ESI for Nanoscale

One-Step Coelectrodeposition-Assisted Layer-by-Layer Assembly of Gold Nanoparticles and Reduced Graphene Oxide and its Self-Healing Three-Dimensional Nanohybrid for Ultrasensitive DNA Sensor

Kumarasamy Jayakumar[a,c,e], María Belén Camarada[b], Venkatraman Dharuman[a,], Huangxian Ju[c], Ramendra Sundar Dey[d,*], and Yangping Wen[e,*],*

[a]Department of Bioelectronics and Biosensors, Alagappa University, Karaikudi-630003, India.E-mail: mail: dharumanudhay@yahoo

[b]Universidad Bernardo OHiggins, Centro Integrative de Biología y Química Aplicada(CIBQA), General Gana 1702, Santiago, Chile

[c] Key Laboratory of Analytical Chemistry for Life Science, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, P. R. China.

[d]Institute of Nano Science and Technology (INST), Habitat Centre, Sector 64, Phase-10, S.A.S. Nagar, Mohali-160064, Punjab, India.
Email: rsdey@inst.ac.in

[e]Institute of Functional Materials and Agricultural Applied Chemistry, Jiangxi Agricultural University, Nanchang 330045, PR China.
Email; wenyangping1980@gmail.com

Synthesis of GO

Graphene oxide (GO) was prepared from graphite following modified Hummers method. Namely, 1 g graphite, 1 g $NaNO_3$, and 50 ml H_2SO_4 were stirred together in an ice bath. Ten minutes later, $KMnO_4$ (3 g) was slowly added under stirring conditions. The temperature was controlled at 20 °C initially for 1 hour and raised to 35°C during subsequent hours. After that, 50 ml de-ionized water was added gradually, and the temperature was increased further to 98 °C. After 15 minutes; the mixture was filtered, washed repeatedly using both 150 ml de-ionized water and 10 ml 30% H_2O_2 solution until the pH of the filtrate was 7 and dried at 65 °C under vacuum. The synthesized GO was characterized by field emission SEM and TEM.

Formula

Equation 1.

$$La = 2.4 \times 10^{-10} \lambda_{laser}{}^{4} \times IG/ID \qquad (1)$$

In the above equation [1], the in-plane size (L_a) of IG and ID are band intensities of G and D bands, λ laser is the wavelength of the used laser (514.5 nm, Ar source).

1. E. Ahn, T. Lee, M. Gu, M. Park, S.H. Min, B.S. Kim. *Chem. Mater.* 2017, **29**, 69-79.

Equation 2.

$$i_p = 2.69 \times 10^5 n^{3/2} \alpha^{1/2} D^{1/2}\, A\, C\, \upsilon^{1/2} \qquad (2)$$

In the above equation [2], I_p is peak current, *n* is a number of electron transfer, *A* is an area of an electrode, α is the transfer coefficient, *D* is diffusion coefficient, v is scan rate, ϑ is transferred coefficient, and *C* is a concentration of the bulk solution.

2. A,J. Bard, L.R. Faulkner, J. Leddy, C.G. Zoski, Electrochemical methods: fundamentals and applications. New York: Wiley, 1980.

Equation 3.

$$K_{et} = RT/n^2F^2AR_{ct}C^0 \qquad (3)$$

In the above equation [3], *K*et is heterogeneous electron transfer rate constant, *A* is an electrod area (cm^2), *R* is gas constant ($J\ K^{-1}mol^{-1}$), *T* is temperature (K), *F* is Faraday constant, n is a number of electrons transfer, R_{ct} is the electronic transfer resistance, and C^O is a concentration of the redox probe in bulk solution.

3. Z.B. Stoynov, B.M. Grafov, B.S. Savova-Stoynov, V.V. Elkin, Electrochemical Impedance, Nauka, Moscow 1991.

Equation 4

$$K_{app} = \psi(\pi nF\upsilon D)^{\frac{1}{2}}\{D_R/D_O\}^{\alpha/2} \quad (4)$$

In the Nicholson equation [4], K_{app} is the apparent heterogeneous rate constant, ψ is a dimensionless charge transfer parameter related to ΔE_p, n is the symbol of the number of electrons transferred during the electrode reaction, α is the transfer coefficient, υ is the scan rate, D_R and D_O are the diffusion coefficient of the reduced and oxidized species, and other symbols have their usual meanings.

4. R.S. Nicholson, Anal. Chem. 1965, **37**(11), 1351-1355.

Equation 5.

$$E_{int} = E_{AB} - E_{A(AB)} - E_{B(AB)}$$

Where E_{int} is BSSE–corrected interaction energy, E_{AB} is the total energy of the complex, $E_{A(AB)}$ represents the total energy of rGO with ghost atoms in place of gold atoms, and $E_{B(AB)}$ corresponds to the total energy of the gold cluster of the complex with ghost atoms for the rest of the system.

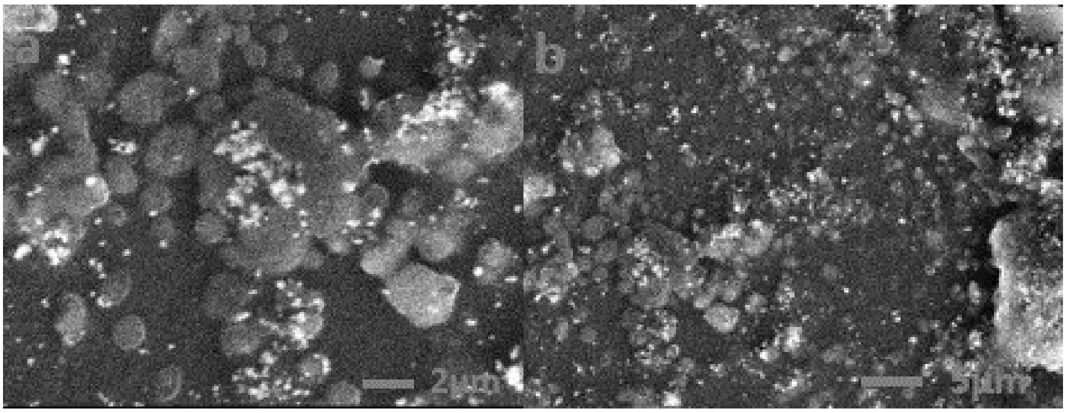

Fig.S1 SEM images of new method (a, AuNPs/rGO /AuNPs-50) and traditional method (b, rGO-AuNPs-50).

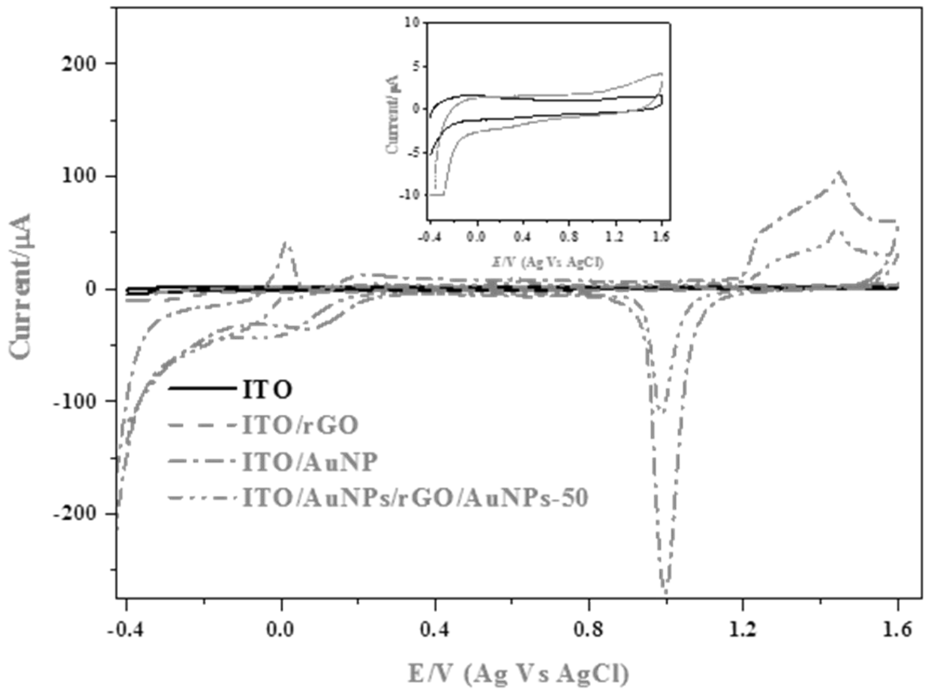

Fig. S2 CVs of bare ITO (a), ITO/rGO (b), ITO/AuNPs (c) and ITO/AuNPs/rGO/AuNPs-50 (d) in the 0.5M H_2SO_4 at scan rates $50mVs^{-1}$.

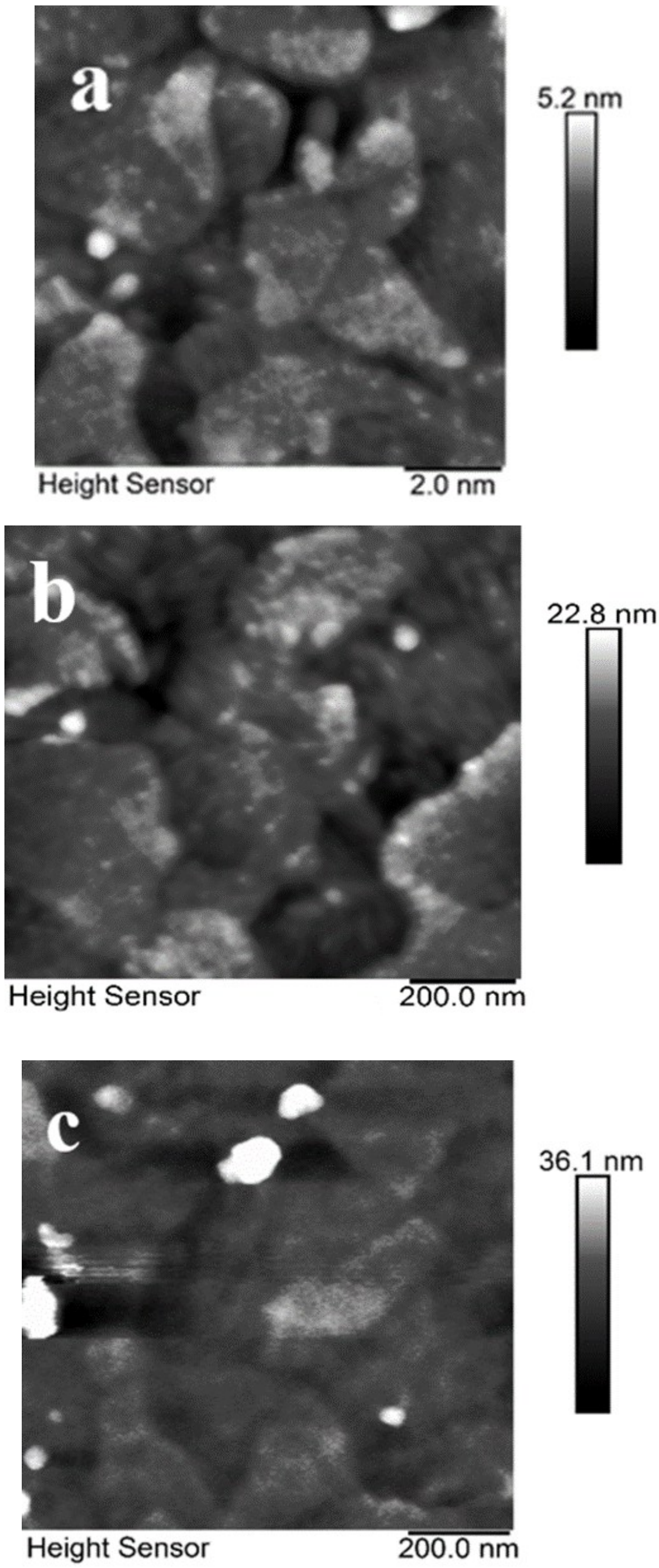

Fig.S3 AFM image of AuNPs/rGO/AuNPs-10 (a), AuNPs/rGO/AuNPs-30 (b), and AuNPs/rGO/AuNPs-50 (c).

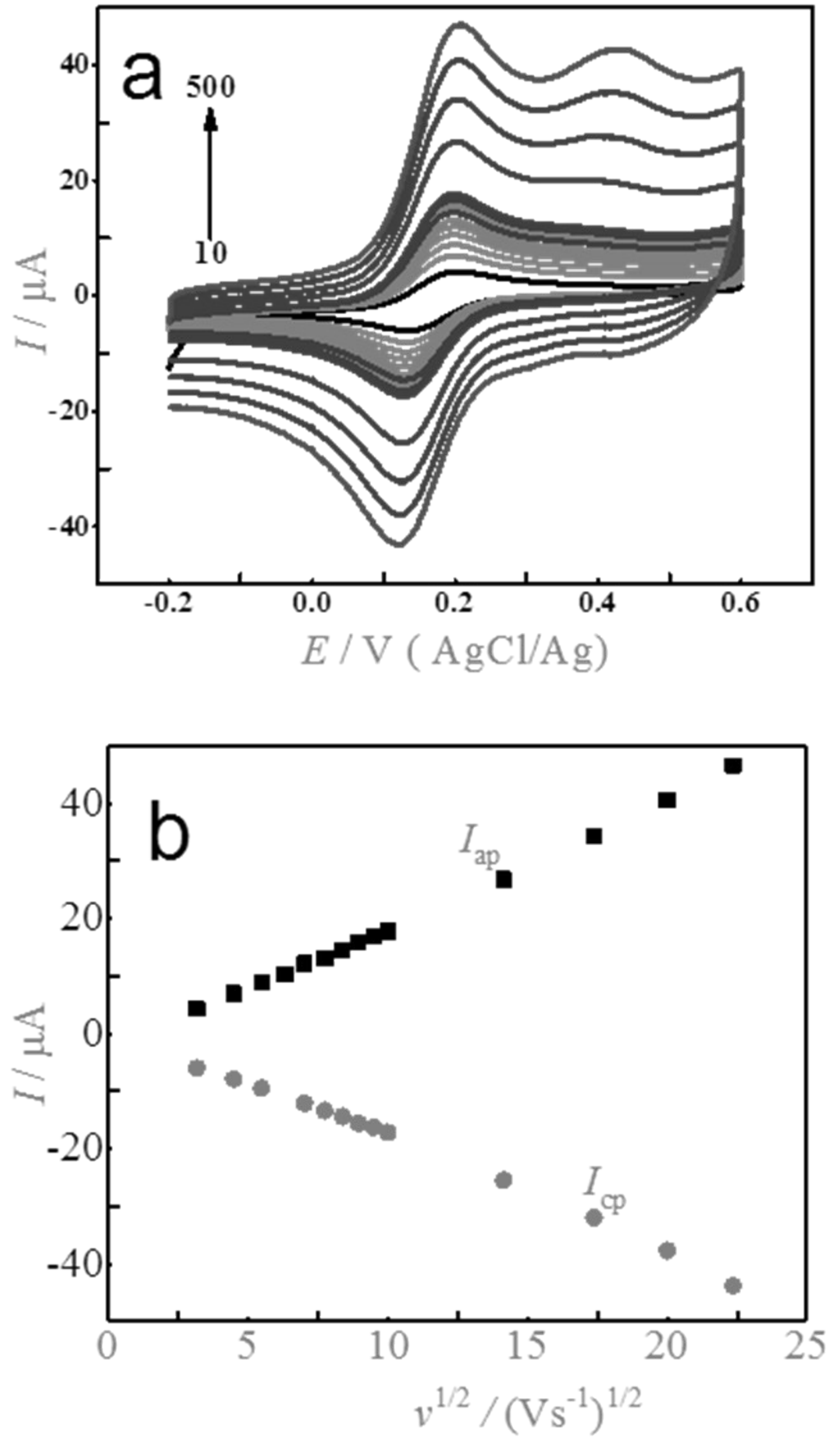

Fig.S4 CVs of GCE/AuNPs/rGO-50 recorded in PBS at different scan rates of 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 200, 300, 400, and 500 mVs^{-1} in presence of 1mM $[Fe(CN)_6]^{3-/4-}$ (a) and the plot of the *I* vs. $v^{1/2}$ (b)

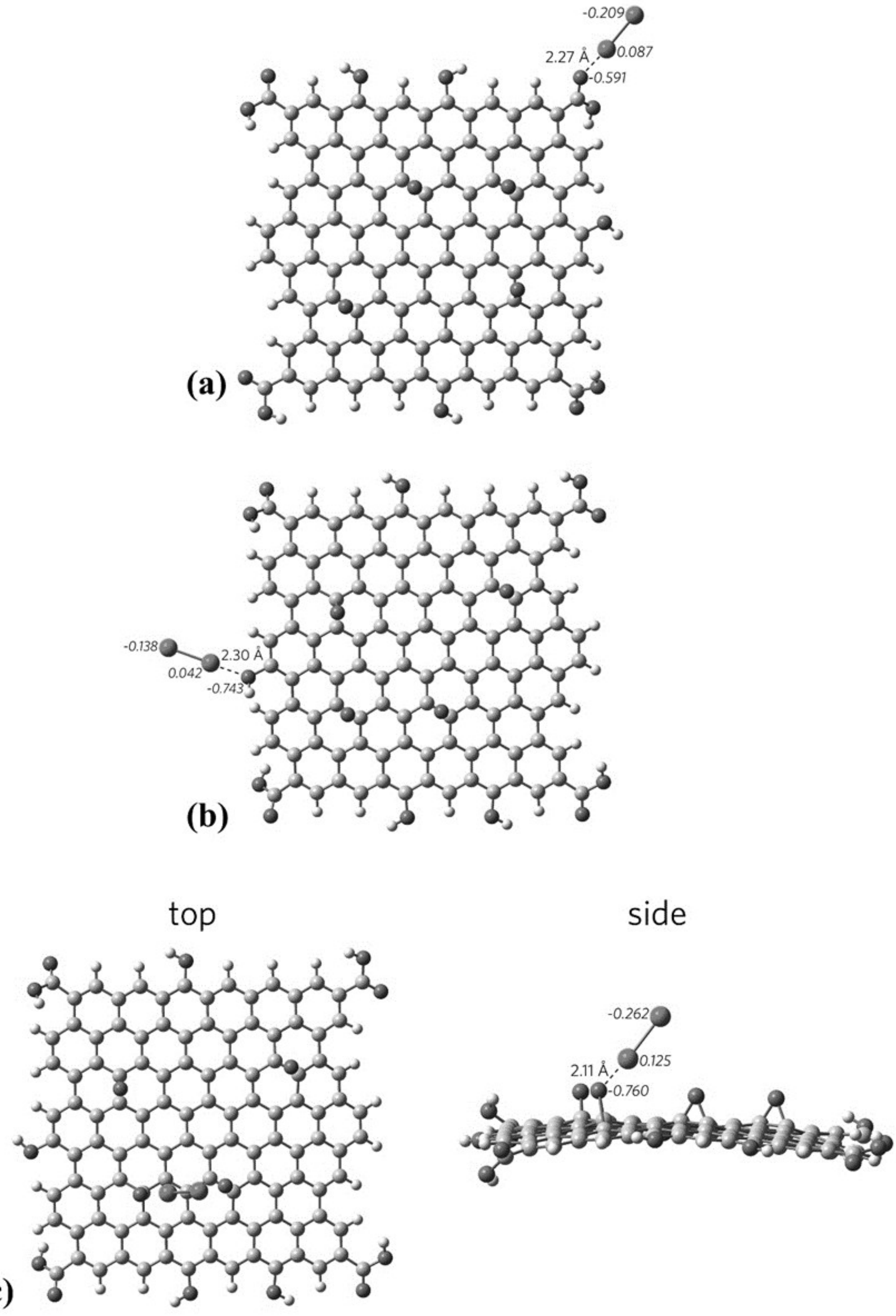

Fig.S5 Ground state structures of Au_2/rGO complexes optimized at the B3LYP/6-31G//LANL2DZ level at different coordination sites: (a) the carboxylic acid group (–COOH), (b) the hydroxyl group (–OH) and (c) the epoxy groups (–O–). NPA charges (a.u.) for selected atoms are displayed in italics, and bond lengths in Å.

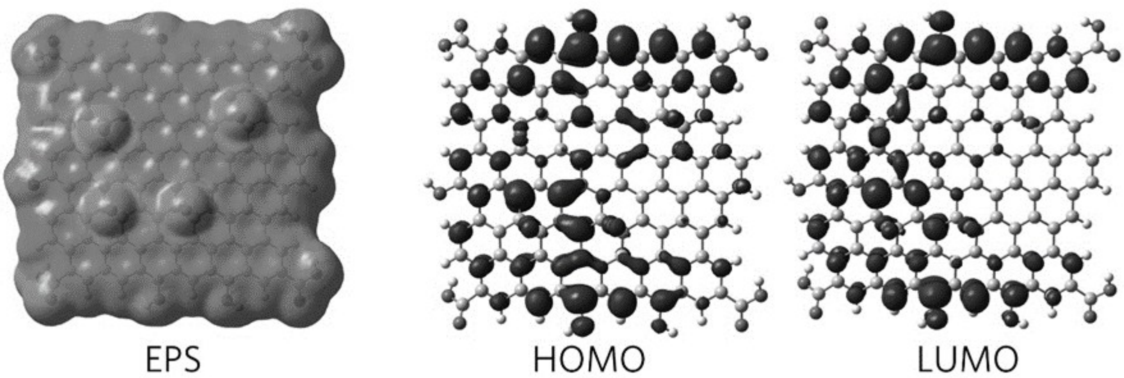

Fig. S6 Electrostatic potential (EPS) and frontier orbitals surfaces of the optimized structure of rGO.

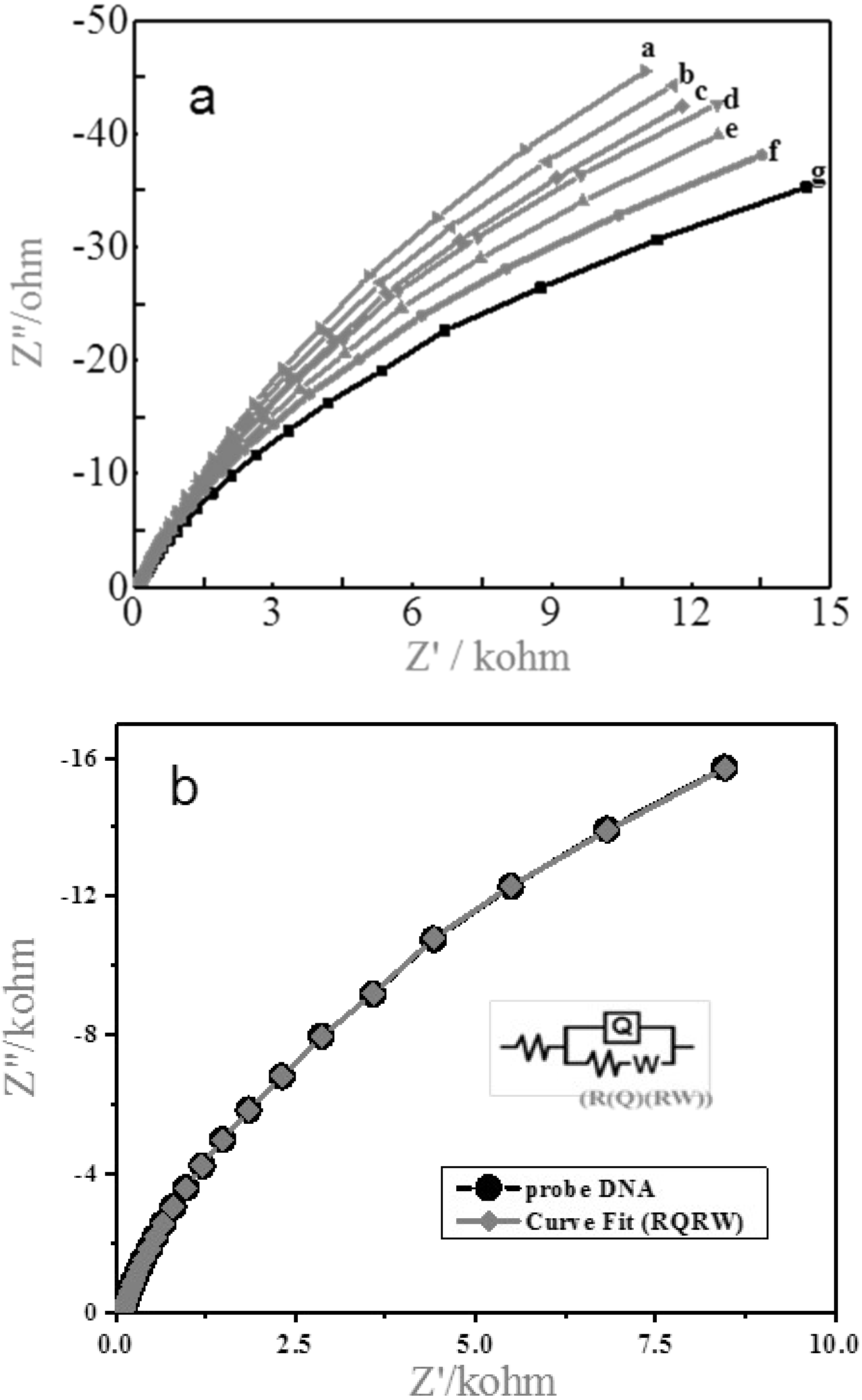

Fig. S7 (a) Impedance behaviors of probe I on the various cDNA concentrations of (a) 1µM, (b) 0.1µM, (c) 0.01µM, (d) 1 nM, (e) 0.1 nM, (f) 0.01 nM and (g) 1 pM. (b) Nyquist curve fit diagrams of prope (I) was recorded at PBS 10 (pH 7.4) containing 0.1M KCl of 1mM $[Fe(CN)_6]^{3-/4-}$ and inset: equivalent circuit fit diagram. Applied DC potential of 250 mV and the AC amplitude of ±5 mV.

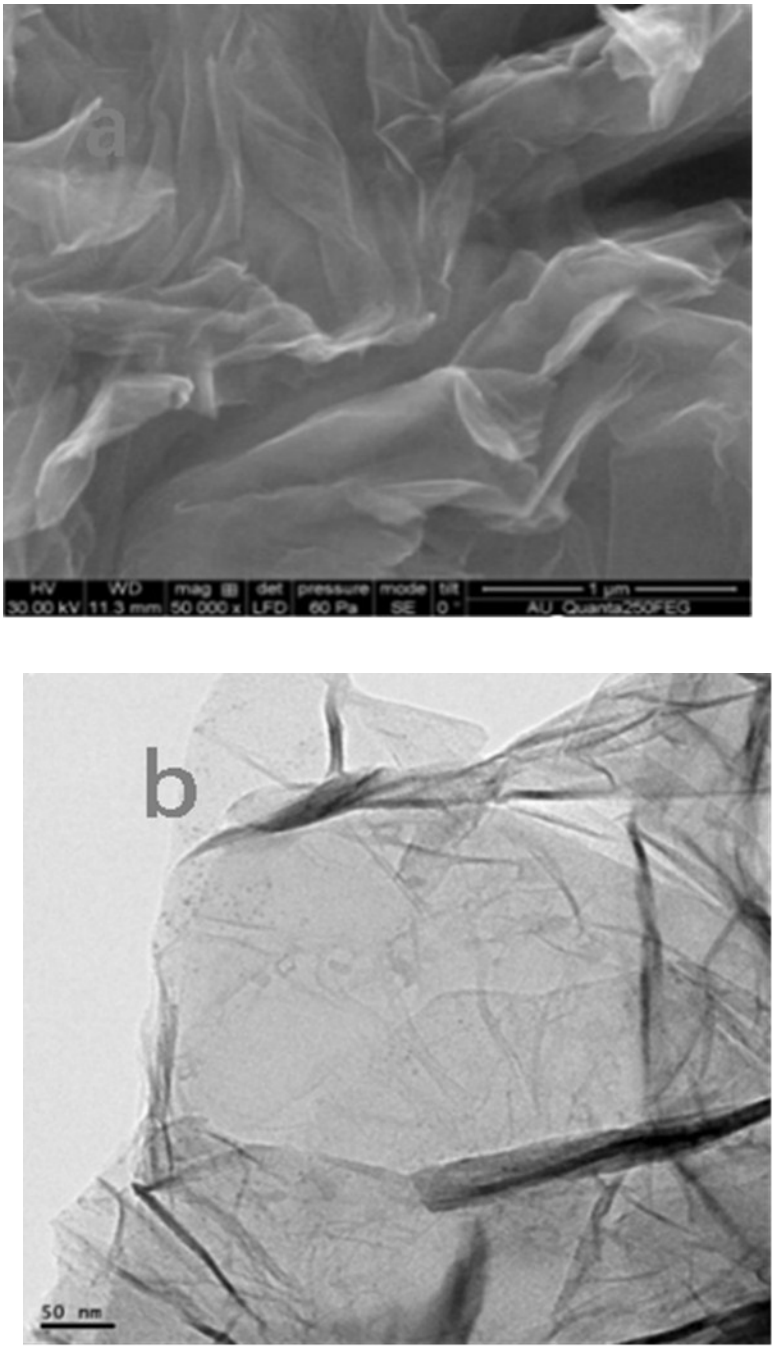

Fig. S8 SEM (a) and TEM images (b) of GO.

Table S1 The relative atomic percentage of GO, rGO and AuNPs/ rGO/AuNPs-50.

Surface	C1*s* %	O1*s %*	C/O ratio
GO	79.28	20.72	0.2613
rGO	49.73	50.26	0.9906
AuNPs/rGO/AuNPs-50	53.46	37.03	1.4436

Table S2 Raman data obtained for GO, rGO and AuNPs/ rGO/AuNPs-50

Electrodes	D cm^{-1}	G cm^{-1}	2D cm^{-1}	D + G cm^{-1}	I_D/I_G ratio	sp^2 graphene size nm	D_{FWHM} cm^{-1}	G_{FWHM} cm^{-1}	D + G_{FWHM} cm^{-1}
GO	1357	1590	2746	2862	1.534	24.76	114	87	1085
rGO	1349	1577	2716	2917	1.61	25.88	96.5	106	240
AuNPs/rGO/AuNPs-10	1345	1580	2716	2924	0.967	16.94	106	79	104
AuNPs/rGO/AuNPs-30	1346	1580	2705	2922	0.98	16.78	113	104	113
AuNPs/rGO/AuNPs-50	1345	1585	2670	3088	0.13	146.21	86	102	78

Table S3 Impedance data obtained for GCE/AuNPs/rGO/AuNPs with 10, 30 and 50 cycles.

GCE/AuNPs/rGO/AuNPs-10

Electrode	R_s (Ω cm^{-2})	Q_{CPE} (F cm^{-2})	n	R_{ct} (Ω cm^{-2})	Warburg (cm s^{-1})	K_{app} (cm s^{-1})
GCE	87.09	2.74×10^{-5}	0.797	0.42×10^{4}	4.71×10^{-5}	
GCE/AuNPs/rGO/AuNPs-10	94.99	1.47×10^{-5}	0.854	0.22×10^{4}	6.27×10^{-5}	1.25×10^{-3}
probe I	88.28	6.26×10^{-6}	0.907	5.57×10^{4}	3.76×10^{-4}	
probe II	88.09	5.75×10^{-5}	0.908	9.12×10^{4}	4.22×10^{-5}	
probe III	106.6	5.18×10^{-6}	0.908	6.61×10^{4}	5.253×10^{-6}	

GCE/AuNPs/rGO/ AuNPs-30

Electrode	R_s (Ω cm^{-2})	Q_{CPE} (F cm^{-2})	n	R_{ct} (Ω cm^{-2})	Warburg (cm s^{-1})	K_{app} (cm s^{-1})
GCE/AuNPs/rGO/AuNPs-30	93.17	1.84×10^{-5}	0.853	1.21×10^{4}	3.16×10^{-5}	1.11×10^{-3}
probe I	93.20	7.82×10^{-6}	0.883	8.46×10^{4}	8.17×10^{-6}	
probe II	93.46	6.76×10^{-6}	0.888	10.00×10^{4}	8.33×10^{-8}	
probe III	85.46	6.62×10^{-6}	0.888	8.49×10^{4}	1.40×10^{-11}	

GCE/AuNPs/rGO/AuNPs-50

Electrode	R_s (Ω cm^{-2})	Q_{CPE} (F cm^{-2})	n	R_{ct} (Ω cm^{-2})	Warburg (cm s^{-1})	K_{app} (cm s^{-1})
GCE/AuNPs/rGO/AuNPs-50	89.23	2.43×10^{-5}	0.861	1.75×10^{4}	2.67×10^{-5}	1.06×10^{-3}
probe I	86.87	9.66×10^{-6}	0.889	5.58×10^{4}	3.97×10^{-6}	
probe II	89.34	7.81×10^{-6}	0.896	9.34×10^{4}	239.8	
probe III	108.4	7.06×10^{-6}	0.889	6.72×10^{4}	2.41×10^{-4}	

Table S4 Cyclic Voltammetric data obtained for GCE/AuNPs/rGO/AuNPs with 10, 30, and 50 cycles.

GCE/AuNPs/rGO /AuNPs-10

Electrode	E_{pa}/V	I_{pa}/A	E_{pc}/V	I_{pc}/A	ΔE_p (V)	K_{et}
GCE	0.2229	8.072×10^{-6}	0.1584	-1.187×10^{-5}	0.64	
AuNPs/rGO/AuNPs-10	0.2329	8.875×10^{-6}	0.1529	-1.185×10^{-5}	0.80	4.83×10^{-4}
probe I	0.2990	4.388×10^{-6}	-0.0017	-8.686×10^{-6}	0.30	
probe II	0.3486	3.579×10^{-6}	-0.0077	-7.799×10^{-6}	0.34	
probe III	0.2968	3.984×10^{-6}	-0.0013	-8.204×10^{-6}	0.30	

GCE/AuNPs/rGO/ AuNPs-30

Electrode	E_{pa}/V	I_{pa}/A	E_{pc}/V	I_{pc}/A	ΔE_p(V)	K_{et}
AuNPs/rGO/AuNPs-30	0.2046	1.082×10^{-5}	0.1220	-1.303×10^{-5}	0.82	2.24×10^{-3}
probe I	0.2637	5.735×10^{-6}	0.0017	-8.599×10^{-5}	0.26	
probe II	0.2826	5.359×10^{-6}	0.0063	-7.658×10^{-5}	0.28	
probe III	0.2708	5.339×10^{-6}	0.0017	-8.599×10^{-5}	0.27	

GCE/AuNPs/rGO/ AuNPs-50

Electrode	E_{pa}/V	I_{pa}/A	E_{pc}/V	I_{pc}/A	ΔE_p (V)	K_{et}
AuNPs/rGO/AuNPs 50	0.1962	1.013×10^{-5}	0.1236	-1.215×10^{-5}	0.72	2.48×10^{-3}
probe I	0.3397	4.671×10^{-6}	0.0352	-8.750×10^{-5}	0.31	
probe II	0.4332	2.767×10^{-6}	0.1096	-7.563×10^{-5}	0.33	
probe III	0.3596	4.106×10^{-6}	0.0004	-8.541×10^{-5}	0.36	

Table S5 Au–X anchor bond distances ($d_{X–Au}$) in Å (X = O or C). NPA derived atomic charges of the anchor atom q_X, the bonded Au atom q_{Au} and the total charge of the Au cluster $\Delta q_{cluster}$ in NPA charges (a.u.). E_{int} (kcal·mol^{-1}) for studying complexes.

Complex	**Site**	**Anchor bond**	$d_{x–Au}$	q_x	q_{Au}	$\Delta q_{cluster}$	E_{int}
Au_2/rGO	(a)	Au–O	2.269	-0.591	0.087	-0.122	13.862
Au_2/rGO	(b)	Au–O	2.298	-0.743	0.042	-0.096	9.672
Au_2/rGO	(c)	Au–O	2.112	-0.760	0.125	-0.137	22.458
Au_2/rGOd	(c)	Au–O	2.124	-0.737	0.123	-0.166	21.740
Au_2/rGO/Au_2	(c)	Au_1–O	2.126	-0.762	0.119	-0.208	34.168
		Au_2–C	2.413	-0.109	0.074	-0.109	
Au_2/rGOd/Au_2	(c)	Au_1–O	2.125	-0.751	0.127	-0.214	32.280
		Au_2–C	2.408	-0.114	0.078	-0.112	

Table S6 The comparison of electrochemical DNA biosensors based on AuNPs and/or GO.

DNA sensors	**Linear ranges (M)**	**LOD**	**Reference**
GCE/GO	1.0×10^{-6} to 1.0×10^{-12}	1.0×10^{-12}	Sun et al., 2012
GO-COOH/PLLy/GCE	1.0×10^{-6} to 1.0×10^{-12}	1.65×10^{-12}	Lu et al., 2016
AuNP/Toluidine blue–GO	2.0×10^{-1} to 1.0×10^{-9}	2.95×10^{-12}	Peng et al., 2015
DNA/AuNP/Cys/PGA	4.8×10^{-9} to 9.1×10^{-11}	4.2×10^{-11}	Zhang et al., 2009
AuNPs/DNA/AuE	5.0×10^{-7} to 1.0×10^{-12}	1×10^{-12}	Yang et al., 2014
AuNPs/TB–GO	1.0×10^{-9} to 1.0×10^{-11}	2.9×10^{-12}	Hu et al., 2012
AuNPs/rGO/AuNPs	**1.0×10^{-6} to 1.0×10^{-13}**	**3.9×10^{-14}**	**This work**

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