

Supporting information

Polymer-Single-Crystal@Nanoparticle Nanosandwich for Surface Enhanced Raman Spectroscopy†

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Experimental Section

Materials and methods: 6nm AuNP was synthesized following the literature method.¹ AuCl₃ (99%), ε-caprolactone (97%), 2-mercaptoethanol (99%), *Candida antarctica* lipase B (CALB) (≥10,000U/g), 1-butanol (≥99.5%), pentyl acetate (99%) and 4-aminothiophenol (4-ATP) (97%) were obtained from Sigma Aldrich Company. Thiol end-functionalized polycaprolactone (PCL-SH) was synthesized using ring-opening polymerization of ε-caprolactone at the presence of 2-mercaptoethanol and CALB catalyst according to the literature.² PCL-SH single crystals were prepared using the self seeding method: 9 mg of PCL-SH was dissolved in 30g 1-butanol at 60°C for 10mins. Then the solution was brought to 5°C for 2hr. The crystal solution was then heated at 46°C for 10mins to obtain the crystal seeds. Finally, the solution was allowed to crystallize at 22°C for 24hrs. The suspension of the single crystals was isothermally filtered to remove uncrystallized polymers. To attach nanoparticles, polymer single crystal's 1-butanol solution was centrifuged and re-dispersed in pentyl acetate. Then, a suspension of the single crystal in pentyl acetate was mixed with AuNP's toluene solution with 5:1 volume ratio and stirred for 24hrs. Free ligands and AuNPs were then removed by centrifugation. Electroless deposition was carried out by adding a certain amount of AuCl₃ into 6nm AuNP-decorated PCL-SH single crystal solution for a period of time. After this, excess AuCl₃ was removed by centrifugation. The as-fabricated AuNP decorated PSC can be dispersed in different solvents, such as water, alcohol, pentyl acetate, etc. through centrifugation. In order to adsorb 4-ATP molecules, 4-ATP solution (1mM in pentyl acetate) was mixed with AuNP decorated PSC for 1hr. Centrifugation was utilized to remove excess 4-ATP molecule in solution. 20nm thick Pt/Pd (80/20) metal film was deposited on silicon wafer using a Cressington 208HR sputter coater (40mA, 60s). This substrate was soaked in 1mM of 4-ATP in pentyl acetate for 1 hr to obtain the self assembled monolayer of 4-ATP. Yeast cells *Saccharomyces cerevisiae* were added into 1ml distilled water and centrifuged. The supernatant was removed and refilled with distilled water. After three times centrifugation, 5μl

solution of the washed yeast cell was placed on a silicon substrate. 5 μ l aqueous solution of PSC@AuNP nanosandwich was then cast on yeast cell for Raman study.

Characterization: UV-vis spectra were collected using an Ocean Optics USB4000 Miniature Fiber Optic Spectrometer at room temperature. TEM experiments were carried out using a JEOL JEM2100 TEM operated at an acceleration voltage of 200kV. To prepare the TEM sample, one drop of single crystal suspension was cast on a carbon-coated nickel grid. After solvent evaporation, the sample was used for TEM observation without further treatment. AFM image was obtained on Digital Instrument nanoscope IIIa. Raman spectroscopy was performed on Renishaw RM1000 VIS Raman Microspectrometer. 8mW power, 785nm excitation laser with a spot size of 2 μ m in diameter was utilized. The acquisition time was 10s.

EF calculation: The enhancement factor (EF) can be calculated from the following equation:

$$EF = (I_{SERS}/N_{ads})/(I_{bulk}/N_{bulk})$$

Where I_{bulk} and I_{SERS} are the intensity of a vibrational mode in solid sample and the SERS spectrum of 4-ATP, respectively. N_{bulk} and N_{ads} stand for the numbers of solid and adsorbed 4-ATP molecules illuminated by a laser light to obtain the corresponding normal Raman and SERS spectra, respectively.

N_{ads} can be obtained according to literature method³:

$$N_{ads} = N_d A_{laser} A_N / \sigma$$

Where N_d denotes the number density of gold nanoparticles. A_{laser} is the area of the focal spot of laser. A_N is the gold nanoparticle footprint area. N_d and A_N can be obtained from the TEM images. And σ is the surface area occupied by an adsorbed 4-ATP molecule (0.2 nm²/molecule).⁴

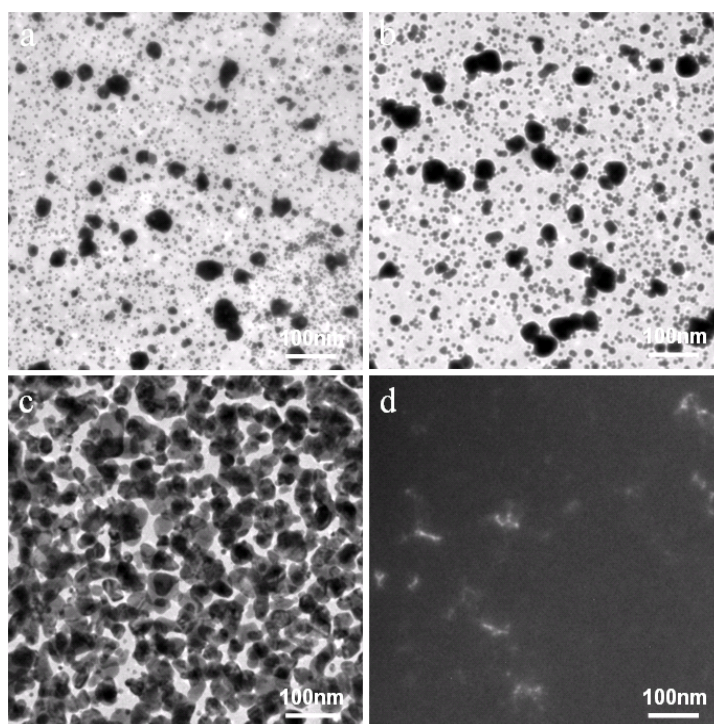


Fig. S1 TEM images of 6nm-AuNP-decorated PCL-SH PSC after AuCl₃ treatment. (a) 1hr in 1mg/ml AuCl₃ solution and (b) 1min, (c) 1hr, (d) 10hrs in 10mg/ml AuCl₃ solution.

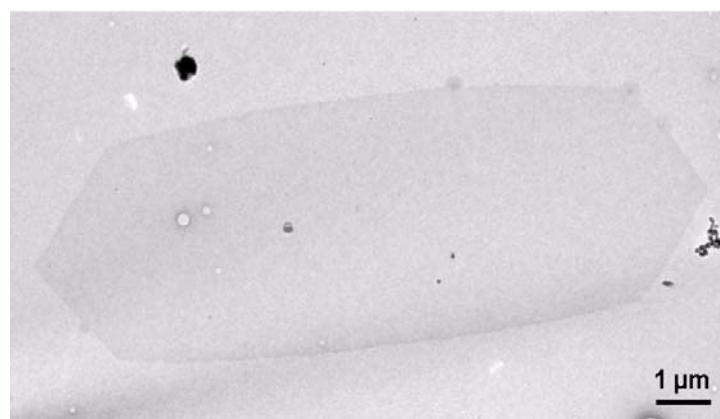


Fig. S2 TEM image of PCL-SH single crystal formed by solution crystallization.

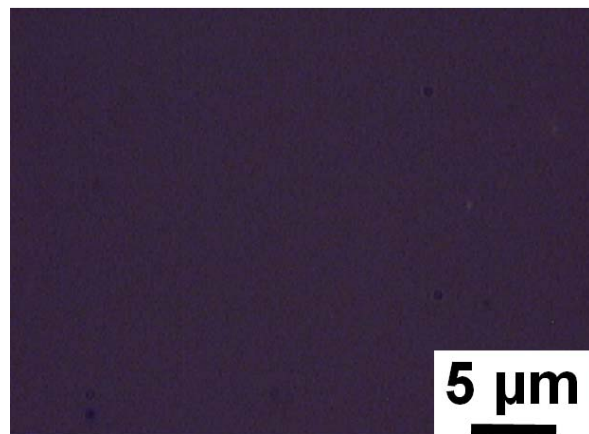


Fig. S3 Optical image showing the PCL-SH single crystal cast on a quartz substrate, which is not visible.

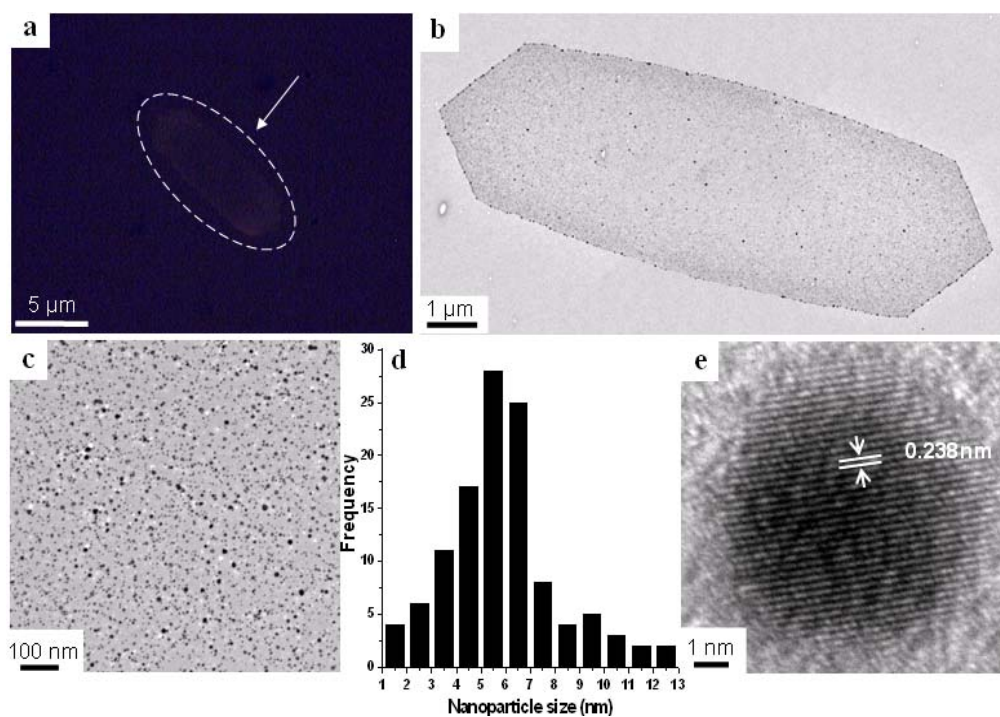


Fig. S4 (a) Optical image of one 6nm-AuNPs-decorated PCL-SH single crystal cast on glass slide. (b,c) TEM images of 6nm-AuNPs-covered PSC at different magnification. (d) Size distribution of AuNPs measured from (c). (e) High resolution image showing the lattice structure of AuNP (111).

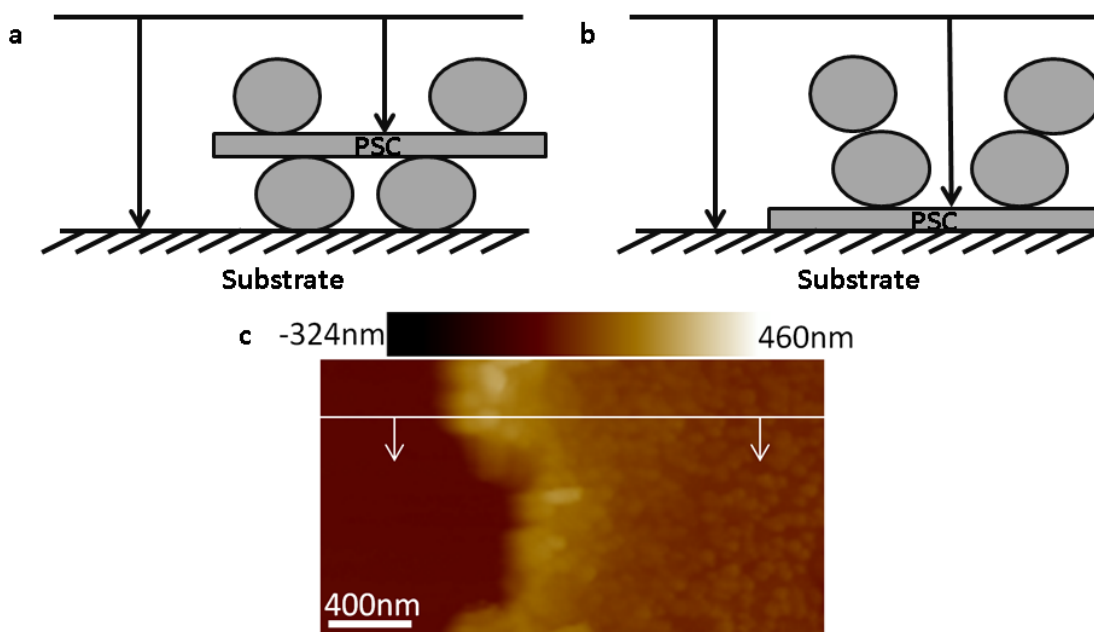


Fig. S5 Two possibilities for the increased thickness as shown in (a) and (b). One possibility is (a) the formation of “nanosandwich” structure, with the height difference between the two arrows being around 50-60nm (the thickness of the 8nm PSC plus the 40-50nm diameter AuNP). The other possibility (b) is the formation of overlapped nanoparticles, where the height difference should be just the thickness of PSC (around 8nm). The measured thickness between two arrows in (c) is around 50nm, demonstrating that our structure is “nanosandwich”.

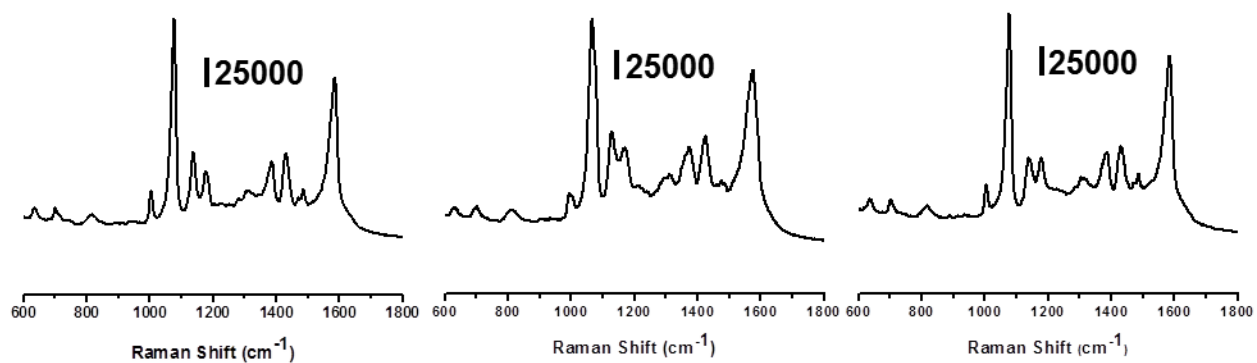


Fig. S6 SERS signals obtained at different locations showing good signal uniformity.

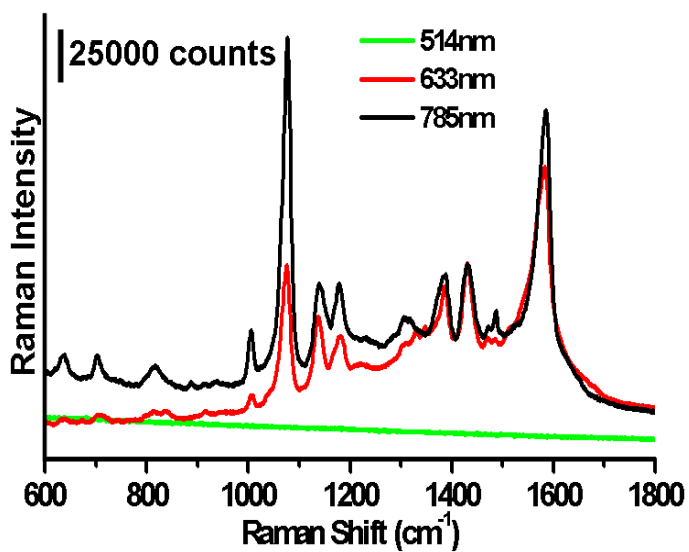


Fig. S7 SERS from 4-ATP molecules chemically adsorbed onto PSC@AuNP under different excitation laser.

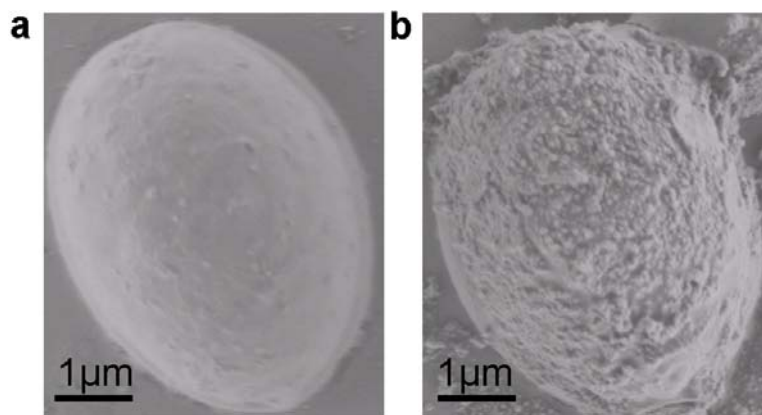


Fig. S8 SEM images showing single yeast cell before (a) and after (b) PSC@AuNP coating.

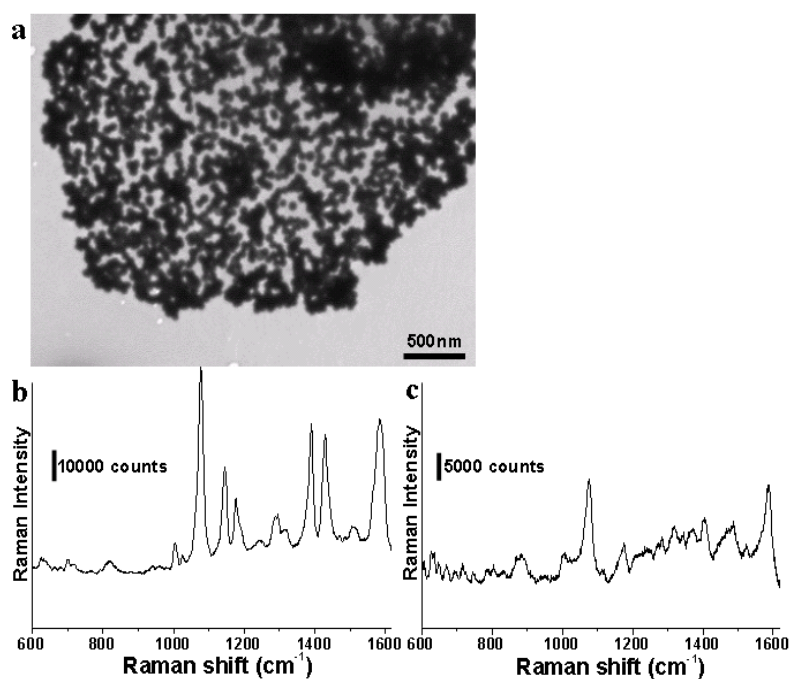


Fig. S9 (a) TEM image showing the regularly sphere-shaped AuNP (50nm in diameter) covering the surface of PCL-SH single crystal which is obtained by self-assembly method. The detailed fabrication process is reported elsewhere.⁵ (b) SERS obtained when 4-ATP is chemically adsorbed onto this structure. (c) SERS obtained by placing this structure on 4-ATP self-assembled monolayer.

Table S1. Raman Spectral Peak Assignment of 4-ATP according to Fig. 3a⁴ in the main text.

bulk ^a	SERS ^a	assignment ^b
1595m	1587s	ν CC, 8a(a ₁)
	1489w	ν CC+ δ CH, 19a(a ₁)
	1433m	ν CC+ δ CH, 19b(b ₂)
1367m	1387m	ν CC+ δ CH, 3(b ₂)
1206m		
	1305w	ν CC+ δ CH, 14(b ₂)
1173m	1180m	δ CH, 9a(a ₁)
	1140m	δ CH, 9b(b ₂)
1089s	1077s	ν CS, 7a(a ₁)
	1006w	γ CC + γ CCC, 18a(a ₁)
	818w	
799m		ν CH+ ν CS+ ν CC, 1(a ₁)
	700w	
634m	639w	γ CCC, 12(a ₁)

a. Units in wavenumber (cm⁻¹). b. ν , stretch; δ and γ , bend; s, strong; m, medium; w, weak.

Table S2. Tentative assignment of SERS spectrum measured from yeast cell surface in Fig. 3d⁶ in the main text.

Raman shift (cm ⁻¹)	Tentative band assignment
1553	N–H, C–H bend, C=C stretch
1505	Amide II
1466	CH ₂ bend (protein, lipid)
1322	C–H bend protein
1176	Phosphate vibration
1032	Phenylalanine
958	C–N stretch
837	Phosphate group
732	Adenine from flavin, C–S, N-acetyl-D-glucosamine

References:

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