Large-scale growth of sharp gold nano-cones for single-molecule SERS detection†

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1. Shape analysis of the nano-cones.

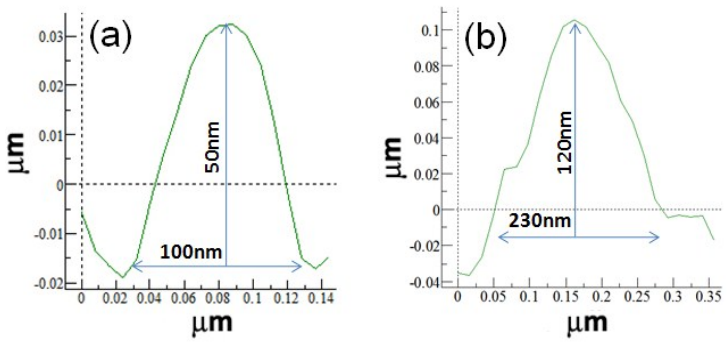
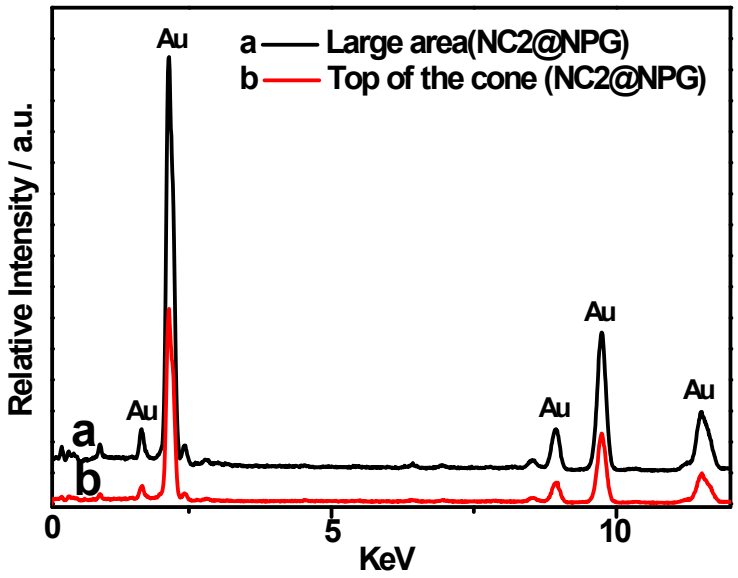


Figure S1. Representative profiles of the nano-cone (NC) from (a) NC1@NPG and (b) NC2@NPG.

From the representative profile of the NC from the two samples, we can see that Although the sizes of individual NC in each sample are different in sizes, but they are very similar to each other in the shape and have a nearly constant length to width ratio. Moreover, the diameter that 5nm away from the apex of all NC is around 20nm.

2. Chemical composition analysis



Region	Sample	Au (Mass%)	Ag(Mass%)
Large Area	NPG	98.14	1.32
	NC1@NPG	98.85	1.15
	NC2@NPG	98.93	1.07
Top of cone	NC2@NPG	99.02	0.98

Figure S2. Chemical analysis of selected area from NC@NPG, and the table below lists the related compositions of NPG template, large area of NC@NPG and the point analysis at the top of the cone.

As shown in Figure S2, the matrix composition of the NC@NPG is gold, and the slightly amount of silver is attributed to residual silver in the ligament of NPG. With the NC growing, the percentage of the Ag keep on decreasing further indicates gold epitaxial growth on the NPG template.

3. Size distribution of nano-cones.

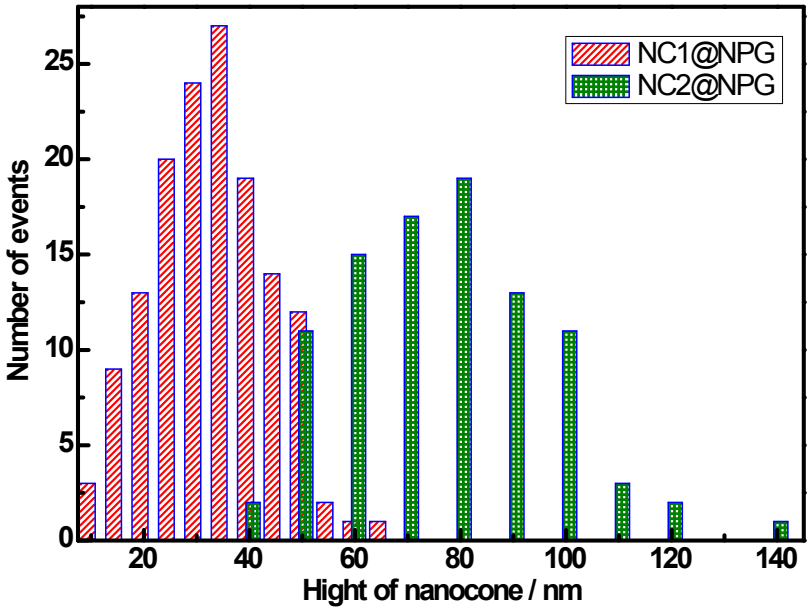


Figure S3. Size distribution of nano-cones on NC1@NPG (2μm × 2μm area) and NC2@NPG (3μm × 3μm area).

With 90mins gold plating, most NC with the size around 30-50nm, and the size of the NC doubled when the plating time extending to 180mins.

4. Normal Raman cross section ($\sigma_{R6G, NR}$) measurement.

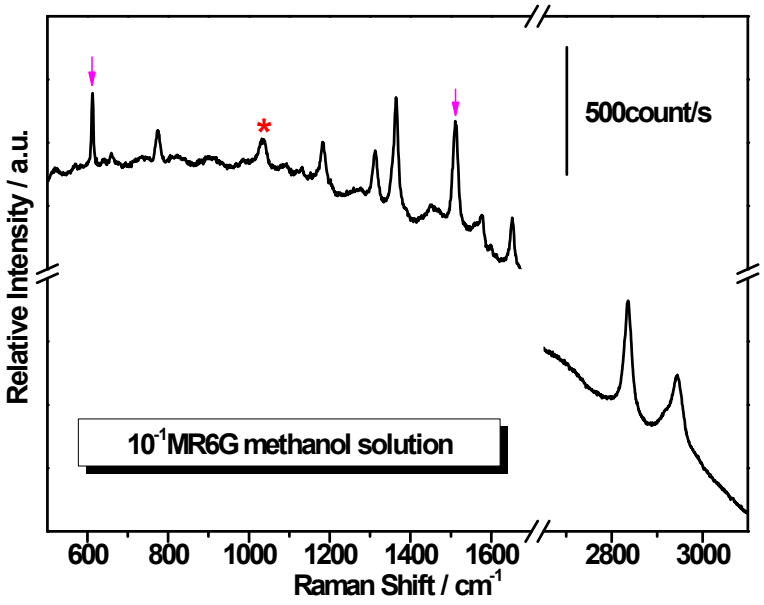


Figure S4. Normal Raman spectrum of 10^{-2}M R6G methanol solution with 632.8nm excitation.

The dye molecule rhodamine 6G (R6G) in methanol is used to measure the SERS enhancement factor (EF) of NC@NPG by comparing the Raman cross section (σ) from the normal Raman (NR) spectrum of R6G with that of the SERS spectrum . [31] **Figure S4** shows the NR spectrum of 10^{-2}M R6G methanol solution with 632.8nm excitation.

The normal Raman cross section ($\sigma_{R6G, NR}$) is estimated by the follow equation:

$$\sigma_{R6G, NR} / \sigma_{meth} = [I_{R6G}/C_{R6G}] / [I_{meth}/C_{meth}],$$

where the IR6G and Imeth are the intensity of the chosen vibrational modes of R6G (marked with arrows) and methanol (marked with star) in Figure S4, respectively.

5. Assignments of the Raman band of DNA adenine in SERS spectra.

Table S1. Comparison and assignment of the Raman bands of DNA adenine in normal Raman and SERS spectra.

NRS[a]	SERS				Plane	Assignment[a,b]
	a	b	c	d		
560	572	578	576		out	wag C2-H, N9-H
623	624				in	def R6 (sqz group C4-C5-C6, N1-C6-N10), R5 (sqz group C5-N7-C8)
723	725				in	ring breath whole molecule (distorted)
797	760		801		in	def R6 (wag C4-C5-C6), wag C8-H
899	869	879	874		in	def R6 (sqz group N1-C2-N3), R5 (str C5-N7)
942	965				in	def R5 (sqz group N7-C8-N9)
1025				1060	in	rock NH2
			992		out	
1126	1116				in	str C8-N9, bend N9-H
1162	1151		1169	1194	in	str C6-N10, N3-C4, C4-N9, bend N9-H, C2-H, N10-H11, C8-H
1234	1222			1242	in	rock NH2, str C5-N7, N1-C2, C2-N3
1308	1320	1320			in	str C2-N3, C5-N7, C5-C6, C5-N7
1333	1341	1348			in	str str C5-N7, N1-C2, bend C2-H, C8-H
1419	1404	1409	1402	1407	in	bend C2-H, N9-H, (str C8-N9, N1-C2)
1463		1457	1455	1467	in	str C2-N3, N1-C6, bend C2-H, sciss NH2
1483	1480	1508		1508	in	str N7-C8, bend C8-H, sciss NH2
1534	1539			1533	in	str N3-C4, N1-C6, C5-N7, bend N9-H
1597				1570	in	sciss NH2

[a] Ref : J. Phys. Chem. B 2002, 106, 101-112.

[b] Def, deforming; rock, rocking; bend, bending; str, stretching; sciss, scissoring; R5, five-membered ring; R6, six-membered ring.