

## Supplementary information

### **Synthesis of Ag nanoparticles-carbon nanotube-reduced graphene oxide hybrids for highly sensitive non-enzymatic hydrogen peroxide detection**

Yong Zhang,<sup>a,b</sup> Ziyang Wang,<sup>a</sup> Ye Ji,<sup>a</sup> Sen Liu<sup>\*a</sup> and Tong Zhang<sup>\*a,b</sup>

<sup>a</sup> State Key Laboratory of Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, Changchun, P. R. China

<sup>b</sup> State Key Laboratory of Transducer Technology, Chinese Academy of Sciences, P. R. China

\* Corresponding authors: E-mail: zhangtong@jlu.edu.cn (T. Zhang); liusen@jlu.edu.cn (S. Liu); Fax: +86 431 85168270; Tel: +86 431 85168385

## Experimental

### 1. Materials and reagents

Graphite powder and dopamine (DA) were purchased from Aladin Ltd. (Shanghai, China). Multi-walled carbon nanotube (MWCNT) was purchased from Nanjing XFNANO Materials Tech, where diameter and length are 10-20 nm and 10-30  $\mu\text{m}$ , respectively.  $\text{NaNO}_3$  (99.0%),  $\text{KMnO}_4$  (99%),  $\text{NaOH}$  (96.0%),  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  (99%),  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  (99%), ascorbic acid (AA), sodium citrate and glucose were purchased from Beijing Chemical Works (Beijing, China).  $\text{AgNO}_3$  (99.8%) was obtained from Shanghai Chemical Corp (Shanghai, China). The solvents including  $\text{H}_2\text{SO}_4$  (98%) and  $\text{H}_2\text{O}_2$  (30wt%) were supplied by Beijing Chemical Works (Beijing, China). All reagents were used directly without further purification. The deionized water used throughout all experiments was purified through a Millipore system. Phosphate buff saline (PBS) was prepared by mixing stock solutions of  $\text{NaH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$  and a fresh solution of  $\text{H}_2\text{O}_2$  was prepared daily.

### 2. Preparation of GO

GO was prepared from natural graphite powder through a modified Hummers' method.<sup>1</sup> In a typical process, 0.1 g of graphite powder was added into 2.3 mL of  $\text{H}_2\text{SO}_4$  (98%), then the mixture was stirred at room temperature for 24 h. After that, 10 mg of  $\text{NaNO}_3$  was introduced into the mixture and stirred for 30 min. Subsequently, the mixture was kept below 5  $^\circ\text{C}$  by ice bath, and 0.3 g of  $\text{KMnO}_4$  was slowly added into the mixture. After being heated to 35~40  $^\circ\text{C}$ , the mixture was stirred for another 10 min. After that, 4.6 mL of water was added into above mixture during 25 min, followed by stirring for another 25 min. Finally, 14.0 mL of water and 1.0 mL of 30 wt%  $\text{H}_2\text{O}_2$  were added into

the mixture to stop the reaction. The unexploited graphite in the resulting mixture was removed and GO was obtained by thorough washing with water and centrifugation. As-synthesized GO was dispersed into individual sheets in water at a concentration of 0.5 mg/mL with the aid of sonication for further use.

### **3. Preparation of AgNPs-CNT-rGO hybrids**

The CNT-GO aqueous dispersion was prepared by dispersing 2.5 mg of CNT into 20.0 mL of GO aqueous solution (0.5 mg/mL) by sonication for 2 h. Then, 105  $\mu$ L of AgNO<sub>3</sub> solution (0.5 M) was mixed with the above CNT-GO aqueous dispersion, followed by stirring 10 min. After the mixture was heated at 80 °C, 2.2 mL of NaOH solution (8 M) was added dropwise into the above mixture. The mixture was washed with water, and the resulting precipitate was dispersed in 20.0 mL of water and stored at 4 °C for characterization and further use.

The AgNPs-rGO hybrids were fabricated by the similar method according to the previous report.<sup>2</sup>

The CNT-rGO composites were also prepared by the similar method for preparation of AgNPs-CNT-rGO hybrids in the absence of AgNO<sub>3</sub>.

The pure AgNPs were prepared via reduction of AgNO<sub>3</sub> by sodium citrate, according to established method.<sup>3</sup>

### **4. Preparation of the modified electrode**

The modified electrodes were prepared by a simple casting method. Prior to the surface coating, the glassy carbon electrode (GCE) was polished with 1.0  $\mu$ m and 0.3  $\mu$ m alumina powder, respectively. Then the GCE was rinsed by sonication in absolute ethanol solution and water successively. 50  $\mu$ L of AgNPs-CNT-rGO aqueous dispersion was

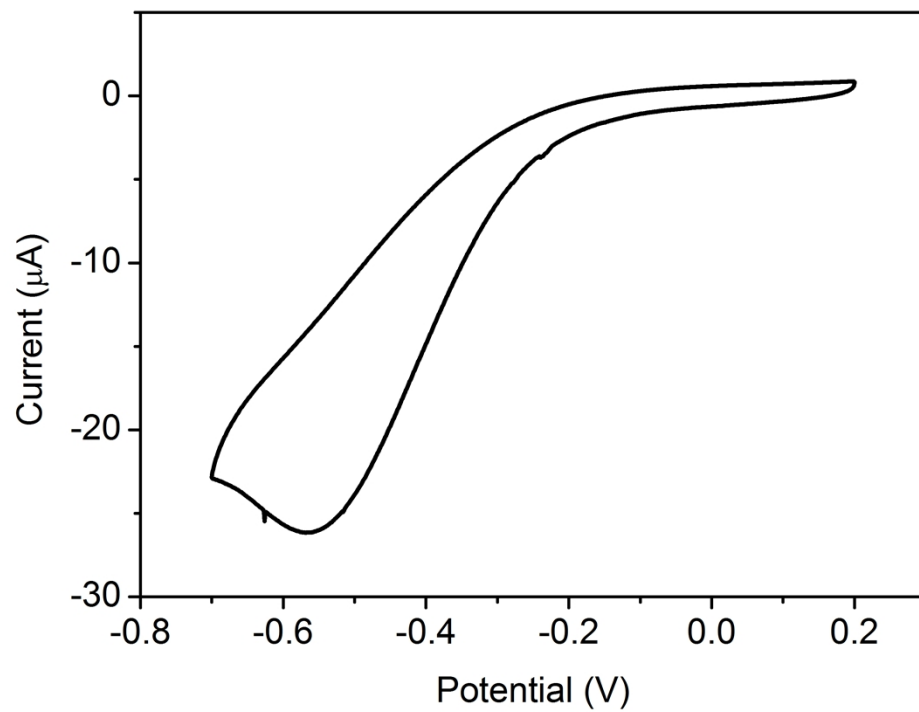
mixed with 50  $\mu\text{L}$  of Nafion solution (5%), followed by sonication 10 min. The 3  $\mu\text{L}$  of mixture dispersion was dropped onto the dry and clean surface of GCE, and dried under infrared lamp. The AgNPs-rGO/GCE was fabricated by the same method.

The AgNPs/GCE was fabricated as follow. 3  $\mu\text{L}$  of as-formed AgNPs dispersion was dropped onto the dry and clean surface of GCE, and dried under infrared lamp.

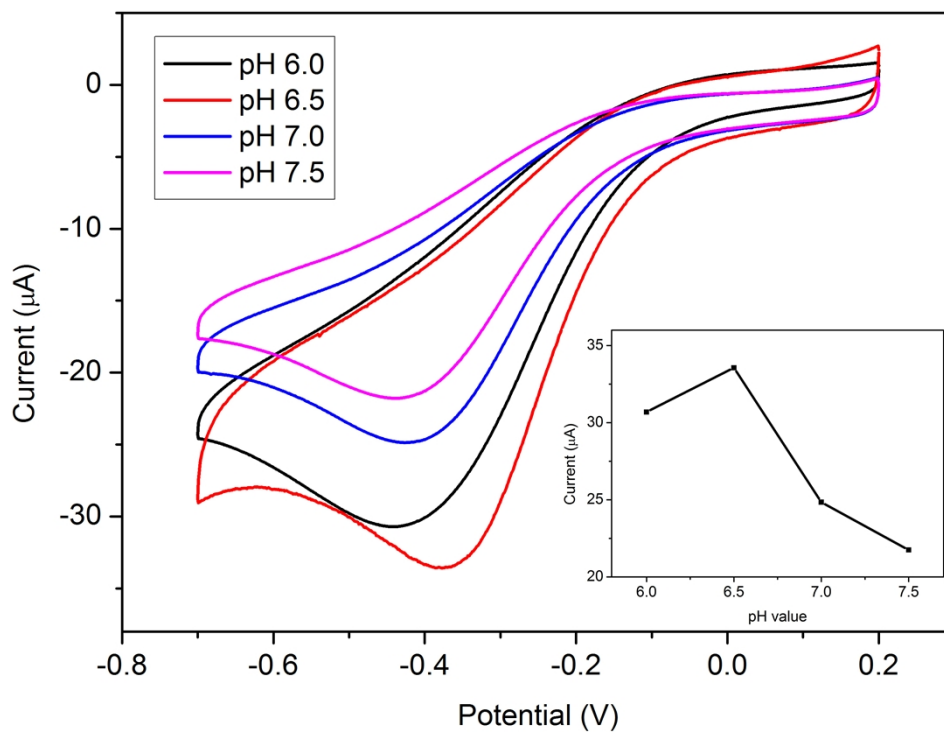
## 5. Characterizations

Raman spectra were obtained on J-Y T64000 Raman spectrometer with 514.5 nm wavelength incident laser light. Powder X-ray diffraction (XRD) data were recorded on a RigakuD/MAX 2550 diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The morphology of the samples was observed by transmission electron microscope (TEM) on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. A Perkin-Elmer TGA 7 unit was used to carry out the thermogravimetric analysis (TGA) in air at a heating rate of 10  $^{\circ}\text{C}/\text{min}$ .

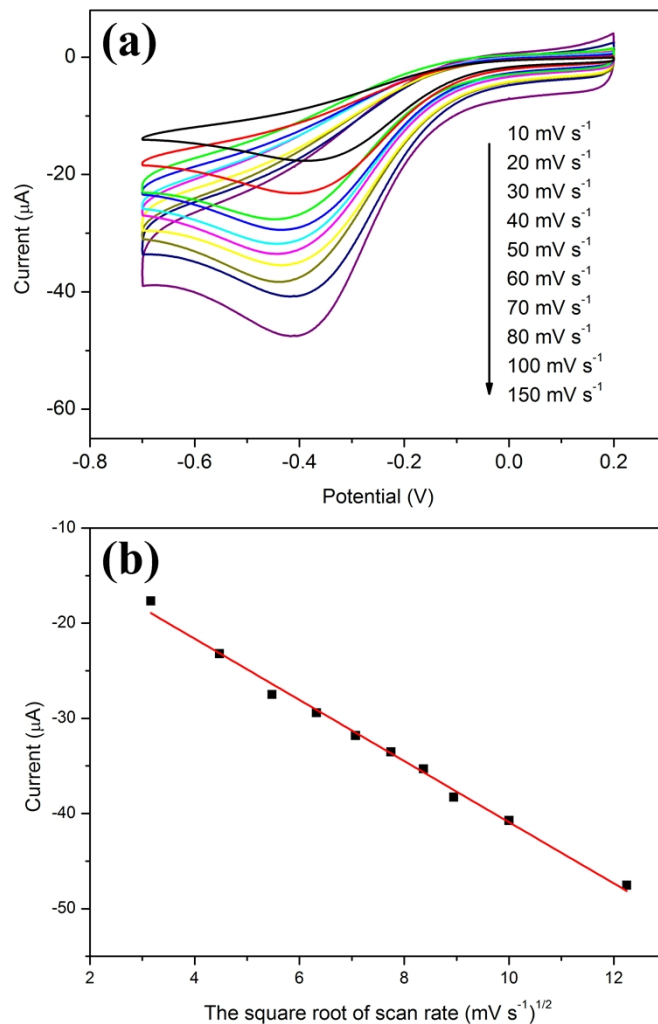
Electrochemical measurements were performed with a CHI 660D electrochemical analyzer (CH Instruments, Inc., Shanghai). A conventional three-electrode cell was used, including a GCE (geometric area = 0.07  $\text{cm}^2$ ) as the working electrode, a Ag/AgCl electrode as the reference electrode, and platinum foil as the counter electrode. All the experiments were carried out at room temperature.



**Fig. S1** Cyclic voltammogram of AgNPs/GCE in N<sub>2</sub>-saturated 0.2 M PBS at pH 6.5 in the presence of 1 mM H<sub>2</sub>O<sub>2</sub> (scan rate: 50 mV s<sup>-1</sup>).



**Fig. S2** Cyclic voltammograms of AgNPs-CNT-rGO/GCE in 0.2 M PBS with different pH from 6.0 to 7.5 (at scan rate  $50 \text{ mV s}^{-1}$  with  $1.0 \text{ mM H}_2\text{O}_2$ ). The inset was the calibration curve.



**Fig. S3** (a) Cyclic voltammograms of AgNPs-CNT-rGO/GCE at scan rates from 10 to 150  $\text{mV s}^{-1}$  (in 0.2 M PBS/ pH 6.5 with 1.0 mM  $\text{H}_2\text{O}_2$ ); (b) calibration plot of the square root of scan rate versus peak current.

**Table S1** Detection of H<sub>2</sub>O<sub>2</sub> at AgNPs-CNT-rGO/GCE in milk sample solutions.

<b>C<sub>added</sub> (μM)</b>	<b>C<sub>detected</sub> (μM)</b>	<b>Recovery (%)</b>
100	97.3	97.3
200	189.8	94.9



## References

- 1 W. S. Hummers Jr, and R. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339-1339.
- 2 J. Tian, S. Liu, Y. Zhang, H. Li, L. Wang, Y. Luo, A. M. Asiri, A. O. Al-Youbi and X. Sun, *Inorg. Chem.*, 2012, **51**, 4742-4746.
- 3 W. Lu, Y. Luo, G. Chang and X. Sun, *Biosens. Bioelectron.*, 2011, **26**, 4791-4797.