

## Electronic Supplementary Information

### In situ synthesis of copper–ruthenium bimetallic nanoparticles on laser-induced graphene as a peroxidase mimic

Dinakaran Thirumalai,<sup>a</sup> Jun-Uk Lee,<sup>a</sup> Hyojeong Choi,<sup>b</sup> Minjeong Kim,<sup>b</sup> Jaewon Lee,<sup>c</sup> Suhkmann Kim,<sup>d</sup>  
Bo-Sung Shin,<sup>\*a</sup> and Seung-Cheol Chang<sup>\*a</sup>

<sup>a</sup>*Department of Cogno-Mechatronics Engineering, College of Nanoscience and Nanotechnology, Pusan National University, Busan 46241, Republic of Korea*

<sup>b</sup>*Department of Optics and Mechatronics Engineering, College of Nanoscience and Nanotechnology, Pusan National University, Busan 46241, Republic of Korea*

<sup>c</sup>*College of Pharmacy, Pusan National University, Busan 46241, Republic of Korea*

<sup>d</sup>*Department of Chemistry, Pusan National University, Busan 46241, Republic of Korea*

## Experimental

### Materials

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30 wt.%), sodium phosphate monobasic (NaH<sub>2</sub>PO<sub>4</sub>), sodium phosphate dibasic (Na<sub>2</sub>HPO<sub>4</sub>), potassium chloride (KCl), potassium ferricyanide (K<sub>3</sub>[Fe(CN)<sub>6</sub>]), copper (II) chloride (CuCl<sub>2</sub>), and ruthenium (III) chloride (RuCl<sub>3</sub>) were purchased from Sigma-Aldrich (USA). All other reagents were of analytical grade and used without further purification. Phosphate-buffered solution (PBS, 50 mM) at pH 7.0 was prepared by mixing NaH<sub>2</sub>PO<sub>4</sub> with Na<sub>2</sub>HPO<sub>4</sub> and 100 mM KCl. All aqueous solutions were prepared using deionized water (Milli-Q water purifying system, 18 MΩ cm).

### Preparation of Cu–Ru/LIG

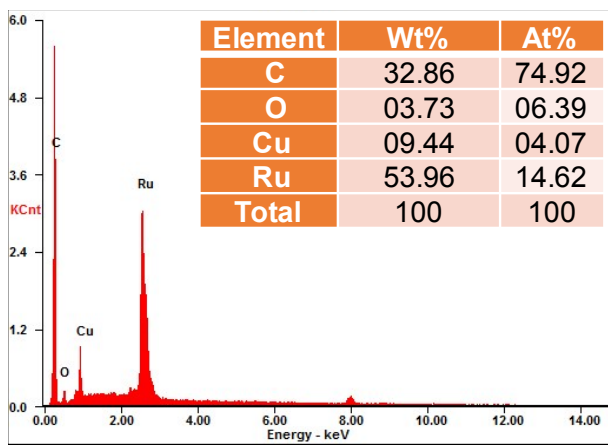
Kapton®, a commercially available polyimide (PI) film, was used to prepare the laser-induced graphene (LIG) because of its high thermal stability and mechanical strength among PI films. The electrode patterns were first designed using drawing software on a computer. After rinsing the PI

film with ethanol and drying in air, the predesigned patterns were directly engraved onto the film using a 355-nm Nd:YVO<sub>4</sub> pulse laser system (power: 1.3 W, speed: 40 mm/s) in air at room temperature to form a black carbonized layer (*i.e.*, LIG). Next, a mixed solution containing 1 M CuCl<sub>2</sub> and 1 M RuCl<sub>3</sub> (volume: 1.0, 3.0, or 5.0  $\mu$ L) was drop-casted and dried at room temperature for 10 min. Then, LIG was lasered again atop the previous pattern under the same conditions. The prepared electrode was named Cu–Ru/LIG.

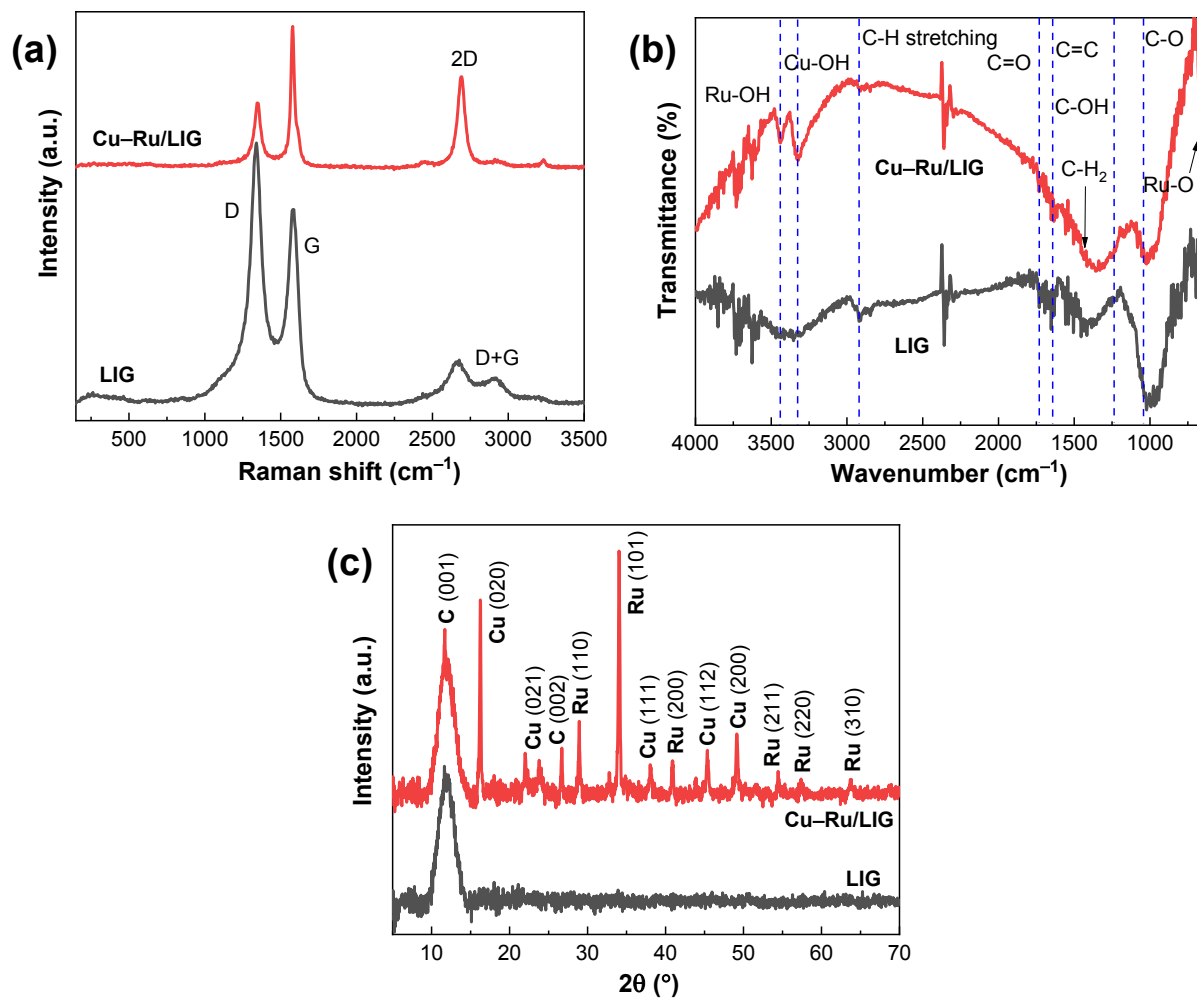
### **Apparatus and Measurements**

The morphologies of LIG and Cu–Ru/LIG were characterized by field emission-scanning electron microscopy (FE-SEM, Zeiss SUPRA 40VP) operated at an accelerating voltage of 5 kV, with energy-dispersive X-ray spectroscopy (EDS) for surface microanalysis. Raman spectra were measured using a Raman spectrometer (NRS-5100 JASCO International Co., Ltd., Tokyo, Japan) with a 532 nm excitation line. Fourier-transform infrared (FT-IR) measurements were conducted using an FTIR-4100 type A instrument with an ATR-PRO 450-S accessory (JASCO International Co., Ltd., Tokyo, Japan). The crystalline structure of Cu–Ru/LIG was characterized by X-ray diffraction (XRD, Panalytical X'Pert-3 PW3050/60 diffractometer, Cu K $\alpha$  radiation at 1.54 Å). X-ray photoelectron spectroscopy (XPS) analysis was performed using a K-Alpha™ X-ray Photoelectron Spectrometer System (Thermo Scientific, Waltham, MA, USA). Cyclic voltammetry (CV) and chronoamperometry (CA) measurements were performed on an electrochemical workstation (model 604E, CH Instruments Inc., Austin, TX, USA). All electrochemical experiments were carried out using a three-electrode system, with the Cu–Ru/LIG sensor as the working electrode, saturated Ag/AgCl as the reference electrode, and Pt wire as the counter electrode.

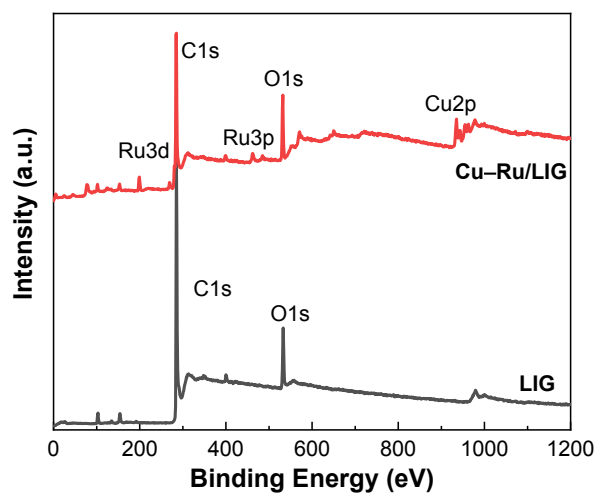
An electrochemical cell was set up using a disposable well (volume: 2 mL) with the sensor, and CA measurements were performed with the sensor. The sensor was inserted into the cell and connected to a potentiostat. An aliquot of PBS (50 mM, 1980  $\mu$ L) was saturated with N<sub>2</sub> for 10 min. Then, the solution was magnetically stirred, and the electrode was polarized at a potential of  $-0.40$  V vs. Ag/AgCl reference electrode. After achieving a stable baseline response with the PBS, 20  $\mu$ L H<sub>2</sub>O<sub>2</sub> sample was added to the cell, and the current responses were recorded as a function of time.



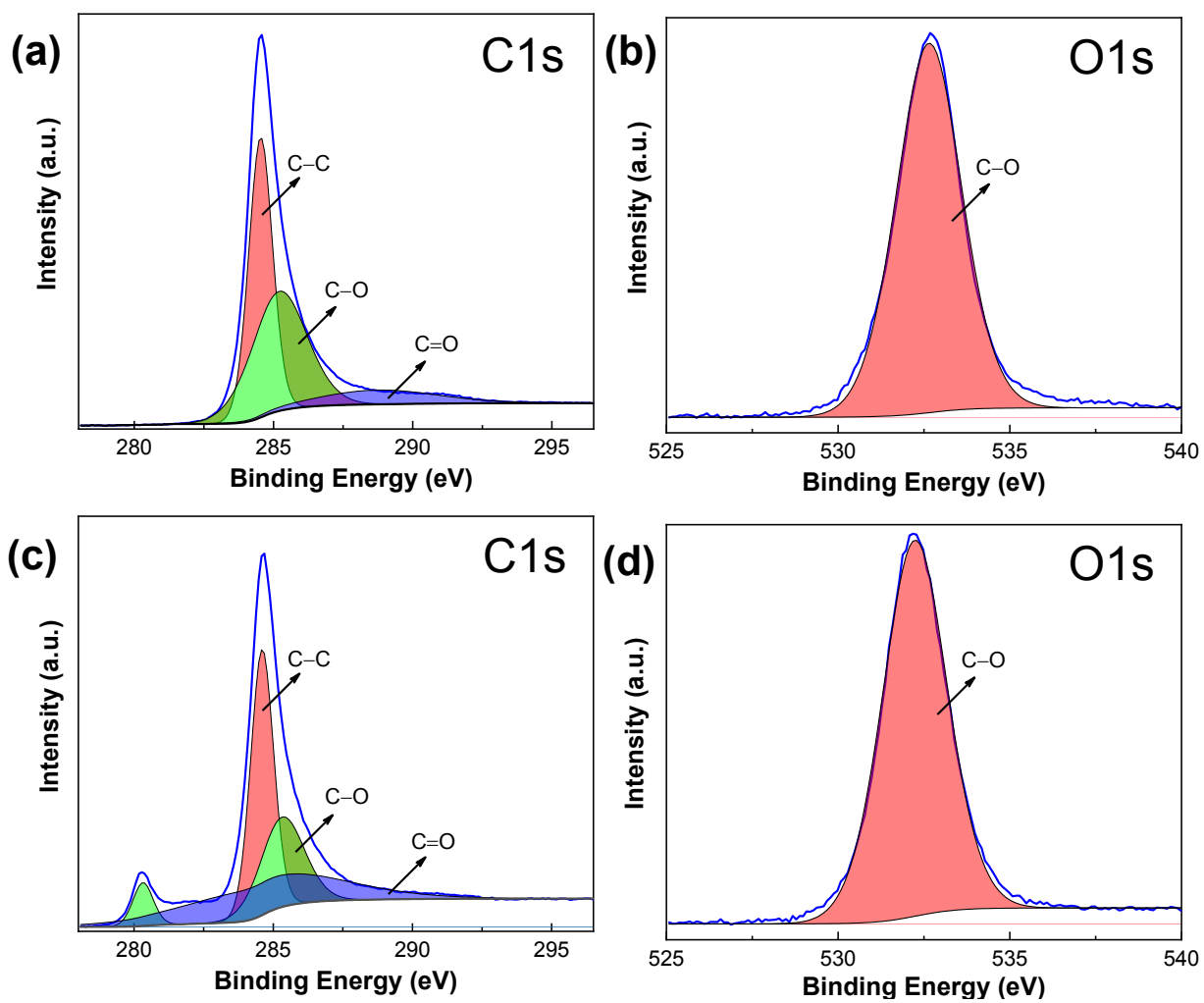
**Fig. S1** EDS spectrum of Cu-Ru/LIG.



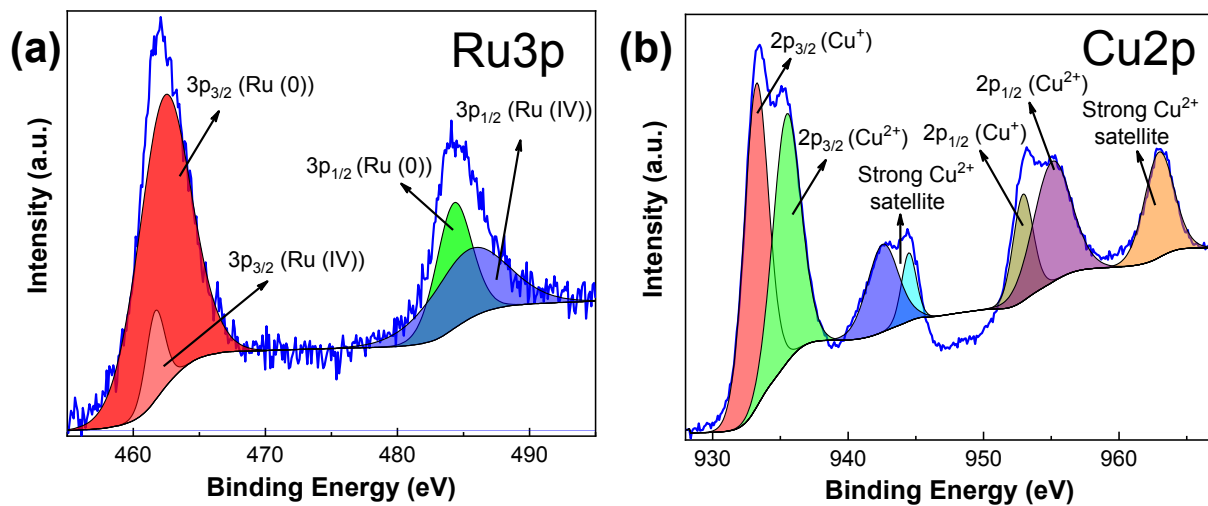
**Fig. S2** (a) Raman, (b) FT-IR, and (c) XRD spectra of LIG and Cu-Ru/LIG.



**Fig. S3** XPS survey spectra of LIG and Cu-Ru/LIG.

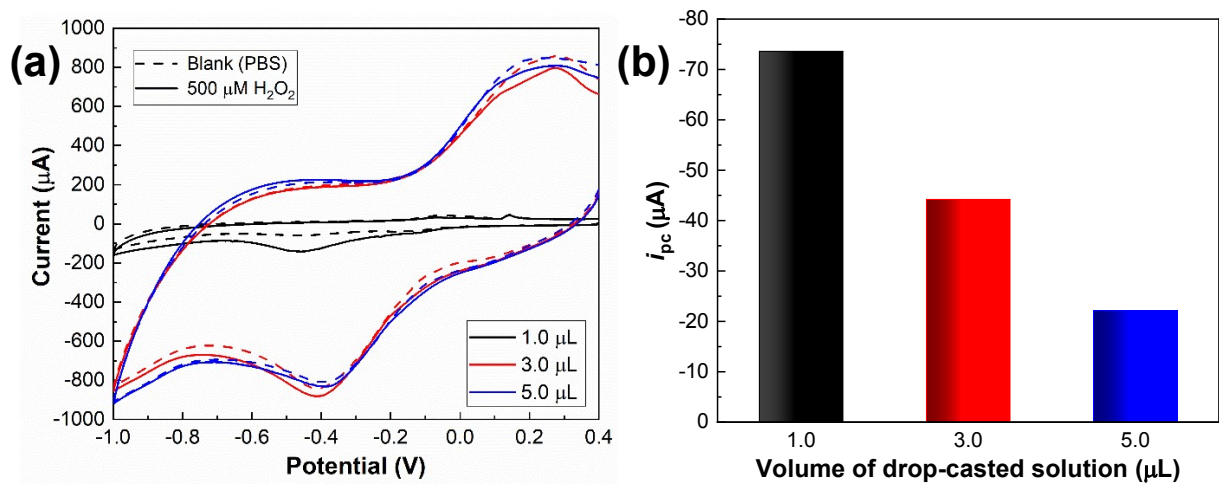


**Fig. S4** Deconvoluted high-resolution XPS spectra of (a) C1s and (b) O1s for LIG, and (c) C1s and (d) O1s for Cu-Ru/LIG.

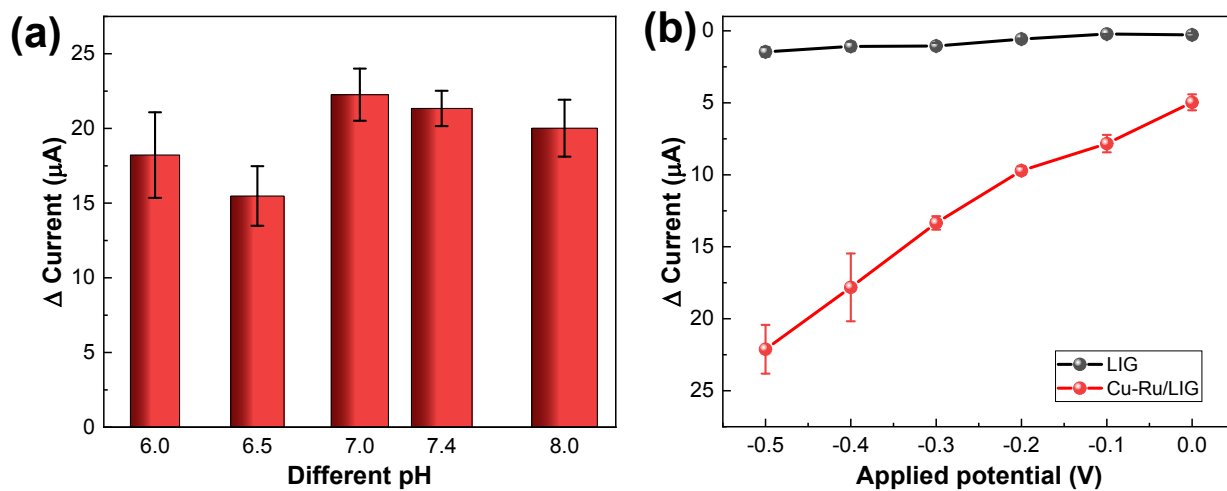


**Fig. S5** Deconvoluted high-resolution XPS spectra of (a) Ru3p and (b) Cu2p for Cu–Ru/LIG.

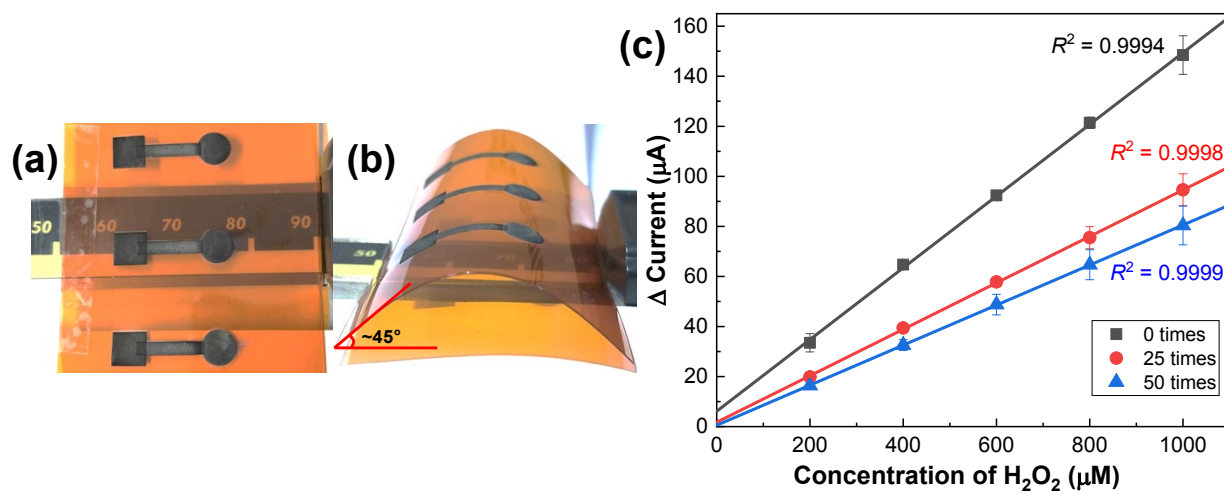




**Fig. S6** (a) CV curves of Cu–Ru/LIG sensors prepared with different volumes of drop-casted precursor solution. (b) The corresponding plot of cathodic peak current ( $i_{pc}$ ) values measured at  $-0.40$  V.



**Fig. S7** (a) Current change under different pH values for Cu-Ru/LIG in 50 mM PBS containing 200  $\mu$ M  $H_2O_2$  at an applied potential of -0.40 V. (b) Current change under different applied potentials for LIG and Cu-Ru/LIG in 50 mM PBS (pH 7.0) containing 200  $\mu$ M  $H_2O_2$ .



**Fig. S8** Photographs of the Cu–Ru/LIG sensor in the (a) flat and (b) bent states. (c) CA current change of Cu–Ru/LIG after continuous bending in 50 mM PBS (pH 7.0) containing different concentrations of  $H_2O_2$ .

**Table S1.** Comparison of flexible electrochemical sensors for H<sub>2</sub>O<sub>2</sub> detection

Sensor	Applied potential (V) vs. Ag/AgCl	Dynamic linear range ( $\mu\text{M}$ )	Sensitivity ( $\mu\text{A mM}^{-1} \text{cm}^{-2}$ )	Limit of detection ( $\mu\text{M}$ )	Ref.
Pt–MnO <sub>2</sub> /rGOP	–0.15	2.0–13330	129.5	1.0	S1
MnO <sub>2</sub> –graphene paper	–0.50	100–45400	59.0	10	S2
Au@PB NPs/graphene paper	–0.10	1.0–30	0.005	0.1	S3
AgNPs/LSG	–0.50	10–10000	32	7.9	S4
C $\mu$ F/Ag NPs–Naf	–0.35	100–80000	-	0.485	S5
Pt/rGOP	–0.25 vs. SCE	0.2–2000 2000–8500	67.5 40.2	0.1	S6
PBEA	–0.10	5.0–1000	-	1.9	S7
Cu–Ru/LIG	–0.40	10–4320	136.7	1.8	This work

Pt – Pt nanoparticles, MnO<sub>2</sub> – manganese (IV) oxide nanowires, rGOP – reduced graphene oxide paper, Au@PB NPs – gold@Prussian blue nanoparticles, AgNPs – silver nanoparticles, LSG – laser scribed graphene, C $\mu$ F – carbon microfibers, Naf – Nafion, rGOP – free-standing reduced graphene oxide paper, SCE – saturated calomel electrode, PBEA – Prussian blue-based electrode array.

## References

- S1. F. Xiao, Y. Li, X. Zan, K. Liao, R. Xu and H. Duan, *Adv. Funct. Mater.*, 2012, **22**, 2487–2494.
- S2. S. Dong, J. Xi, Y. Wu, H. Liu, C. Fu, H. Liu and F. Xiao, *Anal. Chim. Acta*, 2015, **853**, 200–206.
- S3. M. Zhang, A. Halder, C. Hou, J. Ulstrup and Q. Chi, *Bioelectrochemistry*, 2016, **109**, 87–94.
- S4. E. Aparicio-Martínez, A. Ibarra, I. A. Estrada-Moreno, V. Osuna and R. B. Dominguez, *Sens. Actuators, B*, 2019, **301**, 127101.
- S5. M. Gholami and B. Koivisto, *Appl. Surf. Sci.*, 2019, **467**, 112–118.
- S6. R.-M. Song, Z.-H. Li, P.-J. Wei, X.-L. Zhao, C. Chen and Z.-G. Zhu, *Appl. Sci.*, 2018, **8**, 848.
- S7. D. Rojas, J. F. Hernández-Rodríguez, F. Della Pelle, M. Del Carlo, D. Compagnone and A. Escarpa, *Biosens. Bioelectron.*, 2020, **170**, 112669.