3d. Some disordered and aggregated structures can be observed in the image showing thick multiple layers of ERGO deposition on FTO substrate, which confirms the electrochemical reduction of GO.

**Steady state FET measurements.**—Fig. 4a shows the drain current (Id) variation with VGS for VDS of 50mV in liquid gated ERGO FET device which indicates that the ERGO is primarily p-type. It is also observed that there is a small transport gap which may be attributed to certain amount of defects, as observed from the Raman spectra in Fig. 3b. Further the current decreases after antibody immobilization because the antibody molecules are positively charged at a pH of 7.2 which reduces the net carrier concentration in the graphene sheet.

The current traces recorded at ∼−2.5V VGS as a function of time with antibody and different concentration of Hep-B spiked in serum are shown in Fig. 4b. It has been observed that the current becomes steady after a short time of around 10 seconds even in serum and the fluctuations about the baseline value is also negligible, indicating that the sensor is significantly reliable. Hep-B virus being negatively charged at pH 7.2 current increases for negative VGS with increasing antigen concentration due to the increase in the carrier concentration. Importantly, the sensor is also capable of real time sensing, as observed from Fig. 4bi, which is a desirable criteria for point of care diagnostics. The selectivity of the sensor is quite satisfactory, since after application of Hep-C spiked serum at a time instant of 40 seconds, the current again reduces to the baseline within 10 seconds. The variation of current with different concentration of Hep-B surface antigen has been plotted in Fig. 4bii, for both buffer and serum. The change in current has decreased from that in buffer which is obvious since for the same amount of pipetted solution, lesser number of target molecules is captured. It is observed that the detection limit is 1 FM for both buffer and serum but the dynamic range of detection is from 1 FM to 10 pM and 1 FM to 20 pM, for buffer and serum respectively. As the number of captured antigen for the same concentration is lower in serum, the dynamic range increases. However, it can be inferred that the linearity in detection is maintained between 1 FM to 1 pM in buffer and 1 FM to 10 pM in serum. Beyond these limits, the rate of increase in current reduces which may be attributed to the fact that the sensor surface has been occupied by almost the maximum number of antigen.

Non-linearity has been calculated as the maximum deviation of the current characteristics from the linear fit in the range of 1 FM to 1 pM in buffer and 1 FM to 10 pM in serum, in terms of the percentage of full scale output. It is around 5.37%, and 5.53% for buffer and serum.
respectively. Further, it may be inferred from Fig. 4bii that the current sensitivity is 1.4 mA and 1.21 mA for buffer and serum respectively, in the dynamic range of measurement.

For comparison with other reports on virus detection, sensitivity has been calculated as the fractional change in drain-source current and the variations in sensitivity are shown in Fig. 4c for different concentrations of Hep-B in buffer and serum. This representation is convenient for comparison since other reports might have different operating principles and the measurand may not be directly current.

The detection limit achieved from steady state current measurements is higher by one order of magnitude compared to a recent report on ultrasensitive DNA sensor on 3D graphene, though in this report, the researchers have deployed a thick graphene layer with edge defects. A comparison of the ERGO based sensor with other Hep-B sensors is listed in Table I. The signal to noise ratio (SNR) has been calculated from the ratio of change in current after antigen capture to the change in baseline current due to intrinsic fluctuations. It is observed that in most of the recent reports, the limit of detection is much higher than 1 FM. Though some of the research reports 1 FM detection limit with higher sensitivities than ERGO sensor in buffer and serum6,47 their SNRs are lower by at least an order of magnitude than that in the present paper. However, it is evident from Table I that the detection limit achieved with the graphene nanogrid structure is lower by one order of magnitude in buffer. This may be ascribed to the combined effects of increased surface area of 3D graphene nanogrid and increased transconductance owing to its bilayer nature and negligible edge defects. But the SNR at 1 FM in buffer is around 12 for the 3D graphene nanogrid structure whereas, the SNR under similar conditions is 120.75 in the proposed ERGO FET sensor. This feature imparts practical feasibility to ERGO based FET sensor for application in real analyte like serum.

The stability of the sensor has been assessed by storing them at 4°C. They have been characterized at the end of every month. It has been observed that the drift in the baseline current is within 3% after 3 months. The change in current with different concentration of antigen at the end of 3 months has been depicted in Fig. 4d. It is evident, by comparing Fig. 4d with Fig. 4bii, that the current characteristics are significantly repeatable with a maximum deviation of around 10% in serum. Thus, the sensors can be stated to have a good stability of around 12 weeks.

Noise spectroscopy measurements.—As the intrinsic device noise is expected to be lower, it will be interesting to explore the noise spectroscopy measurement with a view to enhance the sensitivity. The noise spectrum of the liquid gated ERGO sensor before antibody functionalization is indicated in Fig. 5a. It is observed that the normalized noise power is almost two orders of magnitude lower than bilayer graphene. This has been reported previously in multilayer graphene fabricated by micromechanical exfoliation of highly oriented pyrolytic graphite. The origin of noise in liquid gated graphene may be ascribed to the ionic fluctuations at the electrolyte graphene interface. Multilayer graphene may enable efficient screening of such potential fluctuations due to the probable existence of parabolic bands with finite density of states at low energies in their nearly three dimensional character. Further, after antibody immobilization, the noise decreases probably due to reduced density of states with increasing carrier concentration.

The noise spectroscopy after antigen capture in serum is indicated in Fig. 5b. It is observed that the noise spectra resembles a low pass filter and deviates from the intrinsic device character. Further, the roll-off frequency shifts toward right with increasing concentration of antigen. It has also been observed that in absence of Hep-B surface antigen, there is no Lorentzian behavior in the noise spectra. Thus the presence of Hep-B is confirmed by the nature of noise spectra, which makes the detection more precise with less false positives or negatives. Also, the fractional change in frequency for a change in concentration of target antigen from 1 FM to 100 FM is around 400% compared to that of around 72% in steady state drain-source current characteristics. Below 1 FM, the capture of antigen is so insignificant that it does not lead to noticeable fluctuations. Thus the proposed ERGO FET sensor can be deployed for point of care diagnostic application since it can yield highly sensitive and reliable detection above 1 FM from the noise characteristics and can operate in real time. This may be explained by revisiting the noise sources in FET biosensors.

After antigen capture, there are two additional sources of noise—firstly, due to association-dissociation kinetics of antibody-antigen capture and secondly, due to the electrons in the vicinity of the Debye length, randomly crossing it, leading to diffusion current noise. These noise sources can be considered to be uncorrelated and each of them induces fluctuations in the gate voltage, which eventually modulates the drain-source current. From Langmuir rate equation, the time constant ($\tau$) of the binding/unbinding fluctuations of gate voltage is given by Equation 4:

$$\frac{1}{\tau} = k_a c + k_d = f$$

where $k_a$, $c$, and $k_d$ are the association and dissociation rate constants and concentration of analyte respectively.

For typical values of $k_a$ and $k_d$ and $c$ within 10 pM, $f$ is of the order of $10^{-2}$ Hz, which is outside the typical range of measurement. On the other hand, the gate voltage noise PSD due to the diffusion current noise is given by Equation 5, which resembles a Lorentzian spectrum.

$$\Delta V_{gs}^2(f) = 4kT R_{layer} \left(1 + \frac{2\pi f R_{layer} C_{eq}^2}{1 + (2\pi f R_{layer} C_{eq}^2)}\right)$$

$$C_{eq} = C_{layer} + C_p = C_{layer} + \left(C_{rec}^{-1} + C_d^{-1} + C_s^{-1}\right)^{-1}$$

$$R_{layer} = \frac{R_0}{N_f} C_{layer} = C_{an} N_f$$

where $R_{layer}$ and $C_{layer}$ are the equivalent resistance and capacitance of the captured molecule layer, $R_0$ and $C_a$ are the resistance and capacitance of each target molecule and $N_f$ is the number of captured molecules. $C_{rec}$, $C_d$ and $C_s$ are the capacitance of the antibody layer, electrical double layer and substrate respectively.
Thus, the frequency and the root mean square noise power is given by Equation 6 from Equation 5:

\[ f = \frac{N_c}{2\pi R_m (C_m N_c + C_p)} \quad \Delta V_{\text{rms}}^2 = \frac{kT}{(C_m N_c + C_p)} \]  

[6]

For typical values of \( R_m, C_m, C_{\text{rec}}, C_B \) and \( C_s \), the noise spectra of the gate voltage fluctuations as obtained from Equation 6 is represented in Fig. 5c. If the gate noise voltage is superimposed, it is observed that it is much lower than the electron number fluctuation noise and hence the overall noise spectra looks like a low pass filter, which explains the experimental results shown in Fig. 5c.

Conclusions

In this paper, fabrication of low noise FET biosensors with electrochemically synthesized reduced GO on FTO glass has been reported. It has been observed that the sensor is capable of detecting 1 fM concentration of Hep-B in serum with a signal to noise ratio of around 80, which is enhanced by more than one order of magnitude compared to the recent reports in serum. Further, the presence of Hep-B can be confirmed by the nature of noise spectra, which makes the detection more precise. Also, the fractional change in frequency for a change in concentration of target antigen from 1 fM to 100 fM is around 400% which is significantly enhanced than any steady state current change reported so far. Thus the proposed ERGO FET sensor, upon integration with microfluidics and readout circuit has the potential to be deployed for point of care diagnostic application.

Acknowledgments

The authors are grateful to Dr. Ramkrishna Dev Das of Saha Institute of Nuclear Physics, Kolkata for carrying out the Raman spectroscopy measurements. The authors acknowledge Visvesvaraya Young Faculty Research fellowship and Institute fellowship for financial support.

ORCID

C. Roychaudhuri 🌐https://orcid.org/0000-0001-9619-4150

References

1. J. Li, S. Pud, M. Petrychuk, A. O. Usser, and E. Vitusevich, Nano Lett.. 14, 3504 (2014).
2. N. Aroonyadet, X. Wang, Y. Song, H. Chen, R. J. Cote, M. E. Thompson, R. H. Datar, and C. Zhou, Nano Letters, 15, 1943 (2015).
3. H. Ghosh and C. RoyChaudhuri, Appl. Phys. Lett., 102, 243701 (2013).
4. C. S. Martinez-Cisneros, S. Sanchez, W. Xi, and O. G. Schmidt, Nano Letters, 14, 2219 (2014).
5. J.-H. Han, D. Lee, C. H. C. Chew, T. Kim, and J. J. Pak, Sensors and Actuators B: Chemical, 228, 36 (2016).
6. S. Guo, D. Wen, Y. Zhai, S. Dong, and E. Wang, ACS Nano, 4(7), 3959 (2010).
7. V. Gupta, Thin Solid Films, 519, 1141 (2010).
8. T. Bertok, A. Sediva, A. Vikartovska, and J. Tkac, *Int. J. Electrochem. Sci.*, 9, 890 (2014).

9. C. Xue, C.-C. Kung, M. Gao, C.-C. Liu, L. Dai, A. Urbas, and Q. Li, *Sensing and Bio-Sensing Research*, 3, 7 (2015).

10. O. Akhavan, E. Ghaderi, and R. Rahighi, *ACS Nano*, 6, 2904 (2012).

11. J. Basu and C. Roychadhuri, *IEEE Electron Device Letters*, 37, 492 (2016).

12. Y. Li, R. Zhao, L. Shi, G. Han, and Y. Xiao, *RSC Advances*, 7, 53570 (2017).

13. T. Terse-Thakoor, S. Badhulika, and A. Mulchandani, *Journal of Materials Research*, 32, 2905 (2017).

14. R. Shu, S. Badhulika, and A. Mulchandani, *Springer Series on Chemical Sensors and Biosensors*, (2017).

15. J. Ping, Y. Wang, K. Fan, J. Wu, and Y. Ying, *Biosensors and Bioelectronics*, 28, 204 (2011).

16. L. Chen, Y. Tang, K. Wang, C. Liu, and S. Luo, *Electrochemistry Communications*, 13, 133 (2011).

17. Z. Wang, M. Shihi, and H. Ogata, *Analyt.* 136, 4903 (2011).

18. G. P. Keeley, A. O’Neill, M. Holzinger, S. Cosnier, J. N. Coleman, and G. S. Duesberg, *Phys. Chem. Chem. Phys.*, 13, 7747 (2011).

19. M. Du, T. Yang, and K. J. Jiao, *Matec Chem.*, 20, 9253 (2010).

20. P.-G. Ren, D.-X. Yan, X. Ji, T. Chen, and Z.-M. Li, *Nanotechnology*, 22, 055705 (2010).

21. S. Gilje, S. Han, M. Wang, K. L. Wang, and R. B. A. Kaner, *Nano Lett.*, 7, 3394 (2007).

22. V. C. Tung, M. J. Allen, Y. Yang, and R. B. Kaner, *Nat. Nanotechnol.*, 4, 25 (2008).

23. B. J. Sanghavi, S. Sitaula, M. H. Griep, S. P. Karna, M. F. Ali, and N. S. Swami, *Analytical Chemistry*, 85, 8158 (2013).

24. B. Yuan, C. Xu, D. Deng, Y. Xing, L. Liu, H. Pang, and D. Zhang, *Electrochimica Acta*, 88, 708 (2013).

25. A. Bonami and M. Pumera, *ACS Nano*, 5, 2356 (2011).

26. M. A. Raj and S. A. John, *The Journal of Physical Chemistry C*, 117, 4326 (2013).

27. H. Tong, J. Zhu, J. Chen, Y. Han, S. Yang, B. Ding, and and X. Zhang, *J Solid State Electrochem.*, 17, 2857 (2013).

28. M. Gao, Y. Xu, W. Yang, S. Sang, and S. Wang, *Electroanalysis*, 28, 1377 (2016).

29. A. N. Pal and A. Ghosh, *Applied Physics Letters*, 95, 082105 (2009).

30. S. E. Rustein, D. Kanwendo, L. Lugali, I. Thengolose, G. Tegha, S. A. Fiscus, J. A. J. Nelson, M. C. Hosseinipour, A. Sarr, S. Gupta, F. Chimbwandrira, R. Mwenda, and R. Mataya, *J. Clin. Virol.*, 60, 392 (2014).

31. R. de la Riva and M. M. Stevens, *Nat. Nanotech.*, 7, 821 (2012).

32. N. Aroonyadet, X. Wang, Y. Song, H. Chen, R. J. Cote, M. E. Thompson, R. H. Datar, and C. Zhou, *Nano Letters*, 15, 1943 (2015).

33. W. Gao, L. B. Alemany, L. Ci, and P. M. Ajayan, *Nat. Chem.*, 1, 403 (2009).

34. J. Basu and C. Roychadhuri, *Sensors*, 16, 1481 (2016).

35. A. Sapper, J. Wegener, and A. Janshoff, *Analytical Chemistry*, 78, 5184 (2006).

36. C. Casiraghi, A. Hartschuh, H. Qian, S. Piscanec, C. Georghi, A. Fasoli, K. S. Novoselov, D. M. Basko, and A. C. Ferrari, *Nano Letters*, 9, 1433 (2009).

37. K. N. Kodin, B. Ozbas, H. C. Schniepp, R. K. Prudhomme, I. A. Aksay, and R. Car, *Nano Letters*, 8, 36 (2008).

38. A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth, and A. K. Geim, *Phys. Rev. Lett.*, 97, 187401 (2006).

39. Y.-H. Choi, G.-Y. Lee, H. Ko, Y. W. Chang, M.-J. Kang, and J.-C. Pyun, *Biosensors and Bioelectronics*, 56, 286 (2014).

40. Y. Wang, K. Chen, Z. Wu, Y. Liu, S. Liu, Z. Zou, S.-H. Chen, and C. Qu, *International Journal of Infectious Diseases*, 29, 31 (2014).

41. M. Shariati, *Biosensors and Bioelectronics*, 105, 58 (2018).

42. Q. Xiang, J. Huang, H. Huang, W. Mao, and Z. Ye, *RSC Advances*, 8, 1820 (2018).

43. M. S. Diware, H. M. Cho, W. Chegal, Y. J. Cho, S. W. O, S.-H. Park, D. S. Kim, K.-S. Kim, Y. G. Min, J. H. Jo, and C. Shin, *Biointerphases*, 12, 01A402 (2017).

44. L. E. Ahangar and M. A. Mehrgardi, *Bioelectrochemistry*, 117, 83 (2017).

45. E. Elkin and A. Erdem, *Electroanalysis*, 28, 2514 (2016).

46. Z. Shakeri, S. Salimian, S. Kharrazi, M. Adabi, and R. Saber, *Analytical and Bioanalytical Chemistry*, 407, 455 (2014).

47. N. Das and C. Roychadhuri, *IEEE Transactions on Device and Materials Reliability*, 15, 402 (2015).

48. K. Georgakopoulou, A. Birbas, and C. Spathis, *Journal of Applied Physics*, 117, 104505 (2015).

49. T. M. Squires, R. J. Messinger, and S. R. Manalis, *Nat. Biotechnol.*, 26, 417 (2008).

50. M. J. Deen, M. W. Shinwari, J. C. Ranuarez, and D. Landheer, *IEEE Transactions on Device and Materials Reliability*, 14017 (2004).

51. F. Patolsky, G. Zheng, O. Hayden, M. Lakadamyali, X. Zhuang, and C. M. Lieber, *Proc. Natl. Acad. Sci. U. S. A.*, 101, 14017 (2004).

Downloaded on 2018-07-20 to IP 207.241.231.80 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).