Supporting Information

Electrochemical DNA Sensor by the Assembly of Graphene and DNA Conjugated Gold Nanoparticles with Silver Enhancement Strategy

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1 Synthesis of graphene

Graphene was synthesized according to previous reports[1,2]. Generally, the pre-oxidized graphite was put into 12 mL concentrated H_2SO_4 (0 ^oC) followed by slowly adding 1.5 g $KMnO_4$ under stirring in ice-bath. After stirring at 35 °C for 4 h, the mixture was diluted with 100 mL deionized water. Then, 2 mL 30% H_2O_2 was added drop by drop. Next, the mixture was filtered, washing with 0.1 M HCl (aq) and deionized water to remove metal ions and acid. The resulting solid was dispersed in deionized water and then purified by dialysis for at least 5 days. Graphite oxide powder was obtained by filtration and dried in vacuum. Graphene was prepared by reduction of graphite oxide. 50 mg graphite oxide powder was dispersed in 50 mL water by sonicating for 1 h. Then, 0.5 mL 80% hydrazine was added and the mixture was kept stirring at 50 ^oC for 24 h. Finally, the resulting mixture was filtered and dried in vacuum to obtain hydrophobic powder of graphene.

2 Preparation of AuNPs and cDNA2 modified AuNPs (Au-cDNA2)

AuNPs were synthesized by citrate reduction of $HAuCl_4$ according to the previous report[3]. Au-cDNA2 was prepared by adding 2 OD cDNA2 to 4 mL aqueous AuNPs solution. After 48 h incubation, the mixture was centrifuged at 12000 rpm for 3 min. The supernatant was separated from the precipitate and then centrifuged at 12000 rpm for another 3 min. This process was repeated several times until the supernatant was

almost colorless. All the red precipitates were collected and washed twice with 0.5×TBE buffer by successive centrifugation and redispersion, and finally dispersed in 4 mL 0.5×TBE buffer. The Na^+ concentration of the solution was gradually increased to 100 mM by slowly adding 2 M NaCl. The solution was allowed to "age" at room temperature for an additional 24 h and then stored at 4 °C for further use.

3 Characterization of AuNPs

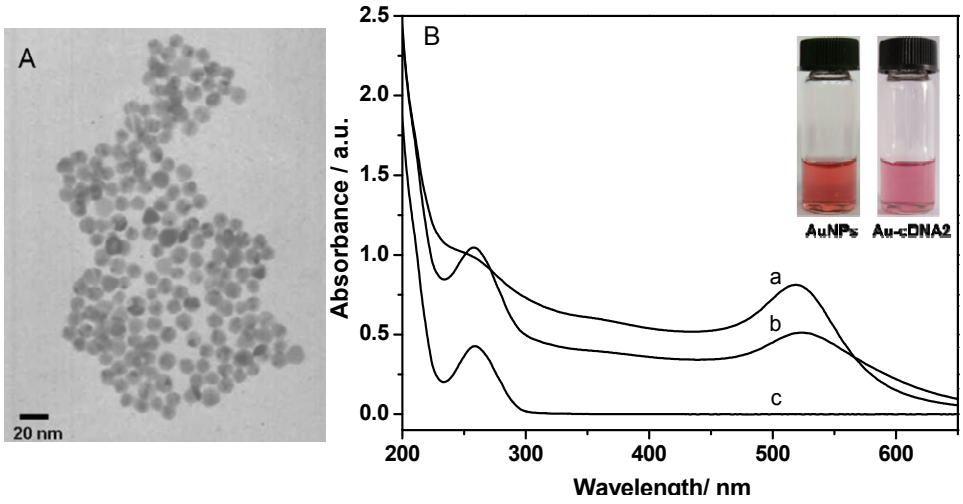

Figure S1. (A) TEM image of the synthesized AuNPs. (B) UV-vis absorption spectra of AuNPs (a), Au-cDNA2 (b), cDNA2 (c). (Inset) Photo images of AuNPs (left) and Au-cDNA2 (right).

4 Characterization of graphene

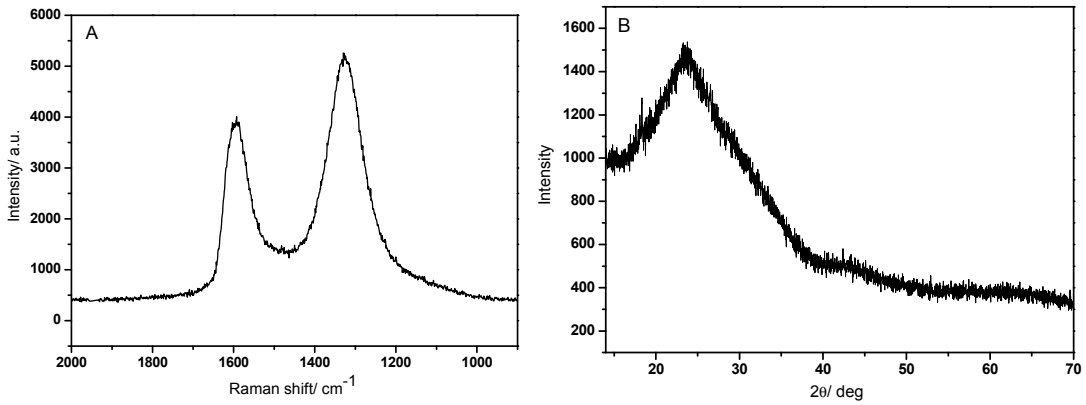

Figure S2. (A) Raman spectra and (B) XRD pattern of graphene.

Two distinct peaks at 1592 and 1329 cm^{-1} shown in Raman spectrum of graphene

correspond to the G and D bands, respectively. As shown in Figure S2(B), the characteristic peak of graphene in the XRD pattern is found at 23.8°.

5 SEM images of graphene

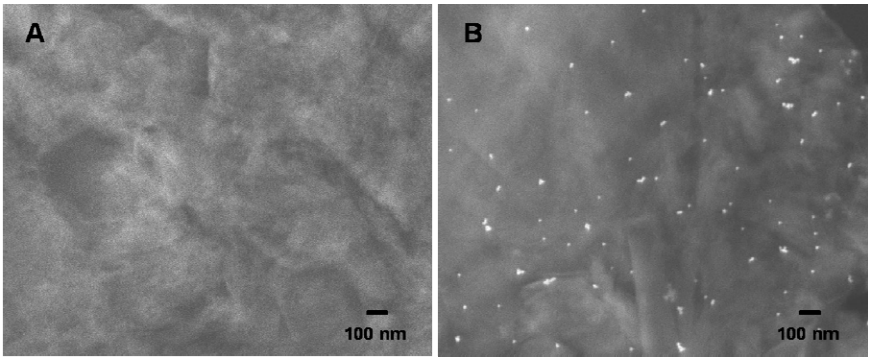

Figure S3. SEM images of (A) graphene and (B) Au-cDNA2 hybridized graphene on the glassy carbon.

Supplementary References

1 W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.

2 Y. Wang, Y. Li, L. Tang, J. Lu and J. Li, *Electrochem. Commun.*, 2009, **11**, 889.

3 K. C. Grabar, R. G. Freeman, M. B. Hommer and M. J. Natan, *Anal. Chem.*, 1995, **67**, 735.