Supporting Information for "Surface-Enhanced Raman Spectroscopy for DNA Detection by Self-Assembly of Ag Nanoparticles onto Ag Nanoparticles/ Graphene Oxide Nanocomposites"

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Synthesis and Characterizations of AgNPs/GO

Ultralarge and single-layer GO nanosheets were prepared by a modified Hummers' method as reported previously [1]. For the synthesis of AgNPs and AgNPs/GO, 10 μ L of AgNO₃ solution (1.5 M) was added to 15 mL of the GO aqueous suspension (0.067 mg/mL). The mixed solution was heated to 100 °C, after which 177 μ L of sodium citrate (0.085 M) was added dropwise. After 10 min reaction, the mixed solution cooled down to room temperature and then was centrifugated at 5000 rpm for 20 min. Then, the supernatant solution mainly consisting of AgNPs and the solid sediment containing AgNPs/GO were separately collected. To prepare the aqueous suspension of AgNPs/GO, the aforementioned solid sediment was washed with distilled water using centrifugation (5000 rpm) to remove free AgNPs. Finally, AgNPs/GO was re-dispersed in water to form a stable dispersion.

To obtain AgNPs with the small sizes, the aforementioned supernatant solution was further centrifugated at 8000 rpm for 20 min to remove GO nanosheets and this centrifugation process was repeated for three times. The averaged diameter of the obtained AgNPs was 15.6 nm as shown in Figure S10.



Figure S1 (a)-(b) Typical TEM images of AgNPs with the large sizes on the carbon support. (c) Histogram of AgNP size. (d) UV/Vis absorption spectrum of AgNPs.

Figure S2 (a) Typical AFM image of a GO nanosheet on SiO_2 / Si substrate. The inset shows that the height difference between the two black arrow heads is approximately 1 nm, which indicates that the GO sheet is monolayered [1]. (b) Raman spectra of 10^{-4} M R6G on three different substrates. The Raman spectra are normalized with respect to the intensity of a Si peak. These Raman spectra were measured using 633 nm laser excitation with a laser power of 1.5 mW.



Figure S3 Histogram of AgNP size for AgNPs/GO. The statistics are based on TEM observation of AgNPs/GO.



Figure S4 (a) Typical AFM image of a AgNPs/GO. The height traces of three lines are shown on the right hand side. (b) Raman spectra of 10⁻⁴ M R6G measured from three different regions in an individual AgNPs/GO. These Raman spectra were measured using 633 nm laser excitation with a laser power of 1.5 mW. (c) UV/Vis absorption spectra of GO nanosheets, AgNPs and AgNPs/GO.

The absorption spectrum of pristine GO shows a broad peak at 228 nm originating from the π plasmon of carbon [2]. Compared with GO, AgNPs/GO shows a new absorption peak at 400 nm due to the SPR of AgNPs [3]. Furthermore, it is noted that the location of the absorption peak in the shorter wavelength remains unchanged, which indicates that the use of sodium citrate in the synthesis of AgNPs/GO principally reduces silver ion rather than GO. (d) Raman spectra of GO nanosheets and AgNPs/GO. The Raman spectra are normalized with respect to the intensity of a Si peak. Two spectra exhibit a D band at 1344 cm⁻¹ and a G band at 1608 cm⁻¹. Furthermore, the D/G intensity ratio of GO (0.91) is nearly identical to that of AgNPs/GO (0.95), which further supports that the influence of sodium citrate on GO is minor. (e) XRD pattern of AgNPs/GO. The broad peak at 20=21.7° corresponds to the background signal of the glass substrate. All the identified peaks can be assigned to the fcc silver (JCPDS card No. 4-783).



Figure S5 SERS spectra of R6G measured from three different clusters of AgNPs. In a typical experiment, a droplet of the mixed solution containing 10^{-4} M R6G and AgNP colloid with an averaged diameter of 15.6 nm was dropped on a SiO₂/Si substrate and SERS spectra were recorded after drying the solvent. These SERS spectra were measured using 633 nm laser excitation with a laser power of 1.5 mW and were normalized with respect to the intensity of a Si peak.



Figure S6 Raman spectrum of 4-MBA powder.



Figure S7 Raman spectrum obtained from AgNPs/GO subject to the incubation with a solution of 4-MBA modified AgNPs and the subsequent rinse in distilled water.



Figure S8 AFM image obtained from probe DNA modified AgNPs/GO subject to the incubation with a solution of AgNPs with the functionalizations of 4-MBA and target DNA and the subsequent dehybridization process. The height trace of a line is shown in the inset.



Figure S9 SERS spectrum recorded after adding a solution of AgNPs functionalized with 4-MBA and 10⁻⁶ M non-complementary target DNAs onto probe DNA modified AgNPs/GO.



Figure S10 AFM images obtained from probe DNA modified AgNPs/GO subject to the incubation with a solution of AgNPs functionalized with (a) 10⁻⁶ M non-complementary and (b) 10⁻⁶ M complementary target DNAs. The height trace of a line is shown in the inset. In the AFM experiments, the AgNPs with the averaged diameter of 57.5nm were used.



Figure S11 (a-c) Typical TEM images of AgNPs with the small size on the carbon support. The inset in (a) shows the size distribution of AgNPs.



Figure S12 AFM images obtained from probe DNA modified AgNPs/GO subject to the incubation with a solution of AgNPs functionalized with (a) 10⁻⁶ M and (b) 10⁻⁹ M of target DNAs. In the AFM experiments, the AgNPs with the averaged diameter of 57.5nm were used.

| DNA name | Sequence (5'-3') |
|-----------------------|-------------------------|
| P1 (Probe DNA No.1) | ACATAGCACATTCGAGGTAG-SH |
| P2 (Probe DNA No.2) | TGCATTACGGAATCTTACTC-SH |
| T1 (Target DNA No.1) | CTACCTCGAATGTGCTATGT-SH |
| T2 (Target DNA No.2) | GAGTAAGATTCCGTAATGCA-SH |
| Non-complementary DNA | TACATCTTGCGACATCGCAG-SH |

Table S1. Sequence of oligonucleotides used in this study

References

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