## **Supplementary Information**

## Hemin/rGO/MWCNT nanocomposites-based dual signal electrochemical aptasensor for sensitive detection of NSE

Huyue Wei<sup>1,2</sup>, Mingzhu Yang<sup>1,2</sup>, Chengshuai Huang<sup>1,2</sup>, Xiaojie Yue<sup>3</sup>, Jiabin Cai<sup>3</sup>, Xinyi Wang<sup>2</sup>, Kai Fan<sup>4</sup>, Linxi Dong<sup>1,2</sup>, Gaofeng Wang<sup>1,2</sup>, Dujuan Li<sup>1,2\*</sup>

<sup>1</sup> Ministry of Education Engineering Research Center of Smart Microsensors and Microsystems, Hangzhou Dianzi University, Hangzhou, 310018, China

<sup>2</sup> School of Electronics and Information, Hangzhou Dianzi University, Hangzhou, 310018, China

<sup>3</sup> The Children's Hospital of Zhejiang University School of Medicine, Hangzhou, 310052, China

<sup>4</sup> School of Automation, Hangzhou Dianzi University, Hangzhou, 310018, China

\* Correspondence: dujuanli@hdu.edu.cn

## 1. SEM raw image



Fig. S1. The original uncropped SEM image of the GO (Fig. 2A).



Fig. S2. The original uncropped SEM image of the MWCNT (Fig. 2B).



Fig. S3. The original uncropped SEM image of the H-rGO-MWCNT (Fig. 2C).



Fig. S4. The original uncropped SEM image of the Partial enlargement of H-rGO-MWCNT (Fig.

## 2. The catalytic mechanism of Hemin on $H_2O_2$ and the enzyme activity validation experiments with H-rGO-MWCNT.

During the electrochemical sensing process, the electrochemical interface provided an electron to reduce Fe (III) to Fe (II), which was later re-oxidized to Fe (III) during the catalytic process. This reversible conversion between FeII and Fe (III) facilitated the catalytic reaction of  $H_2O_2$ . The inferred catalytic mechanism of Hemin on  $H_2O_2$  could be elucidated as follows:

Firstly,  $H_2O_2$  was chemically adsorbed to Fe (II), the center of hemin. The activated  $H_2O_2$  then dissociated an H atom to form the Fe (II)-OOH and the H atom bound to the N atom of hemin. Subsequently, the peroxide bond in Fe (II)-OOH broke, generating Fe (III)-O and -OH. And the -OH reacted with the H atom to form  $H_2O$ . Finally,  $H_2O$  desorbed, completing the catalytic reduction of  $H_2O_2$ .

Fig. S5 depicted the absorbance of H-rGO-MWCNT under different catalytic systems at 650 nm. In the presence of TMB but without  $H_2O_2$ , H-rGO-MWCNT showed no significant absorbance peak (curve c), indicating that the oxidase-like capacity of H-rGO-MWCNT was negligible. In contrast, in the presence of  $H_2O_2$ , H-rGO-MWCNT generated a blue oxidized TMB solution (TMBox) and exhibited a distinct characteristic peak at 650 nm (curve d), demonstrating its excellent peroxidase-like capacity.



**Fig. S5.** The absorbance at 650 nm of H-rGO-MWCNT in different catalytic systems: TMB (a), TMB+H<sub>2</sub>O<sub>2</sub> (b), TMB+H-rGO-MWCNT (c), TMB+H<sub>2</sub>O<sub>2</sub>+H-rGO-MWCNT (d).

Standard concentration	Method	Found (ng/mL)	Relative error (%)
in the sample (ng/mL)			
1.2	DPV	1.417	18.05
1.2	chronoamperometry	1.39	15.83

 Table S1. Results of detecting NSE in human serum samples.