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Modulating of Interparticle Gap for Enhanced SERS Sensitivity in Chemically Stable Ag@Au Hetero-Architectures

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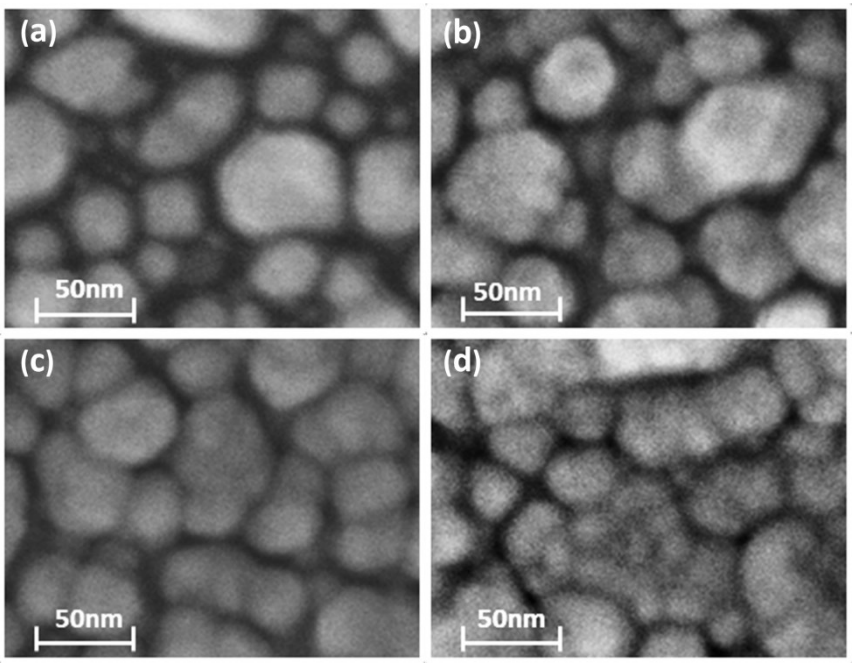

Fig. S1 The magnified SEM images of sample (a) Ag, (b) Ag@Au4, (c) Ag@Au8 and (d) Ag@Ag12.

The magnified SEM images for all samples were shown herein to clearly display morphologies change in the Ag@Au hetero-architectures. Apparently, accompanying with increase in the thickness of Au particle films, the particle sizes of Ag@Au hetero-architectures gradually increased and on the contrary the interparticle gap between two adjacent particles decreased.

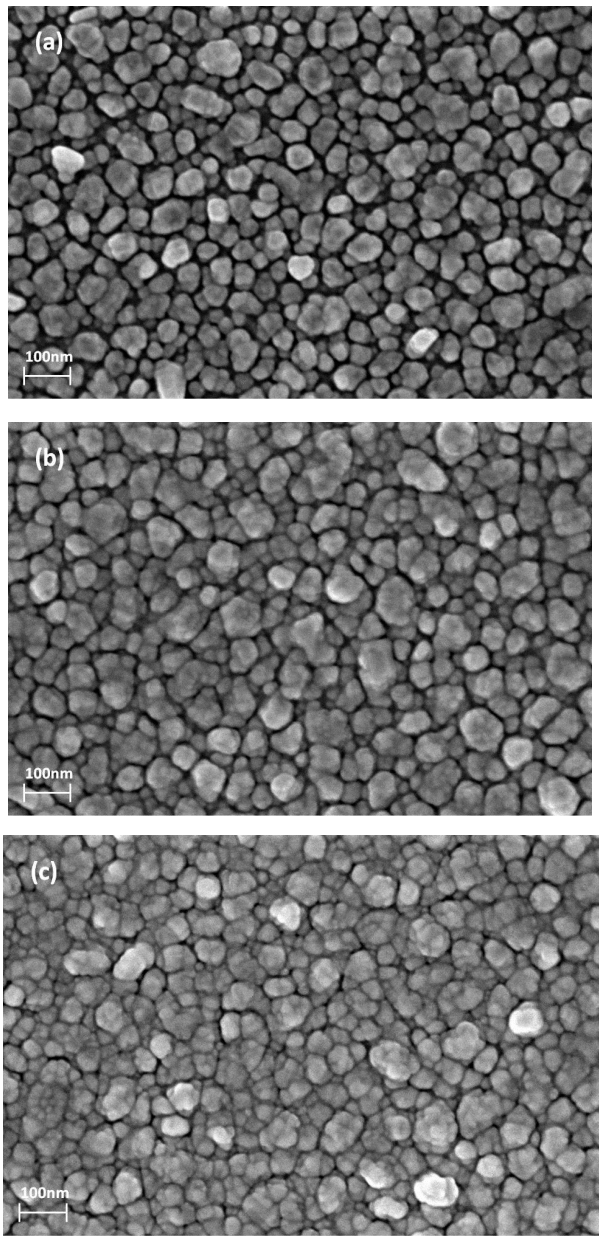

Fig. S2 SEM images of the substrates: (a) Ag@Au4, (b) Ag@Au8 and (c) Ag@Ag12 upon immersion in H_2O_2 solution at concentration of 0.5M for 1h.

To assess the chemical stability of the Ag and Ag@Au substrates, the substrates were submerged in a 0.5 M hydrogen peroxide solution (H_2O_2) for 1 h. It is known that a violent reaction between Ag and H_2O_2 occurs and Ag nanoparticles could be completed dissolved in a short time. The reaction between Ag and H_2O_2 is given in equation (1).

$$Ag_n\,(solid) + 3H_2O_2 + 2H^+ \rightarrow Ag_{n-2}\,(solid) + 2Ag^+ + O_2 + 4H_2O \qquad (1)$$

FE-SEM observations could confirm that no Ag nanoparticles remain on the Si wafer after immersion in the H_2O_2 solution for a while (not shown here). However,

for Ag@Au substrates, the decomposition of Ag nanoparticles by H_2O_2 was greatly reduced due to the protection from Au films. Comparing the FE-SEM images of the Ag@Au substrates before (Fig. 2 b, c, d) and after (Fig. S2 a, b, c) immersion in the H_2O_2 solution, very little change can be observed. However, the formation of bubbles confirmed that reactions do occur between H_2O_2 and both Ag@Au4 and Ag@Au8 substrates. It is probable that the dissolution of some uncoated Ag from the Ag@Au4 and Ag@Au8 nanoparticles by reaction with H_2O_2 results in some pinholes that cannot be detected by FE-SEM.

In order to prove the repeatability of our as-prepared Ag and Ag@Au NPs SERS substrates, we carried out the parallel SERS experiment on another batch of samples to detect R6G molecule. The results of the second batch of substrates (shown in Table S3) demonstrate the similar trend in terms of EF as those listed in Table 3, viz. increasing as thickness of Au layer increases up to 8 nm, then decreasing as it increases.

Table S1 Enhancement factor of four SERS substrates prepared via another batch of experiment

Sample	Test site	Enhancement factor (EF)	Average value of EF	Deviation from average value of EF
Ag	#1	1.72×10^7	1.65×10^7	+4%
	#2	1.54×10^7		-7%
	#3	1.69×10^7		+2%
Ag@Au4	#1	1.85×10^7	1.89×10^7	-2%
	#2	1.77×10^7		-6%
	#3	2.05×10^7		+8%
Ag@Au8	#1	2.20×10^7	2.23×10^7	-1%
	#2	2.36×10^7		+6%
	#3	2.13×10^7		-4%
Ag@Au12	#1	0.53×10^7	0.50×10^7	+6%
	#2	0.46×10^7		-8%
	#3	0.51×10^7		+2%