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Supporting Information for

Seed/Ligand-cooperative Growth of Dense Au Nanospikes on Magnetic Microparticles for SERS Applications

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Supplementary Experimental Section

During the synthesis of Au nanomaterials, all the glassware and stir bar used should be treated aqua regia and piranha solution as follow.

(1) The glassware and stir bars were first cleaned with aqua regia for 15 min and rinsed with deionized water before further use. The aqua regia solution was prepared from a 3:1 (v/v) solution of hydrochloric acid (36.5-38.0%) and nitric acid (68-70%) (*CAUTION: Aqua regia solutions are extremely corrosive, and this solution should be handled with extreme care.*).

(2) This cleaning and rinsing process was repeated using a piranha solution prepared from a 7:2 (v/v) mixture of sulfuric acid (95-98%) and a 30% by volume aqueous solution of hydrogen peroxide (*CAUTION: Piranha solution is a strong oxidizing agent and reacts violently with organic compounds. This solution should be handled with extreme care.*).

1. Synthesis of Au nanoparticles.

The Au nanoparticles was prepared in a 100-mL glass round bottom flask. 2 mL of $HAuCl_4$ (5 mM) and 2 mL of trisodium citrate dihydrate (5 mM) were mixed with 36 mL of H_2O. Under vigorous stirring, 1.2 mL of freshly made ice-cold $NaBH_4$ solution (0.1 M) was quickly injected into the above solution, and the leading to an color change immediately to wine red. After stirring for 4 h, the solution was collected as the seed solution for subsequent seeded growth.

2. Synthesis and Characterization of Gold Nanorods.

The cleaned and rinsed flask and stir bar were dried in an oven at 120 °C for 2 h prior to use in the synthesis of Au nanorods. An aqueous solution of Au seeds was prepared as follows. Typically, chloroauric acid trihydrate ($HAuCl_4 \cdot 3H_2O$, 10 mL of 0.5 mM, 99.0%) was mixed with hexadecyltrimethylammonium bromide (CTAB, 10 mL of 0.2 M, ≥96.0%), and then an ice-cold freshly prepared solution of sodium borohydride ($NaBH_4$, 1.2 mL of 10 mM, 98.0%) was injected into the mixture with vigorous stirring. The mixture was aged for 30 min with continuous stirring before use. In preparation for

the synthesis of Au nanorods, a CTAB solution (100 mL of 0.1 M) was prepared in a glass bottle (500 mL). To this CTAB solution, silver nitrate ($AgNO_3$, 650 μL of 10 mM), $HAuCl_4 \cdot 3H_2O$ (4.2 mL of 10 mM) and ascorbic acid (AA, 700 μL of 0.1 M) were added subsequentially with a gentle stirring. After the above freshly prepared Au seed solution (850 μL) were added, the mixture was left undisturbed for 24 h at 30 °C.

3. Estimation of SERS enhancement factor

The SERS enhancement factors of CV molecules on the film assembled by magnetic Au composite microspheres were estimated according following expression:

$$EF = (I_{SERS}/I_{film})/(N_{SERS}/N_{film})$$

where N_{SERS} and N_{film} are the numbers of CV molecules probed in the film assembled by magnetic Au composite microspheres and reference CV film on glass; and I_{SERS} and I_{film} are the signal intensities of CV molecule Raman spectra probed in the films assembled by magnetic Au composite microspheres and reference CV film on glass. The 20 μl CV (10^{-2} M) was spread on a glass with 1×1 cm^2, and the magnetic Au composite microspheres that dispersed in CV solution (10^{-11} M) were concentrated into 0.2*0.2 cm^2. Previous studies reported that about 10% of the CV molecules were retained after repeated rinsing,[45] and the magnetic Au microparticle aggregated film are about several hundred micrometers in thickness, where only product in one micrometer depth were contributed the SERS signal, thus $N_{SERS}/N_{film} = 20\times10^{-11}\times10\%\times0.01/(2\times10^{-2}\times10^{-2}\times0.04) = 0.25\times10^{-7}$. The ratio of normal Raman intensity of CV film and the SERS signal intensity of probed CV molecules on the films assembled by magnetic Au composite microspheres was estimated to from the height of Raman spectra peak at 1169 cm^{-1}, and then the I_{SERS}/I_{film} was calculated about 0.33 from the Fig. 6d. Therefore EF was roughly calculated to be 1.32×10^7.

Supporting Figures.

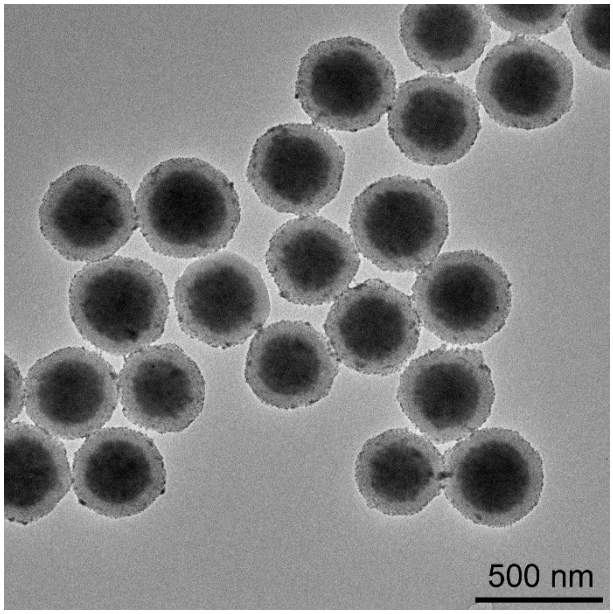

Figure S1. Au nanoparticles-modified magnetic composite microspheres.

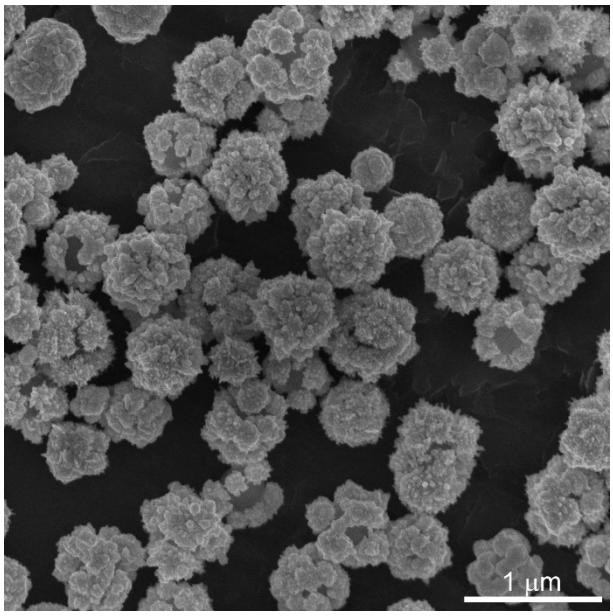

Figure S2. Magnetic Au microparticles with spiky surface by using the CTAB-Ag^{+} complex ions as capping ligands in catechol reaction system.

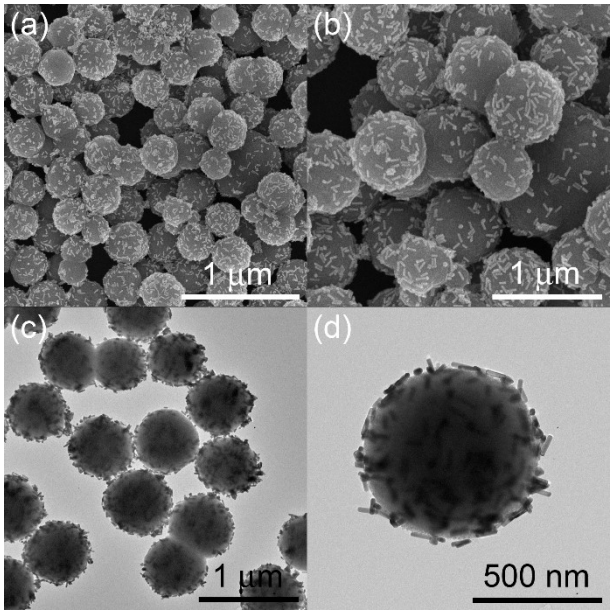

Figure S3. (a) SEM image, (b) high magnified SEM image, (c) TEM image, and (d) high magnified TEM image of magnetic Au composite microspheres with Au nanorods assembled shell.

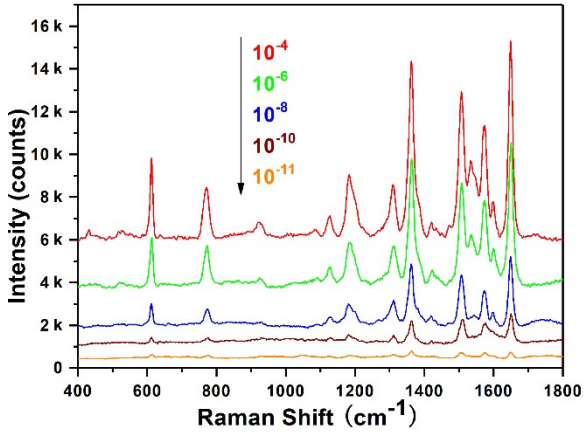

Figure S4. SERS spectra of R6G on MGMNS with concentrations ranging from 10^{-4}-10^{-11} M.

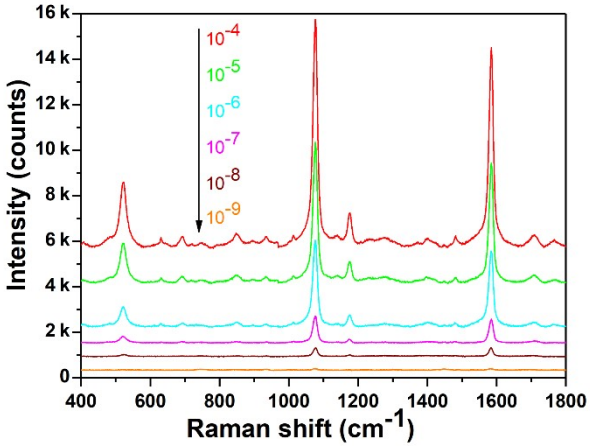

Figure S5. SERS spectra of MBA on MGMNS with concentrations ranging from 10^{-4}-10^{-9} M.