Supporting Information

"Elastic" Property of Mesoporous Silica Shell: for Dynamic SERS Ability Monitoring of Growing Noble Metal Nanostructures via Simplified Spatially Confined Growth Method

Min Lin,[†§] Yunqing Wang,[§]* Xiuyan Sun,[†] Wenhai Wang,[§] and Lingxin Chen[§]*

[†] School of Pharmacy, Yantai University, Yantai 264005, China

[§] Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, China.

E-mail address: yqwang@yic.ac.cn (Y.Q. Wang);

lxchen@yic.ac.cn (L.X. Chen);
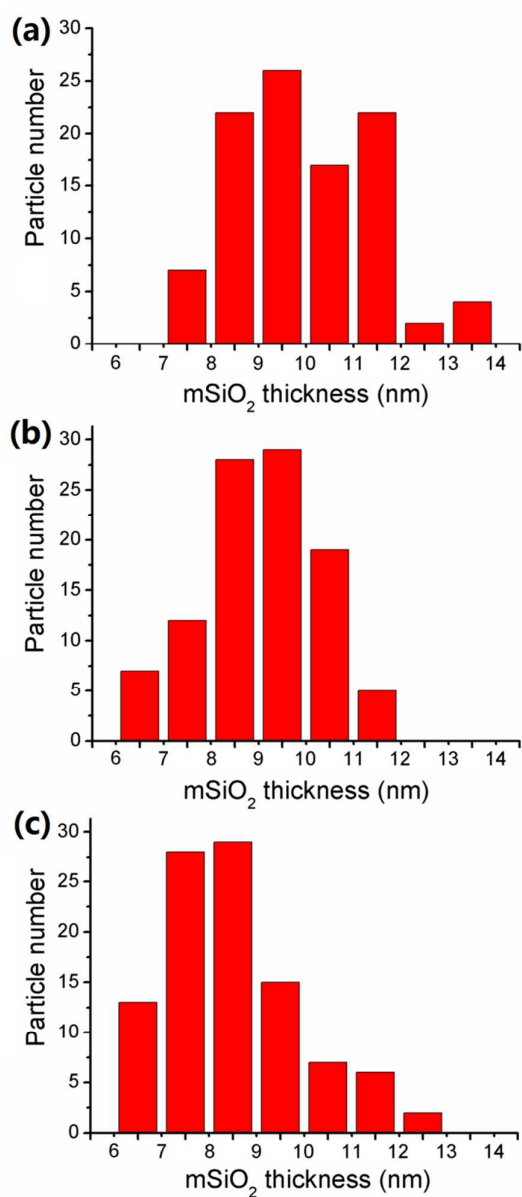
Fax: +86 535 2109130; Tel: +86 535 2109130

Figure S1

Figure S1. Mesoporous silica shell thickness distribution histograms of Au@AgNR@mSiO$_2$ NPs obtained by adding 25 (a), 75 (b) and 150 μL AgNO$_3$. The shell became thinner (from about 10 nm to 8 nm) due to the NP growth induced expansion force.
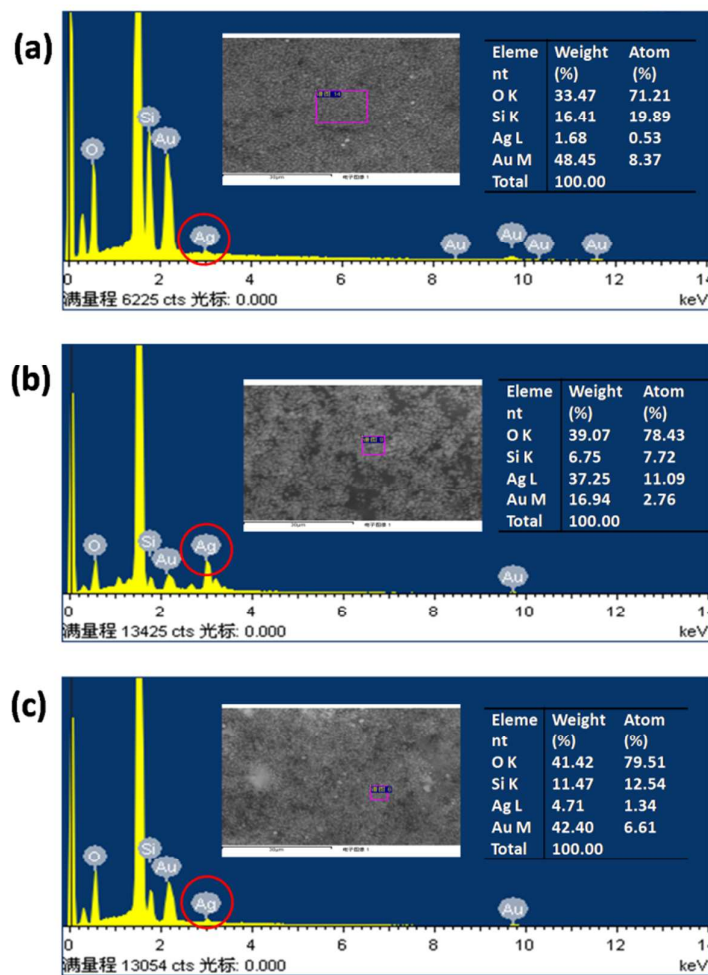
Figure S2

Figure S2. EDX spectra of AuNR@mSiO$_2$ NPs (a), Au@AgNR@mSiO$_2$ NPs synthesized by adding 150 μL AgNO$_3$ before (b) and after (c) silver etching by H$_2$O$_2$. The inset showed the SEM images of the analysis area and the element content analysis results.
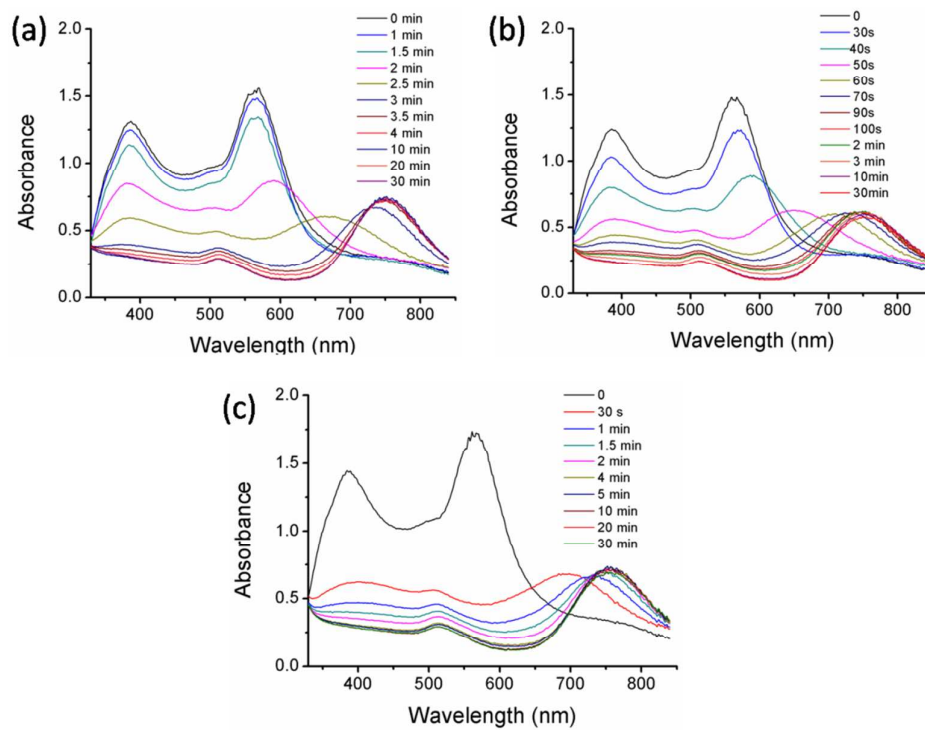
Figure S3

Figure S3. UV-Vis-NIR spectra evolution of Au@AgNR@mSiO$_2$ NPs (1 mL) upon the addition of 20 (a), 50 (b) and 100 µL of H$_2$O$_2$ (30%).
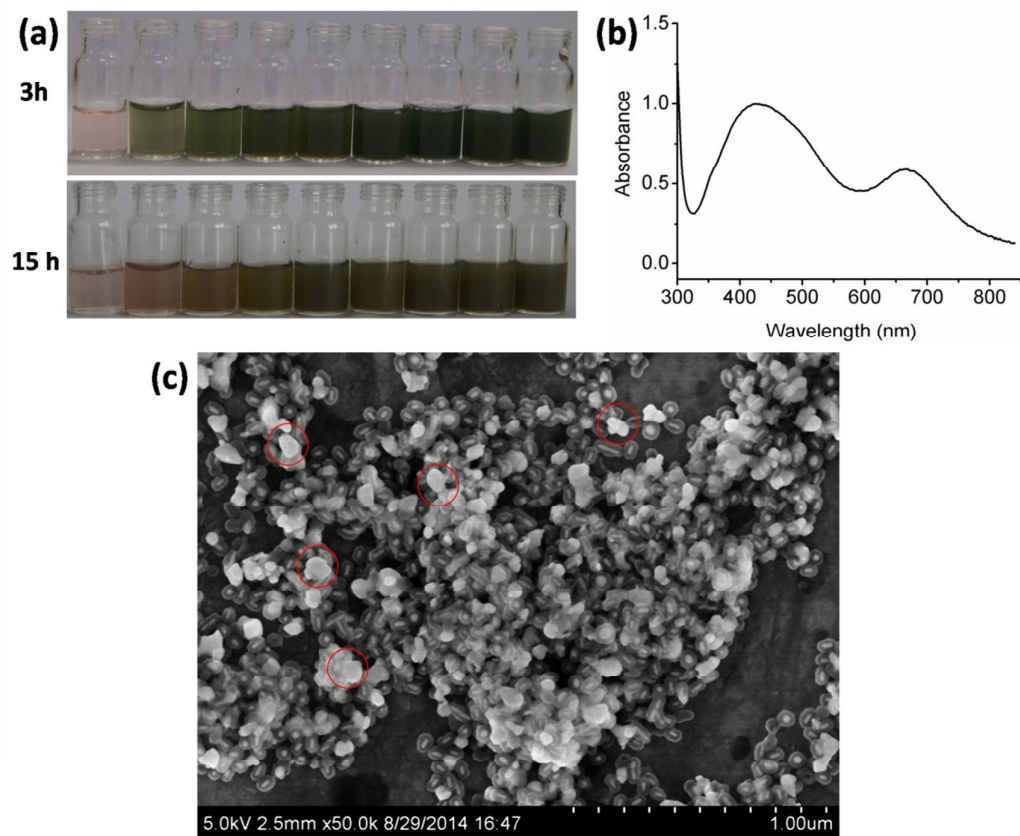
Figure S4

Figure S4. (a) The color of the sample solutions after Ag overcoating reaction performed at 20 $^{\circ}$C for 3 h and 15 h. The adding volume of $AgNO_3$ was 0, 25, 50, 75, 100, 125, 150, 175 and 200 μL, respectively, from left to right. (b) UV-Vis-NIR spectra of the sample of 150 μL $AgNO_3$. The spectra did not show the profile of Au@AgNR@mSiO$_2$ NPs but that of a mixture of AgNP and AuNR. (c) SEM image showed the formation of nonuniform free Ag NPs (marked in red circles) rather than Au@AgNR@mSiO$_2$.
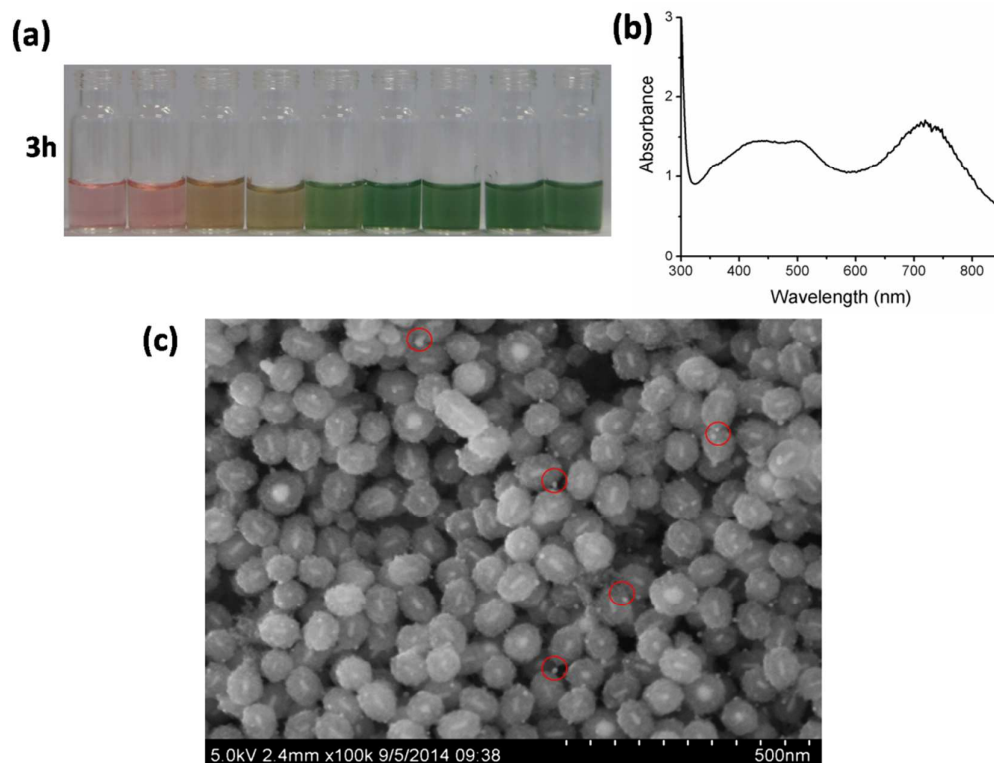
Figure S5

Figure S5. (a) The color of the sample solutions after Ag overcoating reaction performed at 60 °C for 3 h by using AuNR@mSiO$_2$ seeds of 30 nm-thick mSiO$_2$ shells. The adding volume of AgNO$_3$ was 0, 25, 50, 75, 100, 125, 150, 175 and 200 μL, respectively, from left to right. The color stopped at green, indicating the overcoating was hard to proceed. (b) UV-Vis-NIR spectra of the sample after addition of 150 μL AgNO$_3$. It was not the profile of Au@AgNR@mSiO$_2$ NPs but a mixture of the spectra of AgNP and AuNR. (c) SEM image showed the formation of small Ag NPs attached on mSiO$_2$ (marked in red circles) rather than Au@AgNR@mSiO$_2$.
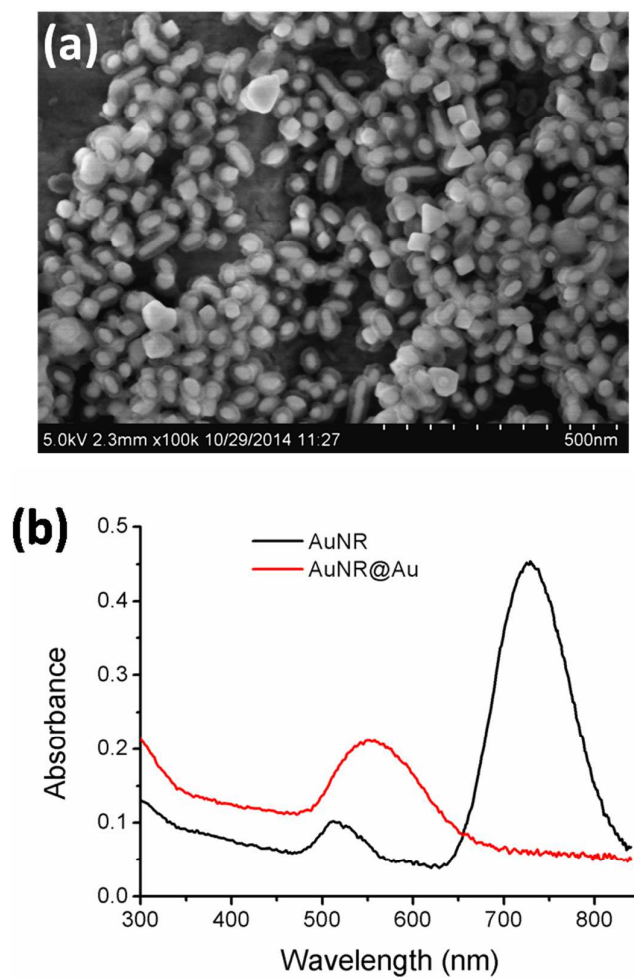
Figure S6

Figure S6. (a) SEM image Au@AuNR@mSiO$_2$ NPs obtained by further Au coating on AuNR seeds. (b) UV-Vis-NIR spectra of AuNR seed and Au@AuNR@mSiO$_2$ NP solutions.
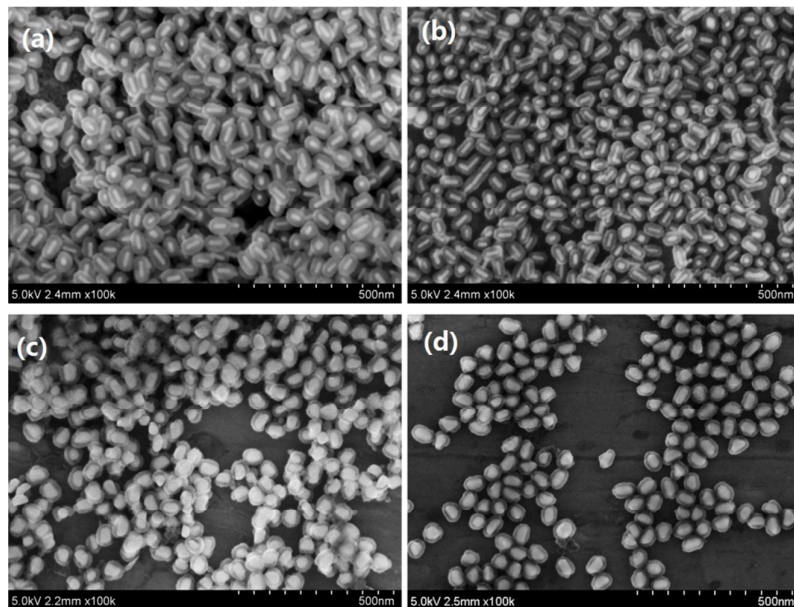
Figure S7

Figure S7. The SEM images of AuNR@mSiO$_2$ (a, b) and Au@AgNR@mSiO$_2$ (synthesized by adding 150 μL AgNO$_3$) (c, d) prepared in two batches.
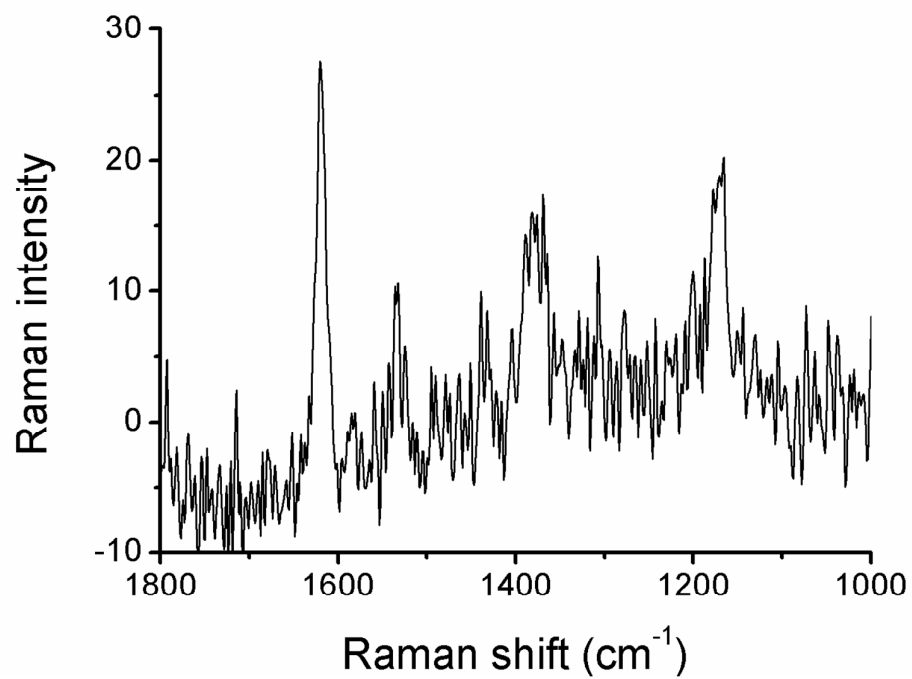
Figure S8

Figure S8. Raman spectrum of the mixture of AuNR@mSiO$_2$ seed NPs and 10^{-6} M crystal violet.
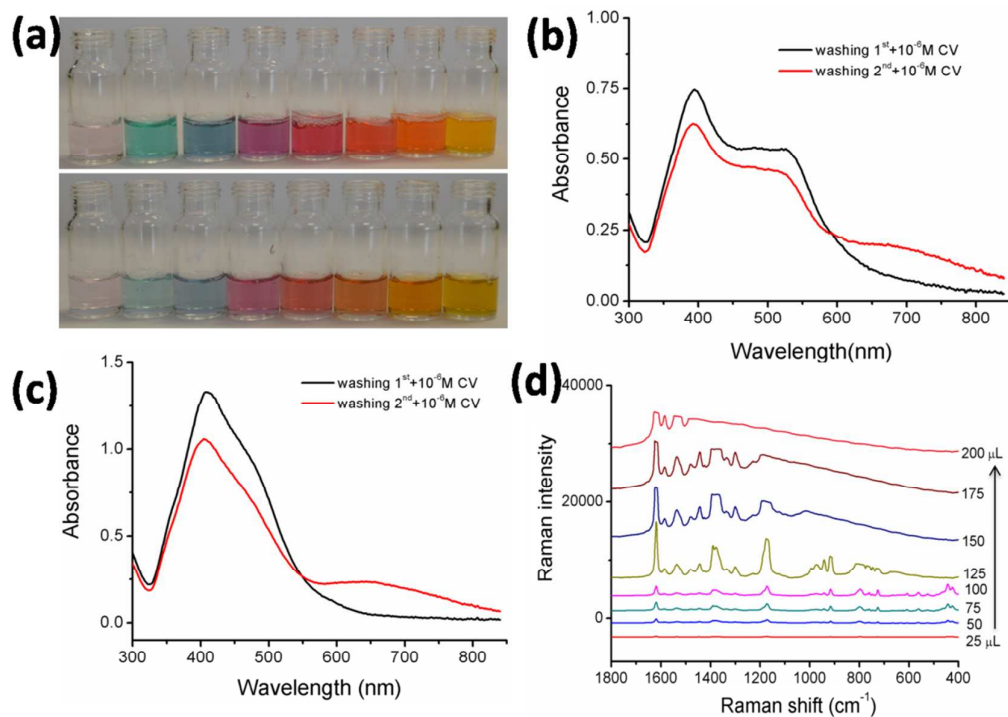
Figure S9

Figure S9. (a) The photoes of the mixture solutions of 10^{-6} M crystal violet and Au@AgNR washed once (the upper panel) and twice (the lower panel). The Au@AgNRs were prepared via free solution method and the adding volume of AgNO$_3$ was 0, 25, 50, 75, 100, 125, 150, 175 and 200 µL, respectively, from left to right. UV-Vis-NIR spectra of the mixtures of 10^{-6} M crystal violet and Au@AgNR prepared with 100 (b) and 150 µL (c) AgNO$_3$ showed that the NPs became aggregate when washed twice. (d) SERS intensity of CV underwent abrupt increase for the NPs with thicker Ag shell due to the aggregation. This would give wrong information when comparing the SERS ability of monodispersed NPs.
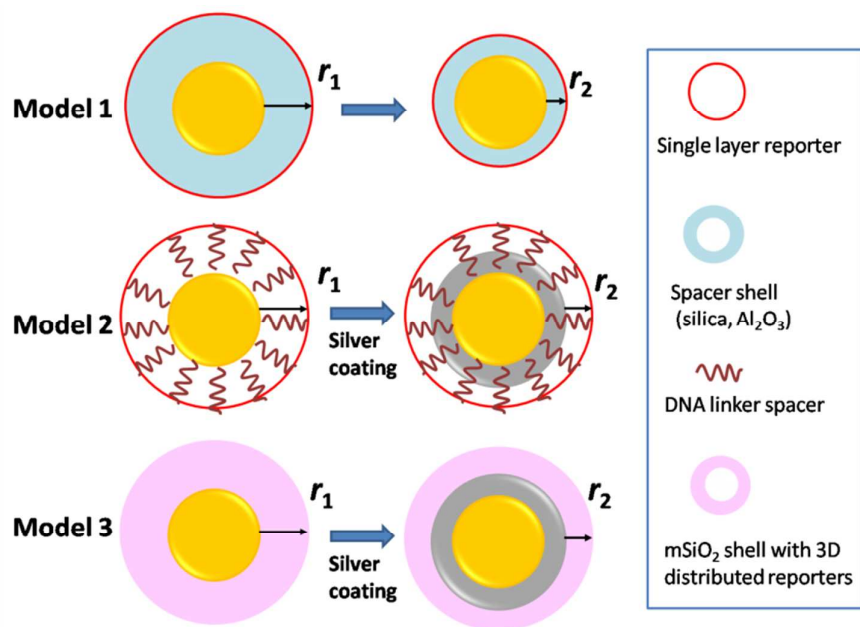
Figure S10

Figure S10. Schematic illustrations of the reported single layer reporter models (Model 1 and 2) and the three-dimensional reporter distribution model proposed in this work (Model 3).
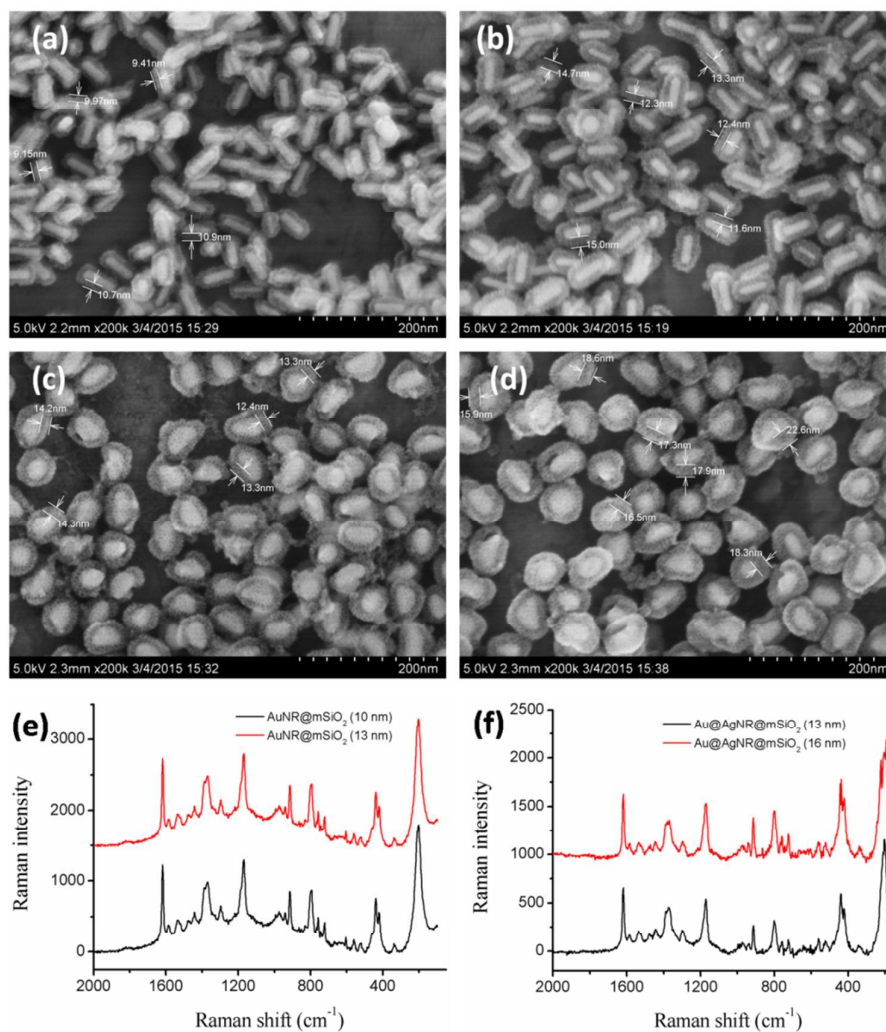
Figure S11

Figure S11. SEM images of AuNR@mSiO$_2$ samples with mSiO$_2$ shell thickness of about 10 nm (a) and 13 nm (b), and Au@AgNR@mSiO$_2$ samples with mSiO$_2$ shell thicknesses about 13 nm (c) and 16 nm (d). (e) and (f) showed the SERS spectra obtained from the mixture of each NP and 10^{-6} M CV solution. The enhancing ability of AuNR is much weaker than Au@AgNR. For acquiring strong enough signals, the concentration of AuNR@mSiO$_2$ NPs was 10 times higher than that of Au@AgNR@mSiO$_2$, thus the SERS intensities in these two figures were not varied so much.