Supporting Information

Facile preparation of SERS-active nanogap-rich Au nanoleaves

Jin-Hyung Hong,[ad] Yong-Kyung Hwang,[ad] Jin-Yeon Hong,[a] Hee-Jin Kim,[b] Sung-Jin Kim,[b]
Yong Sun Won,[c] and Seong Huh[a]*

[a]*Department of Chemistry and Protein Research Center for Bio-Industry, Hankuk University of Foreign Studies,Yongin 449-791, Korea, E-mail: shuh@hufs.ac.kr*

[b]*Department of Chemistry and Division of Nano Science, Ewha Womans University, Seoul 120-750, Korea*

[c]*Department of Chemical Engineering, Pukyong National University, Pusan 608-739, Korea*

[d]*These authors contributed equally.*

Experimetal Details

Powder X-ray diffraction patterns were obtained by using a Rigaku MiniFlex (30 kV, 15 mA). FE-SEM images for metal-coated samples were recorded on a Hitachi S4200 (5 kV). Noncoated sample images were recorded on a Hitachi Ultra-High-Resolution Analytical FE-SEM SU-70 (5 kV). The water suspension of the sample was dropped and dried on Cu grid supported by holey carbon film for TEM measurement, where a JEOL JEM-2100F (200 kV) or a JEM-3000F (300 kV) equipped with an EDAX for EDS spectrum were used. Mass spectrometry was performed on a Thermo Finigan LCQ LC/MS system. XPS data was collected on an ESCA 2000. Cyclic voltammetry of 2-thiophenemethanol (Aldrich) in phosphate buffered saline (PBS, pH 7.0) was performed using a Gamry Series G750 Potentiostat/Galvanostat/ZRA. Au disc electrode with a dimension of 0.0201 cm^2 was used. A Pt coil and an Ag/AgCl electrode were used as a counter electrode and a reference electrode, respectively. The respective scan rate and scan range were 50 mV/s and 0 – 1.3 V.

Micro Raman measurements were performed in backscattering geometry with a Horiba Jobin Yvon LabRam HR system fitted with a liquid-nitrogen cooled CCD multichannel detector. The spectra were collected under ambient conditions using 633 nm line of a He-Ne laser. All Au nanoleaves (GN3) were exposed with 10 μW laser power and 10 s of acquisition time with an area of 1 μm. Control samples were measured at a higher laser power and acquisition time of 1 mW and 60 s, respectively. Methylene blue (MB) was used as a molecular probe for the SERS experiment. The MB dye absorbs at 630 nm and emits at 670 nm. A control experiment on flat gold surface was done by casting of 10^{-5} M MB dye solution (30 μL) on Aldrich gold coated microscope slide. The reaction supernatant in a plastic sample holder was directly measured without any treatments after synthesis of Au nanoleaves. Collected Au nanoleaves (30 mg) were redispersed into H_2O (20 mL) and sonicated. Then the Au nanoleaves suspended solution (30 μL) was drop-casted on Si wafer and dried at 80 °C for 10 min. Repeat this casting and drying step again to the same location spot. The prepared MB aqueous solutions (30 μL) were drop-casted to the premade gold coated surface and dried at room-temperature in the dark.

SERS enhancement factor (EF) by Au nanoleaves was estimated from the following equation according to the literature[S1]:

$$\mathrm{EF} = (I_{\mathrm{SERS}}/I_{\mathrm{Raman}})/(N_{\mathrm{bulk}}/N_{\mathrm{ads}})$$

where I_{SERS} and I_{Raman} indicate the intensity of the selected Raman signal at 1623 cm^{-1} obtained by SERS experiment using Au nanoleaves and the Raman scattering spectrum of the known concentration of a MB bulk solution. The N_{bulk} is the number of MB molecules from the bulk solution. The N_{ads} is the number of MB molecules adsorbed on the Au nanoleaveas. Due to the complex geometry of Au nanoleaves, we could not accurately measure N_{ads}. Therefore, we safely assumed that all MB molecules are located in nanogaps. This approximation will give rise to the minimum range of EF value. The actual EF should be larger than the value obtained by this approximation. Since the Raman spectrometer is same, N_{bulk} and N_{ads} could be replaced by the molar concentrations of the bulk and SERS measurement solution, respectively.[S2] The EF for the SERS detection of MB in our experiment is estimated to be ~2.0×10^{8} (See Fig. S13).

S1) R. Jin, *Angew. Chem. Int. Ed.* **2010**, *49*, 2826-2829.

S2) H. Liu, Q. Yang, *CrystEngComm,* **2011**, *13*, 2281-2288.

Figure S1. Cyclic voltammogram of 2-thiophenemethanol in phosphate buffered saline (PBS, pH 7.0).

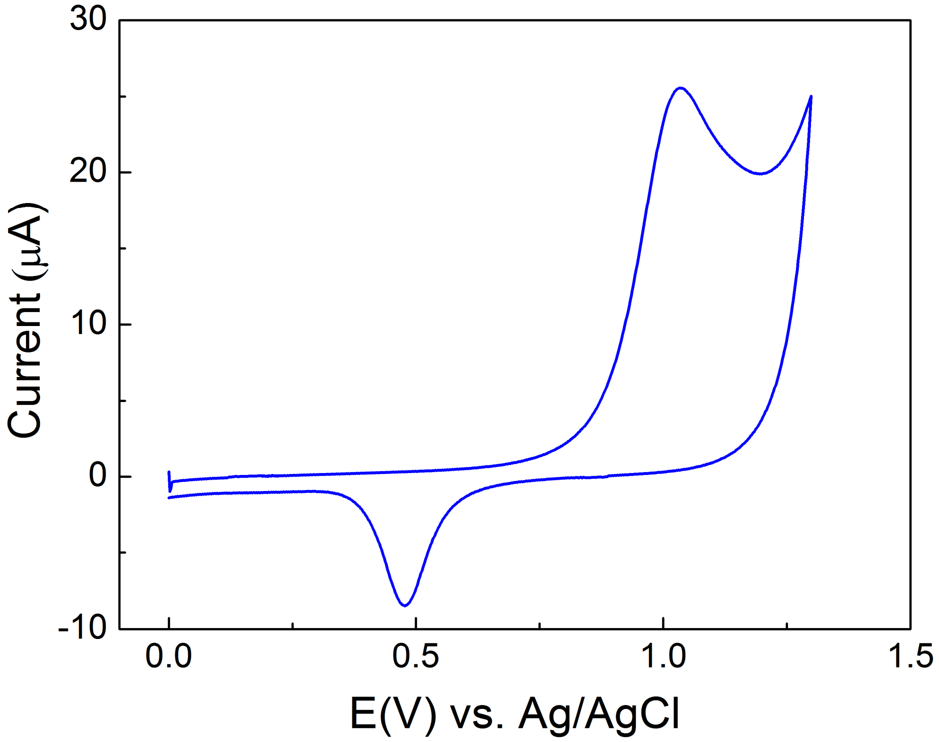

Figure S2. High-Resolution SEM images of Au nanoleaves (GN3) recorded without metallic coating.

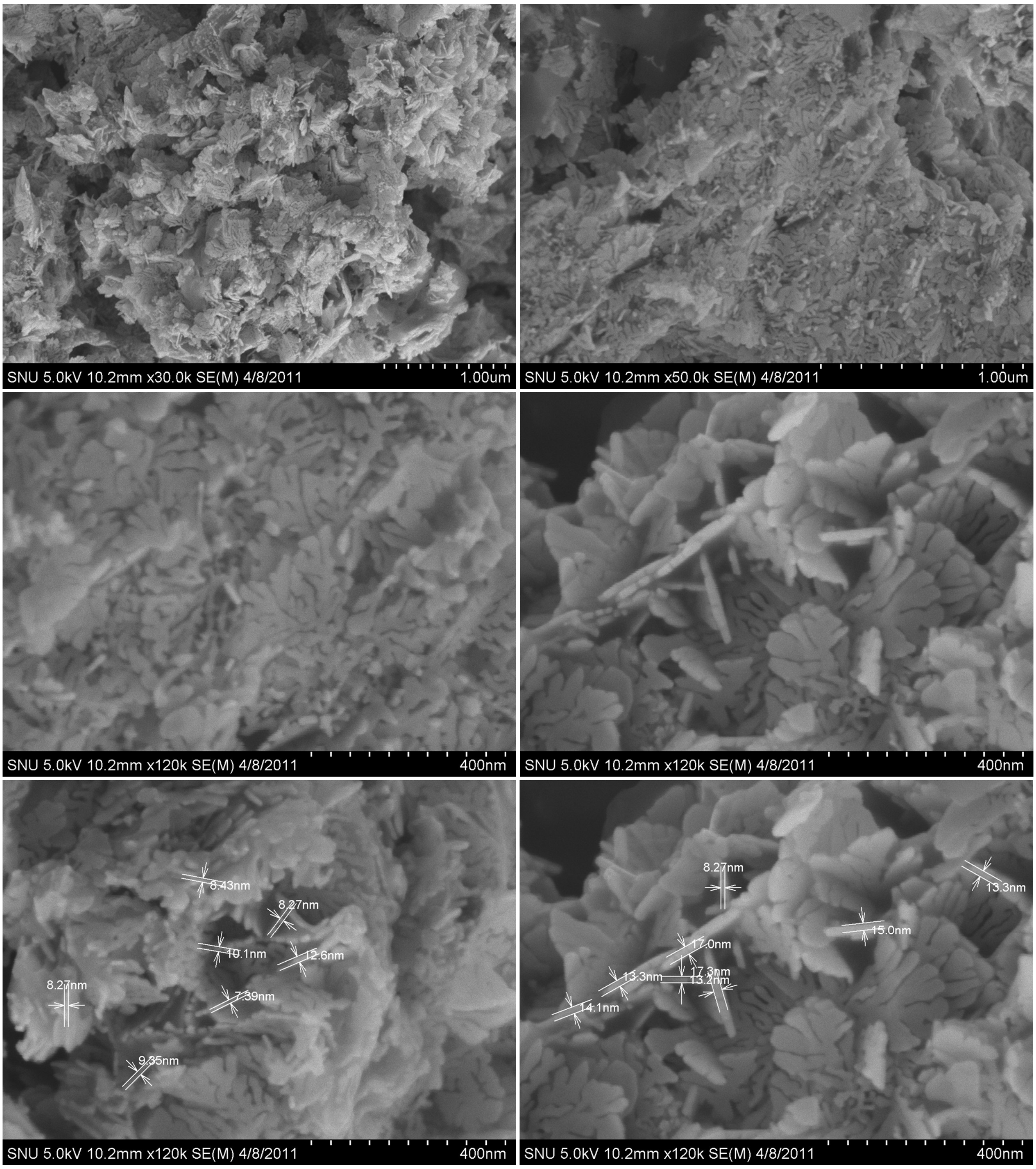

Figure S3. EDS spectrum of GN3 sample obtained by TEM.

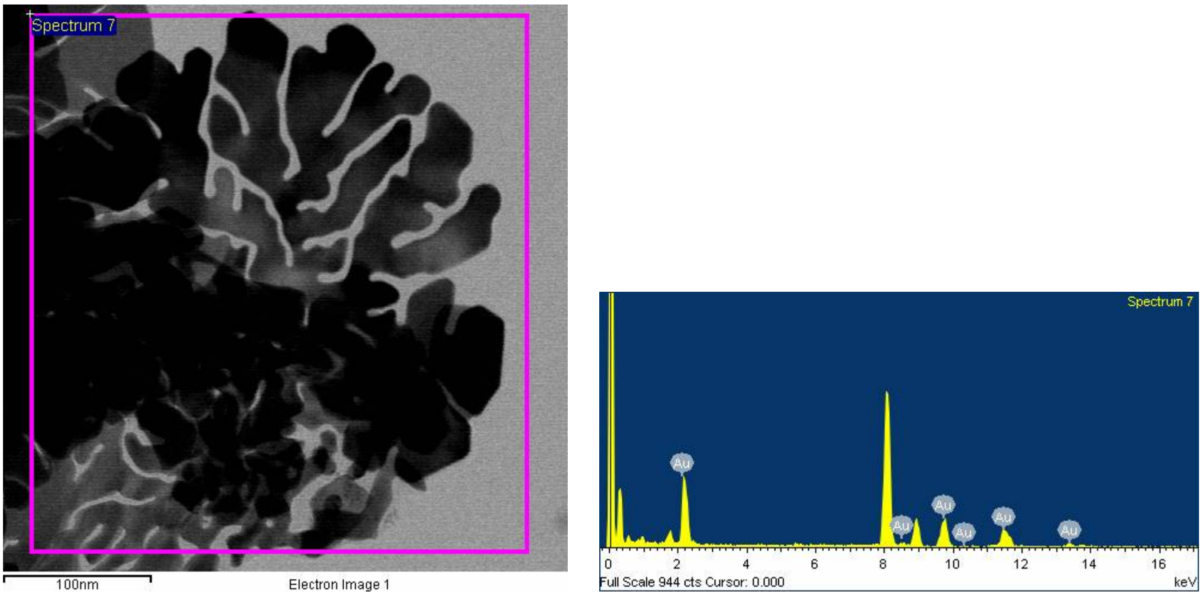

Figure S4. HRTEM image of the nanogap in GN3. The interplanar spacing of 2.35 Å corresponds to Au {111} diffraction plane.

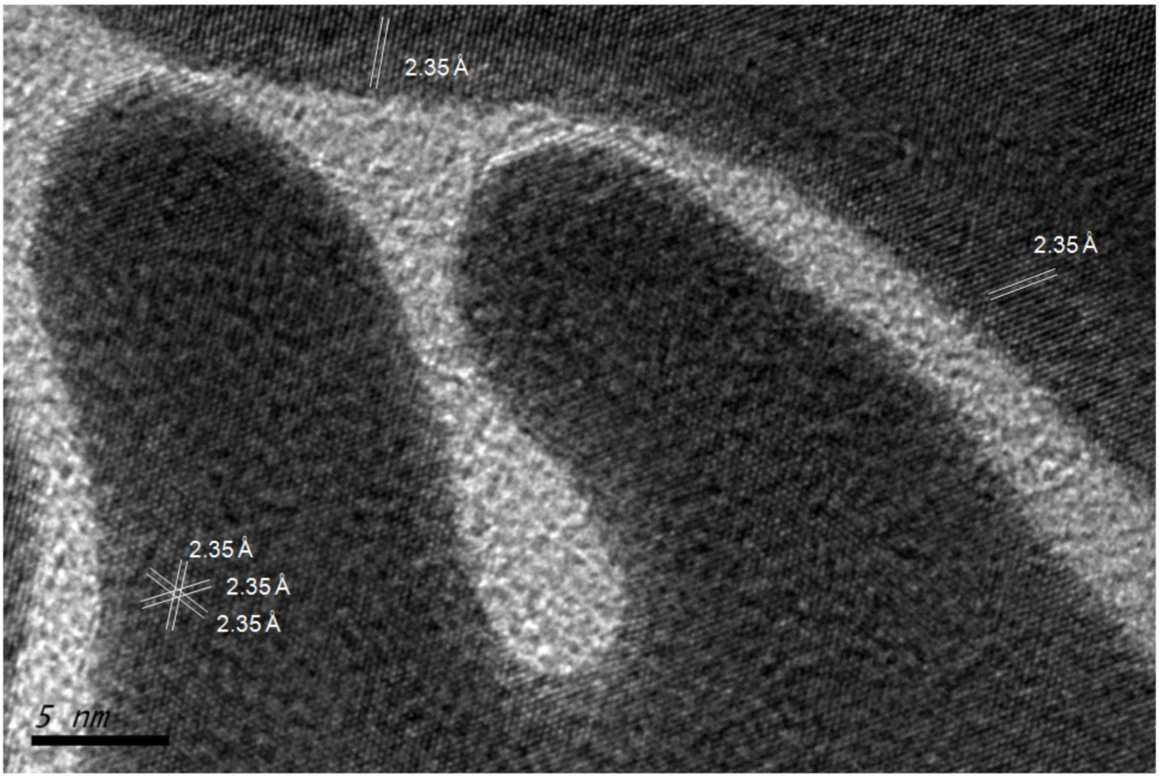

Figure S5. Moiré fringes observed from Au nanoleaves, GN3.

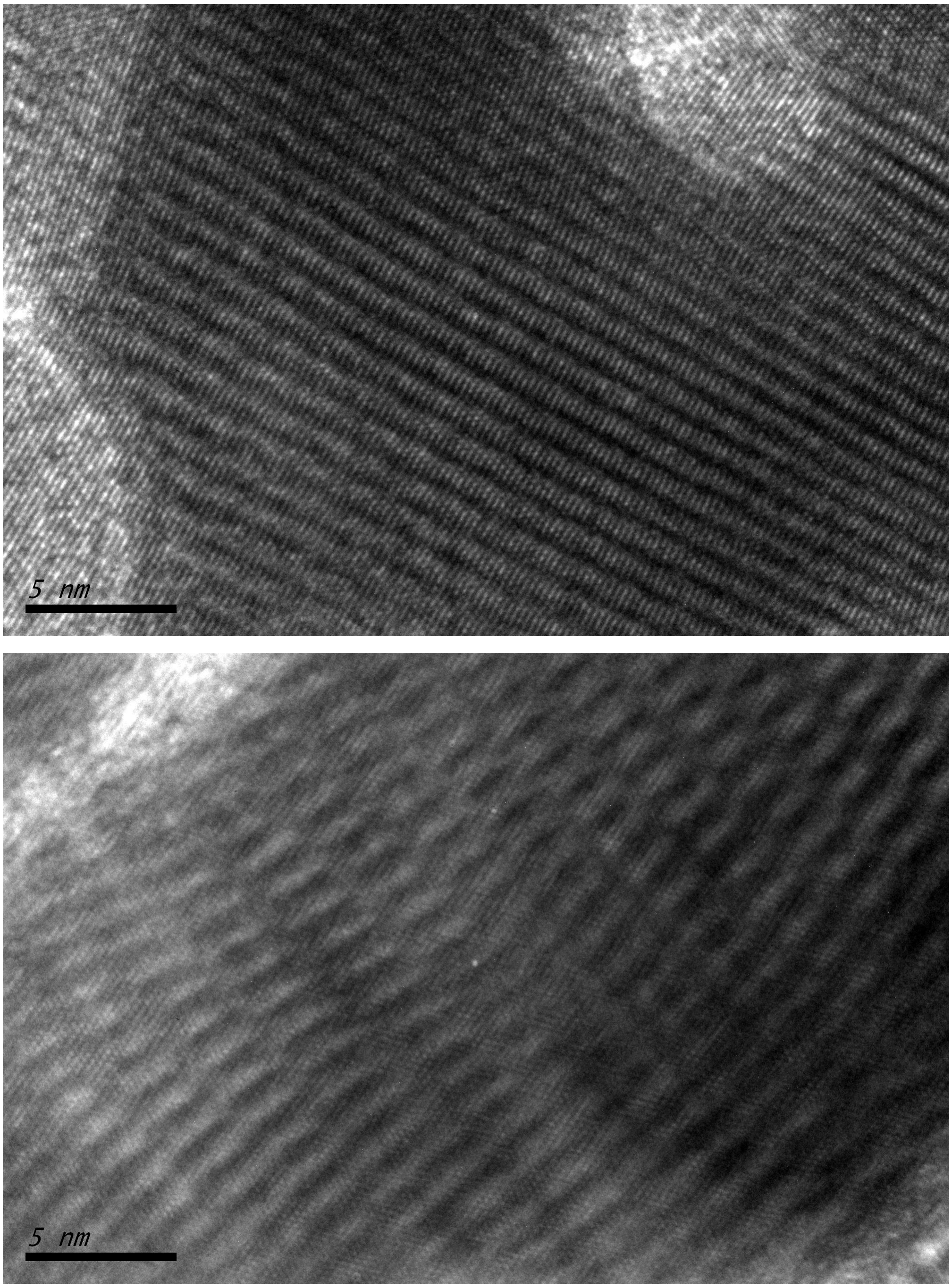

Figure S6. HRTEM image of the nanogap edge along the [011] zone axis. The Fourier transform (FT) patterns for boxes A and B are shown together.

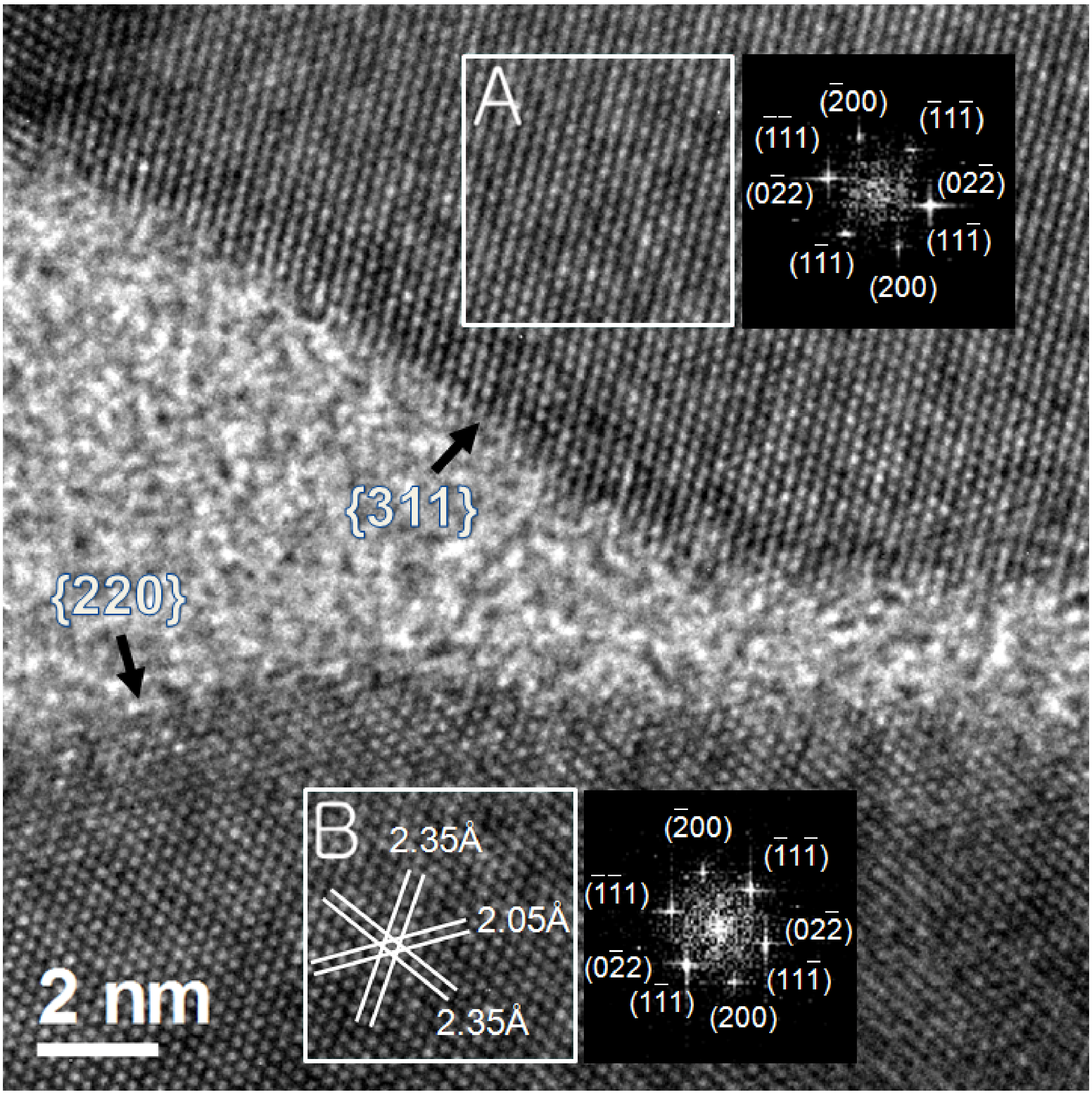

Figure S7. Time-dependent UV/visible absorption spectra during the formation of Au nanoleaves, GN3. Arrows indicate the change of the spectrum as time progresses. From 1 min to 20 min (a), and from 20 min to 120 min (b).

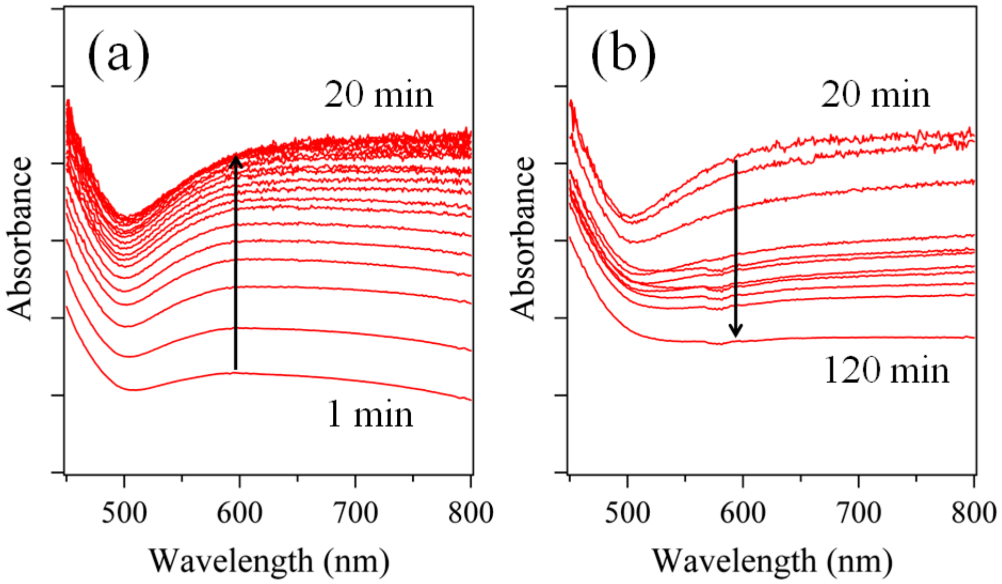

Figure S8. HRTEM images of the aliquots periodically withdrawn from the reaction mixture during Au nanoleaves (GN3) formation.

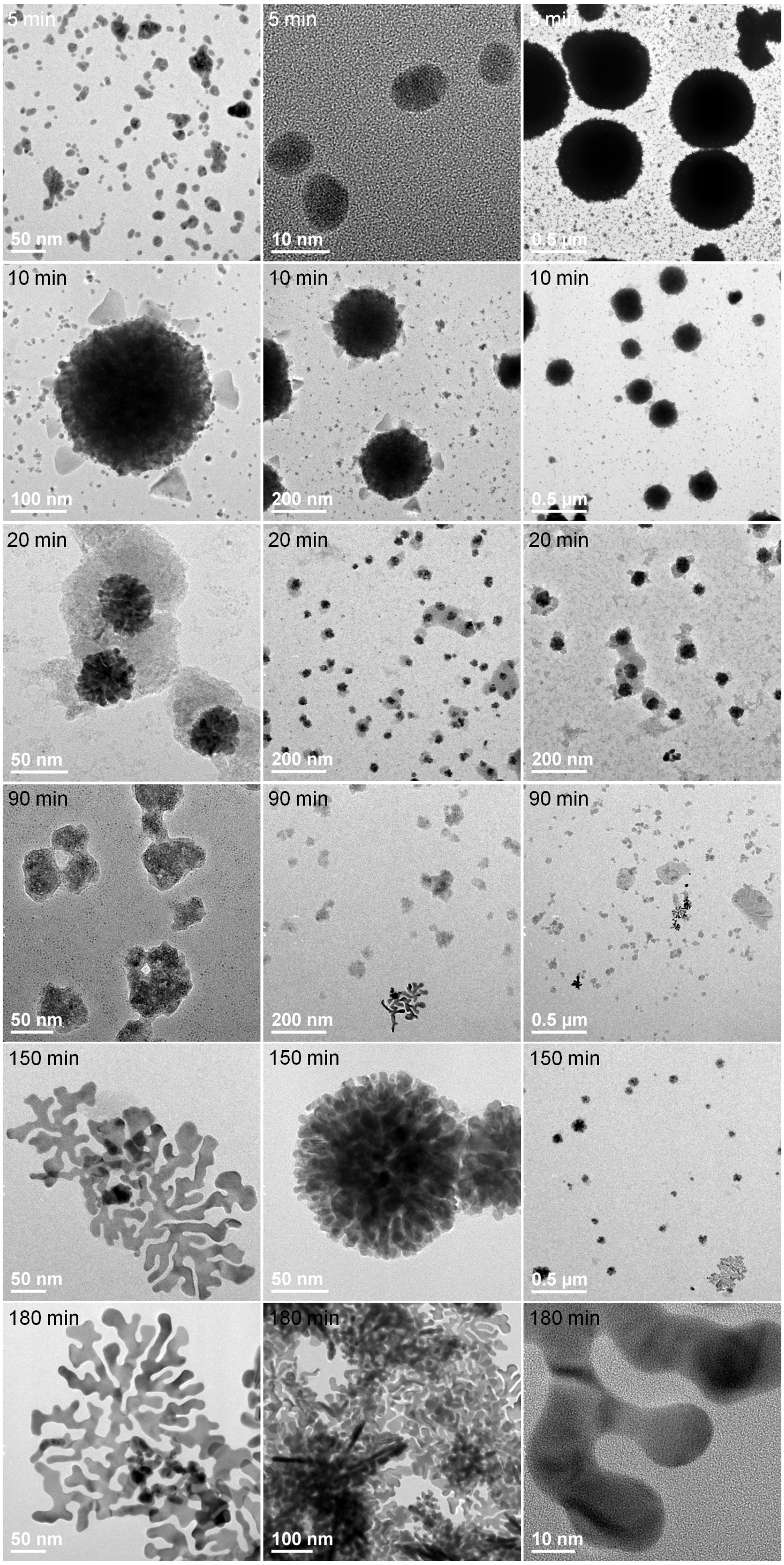

Figure S9. ESI mass spectrum of the reaction supernatant for the preparation of GN3.

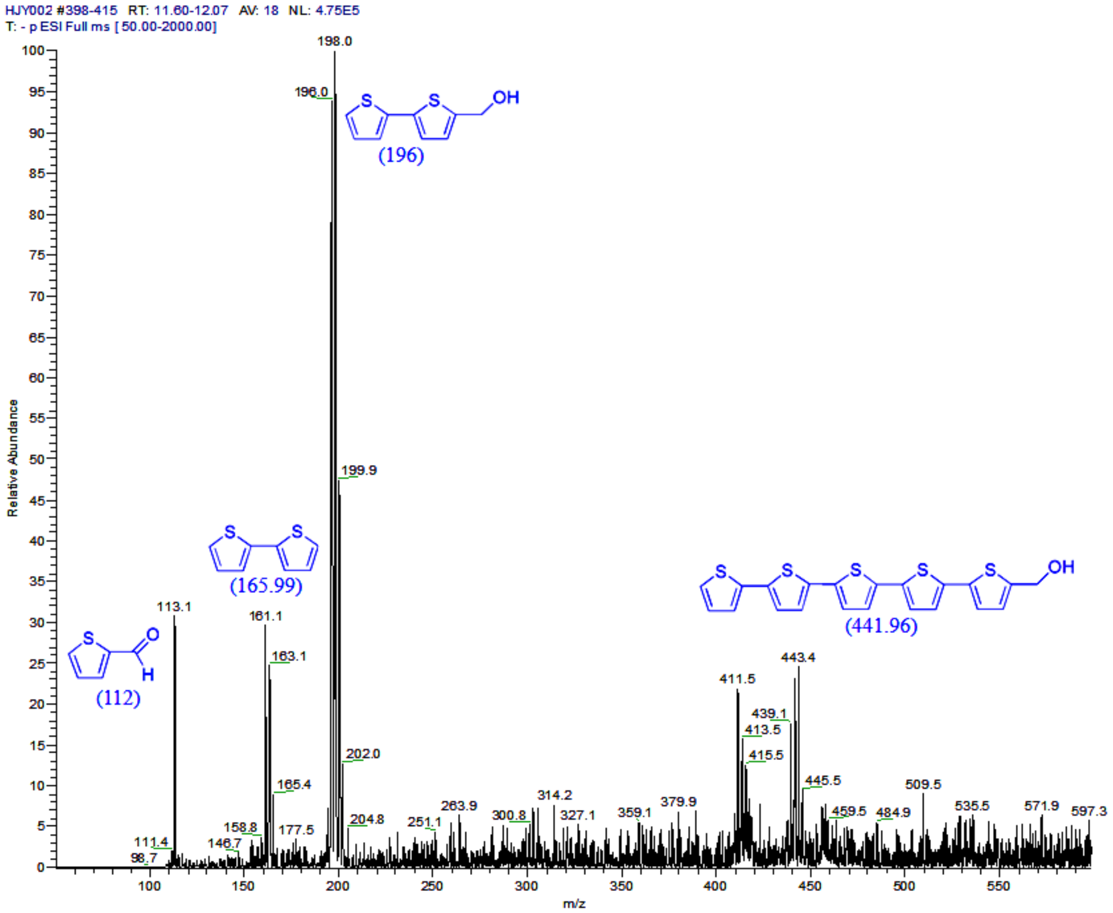

Figure S10. Au 4f XPS spectrum of GN3.

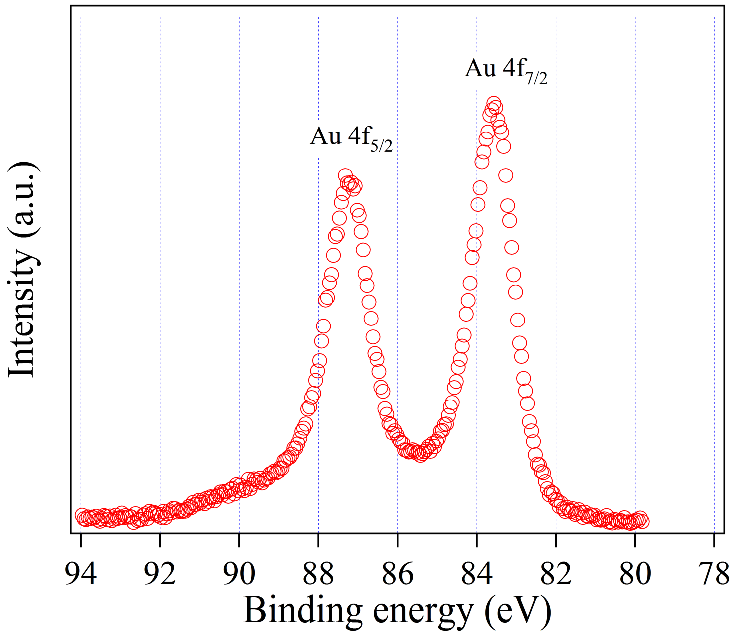

Figure S11. Full range XPS spectrum of GN3.

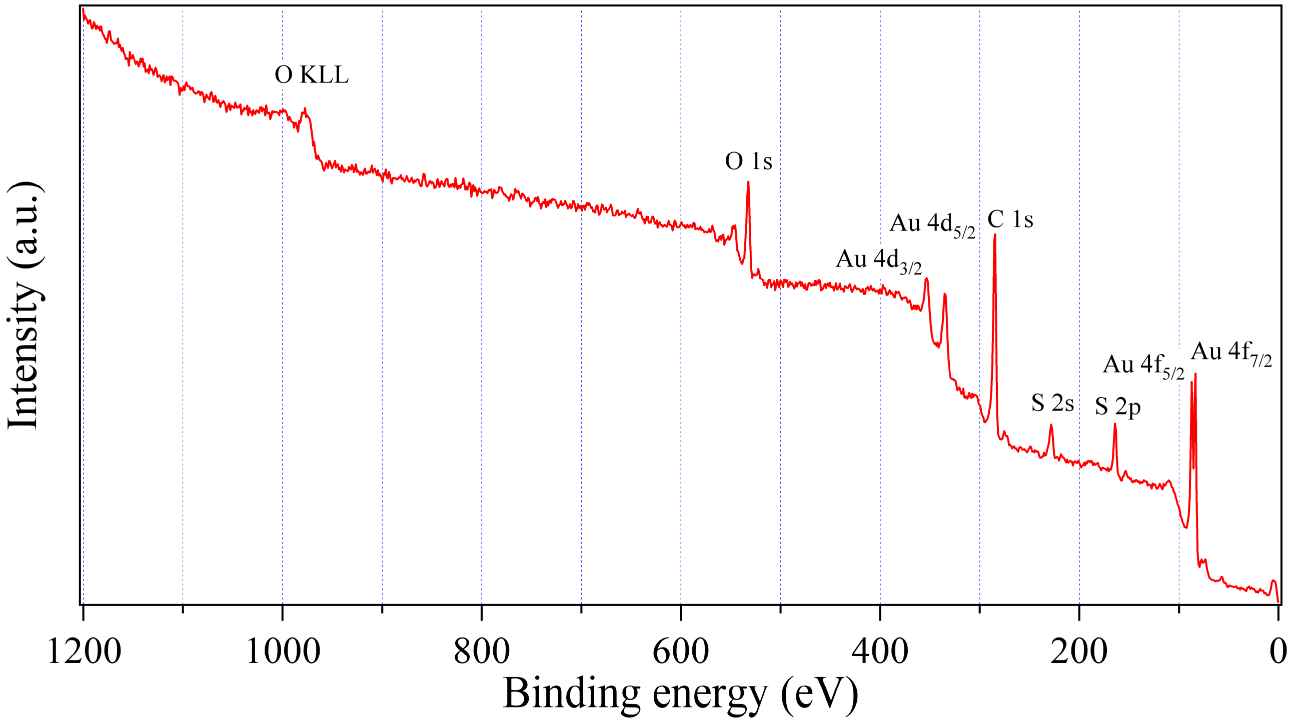

Figure S12. Au nanoparticles encapsulated in polythiophene polymerized from 3-thiophenemethanol. TEM image (a), HRTEM image of the embedded Au nanoparticles (b), Raman spectrum obtained with 633 nm excitation (c).

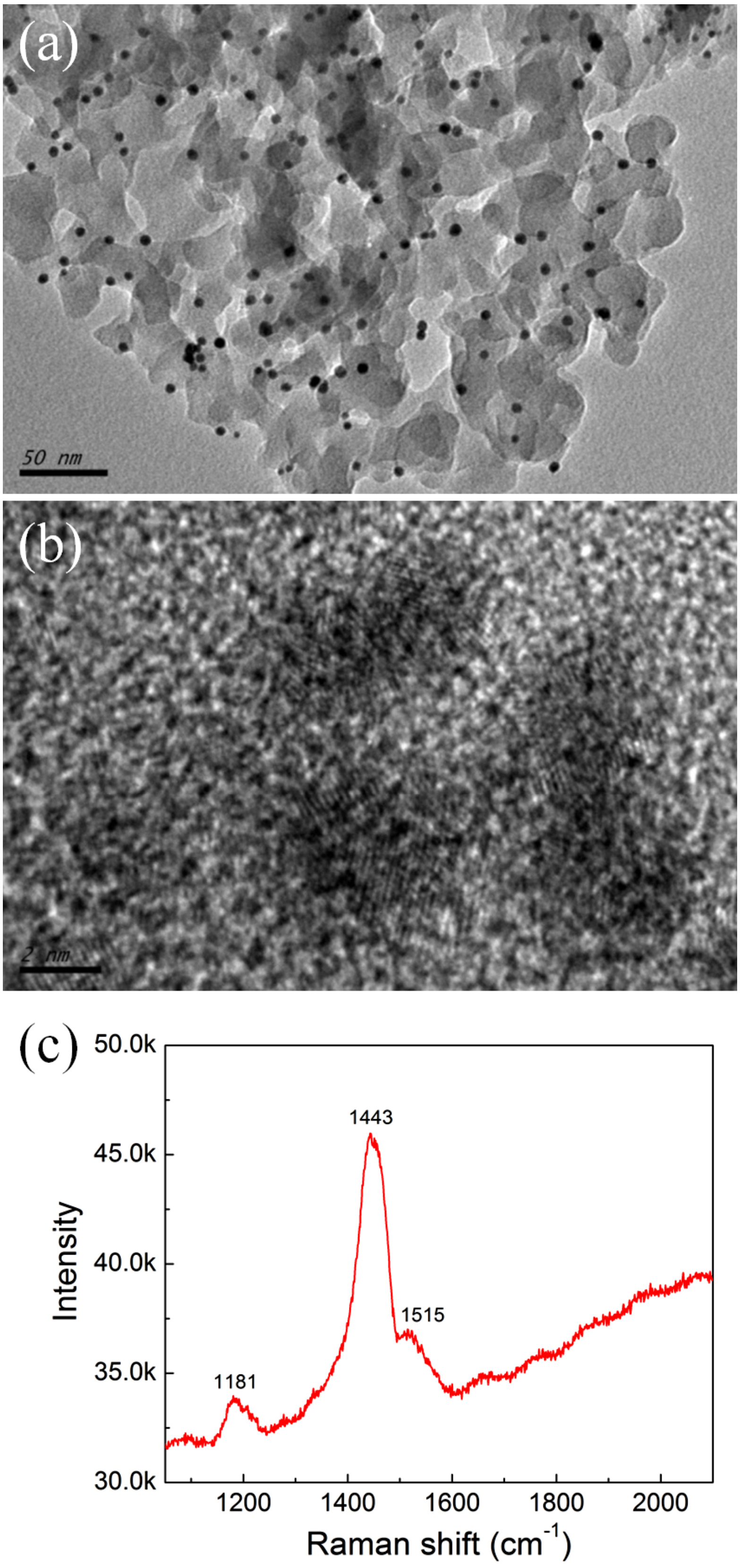

Figure S13. Raman spectrum of the bulk MB solution (1×10^{-1} M) and the SERS spectrum of the MB solution (1×10^{-9} M) on Au nanoleaves (GN3).

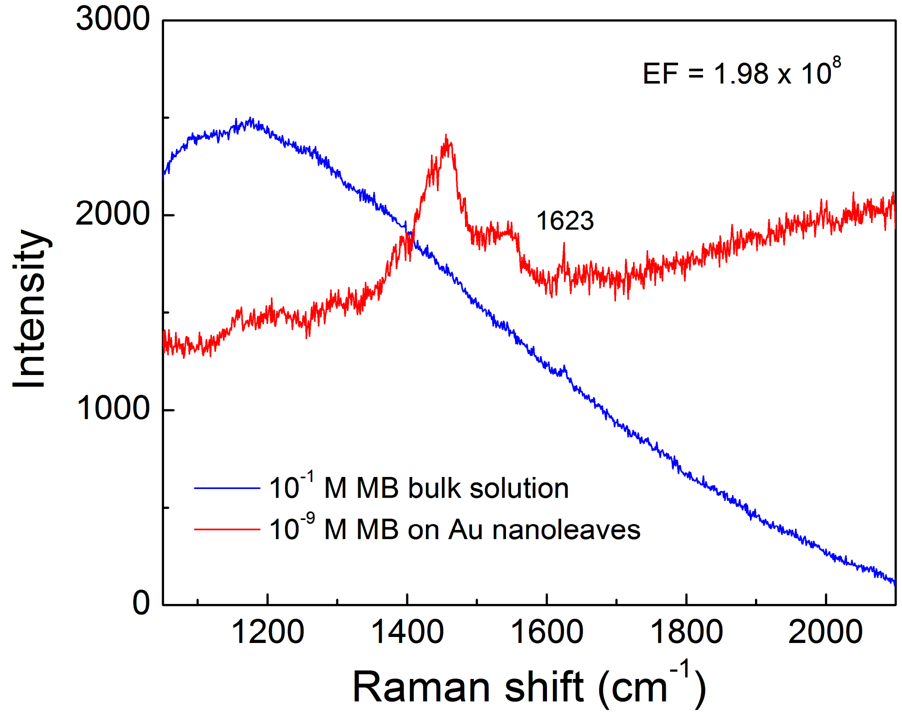

Figure S14. Concentration-dependent Raman spectra of (a) the CV solution (1×10^{-5} M) on flat Au coated glass, (b) the supernatant of the reaction mixture without CV treatment, and CV solutions on GN3 samples on Si wafer (c) 1×10^{-8} M, (d) 1×10^{-7} M, (e) 1×10^{-6} M, and (f) 1×10^{-5} M.

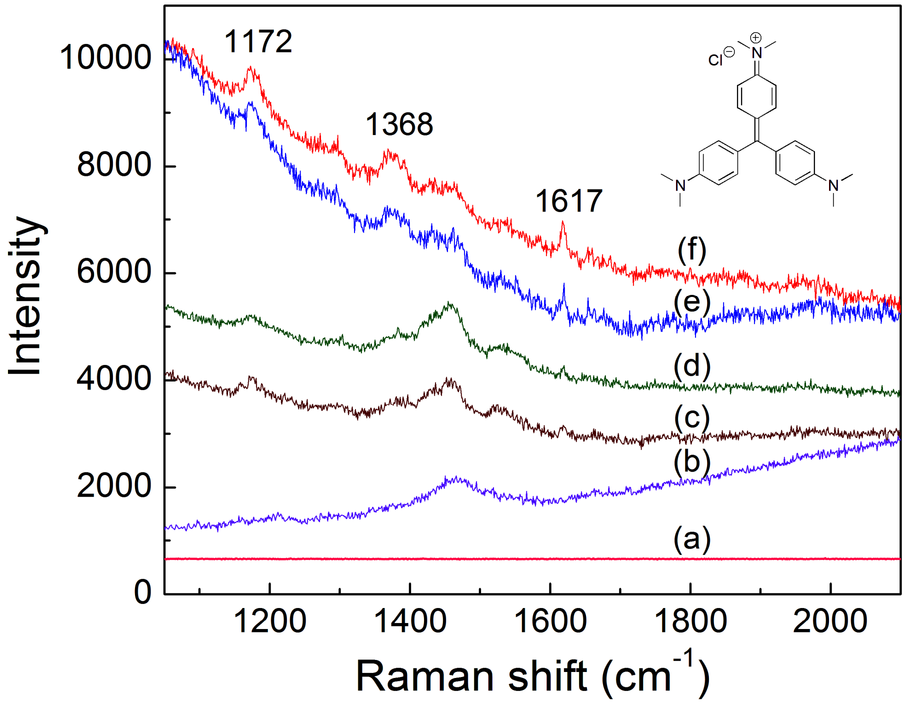

Figure S15. Raman spectra of the MB solution (1×10^{-5} M) on Au nanoleaves (GN3) with different excitation wavelengths.