Electronic Supplementary Information

# $Co_2N_x$/Nitrogen-doped Reduced Graphene Oxide for Enzymeless Glucose Detection

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## Experiment section

### 1.1 Reduced graphene oxide (rGO) modified with poly (diallyldimethylammonium chloride) (PDDA).

In a typical preparation, graphene oxide (GO) was prepared from natural graphite by using a modified Hummers method.[1] 0.1g GO was dispersed with 50 mL of deionized water under sonication. After 30 min, 0.375 mL of aqueous hydrazine ($N_2H_4$, 35 wt%) and 3.75 mL of aqueous ammonia ($NH_3 \cdot H_2O$, 30 wt%) were added to the GO suspension in turn, stirred for 5 h at room temperature. Then, a given amount of PDDA were dropped into the solution and stirred for 5 h. The obtained solids were separated by a centrifuge and washed with deionized water and anhydrous ethanol in turn.

### 1.2 Synthesis of Co nanosheets.

The synthesis of Co nanosheets is according to our previous work.[2] Briefly, 0.2 mmol of $Co(NO_3)_2 \cdot 6H_2O$ was dissolved in 20 mL of deionized water. Equal volume of ethanol solution containing OAm (3.5 mmol $L^{-1}$) was added. After stirring for 3 min, 20 mL of toluene was added and stirred for 5 min. Then, the mixture was transferred to separatory funnel and kept for several minutes. The organic solution in upper layer was separated, washed thoroughly with water and transferred into the three-necked bottle with high-purity $N_2$ protection with stirring. After heated to 45 ºC, aqueous $NaBH_4$ (0.01 mol $L^{-1}$) was added dropwise and reacted for 2 h at the corresponding temperature. The mol ratio of $NaBH_4$ and Co ions is 5:1. After standing, the black products precipitated into water layer and were separated by magnetism. After washing by water and ethanol for several times, the Co nanosheets were obtained.

### 1.3 Electrostatic assembly of Co nanosheets and modified rGO.

A certain amount of modified rGO and Co nanosheets were dispersed into 50 mL deionized water. After 30 min sonication, the mixture was stirred for 5 h at room temperature. During the process, Co nanosheets assembled with the modified rGO through the electrostatic co-precipitation method. The resulting precipitate was washed with anhydrous ethanol, dried at room temperature, and denoted as Co/rGO.

### 1.4 Synthesis of $Co_2N_x$/NG

The prepared Co/rGO was nitrided in a tube furnace at 500 ºC for 2 h with a flowing $NH_3$ rate of 100 mL·min$^{-1}$. After natural cooling, the black $Co_2N_x$/NG samples were obtained. At the same time, in order to study the effect of nitridation temperature and the ratio of Co and rGO on the electrocatalytic performance, the different samples of $Co_2N$/NG were also prepared (the detailed experimental parameters were displayed in **Table S1**). In addition, in order to compare electrocatalytic performance, N-doped reduced graphene oxide (NG) was also prepared by using 3 mol·L$^{-1}$ HCl to remove $Co_2N_x$.

**Table S1** The experimental parameters of the synthesized $Co_2N_x$/NG composites.

| Samples | The initial dosage ratio of Co and rGO (g) | Nitridation temperature (ºC) | Cobalt content calculated from TG analyses (%) |
|---|---|---|---|
| **$Co_2N_x$/NG-500-1** | 5:1 | 500 | 77.70 |
| **$Co_2N_x$/NG-500-2** | 3:1 | 500 | 72.77 |
| **$Co_2N_x$/NG-500-3** | 7:1 | 500 | 82.14 |
| **$Co_2N_x$/NG-400-1** | 5:1 | 400 | 77.70 |
| **$Co_2N_x$/NG-800-1** | 5:1 | 800 | 77.70 |

### 2.1 Characterization

Scanning electron microscopy (SEM) images were recorded with a Hitachi S-4800 field emission scanning electron microscope operating at 15 kV. Transmission electron microscopy (TEM) images were performed on a JEM-3010 electron microscope (JEOL, Japan) with an acceleration voltage of 300 kV. X-ray diffraction (XRD) patterns were obtained by a Rigaku D/max-IIIB diffractometer using Cu Kα radiation ($\lambda$ = 1.5406 Å). X-ray photoelectron spectroscopy (XPS) measures were performed with AXIS UL TRA DLD. Thermogravimetric (TG) analysis was performed on TA Q600 under a stream of air at a heating rate of 10 ºC min$^{-1}$.

### 3.1 Electrochemical measurements

Electrochemical experiments were performed in a conventional three-electrode system, using a saturated calomel electrode (SCE) and a Pt sheet as the reference and the counter electrode, respectively. A 0.4 cm diameter glass carbon (GC) used as working electrode was polished with 30 nm $Al_2O_3$ paste, followed by washing with water and isopropanol. Five milligrams of material mixed with 50 $\mu$L of 5 wt % Nafion ionomer was dispersed in 0.1 mL of ethanol solution. After the material ink was sonicated for 0.5 h, a volume of the ink was dropped on a GC electrode and left to dry. An electrolyte of 0.1 M NaOH solution was used. Electrochemical activity and stability of material to glucose were tested with a BAS 100B electrochemical workstation. Electrochemical impedance spectra (EIS) were performed using Versa STAT 3 in 0.1 M KCl containing 2 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1:1) mixture.

## Results and disccussion

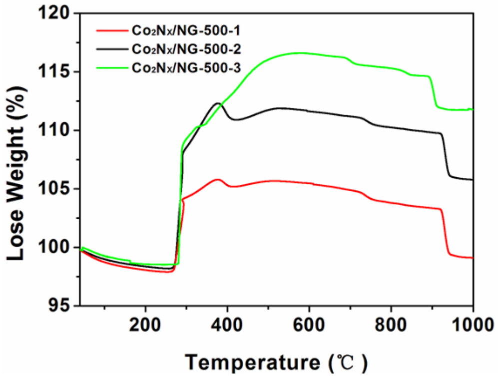

**Fig. S1** TG curves of $Co_2N_x$/NG-500-1, $Co_2N_x$/NG-500-2, and $Co_2N_x$/NG-500-3.

Fig. S2 shows the XRD patterns of $Co_2N_x$/NG nitrided at different temperatures. Diffraction peaks can't be identified until the nitridation temperature reaches 400 ºC. Co gradual transforms into $Co_2N_x$ (including $Co_2N$ and $Co_2N_{0.67}$) and then to $Co_{5.47}N$, as the nitridation temperature increases. When the nitridation temperature reaches 500 ºC, four high-intensity crystal peaks at 41.58º, 42.82º, 44.12º, and 48.51º can be perfectly assigned to the diffraction from (002), (111), (021), and (021) planes of the orthorhombic $Co_2N$, respectively (JCPDS: 06-0647). The crystal peaks at 44.35º can be perfectly assigned to the diffraction from (101) plane of the hexagonal $Co_2N_{0.67}$ (JCPDS: 06-0691). With increasing the nitridation temperature up to 600 ºC, the diffraction peaks of $Co_{5.47}N$ appear and the cubic $Co_{5.47}N$ is the main phase at 800 ºC (JCPDS: 41-0943).

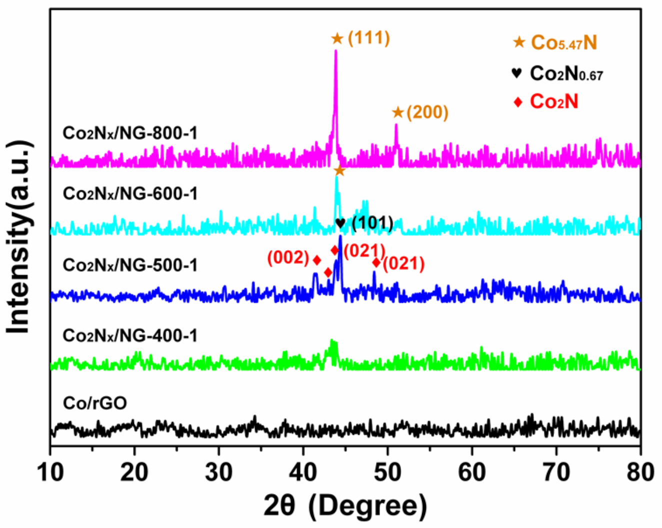

**Fig. S2** Typical XRD patterns of $Co_2N_x$/NG prepared at different nitriding temperature.

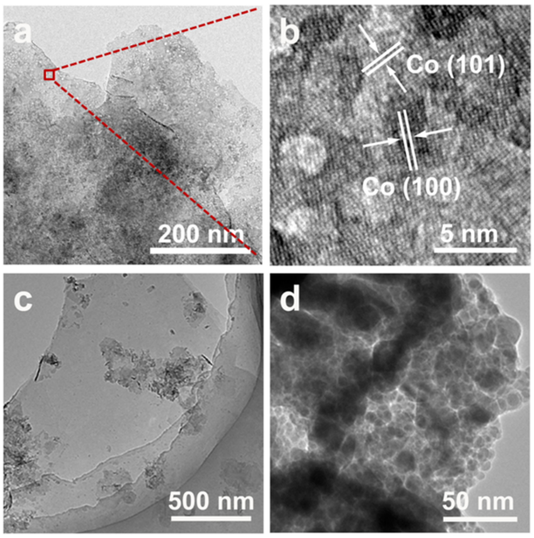

**Fig. S3** Typical TEM images of Co nanosheets (a, b), Co/rGO (c) and $Co_2N_x$ prepared at 500 ºC (d).

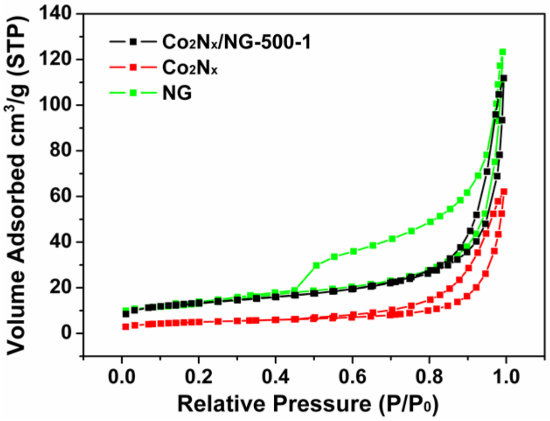

**Fig. S4** $N_2$ adsorption-desorption isotherms of $Co_2N_x$/NG-500-1, NG and $Co_2N_x$.

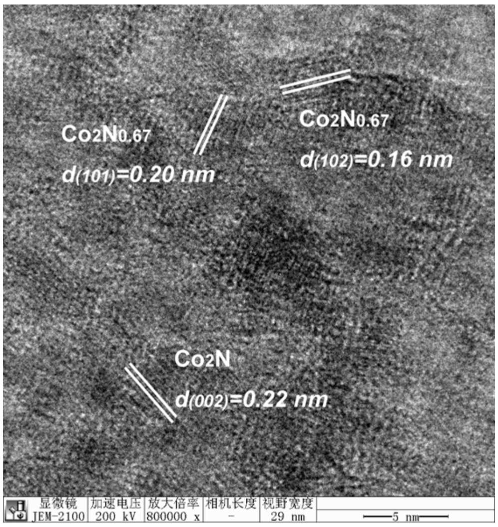

**Fig. S5** HRTEM images of $Co_2N_x$/NG-500-1 (the original image of Fig. 2c)

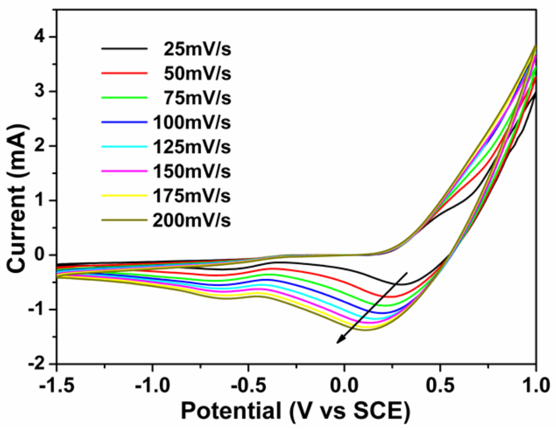

**Fig. S6** CVs of $Co_2N_x$/NG-500-1 electrode in 0.1 M NaOH aqueous solution measured at different scan rates (25-200 mV·s$^{-1}$).

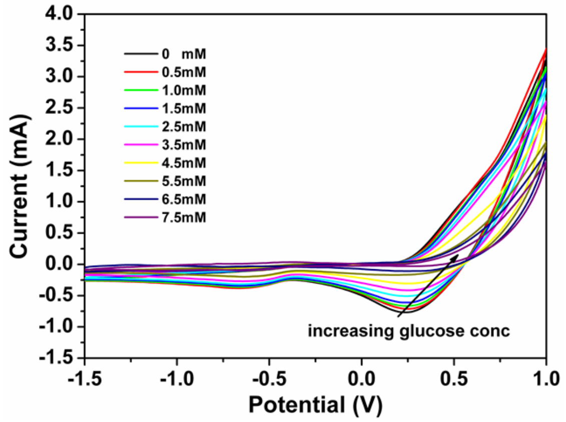

**Fig. S7** CVs of $Co_2N_x$/NG-500-1 electrode in 0.1 M NaOH aqueous solution with different glucose concentrations (0-7.5 mM).

**Table S2.** Comparison of the analytical performance of different glucose biosensors.

| Electrode materials | Detection limit (μM) | Sensitivity (mA mM$^{-1}$ cm$^{-2}$) | Linear range (mM) | Response time (s) | Ref. |
|---|---|---|---|---|---|
| **$Co_3O_4$ NPs** | 0.13 | | 0.005-0.8 | 6 s | 3 |
| **$Fe_3O_4$ NPs** | 200 | | 0.5-10 | | 4 |
| **3D GE/$Co_3O_4$** | 0.025 | 3.39 | --0.08 | | 5 |
| **GE/$Co_3O_4$** | 10 | | 0.05-0.3 | | 6 |
| **Ni-rGO** | 1 | 0.813 | 0.001-0.11 | | 7 |
| **RGO-Ni(OH)$_2$** | 0.6 | 0.011 | 0.002 -3.1 | | 8 |
| **CuO/GO** | 0.69 | 0.263 | 0.028-2.03 | | 9 |
| **Cu-Co-Ni** | 3.05 | 0.105 | 0.01-4.30 | | 10 |
| **$Co_2N_x$/NG-500-1** | **6.93** | **1.167** | **0.01-4.75** | **5 s** | **This work** |

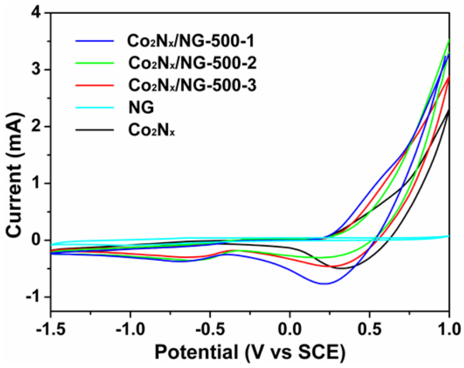

**Fig. S8** CVs of $Co_2N_x$/NG-500-1, $Co_2N_x$/NG-500-2, $Co_2N_x$/NG-500-3, $Co_2N_x$, and NG electrodes in 0.1 M NaOH aqueous solution, scan rate: 50 mV $s^{-1}$.

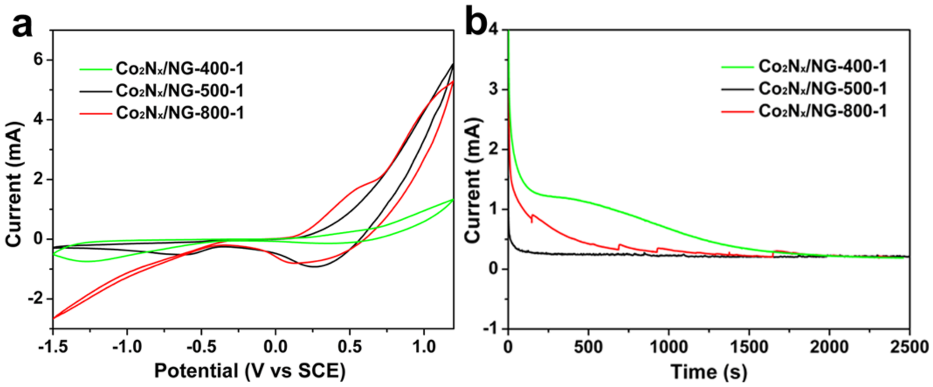

**Fig. S9** (a) CVs of $Co_2N_x$/NG-400-1, $Co_2N_x$/NG-500-1 and $Co_2N_x$/NG-800-1 electrodes in 0.1 M NaOH aqueous solution, scan rate: 50 mV $s^{-1}$. (b) Chronoamperometric curves for $Co_2N_x$/NG-400-1, $Co_2N_x$/NG-500-1 and $Co_2N_x$/NG-800-1, constant voltage test under 0.25 V vs SCE.

## Notes and references

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