

Optimization of a Hybrid Plasmonic Configuration: Particle on Corrugated Film and its SERS Application

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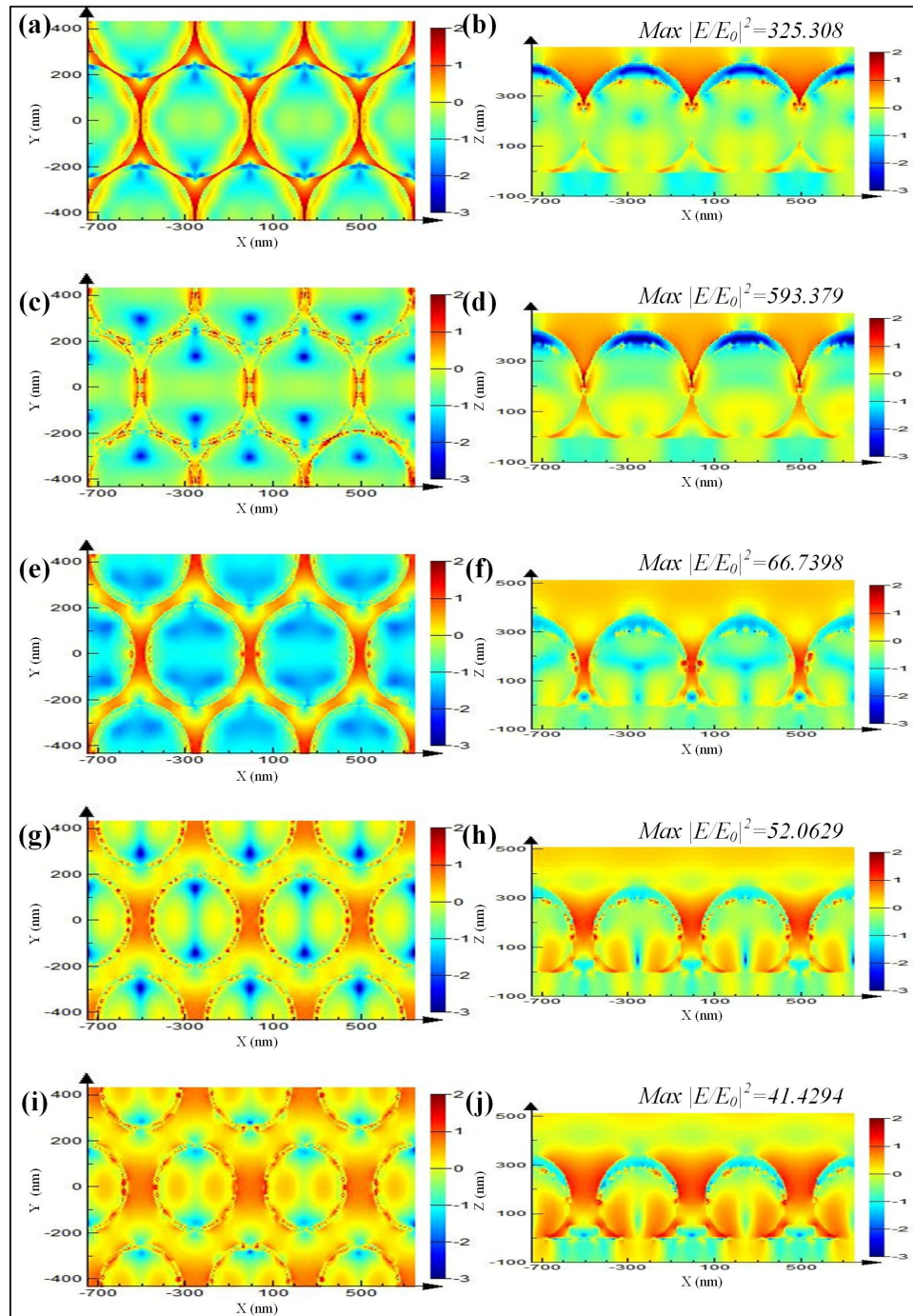


Figure S1. Electromagnetic field distribution of AuFON with various structural sizes.

EM distribution of the corresponding AuFON samples were also conducted by FDTD calculation and the results are shown in Figure S1. Figure S1(a)(c)(e)(g)(i) is the distribution of EM field on the XY plane of Au film on non-etched PS beads, 2min-etched PS beads, 3 min-etched PS beads, 4 min-etched PS beads and 5 min-etched PS beads, respectively. The diameters of the PS beads were set to

be 500 nm, 470 nm, 450 nm, 400 nm, and 350 nm, according to the SEM results of the etched PS beads. Figure S1(b)(d)(f)(h)(j) is the corresponding distribution of EM field on the XOZ plane.

From the picture, we can see that the EM field is mainly concentrated in the position where two AuFON structures are close to each other. This is due to the formation of nanogap between two adjacent structures, which leads to the coupling of EM fields at these locations, resulting in SERS hotspots. In addition to the close position of the AuFON structure, the metal structure on the substrate also produces EM field enhancement, which can be observed more apparently in figure S1(f)(h)(j). The max $|E/E_0|^2$ increases from 325.31 to 593.38, and then decreases to 66.74, 52.06, 41.29, the tendency is consistent with measurement results. We propose an explanation: slight etching could decrease the angle between two adjacent AuFON structures, facilitating the coupling of the EM field, forming high intensity hotspots. But more etching will increase the distance between adjacent AuFON structures too much that decrease the coupling of EM field.

The Au@Ag core-shell nanoparticles were synthesized by Ag ions reduction utilizing the Au seeds as core. Chloric acid was heated to boiling and reduced by adding sodium citrate, forming Au nanoparticle colloid as Au core. After adding the reductant sodium citrate, the silver nitrate solution was added in succession to form the core-shell structure. The SERS effect of the structure can be enhanced by coating the silver shell on the gold core comparing with single silver nanoparticle or gold nanoparticle. Meanwhile, the homogeneity of the particles can be guaranteed by using the gold core as seed. In order to realize controllable preparation of Au@Ag NPs sol with different particle sizes, size of Au core or thickness of Ag shell are controlled. The size of Au core can be effectively adjusted by changing the amount of sodium citrate, which has been reported as a common method. This work mainly discusses the adjustment method of Ag shell thickness by successive addition and sampling. By this way, the thickness of the Ag shell could be controlled precisely. Table S1 describes the details.

Firstly, take Au nanoparticle (25 nm thickness) colloid 100 ml, dilute it to 300 ml and heat it to boiling. Excessive sodium citrate was then added as reductant. And then, 1.5 ml AgNO_3 was added into the Au colloid with sodium citrate. The concentration of AgNO_3 is 10 mM. After 20 mins, the color of the colloid system is stable. Take out 20 ml as sample #1, the concentration of AgNO_3 of

sample #1 is 0.05 mM. There are still 280 ml solution left, 1.4 ml AgNO₃ is added and the added concentration of AgNO₃ is 10 mM/L. Take 20 ml solution out as sample #2, the concentration of AgNO₃ of sample #2 is 0.10 mM. There are 260 ml solution left, 1.3 ml AgNO₃ is added and the added concentration of AgNO₃ is 10 mM/L. Take 20 ml solution out as sample #3, the concentration of AgNO₃ of sample #3 is 0.15 mM. After 10 times, 10 samples were got, the concentration of silver nitrate increases in turn with the concentration gradient of 0.05 mM, as shown in Table S1.

Table S1 Parameters in synthesise Au@Ag NPs by successive sample addition

Sample	Sol system Volume(ml)	Added AgNO₃ Volume(ml)	AddedAgNO₃ concentration (mM)	Sample volume(ml)	ObtainedAgNO₃ concentration(mM)
1st	300	1.50	0.05	20	0.05
2nd	280	1.40	0.05	20	0.10
3rd	260	1.30	0.05	20	0.15
4th	240	1.20	0.05	20	0.20
5th	220	1.10	0.05	20	0.25
6th	200	1.00	0.05	20	0.30
7th	180	0.90	0.05	20	0.35
8th	160	0.80	0.05	20	0.40
9th	140	0.70	0.05	20	0.45
10th	120	0.60	0.05	20	0.50

Based on EM characteristic analysis and SERS performance test, 2-min etching AuFON structure is chosen as the solid substrate of the composite SERS. To optimize the particle size of Au@Ag core-shell structure in the composite SERS substrate, Au@Ag core-shell structure

nanoparticle with different sizes were combined with 2 min etching AuFON structure, following with SERS performance test in which PATP act as Raman marker. Sols with different particle sizes were prepared by adjusting the size of Au core and Ag shell with the method introduced above. The relationship between Au core diameter, Ag ions additive amount, and the grain size of Au@Ag NPs are shown in table S2. The radial dimension of grafted particles varied from 30 nm to 70nm.

The results have shown in figure 4(c-d), while the colloid diameter change form 30 nm-50 nm, the signal intensity increases and reaches the maximum at 50 nm. When the diameter changes from 50 nm to 70 nm, the signal intensity decreases, the result shows that composite SERS substrate with 50 nm diameter Au@Ag core-shell colloid has the highest SERS sensitivity.

Table S2 Relationship between the diameter of Au@Ag NPs and its synthesize parameter

Grain size of Au@Ag NP(nm)	Grain size of Au core(nm)	Addictive amount of AgNO ₃ (ml)
30	25	0.5
35	25	1.0
40	25	1.5
45	25	2.0
50	25	2.5
65	60	1.0
70	60	3.0

The EM field distributions of different sizes Au@Ag NPs were simulated by FDTD, for the Raman signal enhancement mainly originate from SERS hotpots, the models were set as following: two Au@Ag particles get near and thus form a nanogap. The colloid diameter of the Au core spherewasfixed to be 25 nm, and the colloid diameter of the Au@Ag NPs gradually increased with a spacing of 5 nm. The sizes of the Au@Ag NPs in the model range from 30 to 85 nm. Figure S2

shows the EM field distribution of the Au@Ag NPs. Hotspots intensity is marked by color change. From the picture, we can see the max $|E/E_0|^2$ increases from 52.94 to 73.61, 76.70, 67.10, 86.68, 99.06, 118.41, 134.32, 163.39, 184.89, 234.46 to 236.78. The EM field is coupled at the contact position of two particles, the SERS hotspots is just at the nanogap of two particles, which is consistent with our proposal.

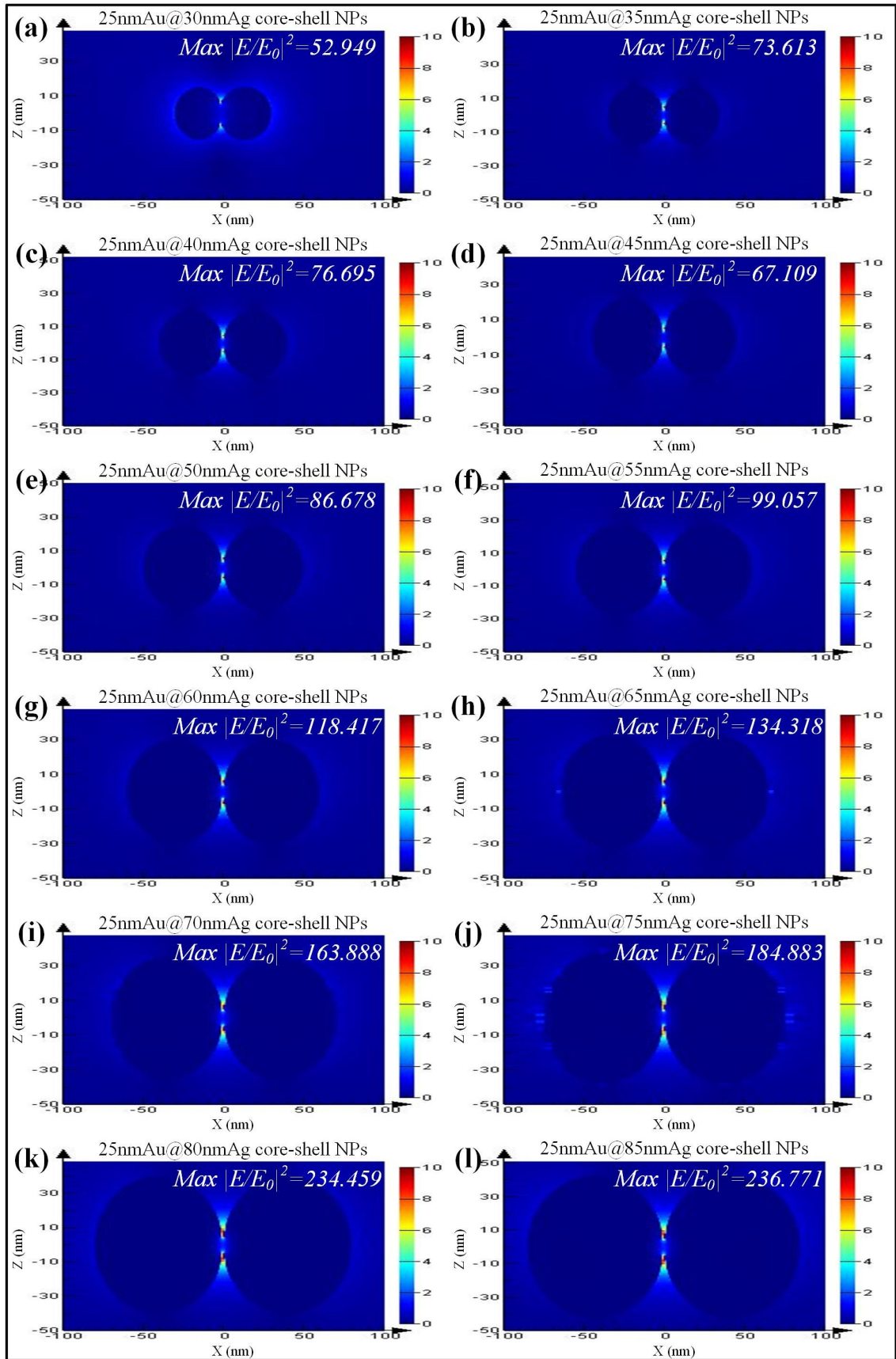


Figure S2. EM field distribution of Au@Ag NPs with various sizes.

According to the EM simulation results, the EM field enhancement characteristics of Au@AgNP can be enhanced with the increase of particle size in this range. However, the performance of the composite SERS substrate with large particle size decreases in practical measurement while the size of Au@Ag NPs exceeds 50 nm. This may be related to the binding efficiency of AuFON structure. Under vibration conditions, the larger the particle size of Au@AgNP, the less likely it is to form a stable connection with the AuFON structure, and the lower its binding rate on the AuFON structure. The number of SERS hot spots decreases correspondingly, which affects the SERS characteristics of composite substrates. In addition, with the passage of time, the SERS performance of composite SERS substrates with larger particle size will gradually weaken. In summary, the Au@Ag NPs with particle size of 50 nm were selected as the liquid sol of composite SERS substrate.

Raman spectra obtained from AuFON, Au@AgNPs, and particle-AuFON structure were shown in figure 5. Its detailed curves when the wavelength range from 1475cm⁻¹ to 1550cm⁻¹ is shown in figure S3.

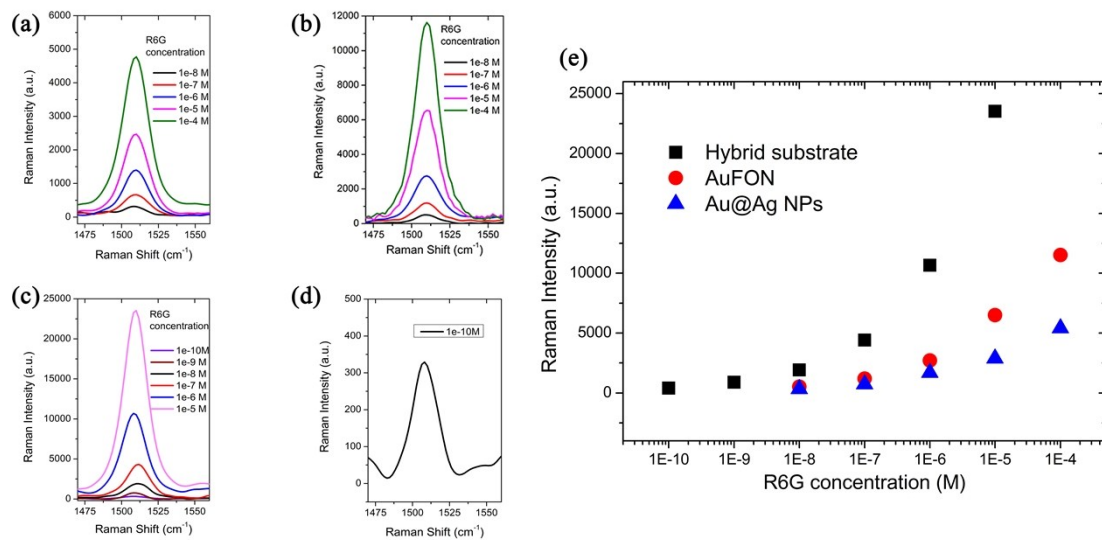


Figure S3 (a-c)The Raman spectra of Au@Ag NPs, AuFON and hybrid substrate with the wavelength ranging from 1475 cm⁻¹ to 1550cm⁻¹,(d) the amplified curve of black line in (c), 10⁻¹⁰M R6G SERS spectrum, (e) The Raman intensity at wavelength 1508cm⁻¹ vs R6G concentration.

The SERS performance has been tested, and the hybrid substrate shows the best performance, in the meantime, uniformity, stability and repeatability are also tested. In the uniformity test, a hybrid

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substrate is immersed in 10^{-6} M PATP solution for 2 hours and dried with nitrogen. Fixed it onto the measurement platform and revolving the X/Y nuts to translate the substrate to 20 test dots, as shown in figure S4. 20 Raman spectra curves show good uniformity in figure 6. The sample is $5\text{ cm} \times 4\text{ cm}$, mark 20 measurements sites along x axis and y axis every 1 cm.

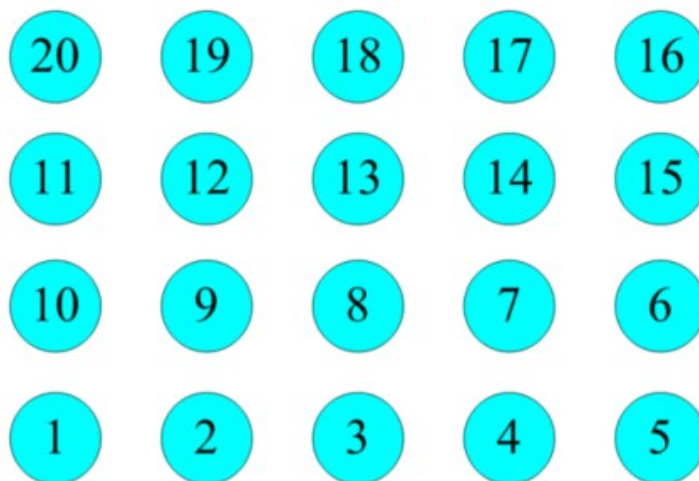


Figure S4. Schematic map of 20 SERS signal acquisition positions.

Quantization of the uniformity of the 20 spectrum curves measured on the hybrid SERS substrate is proposed by introducing relative standard deviation (RSD) to present the degree of dispersion of spectral intensity. The RSD is defined using the following equations:

$$RSD = \frac{\sqrt{\frac{\sum (x - \bar{x})^2}{n-1}}}{\bar{x}}$$

x is the value of the spectrum intensity, \bar{x} is the average value of the sample, n is the number of the samples. The RSD of the hybrid substrate in 1076 cm^{-1} is 10.36% that meets to requirement in practical application.

Figure S5 is the EM field enhancement of a single Au@Ag NPs on plane film. Figure S5(a)(b) shows the refractive index calculation result and EM field enhancement of Au@Ag NPs on silicon substrate. The EM field mainly focus on the upper part of the particle, which shows the EM

enhancement is mainly motivated by the NP itself. Figure S5(c)(d) shows the refractive index calculation result and EM field enhancement of Au@Ag NPs on gold substrate. The EM field mainly focus on the between the cracke of NP and Au substrate, illustrating new SERS hotspots generated by the coupling of Au film and particle. EM field enhancement increases from 0.777 to 1.214.

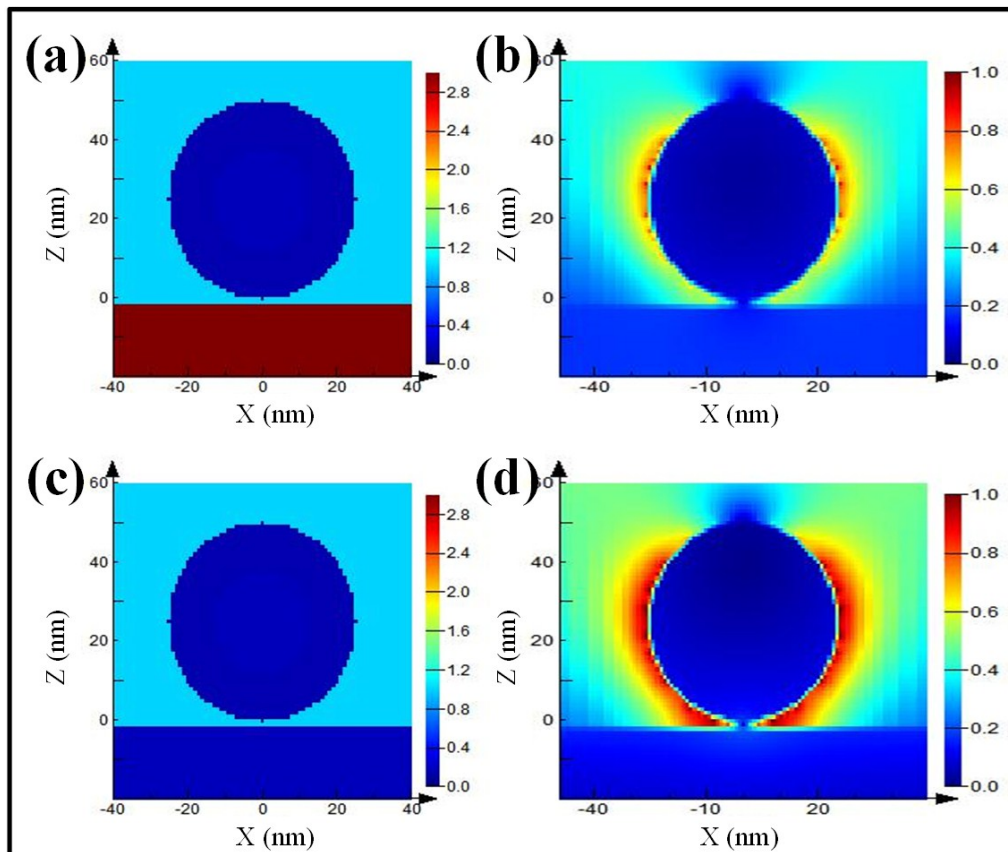


Figure S5. Distribution of dielectric constants and electromagnetic fields of a single Au@Ag NP on silicon/gold substrates.

Au@AgNPs sol is the base of SERS configuration, and its hotspots are mainly located in the nanogap formed between Au@AgNPs. In order to study the EM enhancement effect of Au film on Au@AgNPs clusters, the EM field distribution of Au@AgNPs particle clusters on the Au film substrate was further simulated and analyzed. Figure S6 (a)(c) are the calculated dielectric constants of Au@AgNPs clusters on silicon and gold substrates, respectively, while (b, d) are the distributions of the EM fields of the two structures on the XOZ plane. On the two substrates, the distribution of

EM field is basically the same, mainly concentrated in the gap of Au@AgNPs. The maximum EM field enhancement of Au@AgNPs cluster structure on silicon substrate is 43.336, while that of Au@AgNPs cluster structure on Au film substrate is 77.977. There are no new SERS hotspots between Au@AgNPs and Au@AgNPs sol in Au@AgNPs cluster on the Au film substrate, but the intensity of the original SERS hotspots has been significantly enhanced. This indicates that the hot spots generated between Au@AgNPs and gold film have coupled with the original hot spots of Au@AgNPs cluster.

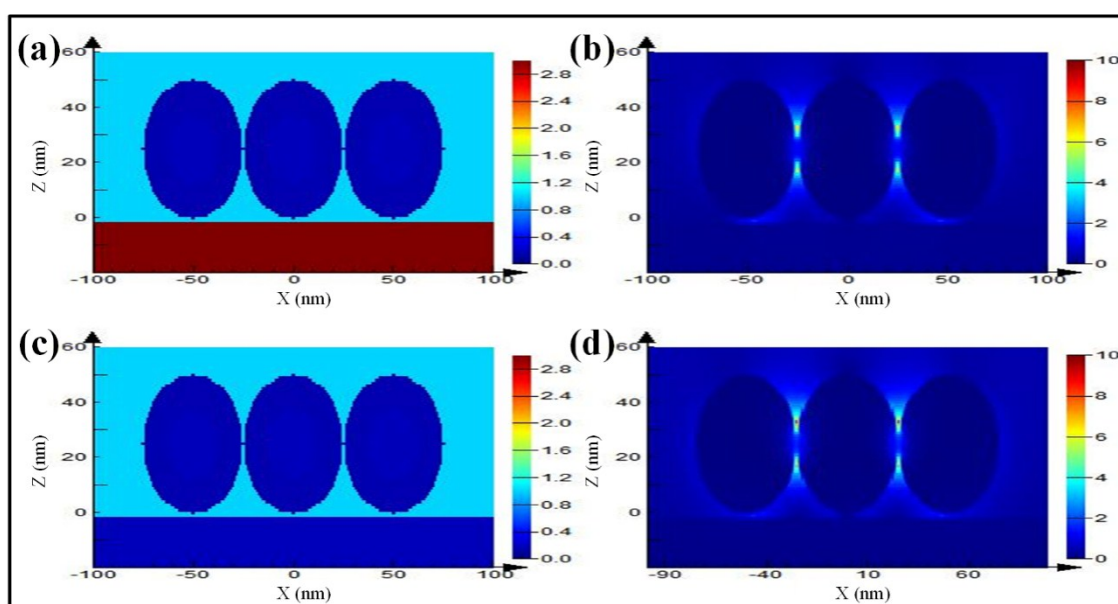


Figure S6. Dielectric constant and EM field distribution of Au@Ag NPs cluster on silicon/Au substrate.

Melamine (1,3,5-triazine-2,4,6-triazine) is a triazine-containing heterocyclic organic compound with a nitrogen content of 66.7% (w/w), so it is also called protein concentrate. At present, the usual method of detecting protein content in food is to determine nitrogen content in food. Adding melamine to milk and other foods can effectively increase its nitrogen content. In 2008, the illegal addition of melamine to Sanlu milk powder broke out in China, which led to kidney stones in infants who ate Sanlu milk powder, and directly resulted in the death of four children. Methods to detect melamine is in urgent. According to the national food safety standards, the content of melamine in infant formula milk powder should not be higher than 1 mg/kg (7.9 ugM), and the content of

melamine in liquid milk, milk powder and other formula milk powder should not be higher than 2.5 mg/kg (19.75 ugM). In the food safety standards formulated by the United Nations, the content of melamine in milk should not be higher than 0.15mg/kg (1.12um). For melamine itself has a intrinsic peak of SERS, the rapid detection of melamine can be realized based on SERS technology. The molecular structure formula and intrinsic Raman spectra of melamine are shown in figure S8. Its main peak locations are in the range of 670 cm^{-1} to 710 cm^{-1} . In this work, the main peak of melamine is located at 681 cm^{-1} . The attribution of melamine SERS peaks is shown in Table S3.

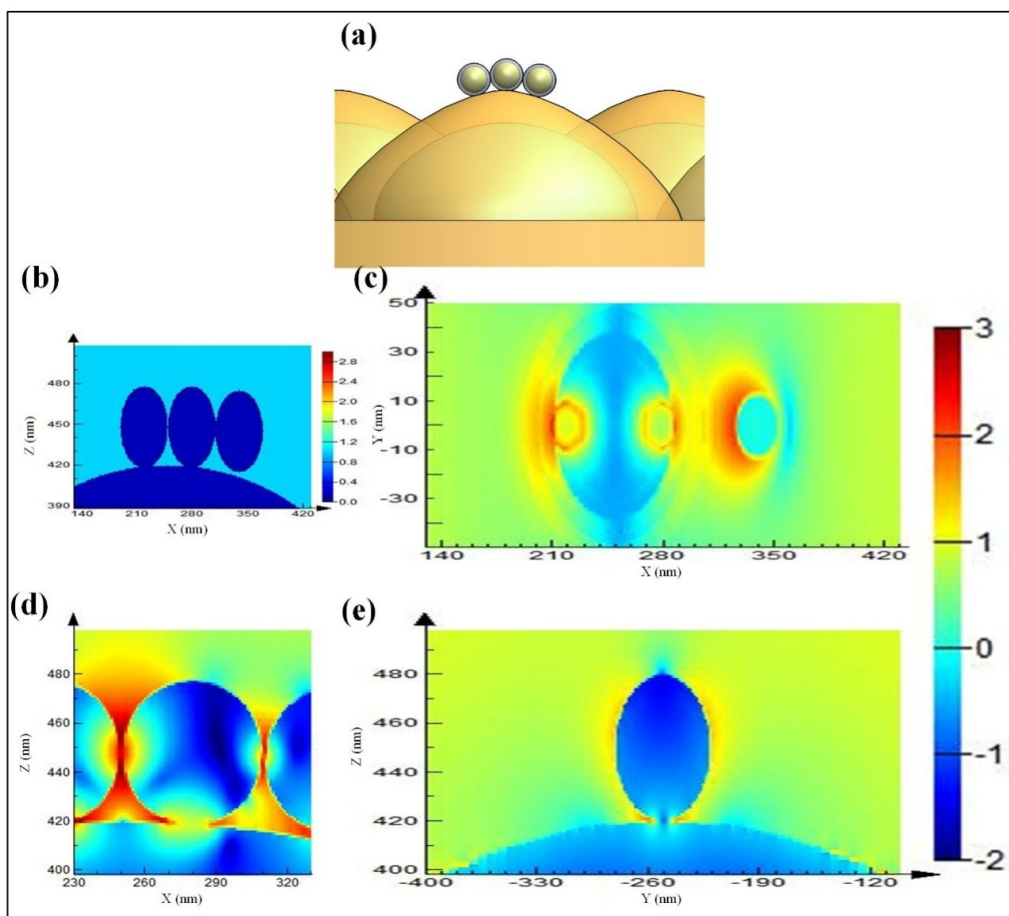


Figure S7. Molecular structure formula and typical SERS spectrum of melamine.

Table S3 Distribution of instinct peaks in SERS spectra of melamine

Position of vibration peak	Attribution of vibration peak
683, 690, 710	Triazine-ring, nitrogen radial in-phase vibration
1070-1090	-RNH ₂ , C-N stretch

1140-1150

-N=C=N-, sym stretch
