Supplementary information

Nanostar probes for tip-enhanced spectroscopy

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Author Contributions

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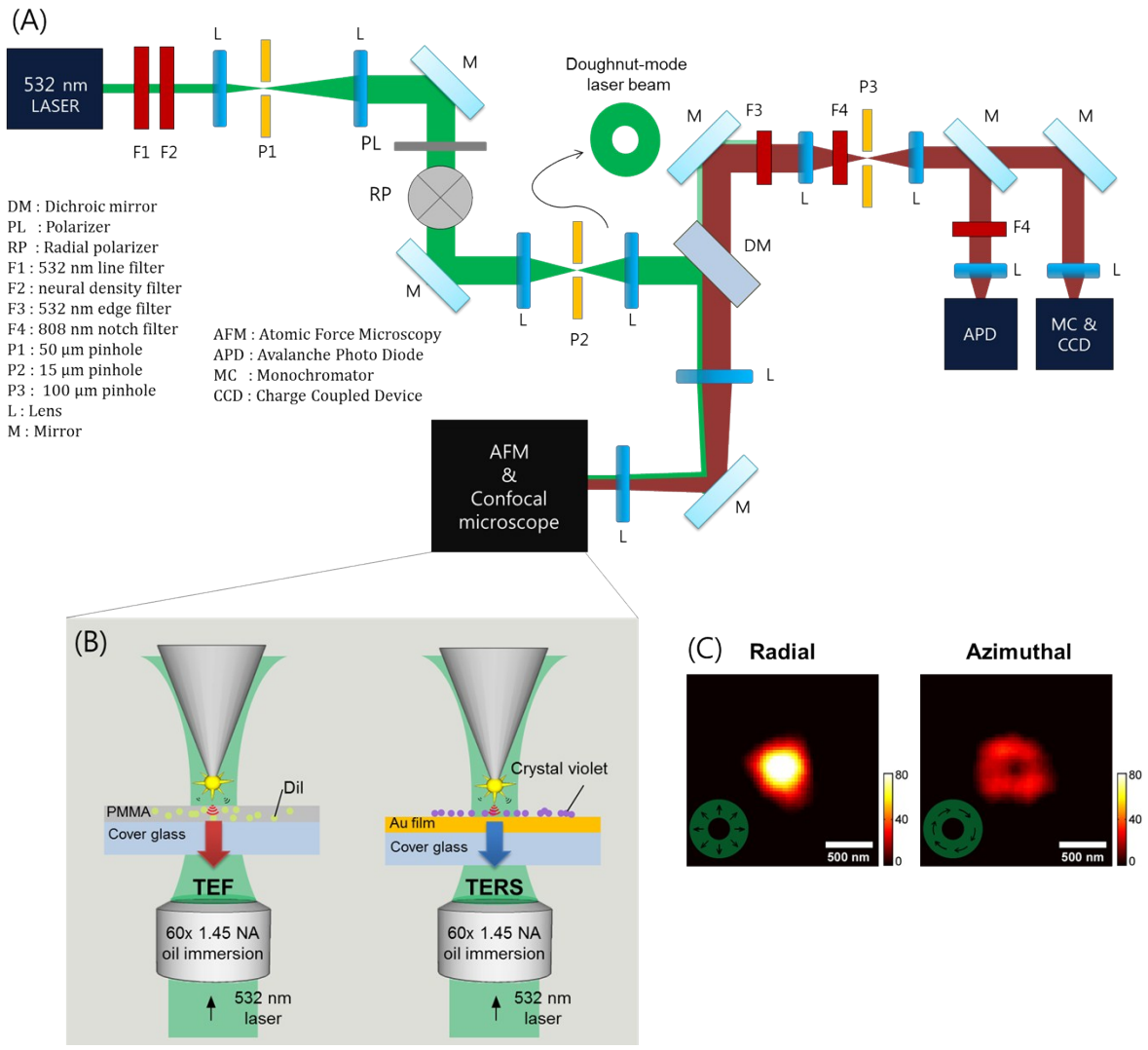

Figure S1. (A) Overall experimental setup. (B) Measurement of tip-enhanced fluorescence (TEF) and tip-enhanced Raman scattering (TERS). (C) Confocal fluorescence images of a fluorescent bead (diameter of 20 nm) on a glass coverslip obtained with a radial polarized laser beam and an azimuthal polarized laser beam, λ = 532 nm. In the experiment described in the main text, the radially polarized laser beam is used to enhance the z-polarized (perpendicular to the sample surface and parallel to the main axis of the tip) electric field component. Such a z-polarized electric field is needed to excite the longitudinal plasmons of vertically (z) oriented spikes of the nanostars at the tip end.

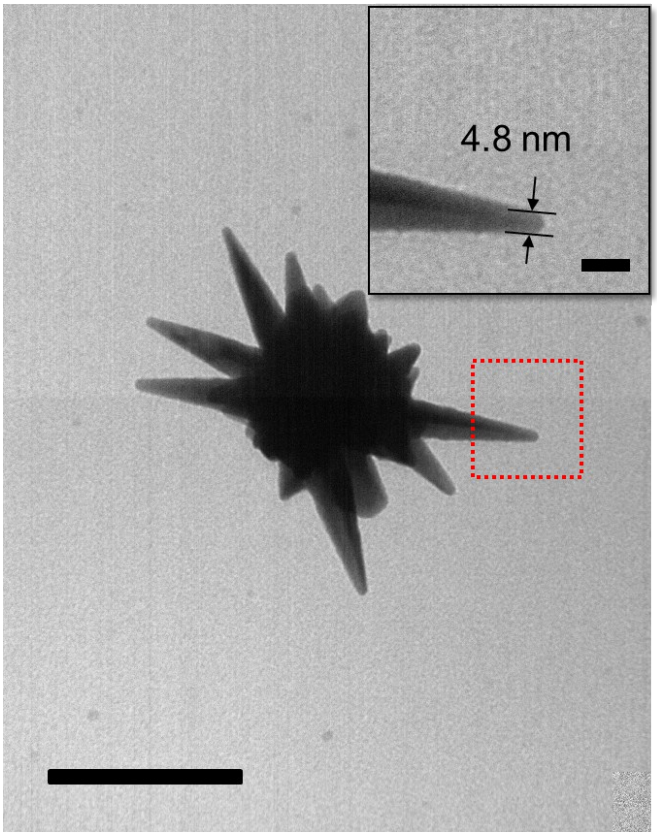

Figure S2. TEM image of a nanostar prepared in solution (scale bar: 100 nm). The inset shows the magnified view of the spikes (scale bar: 10 nm).

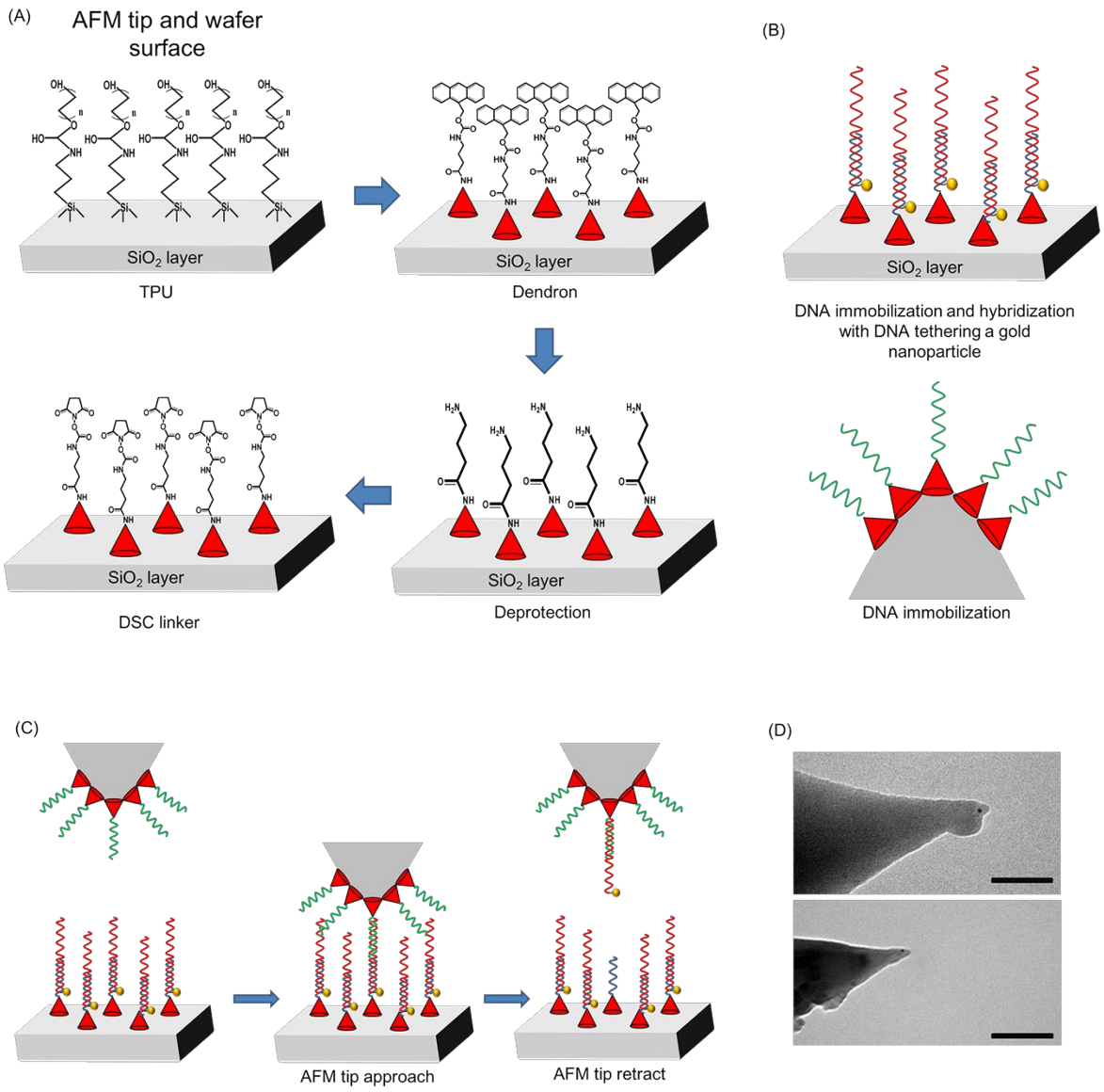

Figure S3. Schematic drawing of the picking process. (A) Preparation of dendron-modified AFM tips and substrates. (B) (top) A substrate that was used to supply gold nanoparticles. Single strand DNA tethering a single AuNP was hybridized to the DNA probe on the substrate. (bottom) Complementary DNA on the tip. (C) A diagram illustrating the steps for transferring a single DNA strand from the substrate to the tip end. (D) TEM images showing the single gold nanoparticle at the end of the tips (scale bar: 100 nm).

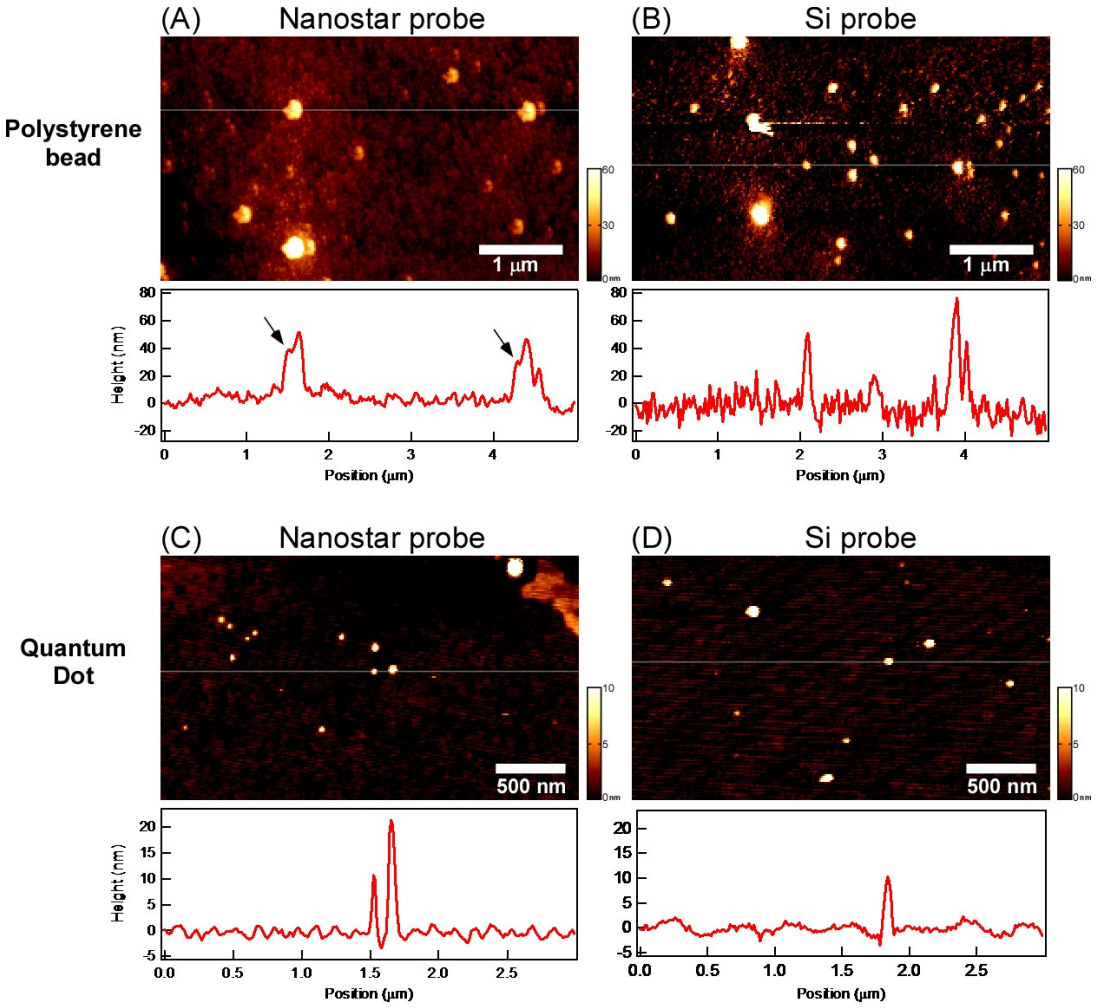

Figure S4. AFM tapping-mode topographic images of polystyrene beads (A and B, PS, average diameter of 20 nm) and CdSe quantum dots (C and D, average diameter of 5-10 nm), obtained with a commercially available Si-tip (B and D; PPP-NCH, Nanosensors) and the nanostar tip (A and C). An associated profile for each image sampled along the white line is presented below of the corresponding image. The black arrows in (A) point the topographic feature arising from the tip-convolution effect.

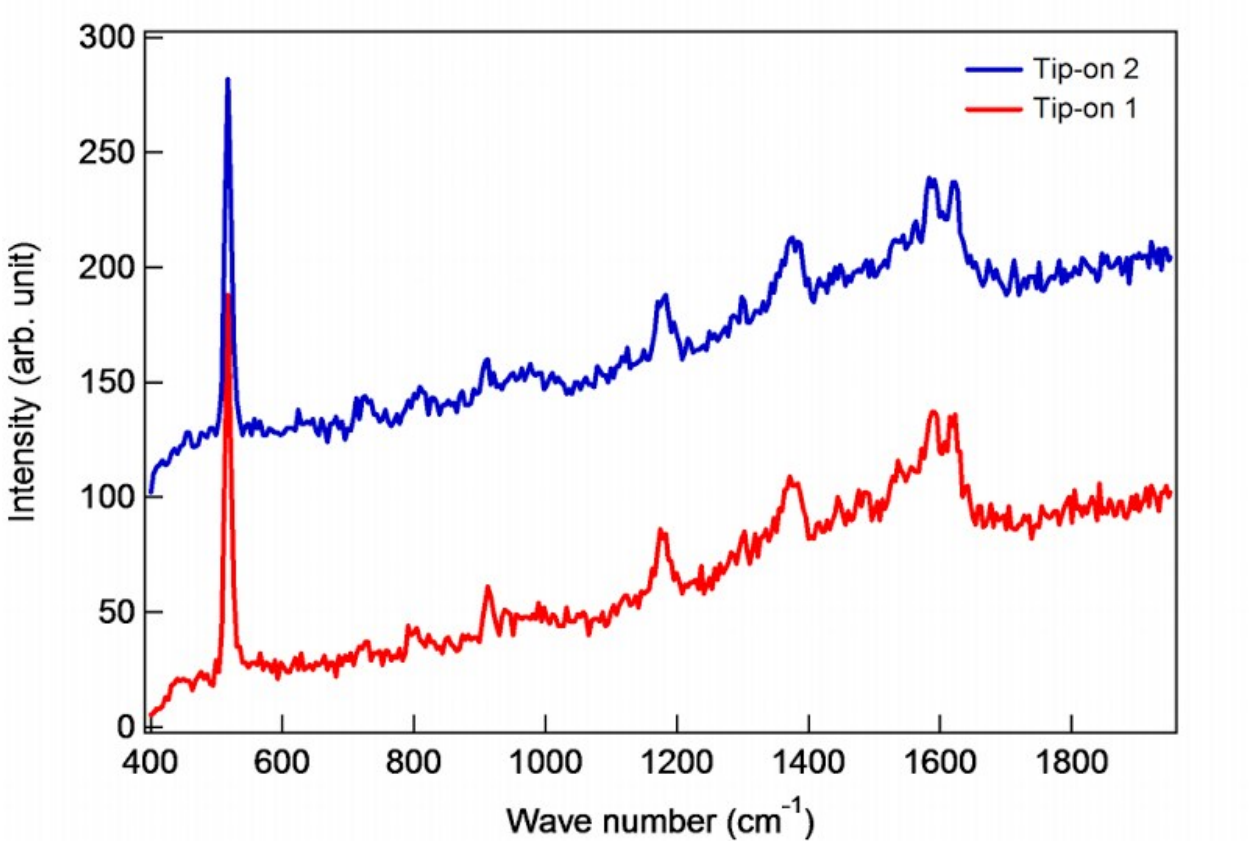

Figure S5. The two consecutive TERS spectra (red → blue) of CV on gold surface obtained from the same tip and the same position in the sample (each with 10 sec of integration time and 80 μW of the laser power). We observed less than 20% of decrease in TERS signal. For the clarity, the second spectrum is displaced along y-axis.

Table-S1. Peak assignments for the Raman and TERS spectra for CV[a] (in cm^{-1})

Peak No.	Raman	TERS	Peak assignments[b]
1	-	804	$\gamma_{as,\ oop,\ \phi\text{-}H}$
2	-	912	
3	1183	1178	$\nu_{as,\ ip,\ C\text{-}H,\ C\text{-}\phi}$
4	1367	1367	$\nu_{as,\ \phi\text{-}C\text{-}\phi,\ C\text{-}N}$
5	1380	1387	ω
6	1536	1536	
7	1583	1591	
8	1622	1618	

a) All of the confocal Raman and TERS spectra were obtained with $\lambda_{ex} = 532$ nm.
b) Vibrational peak assignments and notations.[1-4]
γ : bend, as: antisymmetric, oop: out-of-plane; ν : stretch; ip : in-plane; ω : ring breathing.

References

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