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– Electronic Supplementary Information –

Seeded growth of robust SERS active 2D Au@Ag nanoparticulate films

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Experimental section

Reagents. 3-(trimethoxysilylpropyl)diethylenetriamine) (DEDAS), silver nitrate (99%), ascorbic acid, cetyltrimethylammonium bromide (CTAB), hydrogen tetrachloroaurate(III) hydrate ($HAuCl_4$, 99.9%), and sodium hydroxide (97%) were obtained from Aldrich and used without further purification.

Preparation of Au@Ag nanoparticle films. The substrates for Au@Ag nanoparticle film growth were cut from glass microscope slides. The glass pieces were immersed twice in fresh "piranha" solution (30% H_2O_2:concentrated H_2SO_4, 1:3, v/v) for 20 min (**Caution:** *Piranha solution reacts violently with organic materials and should be handled with extreme care*) followed by extensive rinsing in Milli-Q grade water and then methanol. After being cleaned, the glass slides was dried in a nitrogen stream prior to soaking in a 5 mM solution of DEDAS in toluene for 1 h, followed by successive rinsing with water and ethanol, and drying under a stream of high-purity nitrogen. The resulting SAM functionalized substrate was immersed in a 3 mM $HAuCl_4$ in water for 30

min and then rinsed with copious amounts of water immediately after removal from the solution. The protonated amine groups of the surface-bound DEDAS ligands were neutralized in 5 mM NaOH solution for 20 min to slowly generate metallic gold seeds through a surface-initiated reduction by the DEDAS. The free amines served not only to enhance the reduction of gold (III) species but also to stabilize the resulting metallic gold clusters. Seeded growth of Au nanoparticles on the rinsed microscope slide was finally accomplished by incubation in a gold growth solution consisting of 80 mM CTAB (20 mL), 3 mM $HAuCl_4$ (0.4 mL), and 0.1 M ascorbic acid (0.4 mL) for a specified period ranging from several seconds to several minutes. In order to produce supported Au@Ag core-shell composite nanoparticle films, the above substrate comprising gold colloidal films was further immersed in a silver growth solution (typically, 20 mL of 80 mM CTAB, 0.4 mL of 3 mM $AgNO_3$, 0.4 mL of 0.1 M ascorbic acid, and 50 μL of 1.0 M NaOH) for 10 min, followed by rinsing in a stream of Milli-Q water for 5 min.

Instrumentation. UV–vis transmission absorption spectra were obtained with a Cary 5000 UV-Vis-NIR spectrophotometer. Scanning electron microscope investigations were performed using a JEOL JSM-6060 scanning electron microscope. Raman spectra were recorded with a Renishaw system 1000 Raman spectrometer equipped with an integral microscope (Leica DMLMS/N). Radiation of 632.8 nm from a 25-mW air-cooled He-Ne laser (Renishaw) was used as the excitation source. Raman scattering was collected with a 50 × 0.75 NA dry objective in 180° configuration and focused into a Peltier-cooled CCD camera (400 × 600 pixels). A holographic grating (1800 grooves m^{-1}) and a 50-μm

slit yielded a spectral resolution of 1 cm^{-1}. A silicon wafer with a Raman band at 520 cm^{-1} was used to calibrate the spectrometer; the accuracy of spectral assignments is ±1 cm^{-1}.

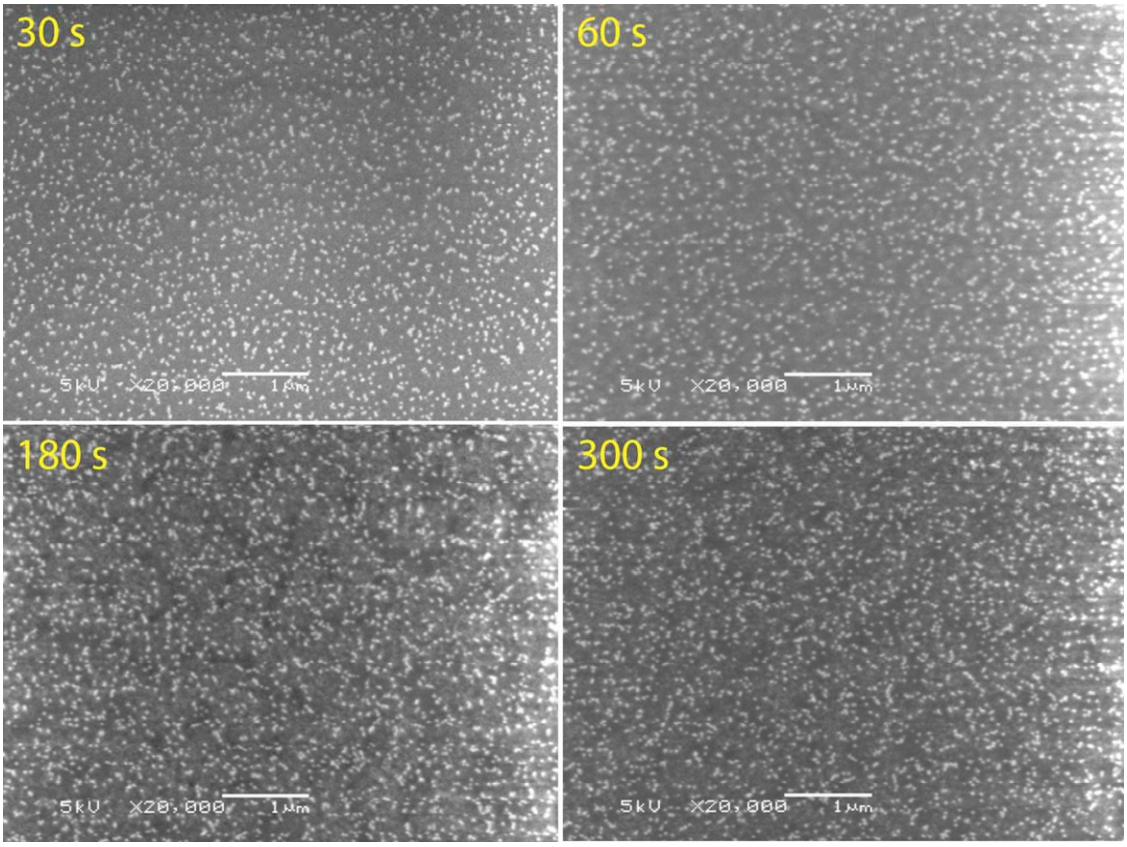

Fig. S1 SEM images showing electroless growth of Au nanoparticle films at various times following the immersion of "seeded" substrates into a growth solution containing CTAB, $HAuCl_4$, and ascorbic acid: 30, 60, 180, and 300 s. The scale bar shown is 1 μm.

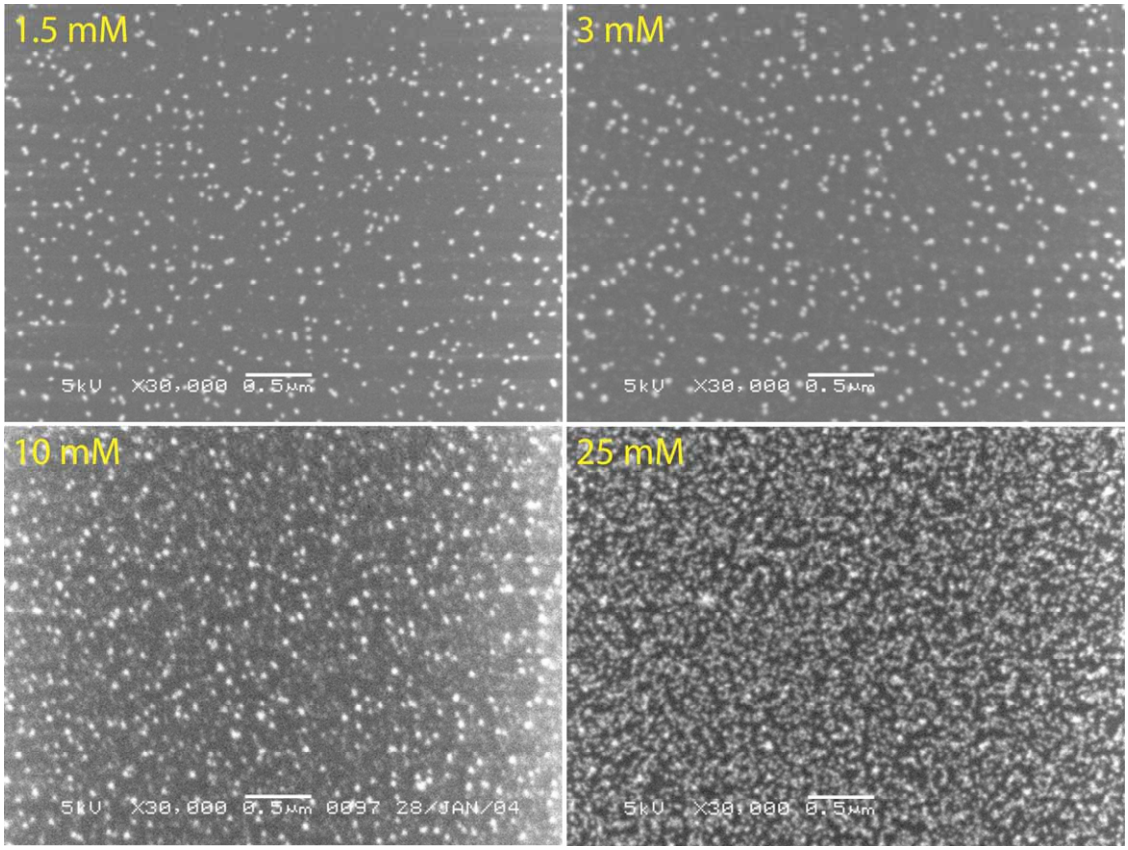

Fig. S2 SEM images demonstrating the effect of Au^{3+} concentration on Au nanoparticle film growth for 1.5, 3, 10, and 25 mM $[Au^{3+}]_0$. The scale bar shown is 0.5 µm.