Laser induced self-N-doped porous graphene as an electrochemical biosensor for femtomolar miRNA detection

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We report a sensitive, yet low-cost biosensor based on laser induced graphene for femtomolar microRNA (miRNA) detection. Combined with the miRNA extraction and magnetic isolation process, the target miRNAs were purified for further detection using laser induced graphene sensor. The laser induced graphene was prepared by direct laser writing on commercial polyimide (PI) and patterned via a computer-aided design system as an electrode for electrochemical biosensing. We found that the laser reduction of PI resulted in nitrogen-doped porous graphene, not only improving its conductivity but also its sensitivity to nucleic acids. Preeclampsia specific miRNA hsa-miR-486-5p was magnetically purified and directly adsorbed on the surface of graphene electrode via graphene-miRNA affinity interaction. Surface attached miRNAs were then electrochemically quantified using [Fe(CN)6]3-/4- redox system. Our assay demonstrates detection of miRNA has-miR-486-5p up to concentrations as low as 10 fM with excellent reproducibility. Owing to its facile fabrication, low cost and high performance, the laser induced N-doped graphene biosensor presented here shows great potential for applications in detecting miRNA in biomedical applications.

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1. Introduction

Numerous carbon-based biosensors have been investigated for highly sensitive and specific detection of proteins [1,2], nucleic acids [3,4], viruses [5,6], and cancer cells [7–9]. MicroRNAs (miRNAs, ~22 nucleotides) are small noncoding, single-stranded RNA molecules that play regulatory roles in cell development, differentiation, proliferation, apoptosis and stress responses and are recognized as important biomarkers for cancer and other complex diseases [10,11]. In the recent decade, graphene has attracted significant interest for use in electrochemical biosensor applications, due to its ability to directly absorb nucleic acid molecules [12]. Studies have suggested that the nature of the direct adsorption of nucleic acids on graphene or graphene oxide surface is a base-dependent phenomenon, and follows conventional physisorption mechanisms [3,13–15]. It has been suggested that the physisorption between individual nucleobases and the graphene is controlled by the polarizabilities of the individual nucleobases. The larger the polarizability the stronger the van der Waals (vdW) interaction. Gowtham et al. and Varghese et al. have suggested that the vdw interaction is the main driving force for adsorption of nucleobases onto the graphene [14,15]. Accurate detection of this adsorption can easily identify the specific DNA, RNA biomarkers and diagnose the diseases of interest. The use of the direct adsorption of DNA or RNA biomarkers on a graphene electrode, rather than the conventional approach of using recognition and
transduction layers [16,17], substantially simplifies the detection method by avoiding the complicated chemistries underlying each step of the sensor fabrication [18–20]. When combined with a magnetic collection and purification method [21–23], the target DNA or RNA biomarkers could be directly adsorbed on the surface of bare graphene electrode via graphene-DNA or graphene-RNA affinity interaction. Subsequently, the adsorbed DNA/RNA (miRNA in present case) could be electrochemically detected in the presence of a solution-phase redox marker [24–26]. This new technology based on graphene-miRNA affinity interaction is recognized as an effective and sensitive platform for detection of miRNA-based biomarkers.

Various methods for graphene fabrication, such as mechanical exfoliation [27], epitaxial growth [28], chemical vapor deposition (CVD) [29] and the reduction of graphene oxide (GO) [30–32], have been investigated. Reliable and scalable fabrication methods for commercial graphene-based biosensors are in great demand to bridge the existing gap between research laboratory and practical applications [33]. Laser direct writing method has attracted significant attention for its efficiency in fabricating graphene devices, showing great advantage for roll-to-roll production and customized patterning. Tour and co-workers have recently reported the fabrication of laser induced graphene (LIG) from commercial polypyrrole (PI) films simply using a CO2 laser [34], which resulted in porous LIG exhibiting high electrical conductivity and specific surface area suitable for both active electrodes and current collectors in micro-supercapacitors. Following works have shown PI-derived LIG can be used in various applications, including electrochemical sensor [35,36], nitrogen sensor [37], strain sensor [38], and acoustic sensor [39]. Recently, the LIG with 3D porous structure and good conductivity was reported for sensing glucose [40], thrombin [41], dopamine (DA) [35,42], hydrogen peroxide (H2O2) [43] and bisphenol A [44]. In addition, direct writing of electrochemical sensors can be integrated with other printed electronic devices such as microsupercapacitors [45], thin film batteries [46], and antennas [47] etc.

To improve the performance of the LIG devices, doping with heteroatoms, such as boron [48], nitrogen [49] has been employed as an effective strategy to tailor the electrochemical properties of LIG and to enhance its electrical conductivity and surface wettability. However, most doping processes rely on the external heteroatom resources, such as the additional precursor of urea [50,51], or plasma treatment with nitrogen gas [52,53]. The abundant N element in the precursor of PI, which can be a potential resource for self-N-doping of LIG have been largely overlooked. Various groups reported different observations on the LIG derived from PI, ranging from no noticeable N [34], insignificant amount of N (2.4%) [54], to 9.48% N [55]. The variations are likely caused by the difference in the used lasers in terms of wavelength, frequency and power and the contents of the precursor. Nevertheless, this self-N-doping which can simultaneously occur during the laser reduction without additional chemicals and processing is of great advantage for the fabrication of N-doped LIG. Due to the excellent electrical conductivity and large surface area of the porous structure, LIG can facilitate the electrolyte accessibility to the electrode surfaces, hence favorable for electrochemical sensing [42]. Also, the heteroatomic electron transfer in the electrochemistry of sp2 carbons is tremendously enhanced due to the rich presence of defects in LIG [56,57].

Herein, we report different observations on the LIG derived from PI, which can be a potential resource for facilitating the electrolyte accessibility to the electrode surfaces, conductivity and large surface area of the porous structure, LIG can additionally offer an opportunity for the chemical sensor [35,36], nitrogen sensor [37], strain sensor [38], chemical sensor [39], thermal sensor [40], humidity sensor [41], target miRNA, and the electrochemical test of the LIG as working electrode. This self-N-doped LIG could be an ideal material for sensitive and selective electrochemical biosensors for miRNA detection.

2. Results and discussion

2.1. Morphological characterization of LIG

Fig. 1 schematically shows the fabrication process of the biosensor with LIG electrode, absorption of the purified target miRNA, and the electrochemical test of the LIG as working electrode. The fabricated LIG as working electrode for absorption (see Fig. 1(b)). Fig. 1(a), the laser written areas appear much darker than the non-scribed area of the PI substrate (light orange). Carbonization is clearly shown in the image of the laser written electrode.

After the irradiation with a CO2 laser, the commercial PI film was converted into porous graphene, which is termed laser induced graphene (LIG). Fig. 1 shows the Raman spectra of LIG with laser power 32 W (fluence 16.6 J cm−2) and scan speed 108 cm/s (energy density 42.3 J cm−2) and of PI sheet. The Raman spectrum of PI shows no obvious peak while that of LIG shows three prominent peaks, including D, G and 2D: the D-band (−1350 cm−1) is derived from defects in the plane structure of graphite due to the presence of oxygen containing groups [58]. The G-band (−1600 cm−1) is induced by an Ezg mode of graphite associated with the stretching motion of sp2 carbon atoms [59] and the 2D Raman band (−2700 cm−1) originated from the second order of zone-boundary phonons [60]. The formation of the graphitic domains is attributed to laser treatment on the PI sheet, which triggers depolymerization, carbonization and eventually graphitization [42].

The SEM image of LIG exhibits porous structures resulting from the rapid liberation of gaseous products. These porous structures increase the accessible surface areas, facilitating electrolyte penetration into the active surface. As mentioned in the experimental section, the target miRNAs were firstly hybridized with complementary biotinylated probes. Subsequently, the hybrids were captured through magnetic beads and the captured miRNAs were released by heating and eventually isolated by a permanent magnet. These purified miRNAs were directly drop-cast onto the LIG electrode for absorption (see Fig. 1(b)). Fig. 1(c) shows how LIG electrode was used as the working electrode in the electrochemical test. For comparison, the released miRNAs mentioned above were drop-cast onto the LIG electrode. The LIG with miRNA shows a decreased DPV current compared to that of bare LIG. This is because the miRNAs were adsorbed onto LIG electrode via miRNA-graphene affinity interaction, covering the effective surface and blocking the [Fe(CN)10]3/4 redox system.

2.2. Influencing laser parameters on LIG

Various laser parameters were investigated and adjusted to achieve successful graphitization of PI, while not incinerating all the material. Fig. 2(a) shows that when the laser parameters (laser
power and laser scanning speed) were in the orange region, no obvious carbonization occurs in the PI film. While for the laser parameters in the light green area, the whole PI material was burned away. Several laser parameters between these two regions were evaluated in the experiments. The study indicated that with the increase of laser power, the laser scanning speed also has to be increased to achieve good graphitization and avoid total burning of PI. To provide a more universal guidance to adjust the properties of
LIG by changing the parameters of the laser, the energy density, ranging from 31.7 to 56.4 J cm\(^{-2}\), can be calculated by laser energy per effective laser scanning area.

The Raman spectra of LIG samples fabricated with various laser power from 8 W (fluence 4.1 J cm\(^{-2}\)) to 64 W (fluence 33.2 J cm\(^{-2}\)) and laser scanning speed from 36 to 162 cm/s were acquired and shown in Fig. 2(b). Fig. S1 in Supporting Information demonstrates that the intensity ratio of D band and G band (I\(_D\)/I\(_G\)), reflecting the degree of disorder in the graphene-structure [61], can be adjusted from 1.46 to 0.9. The larger laser power combined with coordinating scanning speed results in a reduced I\(_D\)/I\(_G\) value, which illustrates the adjustable defects density and structure of LIG. Fig. 2(c) shows the crystalline size in the axis (La), which can be obtained from I\(_D\)/I\(_G\) using the equation [62]

\[
La(nm) = \left(2.4 \times 10^{-10}\right) \times \lambda_i^4 \times \frac{I_D}{I_G}^{-1}
\]

where \(\lambda_i\) is the wavelength of the Raman laser (\(\lambda_i = 514\) nm).

Fig. 2(d) shows the sheet resistance of LIG and I\(_D\)/I\(_G\) at different energy density of laser. The sheet resistance of LIG decreases until it becomes saturated when the laser energy density is varied from 1.46 to 0.9. The larger laser power combined with coordinating scanning speed results in a reduced I\(_D\)/I\(_G\) value, which illustrates the adjustable defects density and structure of LIG. Considering the long wavelength (10.6 \(\mu\)m) of the CO\(_2\) laser used in the experiment, the reduction of PI is mainly caused by the photothermal effect on PI sheet (Fig. 3(b–f)); and the fibrils-like materials covering the top of the porous structure, which is attributed to the further laser ablation of the top surface, leaving the residues with fibrils-like structure, as shown in Fig. 3(g and h). Fig. 3(i and j) shows the cross-section SEM images of the LIG irradiated with laser power 24 W and laser scanning speed of 90 cm/s. We noticed that the laser irradiated region prostrudes from the PI substrate, which likely results from the rapid heating by laser irradiation and the consequent outgassing. The protruded structure is roughly 15 \(\mu\)m above the top surface of PI while the thickness of LIG is about 20 \(\mu\)m. Fig. 3(k and l) show the cross-section SEM images of the LIG irradiated with laser power of 56 W and laser scanning speed of 144 cm/s. The thickness of the laser treated area roughly decreased by 62 \(\mu\)m (the total thickness of PI is about 125 \(\mu\)m) while the thickness of LIG is about 38 \(\mu\)m. This reduction of thickness could be attributed to the laser induced burning effect, removing the mass of the PI and produced LIG on the top surface [63]. The following observations have been made: 1.) the heat generated by the laser induces the carbonization of the PI, accompanied by gasification of the top layer materials; 2.) the heat generated is directly proportional to the laser power exerted per time per area; 3.) the gas production and emission rate in the gasification process is responsible for the morphology difference between the LIG fabricated with various laser parameters.

Fig. 4(a) shows the XPS spectra of LIG fabricated at different laser power and laser scanning speed. The corresponding trend of the percentage of carbon, oxygen and nitrogen with increasing laser power were plotted in Fig. 4(b), which are shown to be adjustable by varying the laser parameters. After the laser treatment, the percentage of carbon components increased from the original 53.5% in PI to 84% in LIG while the percentage of oxygen and nitrogen components decreased from 38.8% to 12% (oxygen) and from 7.7% to 4% (nitrogen), respectively, indicating the effective laser reduction of PI. Fig. 5S shows the C/O ratio can be increased from 1.38 (PI) to 7.0 (LIG 32 W) and the C/N ratio can be enhanced from 6.98 (PI) to 21.11 (LIG 32 W).

Fig. 4(c and d) shows the high resolution C1s XPS spectra of the PI before and after the laser scribing process, respectively. The C1s spectra are deconvoluted into several peaks including [64]: sp\(^2\) hybridized carbon (C–C sp\(^2\) 284.5 eV), sp\(^3\) hybridized carbon and carbon nitrogen bonding (C–C & C–N 285.5 eV), epoxide/hydroxyl (C–O 286.6 eV) and carboxyl (O=C–O 288.6 eV). The oxygen content (mainly the C–O and COOH) significantly decreased after laser treatment, and became C–sp\(^2\) dominant. Table S1 in Supporting Information showing the atomic concentration percentage of chemical bonding states of PI and LIG (32 W) in the XPS spectra reveals a significant increase in C–C sp\(^2\) percentage and the effective reduction of oxygen after laser treatment. Fig. 4(e) shows the high resolution O1s XPS spectrum of PI and LIG (32 W). After laser reduction, the C–O (533.2 eV) peak became more dominant than C–O (531.8 eV), consistent with the C1s spectrum in LIG where the C–O became the major oxygen component. Of note, the intensity of the N1s peak was also significantly altered after laser irradiation as shown in Fig. 4(f); for the untreated Kapton polyimide, only one symmetric peak at 400.4 eV exists in the fitting spectrum of the N1s [65], but the N1s spectrum of the laser treated PI can be deconvoluted into two peaks namely, 400.4 eV (pyrrolic-N; N-5), and 401.5 eV (graphitic-N; N-Q) [66,67]. Fig. 5S6 shows the fitting of N1s XPS spectrum of PI and LIG treated with varying laser power. The percentage of N-Q varied from 2.4% to 4.5% and the percentage of N-5 was adjusted in a range from 1.6% to 4.4%. The ratio of the percentage of N-Q to that of N-5 was modulated from 0.77 to 1.91 by adjusting the laser power, shown in Fig. S5. The high temperature induced by the laser triggered the graphitization process of the PI and some carbon atoms in the graphene skeleton plane were replaced by the nitrogen atom. The effective N-doping into the graphitic structure provides the excess electron in carbon framework, resulting in the high ion diffusion and electrical conductivity [68].
blocks the access of \([\text{Fe(CN)}_6]^{3-/4-}\) molecules to the electrode surface or other complex fabrication methods in our work.

The effect of concentration/density of \(\text{miRNA}\) molecules on the electrochemical measurement is observed in Fig. 4. The DPV current changes for these synthetic samples were a function of the concentration levels of \(\text{miRNA}\) present in the sample. The DPV current changes with respect to the synthetic \(\text{miRNA}\) with varied concentrations from 10 fM to 10 nM. We noted that compared to the baseline current of LIG, the relative current changes for these synthetic samples were a function of the concentration levels of \(\text{miRNA}\) present in the sample. The DPV current generated in the \([\text{Fe(CN)}_6]^{3-/4-}\) system decreases proportionally with the increasing concentration of \(\text{miRNA}\). These results demonstrate the functionality of the capture probes in isolating the target \(\text{miRNA}\) and the effective \(\text{miRNA}\)-graphene adsorption in subsequent electrochemical measurement.

To verify the sensitivity of the system, various concentrations of synthetic target \(\text{miRNA}\) ranging from 10 fM to 10 nM were adsorbed onto the LIG electrode surface for measurement. Fig. 6(a) shows the DPV current changes with respect to the synthetic \(\text{miRNA}\) with varied concentrations from 10 fM to 10 nM. We noticed that compared to the baseline current of LIG, the relative current changes for these synthetic samples were a function of the concentration levels of \(\text{miRNA}\) present in the sample. The DPV current generated in the \([\text{Fe(CN)}_6]^{3-/4-}\) system decreases proportionally with the increasing concentration of \(\text{miRNA}\). Our platform exhibited its capability to detect target \(\text{miRNA}\) up to concentrations as low as 10 fM. This high sensitivity may be attributed to the large surface area and the high conductivity of LIG. As discussed above, the self-doping of N in the form of N-Q considerably enhanced the conductivity of the LIG. However, the role of N-S in this improved sensing performance requires further elucidation.
A simple laser direct writing method to fabricate biosensor with high sensitivity were demonstrated to detect miRNA with concentration as low as 10 fM. The precursor PI and the whole process is ready for roll-to-roll production, showing great potential for commercial application in cancer detection and gene screening. Moreover, due to the simplicity and flexibility of system it can be easily modified to detect virtually any target nucleic acid molecule and can thus be used for diagnostic and prognostic applications in a wide range disease.

3. Conclusions

In conclusion, we fabricated electrochemical biosensors based on laser-induced, self-N-doped porous graphene capable of miRNA detection down to 10 fM. After the laser treatment on PI, the \( I_0/I_c \) ratio of the LIG can be tuned from 1.46 to 0.9, while the C/O ratio can be significantly enhanced from 1.38 to 7.0, demonstrating effective elimination of oxygen components. More importantly, the laser induced graphitization of PI also effectively achieves N-doping (2.4%–4.5%) in the graphene skeleton in the forms of pyrrolic N and
graphitic N, which contribute to the low resistance of LIG and likely improved affinity with nucleic acids. Moreover, by tuning the laser power, we can vary the concentration of the doped N as well as the ratio between graphitic N and pyrrolic N, in turn tuning the electrical and electrochemical properties of the LIG. When fabricated as the electrochemical detector working in conjunction with magnetic particle-assisted miRNA isolation and purification, the patterned LIG with macroporous structure is capable of responding to miRNA concentrations as low as 10 fM, owing to the significantly improved conductivity as a result of self N-doping and large surface contact area. Moreover, the LIG on PI method provides a simple and cost-effective approach that can be easily applied with established industrial processing techniques, which makes it extremely attractive for application in the real world. Therefore, in combination with the magnetic selective extraction method, this self-N-doped LIG biosensor demonstrates great potential as a simple and inexpensive biosensor platform for real world applications.

### 4. Methods

#### 4.1. Materials and apparatus

The DUPONT Kapton HN Film Tape (polyimide, 125-μm thickness) was adopted for laser treatment. Potassium ferrocyanide \([K_4Fe(CN)_6]\) and Potassium ferricyanide \([K_3Fe(CN)_6]\) were purchased from Chem-Supply Pty Ltd (Australia). The phosphate buffer

![](image1.png)  
**Fig. 5.** (a) Differential pulse voltammetric current changes with respect to the miRNA. (b) DPV signal changes while performed on no-template control and negative control. (A colour version of this figure can be viewed online.)

| Table 1: Performance Comparison of miRNA Biosensors Based on Various Materials. |
|---------------------------------|------|------|
| Electrode Material             | Sensitivity | Reference |
| Carbon nanotube                | 1 pM | [17]  |
| Graphene/ZnO                   | 4.3 pM | [4]   |
| Gold                            | 10 fM | [23]  |
| Graphene/Fe₂O₃                 | 1 fM  | [75]  |
| Laser induced graphene         | 10 fM | this work |

![](image2.png)  
**Fig. 6.** (a) Differential pulse voltammetric current with respect to the synthetic miRNA with concentration from 10 fM to 10 nM. (b) Differential pulse voltammetry signal changes respond to different concentrations. Error bars represent the standard deviation of three independent experiments. (A colour version of this figure can be viewed online.)
saline (PBS) tablets were purchased from Fisher Scientific (Australia) and were dissolved with deionized water. All solutions were prepared with Milli Q water system with resistivity 18.2 MΩ cm. Analytical-grade reagents and chemicals were used in the experiment, unless mentioned otherwise.

The scanning electron microscopy (SEM) images were obtained using JEOL JSM-7001F, equipped with the energy-dispersive X-ray spectroscopy (EDX) system. Raman spectra were acquired with Raman Spectrometer Renishaw Invia (using 514-nm excitation wavelength and a 50 × objective, acquisition parameters: 0.05 mW power, 10 s exposure time, 3 accumulations, and 2400 l/m gridding). Peak fittings of the Raman data were carried out using the WiRE3.3 software. The X-ray photoelectron spectroscopy (XPS) measurement was performed with Kratos Axis ULTRA X-ray Photoelectron Spectrometer (with a monochromated Al Kα radiation). The peak fitting of the XPS data was carried out using the CasaXPS software.

4.2. Fabrication of the biosensor

A continuous wave (CW) CO₂ laser cutter system (Rayjet 300 with laser peak power 80 W, wavelength of laser 10.6 μm, laser frequency 5000 Hz) was employed to treat the PI sheet under ambient conditions. The beam size of laser was roughly around 70 μm. The pulses per inch (PPI) setting corresponding to the laser pulses per inch can be adjusted in the range of 1-1000. The laser system was equipped with X-Y control stage with a maximum scan speed of 180 cm/s.

The laser induced graphene was patterned having three parts: an electrode contact (4 mm × 4 mm square), a connection wire (8 mm × 0.5 mm rectangle), and a sensing area (1 mm diameter circle) [75]. During electrochemical testing, the working electrode of the workstation was connected to the electrode contact area. The connection wire was covered with tape serving as passivation layer, while the sensing area was immersed into the aqueous solution for testing. Laser power, scan speed and PPI were optimized to 32 W, 108 cm/s, and 1000 respectively. CorelDRAW software was employed to design the electrode pattern on PI sheet. All the laser scribing experiments were performed under ambient conditions.

4.3. miRNA extraction probe hybridization and magnetic isolation

All buffers and solutions used in miRNA purification procedures were prepared in UltraPure™ DNase/RNase-Free Distilled Water (Invitrogen). We used hsa-miR-486-5p, which was previously shown to be a strong biomarker for differentiating early stage cancer [76]. Briefly, 10 μL of specific target miRNA concentration or total exosomal miRNA was mixed with 15 μL of 10 μM biotinylated complementary capture probe (CP, Tables 2) and 10 μL 5X SSC buffer (pH 4). The mixture was incubated for 1 h at room temperature. Dynabeads MyOne Streptavidin C1 (ThermoFisher; Australia) were prepared as per manufacturer’s instructions. Beads were washed 2 times with 1x binding and wash (B&W) buffer (2X B&W buffer: 10 mM Tris–HCl (pH 7.5), 1 mM EDTA, 2 M NaCl), 2 times with solution A (0.1 M NaOH, 0.05 M NaCl) for 2 min, and one time with solution B (0.1 M NaCl). Washed beads were finally resuspended in 35 μL of solution B and mixed with target-probe mixture from the previous step. Bead target-probe mixture was incubated for 30 min at room temperature with gentle shaking followed by two times washing with 1 × B&W buffer and one time with 50 μL × 5 × SSC buffer to remove excess unbound probes. Target miRNA bound beads were finally resuspended in 20 μL 5 × SSC buffer. Captured target miRNAs were released from capture probes by heating at 95 °C for 5 min and supernatant containing released miRNAs were separated magnetically from the beads.

4.4. Electrochemical measurement

All electrochemical measurements were performed on a CHI1040C electrochemical workstation (CH Instruments, BeeCave, TX, USA) equipped with the three-electrode system consisting of laser induced graphene working electrode of 1-mm diameter, an Ag/AgCl (with saturated KCl) reference electrode and a platinum wire counter electrode. All measurements were performed at room temperature. Differential pulse voltammetry (DPV) experiments were conducted in 10 mM phosphate buffered saline (PBS) solution containing 2 mM K₃Fe(CN)₆ and 2 mM K₄Fe(CN)₆ electrolyte solution. DPV signals were obtained with a potential step of 4 mV, pulse amplitude of 50 mV, pulse width of 50 ms and pulse period of 500 ms.

For synthetic miRNA samples, 10 μL of miRNA sample with different concentrations as mentioned above were adsorbed on laser induced graphene surface. The miRNA solution was dispensed on top of the LIG sensing area and incubated at 25 °C for 20 min in an Eppendorf Thermostirrer with continuous shaking (300 rmp) [23]. The electrodes were then rinsed with PBS and dried prior to perform DPV measurements.

The relative DPV current changes due to the adsorption of miRNA samples were calculated with the following Equation (1).

$$\%_{\text{rel}} = \left( \frac{I_{\text{sample}} - I_{\text{baseline}}}{I_{\text{baseline}}} \right) \times 100\%$$

where the baseline current ($I_{\text{baseline}}$) is the DPV signal without miRNA absorption, and the samples current ($I_{\text{sample}}$) is the DPV signal with miRNA absorption.

Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Zhengfen Wan: Conceptualization, Methodology, Investigation, Data curation, Writing - original draft. Muhammad Umer: Methodology, Resources, Writing - review & editing. Mirko Lobino: Writing - review & editing. David Thiel: Writing - review & editing. Nam-Trung Nguyen: Writing - review & editing. Resources. Adrian Trinch: Writing - review & editing. Muhammad A. Shiddiky: Conceptualization, Methodology, Writing - review & editing. Resources, Supervision. Yongsheng Gao: Writing - review & editing. Funding acquisition. Qin Li: Conceptualization, Methodology, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition.
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Appendix A. Supplementary data

Raman results, laser writing circuits schematics and SEM images, XPS results. This material is available free of charge.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.carbon.2020.03.043.

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