

[Supporting Information]

Fabrication of Nanoelectrode Ensembles by Electrodeposition of Au Nanoparticles on Single-Layer Graphene Oxide Sheets

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In order to characterize the NEEs, SiO₂ was used as substrate to fabricate NEEs in the same experimental conditions shown in Scheme 1. Figure S1 shows the Raman spectrum of GO adsorbed on SiO₂.

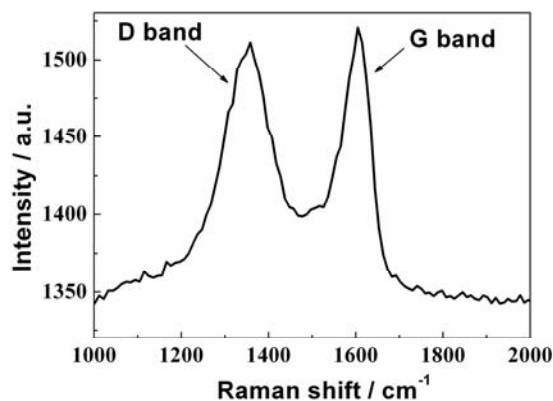


Figure S1. Raman spectrum of GO adsorbed on SiO₂. Laser wavelength: 488 nm.

XPS was used to characterize NEEs formed on SiO₂, *i.e.* SiO₂-GO-AuNP. In Figure S2A, two peaks appeared and they were attributed to C-C and C-O, respectively. In Figure S2B, the peaks at 84.1 and 88.0 eV arose from Au4f_{5/2} and Au4f_{7/2}, respectively, indicating the formation of Au NPs.^[S1]

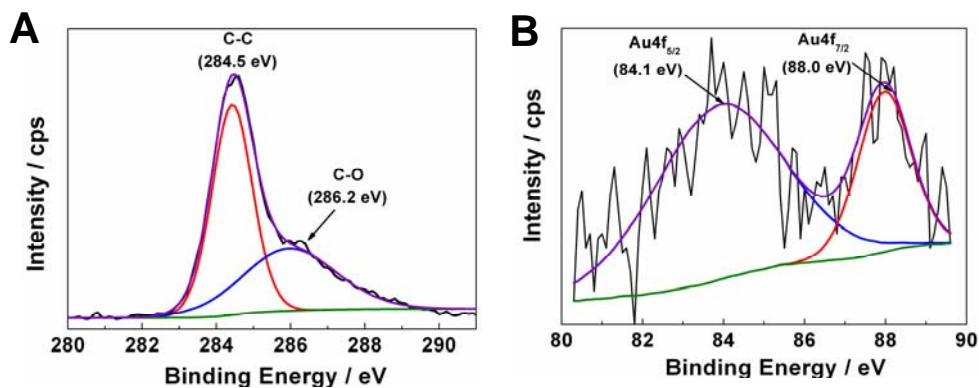


Figure S2. (A) C1s and (B) Au4f XPS of SiO₂-GO-AuNP. Fitting parameters were chosen for a consistent fit for all samples in the series (black lines for raw data, purple lines for total fits, and olive lines for background).

SEM image (Figure S3A) shows the morphology of SiO₂-GO-AuNP electrode. It can be seen that single-layer GO sheets are decorated with AuNPs. The density of AuNPs is low and the average separation between the neighbouring AuNPs is much larger than the size of AuNPs (35 ± 10 nm), which prevent the diffusion layer overlap between the neighboring AuNPs (Figure S3B).^[S2] The density of AuNPs can be controlled by the electrodeposition time. As shown in Figure S4, at electrodeposition time of 0.5 s, the GCE-GO-AuNP electrode gives the CV shape similar to the classic macroelectrode, arising from the high density of AuNPs. When the electrodeposition time is decreased to 0.1 s, the CV curve gives a typical sigmoidal shape. However, if the electrodeposition time is too short, *i.e.* 0.05 and 0.02 s, the conductivity of the GCE-GO-AuNP decreases greatly and NEEs cannot be formed (Figure S4). Therefore, 0.1 s was chosen as the optimal electrodeposition time to fabricate NEEs in our experiments.

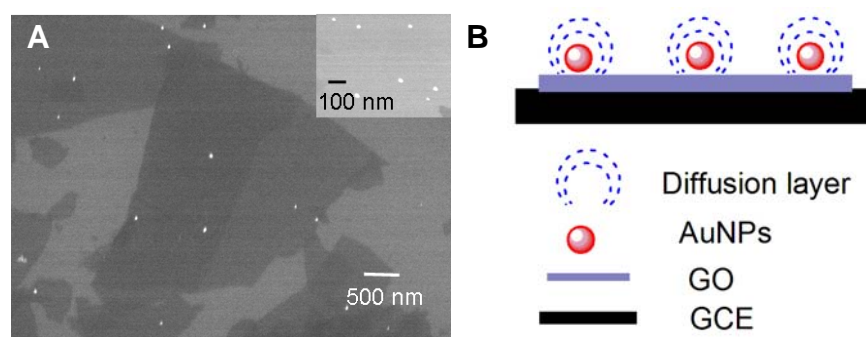


Figure S3. (A) SEM image of AuNPs deposited on GO films adsorbed on APTES-modified SiO₂, *i.e.* SiO₂-GO-AuNP electrode. (B) Schematic illustration of NEEs.

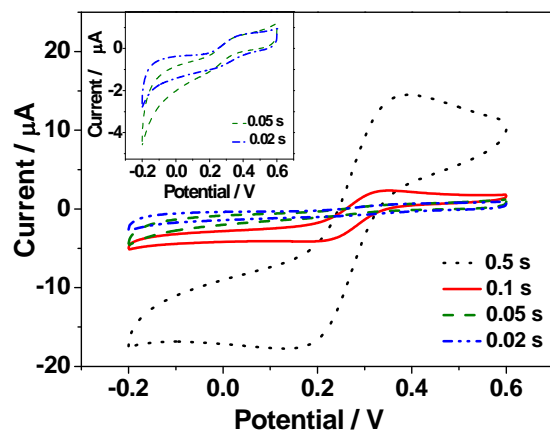


Figure S4. Cyclic voltammograms of $K_3[Fe(CN)_6]$ (5.0 mM) at the GCE-GO-AuNP electrodes prepared at different electrodeposition time (0.02, 0.05, 0.1 and 0.5 s) in 1.0 M KCl solution. Scan rate: 50 mV/s.

GCE modified with 3-Aminopropyltriethoxysilane (APTES), which was referred as to GCE-APTES, was decorated with AuNPs using electrodeposition method. The obtained electrode, GCE-APTES-AuNP, was measured in 5.0 mM $K_3[Fe(CN)_6]$ solution (Figure S5). The results showed that only a few of GCE-APTES-Au electrodes gave sigmoidal shaped voltammetric profiles (dashed line in Figure S5) in different batches of samples. Most of the samples have not shown this kind of profiles (solid line in Figure S5).

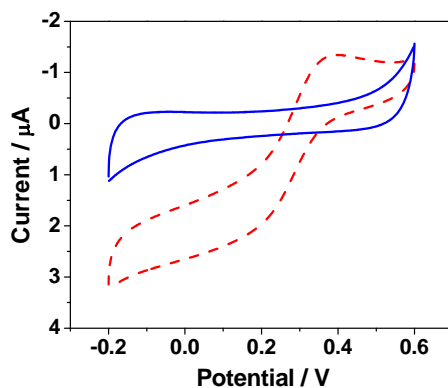


Figure S5. Cyclic voltammograms of $K_3[Fe(CN)_6]$ (5.0 mM) at GCE-APTES-AuNP prepared in different batches in 1.0 M KCl solution. Scan rate: 50 mV/s.

The intercalation time of methylene blue (MB) affects the amount of MB into dsDNA as well as the electrochemical performance. The effect of intercalation time of MB on current was examined and the results are shown in Figure S6. The pronounced electrochemical response at such a low concentration (10 μM) showed that MB molecules were intercalated into dsDNA tightly through the electrostatic and intercalation binding,^[S3] and the electrochemical activity of MB was kept well (Figure S6A). In addition, the current intensity increased gradually with the intercalation time. But when the time was longer than 50 min, the current increased slowly (Figure S6B). Considering the current response and intercalation time, 30 min were chosen as MB intercalation time in all experiments.

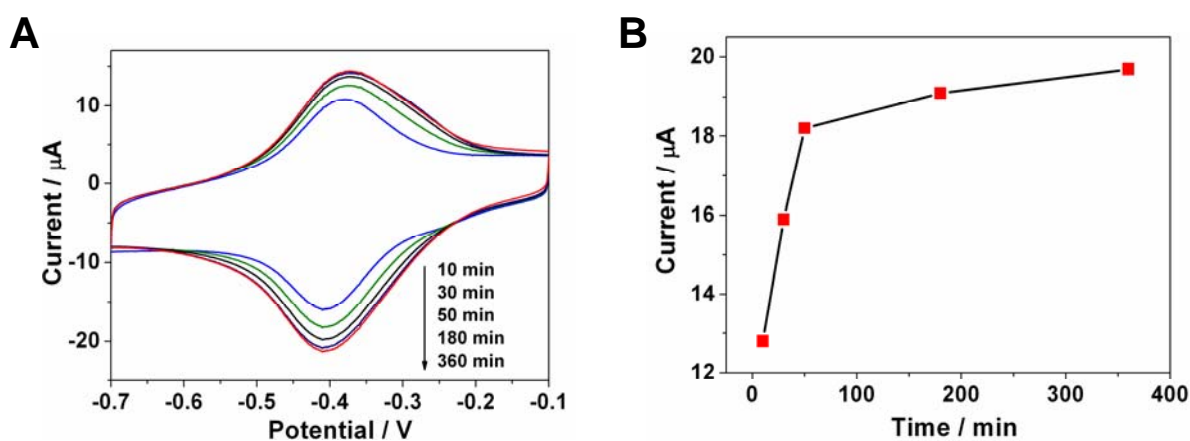


Figure S6. (A) Cyclic voltammograms for the redox reaction of MB intercalated into dsDNA at different intercalation time in 0.01 M PBS buffer containing 0.4 M NaNO_3 . Scan rate: 50 mV/s. (B) Plot of current vs. intercalation time.

The Nyquist plots for GCE-GO, GCE-GO modified with Probe DNA2 (ssDNA) (*i.e.* GCE-GO-ssDNA) and then modified with hybridized DNA (GCE-GO-dsDNA), and the equivalent circuit model for GCE-rGO-dsDNA are shown in Figure S7. The diameter of the semicircle represents the resistance of charge transfer. The impedance of GCE-GO is high due to its poor conductivity. After the adsorption of ssDNA on GCE-GO, the impedance decreased. Compared with GO, ssDNA was described as semiconductor,^[S4] and the impedance decreased although the presence of electrostatic repulsion

between ssDNA and $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox indicators. After hybridization with target DNA, the diameter of semicircle further decreased, which might result from the good conductivity of dsDNA due to its full hybridization.^[S5]

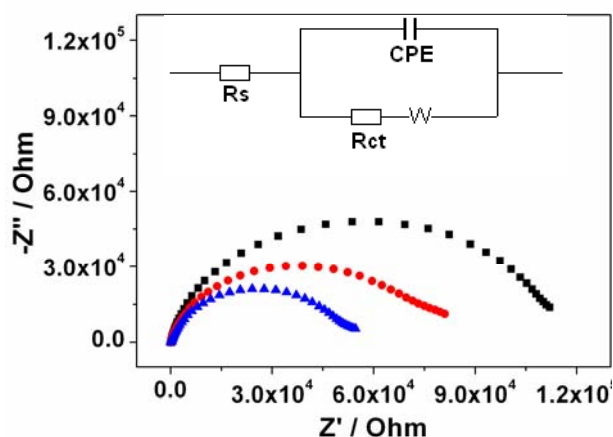


Figure S7. Nyquist plots at bare GCE-GO (■), GCE-GO-ssDNA (●), and GCE-GO-dsDNA (▲). Inset: The equivalent circle model for GCE-rGO-dsDNA. R_s: solution resistance; R_{ct}: resistance of charge transfer; CPE: constant phase element; W: Warburg impedance. The concentration of cDNA used here is 10⁻⁶ M. Frequency range: from 0.1 to 100 000 Hz; Electrolyte: 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ (1:1) in 0.01 M phosphate buffer solution (pH 7.4) containing 0.1 M KCl; amplitude: 5 mV.

The ssDNA can also be anchored on GO surface of NEEs through non-covalent bonding and then hybridized with target DNA, referred to as GCE-GO-AuNP/ssDNA and GCE-GO-AuNP/dsDNA, respectively. After intercalated with MB solution for 30 min at room temperature, GCE-GO-AuNP/dsDNA was scanned in the solution containing 5.0 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$. But there is not any reduction peak for $[\text{Fe}(\text{CN})_6]^{3-}$. Since ssDNA and dsDNA did not connect with AuNPs through the covalent bonding, the electron cannot transfer from the electrode surface to MB through dsDNA, resulting in the termination of reduction of $[\text{Fe}(\text{CN})_6]^{3-}$.

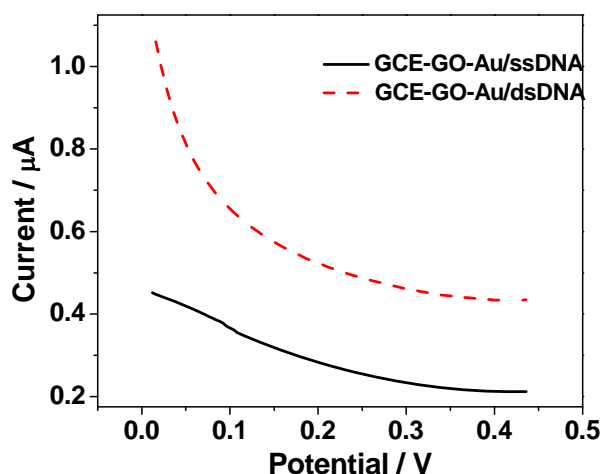


Figure S8. DPV curves for GCE-GO-Au/ssDNA (solid line) and GCE-GO-Au/dsDNA intercalated with MB (dashed line). The concentration of cDNA is 10 μM . Electrolyte: 5.0 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ in 0.01 M PBS buffer containing 0.4 M NaNO_3 . The concentration of MB solution is 10 μM . The intercalation time is 30 min. Scan rate: 50 mV/s.

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