Electronic supplementary information

Gold nanonails for surface-enhanced infrared absorption

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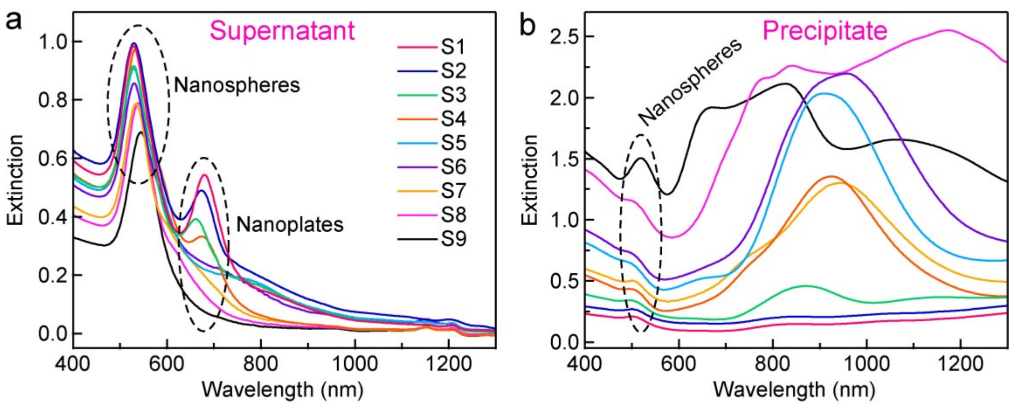

Fig. S1 Extinction spectra of the Au nanorod samples. (a) Extinction spectra of the supernatant. (b) Extinction spectra of the precipitate.

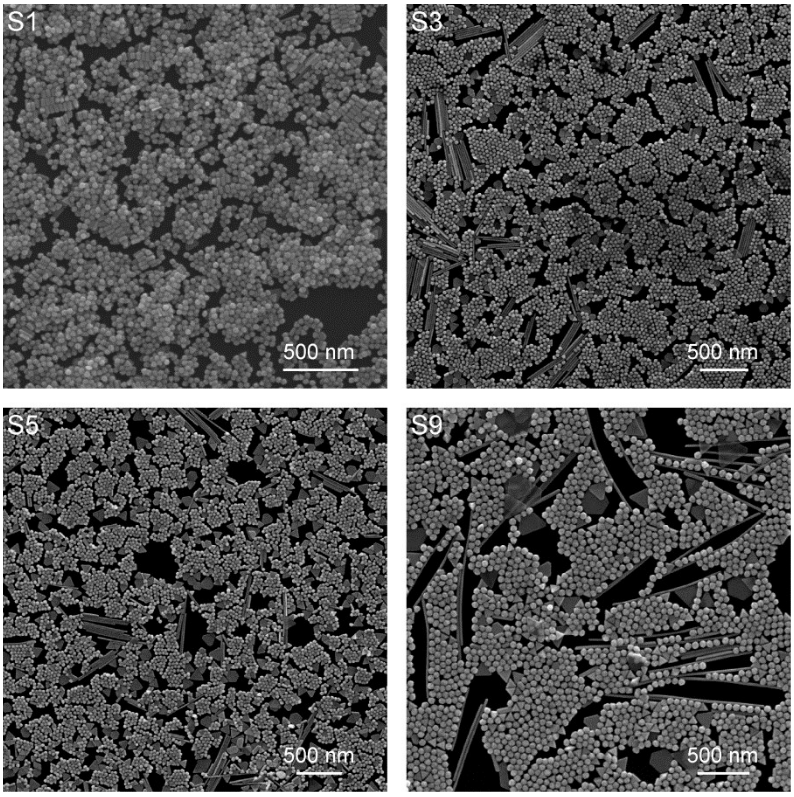

Fig. S2 SEM images of the supernatants in the four representative Au nanorod samples. The pH values of the growth solutions are 6.83, 4.52, 2.06 and 2.06 for the samples 1, 3, 5 and 9, respectively.

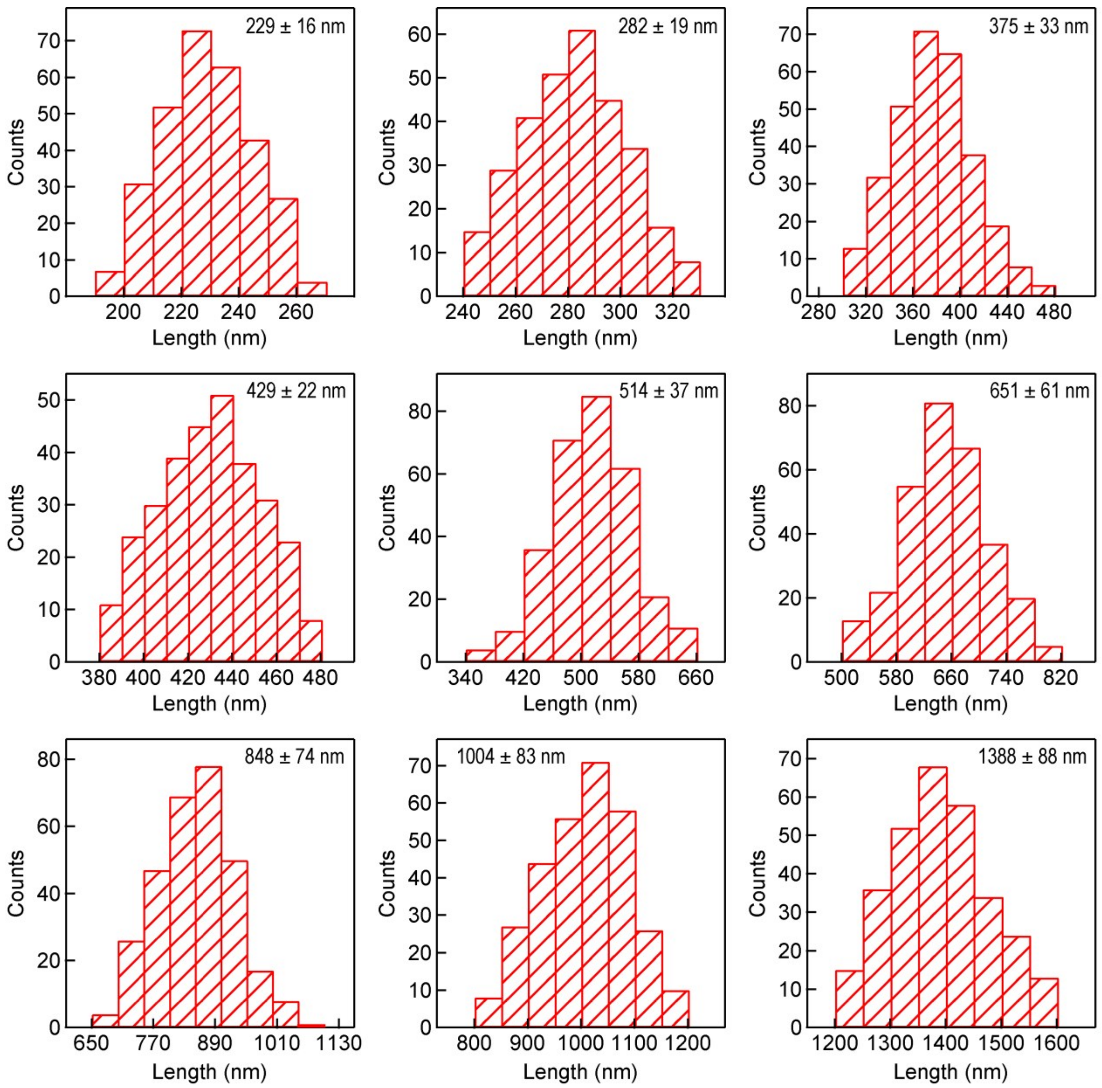

Fig. S3 Histograms of the length distributions of the Au nanorod samples. The average length of each sample is given in the histogram.

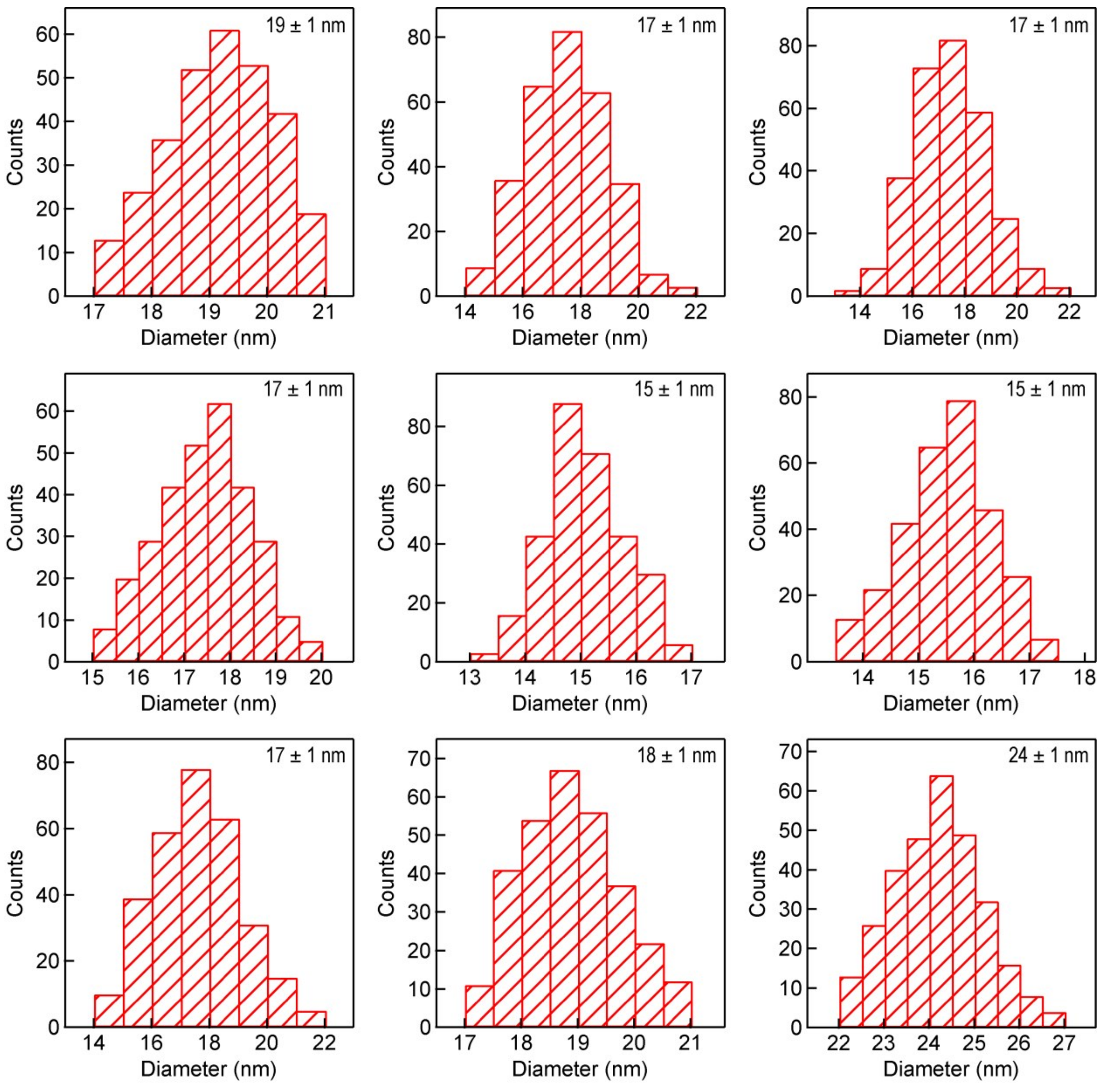

Fig. S4 Histograms of the diameter distributions of the Au nanorod samples. The average diameter of each sample is given in the histogram. The average lengths of these samples are provided in Fig. S3.

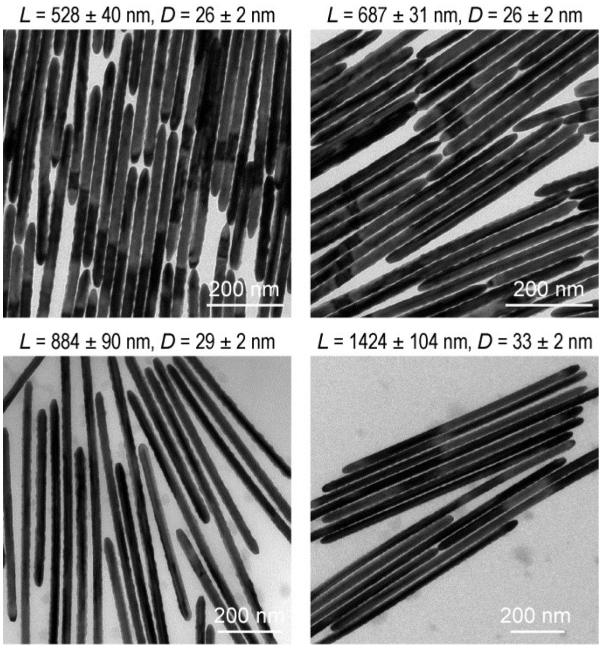

Fig. S5 TEM images of the Au nanonail samples with different dimensions. The average lengths and diameters of the samples are indicated above the TEM images.

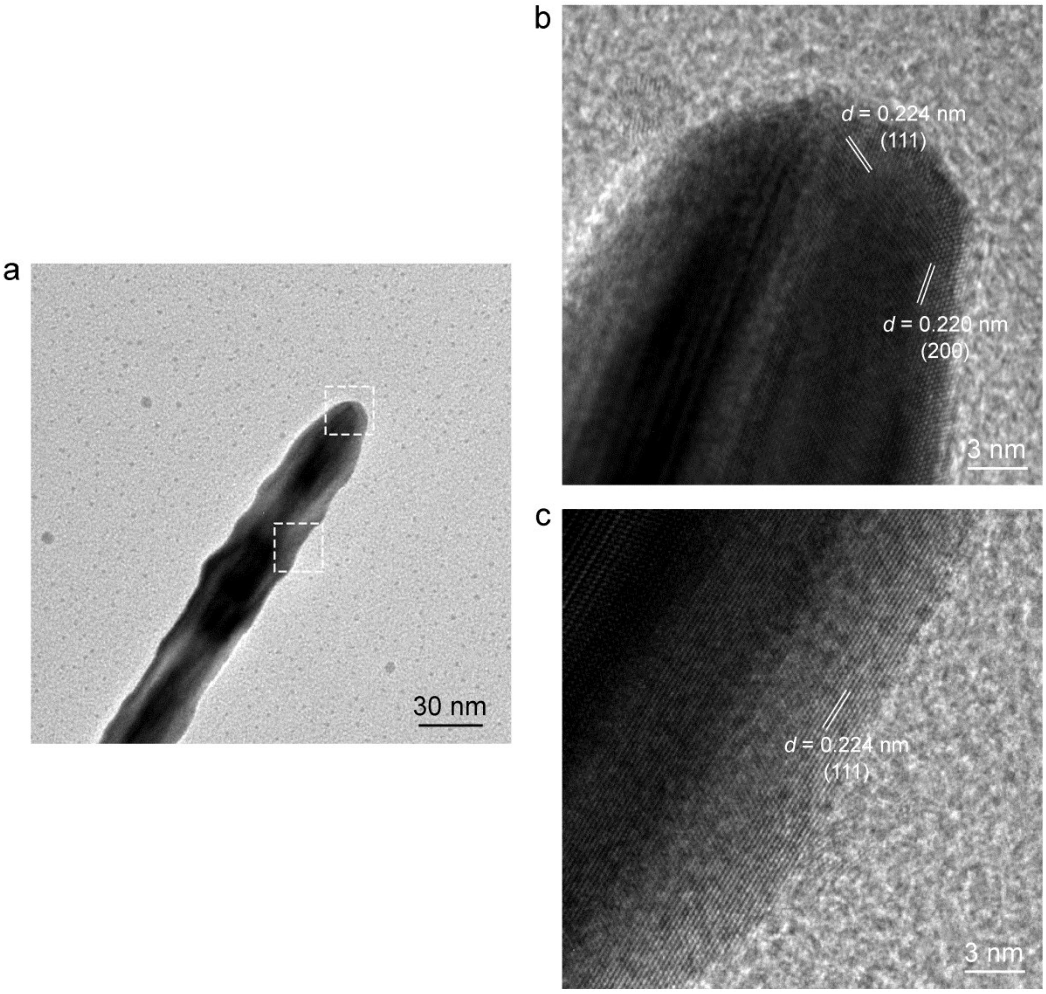

Fig. S6 HRTEM images of a gold nanonail. (a) TEM image of a gold nanonail at low magnification. (b and c) HRTEM images of the tip and side facet regions of the sample shown in (a), respectively. The length and diameter of the Au nanonail are 528 nm and 28 nm, respectively.

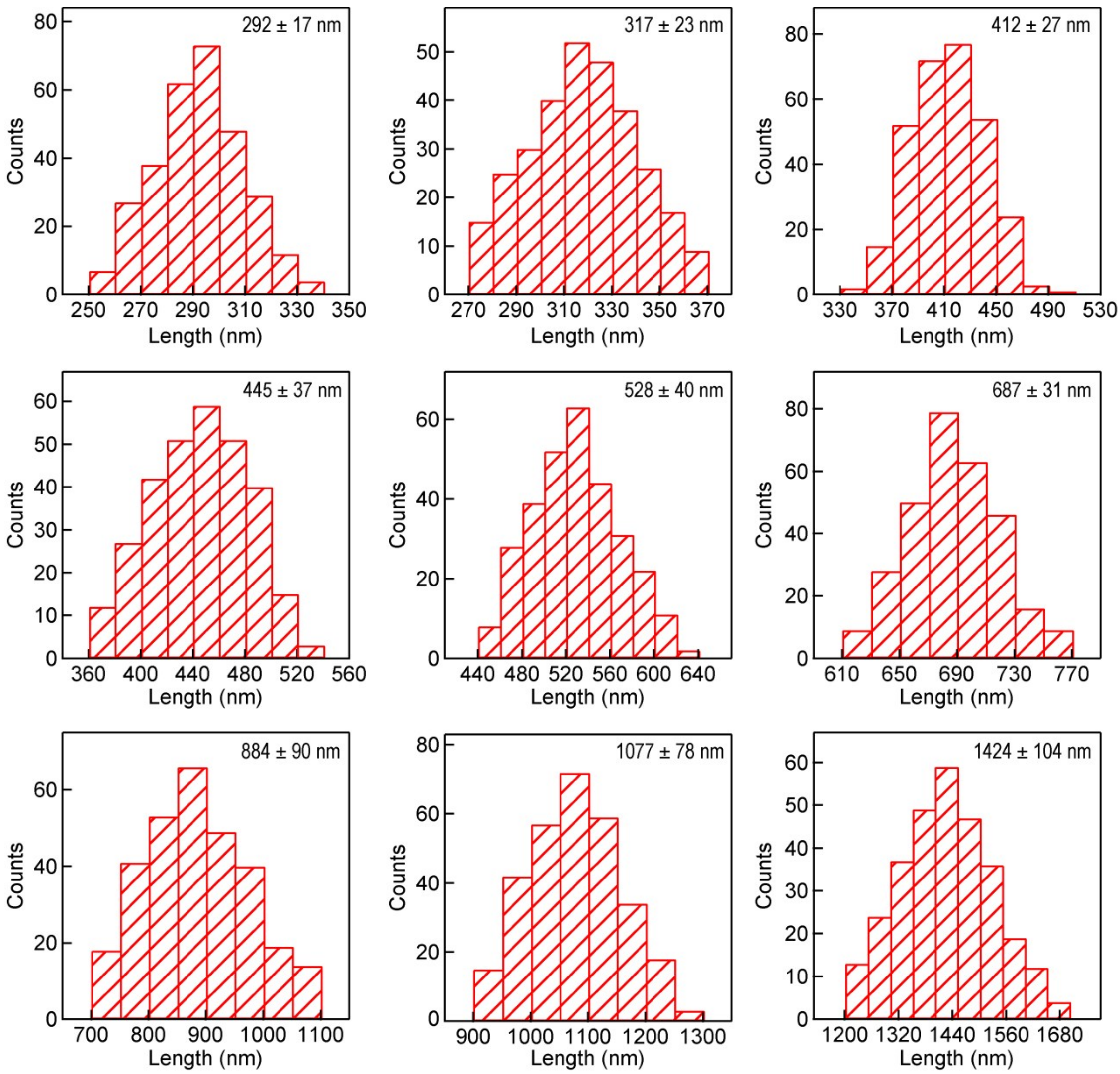

Fig. S7 Histograms of the length distributions of the Au nanonail samples. The average length of each sample is indicated in the histogram.

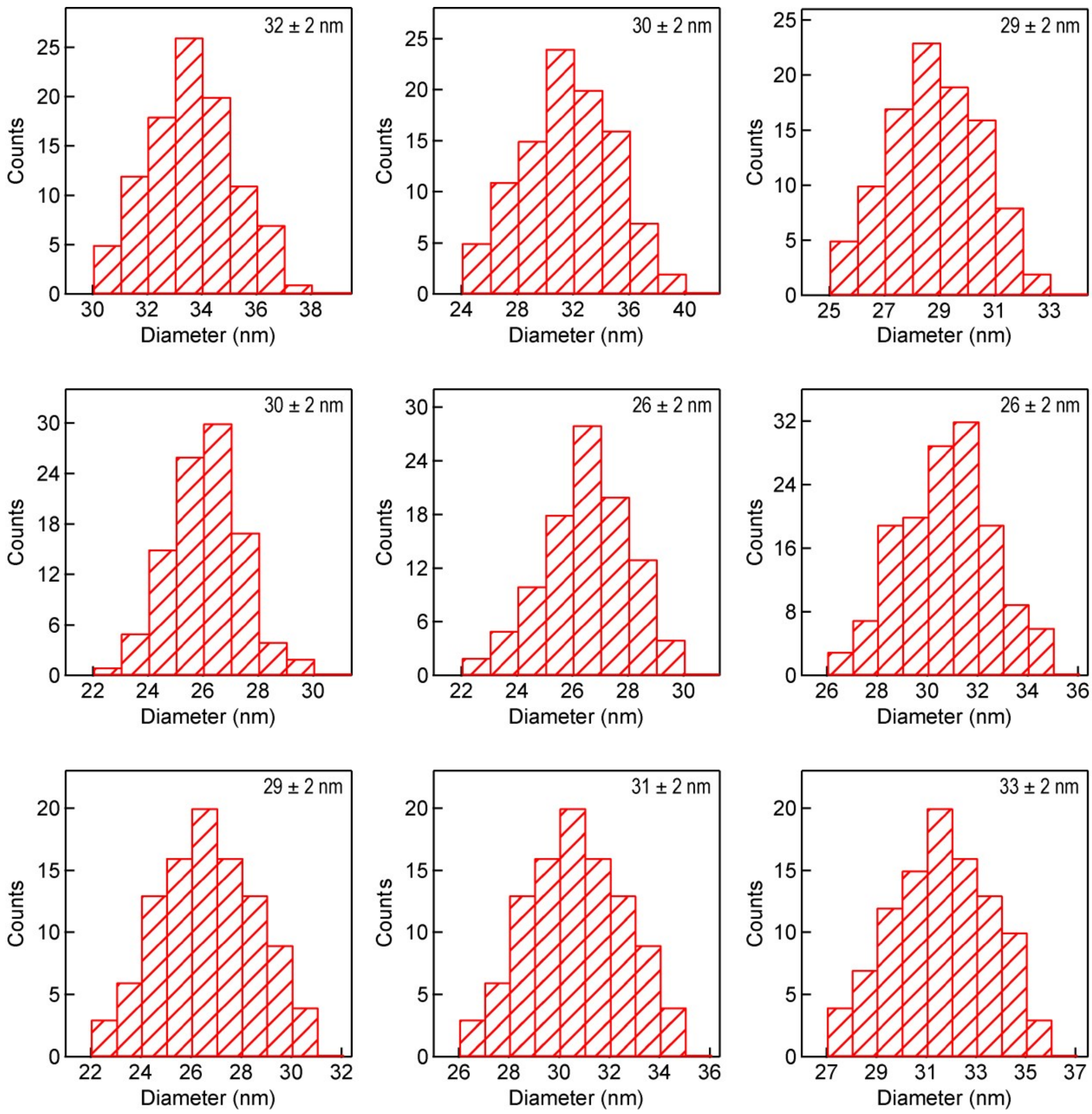

Fig. S8 Histograms of the diameter distributions of the Au nanonail samples. The average diameter of each sample is indicated in the histogram. The average lengths of these samples are given in Fig. S7.

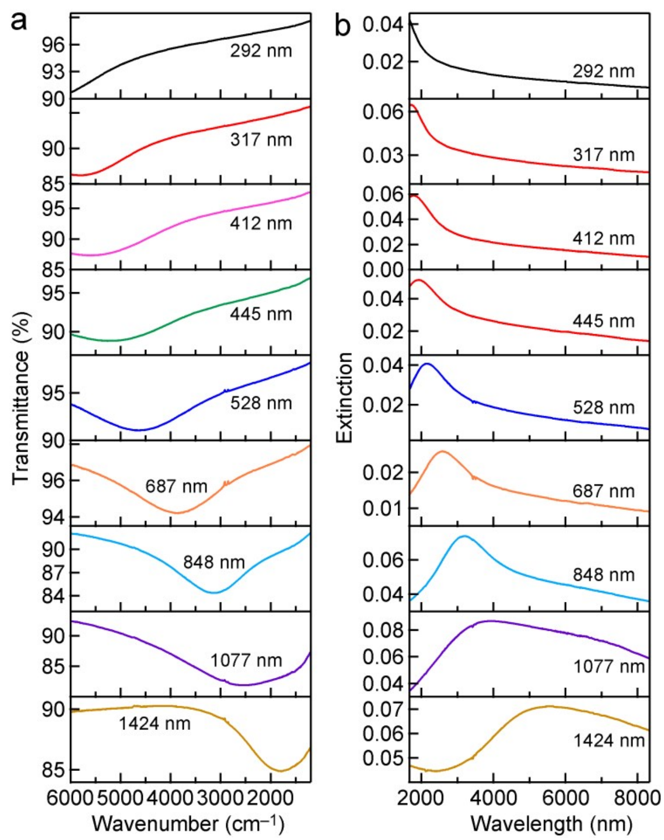

Fig. S9 Transmittance and extinction spectra of the Au nanonail samples. (a) Transmittance spectra. (b) Extinction spectra converted from the corresponding transmittance spectra. The average length of each sample is indicated in the plots of its transmittance and extinction spectra.

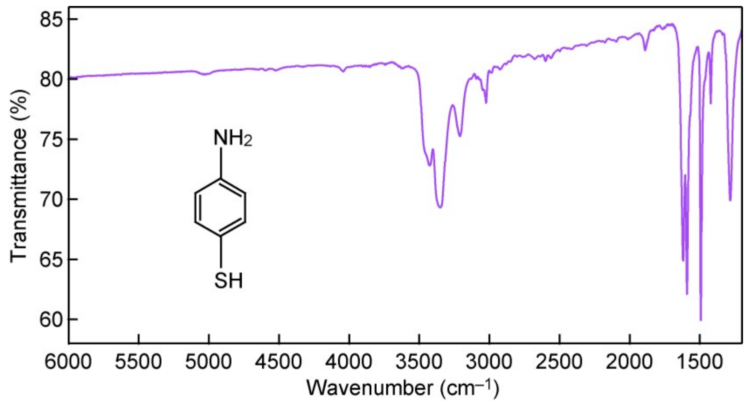

Fig. S10 IR transmittance spectrum of ATP molecules. Four vibrational modes can be identified, including the C–N stretching mode (1282 cm^{-1}), C–C stretching mode (1422, 1491, 1591 cm^{-1}), N–H bending mode (1618 cm^{-1}), and N–H stretching mode (3349 cm^{-1}).

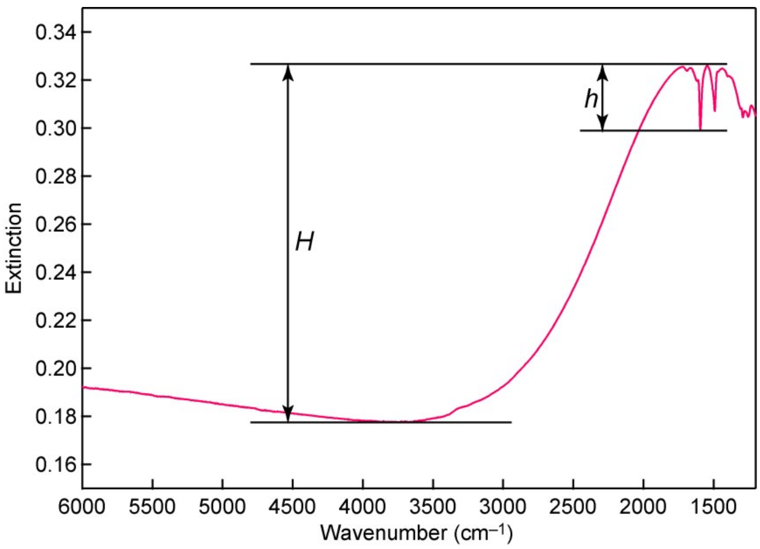

Fig. S11 Definition of the parameters *h* and *H*. *h* represents the enhanced vibrational signal of the probe molecules, and *H* refers to the extinction intensity of the nanoantennas. The IR spectrum was measured from the Au nanonails. The average length and diameter of the Au nanonail sample are 1424 ± 104 nm and 33 ± 2 nm, respectively.

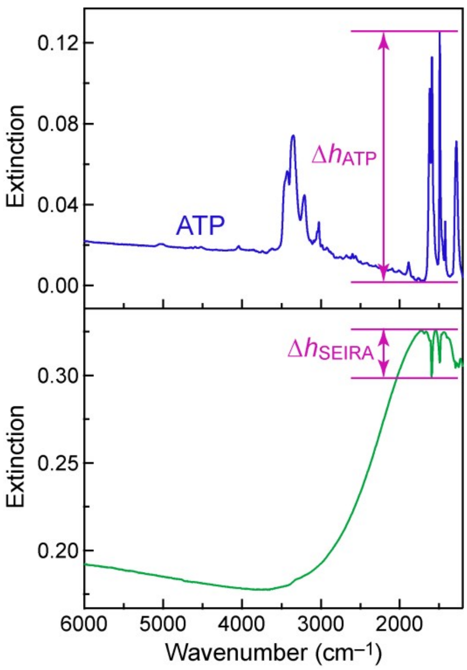

Fig. S12 IR extinction spectra. At the top is the spectrum of pure ATP molecules (0.1 M, in 0.2 mL deionized water). At the bottom is the spectrum of the Au nanonails decorated with ATP molecules. Δh_{ATP} refers to the vibrational signal intensity of ATP molecules dissolved in water. Δh_{SEIRA} represents the enhanced vibrational signal of the probe molecules.

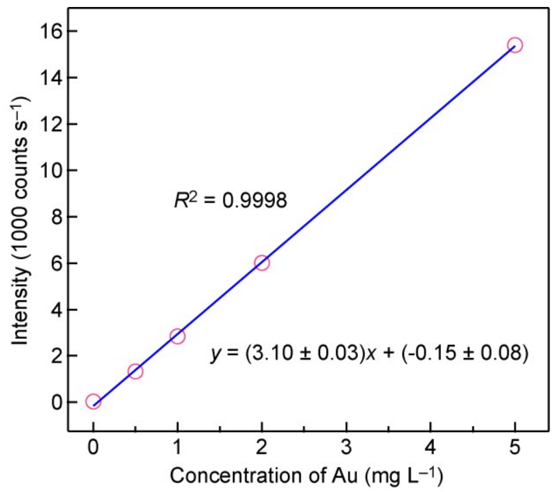

Fig. S13 Linear relationship between the emission intensity and the mass concentration of Au for the ICP-MS measurements. The circles represent the Au concentrations of 0, 0.5, 1.0, 2.0 and 5.0 mg L^{-1}, respectively. The equation obtained from linear fitting is $y = (3.1009 \pm 0.0340)\ x - (-0.1502 \pm 0.0839)$. The coefficient of determination for the linear fitting is $R^2 = 0.9998$. The mass concentration of Au for the Au nanorod and Au nanonail samples were found to be 5.662 mg L^{-1} and 2.512 mg L^{-1}, corresponding to a particle concentration of 1.13×10^9 particles mL^{-1} and 2.69×10^8 particles mL^{-1}, respectively.

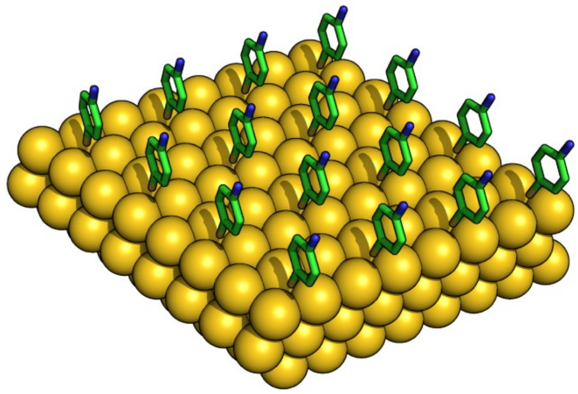

Fig. S14 Optimized structure of ATP molecules adsorbed on the Au (111) surface in the PBC model. The ATP molecule was optimized in the DFT model with the PBE0/631+G(*d,p*) level implemented with the static dielectric constant of water ($\varepsilon = 78.36$) , which was employed to consider the solvent effect. The Au surface was modeled with a (5 × 5) Au (111) surface slab, which contains five Au layers and a 0.15 nm-thick vacuum layer.

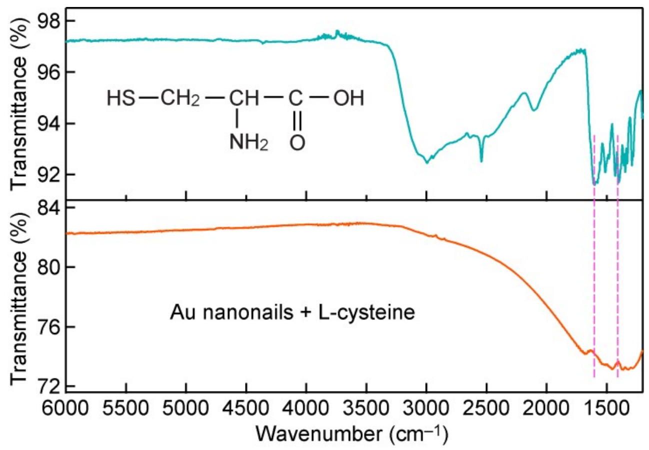

Fig. S15 IR transmittance spectra of pure L-cysteine molecules (upper) and the Au nanonails decorated with L-cysteine molecules (lower). The average length and diameter of the used Au nanonail sample are 1424 ± 104 nm and 33 ± 2 nm, respectively.

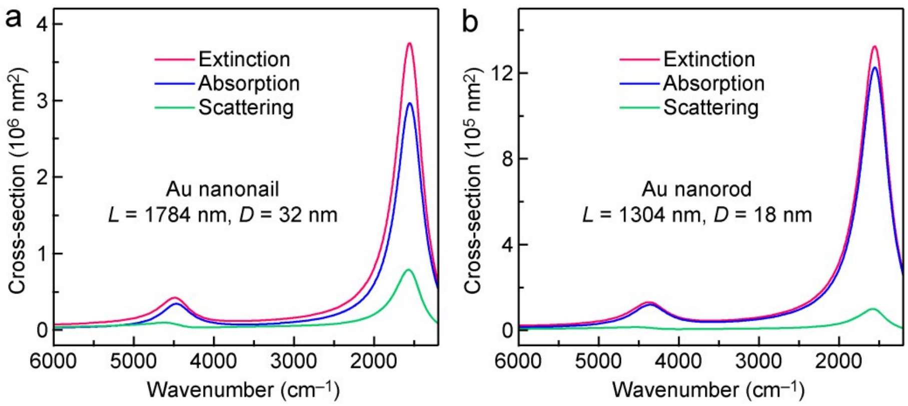

Fig. S16 Simulated extinction, absorption and scattering cross-sections. (a) Au nanonail. (b) Au nanorod.

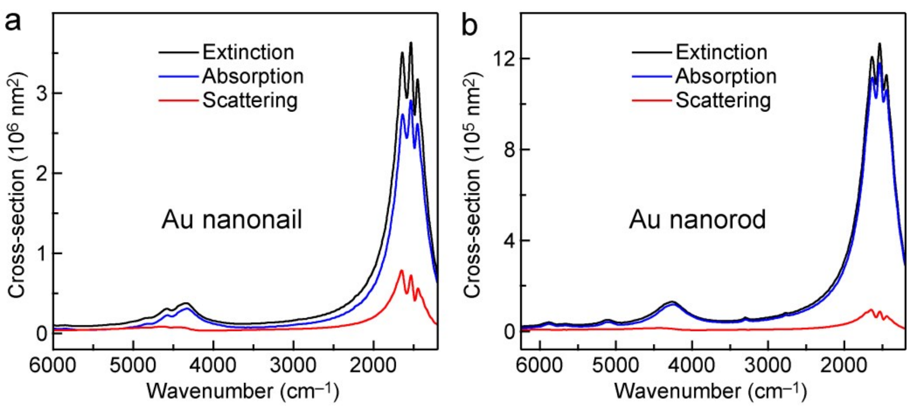

Fig. S17 Simulated extinction, absorption and scattering cross-sections. (a) Au nanonail encapsulated with ATP molecules. (b) Au nanorod encapsulated with ATP molecules.

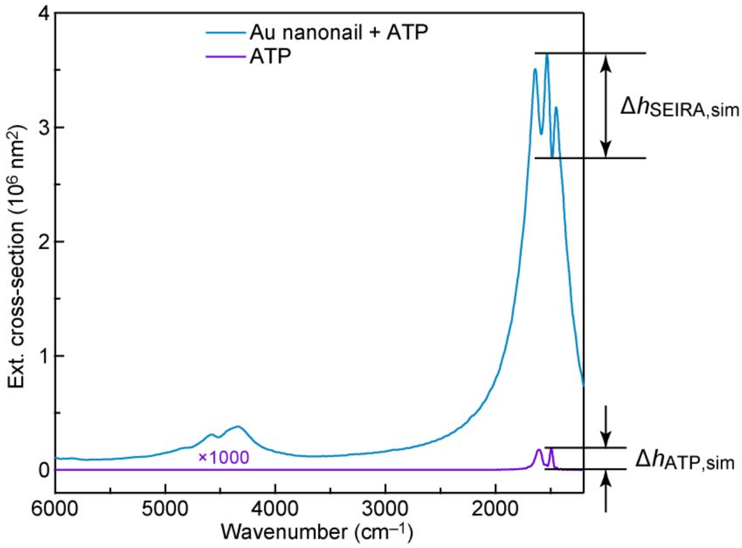

Fig. S18 Definition of $\Delta h_{SEIRA,sim}$ and $\Delta h_{ATP,sim}$. $\Delta h_{ATP,sim}$ refers to the vibrational signal intensity of the ATP molecules in the sole dielectric shell. $\Delta h_{SEIRA,sim}$ represents the enhanced vibrational signal of the probe molecules surrounding the nanoantenna.

Table S1 Growth conditions of the Au nanorods with different dimensions

Sample	NaOH or HNO_3 in the growth solution	pH of the growth solution	Amount of the seeds (mL)	Average length (nm)	Average diameter (nm)	Average aspect ratio
1	0.6 mM NaOH	6.83	1.0	229 ± 16	19 ± 1	12 ± 1
2	0.2 mM NaOH	5.55	1.0	282 ± 19	17 ± 1	16 ± 1
3		4.52	1.0	375 ± 33	17 ± 1	22 ± 2
4		4.52	0.5	429 ± 22	17 ± 1	25 ± 1
5	0.01 M HNO_3	2.06	1.0	514 ± 37	15 ± 1	34 ± 4
6	0.01 M HNO_3	2.06	0.8	651 ± 61	15 ± 1	43 ± 4
7	0.01 M HNO_3	2.06	0.5	848 ± 74	17 ± 1	49 ± 6
8	0.01 M HNO_3	2.06	0.3	1004 ± 83	18 ± 1	55 ± 5
9	0.01 M HNO_3	2.06	0.2	1388 ± 88	24 ± 1	57 ± 4

Table S2 Dimensions of the Au nanorod and nanonail samples

Au nanorods	Average length (nm)	Average diameter (nm)	Average aspect ratio	Au nanonails	Average length (nm)	Average diameter (nm)	Average aspect ratio
1	229 ± 16	19 ± 1	12 ± 1	1	292 ± 17	32 ± 2	9 ± 1
2	282 ± 19	17 ± 1	16 ± 1	2	317 ± 23	30 ± 2	12 ± 1
3	375 ± 33	17 ± 1	22 ± 2	3	412 ± 27	29 ± 2	13 ± 1
4	429 ± 22	17 ± 1	25 ± 1	4	445 ± 37	30 ± 2	14 ± 2
5	514 ± 37	15 ± 1	34 ± 4	5	528 ± 40	26 ± 2	20 ± 2
6	651 ± 61	15 ± 1	43 ± 4	6	687 ± 31	26 ± 2	26 ± 2
7	848 ± 74	17 ± 1	49 ± 6	7	884 ± 90	29 ± 2	33 ± 4
8	1004 ± 83	18 ± 1	55 ± 5	8	1077 ± 78	31 ± 2	35 ± 4
9	1388 ± 88	24 ± 1	57 ± 4	9	1424 ±104	33 ± 2	42 ± 3

Table S3 Relevant parameters for the dielectric function of the probe molecules

Parameter	Value
ε_{bg}	1.66^2
A	10
s_1	1
ω_1	3.0486×10^{14} rad s^{-1}
γ_1	4.5654×10^{12} rad s^{-1}
s_2	1.1679
ω_2	2.9978×10^{14} rad s^{-1}
γ_2	3.8987×10^{12} rad s^{-1}
s_3	1.3064
ω_3	2.8098×10^{14} rad s^{-1}
γ_3	2.1780×10^{12} rad s^{-1}