Supporting Information

Gold/SH-functionalized Nanographene Oxide/ Polyamidamine/Poly(ethylene glycol) Nanocomposite for Enhanced Non-enzymatic Hydrogen Peroxide Detection

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Experimental Section

Materials

Graphite powder (Aldrich, 99.99+%), potassium permanganate (KMnO₄, Aldrich, 99%), sulfuric acid (H₂SO₄, Aldrich, 95~98%), sodium nitrate (NaNO₃, Aldrich, 99%), 2-aminoethanethio (Aladdin, 98%), HAuCl₄·H₂O (Aldrich, 99%), citric sodium (Aldrich, 99%), sodium triacetoxyborohydride ((CH₃COO)₃BHNa, Aldrich, 99%) and hydrogen peroxide (H₂O₂, Aladdin, 30%) were used as received. Six-armed PEG with six amino end groups (6-armed PEG-NH₂, $M_n = 10,000$ g/mol) was purchased from Ponsure Biotech. Inc. (Shanghai, China). *N*-hydroxysuccinimide (NHS, Aldrich, 99%), *N*-(3-(dimethylamino)propyl)-*N*'-ethylcarbodiimide hydrochloride (EDC·HCl, Aldrich, 99%), 3-mercaptopropionic acid (MPA, Aldrich, 99%), Nafion (5% EtOH solution) and polyamidamine dendrimer with amino terminal groups (G1/G3-PAMAM-NH₂) were purchased from J&K Scientific.

Measurements

UV/vis absorption spectra were acquired by a Hitachi U-2910 spectrophotometer. X-ray diffraction (XRD) measurements were run by a Philips X'Pert PRO X-ray powder diffractometer with CuK α (1.541Å) radiation (40 kV, 40 mA), the samples were exposed at a scan rate of $2\theta = 0.04244^{\circ}/s$ in the range from 5° to 80°. Unpolarized Raman scatterings were recorded performed on a Thermo Scientific DXR spectrometer (532 nm line from a semiconductor laser, scan number: 3, power at the sample: ~6.8 mW). Inductively coupled plasma mass spectrometry (ICP-MS) was performed on a PerkinElmer Elan 9000 instrument operating under normal Ar plasma conditions (1400 W forward plasma power, 17 L/ min Ar plasma gas flow, 1.2 L/min auxiliary Ar flow and 0.95 L/min nebulizer Ar flow). Atomic force microscope (AFM) images were taken by a JPK Nano Wizard Sense system in the AC mode of dropping the sample solution onto the freshly exfoliated mica substrate. Scanning electron microscope (SEM) images were taken by a FEI Nova NanoSEM 450 instrument. Transmission electron microscopy (TEM) images were taken by a JEOL JEM-1230 instrument operated at 80 kV. Cyclic voltammetry (CV) measurements were carried out at room temperature using a CH660E instrument. A conventional 3 electrodes system was employed for all the measurements using a glassy carbon electrode ((GCE, 3 mm in diameter), Ag/AgCl (NaCl, 3 M) electrode and a Pt wire as the working, reference and counter electrode, respectively.

Preparation of nanographene oxide

Graphene oxide (GO) was prepared from graphite powder through a modified Hummer's method.¹ Graphite powder was oxidized by concentrated H₂SO₄, NaNO₃ and KMnO₄ in low-temperature (0°C), and room-temperature (35°C) followed by adding H₂O₂ (30%) slowly while the color of solution changed from black to yellow, then the resultant suspension was extensively washed with distilled water by filtration and finally subjected to dialysis to remove residual salts and acids. The preparation of nanographene oxide (NGO) was based on the breakage of GO by ultra-sonication process. The as-prepared GO suspension was subjected to ultra-sonication by a SONICS VCX750 instrument operated at 20 KHz for 1 hour in ice bath.²

Preparation of NGO-PEG

NGO aqueous dispersion was pre-treated with NaOH followed by adding 6-armed PEG-NH₂ and EDC·HCl for sonication at room temperature for 1 h, ultimately the mixed solution was kept stirring vigorously at room temperature for 24 h. The final product, GO-PEG, was obtained by purifying the crude product by dialysis (MW_{cutoff} = 14 kDa) against the double-distilled water for 1 week to remove unbound 6-armed PEG-NH₂.³

Preparation of thiol-modified NGO-PEG

NGO-PEG aqueous dispersion (20 mL, 0.05 wt%) was mixed with cysteamine (10 mg) and KOH (5 mg), the homogeneous dispersion was vigorously stirred at 80°C for 24 h. Finally, the resulting product was dialyzed ($MW_{cutoff} = 3.5$ kDa) against the double-distilled water for several days to remove residual salts and basics.⁴

Preparation of thiol-modified G1/G3-PAMAM-NGO-PEG

NGO-PEG aqueous dispersion (30 mL, 0.05 wt%) was mixed with G1-PAMAM-NH₂ (100 mg) and KOH (6 mg), the homogeneous dispersion was vigorously stirred at 80°C for 12 h. The resulting dispersion was dialyzed ($MW_{cutoff} = 14$ kDa) against the double-distilled water, providing G1-PAMAM-NGO-PEG. MPA (63 mg) was activated by EDC/NHS (molar ratio of MPA:EDC:NHS = 1:4:4) in aqueous solution

at room temperature for 5 h. G1-PAMAM-NGO-PEG dispersion (45 mL) was treated with activated MPA at 30°C for at least 12 h, affording thiol-modified G1-PAMAM-NGO-PEG. Finally, the product was dialyzed ($MW_{cutoff} = 14$ kDa) against the doubledistilled water for several days to remove residual salts and basics.⁵ Similar procedure was utilized for preparing thiol-modified G3-PAMAM-NGO-PEG aqueous solution.

Preparation of AuNPs@NGO-PEG

Thiol-modified NGO-PEG aqueous dispersion (25 mL, 2 mg/mL) was mixed with HAuCl₄·H₂O (0.26 mL, 0.24 mM) followed by vigorous stirring at room temperature for 30 min. Citric sodium (0.92 mL, 0.17 mM) was then added into the solution quickly followed by stirring at 80°C for 1 h. The final product, AuNPs@NGO-PEG dispersion (0.05 mg/mL), was obtained after dialysis (MW_{cutoff} = 14 kDa) against the double- distilled water. The concentration of Au in AuNPs@NGO-PEG dispersion was determined to be ~1.21 mg/L by ICP-MS.⁶

Preparation of AuNPs@G1/G3-PAMAM-NGO-PEG

Thiol-modified G1-PAMAM-NGO-PEG aqueous dispersion (2 mL, 0.4 mg/mL) was mixed with HAuCl₄·H₂O (0.05 mL, 0.24 mM) followed by vigorous stirring at room temperature for 10 min. (CH₃COO)₃BHNa (0.05 mL, 1.0 mM) was then added into the solution quickly followed by stirring at room temperature for 8 h. The final product, AuNPs@G1-PAMAM-NGO-PEG dispersion (0.2 mg/mL), was obtained after dialysis (MW_{cutoff} = 14 kDa) against the double-distilled water. Similar

procedure was used for preparing AuNPs@G3-PAMAM-NGO-PEG aqueous solution. The concentration of Au in AuNPs@G1-PAMAM-NGO-PEG and AuNPs@G3- PAMAM-NGO-PEG dispersion were determined to be ~3.72 mg/L and ~4.02 mg/L, respectively, by ICP-MS.⁶

Modification of electrode and electrochemical analysis

Prior to use, a glassy carbon electrode (GCE) was cleaned through mechanical polishing by using 1.0 μ m and 0.3 μ m alumina slurry for 2 min, following by sonication in deionized water for 30 s and rinsed with ultrapure water. Modification of GCE surface with AuNPs@NGO-PEG, AuNPs@G1-PAMAM-NGO-PEG and AuNPs@G3-PAMAM-NGO-PEG dispersion was performed by drop casting of 20 μ L of dispersion and drying at 50°C for 20 min. The resulting electrodes were labeled as GCE/AuNPs@NGO-PEG, GCE/AuNPs@G1-PAMAM-NGO-PEG and GCE/AuNPs@G3-PAMAM-NGO-PEG. All the CV measurements were carried out 5 times for presenting average results. For the electrochemical detection of H₂O₂, different amounts of H₂O₂ were added to PBS solution (0.1 M, 6 mL) to record the corresponding current. Current *vs.* time curve was conducted at -0.4 V in 6 mL of stirred solution.⁷



Scheme S1. Preparation of AuNPs loading on thiol-modified PEG-functionalized NGO (AuNPs@NGO-PEG).



Scheme S2. Preparation of AuNPs loading on thiol-modified PEG and PAMAM dualfunctionalized NGO (AuNPs@G1/G3PAMAM-NGO-PEG).



Figure S1. TGA (in N₂) curves of NGO, PEG, PAMAM, thiol modified NGO-PEG, thiol modified G1-PAMAM-NGO-PEG and thiol modified G3-PAMAM-NGO-PEG with a heating rate of 10°C/min.



Figure S2. (A) UV/vis absorption spectrum, (B) XRD pattern, (C) TEM image and

(D) AFM image and lateral dimension statistic of AuNPs@G3-PAMAM-NGO-PEG.



Figure S3. (A) UV/vis absorption spectrum, (B) XRD pattern, (C) TEM image and

(D) AFM image and lateral dimension statistic of AuNPs@NGO-PEG.



Figure S4. SEM images of (A) AuNPs@NGO-PEG, (B) AuNPs@G1-PAMAM-NGO-PEG and (C) AuNPs@G3-PAMAM-NGO-PEG; and (D) Raman spectra of AuNPs@NGO-PEG, AuNPs@G1-PAMAM-NGO-PEG and AuNPs@G3-PAMAM-NGO-PEG (the spectra consist of D, G, 2D and D+D' bands located at 1343, 1599, 2679 and 2934 cm⁻¹).



Figure S5. CV curves of GCE/AuNPs@G1-PAMAM-NGO-PEG response to (A) different H_2O_2 concentrations (scan rate: 50 mV s⁻¹) and (B) H_2O_2 (20 mM) at varied scan rates.



Figure S6. CV curves of GCE/AuNPs@G3-PAMAM-NGO-PEG response to different H_2O_2 concentrations (scan rate: 50 mV s⁻¹).



Figure S7. Typical ready-state amperometric responses to increased H₂O₂ concentration for GCE/AuNPs@NGO-PEG and GCE/AuNPs@G1-PAMAM-NGO-PEG.

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