Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information for:

Bimetallic Gold Core - Silver Shell Nanorods Performance for Surface Enhanced Raman Spectroscopy

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1- XPS data[S1]

A Thermo Scientific Model K-Alpha x-ray photoelectron spectroscopy (XPS) instrument (Thermo Scientific LLC, Madison, WI) using monochromatic Al Kα radiation (1486.7 eV) generated XPS data for the assessment of the silver layer formation and chemical composition for four classes of AuNR/Ag. The spot sizes of x-ray used in this study were 200 or 400 μm. The electrons emitted from the sample surfaces were analyzed with a 128 multi-channel hemispherical electron energy analyzer. The analyzer pass energies for survey spectra and high-resolution (narrow scan) spectra were set to 200 eV and 50 eV, respectively. The base vacuum pressure maintained in the analysis chamber was typically $\sim 1\times10^{-9}$ mBar.

Several drops of the thiolated polyethylene glycol- (HS-PEG) coated samples were dried on glass microscope slides and mounted to the sample platen using copper clips. The food gun, utilizing a combination of low energy electrons and argon ions, was turned on for charge neutralization during all spectra collection, causing the vacuum in the analysis chamber to rise to $\sim 2\times10^{-7}$ mBar during the measurements. The Thermo Scientific Avantage XPS software package® was used to collect and analyze all spectra. All spectra were charge-corrected by shifting the lowest energy C1s peak to the value of 284.8 eV, corresponding to C–C or C–H bonds confirmed by the pure metallic $Au4f_{7/2}$ peak at 84.0 eV. XPS peaks were fitted by mixed Gaussian/Lorentzian peaks after Shirley-Smart background subtraction. In our XPS studies, the binding energies of C1s, $Au4f_{7/2}$, $Ag3d_{5/2}$, O1s, N1s, and $S2p_{3/2}$, were investigated.

XPS data analysis was conducted to analyze the surface chemical compositions of (0, 1, 2, 3,

and 4 nm) silver-coated gold nanorods. Table S1 and Figure S1 reveal that as the silver layer thickness increased, the atomic percentage amount of the silver increased. However, increasing the amount of silver on the outermost layer of the nanorods decreased the signal from the gold core gradually, which confirms the formation and thickness of the silver layer.

Table S1: XPS atomic percentage of elemental chemical composition of the gold nanorod (AuNR\Ag(0)) and four classes of silver-coated gold SERS substrates.

Silver layer thickness (nm)	**Ag atomic % ($Ag3d_{5/2}$)**	**Au atomic % ($Au4f_{7/2}$)**
AuNR\Ag(0)	0	0.54
AuNR\Ag(1)	2.63	3.08
AuNR\Ag(2)	2.61	1.88
AuNR\Ag(3)	3.94	1
AuNR\Ag(4)	8.13	0.42

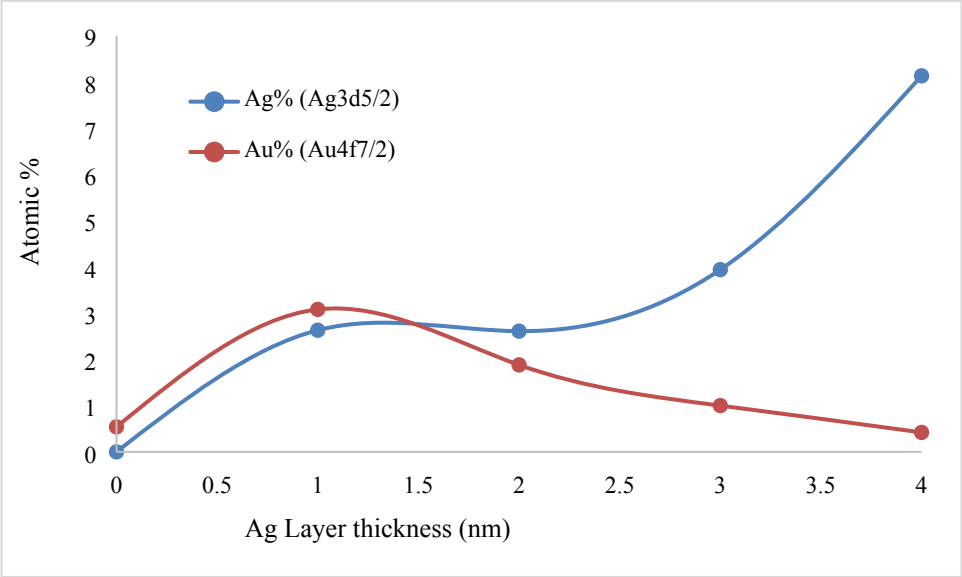


Figure S1: Atomic percentage of silver-coated gold nanorods.

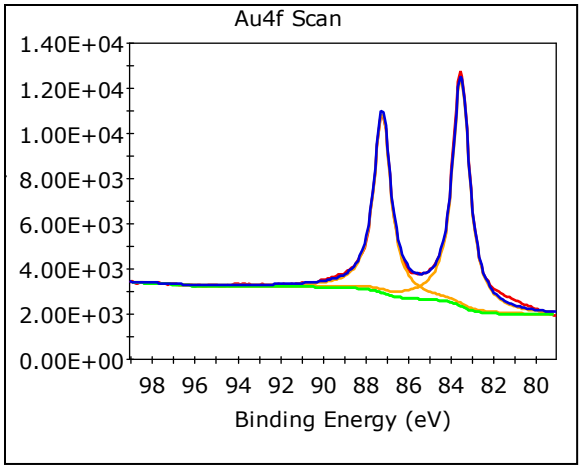


Figure S2 and Figure S2: AuNR\Ag(0) (Ag = 0 nm)

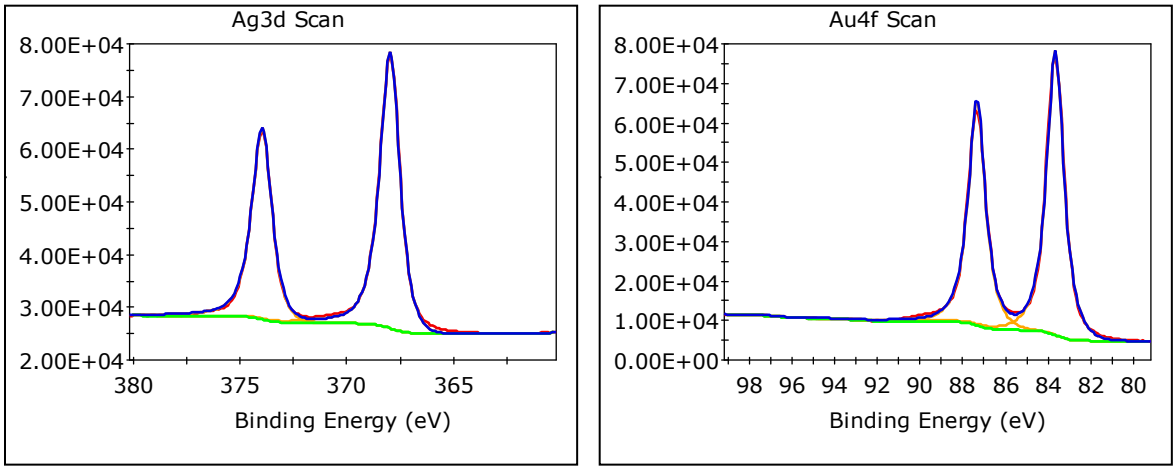


Figure S3 and Figure S3: AuNR\Ag(1) (Ag = 1 nm)

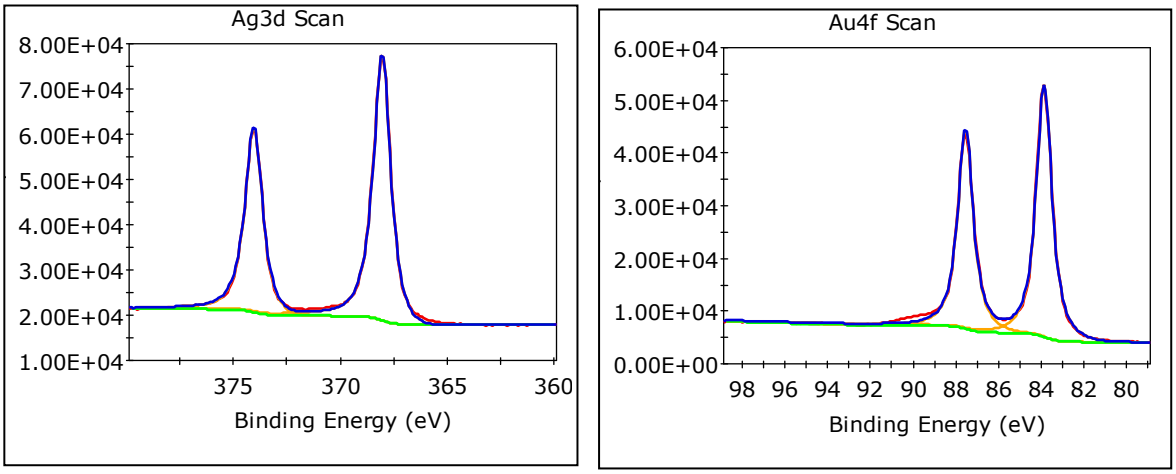


Figure S4 and Figure S4: AuNR\Ag(2) (Ag = 2 nm)

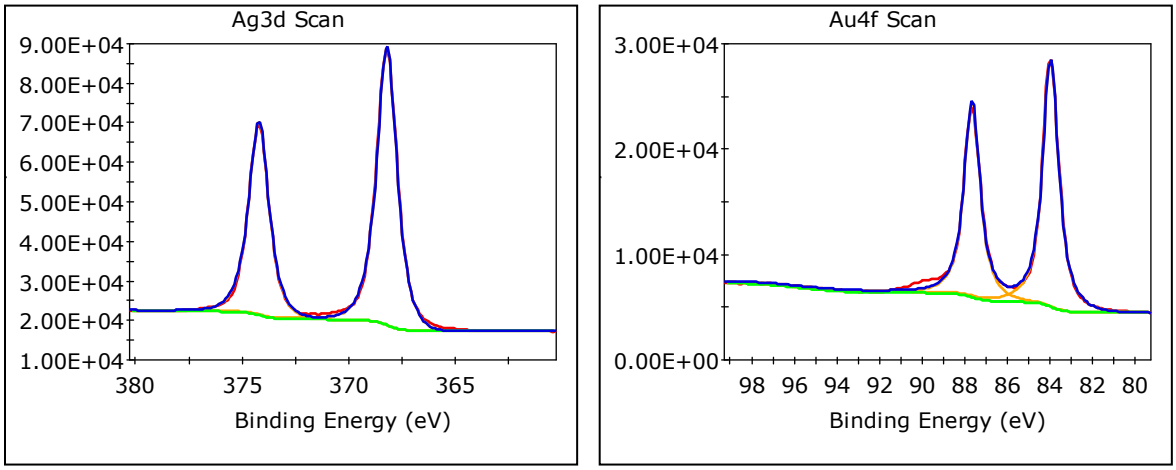


Figure S5 and Figure S5: AuNR\Ag(3) (Ag = 3 nm)

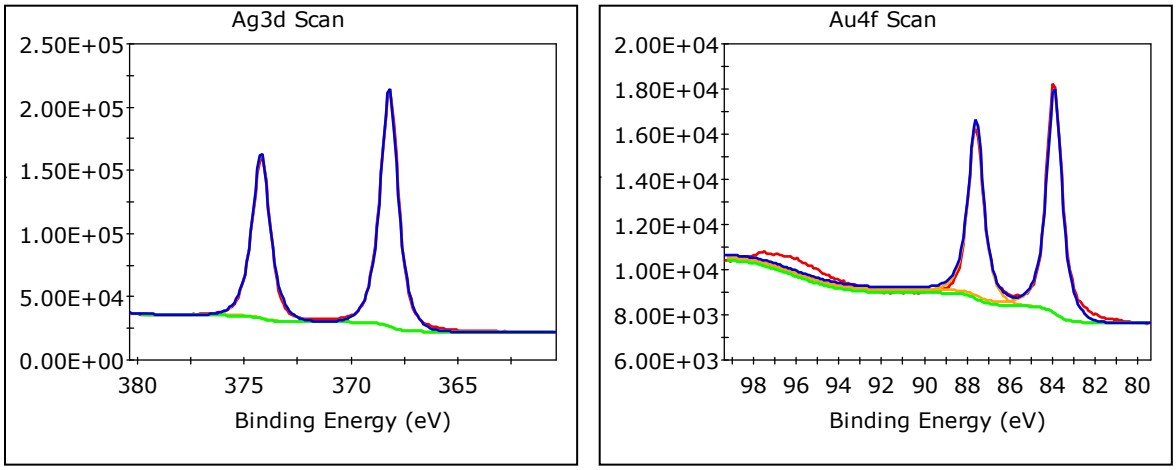


Figure S6 and Figure S6: AuNR\Ag(4) (Ag = 4 nm)

2- Zeta Potential

Zeta potential for the following samples were conducted using ZetaView®, from Electrophoresis and Brownian Motion Video Analysis Laser Scattering Microscopy.

Table S2: Zeta potential analysis of nanorods samples

Sample	**Zeta Potential (mV)**	**Number of traced particles**
AuNR-Ag(0)	-44.69	552
AuNR-Ag(1)	43.55	676
AuNR-Ag(2)	40.59	661
AuNR-Ag(3)	32.28	446
AuNR-Ag(3)	45.94	418
AuNR-Ag(2)-PATP	-28.76	312

Following images are the analysis report for each kind:

1) AuNR-Ag(0)

PARTICLEMETRIX
www.particle-metrix.de

Electrophoresis & Brownian Motion
Video Analysis
Laser Scattering Microscopy

Operator (Report): ZetaView
Video Operator: ZetaView

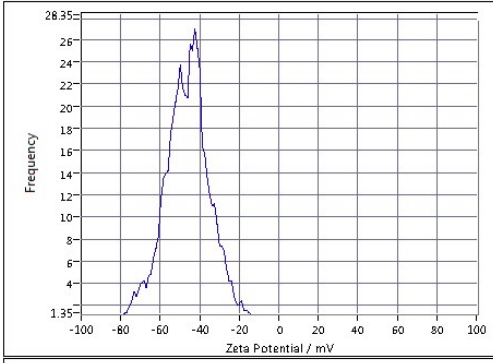
Sample Parameters
Sample Name: \\AuNRx1000
\\AuNR
Comment: sen 89, shutter 40, calib 325000
Electrolyte: PBS, Concentration: 135.000 N
Temperature: 27.01 °C sensed
pH 7.4 entered
Conductivity: 37.81 µS/cm sensed

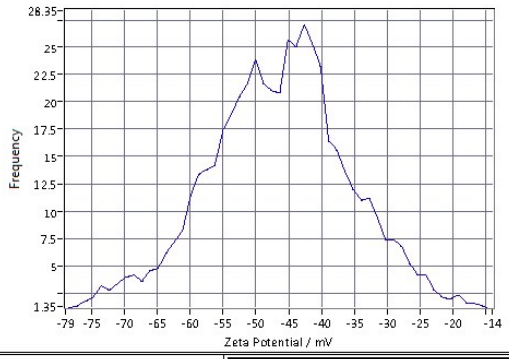
Measurement Parameters
Cell S/N: CA0020_0062b
Sensed Electric Field: 4.18 V/cm
Measurement Mode: Stationary 4 Cycles

Result
Mobility: -3.78 FWHM 1.72 µm/sec/V/cm, @ 25°C: -3.65 µm/sec/V/cm
ZP Factor 12.4 (Smoluchowski):
Zeta Potential @ 25 °C: -46.72 FWHM 12.58 mV
Concentration 31.75E+6 Particles / mL

Quality
Number of Traced Particles: 552
ΔSL: 20.02 mV

Analysis Parameters
Max Size: 702, Min Size: 20, Min Brightness: 30

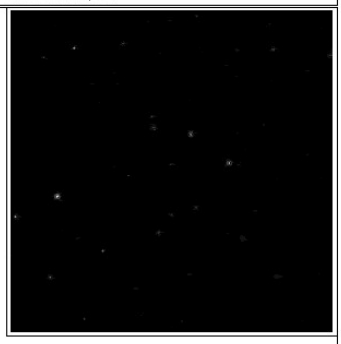




Stationary Layers	Rel. Position
SL1	0.149
SL2	0.851

Peak Analysis (25 °C)

Zeta Potential / mV	Frequency	FWHM / mV	Percentage
-44.6920	25.3960	22.0154	100.0000



Comment

(Signature)

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ZetaVIEW S/N 201, Software ZetaView 8.02.28, Camera 0.703 µm/px

Experiment: 2015-09-11 13:46, Report: 2015-09-11 13:48

2) AuNR-Ag(1)

PARTICLEMETRIX
www.particle-metrix.de

Electrophoresis & Brownian Motion
Video Analysis
Laser Scattering Microscopy

Operator (Report): ZetaView
Video Operator: ZetaView

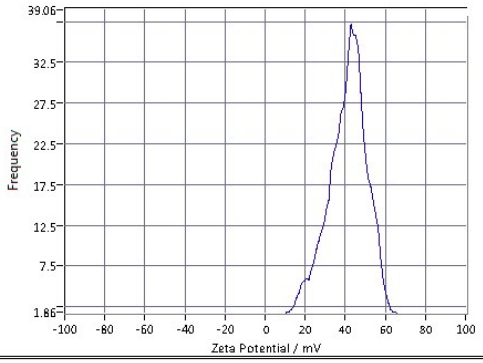
Sample Parameters
Sample Name: \\AuNR-PEG
\\AuNR-Ag-1
Comment: sen 89, shutter 40, calib 325000
Electrolyte: PBS, Concentration: 135.000 N
Temperature: 26.94 °C sensed
pH 7.4 entered
Conductivity: 28.00 µS/cm sensed

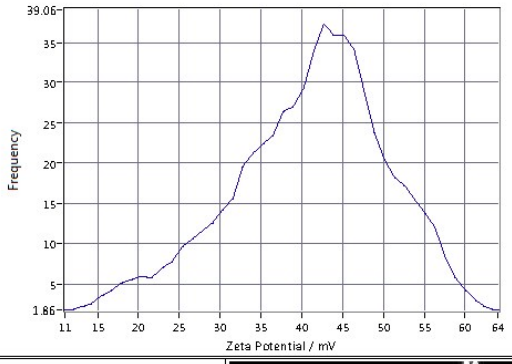
Measurement Parameters
Cell S/N: CA0020_0062b
Sensed Electric Field: 3.77 V/cm
Measurement Mode: Stationary 4 Cycles

Result
Mobility: 3.30 FWHM 1.46 µm/sec/V/cm, @ 25° C: 3.18 µm/sec/V/cm
ZP Factor 12.4 (Smoluchowski):
Zeta Potential @ 25 °C: 40.79 FWHM 12.34 mV
Concentration 30.49E+6 Particles / mL

Quality
Number of Traced Particles: 676
ΔSL: 11.74 mV

Analysis Parameters
Max Size: 702, Min Size: 20, Min Brightness: 30

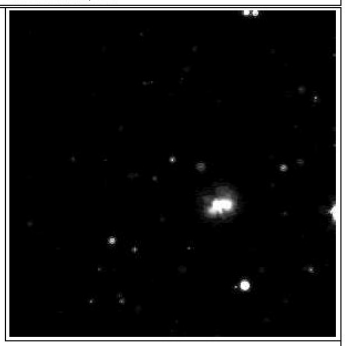




Stationary Layers	Rel. Position
SL1	0.149
SL2	0.851

Peak Analysis (25 °C)

Zeta Potential / mV	Frequency	FWHM / mV	Percentage
43.5469	36.2333	18.6463	100.0000



Comment

(Signature)

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ZetaVIEW S/N 201, Software ZetaView 8.02.28, Camera 0.703 µm/px

Experiment: 2015-09-11 14:26, Report: 2015-09-11 14:28

3) AuNR-Ag(2)

PARTICLEMETRIX
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Electrophoresis & Brownian Motion
Video Analysis
Laser Scattering Microscopy

Operator (Report): ZetaView
Video Operator: ZetaView

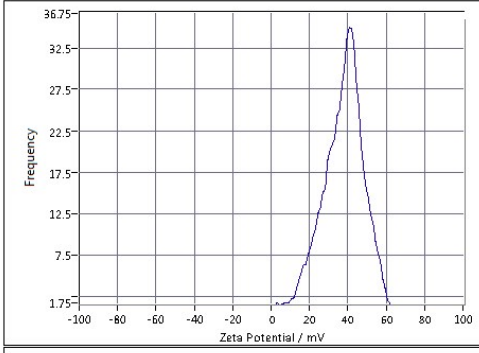
Sample Parameters
Sample Name: \\AuNR-PEG
\\AuNR-Ag-2
Comment: sen 89, shutter 40, calib 325000
Electrolyte: PBS, Concentration: 135.000 N
Temperature: 26.45 °C sensed
pH 7.4 entered
Conductivity: 21.21 µS/cm sensed

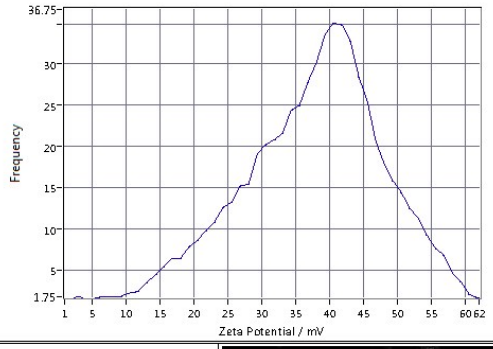
Measurement Parameters
Cell S/N: CA0020_0062b
Sensed Electric Field: 3.71 V/cm
Measurement Mode: Stationary 4 Cycles

Result
Mobility: 3.00 FWHM 1.52 µm/sec/V/cm, @ 25°C: 2.92 µm/sec/V/cm
ZP Factor 12.5 (Smoluchowski):
Zeta Potential @ 25 °C: 37.47 FWHM 12.59 mV
Concentration 33.72E+6 Particles / mL

Quality
Number of Traced Particles: 661
ΔSL: 7.59 mV

Analysis Parameters
Max Size: 702, Min Size: 20, Min Brightness: 30

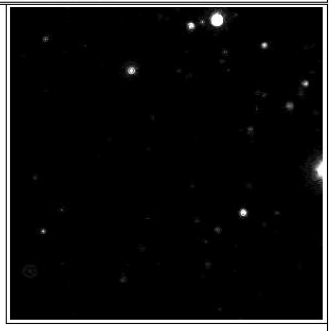




Stationary Layers	Rel. Position
SL1	0.149
SL2	0.851

Peak Analysis (25 °C)

Zeta Potential / mV	Frequency	FWHM / mV	Percentage
40.5931	34.9956	19.4297	100.0000



Comment

(Signature)

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ZetaVIEW S/N 201, Software ZetaView 8.02.28, Camera 0.703 µm/px

Experiment: 2015-09-11 14:54, Report: 2015-09-11 14:56

4) AuNR-Ag(3)

PARTICLEMETRIX
www.particle-metrix.de

Electrophoresis & Brownian Motion
Video Analysis
Laser Scattering Microscopy

Operator (Report): ZetaView
Video Operator: ZetaView

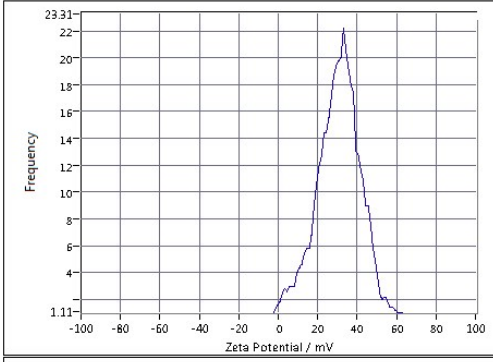
Sample Parameters
Sample Name: \\AuNR-PEG
\\AuNR-Ag-3
Comment: sen 89, shutter 40, calib 325000
Electrolyte: PBS, Concentration: 135.000 N
Temperature: 26.63 °C sensed
pH 7.4 entered
Conductivity: 25.91 µS/cm sensed

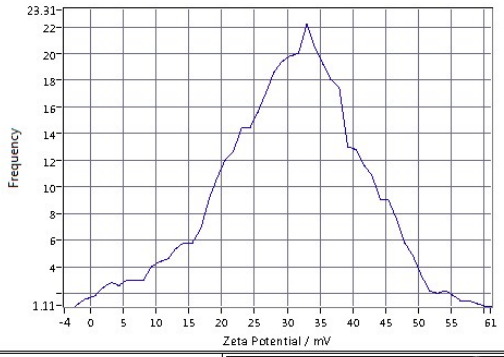
Measurement Parameters
Cell S/N: CA0020_0062b
Sensed Electric Field: 3.61 V/cm
Measurement Mode: Stationary 4 Cycles

Result
Mobility: 2.46 FWHM 1.77 µm/sec/V/cm, @ 25°C: 2.39 µm/sec/V/cm
ZP Factor 12.4 (Smoluchowski):
Zeta Potential @ 25 °C: 30.59 FWHM 12.15 mV
Concentration 17.59E+6 Particles / mL

Quality
Number of Traced Particles: 446
ΔSL: 2.90 mV

Analysis Parameters
Max Size: 702, Min Size: 20, Min Brightness: 30

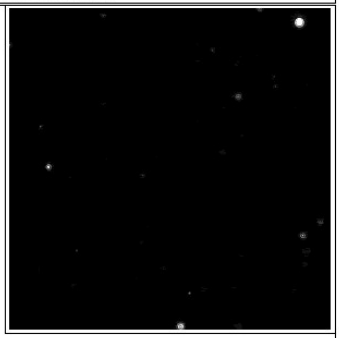




Stationary Layers	Rel. Position
SL1	0.149
SL2	0.851

Peak Analysis (25 °C)

Zeta Potential / mV	Frequency	FWHM / mV	Percentage
32.2763	20.9706	22.7290	100.0000



Comment

(Signature)

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ZetaVIEW S/N 201, Software ZetaView 8.02.28, Camera 0.703 µm/px

Experiment: 2015-09-11 14:36, Report: 2015-09-11 14:38

5) AuNR-Ag(4)

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Electrophoresis & Brownian Motion
Video Analysis
Laser Scattering Microscopy

Operator (Report): ZetaView
Video Operator: ZetaView

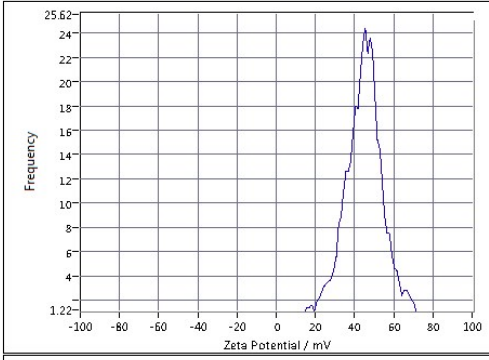
Sample Parameters
Sample Name: \\AuNR-PEG
\\AuNR-Ag-4
Comment: sen 89, shutter 40, calib 325000
Electrolyte: PBS, Concentration: 135.000 N
Temperature: 26.72 °C sensed
pH 7.4 entered
Conductivity: 19.77 µS/cm sensed

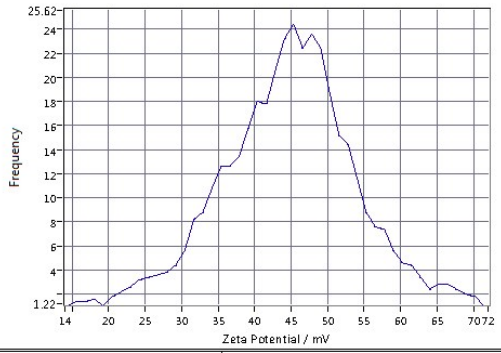
Measurement Parameters
Cell S/N: CA0020_0062b
Sensed Electric Field: 3.78 V/cm
Measurement Mode: Stationary 4 Cycles

Result
Mobility: 3.57 FWHM 1.46 µm/sec/V/cm, @ 25°C: 3.47 µm/sec/V/cm
ZP Factor 12.4 (Smoluchowski):
Zeta Potential @ 25 °C: 44.39 FWHM 11.50 mV
Concentration 19.68E+6 Particles / mL

Quality
Number of Traced Particles: 418
ΔSL: 11.18 mV

Analysis Parameters
Max Size: 702, Min Size: 20, Min Brightness: 30

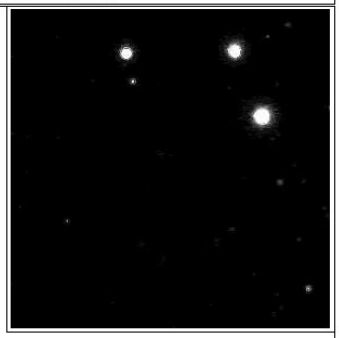




Stationary Layers	Rel. Position
SL1	0.149
SL2	0.851

Peak Analysis (25 °C)

Zeta Potential / mV	Frequency	FWHM / mV	Percentage
45.9442	23.4303	18.6435	100.0000



Comment

(Signature)

Analyzed Video: C:\Users\Zeta View\Documents\LabVIEW Data\Test\20150911_0037_AuNR-Ag-4_SL.avi

ZetaVIEW S/N 201, Software ZetaView 8.02.28, Camera 0.703 µm/px

Experiment: 2015-09-11 15:07, Report: 2015-09-11 15:08

6) AuNR-Ag(2)-PATP

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Electrophoresis & Brownian Motion
Video Analysis
Laser Scattering Microscopy

Operator (Report): ZetaView
Video Operator: ZetaView

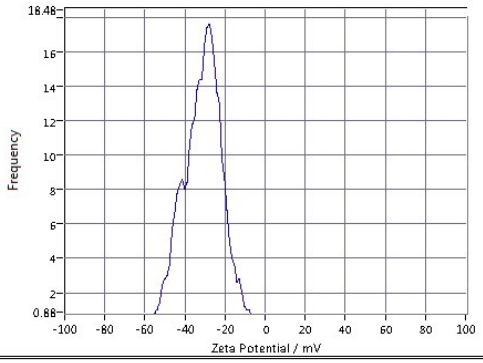
Sample Parameters
Sample Name: \\AuNR-PATP
\\AuNR-Ag2-PATP
Comment: sen 89, shutter 40, calib 325000
Electrolyte: PBS, Concentration: 135.000 N
Temperature: 26.67 °C sensed
pH 7.4 entered
Conductivity: 18.41 µS/cm sensed

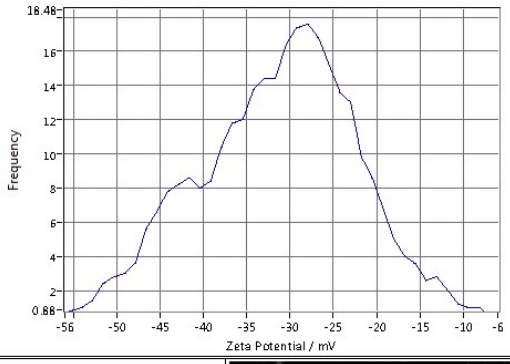
Measurement Parameters
Cell S/N: CA0020_0062b
Sensed Electric Field: 3.72 V/cm
Measurement Mode: Stationary 4 Cycles

Result
Mobility: -2.47 FWHM 1.42 µm/sec/V/cm, @ 25° C: -2.40 µm/sec/V/cm
ZP Factor 12.4 (Smoluchowski):
Zeta Potential @ 25 °C: -30.69 FWHM 10.85 mV
Concentration 14.08E+6 Particles / mL

Quality
Number of Traced Particles: 312
ΔSL: 16.28 mV

Analysis Parameters
Max Size: 702, Min Size: 20, Min Brightness: 30

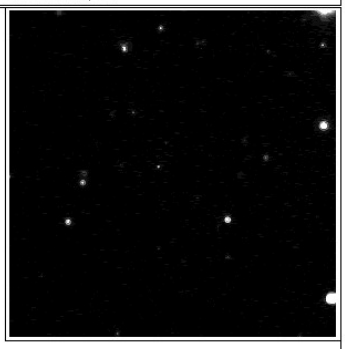




Stationary Layers	Rel. Position
SL1	0.149
SL2	0.851

Peak Analysis (25 °C)

Zeta Potential / mV	Frequency	FWHM / mV	Percentage
-28.7571	17.4742	18.1941	100.0000



Comment

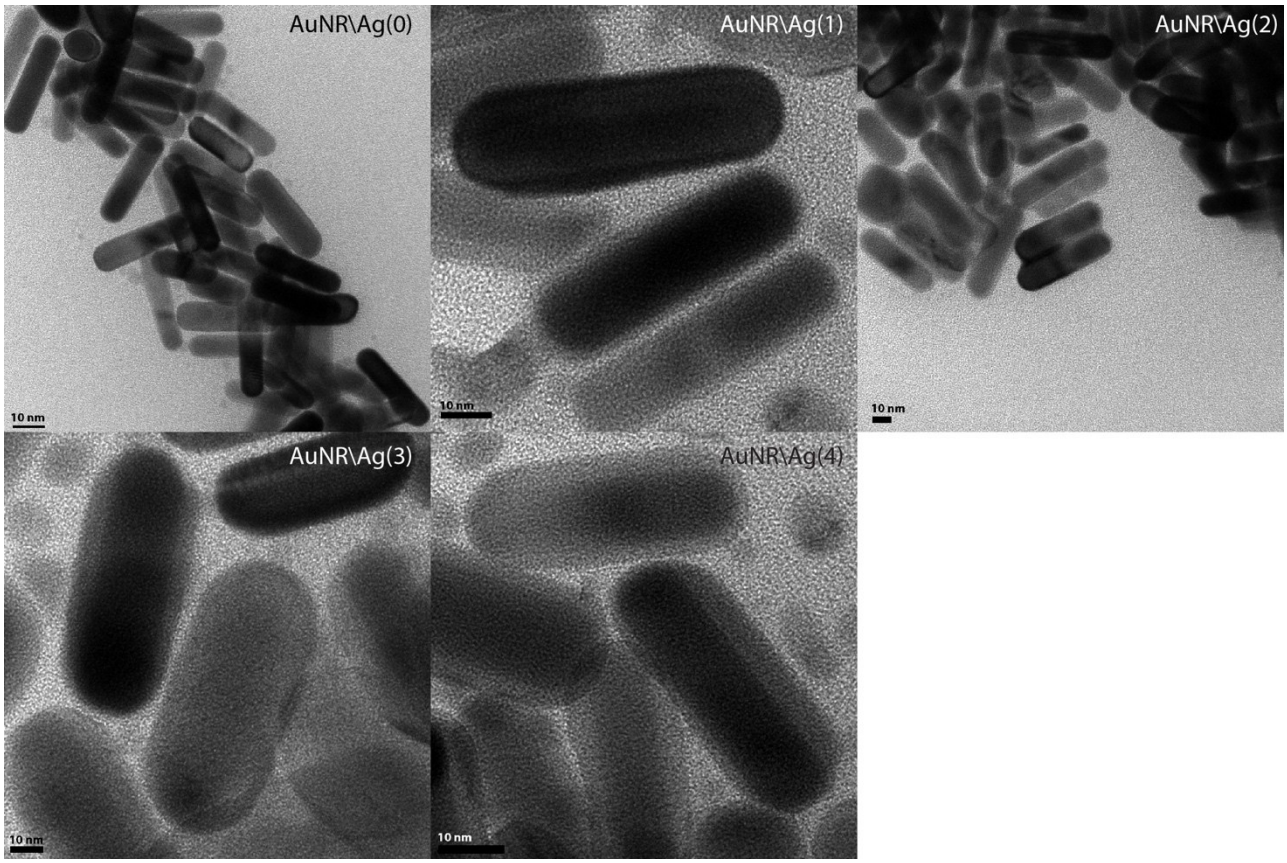
(Signature)

Analyzed Video: C:\Users\Zeta View\Documents\LabVIEW Data\Test\20150911_0024_AuNR-Ag2-PATP_SL.avi

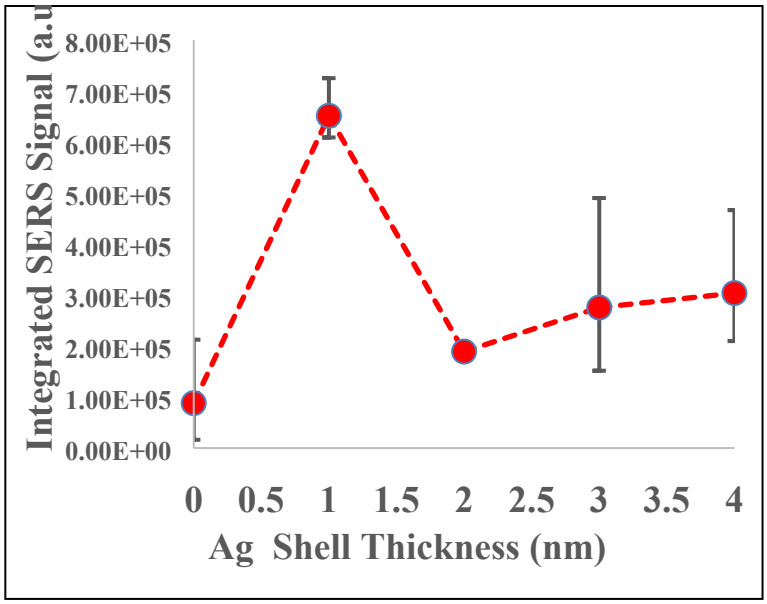
ZetaVIEW S/N 201, Software ZetaView 8.02.28, Camera 0.703 µm/px

Experiment: 2015-09-11 13:52, Report: 2015-09-11 13:55

3- TEM images

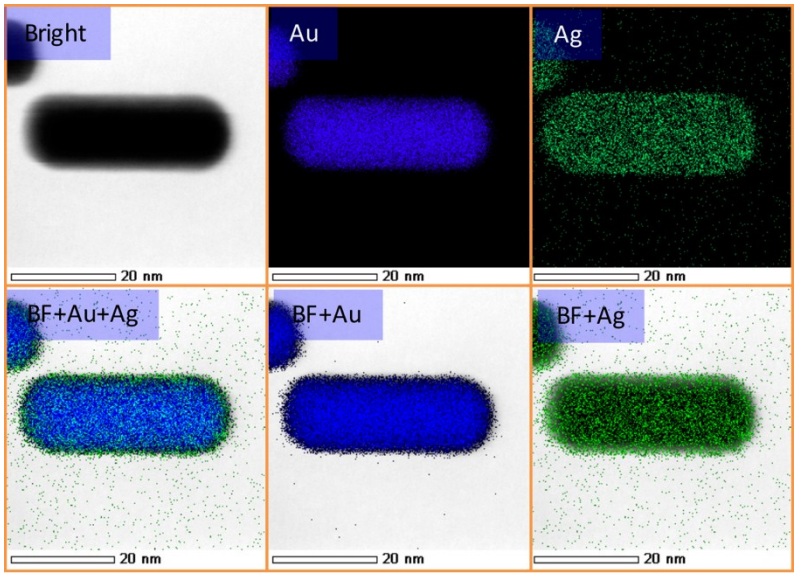


4- SERS experimental error bars

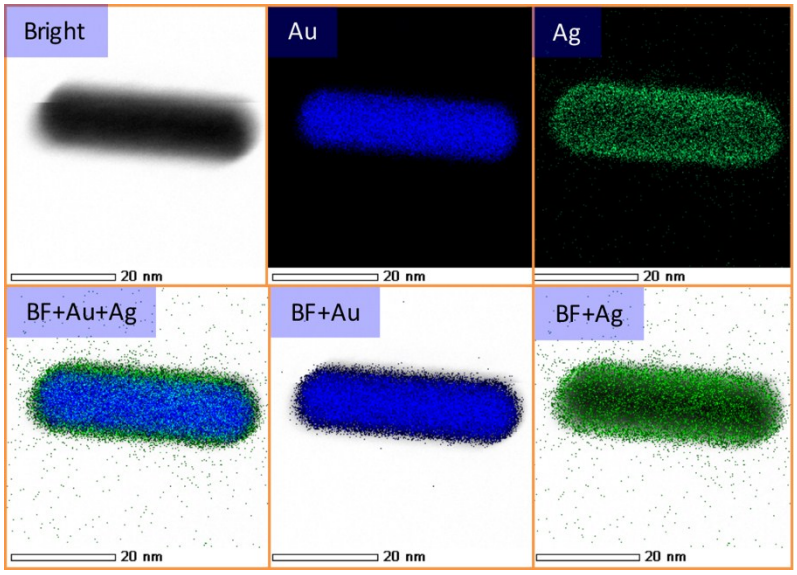


5- STEM images

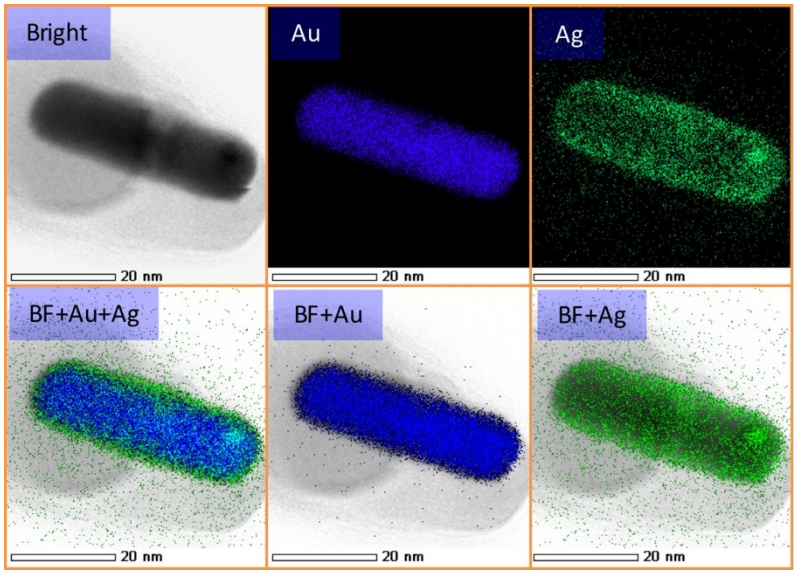
AuNR\Ag(1)



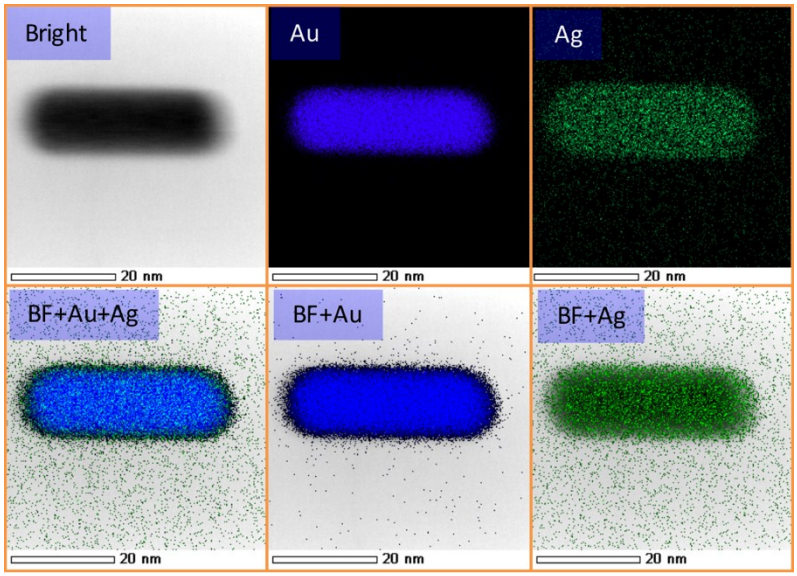
AuNR\Ag(2)



AuNR\Ag(3)



AuNR\Ag(4)



References

(S1): Fumiya, W.; Zeid, A. N.; Takumi, H.; Masatoshi, M.; Minoru, N.; Alexandru, S. B. X-ray photoelectron spectroscopy and transmission electron microscopy analysis of silver-coated gold nanorods designed for bionanotechnology applications. *Nanotechnology* 2017, *28* (2), 025704.