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### SUPPORTING INFORMATION

# LASER-INDUCED GRAPHENE INCORPORATED WITH SILVER NANOPARTICLES APPLIED TO A HEAVY METAL MULTI-DETECTION

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### Preparation of sample solution

Two different types of test solutions were prepared. Cd, Pd and Cu ions in acetate buffer (0.1 M, pH 4.5) for sensor performance optimization and Cd, Pd and Cu ions in drinking and tap water for real sample analysis. For performance testing solutions, 1 L of acetate buffer (0.1 M, pH 4.5) was prepared by mixing 3.692 g of sodium acetate and 3.302 g of acetic acid in 800 mL of DI water and adjusting the resulting solution's pH to 4.5. For real sample testing solutions, Cd, Pd and Cu in DI and tap water were prepared simply by adding various concentrations Cd and Pd standard solutions.

### Roadmap of fabrication and measurement

First, design the electrode with CAD, input the design file into the laser, and then irradiate the laser on the PI film to make LIG electrode. After LIG is formed, a reference electrode is prepared using Ag/AgCl, and passivation is performed to have the same area of working, reference, and counter elec-trode using PI films. Afterwards, the AgNPs/LIG electrode is fabricated by electroplating the AgNPs, and the peak current can be checked with SWASV by putting the heavy metal to be measured in a 0.1M acetate buffer solution of pH 4.5 using the fabricated electrode.

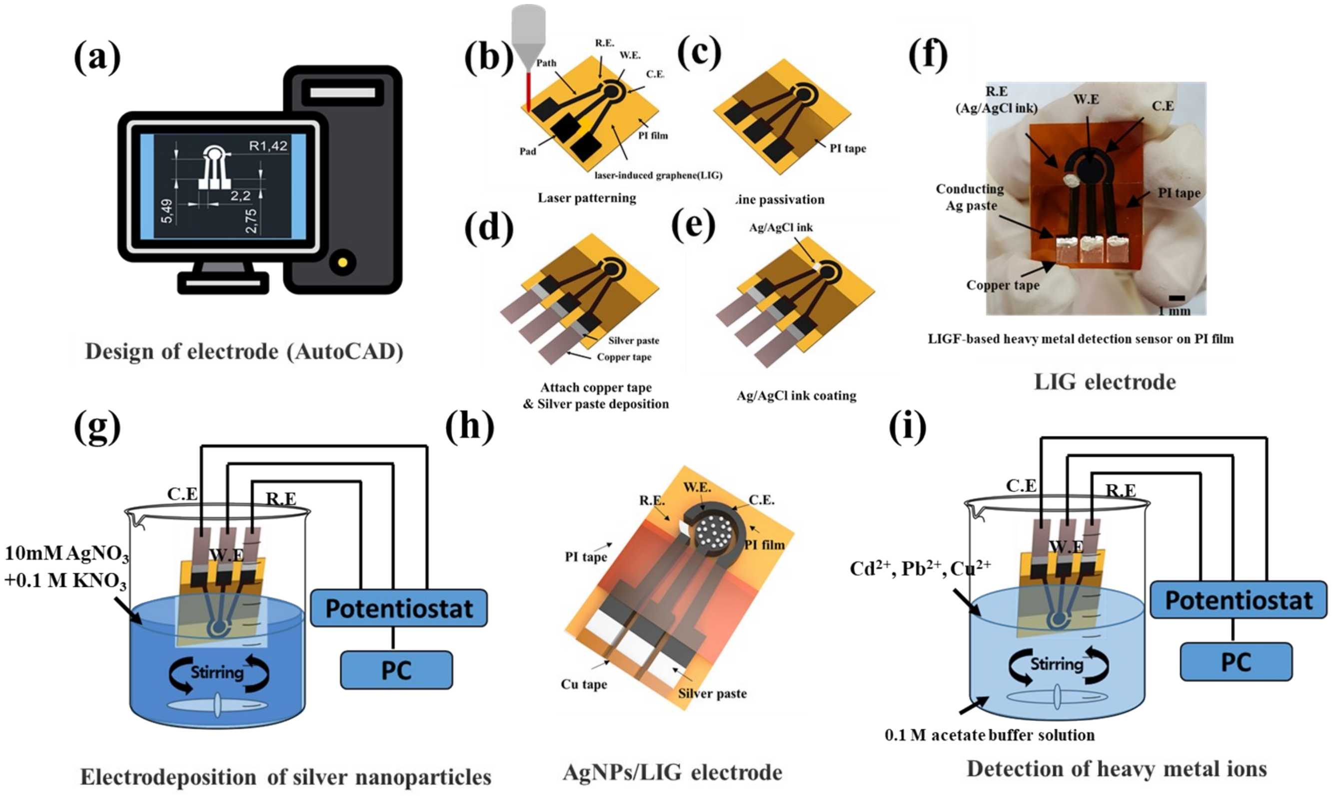

**Fig. S1.** Roadmap of the whole process from sensor preparation to detection. (a) Design and fabrication (b-e) of electrode, (f) LIG electrode, (g) Electrodeposition of silver nanoparticles, (h) AgNPs/LIG electrode, (i) Detection of heavy metal ions

## Active surface area of the working electrode

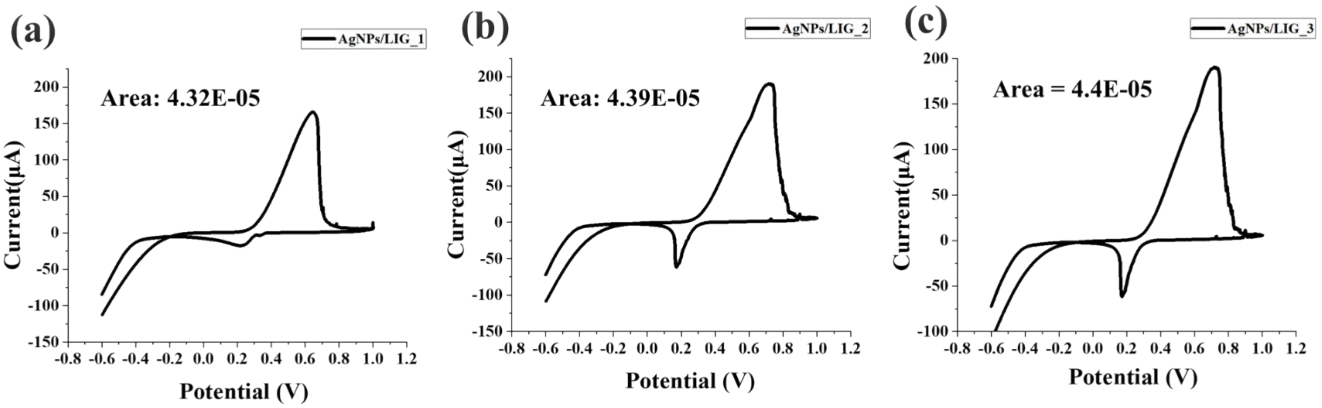

**Fig. S2** (a) Cyclic voltammetry. (a-c) Three AgNPs/LIG (1 M sulfuric acid, scan rate: 50 mV/s)

## DRX analysis

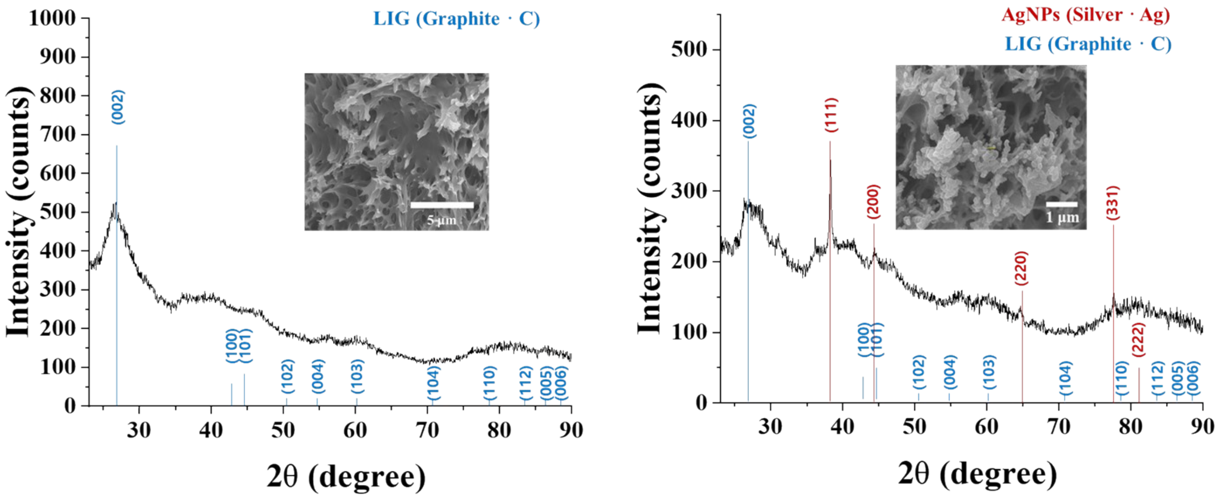

**Fig. S3** DRX analysis results. (a) LIG and (b) AgNPs/LIG.

**SEM images of AgNPs/LIG, AuNPs/LIG and PtNPs/LIG according to fabrication conditions**

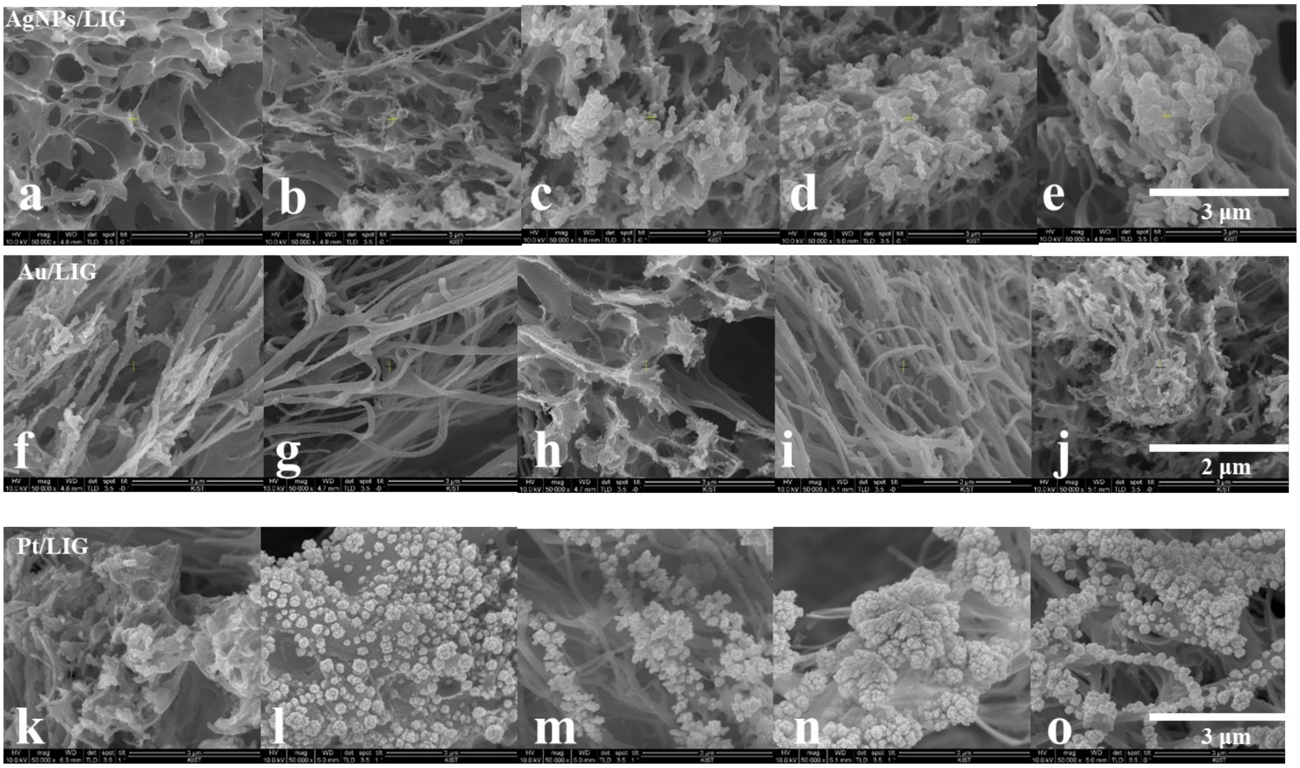

**Fig. S4.** SEM image of AgNPs/LIG deposited at potential of −0.2V, time at a 10 s, b 30 s, (c) 60 s, (d) 100 s, (e) 150 s (x50000). SEM image of AuNPs/LIG deposited at potential of −0.1V at (f) 100 s, (g) 200 s, (h) 300 s, (i) 400 s, (g) 500 s (x50000)**.** SEM image of PtNPs/LIG deposited at potential of −0.2V at (k) 50 s, (l) 100 s, (m) 150 s, (n) 200 s, (o) 250 s (x50000).

**Effect of 0.1 M Acetate Buffer Solution at pH 4.5 Experiment on AgNPs/LIG Electrode**

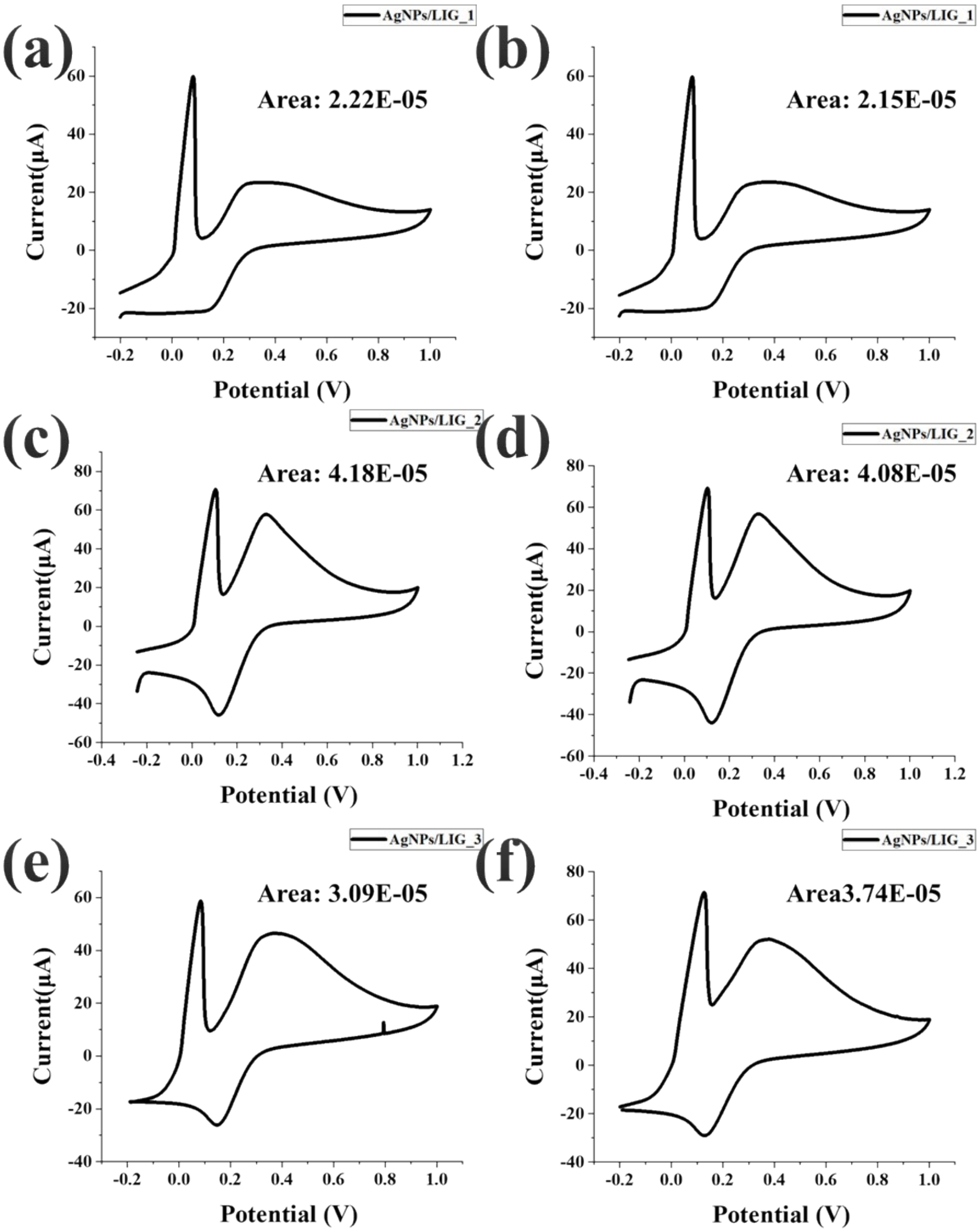

**Fig. S5** Cyclic Voltammogram (a, c, e) before and after (b, d, f) soaking in 0.1M acetate buffer solution at pH 4.5 for 300 s.

## Optimization of various experimental parameters of SWASV

Like the experiments on the effects of heavy metal measurement conditions, we conducted experiments to find the optimal conditions depending on the frequency, amplitude, and E-step of the SWASV conditions. First of all, in Fig. S6(a), we changed the amplitude in the range of 0 to 250 mV with the frequency fixed at 25 Hz. The Peak current increased and the baseline became higher when the amplitude changed from 0 to 200 mV. As the amplitude increased, the peak current increased gradually, and the largest value of the peak current that was measured was 200 mV. Therefore, the amplitude was selected as 200 mV. As shown in Fig. S6(b), we measured the peak current while changing the frequency from 1 Hz to 20 Hz with the amplitude fixed at 50 mV and the E-step at 5 mV. The peak current increased as the frequency increased from 1 Hz to 5 Hz and it decreased after 5 Hz. Therefore, the frequency was selected as 5 Hz. The increasing frequency proceeded at the speed of 25 Hz. As shown in Fig. S6(C), we changed the E-step from 0.5 to 10 mV with the amplitude and frequency fixed. The peak current increased as the E-step increased from 0.5 to 5 mV, yet, after 5 mV, the number of data decreased, and the shape of the voltage-current curve was not smooth. From these results, for the SWASV optimal conditions, we determined the amplitude to be 200 mV, the frequency to be 5 Hz, and the E-step to be 5 mV.

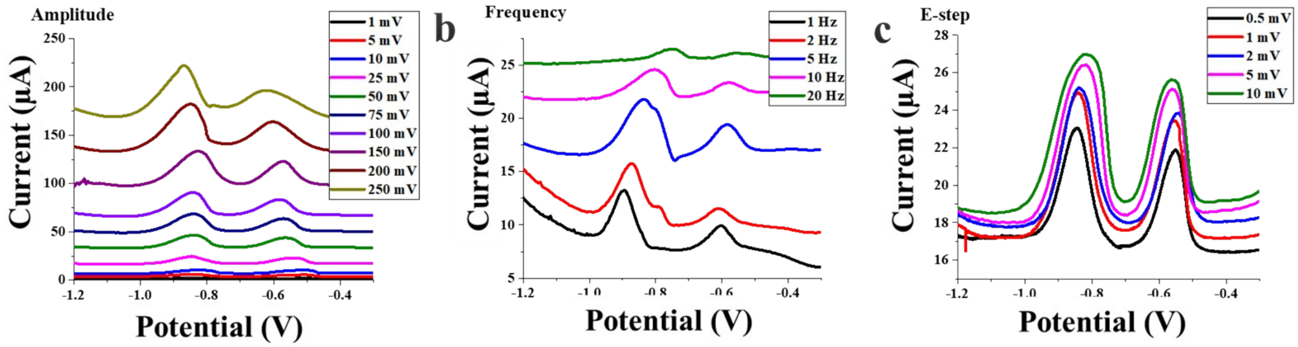

**Fig. S6.** SWASV measurments of SWASV parameters depending on (a) amplitude, (b) frequency, and (c) E-step in acetate-buffer solution containing 200 μg L$^{-1}$ of Cd and Pb ions.

## Analytical performance for the multi-detection of BiNPs/LIG electrode for Cd, Pb, and Cu ions

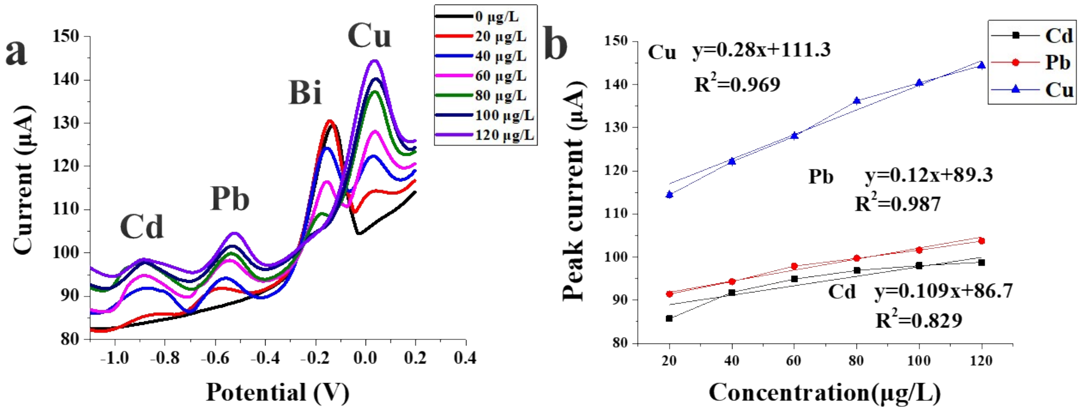

**Fig. S7.** SWASV for the multi-detection of Cd, Pb and Cu ions with BiNPs/LIG in 0.1 M acetate-buffer solution. Stripping currents when (a) multi-detection of Cd, Pb and Cu are at 0, 20, 40, 60, 80, 100, 120 μg/L. (b) Show the calibration curves of the Cd, Pb and Cu ions. Data are presented with the mean of three replicates.

### Limit of Detection (LOD) for Cd, Pb, and Cu ion multi-detection

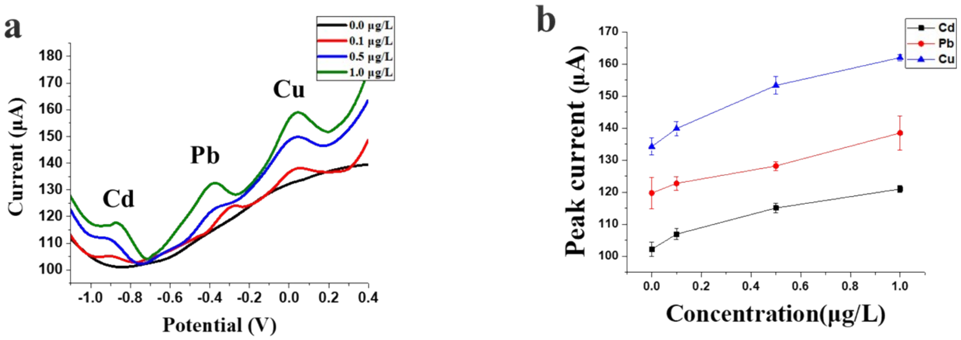

**Fig. S8.** SWASV for the multi-detection of Cd, Pb and Cu ions with AgNPs/LIG in 0.1 M acetate-buffer solution at pH 4.5. Stripping currents when Cd and Pb ion concentrations are at (a) 0.1, 0.5, 1 µg/L. (b) show the calibration curves of the Cd, Pb and Cu ions. Data are presented with the mean of three replicates.

### Interference experiments with other metal ions and organics

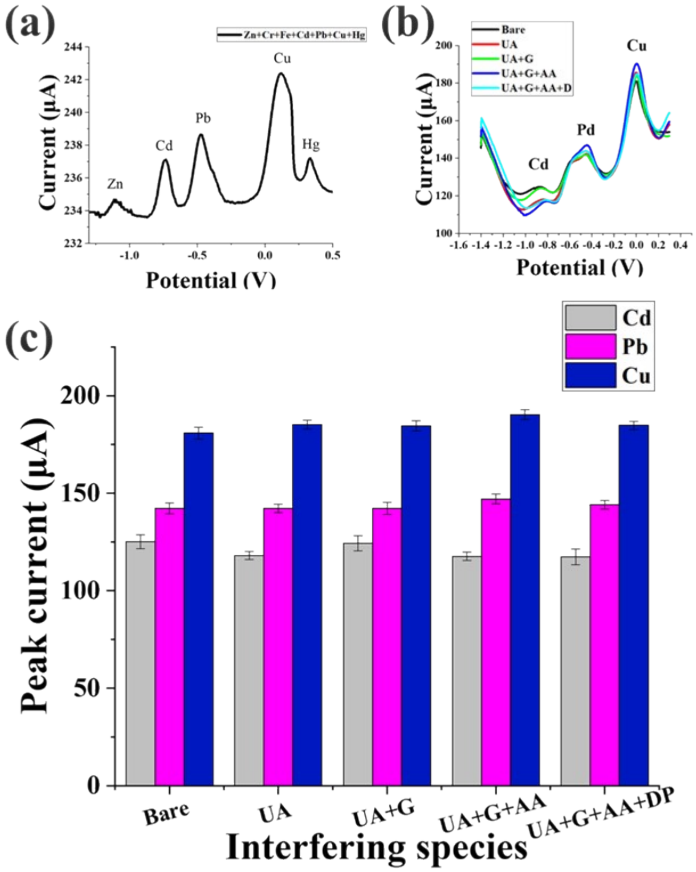

**Fig. S9** Interfering species experiment (a) Zn, Hg ions, (b), (c) organics (uric acid, glucose, ascorbic acid, and dopamine)

**Table S1. $CO_2$ laser irradiation parameters for LIG fabrication.**

| Electrode | Mode | PPI | Laser power | Speed | Z-distance |
|---|---|---|---|---|---|
| LIG | Raster | 500 PPI | 10 W | 8.82 cm/s | 0.5 mm* |

* This is the number reported by the laser control software. The actual distance measured from the surface of the PI film to the tip of the air-assist cone (where the laser beam exits towards the irradiation surface) was roughly 15 mm.

**Table S2. Number of graphene layers according to intensity ratio ($I_{2D}/I_G$).**

| $I_{2D}/I_G$ | Number of graphene layers |
|---|---|
| $I_{2D}/I_G > 1.8$ | Monolayer graphene |
| $0.8 < I_{2D}/I_G < 1.8$ | Graphene with 10 layers or less |
| $I_{2D}/I_G < 0.8$ | Multilayer graphene with 10 layers or more |

**Table S3. Electroplating fabrication conditions for Au/LIG, Pt/LIG and Ag/LIG.**

| Electrode | Solution | Deposition potential(V) | Deposition time(s) |
|---|---|---|---|
| Ag/LIG | 1.0 mM $H_2PtCl$+0.1M $H_2SO_4$ | -0.2 | 300 |
| Au/LIG | 1 mM $HAuCl_43H_2O$ | -0.1 | 150 |
| PT/LIG | 1mM $AgNO_3$+0.1 M $KNO_3$ | -0.2 | 150 |