Supporting Information

Nanoporous Gold Nanoframes with Minimalistic Architectures: Lower Porosity Generates Stronger Surface-Enhanced Raman Scattering Capabilities

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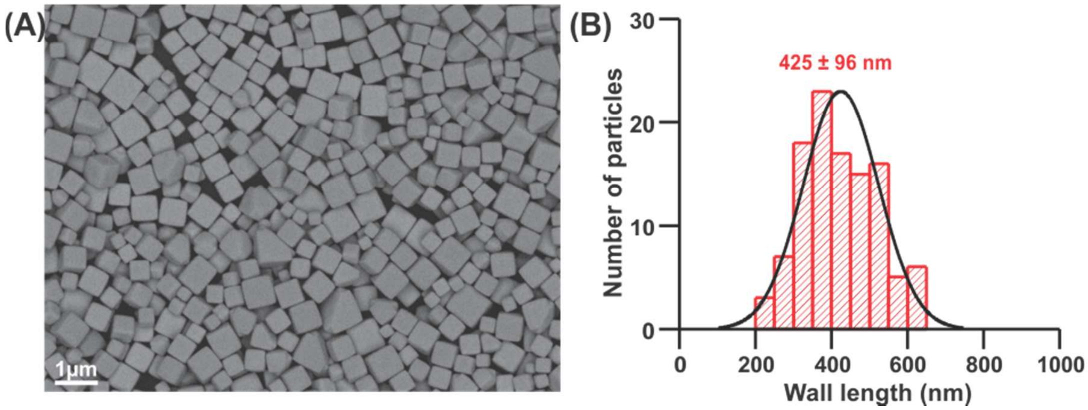


Figure S1. (A) AgCl template synthesized with distinct edges and corners. (B) Size distribution of the AgCl template.

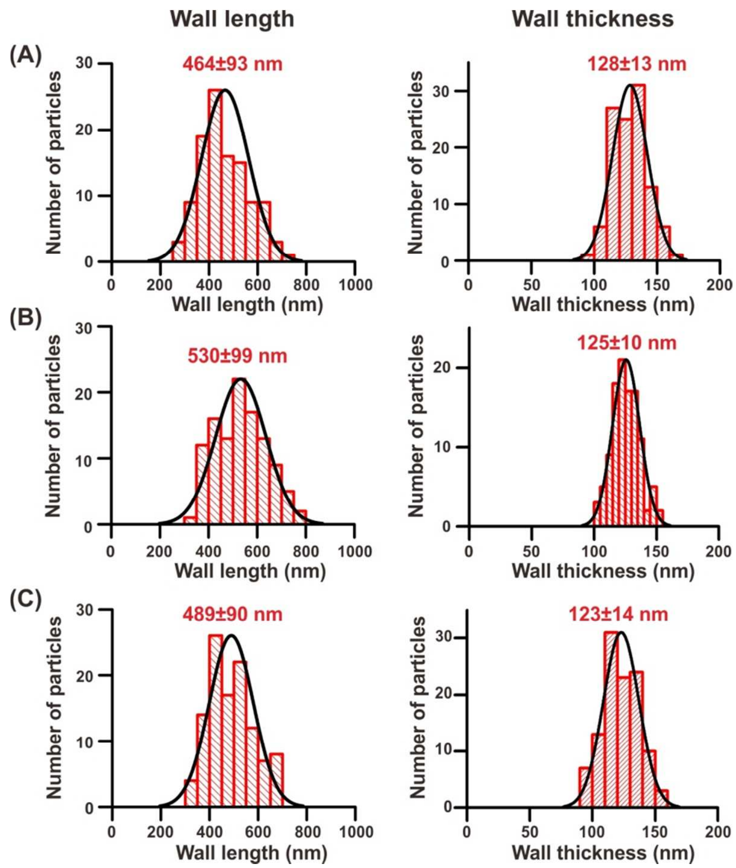


Figure S2. Wall length and wall thickness of (A) NGN1, (B) NGN2, and NGN3.

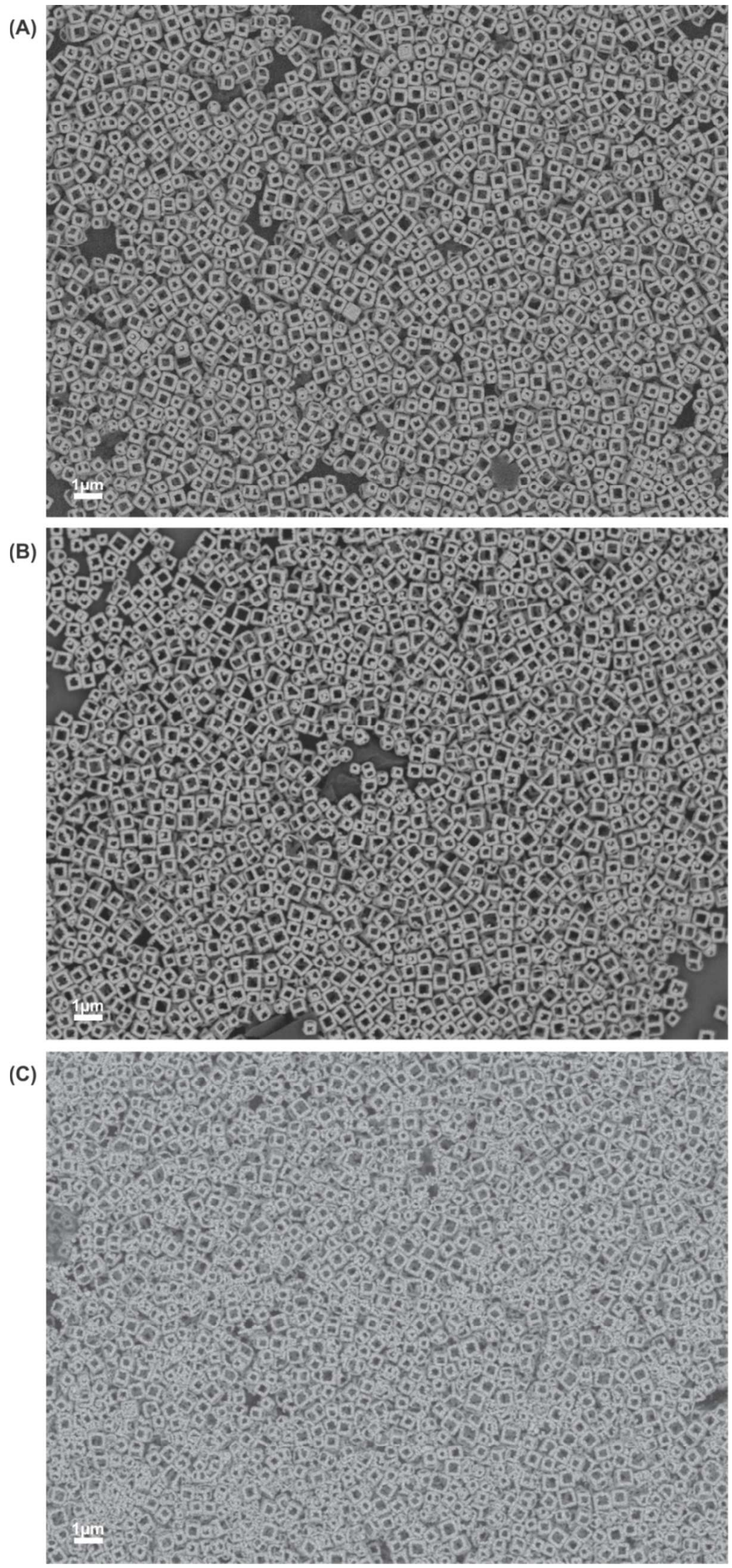


Figure S3. (A-C) SEM images of NGN1, NGN2, and NGN3, respectively, indicating yield of close to 100%.

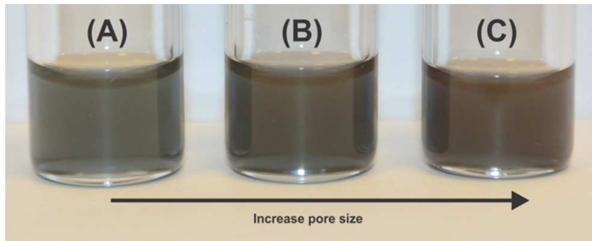


Figure S4. (A-C) Solution colour of NGN1, NGN2, and NGN3, respectively. As the pore size increases from left to right, the colour changes from bluish-grey to reddish-blue.

Calculation of crystallite grain size

Scherrer equation:

Crystallite grain size = $\frac{K\lambda}{\beta cos\theta}$

K = shape factor (0.94)

λ = X-ray wavelength (1.5406 Å = 0.15406 nm)

β = Full-width half maximum (FWHM)

θ = Bragg angle (2θ = 38.3; θ = 19.15)

For NGN1

FWHM = 1.88° = 0.03288 radian

Crystallite grain size = (0.94 × 0.15406) ÷ (0.03288 × cos19.15)

= 4.7 nm

For NGN2

FWHM = 0.87° = 0.01513 radian

Crystallite grain size = (0.94 × 0.15406) ÷ (0.01513 × cos19.15)

= 10.1 nm

For NGN3

FWHM = 0.68° = 0.01178 radian

Crystallite grain size = (0.94 × 0.15406) ÷ (0.01178 × cos19.15)

= 13.0 nm

(A)

(B)

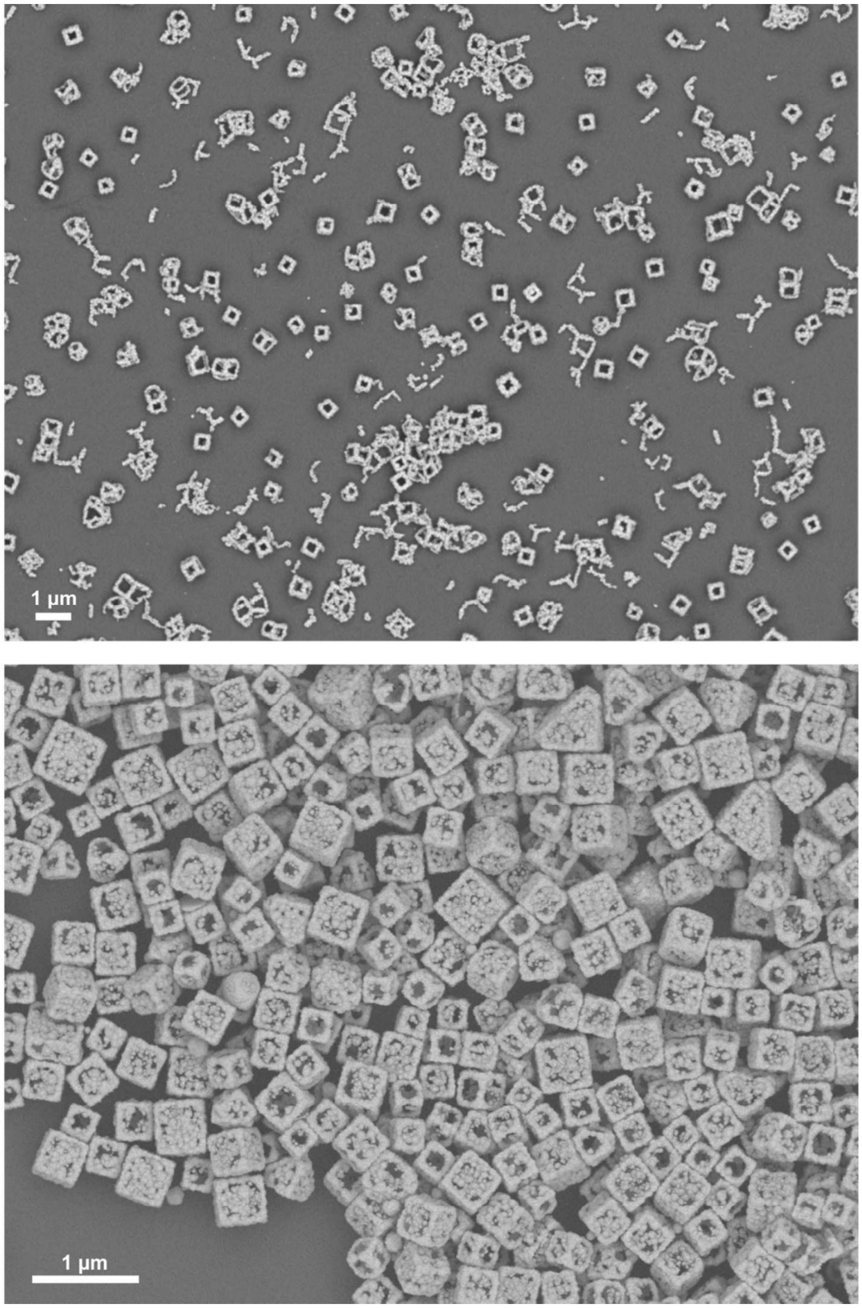
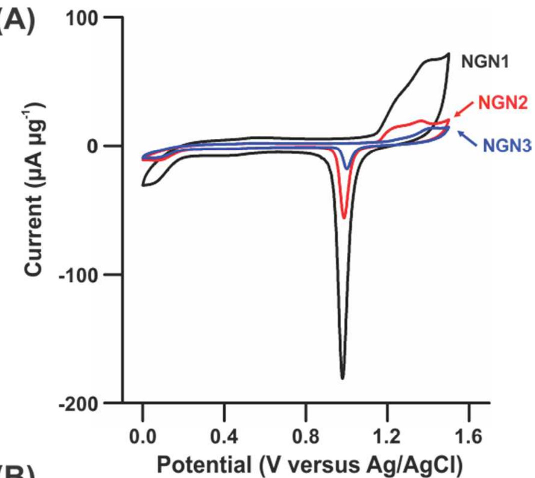


Figure S5. Control experiment to determine the effect of the molar ratio of hydroquinone to $HAuCl_4$ in which at lower molar ratio of 1.0 (A) the reducing agent is not enough to reduce the Au^+ causing the growth of incomplete NGN as observed with strands of Au nanoparticles and incomplete NGN; and at higher molar ratio of 2.0 (B) the excess amount of reducing agent reacts with the Ag^+ from the AgCl template leading to the formation of nanoboxes instead of NGN.

(A)



(B)

Sample	Gold oxide stripping peak (μC)	Electro-active surface area (m^2g^{-1})
NGN1	871.5	35.3
NGN2	616.3	10.2
NGN3	224.8	3.4

Figure S6. (A) Cyclic voltammogram of NGN1, NGN2, and NGN3. (B) Calculated electrochemically active surface area (ECSA) of the NGNs showing the decrease of surface area as the porosity increases from NGN1 to NGN2 to NGN3.

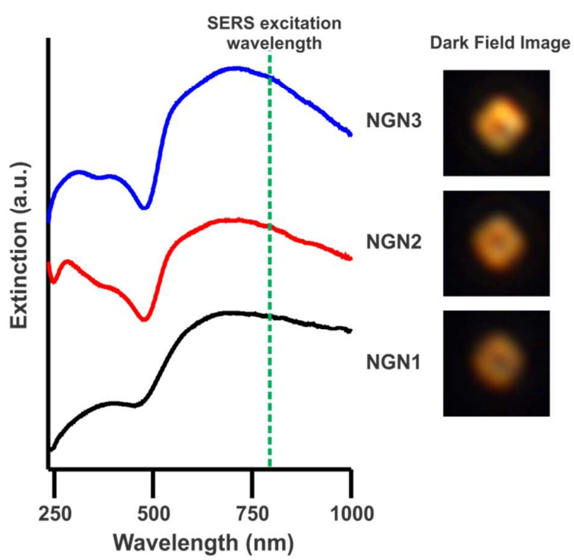


Figure S7. UV-Vis spectra of the NGNs with the vertical dashed line representing the excitation wavelength at 785 nm. They all exhibit broad peak across the visible to the near-IR region which is consistent with the unique characteristic of GNFs whereby their LSPR are extended to the near-IR region. Dark field images shows the change in colour from reddish to orangey as the porosity changes.

Calculation of enhancement factor (EF)

The enhancement factor is calculated using the equation below:

$$\text{EF} = \frac{I_{SERS}}{I_{NORMAL}} \times \frac{N_{NORMAL}}{N_{SERS}}$$

We chose the peak at 1080 cm^{-1} to calculate the enhancement factor.

I_{NORMAL} = 167.2 cm^{-1}/3600 s

= 0.46 cm^{-1} (based on 0.5 M 4-MBT solution, 100 × objective lens, line scan, 3600 s/line)

N_{NORMAL} = number of molecules within the measured laser spot

= V solution × concentration of molecules × Avogadro's number

V solution = π × x × y × z (x=1.20/2=0.60 µm, y=1.18/2=0.59 µm, z=14.76 µm)

= 3.142 × 600 nm × 590 nm × 14760 nm

= 1.64×10^{10} nm^3

N_{NORMAL} = 1.64×10^{10} nm^3 (=1.64×10^{-17} m^3) × 0.5M (=500 mol/m^3) × 6.022×10^{23}

= 4.94×10^9

N_{SERS} = number of molecules on the surface of the nanoparticles within the measured laser spot

Laser spot diameter = 610 nm (100 × objective lens) > diameter of the nanoparticles

N_{SERS} **=** surface area of single nanoparticle ÷ surface area of 4-MBT

Surface area of 4-MBT = 2.3 × 2.3Å^2 / molecule = 0.0529 nm^2/molecule

Assuming the Au nanoparticle seeds making up the NGN are uniform in size with simple cubic packing throughout the NGN, the amount of Au particle seed in a NGN could be calculated. Thus the volume of a NGN could be estimated through the following reaction using the dimension in Figure S9 and S10:

Number of Au seeds in a plane (χ) = $\left(\frac{127}{Au\ seed\ diameter}\right)^2 - \left(\frac{64}{Au\ seed\ diameter}\right)^2$

Number of Au seeds in 4 long walls ($\boldsymbol{\alpha}$) = $4\left(\frac{500}{Au\ seed\ diameter}\right) \times \boldsymbol{\chi}$

Number of Au seeds in 8 short walls ($\boldsymbol{\beta}$) = $8\left(\frac{246}{Au\ seed\ diameter}\right) \times \boldsymbol{\chi}$

Volume of NGN = ($\boldsymbol{\alpha} + \boldsymbol{\beta}$) × *Au seed volume*

By estimating the volume of a NGN we could calculate the mass of a single NGN and thus the surface area of the NGN.

The calculation carried out on NGN1, NGN2, and NGN3 using the Au seed diameter of 4.7 nm, 10.1 nm, and 13.0 nm respectively yield a similar volume of 2.5×10^{7} nm^3

Thus, the estimated mass of a NGN would be:

Mass = Volume × Density

= $(2.5 \times 10^{-14}\ cm^3) \times (19.30\ g/cm^3)$

= 4.825×10^{-13} g

Therefore, the surface area of a single nanoparticle would be the ECSA value multiplied with the estimated mass above.

For NGN1

I_{SERS} = 30

Surface area = 35.3 m^2g^{-1}

Surface area of single nanoparticle = 35.3 $m^2g^{-1} \times 4.825 \times 10^{-13}$ g

= 1.70×10^{7} nm^2

N_{SERS} = 1.70×10^{7} $nm^2 \div 0.0529$ nm^2/molecule

= 3.22×10^{8} molecule

EF = $[30/0.46] \times [4.94 \times 10^{9}/3.22 \times 10^{8}]$

= 1.00×10^{3}

For NGN2

I_{SERS} = 154

Surface area = 10.2 m^2g^{-1}

Surface area of single nanoparticle = 10.2 $m^2g^{-1} \times 4.825 \times 10^{-13}$ g

$= 4.92 \times 10^6$ nm^2

N$_{SERS}$ = 4.92×10^6 nm^2 ÷ 0.0529 nm^2/molecule

= 9.30×10^7 molecule

EF = [154/0.46] × [4.94×10^9/9.30×10^7]

= 1.78×10^4

For NGN3

I$_{SERS}$ = 257

Surface area = 3.4 m^{2}g^{-1}

Surface area of single nanoparticle = 3.4 m^{2}g^{-1} × 4.825×10^{-13} g

= 1.64×10^6 nm^2

N$_{SERS}$ = 1.64×10^6 nm^2 ÷ 0.0529 nm^2/molecule

= 3.10×10^7 molecule

EF = [257/0.46] × [4.94×10^9/3.10×10^7]

= 8.90×10^4

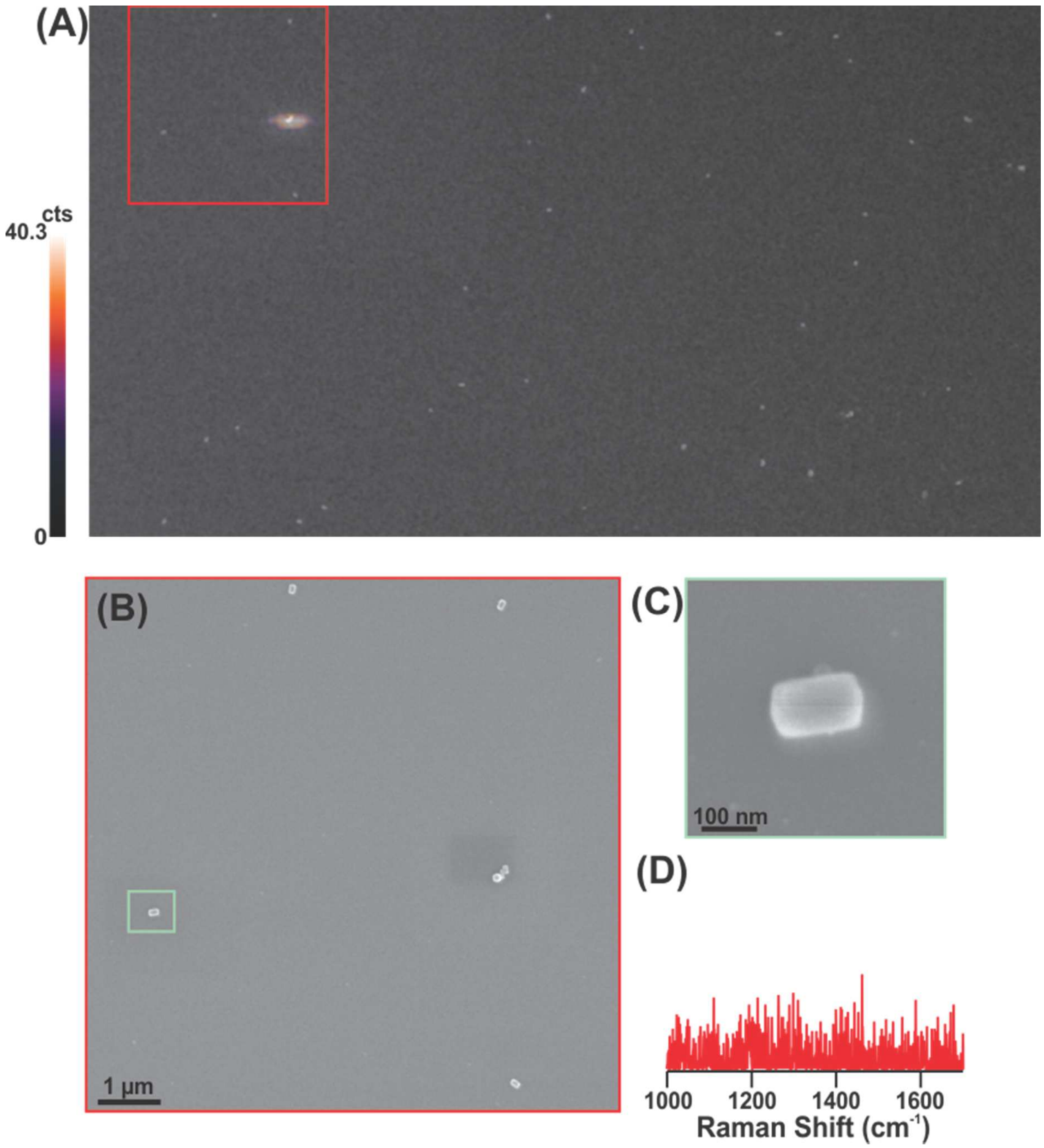


Figure S8. (A) Overlaid SERS and SEM images of gold nanorods with excitation laser wavelength of 785 nm and an excitation power of 0.05 mW, similar to NGNs, but with an exposure time of 6 minutes/line, 36 times longer than the exposure time used for the NGNs. (B) Zoom-in SEM image of the red border area shows 4 single gold nanorods, which shows no SERS enhancement, with one gold nanorod trimer showing SERS enhancement. (C-D) Zoom-in SEM image of the green border area shows a single gold nanorod with its SERS spectrum.

Scientific Control

After an exposure time of 6 minutes/line for gold nanorods, with the width and length of approx. 100 nm and 150 nm respectively, at similar excitation laser wavelength and power used for NGNs, the SERS spectra yields no clear major characteristic peaks of 4-MBT at 1080 cm^{-1} and 1578 cm^{-1}.

Assuming the value of the gold nanorods spectra as 1 counts, the counts normalized to the exposure time of NGNs (10 seconds/line) would be 1/36 counts, which is 0.028 counts.

Thus NGN1 (30 ± 16 counts), NGN2 (154 ± 36 counts), and NGN3 (257 ± 63 counts) are better than gold nanorods for SERS detection of 4-MBT by 1054-fold, 5500-fold, and 9179-fold respectively.

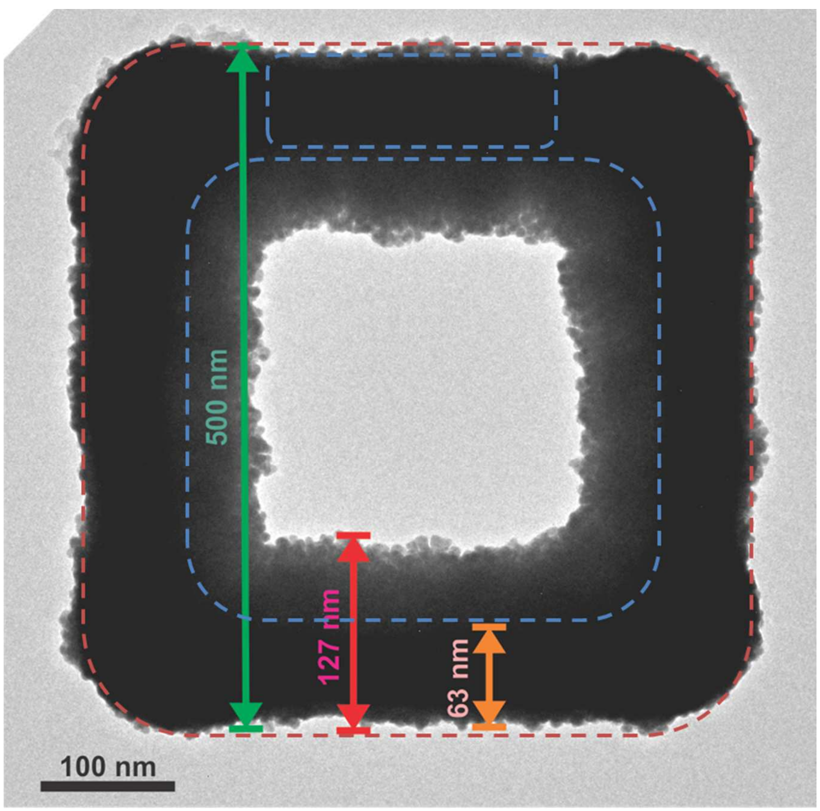


Figure S9. Estimation of the dimension of a NGN using TEM image. The darker outline is assumed to be the overlay of the wall thickness.

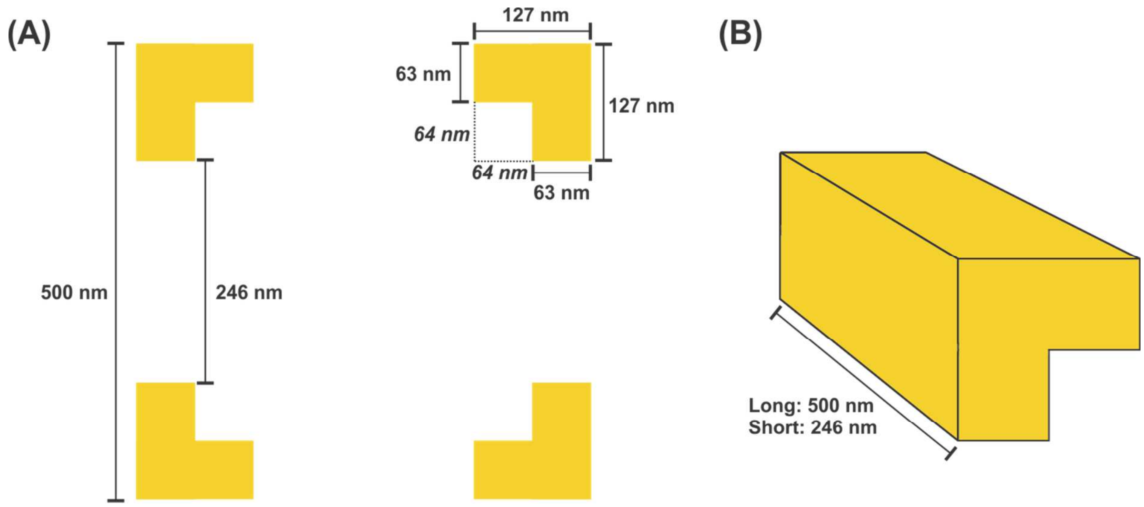


Figure S10. (A) Cross section dimension of the NGNs from the TEM image. (B) A wall of the NGN which consist of 4 long walls and 8 short walls.