Supplementary material for

Self-patterning of Graphene-encapsulated Gold Nanoparticles for Surface-enhanced Raman Spectroscopy

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S1. Experimental section

S1.1. Materials and Methods

Si wafers (111) were purchased from IWS (Colfax, CA). Potassium gold (III) chloride was purchased from Sigma-Aldrich (St. Louis, MO). Hydrogen fluoride (50%) was purchased from VWR (Atlanta, GA). Ammonium fluoride was purchased from Alfa Aesar (Ward Hill, MA). Xylene used for CVD growth of multilayer graphene shell was purchased from Fisher Scientific (Pittsburg, PA). Rhodamine 6G (R6G) and Methylene blue (MB) were purchased from Alfa Aesar (Ward Hill, MA). All chemicals were used without further purification. Buffered oxide etch (BOE) solution was prepared by mixing 40% NH_4F and 50% HF in DI-water with a volume ratio of 6:1. DI water (18.1 MΩ-cm) was obtained using a Barnstead International DI water system (E-pure D4641). High-temperature annealing was conducted using a CMF 1100 oven furnace (MTI Corporation). Growth of multilayer graphene shell was carried out in in a Lindberg blue three-zone tube furnace (Watertown, WI) with a quartz tube from ChemGlass (Vineland, NJ). Plasma treatment was conducted in a Nordson March Jupiter III Reactive Ion Etcher (Concord, CA).

S1.2. Patterning of Au nanoparticles on Si wafer

Gold (Au) film was deposited onto the Si wafer by a galvanic deposition process [S1,S2]. Briefly, Si wafers were cleaned in acetone for 10 min under sonication. The wafer was further treated in BOE solution for 30 s to remove the surface oxide layer. This was followed by directly immersing the wafer in the galvanic deposition solution (1 mM $KAuCl_4$ + 1% HF) for 1 min. The obtained

Au film was rinsed with DI-water and dried in flowing N_2. Subsequently, the sample was inserted in a box oven and annealed for 10 min at 850 ˚C to form uniformly dispersed Au nanoparticles.

S1.3. Growth of multilayer graphene shell on Au nanoparticles

Formation of multilayer graphene shell on the Au nanoparticles was achieved *via* a xylene-based CVD process reported by the authors.[**Error! Bookmark not defined.**-**Error! Bookmark not defined.**] Briefly, Au nanoparticles patterned on the Si wafer were oxidized with oxygen plasma for 15 min to produce a gold oxide surface layer. The samples after plasma oxidation were put in the center of the quartz tube furnace. The growth process was carried out at 675 ˚C for 1 h. Xylene was used as the carbon source with a feeding rate of 10 mL/h, which was carried by 10% H_2/Ar with a total flow rate of ~1.15 SLM. For the purpose of modifying the shell structure and thickness, the as-produced GNPs were treated with oxygen plasma for 15 s.

S1.4. Anchoring of organic dyes on Au nanoparticle and GNP substrates

The Au nanoparticles- or GNPs-decorated Si wafers were used as SERS substrates for detection of MB and R6G. The substrates were treated in BOE solution for 10 s, washed with DI-water, and dried in flowing N_2. This was followed by incubating the substrates in aqueous solution of R6G and/or MB (10^{-6} M) for 10 h. The substrate were then washed with DI-water and dried in flowing N_2. Raman spectra of R6G and/or MB were directly collected from various spots on these substrates. The average Raman intensity with standard deviation was further calculated.

S1.5. Characterizations

FE-SEM JEOL-7000 Scanning Electron Microscopy (SEM) and Tecnai F-20 Transmission Electron Microscopy (TEM) were used to characterize the morphology and structure of Au nanoparticles, as-produced GNPs, as well as the GNPs after plasma treatment. Philips X'Pert-MPD X-ray Diffraction (XRD) System was used for the phase analysis of the Au film after galvanic deposition. Raman spectra were collected using a Bruker Senterra system (Bruker Optics Inc. Woodlands, TX) equipped with a 785 nm laser source. The laser power for all the measurement are 10 mW. The integral time and co-additions were set as 15 s and 2, respectively.

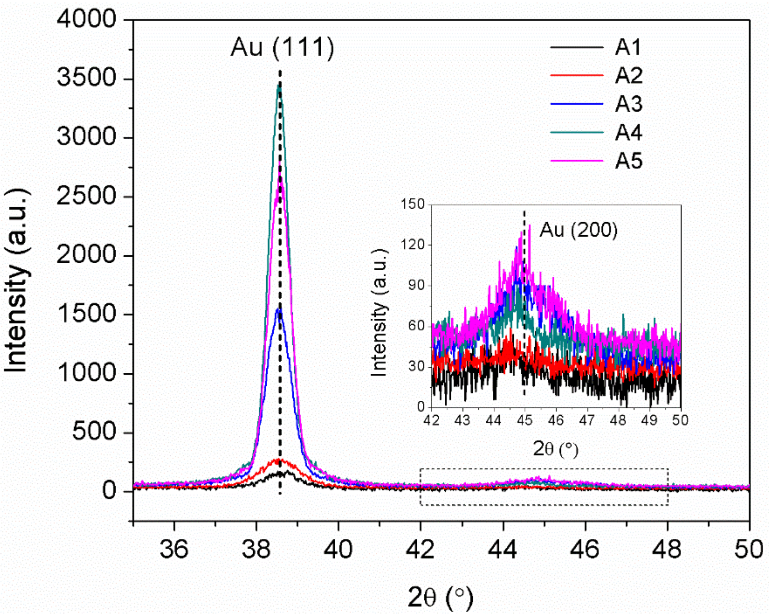
References

S1. S.Y. Sayed, F. Wang, M. Malac, A. Meldrum, R.F. Egerton, J. M. Buriak: Heteroepitaxial Growth of Gold Nanostructures on Silicon by Galvanic Displacement. *ACS Nano* **3**, 2809 (2009).

S2. S.Y. Sayed, F. Wang, M. Malac, P. Li, D. Wang, J. Buriak: Preferential face deposition of gold nanoparticles on silicon nanowires by galvanic displacement. *CrystEngComm.* **14**, 5230 (2012).

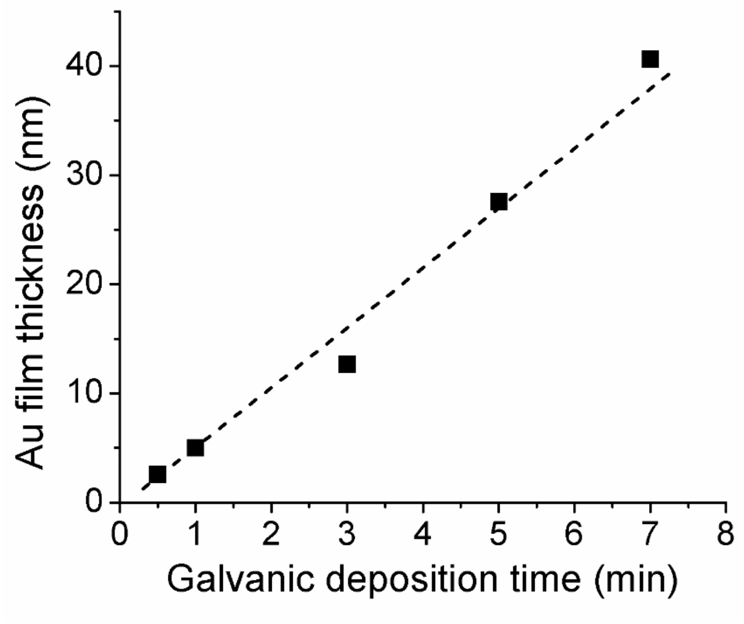
S2. Supplementary figures

FIG. S1 XRD patterns for the as-deposited Au films corresponding to Figure 2A-E.



XRD patterns were collected to identify the crystal structure of the Au films. The dominant Au (111) peak was observed consistently for all the samples while a small Au (200) peak was also observed.

FIG. S2 Au film thickness calculated according the density and size of Au nanoparticle in Figure 2F-J.



The author realizes such size and spatial density information can be reversely used to estimate the thickness of Au film after step 1 in Fig. 1A. As shown in Fig. S2, a linear trend of film thickness was observed as a function of galvanic deposition time, indicating the formation of Au film have no significant effect on the contact of electrolyte and the Si wafer due to the existence of inter-grain cracks and this wet-chemical deposition process is continued uniformly with 7 min. This estimation is critical since it further confirms the control of particle size and distribution of Au nanoparticles and GNPs by simply varying the galvanic deposition time.

FIG. S3 (A,B) SERS spectra of MB. These spectra correspond to the Au nanoparticle (A) and GNP (B) samples immersed in MB solution with various concentration. The peak locations (cm^{-1}) were mark on the top of these spectra. (C) Average Raman intensity MB corresponding to A and B. *Note: The Raman intensity of MB was estimated using the peak centered at 1390 cm^{-1}.*