## Supporting Information

## Graphene-Silver Nanohybrids for Ultrasensitive Surface Enhanced Raman Spectroscopy: Size Dependence of Silver Nanoparticles

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**Synthesis of GE-Ag NPs Nanohybrid:** Firstly, the GO-silver ions (GO-Ag<sup>+</sup>) precursor was fabricated by self-assembly method. GO (100 mg) was dispersed into absolute ethanol (100 mL) with sonication for 30 min. Then AgNO<sub>3</sub> ethanol solution (0.059 M, 10 mL) was added into the GO solution with sonication for 30 min at room temperature, then centrifuged and washed copiously with ethanol. The obtained sample was dried in a vacuum at 30 °C for 24 h and labeled as GO–Ag<sup>+</sup>. The GE-Ag NPs hybrids can be fabricated by reduction of GO-Ag<sup>+</sup> precursor.

Synthesis of GE-Ag NPs Nanohybrid using NaBH<sub>4</sub> as a Reducing Agent: GO-Ag<sup>+</sup> (50 mg) was dispersed into sodium citrate aqueous solution (0.12 mol L<sup>-1</sup>, 50 mL) with sonication for 30 min at room temperature, sodium borohydride (0.25 mg) was dispersed into sodium citrate aqueous solution (0.12 mol L<sup>-1</sup>, 50 mL) with stirring for 2 min. Then the GO-Ag<sup>+</sup> mixture were dropped slowly into the fresh sodium borohydride and sodium citrate aqueous solution with stirring. Then the reaction mixture was adjusted to a pH value of 11 with NaOH solution (0.5 mol L<sup>-1</sup>), and stirred for 70 min. The slurry-like product was centrifuged and washed with

de-ionized water and ethanol repeatedly to remove any impurities and the obtained products were dried overnight in a vacuum at 30 °C and the obtained products were labeled as G–Ag(SB).

Synthesis of GE-Ag NPs Nanohybrid using the Solvothermal Method:  $GO-Ag^+$  (25 mg) was mixed with de-ionized water (25 mL) with hydrazine (50 µL, 35 wt % in water) solution or ethylene glycol (25 mL), under sonication for 30 min, and the resulting mixtures were transferred into two 25 mL stainless steel Teflon-lined autoclaves. The autoclaves were sealed, kept at 140 °C for 2.5 h, and then naturally cooled to room temperature. After the reaction, the solution was centrifuged, washed with ethanol and de-ionized water three times each, dried overnight in a vacuum at 30 °C and the obtained products were labeled as G-Ag(Hy) and G-Ag(EG) for different reducing agent of N<sub>2</sub>H<sub>4</sub> and EG, respectively.

Synthesis of Pure GE: GO aqueous solution (1 g L<sup>-1</sup>, 25 mL) was mixed with hydrazine (50  $\mu$ L), and the resulting mixture was transferred into 25 mL stainless steel Teflon-line autoclave. The autoclave was sealed, kept at 140 °C for 2.5 h, and then naturally cooled to room temperature. After the reaction, the solution was centrifuged, washed with ethanol and de-ionized water three times each, dried overnight in a vacuum at 30 °C and the obtained product was labeled as G–(Hy).

**Synthesis of pure Ag NPs Colloid:** Silver nitrate powder (90 mg) was dispersed in deionized water (10 mL), and then was mixed with polyelectrolyte-poly (diallyldimethylammonium chloride) (PDDA) (5 g L<sup>-1</sup>, 30 mL) under stirring. Subsequently, this mixture was added slowly to fresh sodium borohydride solution (2.1 mol L<sup>-1</sup>, 10 mL) under stirring for 24 h. After the reaction, the Ag NPs colloid was centrifuged, washed with acetone and de-ionized water three times each, and it is kept in brown beaker.

**Preparation of Sample for Raman Measurement:** For G-(Hy), G-Ag(SB), G-Ag(Hy) and G-Ag(EG) samples, R6G ethanol solution  $(1 \times 10^{-5} \text{ M}, 1 \text{ mL})$  was dropped into the as-prepared samples ethanol solution (0.1 g L<sup>-1</sup>, 10 mL) and it was stirred at room temperature for 12 h.

Finally the samples were centrifuged and washed with ethanol to remove unbound R6G molecules and dried at room temperature to evaporate all of the ethanol. For the control sample of Ag NPs, the Ag NPs colloid as-prepared was dripped onto the glass and dried at room temperature. Then, the R6G ethanol solution  $(1 \times 10^{-6} \text{ M}, 50 \text{ }\mu\text{L})$  was dropped onto the surface of Ag NPs film and dried at room temperature. For the GE-Ag NPs hybrids film, the hybrids films were immersed in R6G ethanol solution  $(1 \times 10^{-6} \text{ to } 1 \times 10^{-12} \text{ M}, 50 \text{ mL})$  and CV ethanol solution  $(1 \times 10^{-8} \text{ M})$  for 12 h and then dried at room temperature.



**Fig. S1** a) Typical XRD pattern of GO-Ag<sup>+</sup> precursor, the inset is GO powders; b) Typical XRD patterns of A) G-Ag(SB), B) G-Ag(Hy) and C) G-Ag(EG) powders.



Fig. S2 The typical Raman spectrum of GO.



Fig. S3 TGA data obtained for GO, G-Ag(SB), G-Ag(Hy) and G-Ag(EG) heated in air



Fig. S4 a) Photographs of GO aqueous dispersion before and after the reduction by  $N_2H_4$  as well as the resultant GE aqueous dispersion after washing and redispersing in water. b) XRD pattern of GE. c) TEM image GE sheets. d) UV-vis spectra of GE aqueous dispersions. e) XPS general spectra of dried GE.



**Fig. S5** a) The typical UV-Vis spectrum of Ag NPs colloid and the inset is its digital image. b) the TEM image of Ag NPs.

The as-prepared Ag NPs colloid has good stability and well-dispersion property. The photograph inset of Fig. S5a is the aqueous dispersions of the Ag NPs, without precipitate occurring for more than two months at room temperature. The UV-Vis spectrum of Ag NPs colloid was shown in Fig. S5a. It is clear seen that a typical absorbance peak of Ag NPs appeared at 420 nm. TEM image gave the morphology of Ag NPs, which can be seen in Fig. S5b. And the average size of Ag NPs was about 35 nm.



**Fig. S6** SERS spectra of R6G molecules with  $1 \times 10^{-6}$  M concentration adsorbed on G-Ag(EG) nanohybrids.

The approximate calculation of EF. The EF can be estimated as follows:  $EF = (I_{SERS}/I_{bulk}) / (N_{ads}/N_{bulk})$ . In calculating N<sub>bulk</sub>, the volume of the laser waist is approximately to a cylinder with a radius of 25 µm and a depth in the sample of 3 mm. The calculated volume is ca.  $5.9 \times 10^{-12}$  m<sup>3</sup>. Thus, the estimated value for N<sub>bulk</sub> is ca.  $1.03 \times 10^{13}$ . N<sub>ads</sub> is the number of molecules constituting the first monolayer adsorbed on the grating under the laser spot area of 2.1 µm. In the calculation, the surface area of one CV molecule of  $1.35 \times 10^{-18}$  m<sup>2</sup>/molecule was used. Thus, the estimated maximum value for N<sub>ads</sub> is ca.  $2.56 \times 10^{6}$ . The I<sub>SERS</sub>/I<sub>bulk</sub> can be obtained from the SERS spectra. Thus, the EF value can be calculated. This hypothesis represents a theoretical maximum number of CV molecules absorbed on the surface of Ag NPs and is surely an overestimate, thus the EF reported here is likely an underestimate rather than an overestimate of the actual EF value.

**Table S1.** XPS data of C1s of GO, G-Ag(SB), G-Ag(Hy) and G-Ag(EG) hybrids. The results of the four main peaks are tabulated below as binding energies and area percentages (in parentheses).

Samples	C/O ratio	C1s fitting Binding energy (eV) (relative area percentage %)				
		sp <sup>2</sup>	C-0	C-O-C	C=O/O-C(O)	
GO	2.6	284.8 (31.6%)	285.6 (7.0%)	286.7 (57.0%)	288.5 (4.4%)	
G-Ag(SB)	4.4	284.6 (67.6%)	285.6 (10.1%)	286.7 (13.5%)	288.2 (8.8%)	
		sp <sup>2</sup>	C-N	C-O/C-O-C	C=O/O-C(O)	
G-Ag(Hy)	5.9	284.4 (72.9%)	285.6	286.7 (10.2%)	288.2 (4.3%)/ 289.5 (7.8%)	
G-Ag(EG)	3.9	284.8 (56.7%)		286.3 (26.4%)	288.5 (13.9%)/ 290.0 (3.0%)	

Table S2. The ratio of D and G band in Raman spectra.

Sample	GO	G-(Hy)	G-Ag(SB)	G-Ag(Hy)	G-Ag(EG)
I <sub>D</sub> /I <sub>G</sub>	0.78	1.22	1.04	1.07	0.92

Table S3. RSD values for the major peaks of the CV SERS spectrum.

Peak position (cm <sup>-1</sup> )	809	915	1171	1370	1535	1588	1619
RSD value	0.10	0.13	0.10	0.08	0.05	0.06	0.09