Supporting Information

Perylene Derivatives Bridged Au-Graphene Nanohybrid for Label-Free HpDNA Biosensor

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10 **Materials**

Graphite powder (320 mesh) was of spectroscopically pure reagent and purchased from Shanghai Chemicals, China. $HAuCl_4 \cdot 3H_2O$ (99.9%), 3,4,9,10-Perylene tetracarboxylicdianhydride (PTCDA, 97%), and tris(hydroxymethyl)aminomethane (Tris) were got from Sigma-Aldrich, USA. N-(3-Aminopropyl)-imidazole (98%) and 3-bromopropylamine 15 hydrobromide (98%) were obtained from Alfa Aesar, USA. Hydrazine solution (50% in water) was obtained from Beijing Yili Chemicals, China. Ammonia solution (25% in water) was got from Beijing Chemicals, China. Sodium dodecylsulfate (SDS) was purchased from Shanghai Reagent Company, China. Other reagents were of analytical grade and used as received. All aqueous solutions were prepared with ultrapure water from a Millipore Milli-Q Plus (>18 MΩ) 20 system.

The 32-base synthetic oligonucleotide probe (hpDNA), its complementary DNA (cDNA) (target DNA, conserved sequence of the human immunodeficiency virus 1 (HIV-1) pol gene) and single-base mismatched sequence were all obtained from Sangon Biotechnology Inc. (Shanghai, China). The corresponding base sequences were shown as following: hpDNA: 5′-
25 SH-$(CH_2)_6$-<u>CGGCCA</u> GCT TGC CAA TGA T*C*T GTC CA<u>T</u> <u>GGC</u> <u>CG</u>-3′; cDNA: 5′-TGG ACA GAT CAT TGG CAA GC-3′; single-base mismatched DNA: 5′-TGG ACA *A*AT CAT

TGG CAA GC-3′. All oligonucleotide stock solutions (1.0×10^{-4} M) were prepared by using Tris-HCl solution (pH 7.0), then stored at 4 °C for further use. More diluted solutions were obtained by diluting the stock solution with ultrapure water. The hybridization solution was diluted with $2 \times$ SSC (pH 7.0), which is made up of NaCl (0.30 M) and sodium citrate tribasic

5 dihydrate ($C_6H_5Na_3O_7 \cdot 2H_2O$; 0.030 M).

Apparatus and characterization

Fourier transform infrared (FTIR) spectroscopy was recorded on a Bruker Tensor 27 Spectrometer. Ultraviolet-visible (UV-Vis) absorption spectra were recorded on a Hitachi U-3900 spectrophotometer. Fluorescence emission spectra were recorded using a Hitachi F-4600

10 fluorescence spectrophotometer with an excitation wavelength of 491 nm. Zeta potentials were measured by dynamic light scattering (Malvern Nano-ZS, U.K.). X-ray photoelectron spectrum (XPS) was carried out on an ESCALAB MK II X-ray photoelectron spectrometer to evaluate the composition of the samples. Transmission electron microscopy (TEM) was applied to observe the morphology and size of graphene and AuNPs, which was conducted using a JEOL

15 2000 transmission electron microscope at an accelerating voltage of 200 kV.

Cyclic Voltammetry (CV) were performed using a conventional three-electrode cell with glassy carbon electrode(GCE) (3-mm diameter) as the working electrode, Ag/AgCl (KCl-saturated) as reference electrode and a platinum wire as the counter electrode in a CHI 660 Electrochemical Work-station (CHI). Electrochemical impedance spectroscopy (EIS)

20 measurements were performed under open-circuit conditions in Solartron 1255B Frequency Response Analyzer (Solartron Inc., U.K.) with the frequency range from 100 kHz to 1 mHz and an alternate voltage of 5 mV. The supporting electrolyte was 2.0 mM $K_3[Fe(CN)_6]$ and 2.0 mM $K_4[Fe(CN)_6]$ (1:1) solution containing 0.1 M KCl.
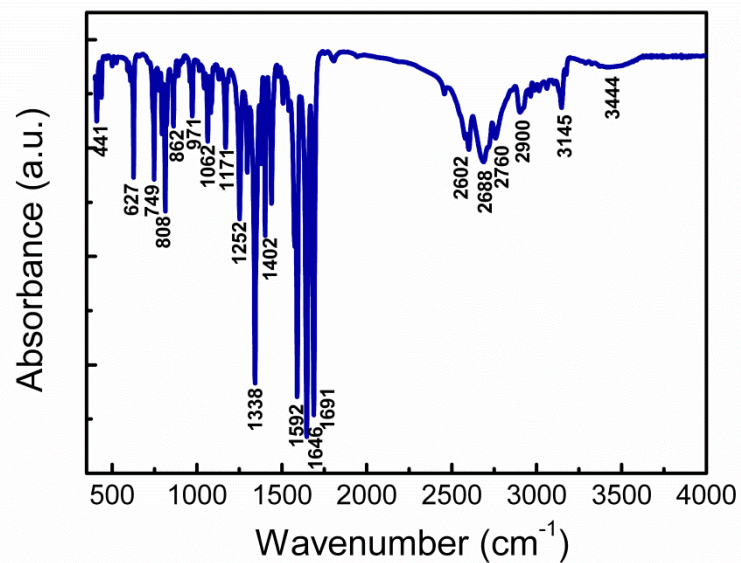
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Fig. S1. FTIR spectrum of PDI molecule

Table S1

The characteristic peaks of GO, graphene, PDI and PDI-graphene.

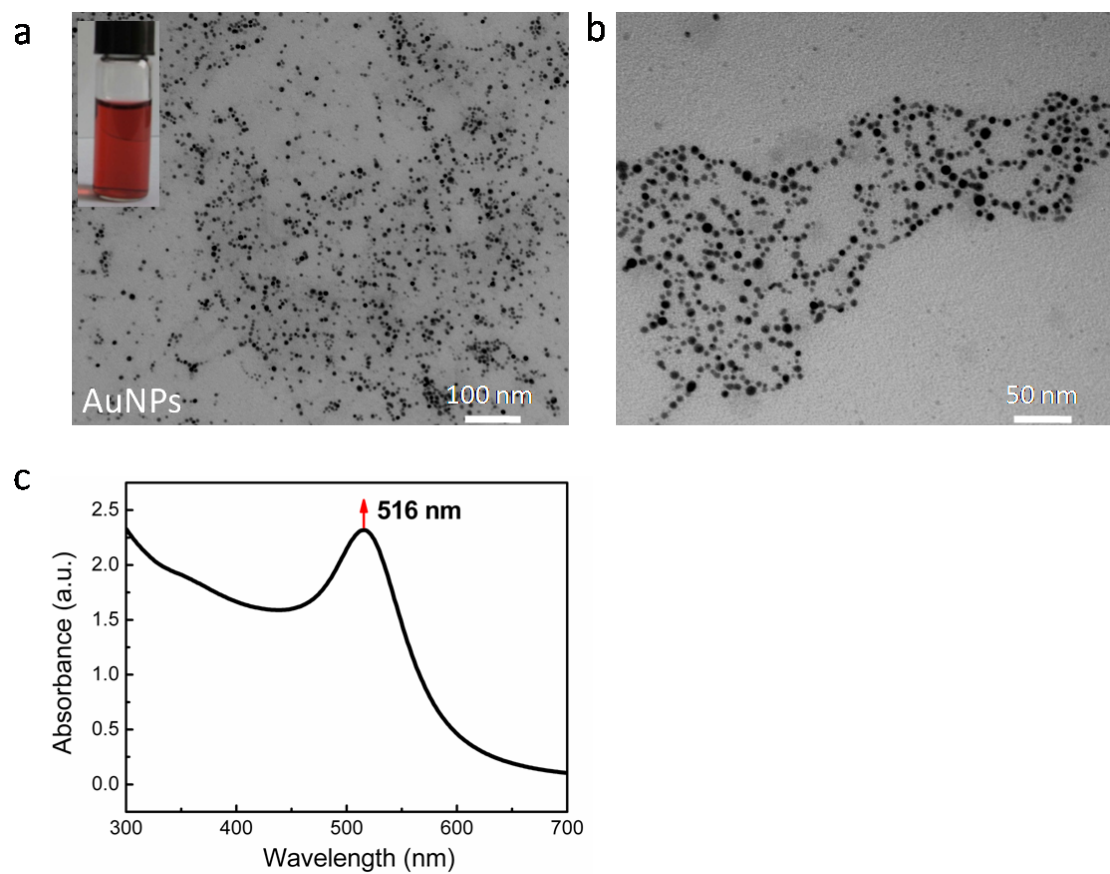|	υ(O-H)/cm^{-1}	υ(C=C)/cm^{-1}	υ(C=O)/ cm^{-1}	υ(N-C=O)/cm^{-1}	υ(N-H)/cm^{-1}
GO	3258	1637	1727	–	–
graphene	–	1573	1654	–	–
PDI	–	1592	1691	1646	3444
PDI-graphene	–	1591	1687	1648	3380

[a] Footnote text.

Fig. S2† TEM images of AuNPs at low magnification (a) and high magnification (b), Inset: the photograph of AuNPs dispersions in ultrapure water; (c) The UV-vis spectrum of AuNPs.
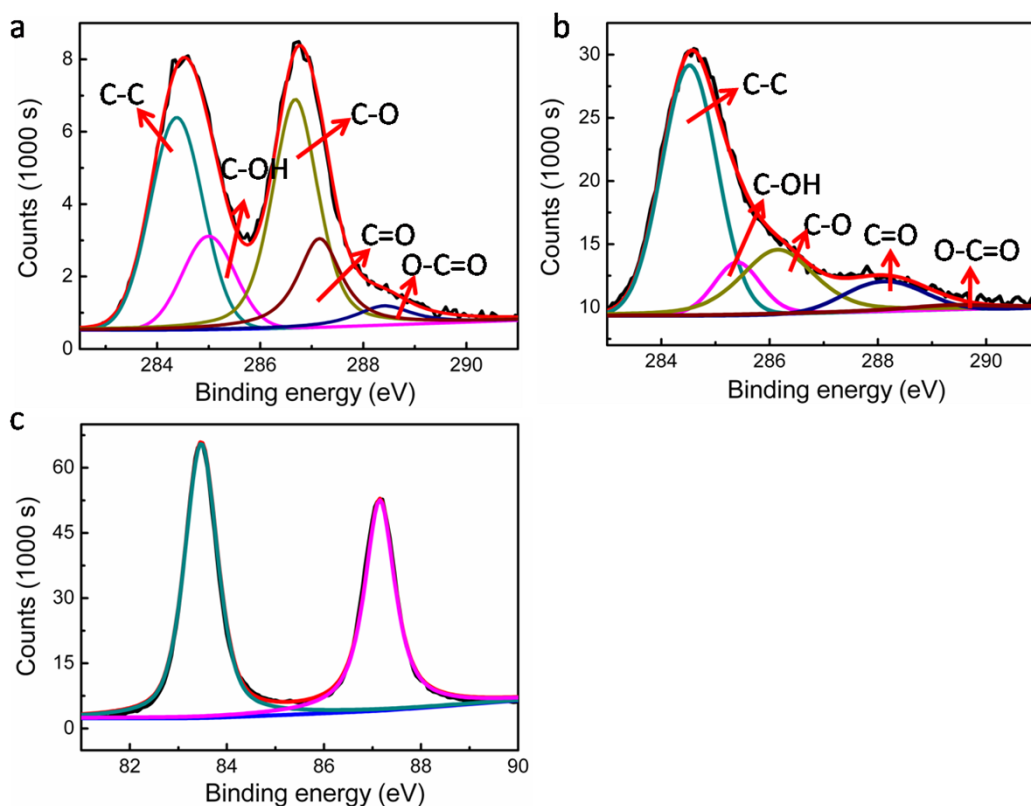
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Fig. S3† The XPS spectra the C1s of GO (a) and graphene (b), Au4f of AuNPs on Au-PDI-graphene platform (c). The decomposition in curve components is shown in different color curve underneath the experimental data points.

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Table S2 Comparison of the proposed platform with others for specific DNA sequence hybridization detection using EIS.

Method	1	2	3	This work
Platform	four layer graphene	Au-graphene	PDI-graphene	Au-PDI-graphene
Detection range(M)	$3\times10^{-13}\sim3\times10^{-10}$	$5\times10^{-14}\sim5\times10^{-9}$	$1.0\times10^{-12}\sim1.0\times10^{-6}$	$1.0\times10^{-14}\sim1.0\times10^{-10}$
Detection limit(M)	6.6×10^{-12}	1×10^{-14}	5.5×10^{-13}	1.2×10^{-15}

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