Supplemental Information

3D graphene network@WO₃ nanowires composite: a multifunctional

colorimetric and electrochemical biosensing platform

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1. Experimental

1.1. 3DGN

As described in previous study¹, the 3DGN was synthesized by CVD on 1.5 mm \times 1 cm \times 1 cm

nickel foam under atmosphere pressure. The samples were first heated to 1000 $^{\circ}$ C with the flow of H₂ and Ar (H₂/Ar = 150:300 sccm). Then 15 sccm CH₄ was introduced into the quartz tube to synthesize the graphene in 10 min. After the growth, the samples were rapidly cooled down to room temperature in 10 min with the protection of H₂ and Ar to get the Ni/graphene 3D network.

1.2. 3DGN@WO₃ nanowires

12.5 mmol Na₂WO₄, 35 mmol H₂C₂O₄ and 100 mmol (NH₄)₂SO₄ was dissolved into 250 mL deionized water, which resulted in the formation of yellowish precursor. Then the as-prepared 40 mL precursor was transferred into a Teflon-lined stainless autoclave (50 mL volume), and 0, 200, 500 or 1000 μ L HCl was added to the solution to control the morphology of WO₃ product. For the next step, put 1 cm ×1 cm as prepared Ni/graphene 3D network into the autoclave and heated to 180 $^{\circ}$ C for 18 hours. At last, the products were immersed into 1 M HCl and 1 M FeCl₃ solution at 80 $^{\circ}$ C to etch away the nickel foam.

1.3. WO₃/GCE

Glass carbon electrode (GCE, diameter 3 mm) was first polished with 0.3 and 0.05 μ m alumina slurries and washed with ethanol and double-distilled water three times, then GCE was dried at room temperature. 10 mg as prepared WO₃ powder was dispersed into 5 ml 1% (wt%) chitosan solution. Then 20 μ l solution was dropped onto the GCE and dried overnight naturally.

1.4. Instruments and Characterization

The morphology of samples were characterized with HITACHI S-4800 electron microscopy (SEM) and Tecnai F20 transmission electron microscopy (TEM). Raman spectra were recorded at ambient temperature on a Labor Raman HR-800 system with 514.532 nm wavelength laser. The X-ray diffraction (XRD) was carried out on a PANalytical B.V. Empyrean 200895 (Netherland) using Cu K α radiation. X-ray photoelectron spectroscopy were tested by ESCALAB 250Xi.

The UV-Vis absorption spectra were obtained with a SHIMADZU UV-3600 spectrophotometer (Japan). When testing the colorimetric sensing property, one piece of 1.5 mm ×0.5 cm ×0.5 cm 3DGN or $3DGN@WO_3$, or 1.33 mg WO₃ powder (the same weight with $3DGN@WO_3$) were dropped into 10 ml 0.5 mM TMB solution with continuous stirring.

The typical procedure of recycling in colorimetric sensing of H_2O_2 and AA is like this: after the introduction of $3DGN@WO_3$ and $400 \ \mu M \ H_2O_2$, the solution would turn into sky blue in five minutes and then its absorbance at 652 nm was measured through which the sensitivity to H_2O_2 can be calculated. After that, $60 \ \mu M$ AA was dropped into the solution with continuous stirring and in one minute, the reaction would reach a balance when the absorbance at 652 nm was measured and the according sensitivity to AA was calculated. After that, the piece of $3DGN@WO_3$ was recollected from the solution by tweezers and washed by ethanol and water twice. To begin the next round of testing, one only need to repeat the procedure above using the same piece of $3DGN@WO_3$.

All the electrochemical experiments were carried out with a CHI 760e (U.S.) electrochemical workstation. A three-electrode system was employed in all the electrochemical experiments. Rinsed by ethanol and water twice, the $3DGN@WO_3$ were griped by a Pt clip which is connected to the electrochemical workstation. The $3DGN@WO_3$ composite served as the working electrode, while a platinum electrode and a Ag/AgCl electrode were used as the counter and reference electrodes respectively. All the experiments were carried out in 0.1 M pH = 7.2 PBS solution.

Procedure of stability tests: Twelve samples were used in the stability test and these samples were stored in open air condition. Every four days three samples were picked to test their colorimetric and electrochemical sensing of H_2O_2 , AA and DA. The whole test lasted for 12 days.

2. Results and Discussions



Fig. S1 SEM/TEM images of WO₃ NWs powder and 3DGN. (a-b) low to high magnification SEM images of WO₃ NWs powder; (c-d) low to high magnification TEM images of WO₃ NWs powder, (d inset) SEAD of WO₃ NWs powder; (e-g) low to high magnification SEM images of 3DGN; (h) TEM image of crushed 3DGN pieces.



Fig. S2 the XRD spectra of 3DGN and 3DGN@WO₃.



Fig. S3 Raman spectra of 3DGN. Two characteristic peaks, G and 2D peaks at 1581 cm⁻¹ and 2725 cm⁻¹ respectively can be easily observed and no peaks at 1350 cm⁻¹ indicates good quality and the lack of defects.



Fig. S4 XPS of 3DGN@WO₃. The three characteristic peak of WO₃ i.e., W4f_{7/2} at 35.7 eV, W4f_{5/2} at 37.8 eV and W5p_{3/2} at 41.7 eV can be observed.



Fig. S5 Nyquist plots of electrochemical impedance spectroscopy of WO_3/GCE , 3DGN and 3DGN@WO₃ in 0.1 M PBS (pH 7.2) in the frequency range of 0.1 Hz to 100 kHz.



Fig. S6 Time-dependent absorbance changes at 652 nm of WO $_3$ NWs powder, 3DGN and 3DGN@WO $_3$ in 0.5 mM TMB 0.4 mM H $_2O_2$ solution.



Fig. S7 CV curves of 3DGN@WO₃ at different scan rates (50, 60, 70, 80, 90 and 100 mV/s) in 0.4 mM dopamine solution. Inset is the plot of anodic peak current vs. V^{1/2}. The peak at about 0.49 V corresponds to the oxidation of DA while the peak at about -0.07 V corresponds to the intercalation of protons in WO₃.²



Fig. S8 Stability of $3DGN@WO_3$ sensing H_2O_2 , AA and DA. We can see the overall sensitivity can still be above 98% in 12 days.



Fig. S9 3DGN@WO₃ DPV responses to AA and DA with 20 mV modulation amplitude and 5 mV step potential. Two peaks at -0.02 V and 1.5 V can be ascribed to AA and DA respectively. And the response to DA is much stronger than that to AA which further confirm the good selectivity to DA.

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- 2. D. J. Kim, S. I. Pyun and Y. M. Choi, *Solid State Ion.*, 1998, **109**, 81-87.