Supplementary Information (SI) for RSC Applied Interfaces.

Supporting Information

Probing Raman Enhancements for a Colloidal Metasurface with Optical Gap Distances in the Quantum Regime

Yuan Zeng[1,2*], Yu Xie[1*], Andrea L. Rodarte[1], Tyler J. Dill[1], and Andrea R. Tao[1,2‡]

[1]Aiiso Yufeng Li Family Department of Chemical and Nano Engineering, University of California, San Diego, 9500 Gilman Drive MC 0448, La Jolla, California 92093-0448

[2]Materials Science and Engineering, University of California, San Diego, 9500 Gilman Drive, La Jolla, California 92093

[*]These authors contributed equally to this work.

[‡]Email: atao@ucsd.edu

Figure S1

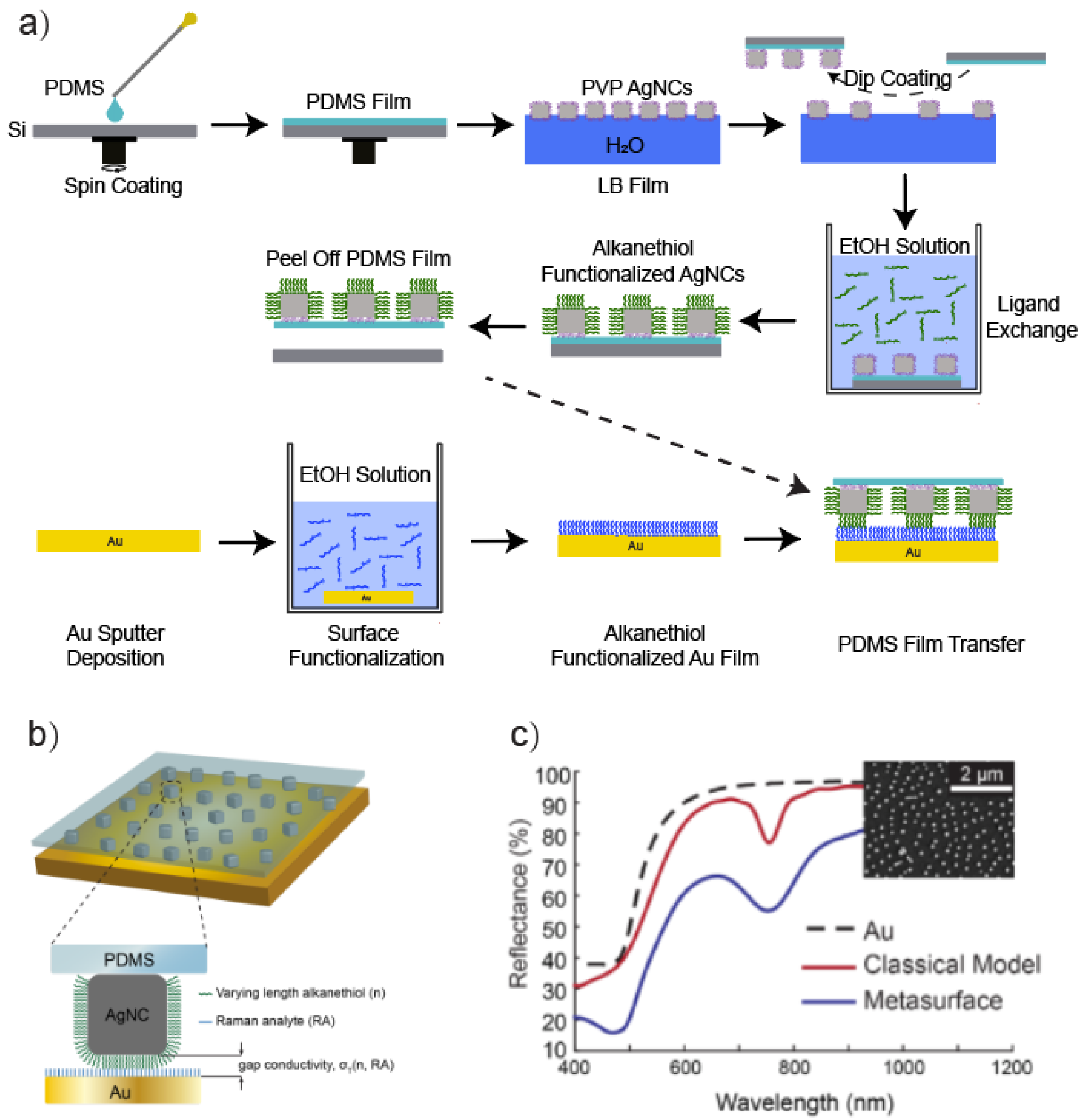

Figure S1. Schematic and far field spectra of metasurface: (a) Schematic of colloidal metasurface fabrication using PDMS stamping method (b) Schematic of a single meta-atom formed by AgNC and Au thin-film and separated by a dielectric gap consist of Raman analyte (dHDT) and alkanethiol (DDT). (c) Experimental (blue) reflectance spectra for an AgNC metasurface in classical regime (d = 3.27 nm) and simulated (red) reflectance spectra with classical model (h = 3 nm, $\sigma_T = 0$). The inset shows an SEM image of AgNCs (73.6 ± 3.7 nm) deposited on PDMS prior to adhesion to an Au substrate, dashed line shows the reflectance spectra of PDMS adhered to Au with no AgNCs.

Due to the 150 μm thick PDMS cap above the nanojunctions, we did not image the PDMS-AgNC on Au directly. However, because the gap mode resonance is identical to the AgNC on Au metasurface (Figure S1c), we believe the PDMS-AgNC nanojunction axes lie similarly in an out-of-plane direction where the AgNC flat facet in parallel to Au film.

Table S1: Raman Intensity (@ 999cm^{-1}) vs. gap height

	h (nm)	Ex @ 633 nm	Ex @ 785 nm
Cn = 0	0.932	321.4	4228.2
Cn = 1	1.058	9285.5	33035.5
Cn = 2	1.184	16075.4	52462.3
Cn = 3	1.31	48220.7	54790.3
Cn = 4	1.436	26287.9	53766.9
Cn = 6	1.688	17997.2	33594.2
Cn = 8	1.94	12623.9	28294.7
Cn = 12	2.444	5174.8	18247.1
Cn = 16	2.948	684.5	4674.5
Cn = 18	3.2	824.7	2863.0

Figure S2

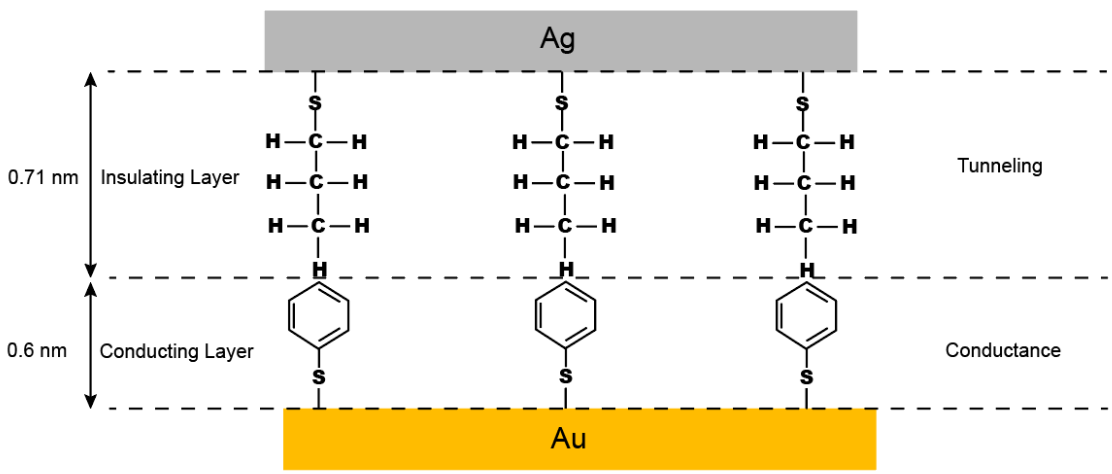

Figure S2. Schematic of Nanojunction

A schematic of nanojunction (alkanethiol Cn = 3) is shown in Figure S2. The alkanethiol monolayer (Cn = 3) is 0.71 nm thick and the PhSH monolayer is 0.6 nm thick. This nanojunction can thus be approximated by a 0.71 nm thick insulating layer (alkanethiol) for which electron tunneling plays a dominant role in charge transfer and a 0.6 nm thick conductive layer (PhSH) for which conductance plays a dominant role due to π-π stacking. However, it is not clear which charge transfer effect is more dominant in the overall nanojunction and would benefit from future studies on the fundamental physical mechanisms at play in these metasurface architectures.

Figure S3

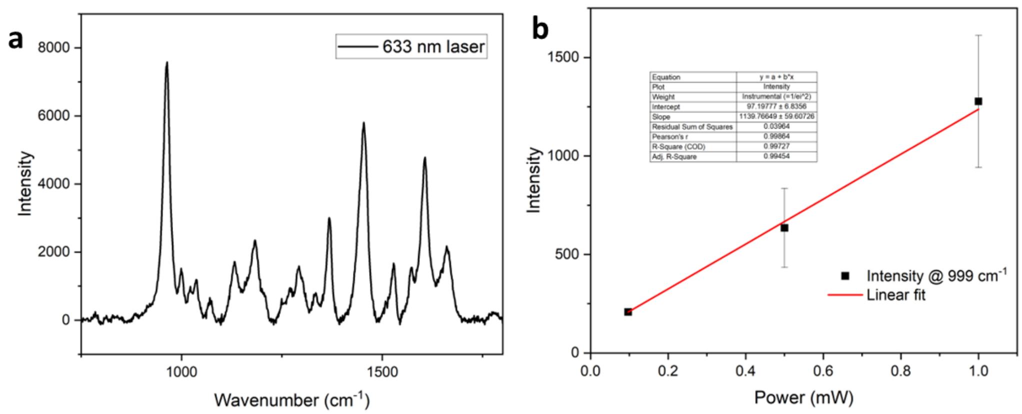

Figure S3. mSERS measurements as a function of 633 nm laser power. A) mSERS spectrum for a metasurface functionalized with benzenethiol. b) Plot of mSERs intensity at the 999 cm^{-1} Raman band as a function of laser power showing a linear response.

Figure S4

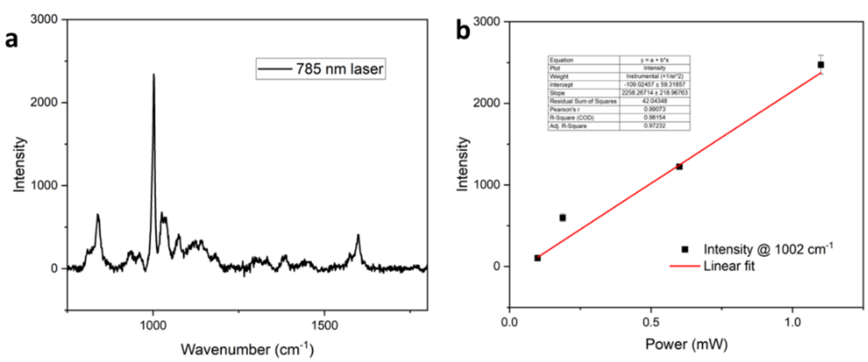

Figure S4. mSERS measurements as a function of 785 nm laser power. A) mSERS spectrum for a metasurface functionalized with benzenethiol. b) Plot of mSERs intensity at the 1002 cm^{-1} Raman band as a function of laser power showing a linear response.