Supplementary Information (SI) for Analyst.

Neural network-shaped composite of α-MnO_2 with N-doped graphene for electrocatalytic reduction of hydrogen peroxide in human urine sample

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S1-1 Regents and Instrumentation

$MnSO_4 \cdot H_2O$, $AgNO_3$ and $(NH_4)_2S_2O_8$ were all purchased from Beijing Chemical reagent Co., Beijing, China; Chitosan (Cs) were bought from Aldrich Co., USA; H_2O_2, KCl, NaCl, $CaCl_2$, KNO_3, $CuSO_4$, Na_2SO_4, $NaNO_3$ and NH_4Cl, ascorbic acid and uric acid were brought from Tianjin Tianli Chemical reagent Co., Tianjin, China; H_2O_2 aqueous was diluted when it would be used. Appropriate proportions of KH_2PO_4 and K_2HPO_4 was used to prepare phosphate buffer (0.05 $mol \cdot L^{-1}$, pH 7.4) as the supporting electrolyte.

X-ray diffraction meter (XRD, D/MAX-III-B-40kV, Japan) was adopted to investigate the N@Gr/α-MnO_2 composite with Cu K_α radiation (λ = 1.5406) during the bragg range from 10 to 80 degree. Micromorphology of N@Gr/α-MnO_2 were performed on scanning electron microscope (SEM, Hitachi S-4800, Hitachi, Japan) at the operational power of 15.0 kV. X-ray photoelectron spectroscopy (XPS, Kratos Amicus, Manchestert, England, $h\nu$ = 1486.6 eV) was used to determine the valence state of the product within ± 0.2 eV deviation in the binding energy position with Al K_α radiation.

Tests about electrochemical were all performed on an electrochemical workstation (CHI-760E, Shanghai Chenhua

Apparatus Co., Shanghai, China) equipped with standard three-electrode system, in which the modified glassy carbon electrode with diameter of 5 mm was selected as working electrode. Platinum wire and saturated calomel electrode (SCE) were used as the auxiliary electrode and reference electrode, respectively.

S1-2 Pretreatment process of glassy carbon electrode

GCE (d=5 mm) was polished via using different sizes of alumina slurry (0.3, 0.1 and 0.05 μm) consecutively, and then treated by ultrasound wave in 50% nitric acid aqueous, absolute ethanol and deionized water, successively. Thereafter, the electrode was activated in 0.25 mol·L^{-1} H_2SO_4 by the cycled (20 cycles) potential ranged from -1.0 V to 1.0 V.

S1-3 Investigation of experiment conditions

The optimal applied potential used in this work was chosen according to comparision of amperometric response to equal amount of H_2O_2 (Fig. S1). The catalytic current of H_2O_2 increases with the decreasing of the applied potential (-0.2, -0.3, -0.4 and -0.5 V); however, the noise current also increases. When catalytic response and noise current are considered together, -0.4 V is chosen as the optimal potential in the whole determination process of H_2O_2.

Fig. S1

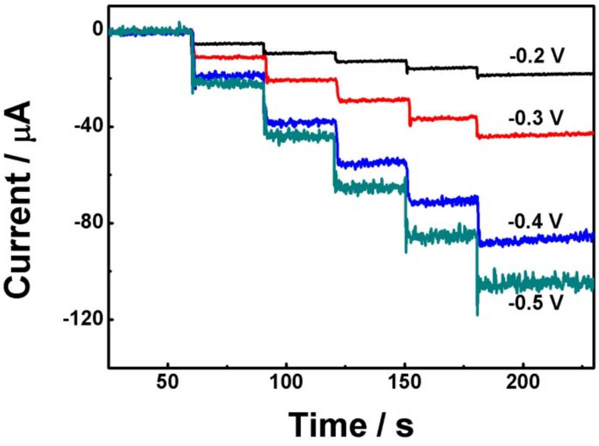

Fig. S1 Amperometric responses obtained from N@Gr/α-MnO_2/GCE in addition of H_2O_2 at different applied potentials in phosphate buffer (pH 7.4).

The effect of different pH values (5.6, 6.2, 6.8, 7.4, 8.0 and 8.6) of phosphate buffer on H_2O_2 (Fig. S2) catalytic response was also investigated. As shown in Fig. S2, the catalytic current of the system (pH = 7.4) is larger than those of other five pH values, thus, 7.4 is chosen as the optimal pH in the later experiments.

Fig. S2

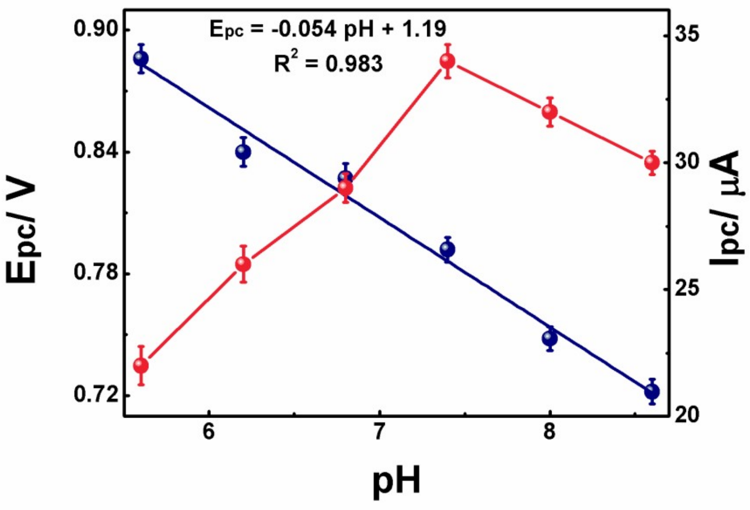

Fig. S2 The relationship of E_{pc} and I_{pc} of H_2O_2 against different pH (5.6、6.2、6.8、7.4、8.0 and 8.6) values.

The modifier content of N@Gr/α-MnO_2 (5, 10, 15, and 20 μL) on GCE was also investigated. As shown in Fig. S3, the catalytic current of 10 μL is the largest for H_2O_2 among the four modifier content. Therefore, 10 μL is chosen as the optimal modifier content.

Fig. S3

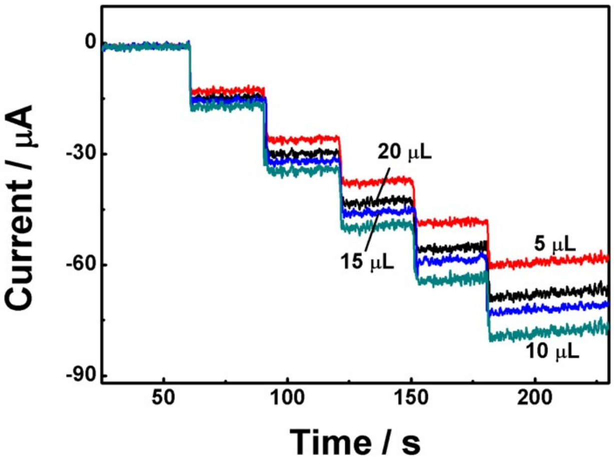

Fig. S3 Amperometric responses obtained from N@Gr/α-MnO_2/GCE with different modifier contents in phosphate buffer (pH 7.4) for H_2O_2 (applied potential : -0.4 V (vs. SCE)).

Fig. S4

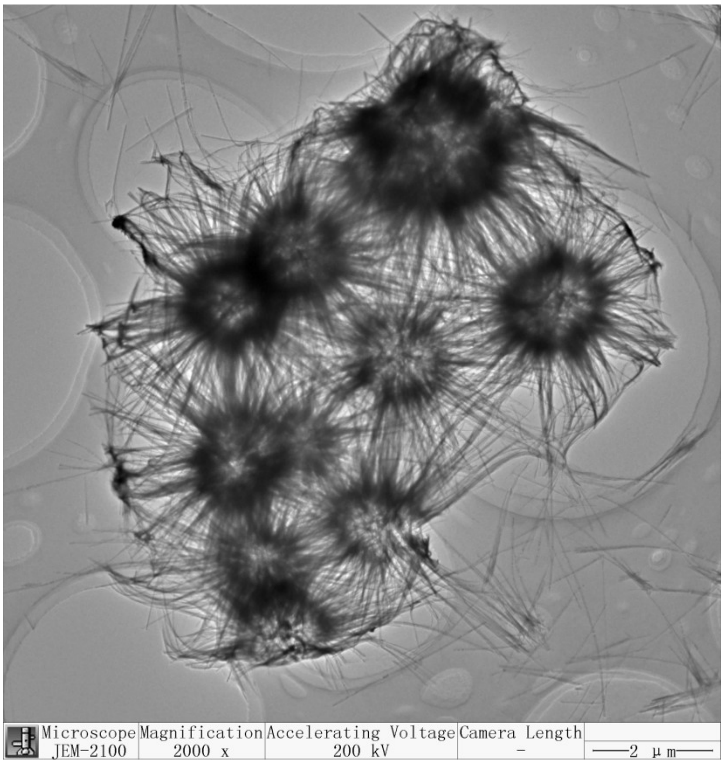

Fig. S4 TEM image of neuron-like shape of N@Gr/α-MnO$_2$

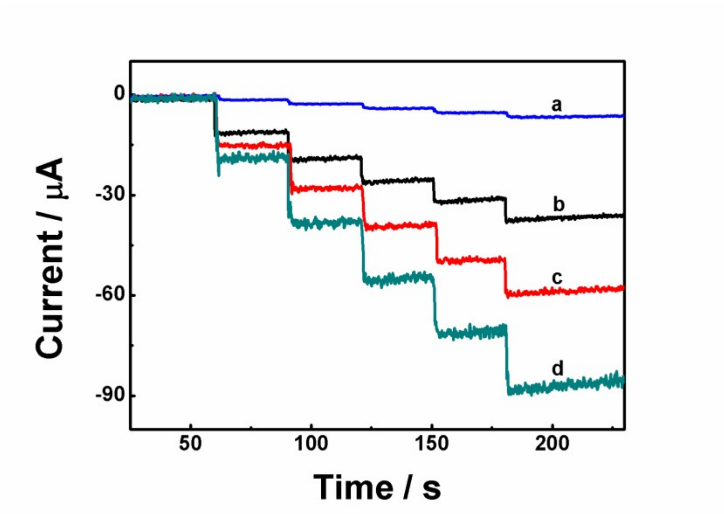

Fig. S5 Amperometric responses of different modified electrodes in H_2O_2 (a) (a: GCE; b: α-MnO_2/GCE; c: N@Gr/GCE; d: N@Gr/α-MnO_2/GCE)

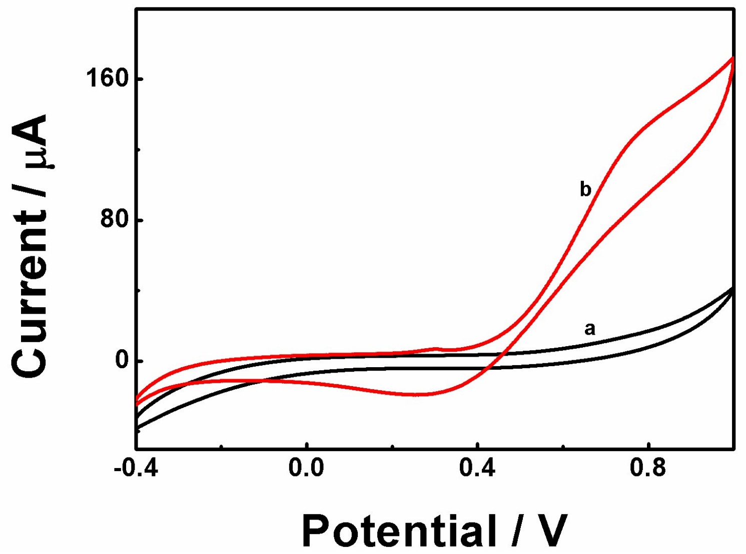

Fig. S6 CV performed without (a) and with (b) the addition of H_2O_2 under exactly the same experimental conditions