1st Nov, 2008

Paper Presentation on

"Surface-enhanced Raman scattering spectroscopy via gold nanostars"

E. Nalbant Esenturk and A. R. HightWalker

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Physics Laboratory,
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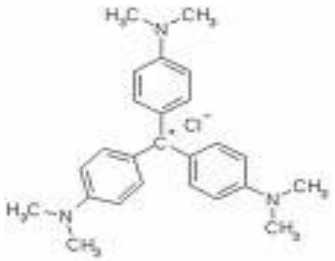
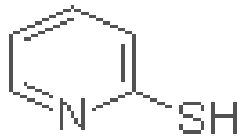
Gaithersburg, MD, USA.





DOI 10.1002/jrs.2084 *J. Raman Spectrosc.* **(2008)** Early View @ Wiley Interscience

Journal of RAMAN SPECTROSCOPY

SERS Origin

Chemical Enhancements

- The nature of the molecule
- An increased molecular polarizability by formation of a CT complex
- Molecules with delocalized electrons often show strong Raman enhancement.
- Different EFs for different molecules on identical SERS substrates

Electromagnetic Enhancements

- Results from an increased field at the metallic NP surface.
- Results from surface plasmons, or collective oscillations of the metal electrons.
- Aggregates of metallic NPs generate intense enhancement at the junction between two NPs, called 'hot spots'.
- Results from the tips of NPs with sharp features

Applications of SERS Substrates

- Chemical Analysis
- Bioanalytical sensing and imaging
- Detection of Metal ions (As)
- Detection of molecules at very low conc. (At nM and μM)

Preparation of Gold Nanostar

- 0.2ml of 0.01M $HAuCl_4.H_2O$
- 4.5ml of 0.1M CTAB
- 0.03ml of 0.01M $AgNO_3$
- 0.032ml of 0.1M Ascorbic acid
- 10µl of 10nm commercially available seed solution
- Gentle mixing
- Kept in a water bath at room temperature undisturbed for 3 h.
- Blue-purple color

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Preparation of Gold Nanorod

Preparation of Gold Seed

- 0.25ml of 0.01M $HAuCl_4.H_2O$
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- Gentle mixing
- 0.6ml of 0.01M $NaBH_4$ ice-cold
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Nanorod ~ 65 x 30 nm **UV-VIS absorption spectra @ 550 & 700 nm**

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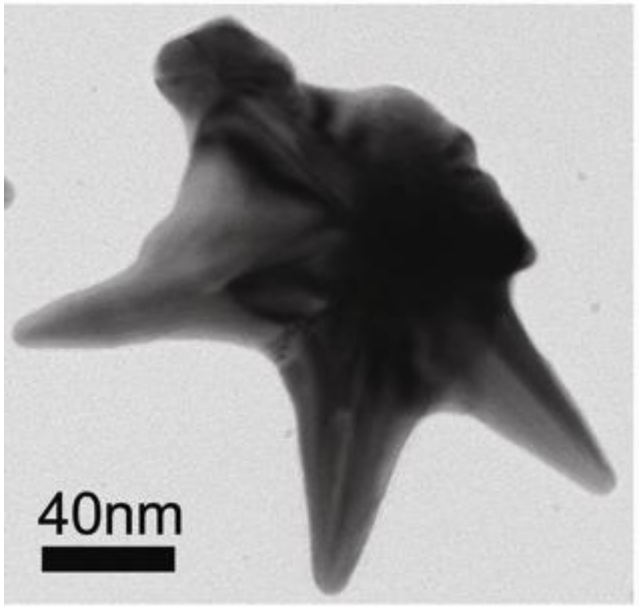

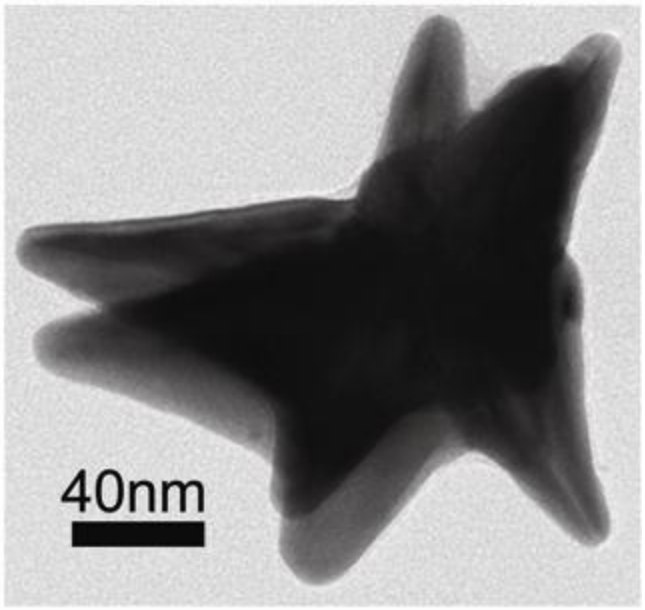

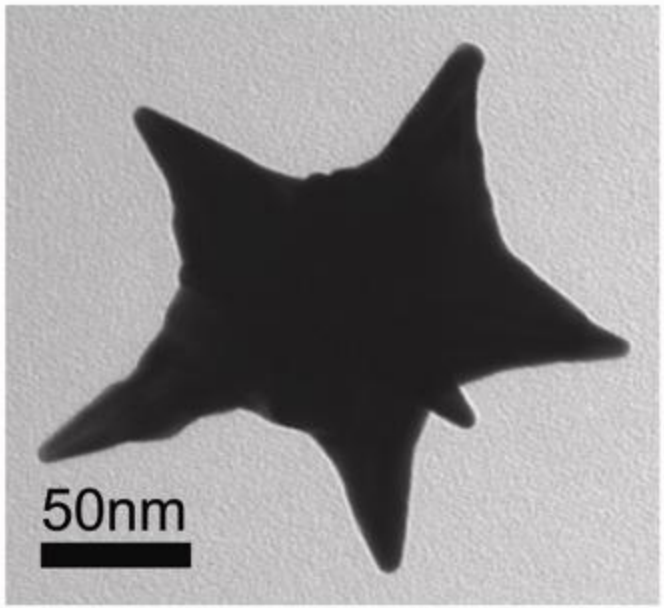

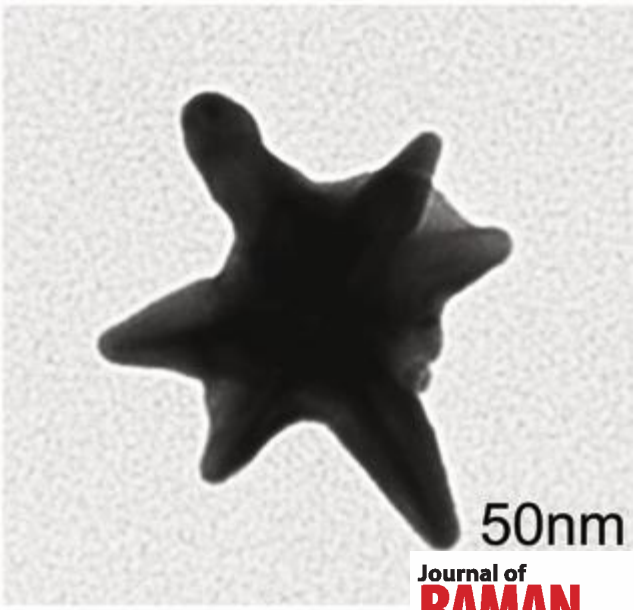

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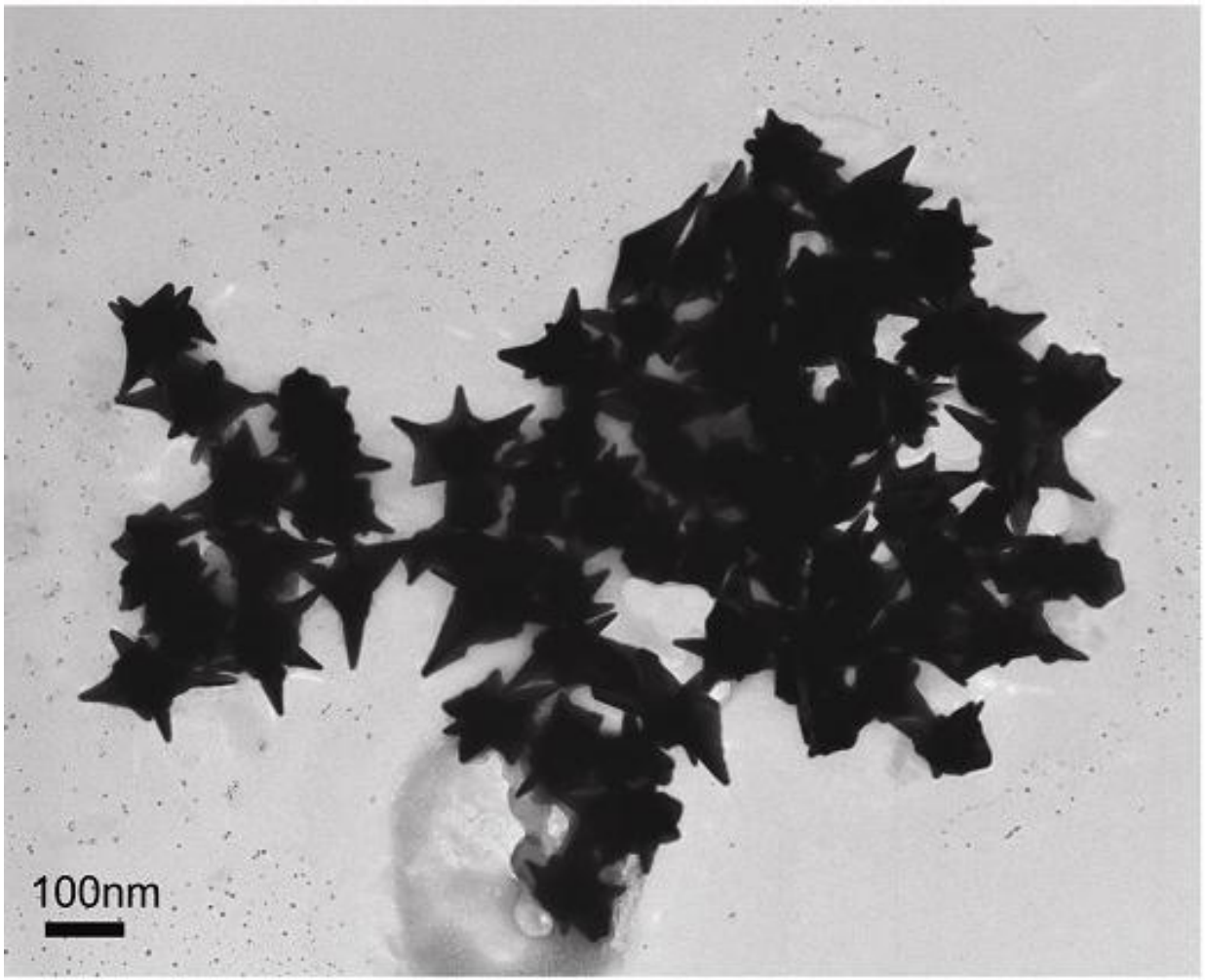

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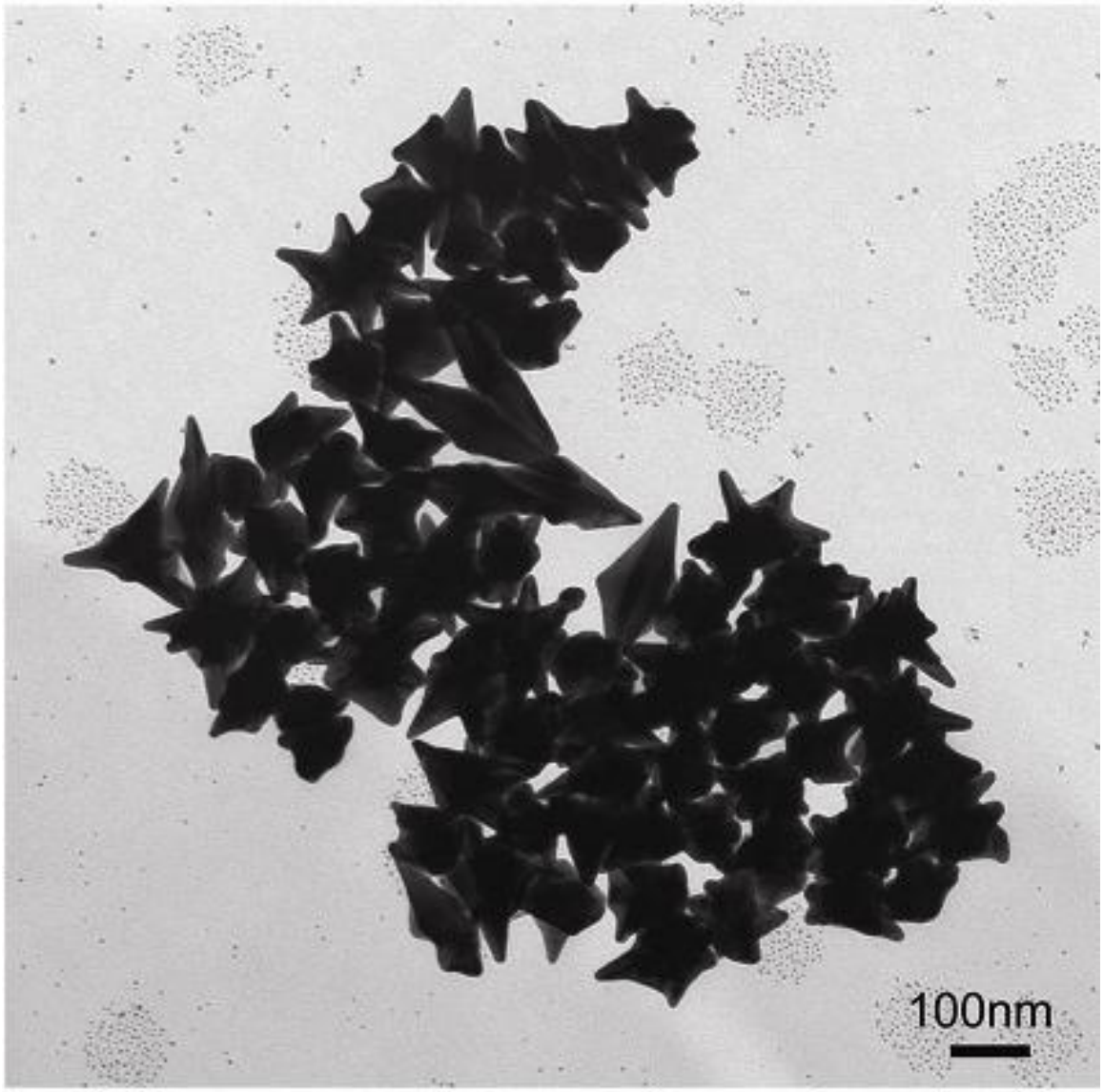

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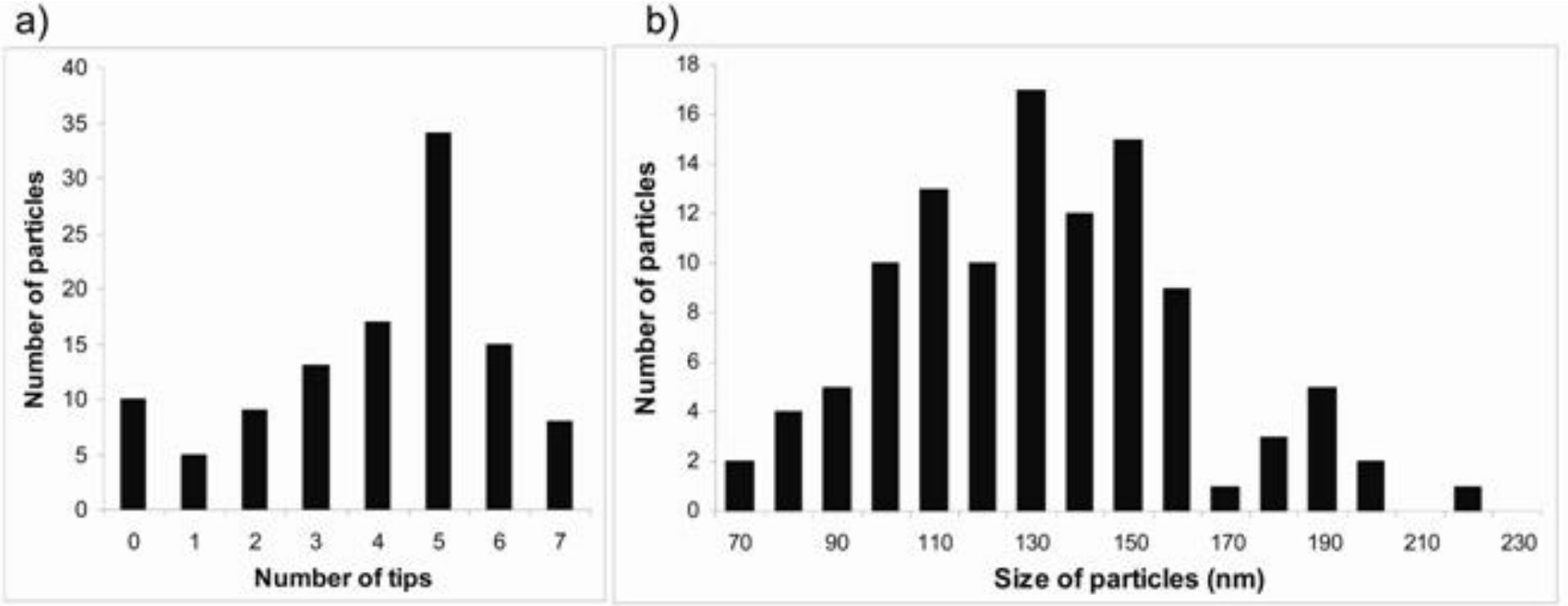

a) Number of tip, and (b) Size distribution of nanostars based on TEM images

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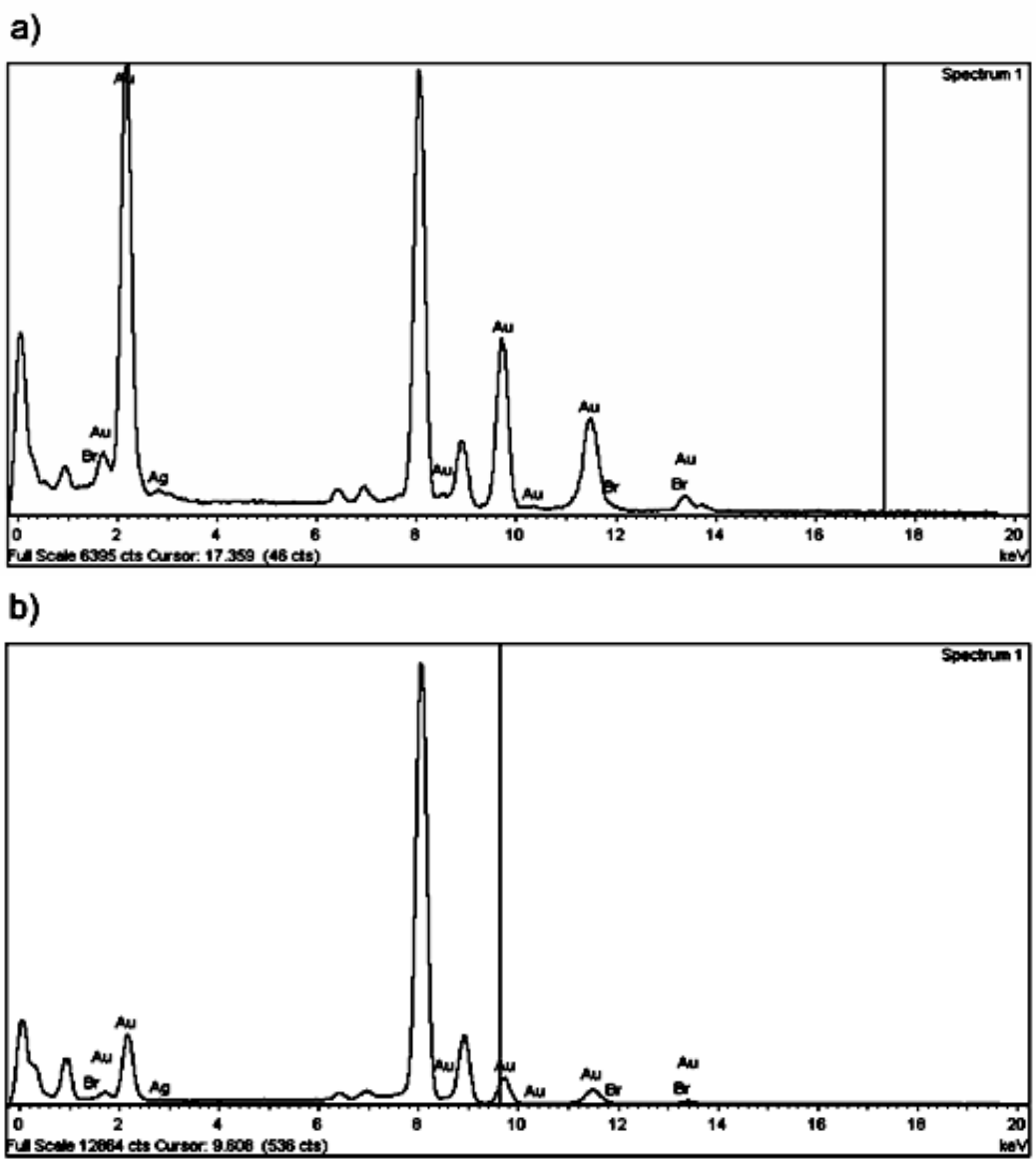

EDX spectra of a) nanostar and b) nanorod particles.
Analysis showed ca. 96% Au, ca. 2% Ag and ca. 2% Br for both type of nanoparticle

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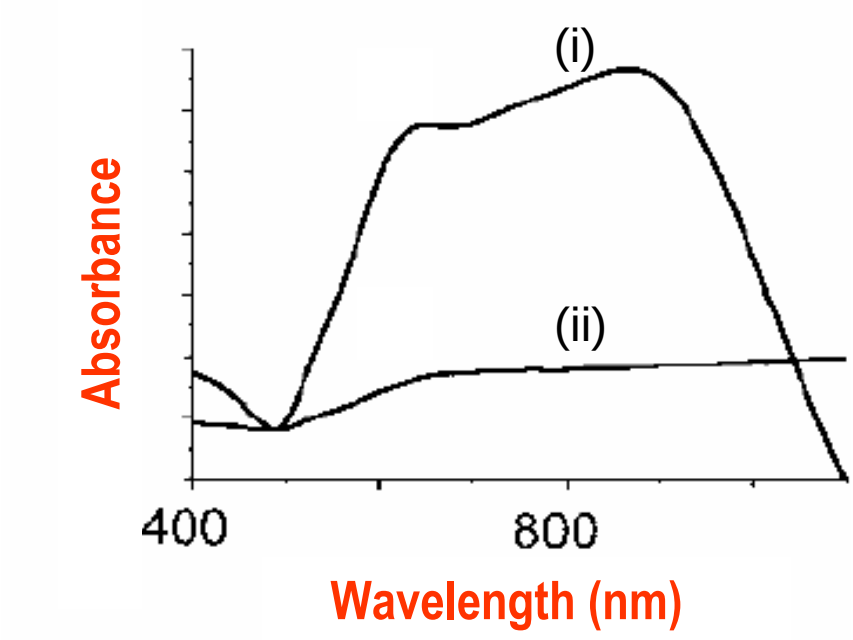

UV–vis spectra of (i) before NaCl addition (only nanostar solution) and (ii) after NaCl addition (50 mM to SERS sample).

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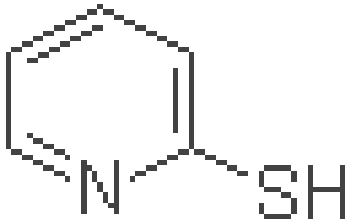
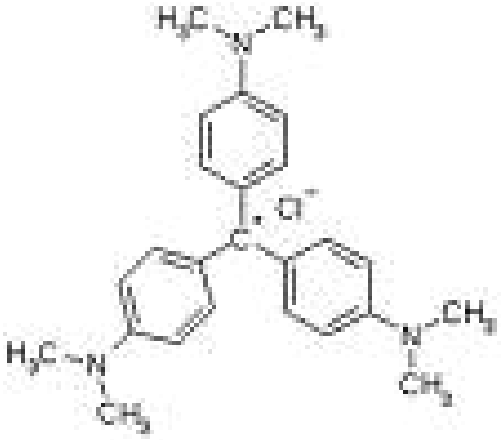
Surface-enhanced Raman scattering analytes



2-mercaptopyridine (2-MPy)



crystal violet (CV)

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Preparation of SERS samples

❖ 1 ml of Au colloid solution

❖ 0.1 ml of aqueous probe molecule (2-MPy or CV) at varying concentrations.

❖ The samples were sonicated for 10 mins prior to the measurements

❖ 1 ml of NaCl solution was added to 1 ml of Au NP solution to induce the aggregation

❖ 10 min of sonication,

❖ 0.1 ml probe molecule solution

❖ sonicated for 10 min before acquiring the SERS spectra.

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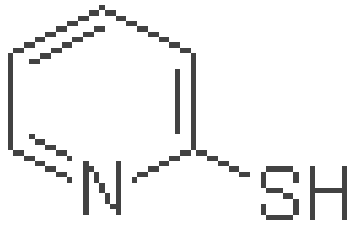
Surface-enhanced Raman scattering - analytes I



2-mercaptopyridine (2-MPy)

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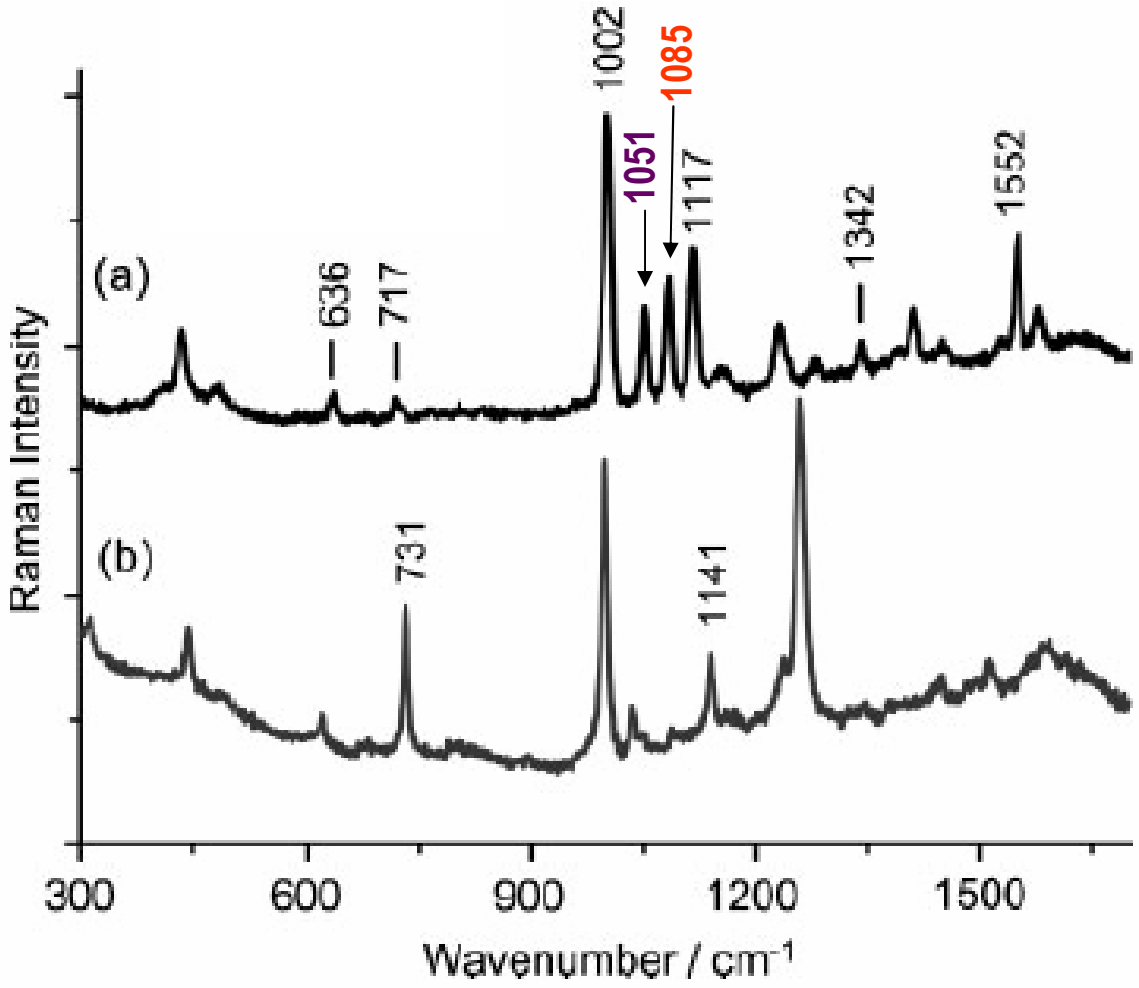
ν(C–S) at 731 cm−1 to 717 cm−1
Ring breathing (RB)/*ν*(C–S) band at 1141 to 1117 cm−1

ν(C C) at 1552 cm−1
ν(C–H) at 1085 cm−1
RB at 1002 cm−1
RB/*ν*(C–S) at 1117 cm−1

γ (CCC) at 636 cm−1
γ (CH) at 1342 cm−1
β(CH) at 1051 cm−1



(a) SERS spectra of 1 μM 2-MPy on Au nanostars
(b) and (b) Raman spectra of 0.1 M 2-MPy.
Traces are offset for clarity.

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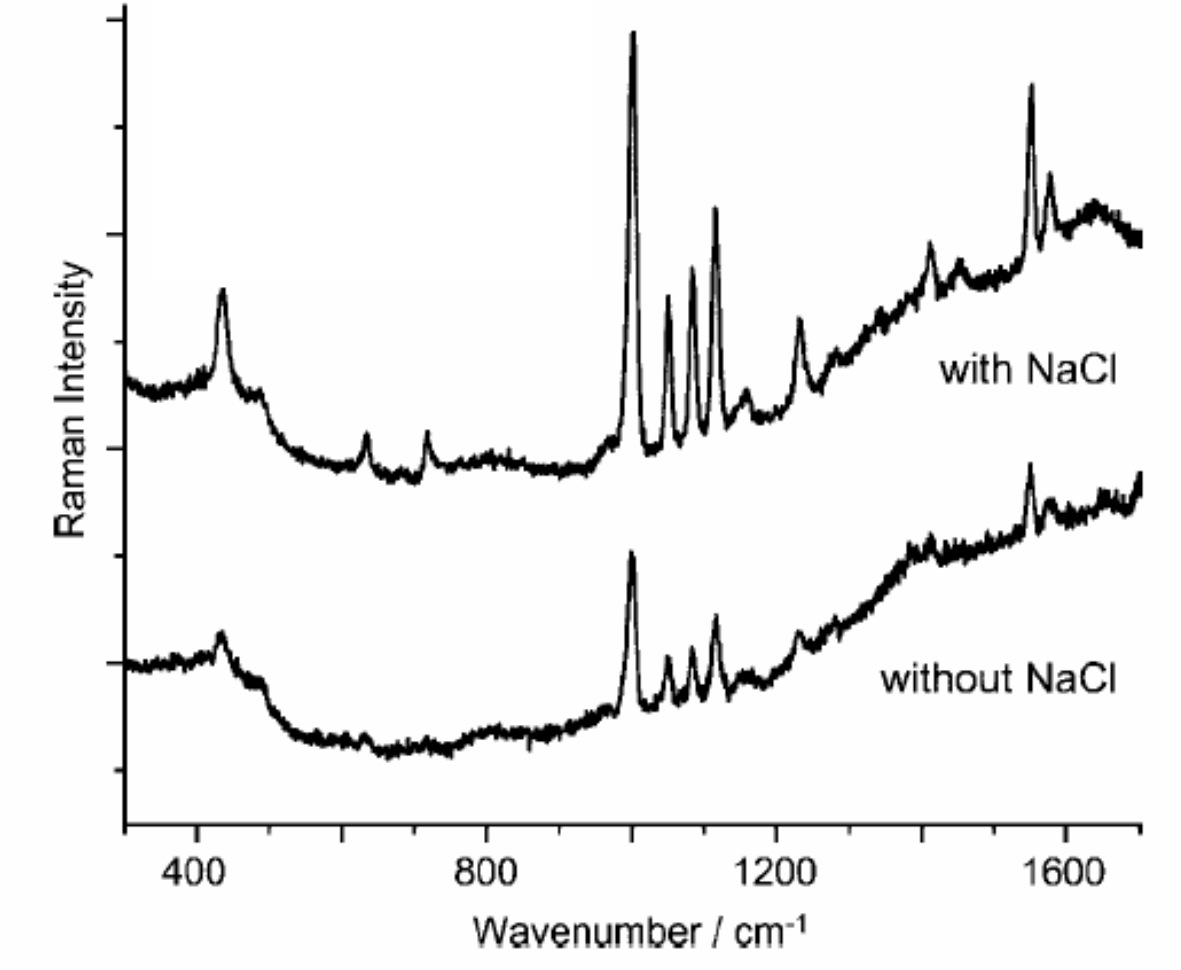

SERS activity of Au nanostars as a function of NaCl addition. 2-MPy concentration was kept constant at 1 μM in SERS sample. Traces are offset for clarity.

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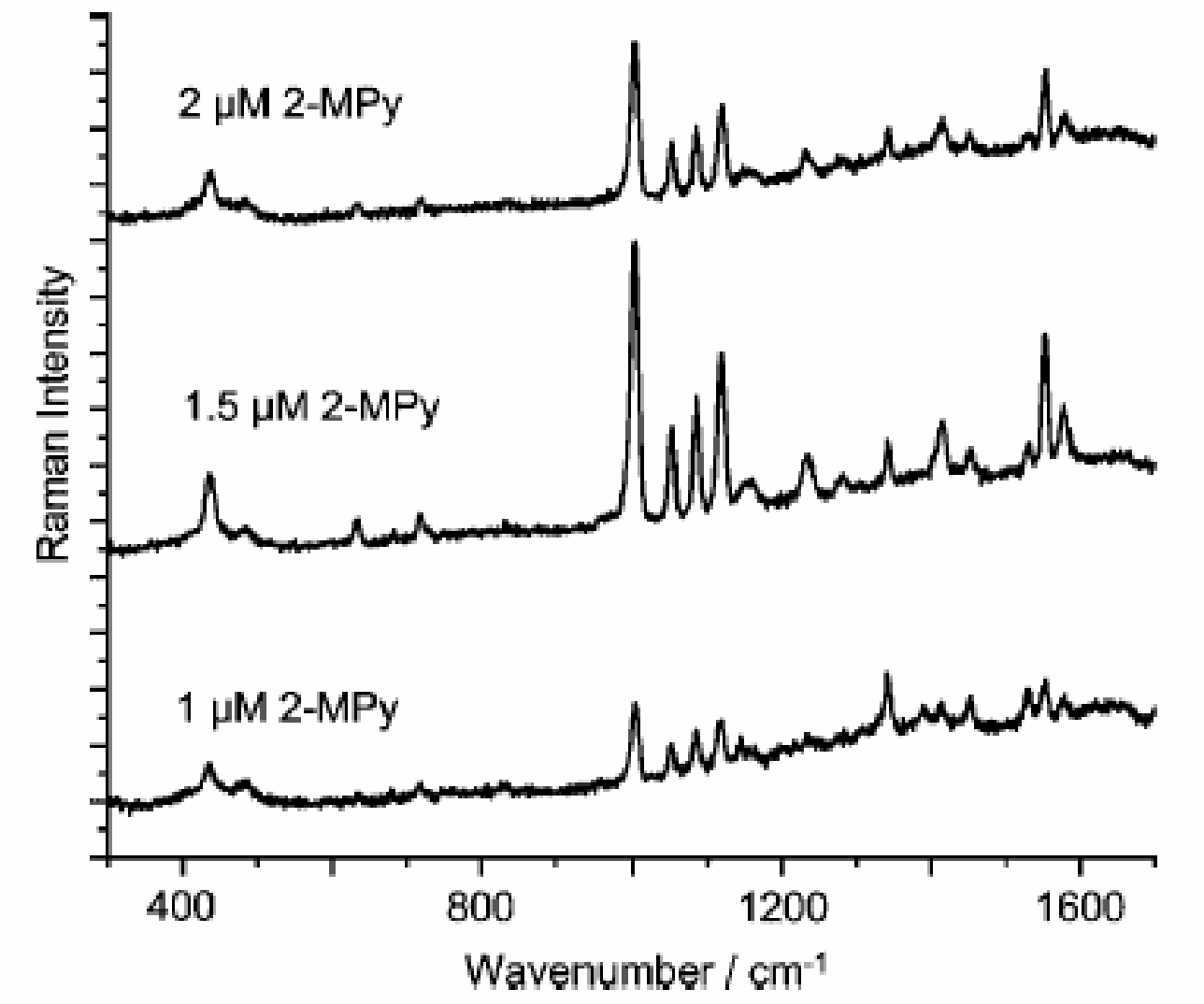

SERS activity of Au nanostars as a function of 2-MPy concentration.
NaCl concentration was kept constant at 50 mM. Traces are offset for clarity.

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Optimizing (equal) NPs concentration

Nanostars (ca. 140 nm), Nanorods (ca. (65 nm x 30 nm)) & Nanospheres (ca. 150 nm)

	# particles / mL (**N**)[1]	Surface area (nm^2) of each nanoparticle (**A**)[2]	Total surface area of nanoparticle / mL (= **N** x **A**)
nanostar*	~ 3×10^{10}	~ 17000	5×10^{14}
nanorod	~ 8×10^{10}	~ 10400	8×10^{14}
nanosphere	~ 3×10^{9}	~ 71000	2×10^{14}

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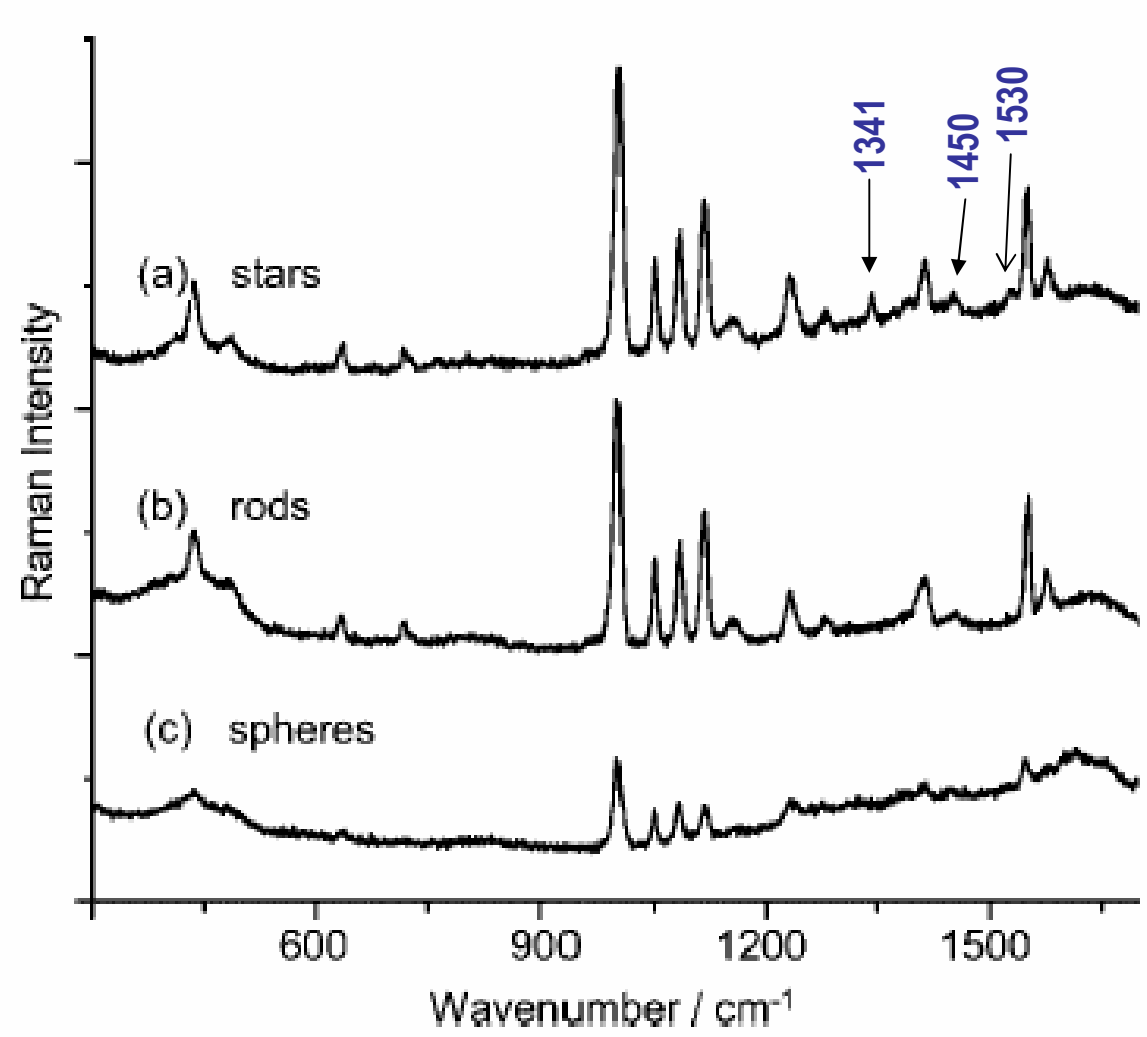
γ (CH) at 1341 cm−1
ν(C=C/C=N) at 1530 cm−1
ν(C=C/C=N) at 1450 cm−1



SERS spectra comparison of 2-MPy adsorbed on Au
(a) Nanostars (*ca* 140 nm),
(b) Nanorods (*ca* 65 nm × 30 nm (length × width)), and
(c) Nanospheres (*ca* 150 nm).
Traces are offset for clarity.

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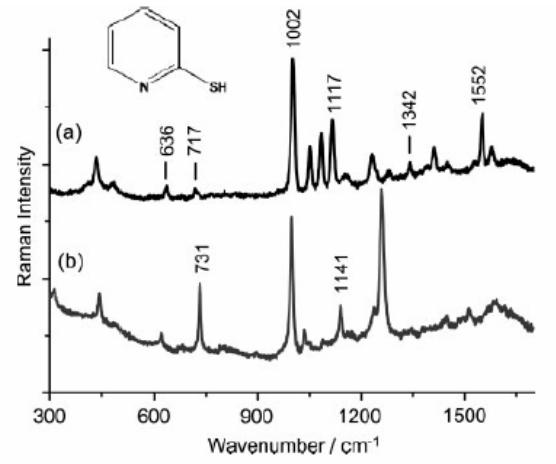
Calculation of Enhancement Factor for aggregated nanostar (2-MPy)

$$EF = \frac{[I_{SERS\ of\ Nanostar}]\ [M_{bulk}]}{[I_{Raman}]\ [M_{ads.}]}$$

$[M_{bulk}] = 0.1$ M
$[M_{ads.}] = 1 \times 10^{-6}$ M

$EF_{nanostar}$ = ~10^5 times higher than Bulk raman spectra



No. of Nanostar ~ 3×10^{10} / mL

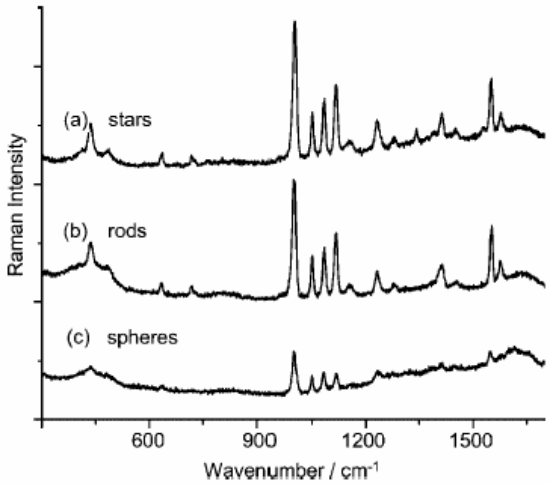
$$EF = \frac{[I_{SERS\ of\ Spherical\ NP}]\ [M_{bulk}]}{[I_{Raman}]\ [M_{ads.}]}$$

$[M_{bulk}] = 0.1$ M
$[M_{ads.}] = 5 \times 10^{-7}$ M

$EF_{sp\ NP}$ = ~4×10^4 times higher than Bulk raman spectra

$EF_{nanostar}$ = ~4 times higher than $EF_{sp\ NP}$ = ~2×10^5

$EF_{nanostar}$ = ~ $EF_{nanorod}$



No. of spherical NP ~ 3×10^9 / mL

Area required for each 2-MPy ~ 0.18 nm^2

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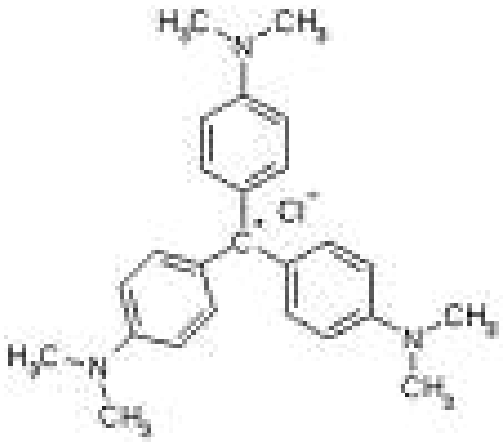
Surface-enhanced Raman scattering- analyte II



crystal violet (CV)

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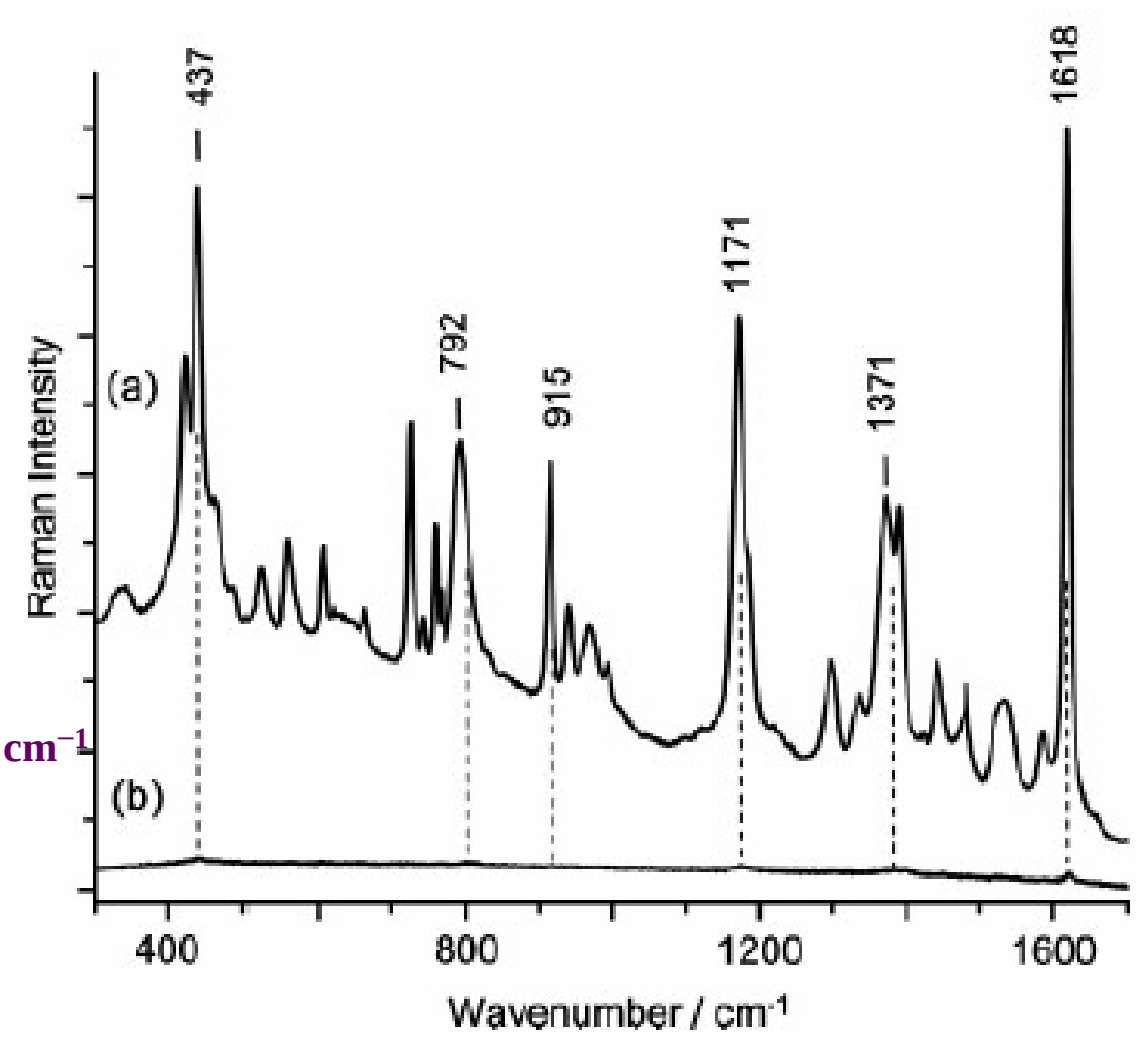
C+ – ph vib. up to 450 cm^{-1}

N–ph str. between 1350 and 1400 cm^{-1}

ph rings ske. ring vib. and ring C–H deform. between 400 and 1300 cm^{-1}
ring str. above 1400 cm^{-1}

C+ – ph bending at 336 cm^{-1}
ring C–H bending at 792 & 1171 cm^{-1}
ring ske.vib. of radical orientation at 915 cm^{-1}
N–phenyl stretching at 1371 & 1391 cm^{-1}
ring C–C stretching at 1531 & 1618 cm^{-1}



(a) SERS spectra of 0.1 μM CV on Au nanostars and (b) Raman spectra of 1 mMCV. Traces are offset for clarity. Vertical lines mark positions of some characteristic vibrational bands of CV.

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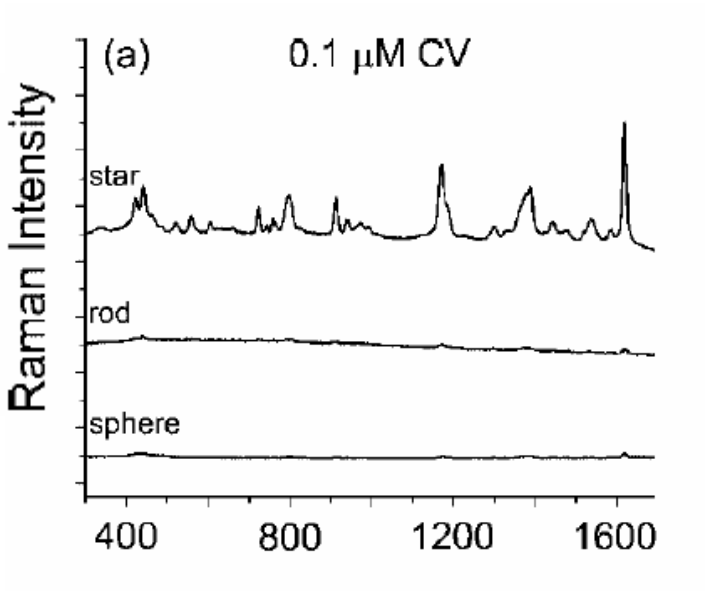

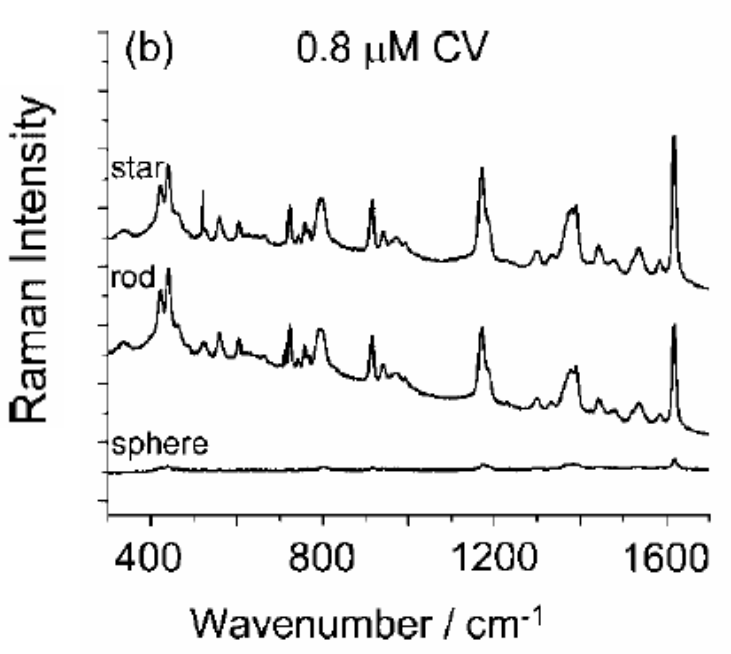

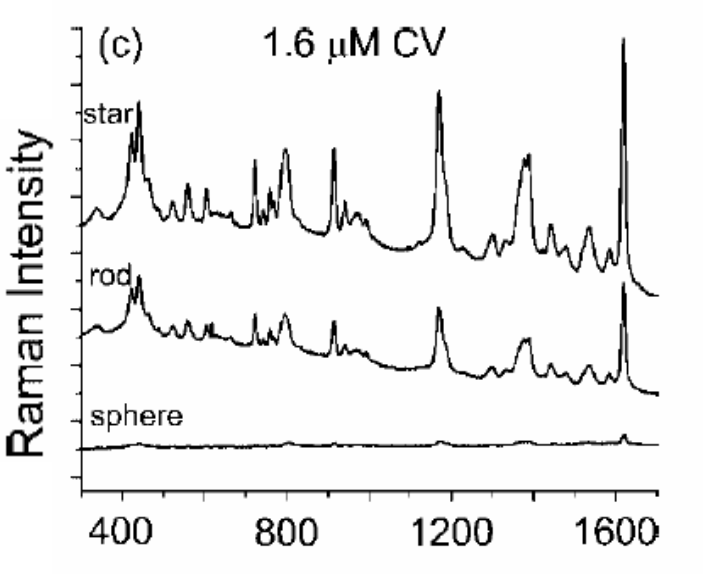

Comparison of SERS activity of Au NPs:
nanostars, nanorods, nanospheres

The intensity scale of all three images is equivalent and the traces are offset for clarity.

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Calculation of Enhancement Factor for aggregated nanostar (CV)

$$EF = \frac{[I_{SERS\ of\ Nanostar}]\ [M_{bulk}]}{[I_{Raman}]\ [M_{ads.}]}$$

$[M_{bulk}]$ = 1 m M
$[M_{ads.}]$ = 0.1×10^{-6} M

$EF_{nanostar}$ = ~ 5×10^5 times higher than Bulk raman spectra

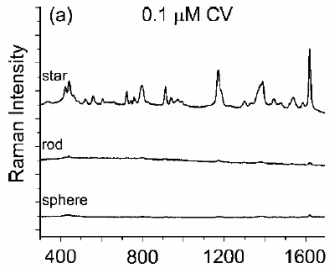
$EF_{nanorod}$ = ~ 1×10^4 times higher than Bulk raman spectra

$EF_{sp\ NP}$ = ~ 8×10^3 times higher than Bulk raman spectra

No. of Nanostar ~ 3×10^{10} / mL

$$EF = \frac{[I_{SERS\ of\ Spherical\ NP}]\ [M_{bulk}]}{[I_{Raman}]\ [M_{ads.}]}$$

$[M_{bulk}]$ = 1 m M
$[M_{ads.}]$ = 5×10^{-7} M and 5×10^{-8} M



$EF_{sp\ NP}$ = ~4×10^3 times higher than Bulk (Perpendicular)
&
= ~ 4×10^4 times higher than bulk (Parallel)

$EF_{nanorod}$ = ~5×10^4 times higher than Bulk (Perpendicular)
&
= ~ 5×10^5 times higher than bulk (Parallel)

$EF_{Nanostar}$ = ~1×10^5 times higher than Bulk (Perpendicular)
&
= ~ 1×10^6 times higher than bulk (Parallel)

No. of spherical NP ~ 3×10^9 / mL

Area required for each CV ~ 0.4 and 4 nm^2

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Conclusion

The Raman enhancement by nanostars and nanorods was similar for 2-MPy at all studied concentrations of the molecule

the Raman enhancement was significantly higher for nanostars compared to nanorods for CV

With nanostars, most of the CV modes were detectable even at lower CV concentrations such as at 1 nM.

Certain modes were not at all detectable at 100 nM of CV concentration in the nanosphere or nanorod solutions.

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The number of molecules adsorbed either on ‘hot spots’ or on the rest of the NP surface is not known.

The use of different surfactants to stabilize the NPs, may produce differences in surface chemistries, and also in NP concentrations in solutions.

Accurate concentration and surface area of nanostars is not known, because of their nonuniform 3D structure

NP concentration, shape, and aggregation state differences

Thank you

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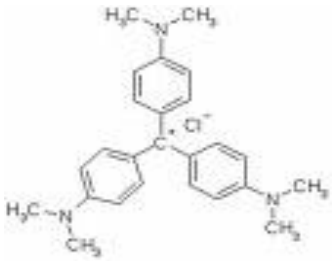

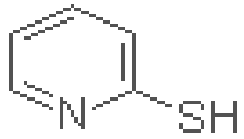

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- Results from an increased field at the metallic NP surface.
- Results from surface plasmons, or collective oscillations of the metal electrons.
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- Detection of Metal ions (As)
- Detection of molecules at very low conc. (At nM and μM)

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- 0.032ml of 0.1M Ascorbic acid
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C. L. Nehl, H. Liao, J. H. Hafner, *Nano Lett.* **2006**, *6*, 683.

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Nanorod ~ 65 x 30 nm **UV-VIS absorption spectra @ 550 & 700 nm**

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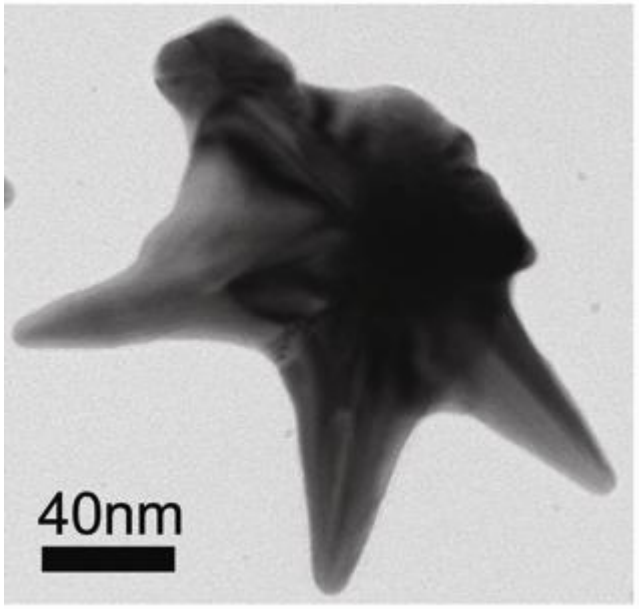

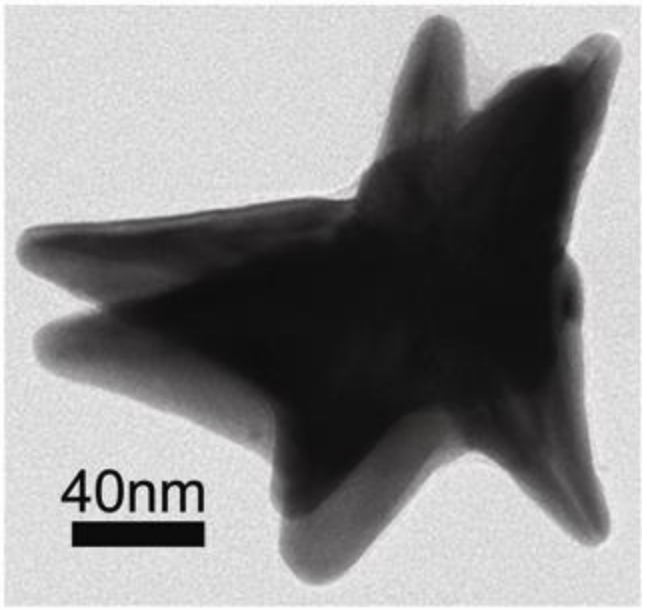

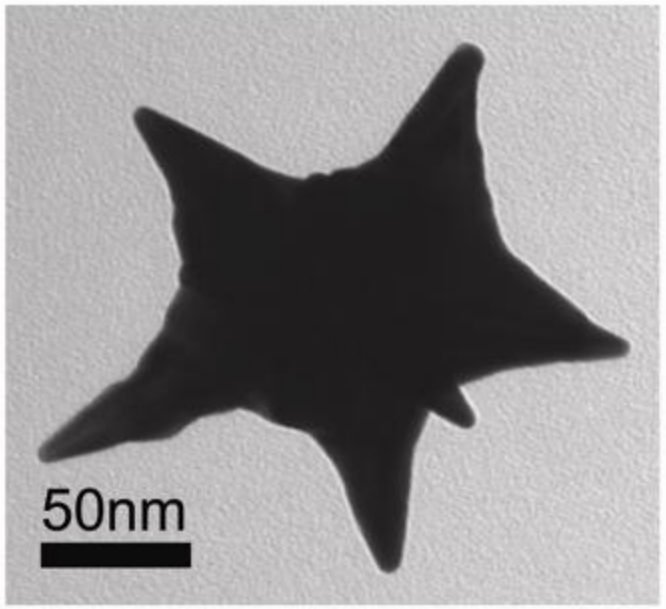

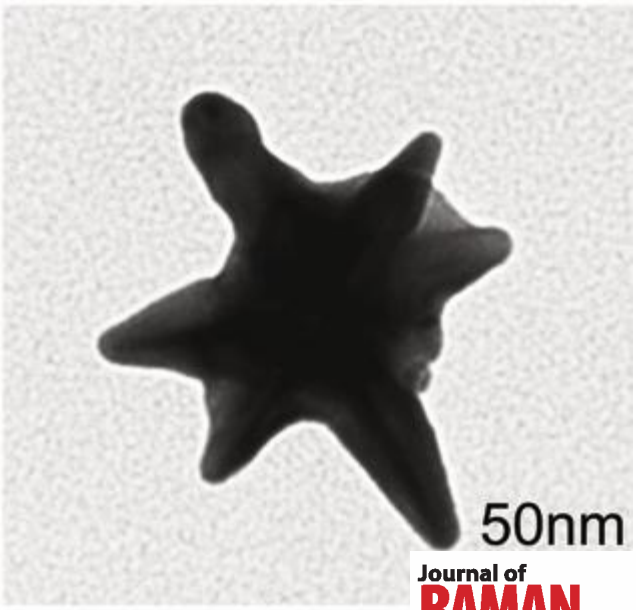

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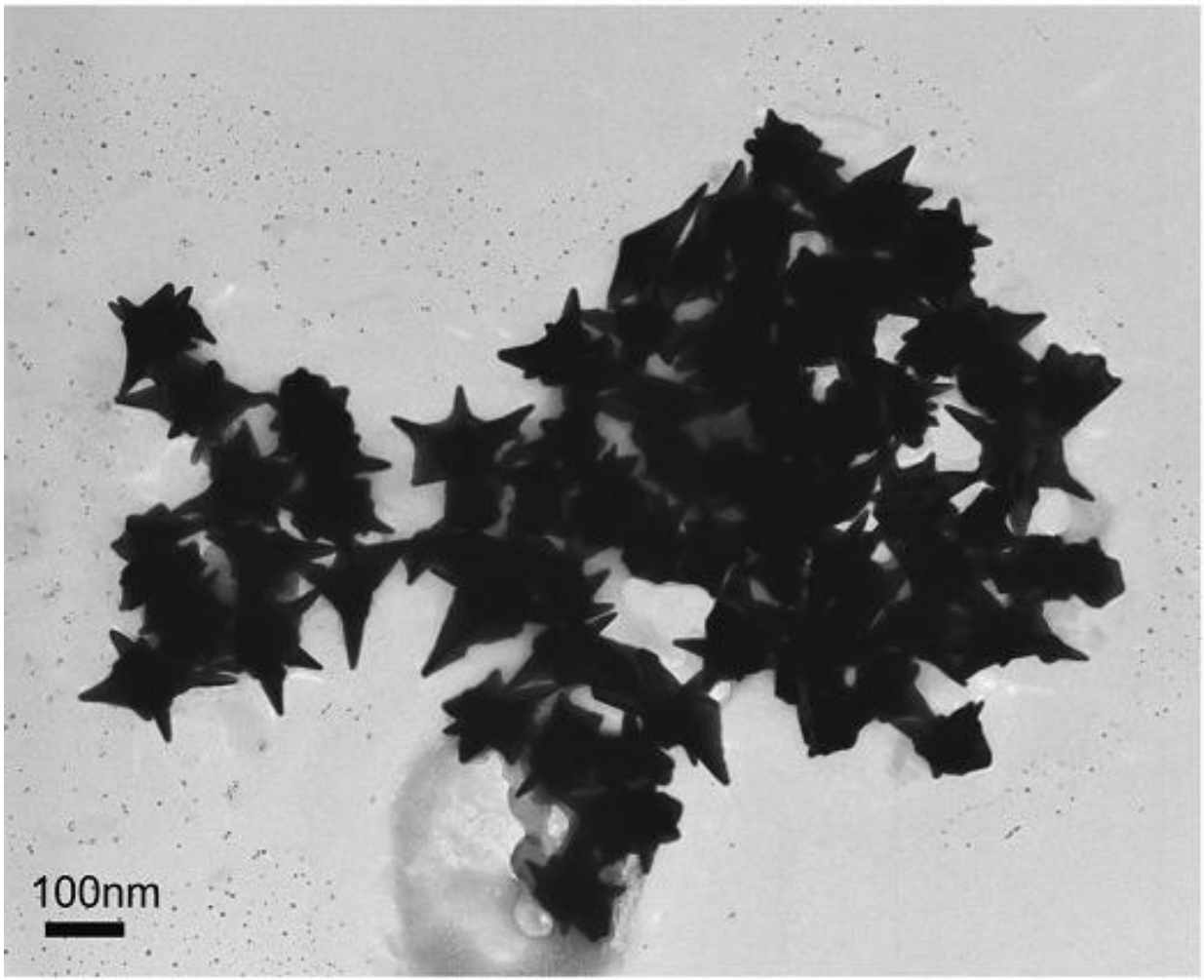

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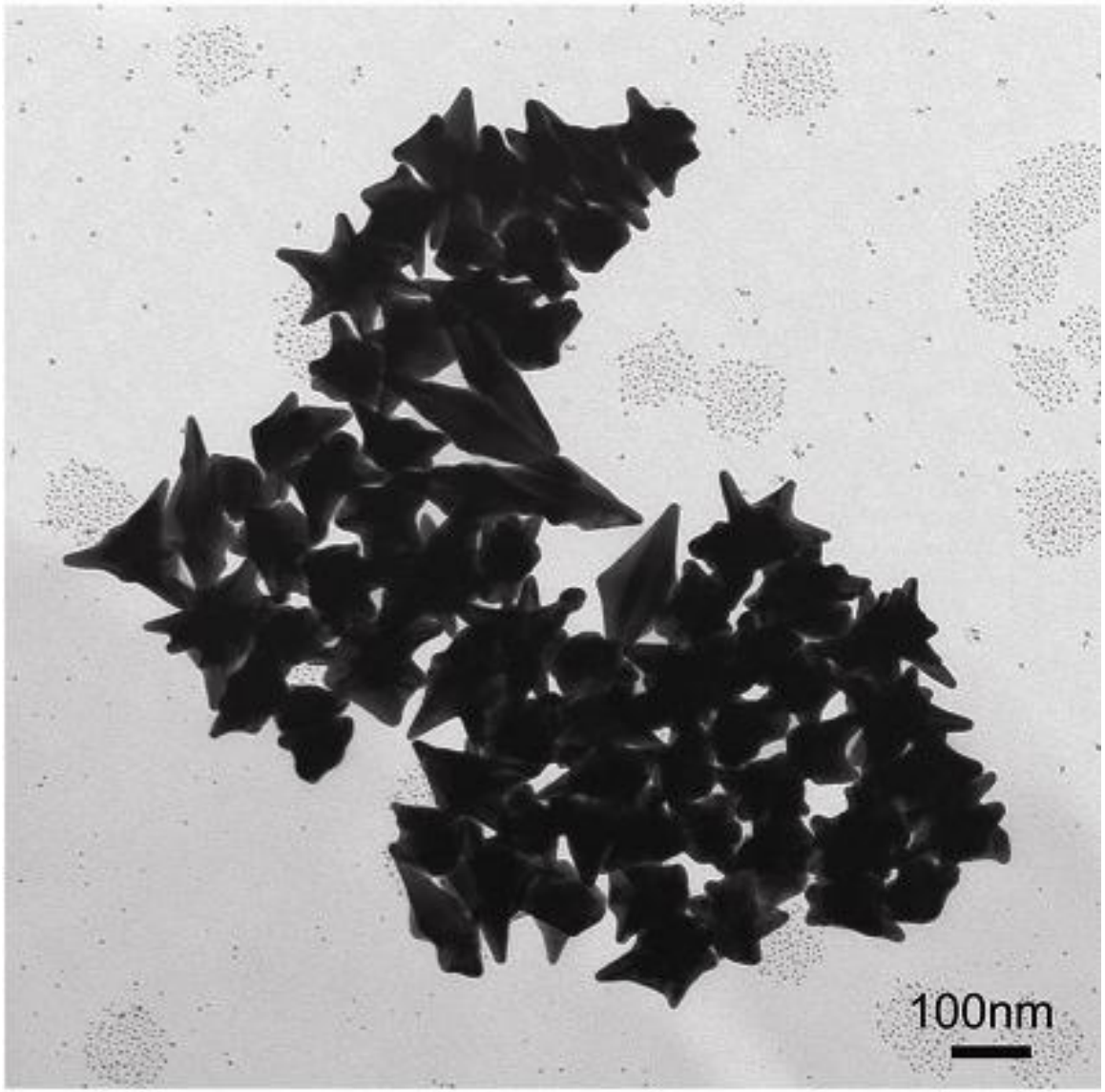

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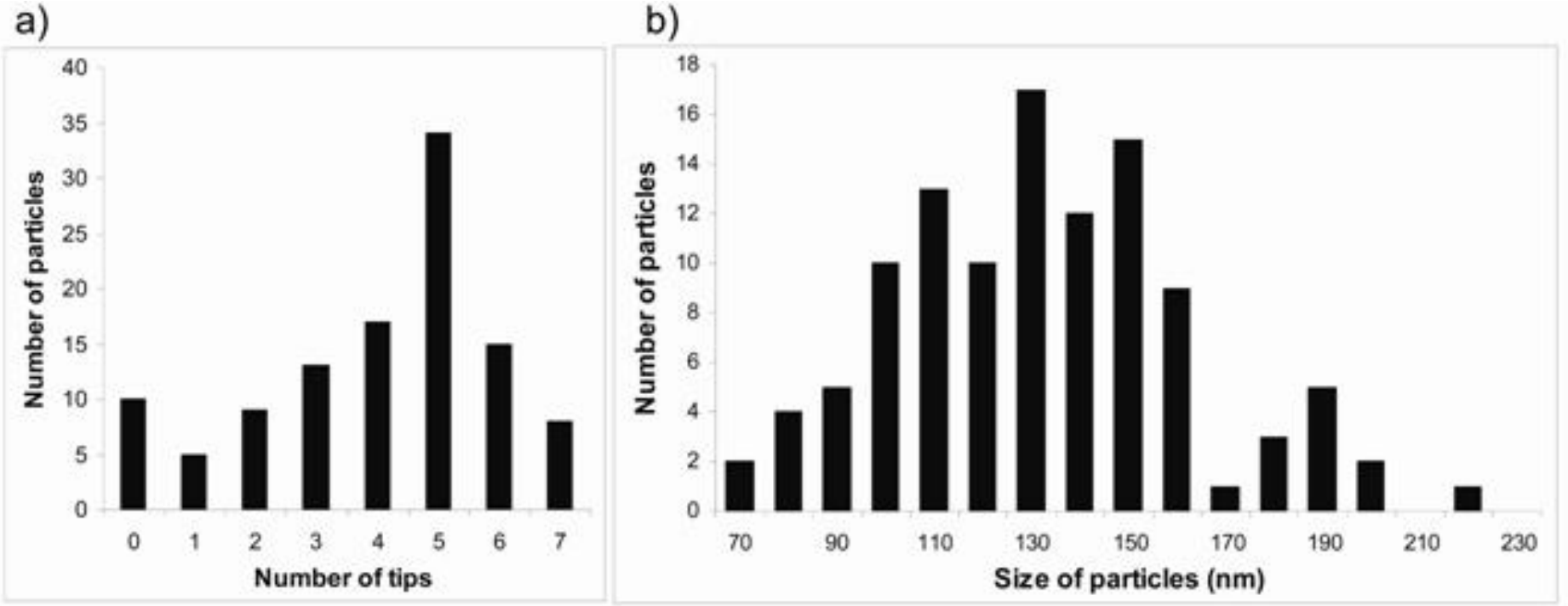

a) Number of tip, and (b) Size distribution of nanostars based on TEM images

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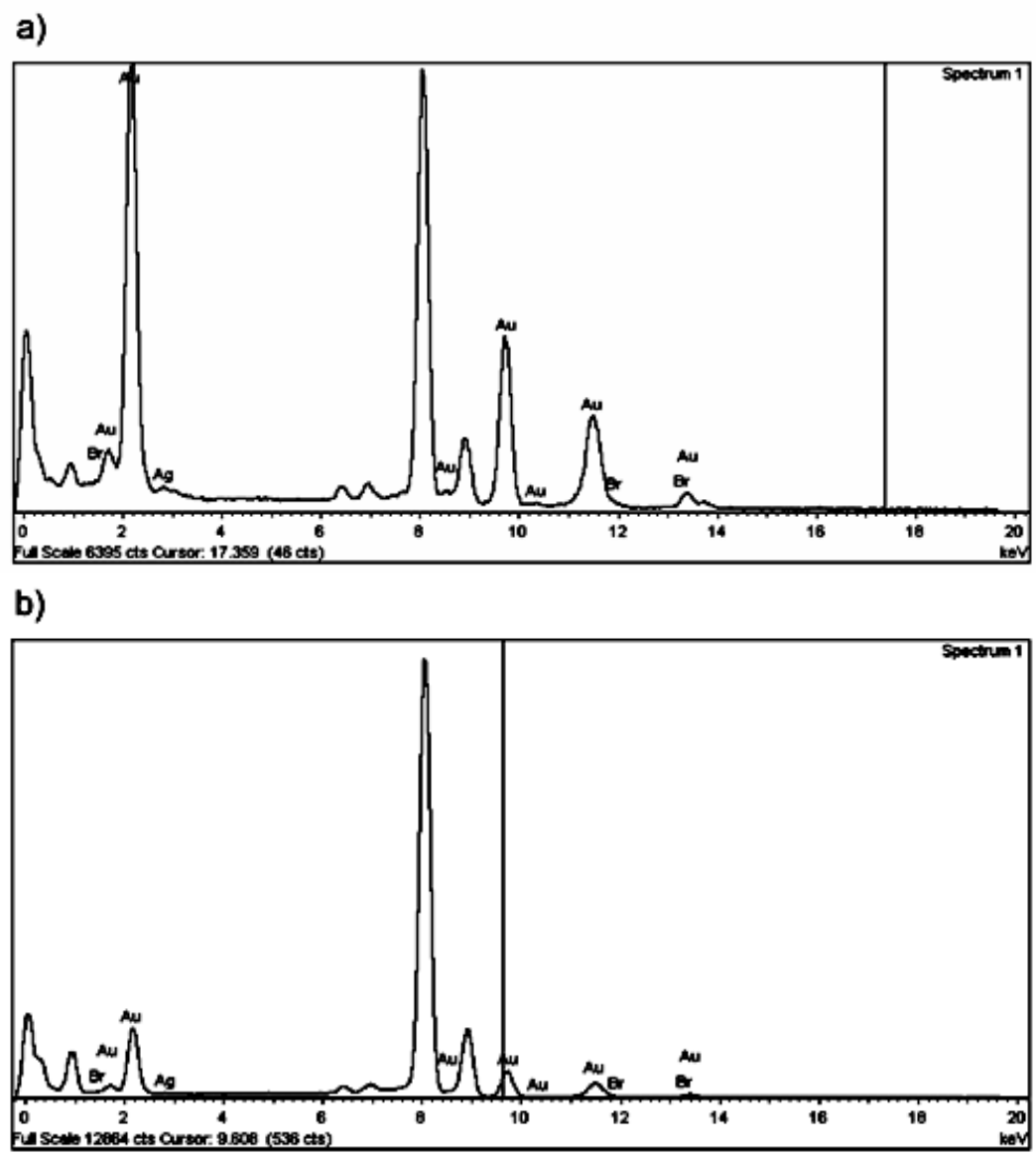

EDX spectra of a) nanostar and b) nanorod particles.
Analysis showed ca. 96% Au, ca. 2% Ag and ca. 2% Br for both type of nanoparticle

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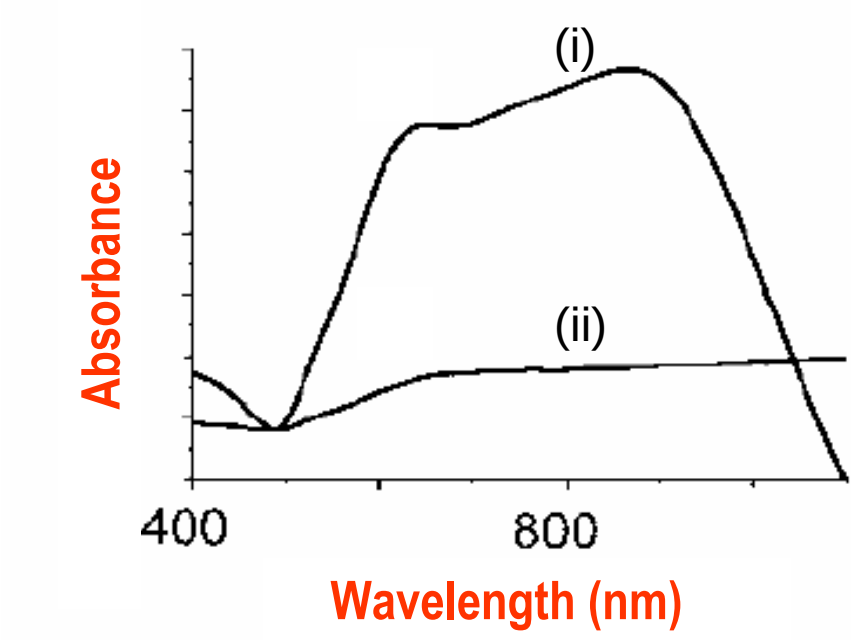

UV–vis spectra of (i) before NaCl addition (only nanostar solution) and (ii) after NaCl addition (50 mM to SERS sample).

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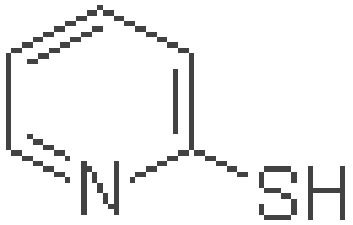
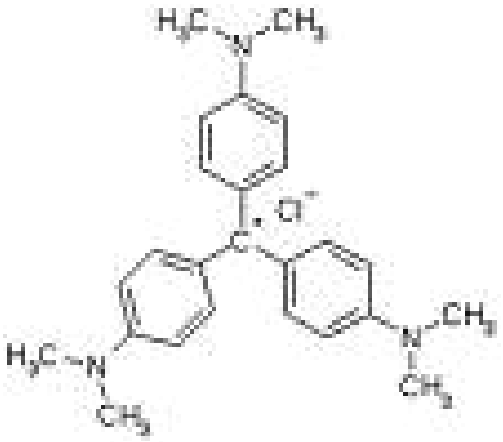
Surface-enhanced Raman scattering analytes



2-mercaptopyridine (2-MPy)



crystal violet (CV)

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Preparation of SERS samples

❖ 1 ml of Au colloid solution

❖ 0.1 ml of aqueous probe molecule (2-MPy or CV) at varying concentrations.

❖ The samples were sonicated for 10 mins prior to the measurements

❖ 1 ml of NaCl solution was added to 1 ml of Au NP solution to induce the aggregation

❖ 10 min of sonication,

❖ 0.1 ml probe molecule solution

❖ sonicated for 10 min before acquiring the SERS spectra.

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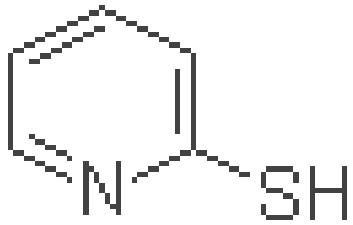
Surface-enhanced Raman scattering - analytes I



2-mercaptopyridine (2-MPy)

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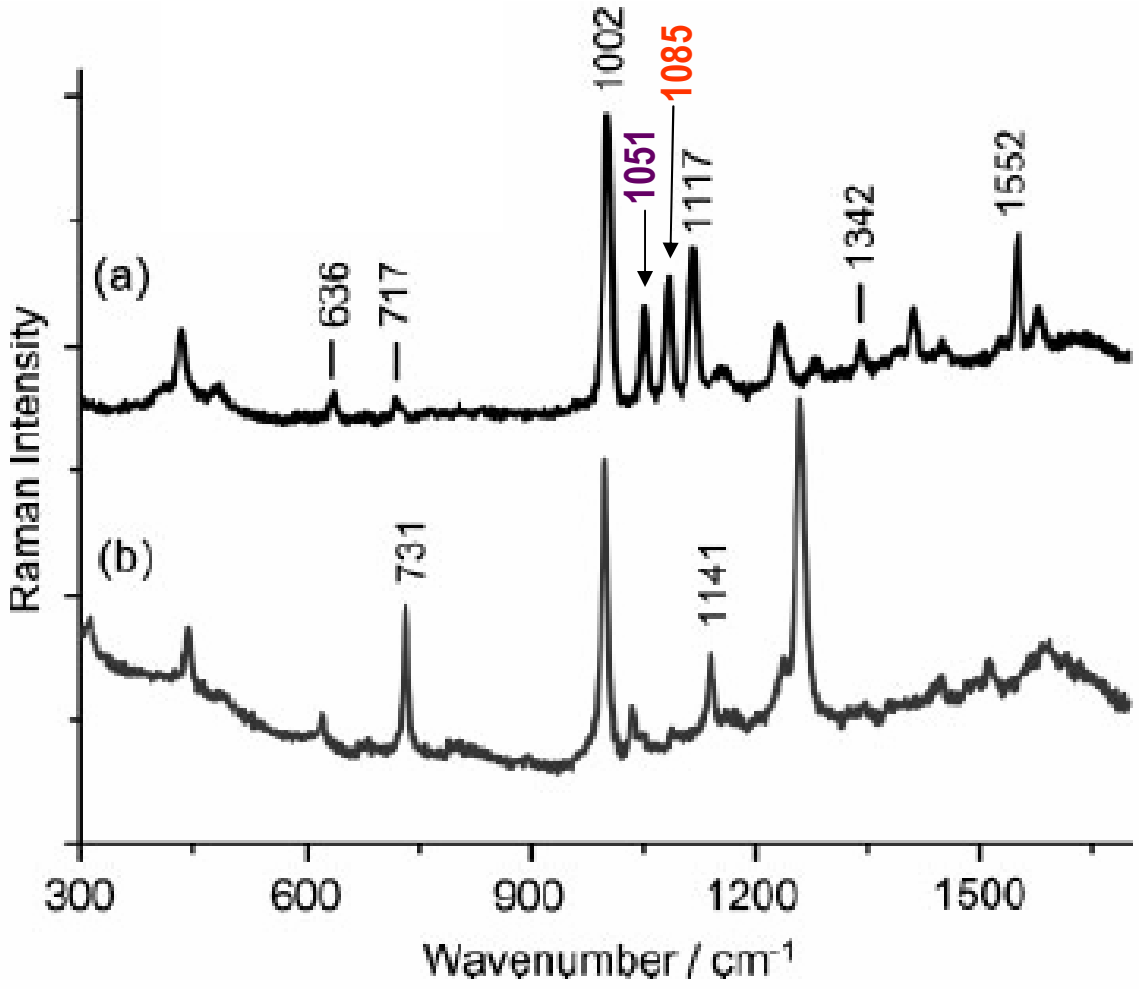
ν(C–S) at 731 cm−1 to 717 cm−1
Ring breathing (RB)/*ν*(C–S) band at 1141 to 1117 cm−1

ν(C C) at 1552 cm−1
ν(C–H) at 1085 cm−1
RB at 1002 cm−1
RB/*ν*(C–S) at 1117 cm−1

γ (CCC) at 636 cm−1
γ (CH) at 1342 cm−1
β(CH) at 1051 cm−1



(a) SERS spectra of 1 μM 2-MPy on Au nanostars
(b) and (b) Raman spectra of 0.1 M 2-MPy.
Traces are offset for clarity.

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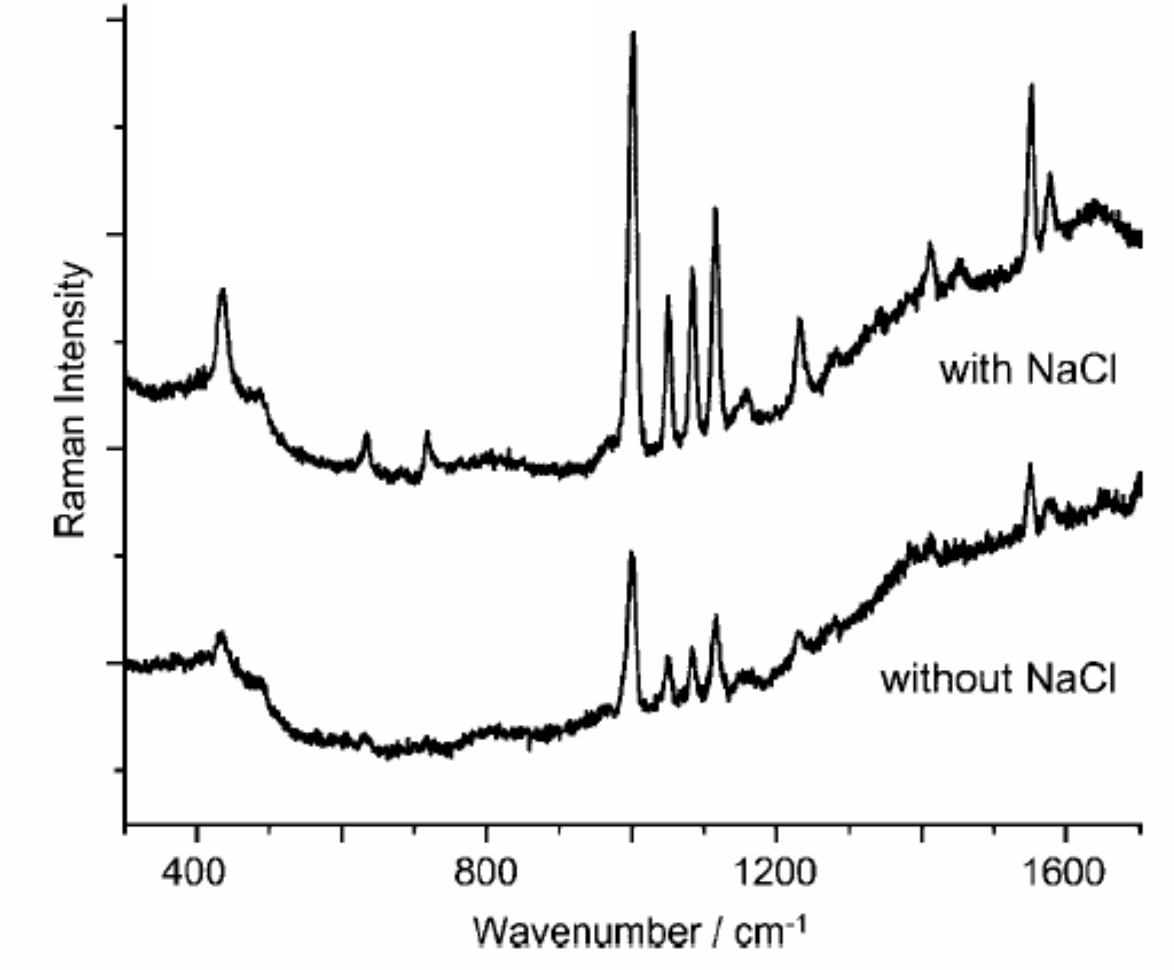

SERS activity of Au nanostars as a function of NaCl addition. 2-MPy concentration was kept constant at 1 μM in SERS sample. Traces are offset for clarity.

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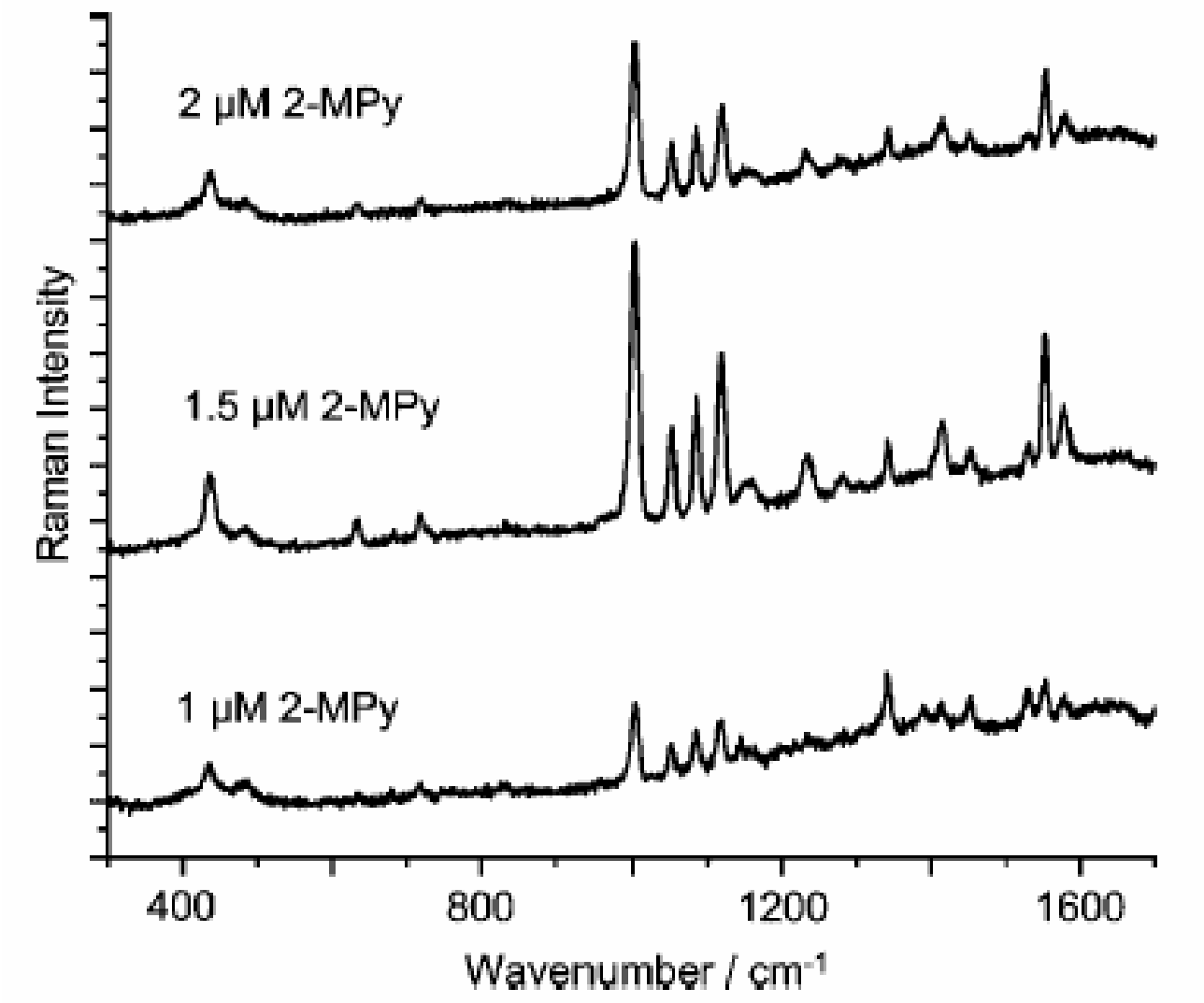

SERS activity of Au nanostars as a function of 2-MPy concentration.
NaCl concentration was kept constant at 50 mM. Traces are offset for clarity.

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Optimizing (equal) NPs concentration

Nanostars (ca. 140 nm), Nanorods (ca. (65 nm x 30 nm)) & Nanospheres (ca. 150 nm)

	# particles / mL (**N**)[1]	Surface area (nm^2) of each nanoparticle (**A**)[2]	Total surface area of nanoparticle / mL (= **N** x **A**)
nanostar*	~ 3×10^{10}	~ 17000	5×10^{14}
nanorod	~ 8×10^{10}	~ 10400	8×10^{14}
nanosphere	~ 3×10^{9}	~ 71000	2×10^{14}

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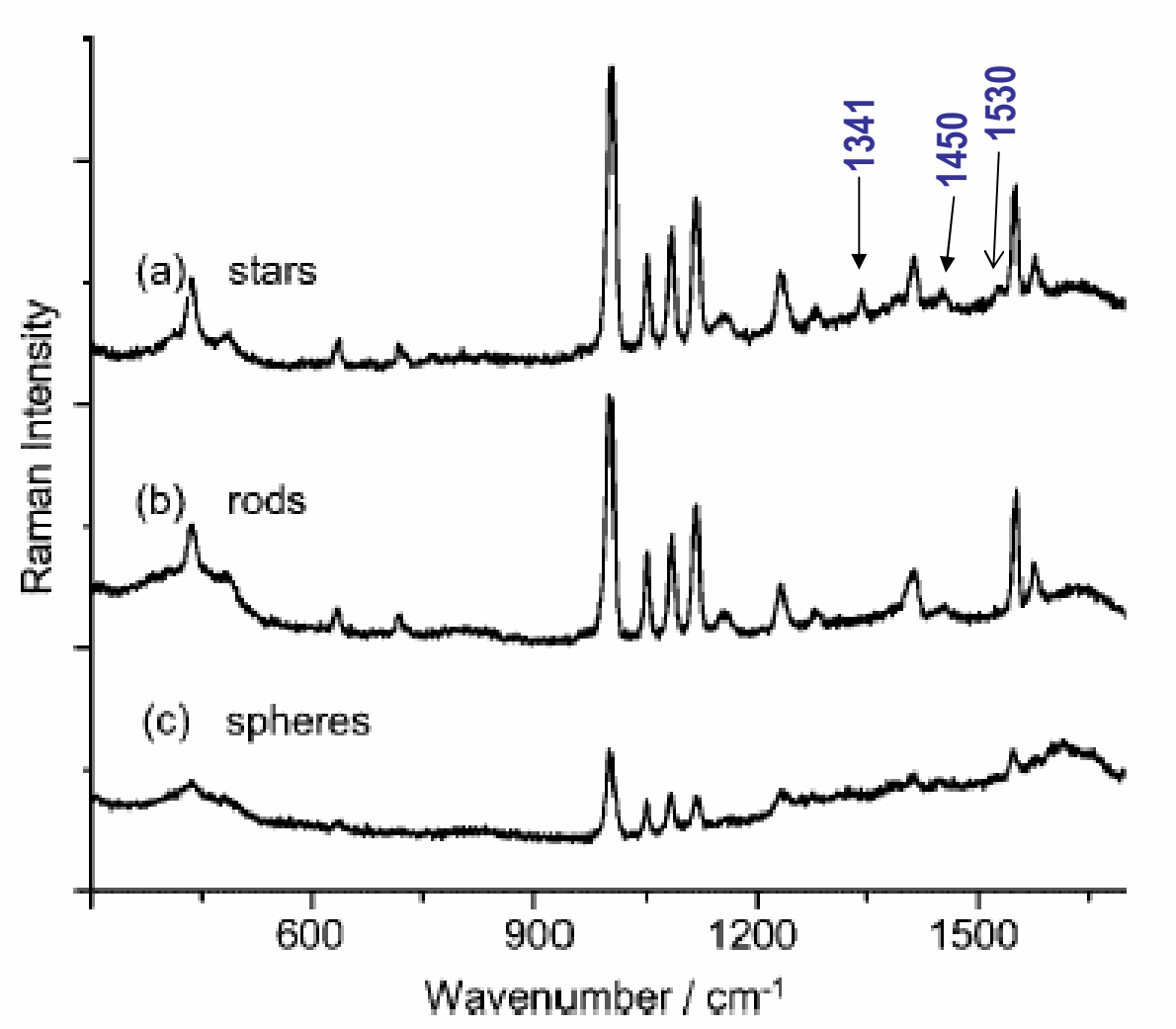
γ (CH) at 1341 cm−1
ν(C=C/C=N) at 1530 cm−1
ν(C=C/C=N) at 1450 cm−1



SERS spectra comparison of 2-MPy adsorbed on Au
(a) Nanostars (*ca* 140 nm),
(b) Nanorods (*ca* 65 nm × 30 nm (length × width)), and
(c) Nanospheres (*ca* 150 nm).
Traces are offset for clarity.

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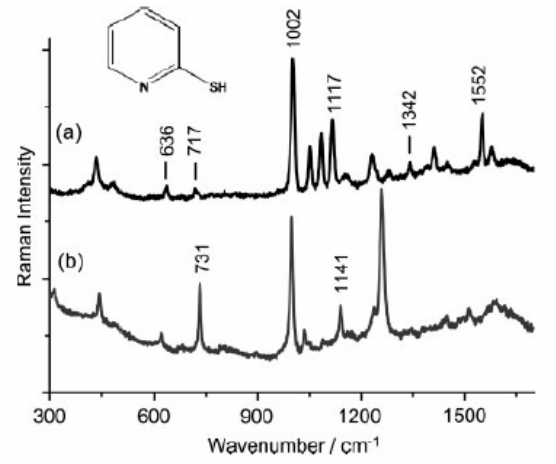
Calculation of Enhancement Factor for aggregated nanostar (2-MPy)

$$EF = \frac{[I_{SERS\ of\ Nanostar}]\ [M_{bulk}]}{[I_{Raman}]\ [M_{ads.}]}$$

$[M_{bulk}] = 0.1$ M
$[M_{ads.}] = 1 \times 10^{-6}$ M

$EF_{nanostar}$ = ~10^5 times higher than Bulk raman spectra



No. of Nanostar ~ 3×10^{10} / mL

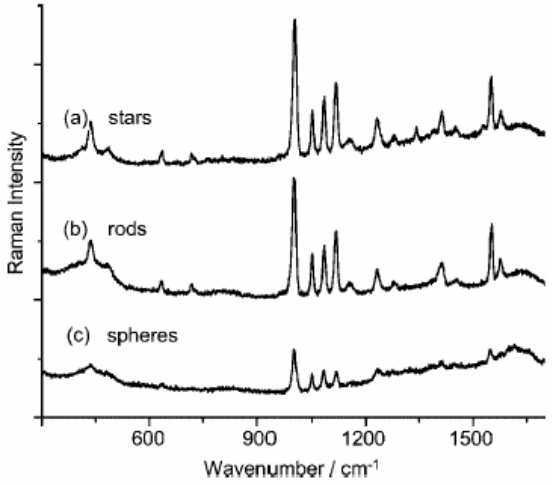
$$EF = \frac{[I_{SERS\ of\ Spherical\ NP}]\ [M_{bulk}]}{[I_{Raman}]\ [M_{ads.}]}$$

$[M_{bulk}] = 0.1$ M
$[M_{ads.}] = 5 \times 10^{-7}$ M

$EF_{sp\ NP}$ = ~4×10^4 times higher than Bulk raman spectra

$EF_{nanostar}$ = ~4 times higher than $EF_{sp\ NP}$ = ~2×10^5

$EF_{nanostar}$ = ~ $EF_{nanorod}$



No. of spherical NP ~ 3×10^9 / mL

Area required for each 2-MPy ~ 0.18 nm^2

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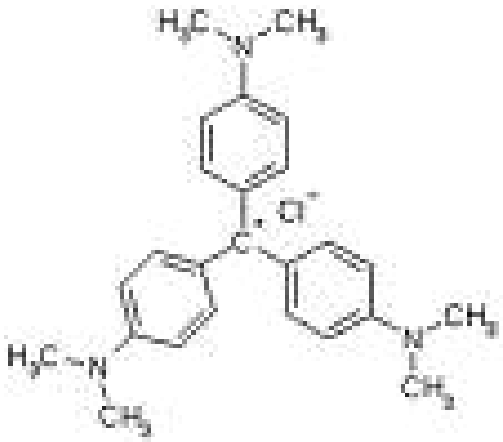
Surface-enhanced Raman scattering- analyte II



crystal violet (CV)

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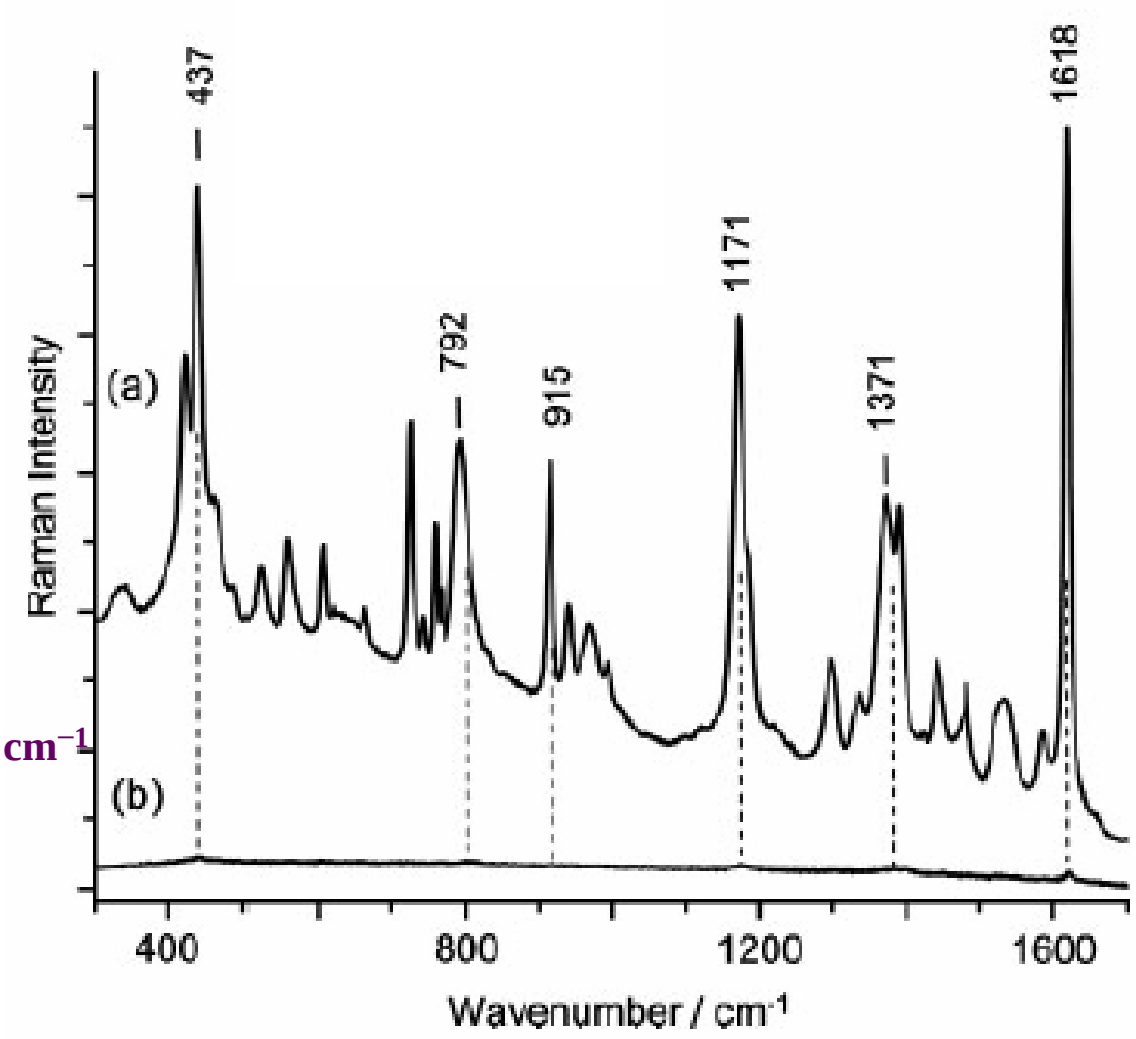
C+ – ph vib. up to 450 cm^{-1}

N–ph str. between 1350 and 1400 cm^{-1}

ph rings ske. ring vib. and ring C–H deform. between 400 and 1300 cm^{-1}
ring str. above 1400 cm^{-1}

C+ – ph bending at 336 cm^{-1}
ring C–H bending at 792 & 1171 cm^{-1}
ring ske.vib. of radical orientation at 915 cm^{-1}
N–phenyl stretching at 1371 & 1391 cm^{-1}
ring C–C stretching at 1531 & 1618 cm^{-1}



(a) SERS spectra of 0.1 μM CV on Au nanostars and (b) Raman spectra of 1 mMCV. Traces are offset for clarity. Vertical lines mark positions of some characteristic vibrational bands of CV.

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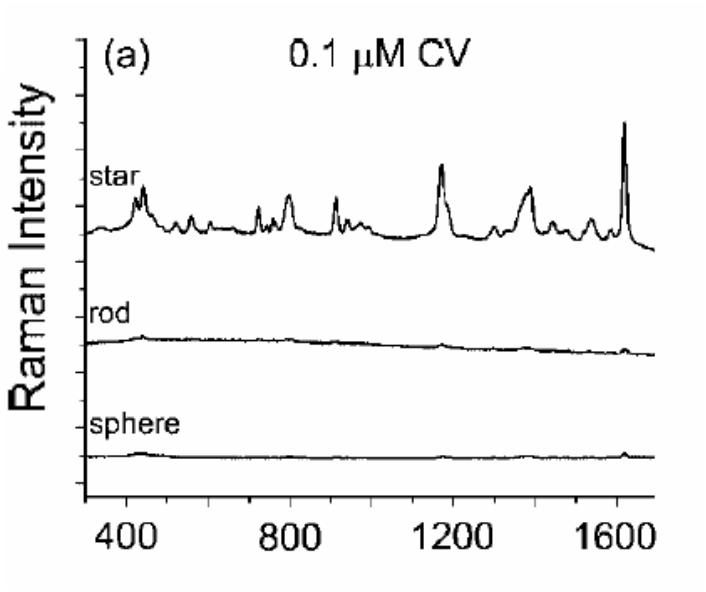

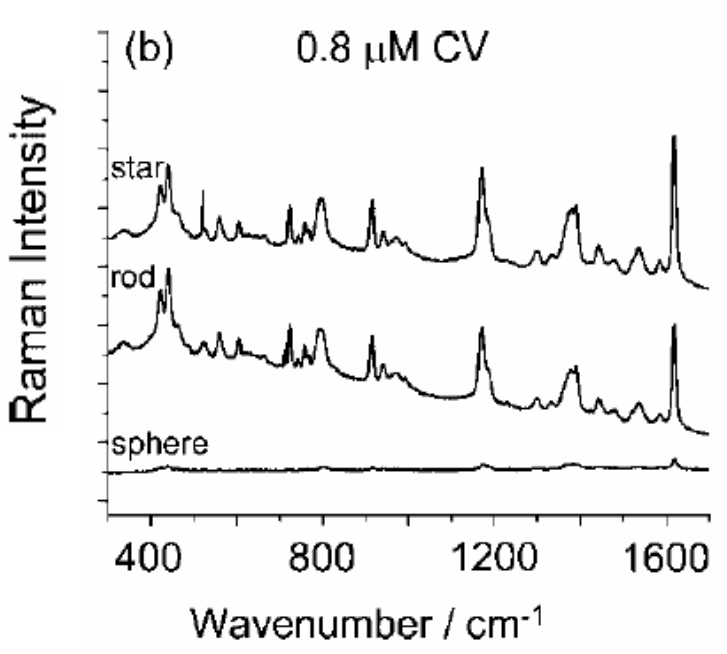

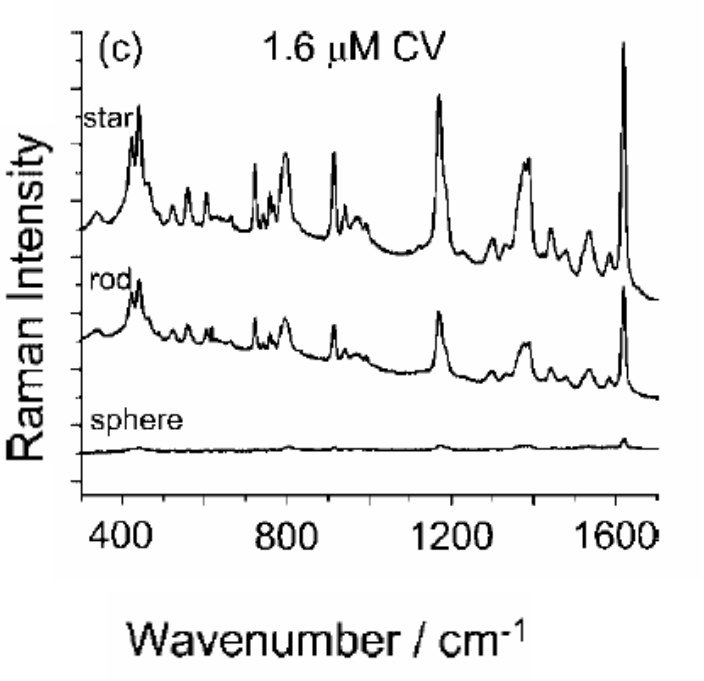

Comparison of SERS activity of Au NPs:
nanostars, nanorods, nanospheres

The intensity scale of all three images is equivalent and the traces are offset for clarity.

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Calculation of Enhancement Factor for aggregated nanostar (CV)

$$EF = \frac{[I_{SERS\ of\ Nanostar}]\ [M_{bulk}]}{[I_{Raman}]\ [M_{ads.}]}$$

$[M_{bulk}]$ = 1 m M
$[M_{ads.}]$ = 0.1 x 10^{-6} M

$EF_{nanostar}$ = ~ 5x 10^5 times higher than Bulk raman spectra

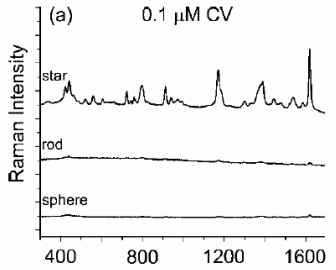
$EF_{nanorod}$ = ~ 1x 10^4 times higher than Bulk raman spectra

$EF_{sp\ NP}$ = ~ 8x 10^3 times higher than Bulk raman spectra

No. of Nanostar ~ 3 x 10^{10} / mL

$$EF = \frac{[I_{SERS\ of\ Spherical\ NP}]\ [M_{bulk}]}{[I_{Raman}]\ [M_{ads.}]}$$

$[M_{bulk}]$ = 1 m M
$[M_{ads.}]$ = 5 x 10^{-7} M and 5 x 10^{-8} M



$EF_{sp\ NP}$ = ~4 x 10^3 times higher than Bulk (Perpendicular)
&
= ~ 4 x 10^4 times higher than bulk (Parallel)

$EF_{nanorod}$ = ~5 x 10^4 times higher than Bulk (Perpendicular)
&
= ~ 5 x 10^5 times higher than bulk (Parallel)

$EF_{Nanostar}$ = ~1 x 10^5 times higher than Bulk (Perpendicular)
&
= ~ 1 x 10^6 times higher than bulk (Parallel)

No. of spherical NP ~ 3 x 10^9 / mL

Area required for each CV ~ 0.4 and 4 nm^2

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Conclusion

The Raman enhancement by nanostars and nanorods was similar for 2-MPy at all studied concentrations of the molecule

the Raman enhancement was significantly higher for nanostars compared to nanorods for CV

With nanostars, most of the CV modes were detectable even at lower CV concentrations such as at 1 nM.

Certain modes were not at all detectable at 100 nM of CV concentration in the nanosphere or nanorod solutions.

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The number of molecules adsorbed either on ‘hot spots’ or on the rest of the NP surface is not known.

The use of different surfactants to stabilize the NPs, may produce differences in surface chemistries, and also in NP concentrations in solutions.

Accurate concentration and surface area of nanostars is not known, because of their nonuniform 3D structure

NP concentration, shape, and aggregation state differences

Thank you

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