Electronic Supplementary Information

Size-controllable and uniform gold bumpy nanocubes for single-particle-level surface-enhanced Raman scattering sensitivity

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Table S1. Growth conditions for samples (i)–(vi)

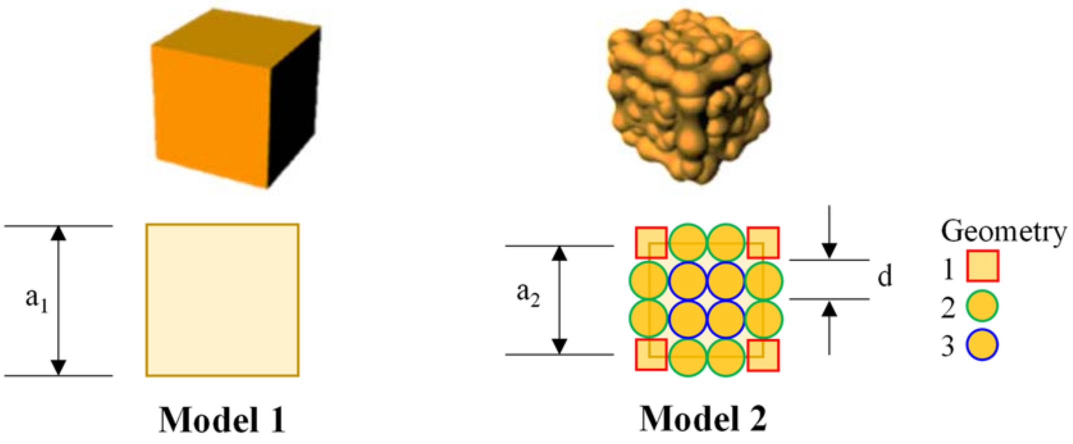
	CTAB	$HAuCl_4 \cdot 3H_2O$	Ascorbic Acid	4-ATP	Au Nanocubes	ATP : Au^{3+}
	4.7 mL	*0.1 mL*	*0.475 mL*	*0.5 μL*	*50 μL*	
(i)	1.7 mM	0.5 mM	5 mM	10 mM	3×10^{10} /mL	1 : 10
(ii)		1 mM	10 mM			1 : 20
(iii)		2 mM	20 mM			1 : 40
(iv)		4 mM	40 mM			1 : 80
(v)		6 mM	60 mM			1 : 120
(vi)		10 mM	100 mM			1 : 200

Table S2. Size distributions of samples (i)–(vi)

	Mean (nm)
Cube (seed)	*44 ± 4*
(i)	53 ± 4
(ii)	67 ± 5
(iii)	76 ± 5
(iv)	112 ± 6
(v)	127 ± 8
(vi)	156 ± 9

Modeling and Calculation

We can assess the effect of increasing surface area due to bumpy cubic structures, which is referred as 'morphology factor'. Model 1 is for simple cubic structure as a control and model 2 is for a bumpy cubic structure, including small structures on cubic structure.



a_1: Edge length of Au NC (Model 1) and Au BNC (Model 2).

d: Edge length of small cubes or diameter of spheres on a core cube in Model 2.

Geometry 1: small cubes on vertex which have partially (7/8) exposed surface

Geometry 2: spheres on edge which have partially (3/4) exposed surface

Geometry 3: hemispheres on side area

The value of d is approximated as a quarter of a_1 based on TEM images of Figure 1.

a_2: a_2 is defined as $a_2 + d = a_1$.

Then, the surface area of Model 1 is

Area 1 $= 6(a_1)^2 = 96d^2$

And the surface area of Model 2 is the sum of exposed surface areas from cubes or spheres on each geometry (1, 2 and 3) multiplied by the number of cubes or spheres on each geometry (1, 2 and 3) and the exposed surface area from a core cube as:

Area 2 $= [(21/4)d^2 \times 8] + [3\pi(d/2)^2 \times (2\times12)] + [2\pi(d/2)^2 \times (4\times6)] + 6[(a_2)^2 - 8\times\pi(d/2)^2]$

$= [72\pi+36](d/2)^2$

Therefore, morphology factor = Area 2 / Area 1 = 1.12

This estimation reveals that the bumpy structure effect on surface area increase is not significant. Another contribution of surface area is the size of cubic body as shown in TEM images of Fig. 1. Surface area of a cubic body increases with square of edge length and the edge length increases from 44 nm to 156 nm from seed to Au BNC (vi), which is much larger than the morphology factor. Including the morphology factor (1.12), we estimated the surface area of each nanoparticle, and compared their SERS intensity of 385 cm^{-1} band as shown in Table S3.

Table S3. Estimated surface area and observed SERS intensity for Au BNC (i)–(vi)

Type of particle	Edge length (nm)	Surface area of a particle (nm^2)	Intensity of 385 cm^{-1} (a.u.)
Seed	44	1.16.E+04	6.5.E+02
Au BNC (i)	53	1.89.E+04	7.1.E+02
Au BNC (ii)	67	3.02.E+04	2.1.E+03
Au BNC (iii)	76	3.88.E+04	6.8.E+03
Au BNC (iv)	112	8.43.E+04	4.9.E+03
Au BNC (v)	127	1.08.E+05	3.8.E+03
Au BNC (vi)	156	1.64.E+05	2.4.E+03

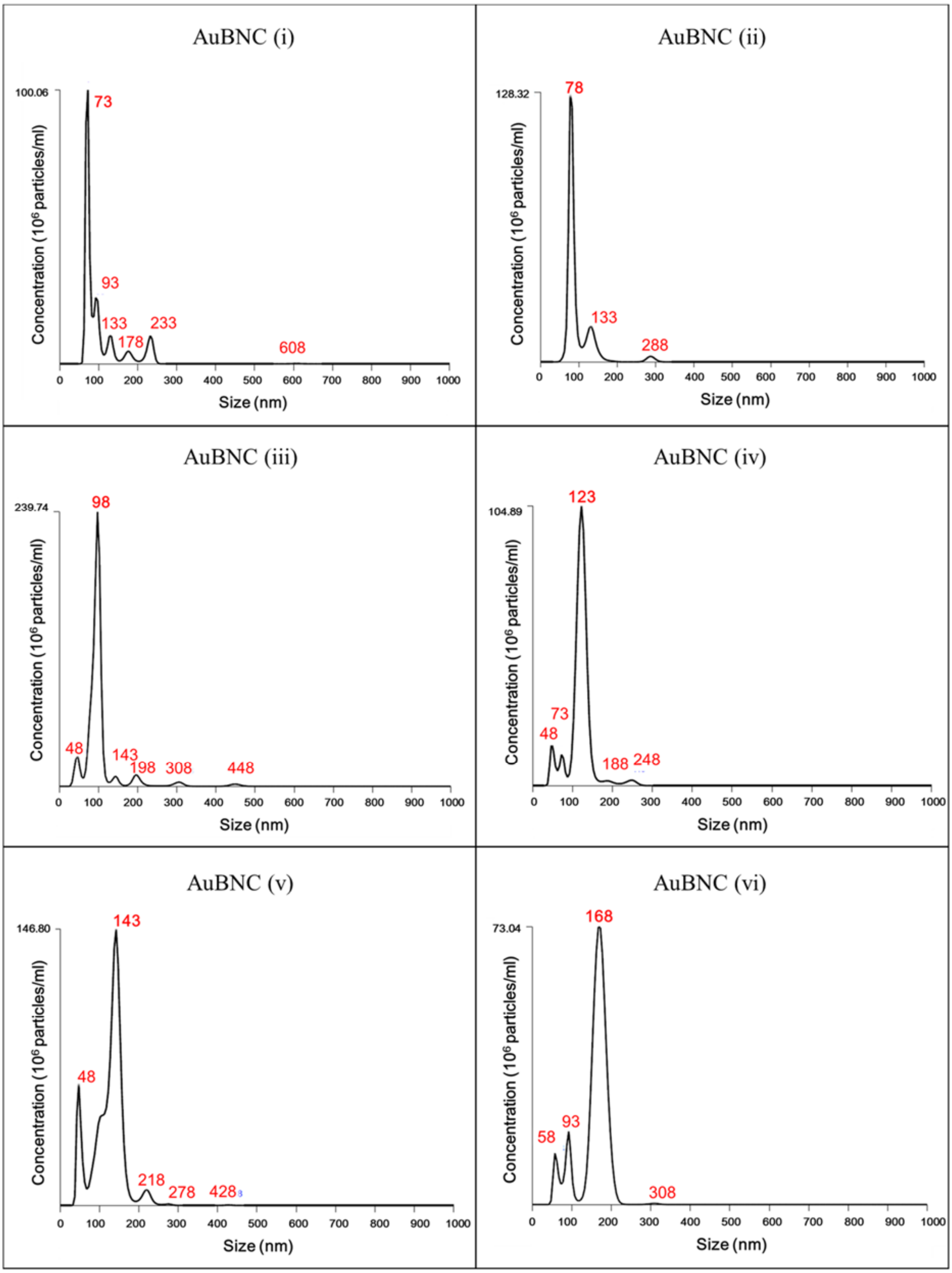


Fig. S1. Particle size distributions of Au BNCs obtained by Nanoparticle Tracking Analysis.

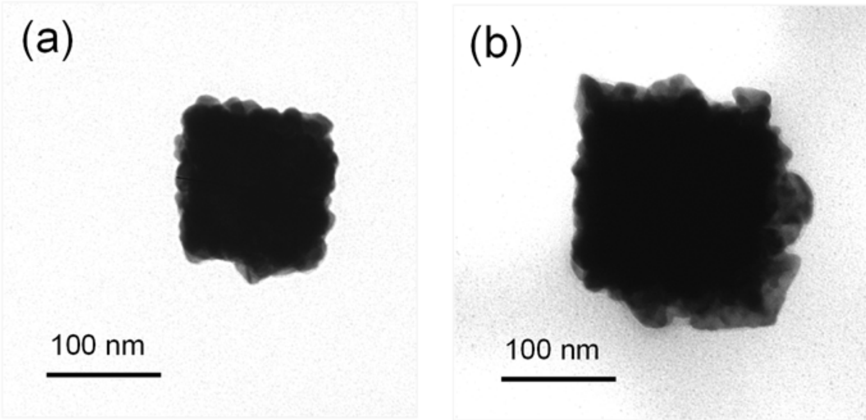


Fig. S2. TEM images of (a) Au BNCs (v) and (b) Au BNCs (vi)

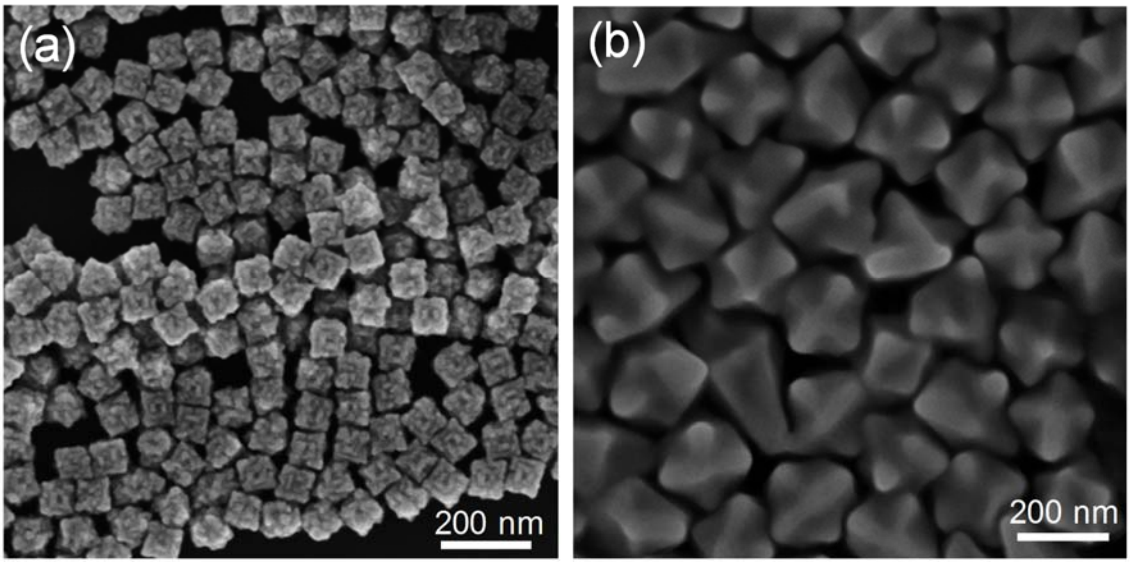
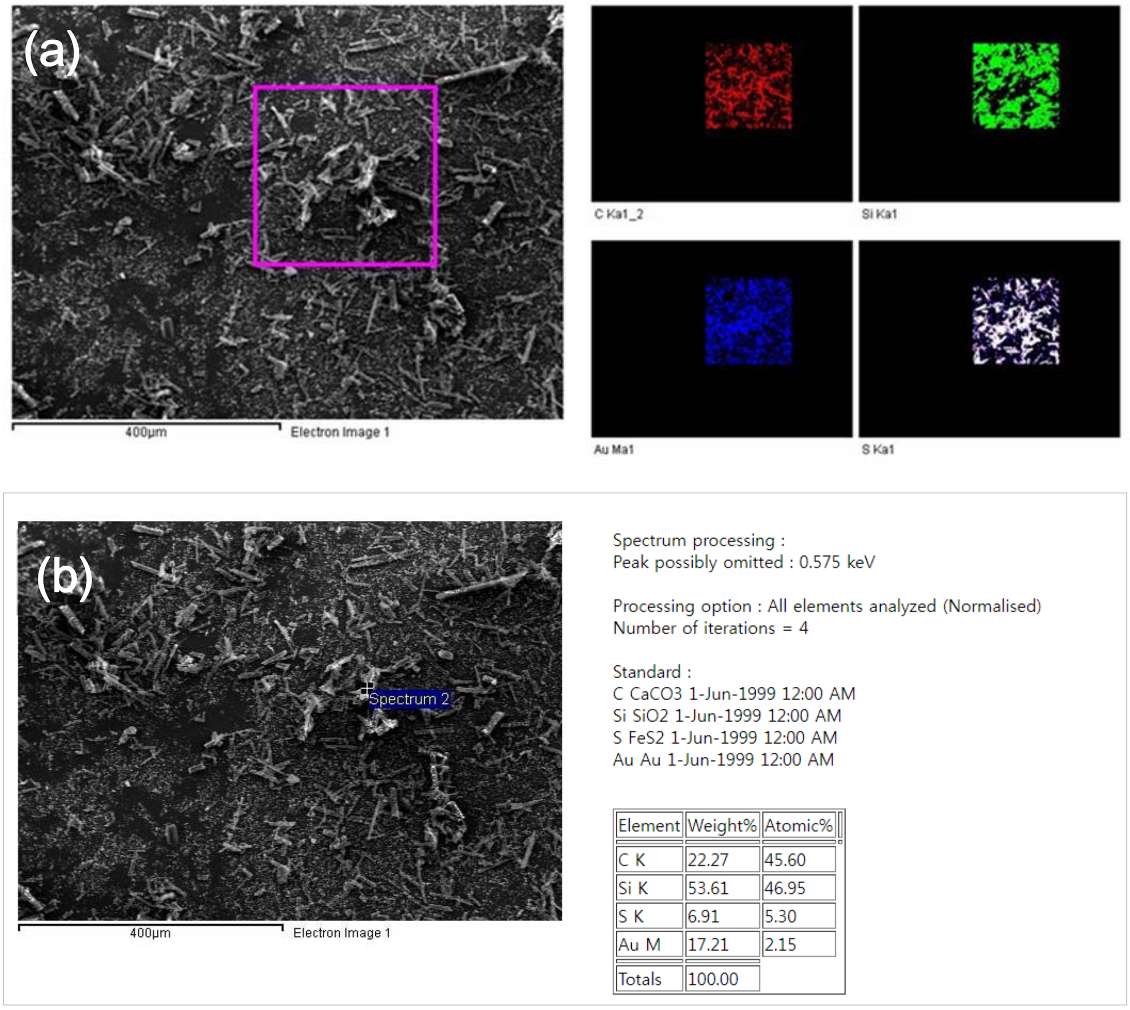


Fig. S3. SEM images of (a) Au BNCs with average size of 67 nm (iii) at low magnification and (b) trisoctahedron (TOH) nanocrystals with average size of 140 nm obtained by growth of nanocubes under the same conditions as (iii) without 4-ATP.



Element	Weight%	Atomic%
C K	22.27	45.60
Si K	53.61	46.95
S K	6.91	5.30
Au M	17.21	2.15
Totals	100.00	

Fig. S4. Energy-dispersive X-ray spectroscopy analysis of Au BNCs. (a) SEM image of Au BNC aggregates on the Silicon wafer and EDX mapping image. Red, green, blue and white colors mean C, Si, Au, and S elements respectively. Au and S appeared at the same location on the SEM image. (b) Quantitative EDX analysis on Au BNC aggregates.

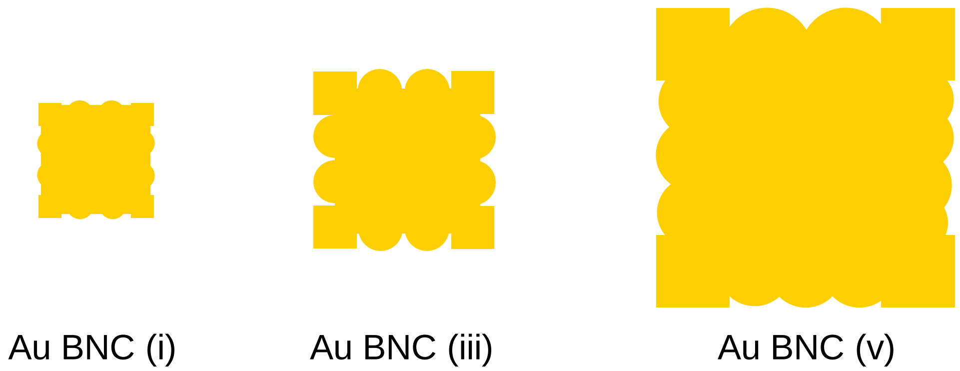


Fig. S5. Schematic illustration for development of surface morphology as Au BNCs grow larger. In the early case of Au BNC (e.g. Au BNC (i)), bumpy structures are less developed and their numbers are low, illustrating that their SERS effect is not significant. In the case of Au BNC (iii), bumpy structures are much grown to have many interstitial gaps between bumpy particles, illustrating that this structure is more effective in SERS effect than the earlier ones. However, as the Au BNCs grow further as in the case of Au BNC (v), merging the bumpy structures flatterns and smoothens the gap structure, which becomes less effective in SERS effect.

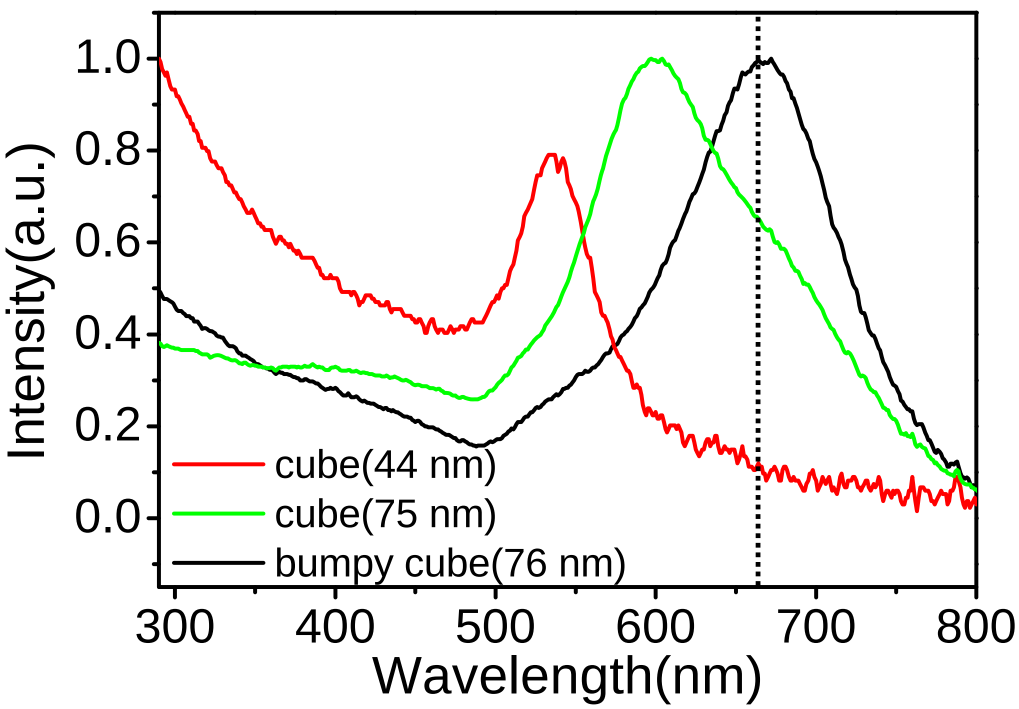


Fig. S6. Extinction spectra of Au nanocubes (44 nm), Au nanocubes (75 nm), and Au bumpy nanocubes (76 nm).

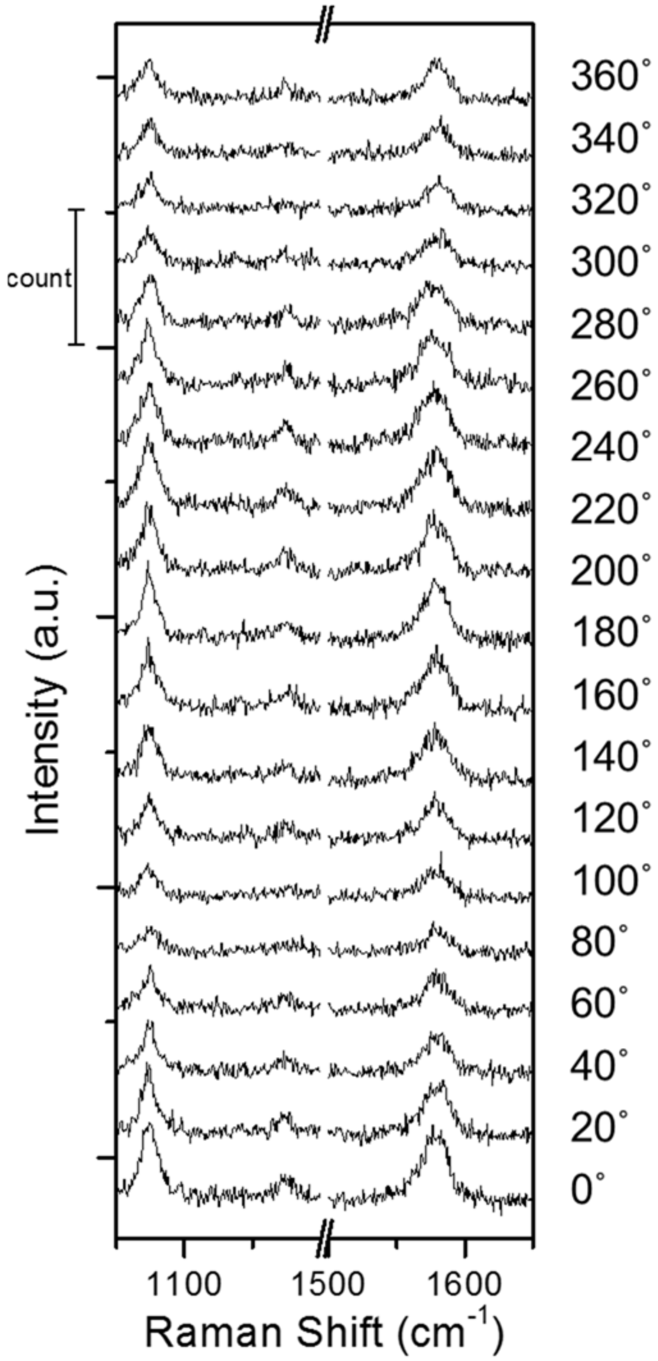


Fig. S7. Polarization-dependent SERS spectra from the single Au BNC shown in Fig. 5d.