Supplementary Information

Ultra-Sensitive and Specific Detection of Ascorbic Acid using a Laser-Engraved Graphene Electrode Modified with Molecularly Imprinted Polymer

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1. Optimization of laser defocus distance for LEG electrode fabrication

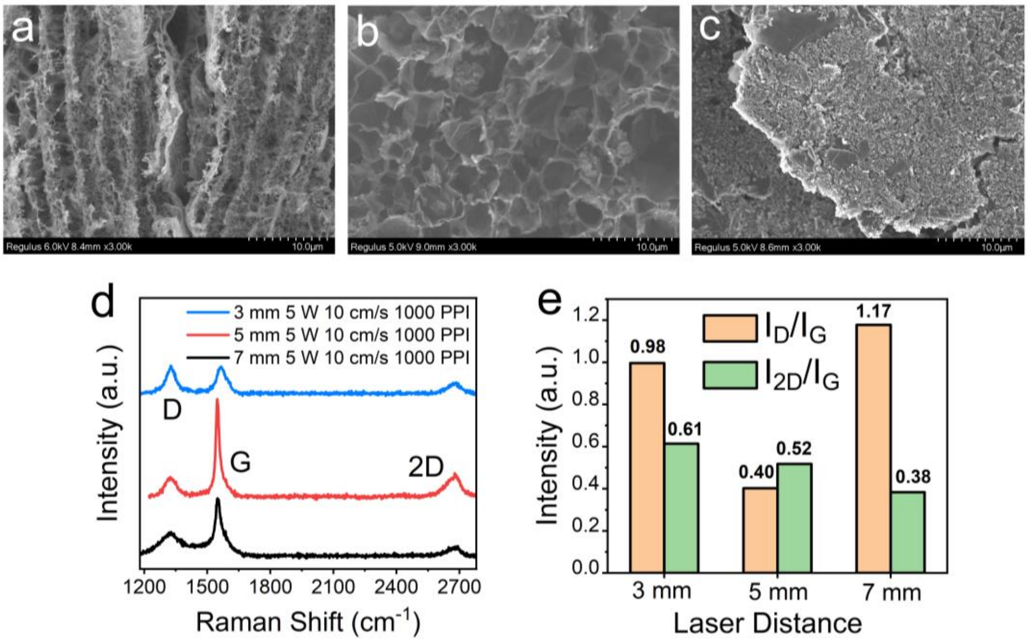

Fig. S1 (a-c) Under the CO_2 laser parameters of a laser power of 5 W, a scanning speed of 10 cm/s, and a PPI of 1000, the SEM images of different LEG electrodes with a defocus distance of (a) 3 mm, (b) 5 mm and (c) 7 mm. (d-e) Raman spectra and the ratio of different peak intensities of fabricated LEG electrodes.

To investigate the effect of laser defocus distance on the structure of graphene, the LEG electrodes with defocus distances of 3 mm, 5 mm, and 7 mm, maintaining a constant laser power of 5 W, scanning speed of 10 cm/s, and pulses per inch (PPI) of 1000 were fabricated. The prepared electrodes were characterized via SEM. In Fig. S1a, the three-dimensional (3D), linearly arranged pore-like structures emerged at a 3 mm defocus distance. Fig. S1b shows the regular porous structure obtained at the 5 mm defocus distance, while Fig. S1c shows the granular morphology at the 7 mm defocus distance. The Raman spectra presented in Fig. S1d for LEG electrodes exhibit clear D, G, and 2D peaks, indicating that the fabricated LEG electrodes have the typical characteristics of graphene material. Generally, the value of I_D/I_G can be used to estimate the disorder degree or defect density of graphene.[1] The larger the I_D/I_G ratio, the higher the degree of defects in the sample. Similarly, the value of I_{2D}/I_G can be utilized to evaluate the number of graphene layers.[2] Typically, as the number of graphene layers increases, the value of I_{2D}/I_G decreases. It can be observed from Fig. S1e that when the defocus distance is 5 mm, the number of graphene layers prepared is the least amount, and the degree of defects is also relatively low.

Reference

1. W. Yu, W. Zhao, S. Wang, Q. Chen and X. Liu, *Advanced Materials*, 2023, **35**, 2209545.
2. L. Cheng, C. S. Yeung, L. Huang, G. Ye, J. Yan, W. Li, C. Yiu, F.-R. Chen, H. Shen, B. Z. Tang, Y. Ren, X. Yu and R. Ye, *Nature Communications*, 2024, **15**, 2925.

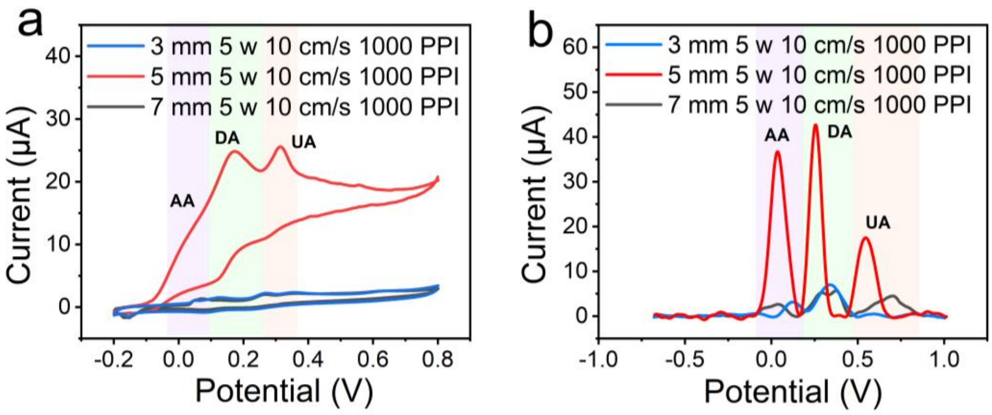

Fig. S2 (a) Cyclic voltammetry (CV) and (b) differential pulse voltammetry (DPV) measurements of different LEG electrodes with defocus distance of 3 mm, 5 mm and 7 mm in a PBS buffer solution containing 2 mM AA, DA and UA.

The fabricated LEG electrodes were characterized using CV technique in a potential range from -0.2 V to 0.8 V vs. Ag/AgCl at a scan rate of 100 mV/s. As shown in Fig. S2a, the LEG electrodes prepared with a defocus distance of 5 mm exhibits oxidation peaks at approximately 0.02 V (assigned to AA), 0.16 V (assigned to DA), and 0.31 V (assigned to UA) vs. Ag/AgCl. Conversely, LEG electrodes prepared with laser defocus distances of 3 mm and 7 mm do not exhibit significant oxidation peaks for these analytes. Similarly, when the defocus distance is 5 mm, the prepared LEG electrode exhibits obvious oxidation peaks at about 0.02 V, 0.25 V, and 0.5 V vs. Ag/AgCl (Fig. S2b). In contrast, when the defocus distance is 3 mm or 7 mm, the prepared LEG electrodes show relatively weak DPV response signals to the above three molecules (AA, UA, and DA), and the oxidation peak potentials shift to higher values. This highlights the specific and enhanced response of LEG electrodes prepared at a laser defocus distance of 5 mm to these three molecules. This may be due to the varying parameters of laser engraving, which result in differences in the structure of the prepared graphene electrode materials, thereby leading to different electrochemical properties. In conclusion, it can be seen that the LEG electrode prepared at the defocusing distance of 5 mm exhibits a high current response and can effectively differentiate between AA, DA and UA, demonstrating excellent electrochemical sensing performance.

2. Optimization of laser power for LEG electrode fabrication

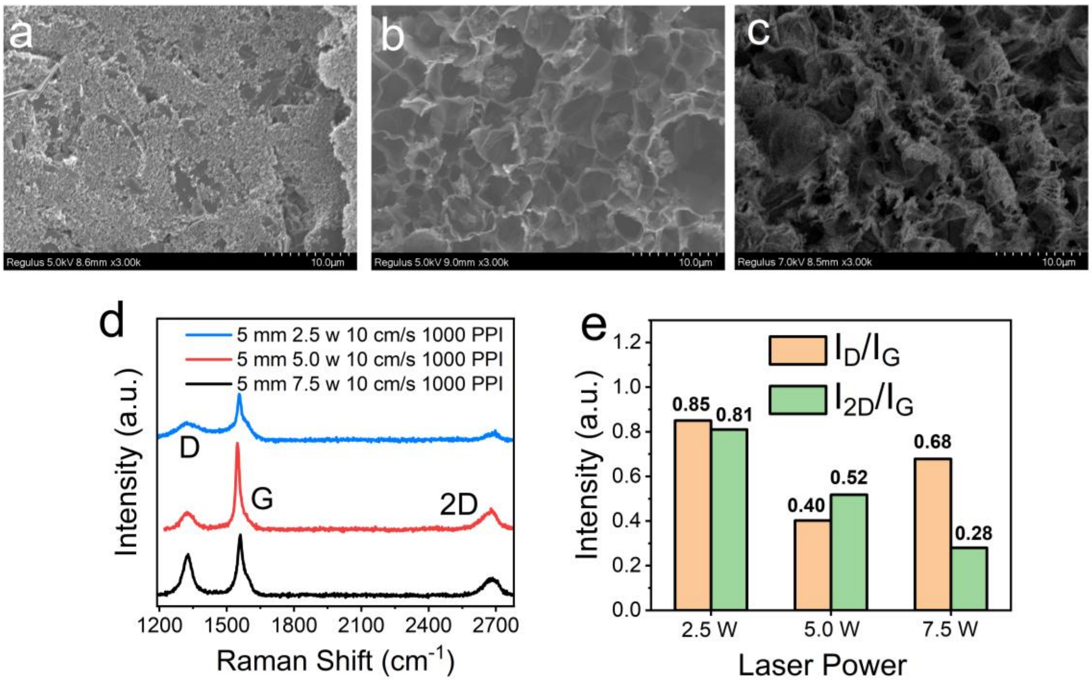

Fig. S3 (a-c) Under the CO_2 laser parameters of defocus distance of 5 mm, a scanning speed of 10 cm/s, and a PPI of 1000, the SEM images of different LEG electrodes with a laser power of (a) 2.5 W, (b) 5 W and (c) 7.5 W. (d-e) Raman spectra and the ratio of different peak intensities of fabricated LEG electrodes.

The LEG electrodes were then optimized under three laser powers of 2.5 W, 5 W, and 7.5 W, while maintaining a defocus distance of 5 mm, a scanning speed of 10 cm/s, and PPI of 1000. In Fig. S3a, when a laser power of 2.5 W is applied, the LEG electrode displays the morphology of particle aggregates. Conversely, Fig. S3b illustrates the successful achievement of a regular porous structure at a laser power of 5 W. The electrode processed at a laser power of 7.5 W (Fig. S3c) exhibits a disordered folded structure. The Raman spectra presented in Fig. S3d demonstrates that the graphene electrodes were successfully fabricated under different laser powers. Furthermore, by thoroughly comparing the ratios of I_D/I_G and I_{2D}/I_G presented in Fig. S3e, it is evident that the quality of the LEG electrode reaches its optimum when processed at a laser power of 5 W.

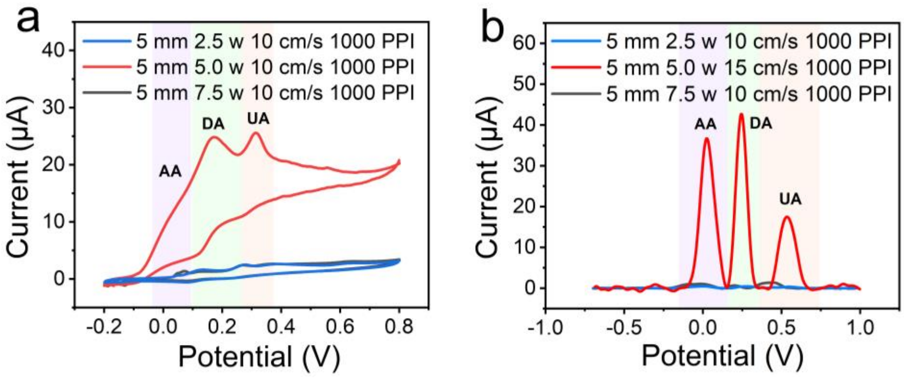

Fig. S4 (a) CV and (b) DPV measurements of different LEG electrodes with laser power of 2.5 W, 5 W and 7.5 W in PBS buffer solution containing 2 mM AA, DA and UA.

In Fig. S4a, the LEG electrode fabricated using laser power of 5 W displays significant oxidation peaks from AA, DA, and UA. However, the electrode prepared using laser powers of 2.5 W and 7.5 W have almost no electrochemical response for the three molecules. The result of DPV measurements is consistent with the CV tests, indicating that the LEG electrodes fabricated at a laser power of 5 W possess satisfactory electrochemical properties (Fig. S4b).

3. Optimization of laser scanning speed for LEG electrode fabrication

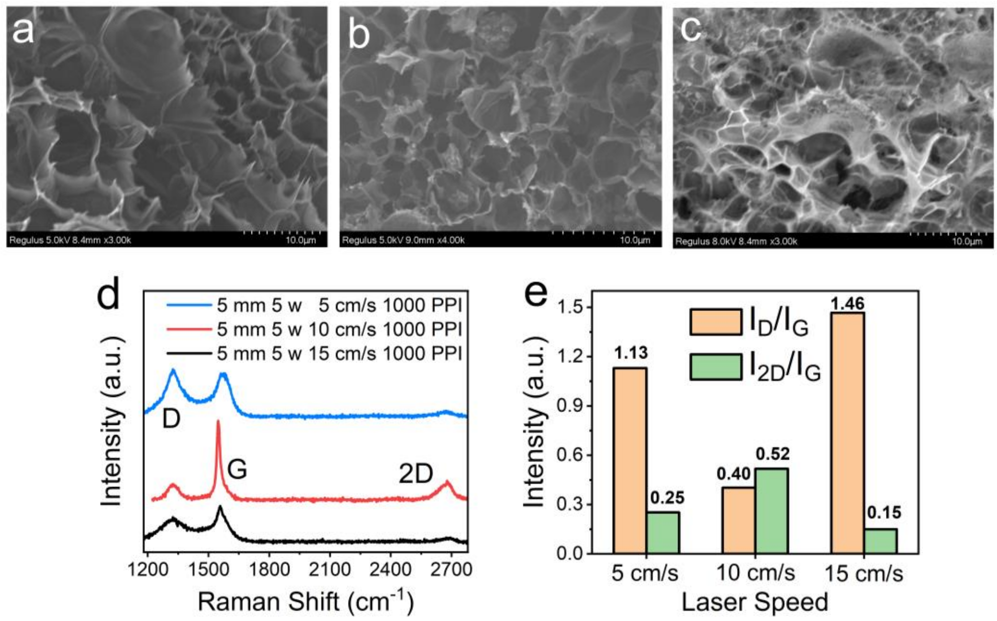

Fig. S5 (a-c) Under the CO_2 laser parameters of defocus distance of 5 mm, a laser power of 5 W, and a PPI of 1000, the SEM images of different LEG electrodes with a scanning speed of (a) 5 cm/s, (b) 10 cm/s and (c) 15 cm/s. (d-e) Raman spectra and the ratio of different peak intensities of fabricated LEG electrodes.

Subsequently, the laser scanning speed for LEG electrodes was optimized under the conditions of a fixed defocus distance of 5 mm, a laser power of 5 W, and a PPI of 1000, with three speeds tested: 5 cm/s, 10 cm/s, and 15 cm/s. Porous structures of graphene were observed at all three scanning speeds (Fig. S5a-c). However, compared to the graphene prepared at the other speeds, the graphene fabricated at a scanning speed of 10 cm/s exhibited a more regular 3D porous morphology (Fig. S5b). Raman spectra displayed clear characteristic peaks of graphene (Fig. S5d), indicating the successful formation of graphene materials at all three scanning speeds. Specifically, when scanned at a speed of 10 cm/s, the prepared LEG electrode demonstrated higher I_{2D}/I_G ratio, suggesting the presence of the least number of graphene layers during this scanning process.

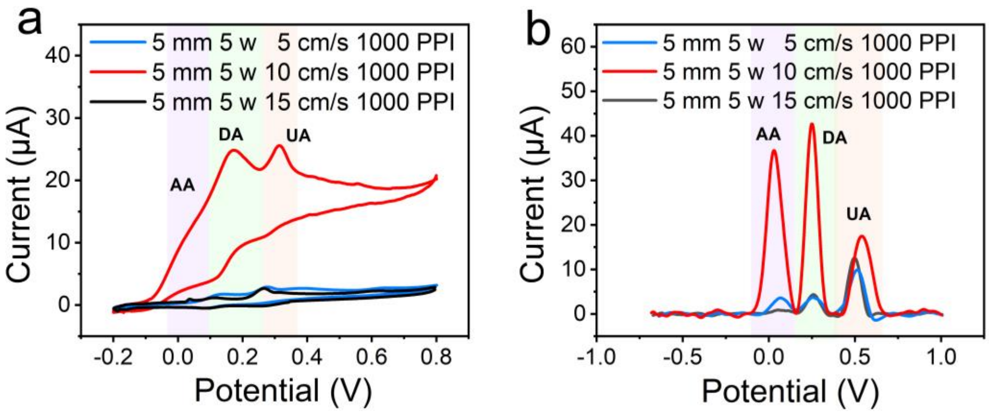

Fig. S6 (a) CV and (b) DPV measurements of different LEG electrodes with scanning speed 5 cm/s, 10 cm/s and 15 cm/s in a PBS buffer solution containing 2 mM AA, DA and UA.

Fig. S6a illustrates that the produced LEG electrodes exhibit weak oxidation peaks to AA, DA, and UA when the laser scanning speed setting at 5 cm/s and 15 cm/s, respectively. On the contrary, the prepared LEG electrode at a scanning speed of 10 cm/s shows a significant current response for the three analytes (Fig. S6a). The DPV measurements clearly reveal that the LEG electrode under the scanning speed of 10 cm/s can distinguish between the three molecules (Fig. S6b). Considering the above results, the electrochemical sensing performance of the LEG electrode is optimal at a laser scanning speed of 10 cm/s.

4. Optimization of PPI for LEG electrode fabrication

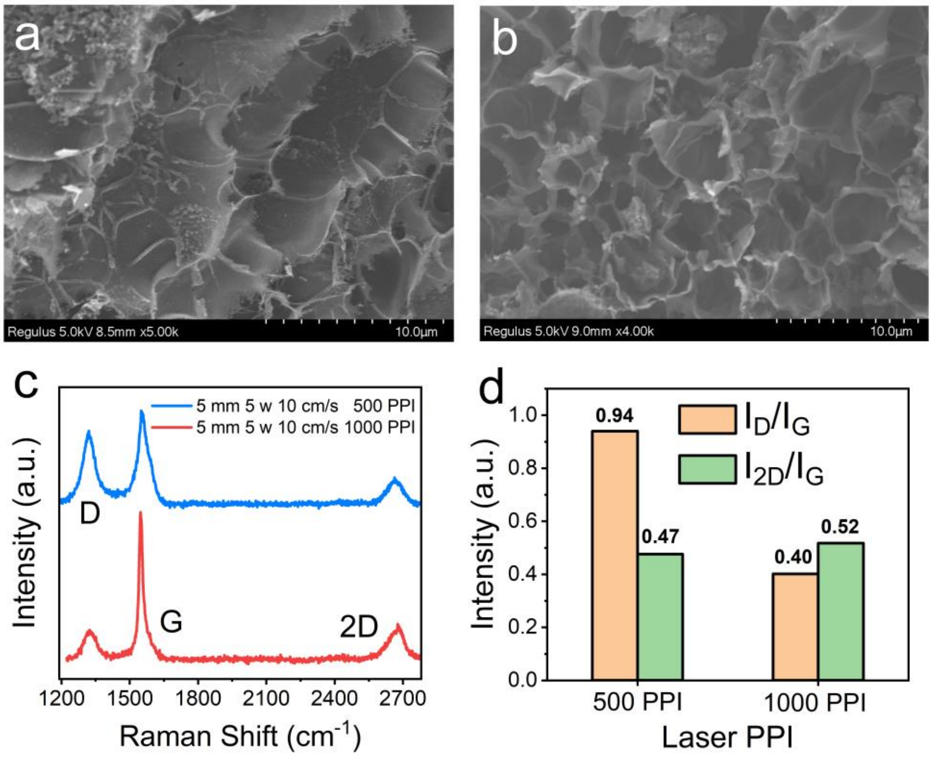

Fig. S7 (a-b) Under the CO_2 laser parameters of defocus distance of 5 mm, a laser power of 5 W, and a scanning speed of 10 cm/s, the SEM images of different LEG electrodes with a PPI of (a) 500 and (b) 1000. (c-d) Raman spectra and the ratio of different peak intensities of fabricated LEG electrodes.

Furthermore, the laser PPI value of LEG electrodes was optimized under the CO_2 laser parameters of a defocus distance of 5 mm, a laser power of 5 W, and a scanning speed of 10 cm/s. As shown in Fig. S7a, the graphene prepared at 500 PPI exhibits wrinkled morphology and lacks a distinct porous structure. The relatively low I_D/I_G ratio and the high I_{2D}/I_G ratio indicate that the graphene prepared under the processing parameter of 1000 PPI has relatively fewer defects and a thinner graphene layer.

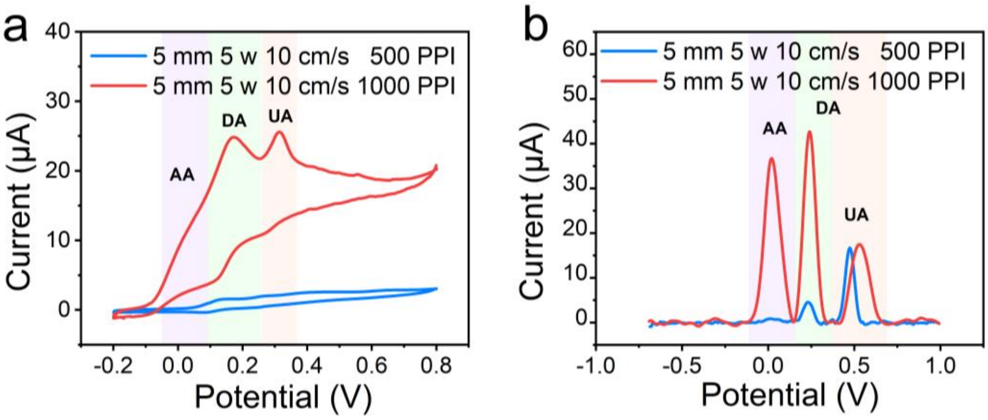

Fig. S8 (a) CV and (b) DPV measurements of different LEG electrodes with PPI of 500 and 1000 in a PBS buffer solution containing 2 mM AA, DA and UA.

As demonstrated in Fig. S8a, the CV curve clearly shows three separate oxidation peaks corresponding to AA, DA, and UA at a PPI of 1000. In contrast, the LEG electrode prepared with a PPI of 500 demonstrates a minimal response to these three molecules. In the DPV test, the LEG electrode with a PPI of 500 exhibits virtually no response to AA, DA, and UA in contrast to the LEG electrode with a PPI of 1000. In summary, the optimal performance of the LEG electrode has achieved at a laser power of 5 W, a defocus distance of 5 mm, a scanning speed of 10 cm/s, and a PPI of 1000.

5. Characterization of LEG electrode

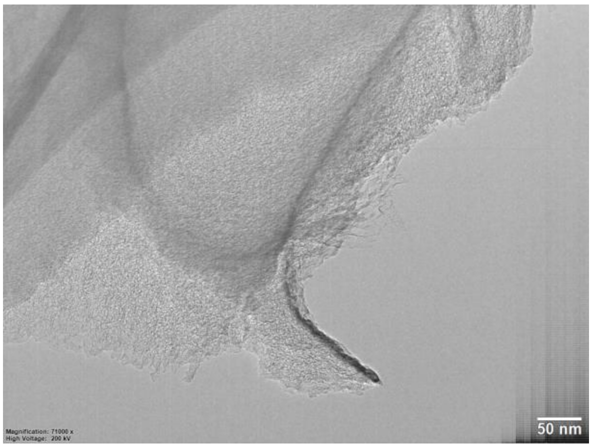

Fig. S9 The TEM characterization of graphene on LEG electrode. TEM characterization clearly reveals the structural features of ultrathin graphene.

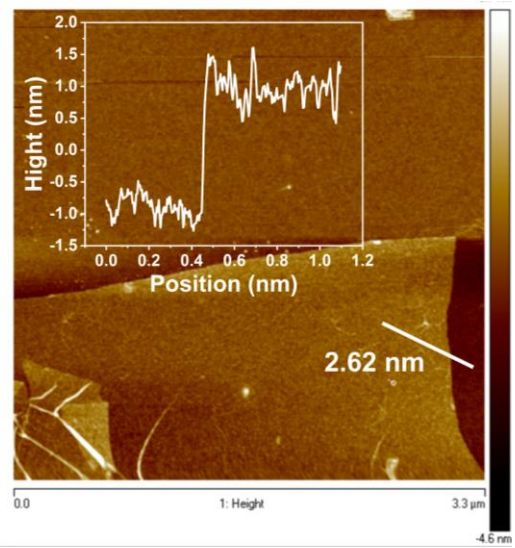

Fig. S10 The AFM characterization of graphene on LEG electrode. AFM characterization shows that the thickness of the prepared graphene is about 2.62 nm.

6. Fitting results obtained from Nyquist plots

Table S1. The values of R_S, R_{ct}, C_{dl}, and Z_w for the equivalent circuit model.

	R_s ($\Omega\cdot cm^2$)	R_{ct} ($\Omega\cdot cm^2$)	C_{dl} ($\Omega^{-1}\cdot cm^{-2}\cdot s^a$)	Z_w ($\Omega\cdot cm^2$)
LEG	170.6	0.5	33.1	3883.2
PPD/LEG	146.7	0.6	56.5	1537.3

*a is the exponent in the equation for the constant phase element (CPE) ($Z_{CPE} = Z_{dl}(j\omega)^{-a}$).