

Supporting Information

Photosynthesis of Stable Ag@Graphene Oxide Nanocolloid Core@Shell Nanoparticles with Sustained Surface Plasmon Resonance under Harsh Conditions

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Experimental section

Materials: Natural graphite (FP 99.95% pure) was purchased from Graphit Kropfmühl AG (Hauzenberg, Germany). Graphite nanofiber (300 nm in diameter, 30 μm in length) was purchased from Carbon Nanomaterial Technology (Pohang, Korea). Ethanol was purchased from Merck (Darmstadt, Germany). Silver nitrate, potassium permanganate and 3-aminopropyltriethoxysilane (APTES) were purchased from Aldrich Chemical Co. (Milwaukee, WI, USA). Hydrogen peroxide (30%), sodium sulfate, sodium nitrate, potassium persulfate, phosphorus pentoxide and toluene were purchased from Junsei Chemical Co. (Tokyo, Japan). Sulfuric and hydrochloric acid was purchased from Samchun (Seoul, Korea). 500-nm $\text{SiO}_2/\text{P}^{++}$ Si substrates (500 μm in thickness) was respectively purchased from STC (Japan). All chemicals were used as received.

Synthesis of graphene oxide nanocolloid (GON): 1.5 g of potassium persulfate and 1.5 g of phosphorus pentoxide were added to 50 mL of sulfuric acid at 80 $^{\circ}\text{C}$ and stirred until the reagents are dissolved. 2.0 g of graphite nanofiber was added to the acid mixture and stirred at 80 $^{\circ}\text{C}$ for 4.5 h, then the mixture was cooled to room temperature and diluted by addition of 250 mL of water. The diluted mixture was filtered with filter paper (Whatman, Grade No. 4), washed with 1 L of water to remove residual reagents and dried under vacuum. The filtered cake was added to 250 mL of sulfuric acid in an ice bath. 10 g of potassium permanganate was slowly added to the mixture with stirring and maintaining the temperature below 10 $^{\circ}\text{C}$. The reaction mixture was transferred to 35 $^{\circ}\text{C}$ water bath and stirred for 12 h. After 12 h, the mixture was diluted with addition of 1 L of water in an ice bath while maintaining the temperature below 55 $^{\circ}\text{C}$. Then, 50 mL of hydrogen peroxide (30%) was added to the mixture. The mixture was centrifuged at 8228 rcf, washed with 3.4% hydrochloric acid solution (3 time) and rinsed with acetone (3 time). The brown supernatant of acetone was collected and evaporated under vacuum to remove acetone. 100 mL of water was added to the obtained slurry and sonicated for 10 min. Then, the suspension was dialyzed with 1000 Da membrane tube until it was neutralized. Finally, the suspension was lyophilized to obtain GON powder.

Synthesis of graphene oxide (GO): 3 g of graphite and 1 g of sodium nitrate were added in 46 mL of sulfuric acid and stirred. 6 g of potassium permanganate was gradually added to the acid mixture

with stirring in an ice bath and the mixture was transferred to a water bath at 35 °C. The mixture was stirred for an hour. 40 mL of water was slowly added to the mixture, further stirred for 30 min and diluted with 100 mL of water in an ice bath to prevent rapid boiling by extremely exothermic reaction. Finally, 6 mL of hydrogen peroxide (30%) was slowly added to the mixture. The final mixture was filtered with filter paper (Whatman, Grade No. 3) and washed with water until the filtrate was neutralized. The filtered solid was dried in air for 48 h.

Preparation of APTES treated quartz and Si substrates: The quartz and Si substrates were cleaned in Piranha solution (sulfuric acid: hydrogen peroxide (30%) = 3:1, WARNING: Piranha solution is extremely explosive and corrosive.) for 10 min at 125 °C, washed with water and ethanol, and dried under a stream of nitrogen. The substrates were immersed in a 10 mM anhydrous toluene solution of APTES for 30 min, briefly sonicated in toluene for 2 min, rinsed with ethanol and water and dried under a stream of nitrogen.

Synthesis of Ag NPs. 0.5 mL of 59 mM AgNO₃ and 1.0 mL of 34 mM sodium citrate were added to 98 mL of aqueous solution with stirring. 0.5 mL of an aqueous 20 mM sodium borohydride was added at once. The reaction mixture was stirred for 1 h and aged for 24 h at room temperature.

Supporting figure

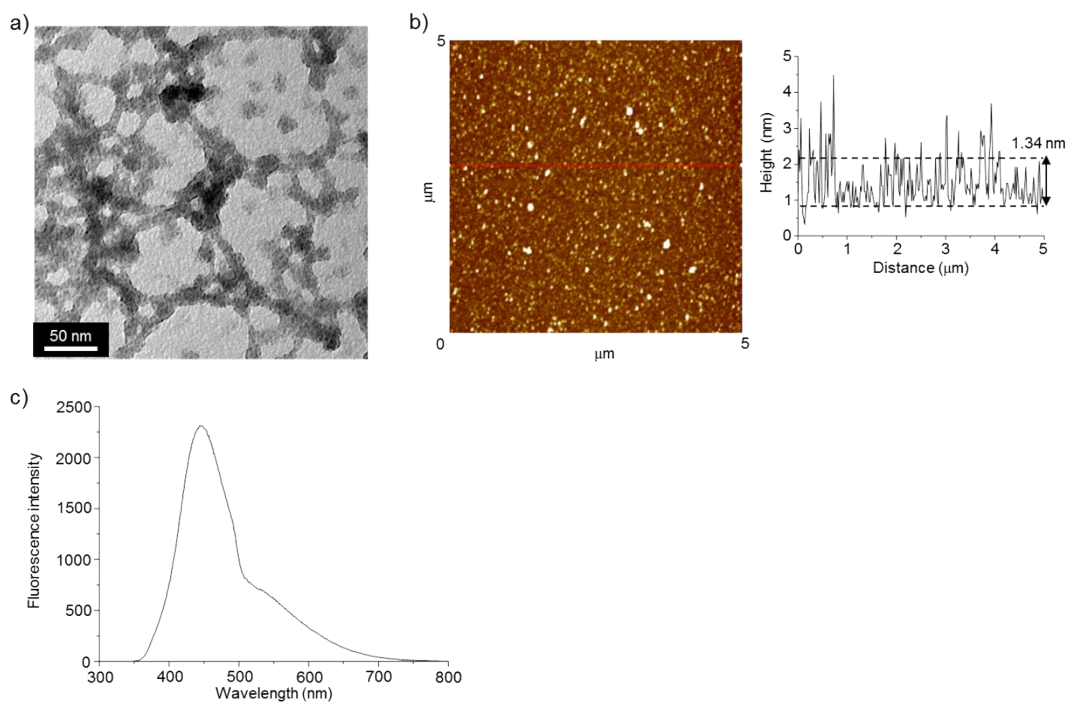


Figure S1. TEM image (a), AFM image and Line profile (b) of graphene oxide nanocolloid (GON). The synthesized GON showed narrow size distribution from 10 to 15 nm with around 1.3 nm in thickness. Fluorescence spectrum (c) of 0.2 mg mL^{-1} GON. Fluorescence spectrum was obtained with 335 nm excitation wavelength.

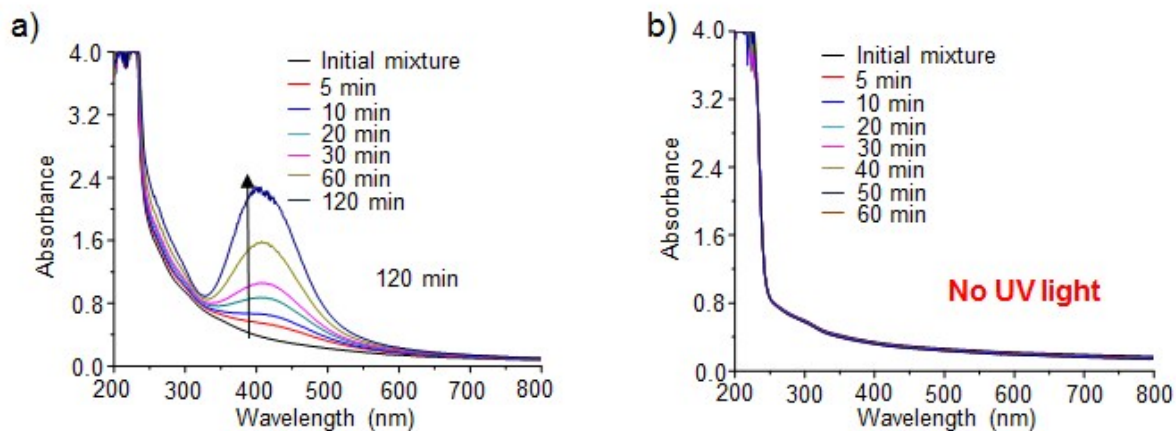


Figure S2. UV-vis spectra of reaction mixtures (1:1 volume ratio of 10 mM AgNO₃ solution and 0.1 mg mL⁻¹ GON suspension) for the synthesis of Ag@GON NPs as a function of incubation time with UV exposure (a) and without UV exposure (b).

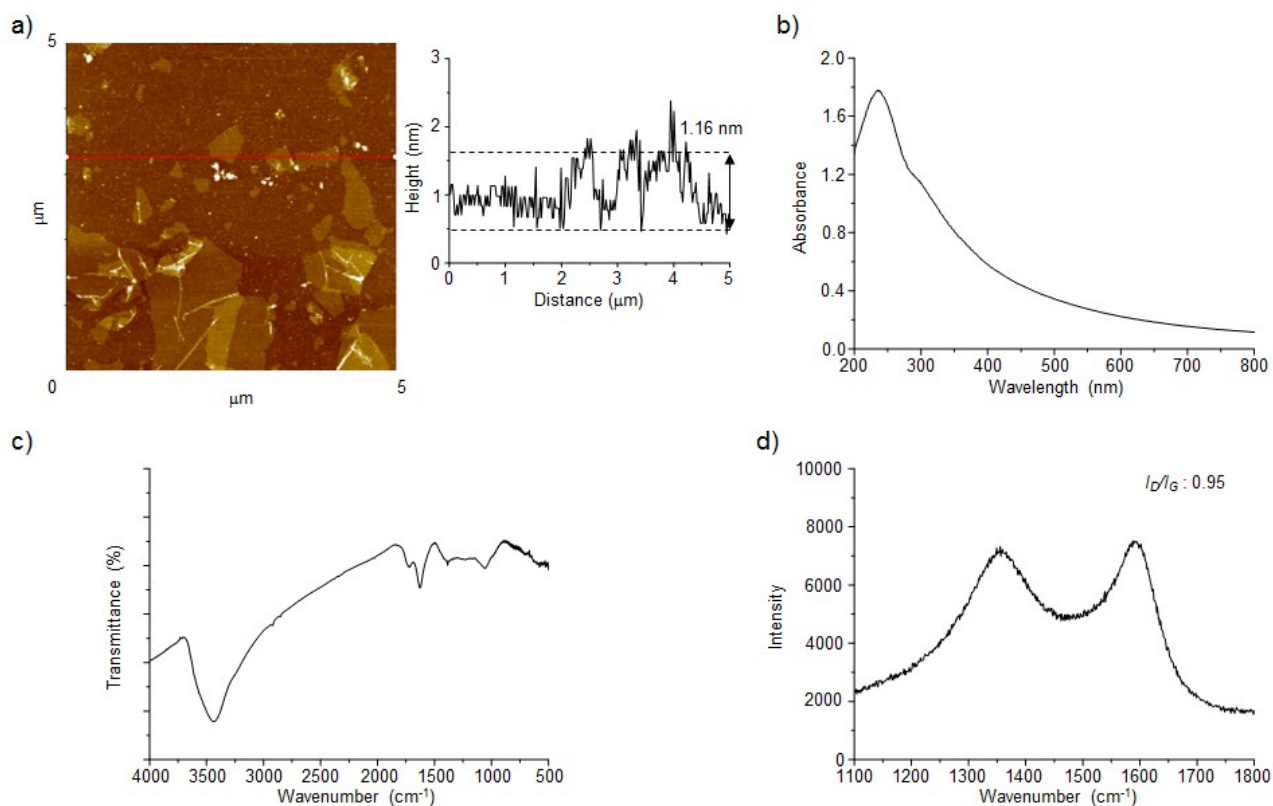


Figure S3. a) AFM image and line profile of GO showed that GO has broad size distribution (0.1 ~ 3 μm and 1.16 nm thickness corresponding to single layered structure. b) UV-vis spectra of GO showed typical π - π^* transition peak around 230 nm. c) FT-IR spectrum of GO showed typical peaks of oxygen-containing functional groups at 1055 cm^{-1} from C-O stretching, 1627 cm^{-1} from skeletal vibration of oxidized aromatic C-C bonds, 1723 cm^{-1} from C=O stretching and 3437 cm^{-1} from O-H vibration with weak aliphatic C-H stretching at 2852 and 2923 cm^{-1} . d) Raman spectrum of GO showed characteristic D- and G-peak at 1352 and 1594 cm^{-1} , respectively. All of the characterization results supported that the GO was successfully synthesized and exfoliated.

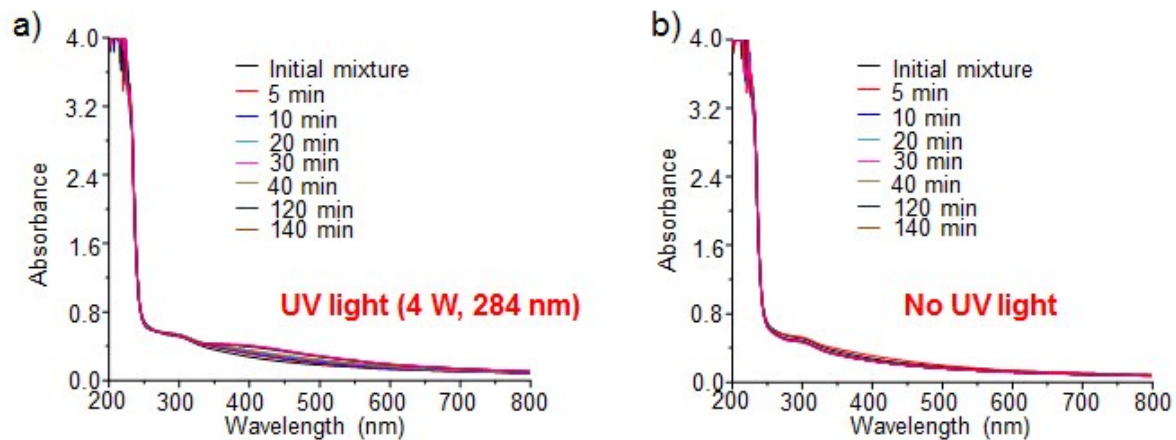


Figure S4. a) UV-vis spectra of reaction mixtures (1:1 volume ratio of 10 mM of AgNO_3 solution and 0.1 mg mL^{-1} GO suspension) for control experiment as a function of incubation time with UV exposure and without UV exposure (b) (for characterization of GO, see Fig. S3). The control experiments clearly supported that Ag@GON NPs were synthesized by photo-induced reduction of Ag^+ ion and thus fluorescence and many oxygen functional groups of GON played an important role for the synthesis of Ag@GON NPs.

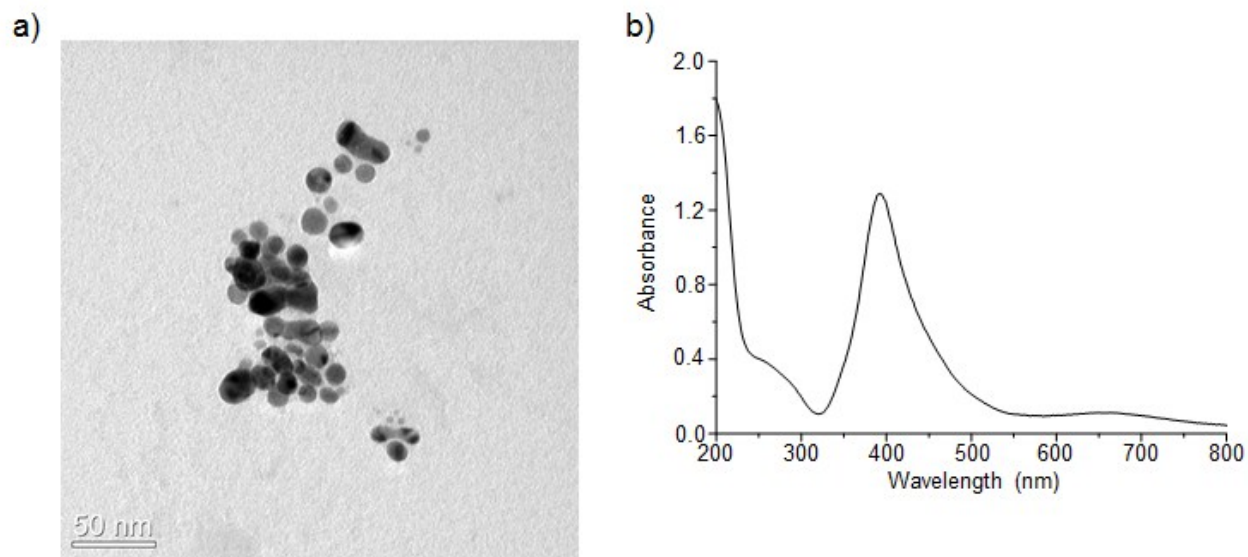


Figure S5. TEM image (a) and UV-vis spectrum (b) of Ag NPs.

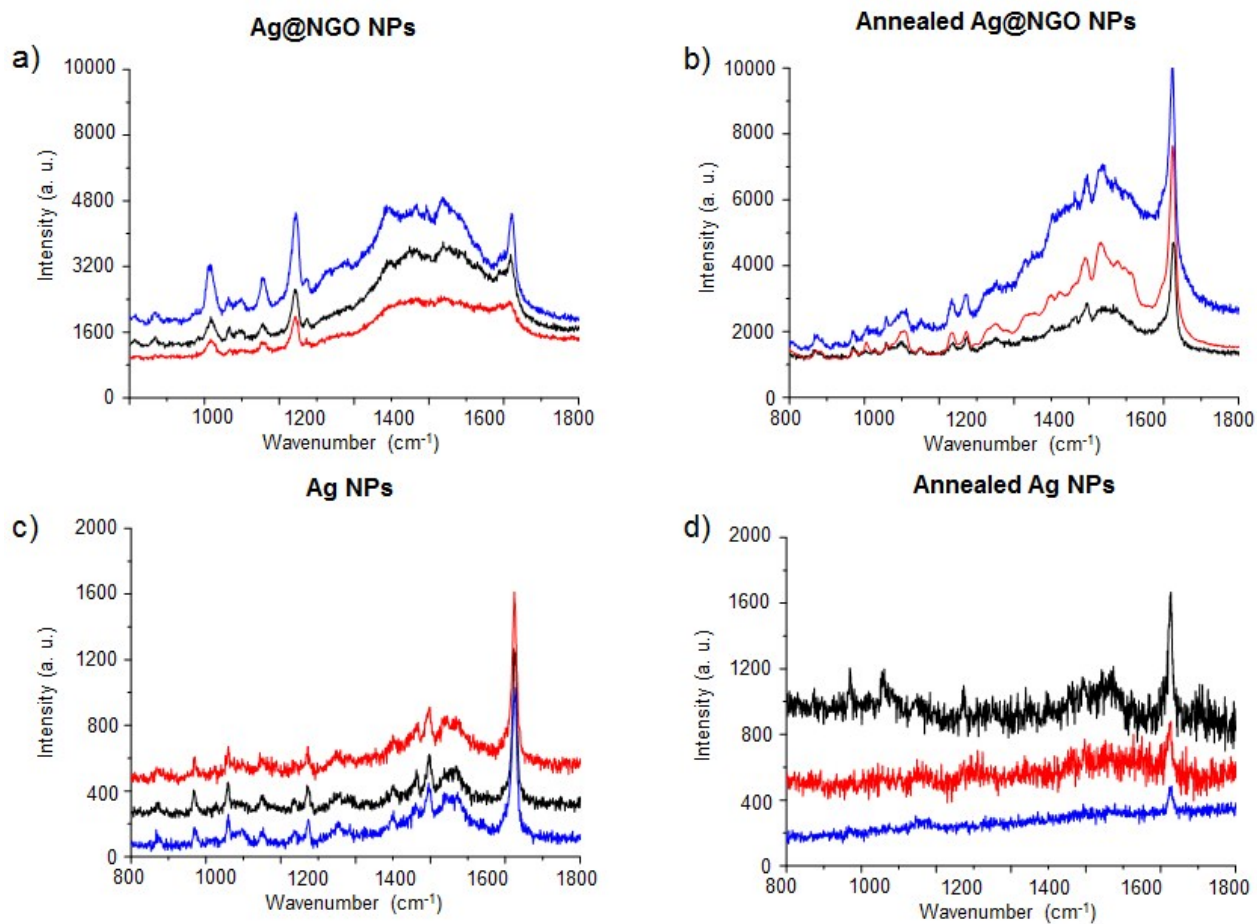


Figure S6. SERS spectra of methylene blue (MB) on surface immobilized Ag@GON NPs before (a) and after thermal treatment (b). SERS spectra of MB on surface immobilized Ag NPs before (c) and after thermal treatment (d).

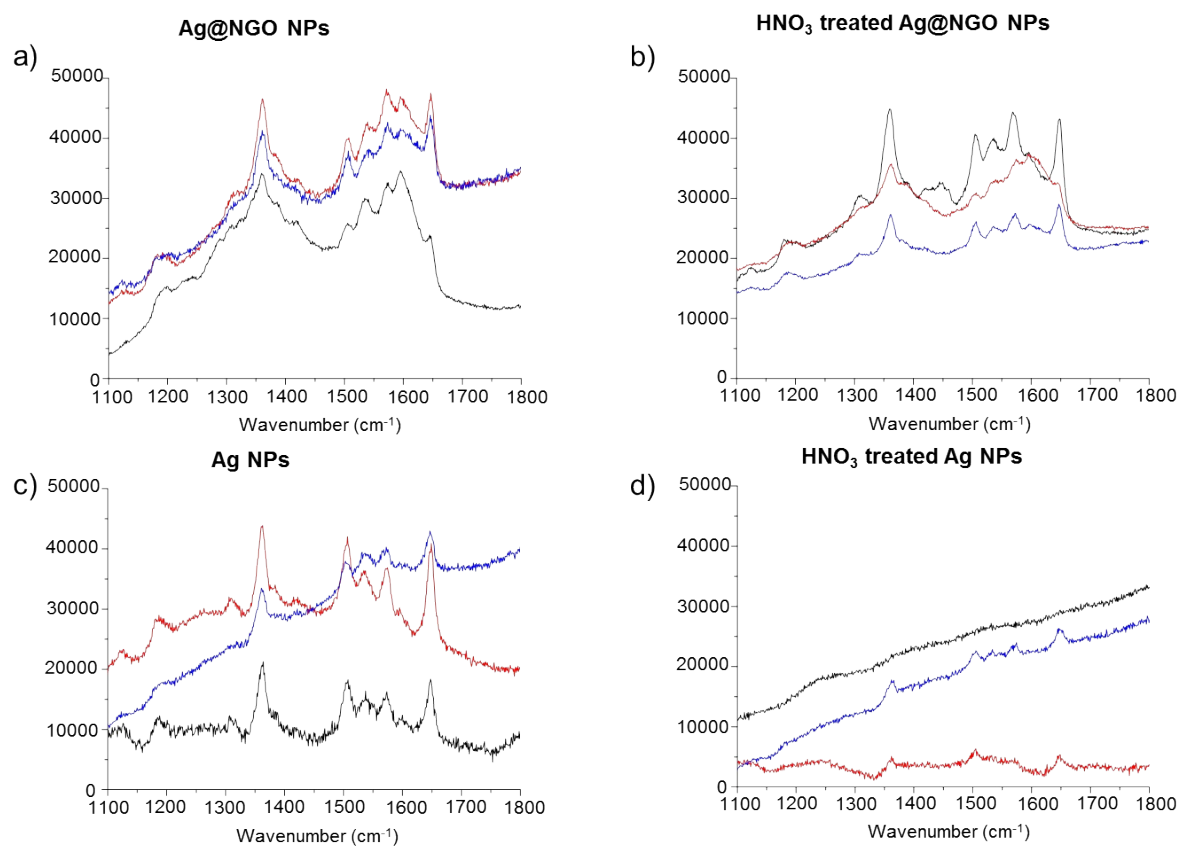


Figure S7. SERS spectra of R6G with colloidal Ag@GON NPs before (a) and after 1.0 mM HNO₃ treatment for 1 h (b). SERS spectra of R6G with colloidal Ag NPs before (c) and after 1.0 mM HNO₃ treatment for 1 h (d).

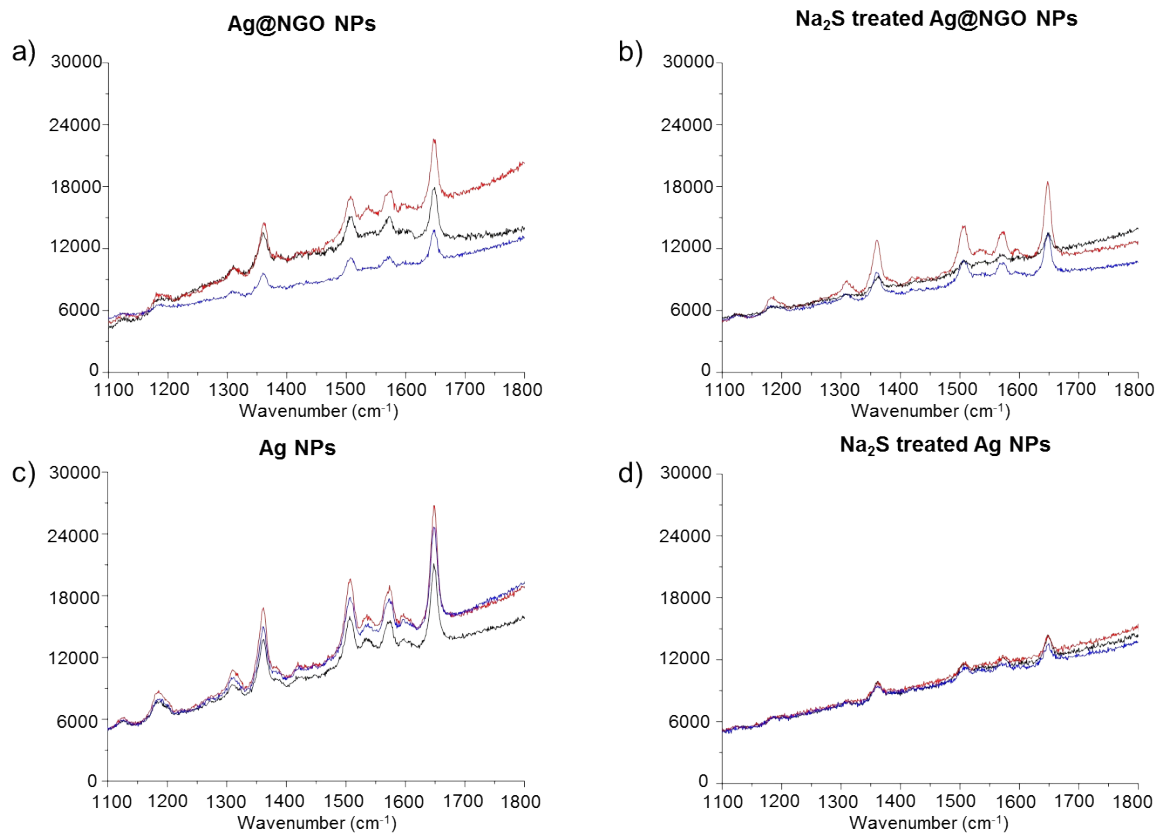


Figure S8. SERS spectra of R6G with colloidal Ag@GON NPs before (a) and after 0.1 mM Na₂S treatment for 1 h (b). SERS spectra of R6G with colloidal Ag NPs before (c) and after 0.1 mM Na₂S treatment for 1 h (d).

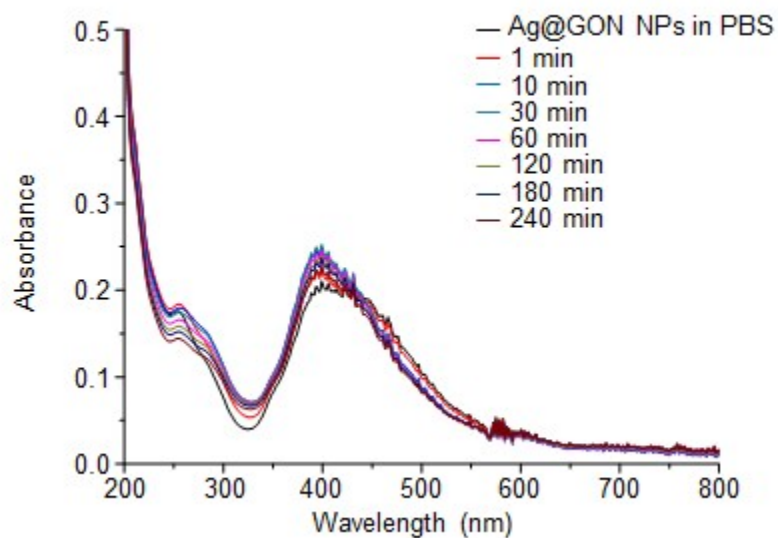


Figure S9. The changes of UV-vis spectra of Ag@GON NPs as a function of incubation time in phosphate buffered saline (PBS) buffer. The SPR band of Ag@GON NPs was almost maintained for 240 min in PBS. This result showed the high colloidal stability of Ag@GON NPs.

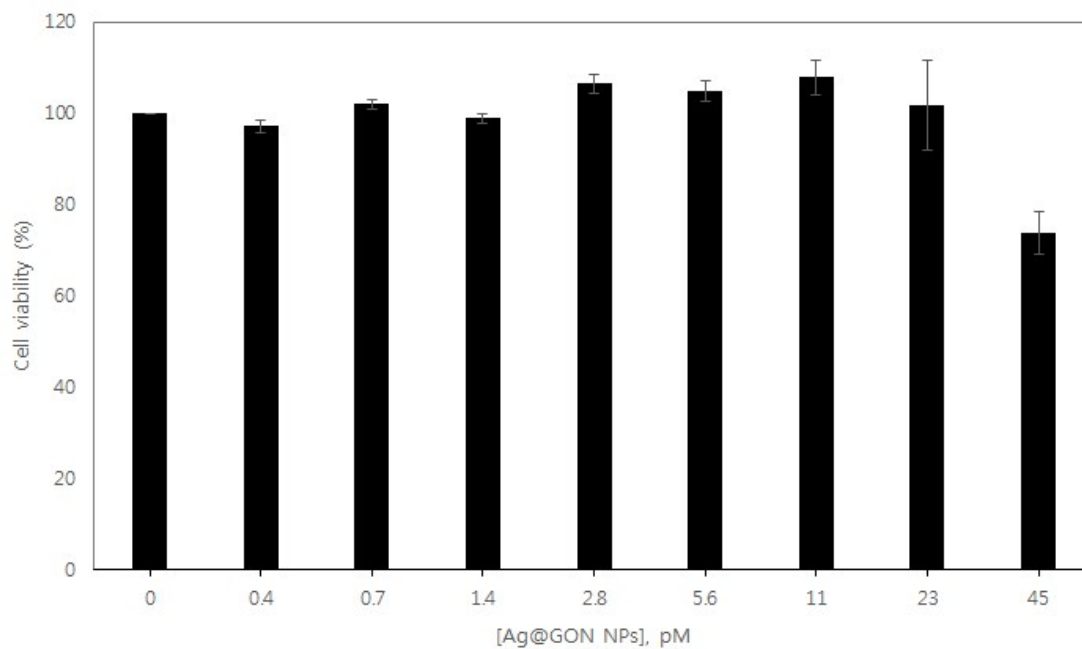


Figure S10. Cytotoxicity was estimated by treatment of varying concentration Ag@GON NPs from 0 – 45 pM to HeLa cell. Cell viability was evaluated by CCK-8 assay.

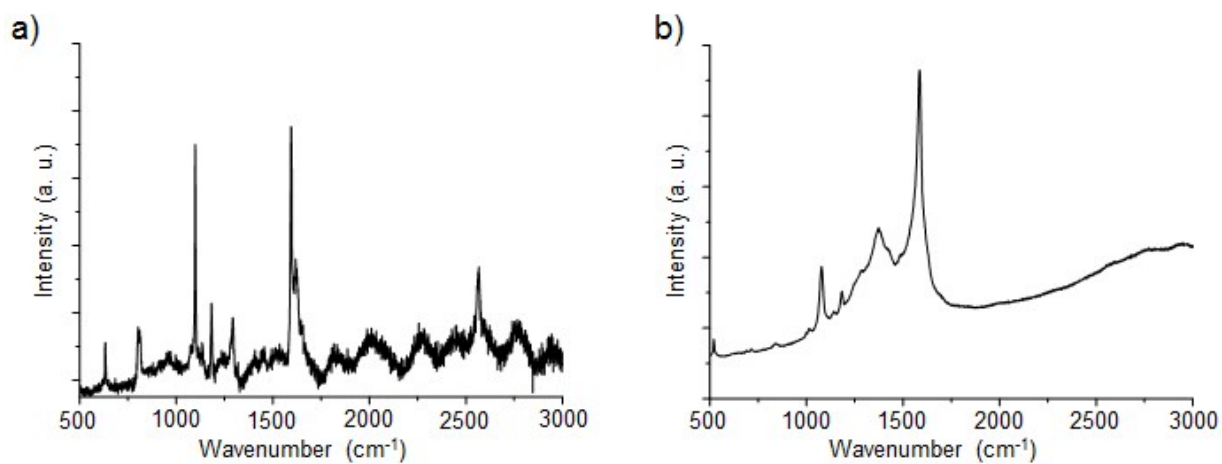


Figure S11. Normal Raman spectrum of 4-mercaptobenzoic acid (MBA) (a) and SERS spectrum of MBA on Ag@GON NPs.

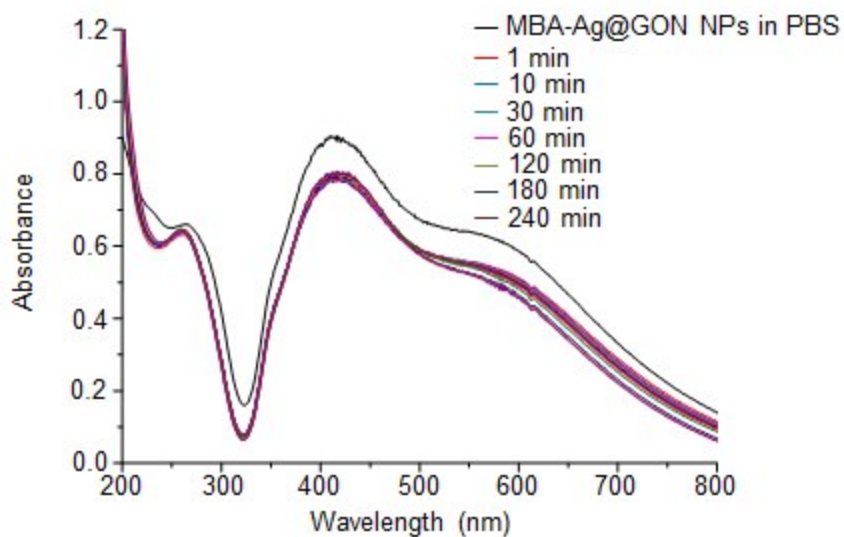


Figure S12. The changes of UV-vis spectra of MBA-Ag@GON NPs as a function of incubation time in phosphate buffered saline (PBS) buffer. The SPR band of MBA-Ag@GON NPs was almost maintained for 240 min in PBS. This result showed the high colloidal stability of MBA-Ag@GON NPs.

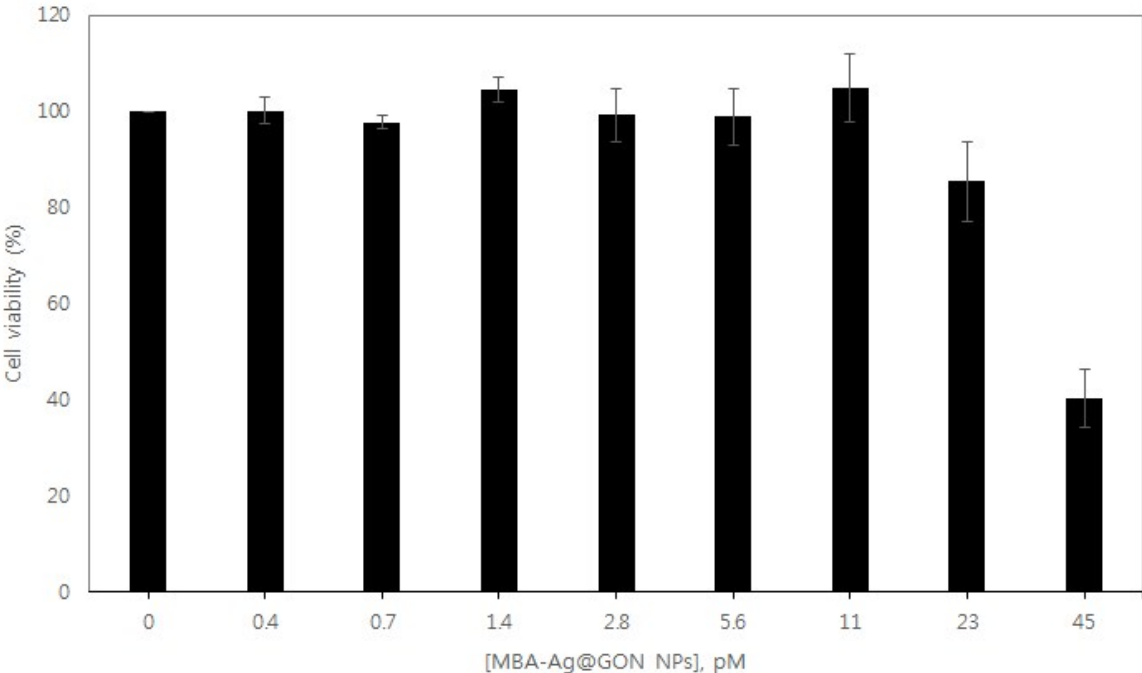


Figure S13. Cytotoxicity was estimated by treatment of varying concentration MBA-Ag@GON NPs from 0 – 45 pM to HeLa cell. Cell viability was evaluated by CCK-8 assay.

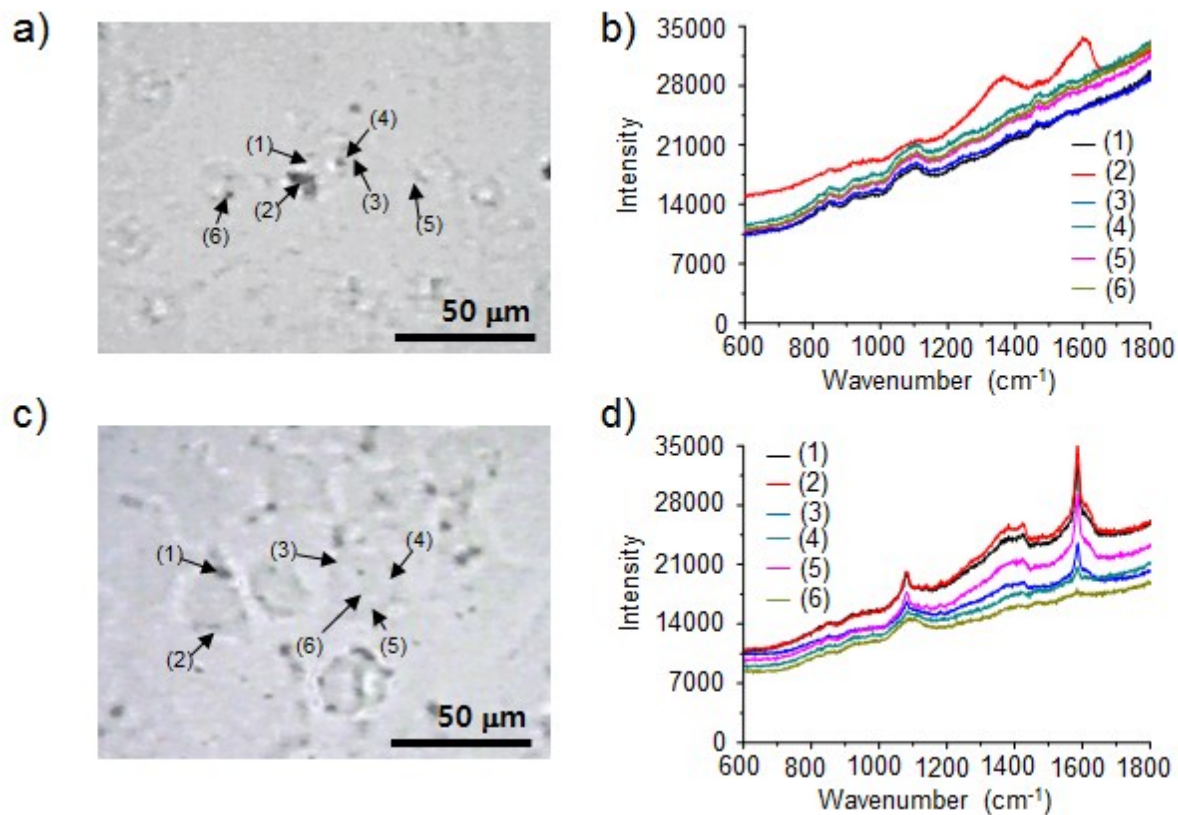


Figure S14. Bright field microscopy image (a) and Raman spectra (b) obtained from Ag@GON NPs treated HeLa cells. Bright field image (c) and Raman spectra (d) obtained from MBA-Ag@GON NPs treated HeLa cells. Each numbered arrow indicates the positions of analyzed spots of their corresponding HeLa cells images. All of Raman spectra were obtained by using 514 nm excitation source with 0.8 mW power.

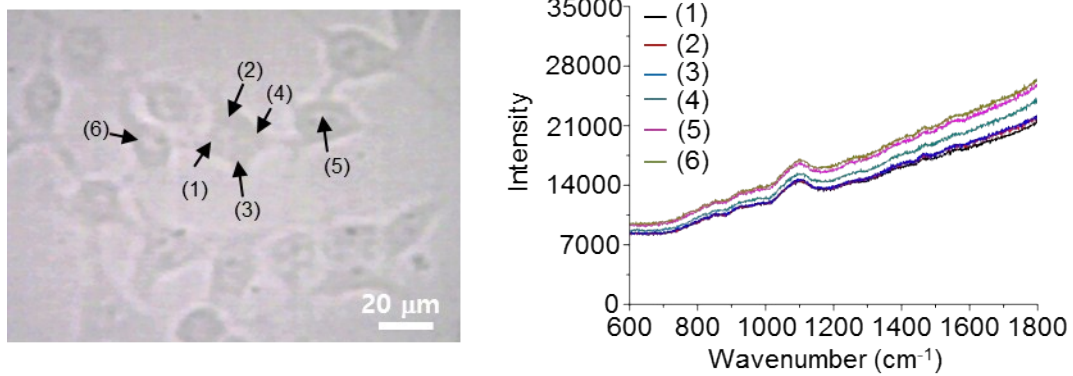


Figure S15. Raman analysis of HeLa cells without any treatment.