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Supplementary Information

Ag-TiO₂-reduced graphene oxide hybrid film for electrochemical detection of 8-hydroxy-2'-deoxyguanosine as an oxidative DNA damage biomarker

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[†]Electronic supplementary information (ESI) available: UV and FTIR spectra, EIS spectroscopy results and stability measurements.



The UV–Vis spectroscopy of GO and rGO was shown in Fig. S1[†]. The strong absorption peak at 231 nm is a characteristic peak of GO which is assigned to π – π * transition of aromatic C=C bond, and a shoulder at around 300 nm is due to n– π * transition of C=O bond in the structure of GO. In the spectrum of rGO, a gradual red shift of the 231 nm peak towards 260 nm can be seen that suggesting the restoration of π -conjugation network of rGO after the reduction of GO. Furthermore, the gradual disappearance of plasmon peak at 300 nm confirms the removal of oxygen groups in rGO.^{S1}



Fig. S2 FT-IR (a) and Raman (b) spectra of GO and rGO.

FT-IR and Raman spectra were recorded and the obtained spectrum of GO and rGO confirmed the successful reduction of GO (Fig. S2[†]). The peaks of GO at 1030 cm⁻¹, 1150 cm⁻¹, 1610 cm⁻¹, 1720 cm⁻¹, and 3300 cm⁻¹ represented C–O, C–OH, C=C, C=O, and O–H, respectively. As illustrated in Fig. S2a, all the intensities of the peaks corresponding to the oxygen groups in the structure of rGO were decreased as compared with those of GO and even some were disappeared.^{S2} This result confirms that GO is successfully reduced to rGO by hydrazine. In Fig. S2b, the Raman spectrum of GO and rGO indicated the appearance of D and G peaks at around 1350 cm⁻¹ and 1600 cm⁻¹, respectively that show the lattice distortions. The ratios of I_D/I_G peak intensity were also calculated as 0.93 for GO and 1.03 for rGO.^{S3} These results show that GO was successfully reduced to rGO.

Electrochemical impedance spectroscopy (EIS) can determine the interfacial changes of modified electrodes. Fig. S3[†] illustrates the Nyquist plots of EIS in the presence of 0.01 M Fe(CN)₆^{3-/4-} in 0.1 M KCl solution for bare electrode, rGO modified electrode and Ag-TiO₂-rGO modified electrode. The electron transfer resistance (R_{ct}) at the modified electrodes can be estimated from the diameter of the semicircle. The R_{ct} value of the bare electrode (8000 Ω) is larger than that of the Ag-TiO₂-rGO modified electrode (2000 Ω). The R_{ct} value of the Ag-TiO₂-rGO has the lowest semicircle compared to the other modified electrode.^{S4} On the other hand; the rGO plot showed similar result with that of previous study.^{S5} These results indicate that the modification of electrode with Ag-TiO₂-rGO enhanced the conductivity between the analyte and the electrode surface.



Fig. S3 Electrochemical impedance spectroscopy (EIS) of the bare electrode, rGO modified electrode and Ag-TiO₂-rGO modified electrode.

The electrochemically active surface areas of various modified electrodes (bare SPE, rGO/SPE, Ag-TiO₂/SPE, and Ag-TiO₂-rGO/SPE) were calculated by the Randles-Sevcik equation.^{S6} The calculated surface areas for bare SPE, rGO/SPE, Ag-TiO₂/SPE, and Ag-TiO₂-rGO/SPE were 0.0828, 0.100, 0.102, and 0.113 cm², respectively. The higher surface area value of Ag-TiO₂-rGO/SPE showed the effect of used nano-hybrid as an effective sensing material, which facilitates the electron transfer between the electrode surface and the target compound.^{S7}



Fig. S4 Stability of Ag-TiO₂-rGO/SPE (Each data point of graph is based on measuring the current response of 2 μ M 8-OHdG in 0.1 M PBS, pH 7.4).

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