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Supporting Information

SERS-Fluorescence-Superresolution Triple-mode Nanoprobe based on Surface Enhanced Raman Scattering and Surface Enhanced Fluorescence

Shenfei Zong [1], Hailong Tang [1], Kuo Yang[1], Hong Wang [2], Zhuyuan Wang [1], Yiping Cui [1]**

[1] Advanced Photonics Center, Southeast University, Nanjing 210096, Jiangsu, China

[2] Department of Laboratory Medicine, the First Affiliated Hospital of Nanjing Medical University, Nanjing 210029, China

*wangzy@seu.edu.cn cyp@seu.edu.cn

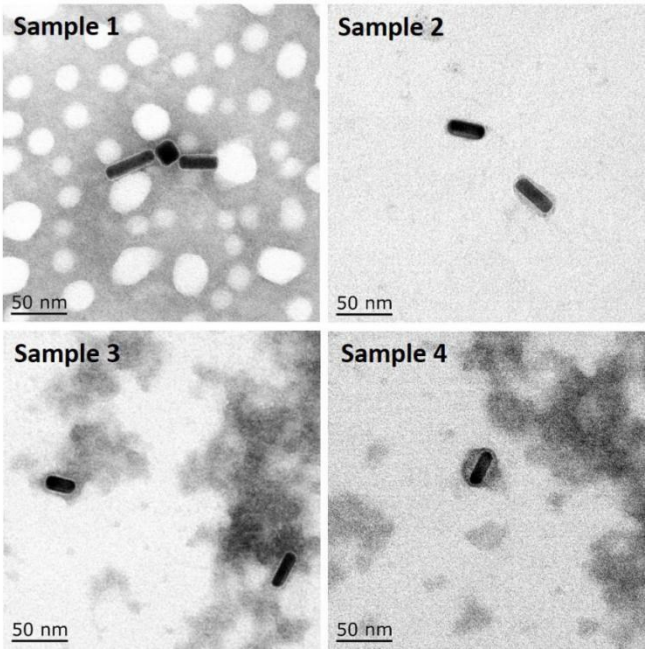

Figure S1. TEM image of **Sample 1** to **Sample 4**. The samples were stained by phosphotungstic acid (2wt %, pH adjusted to 7 by adding NaOH) before TEM imaging.

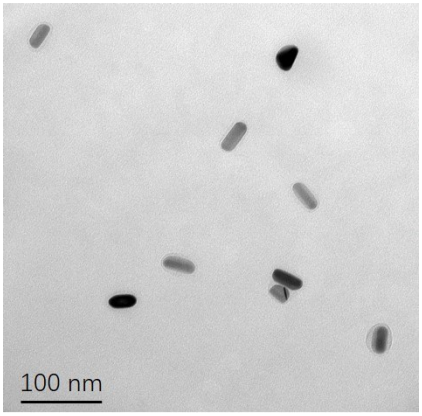

Figure S2. TEM image of PEs coated Ag NRs (**Sample 5**) without phosphotungstic acid staining.

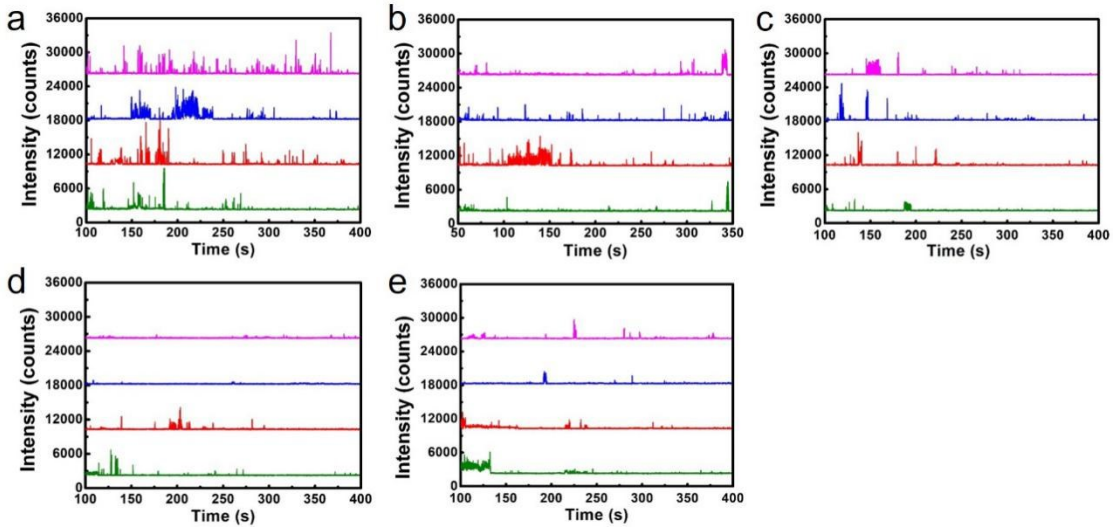

Figure S3. Typical photo-switching curves of different nanoprobes. (a) **Sample 3**, (b) **Sample 2**, (c) **Sample 4**, (d) **Sample 1**, (e) **Sample 5**. The curves are placed in parallel for clarity.

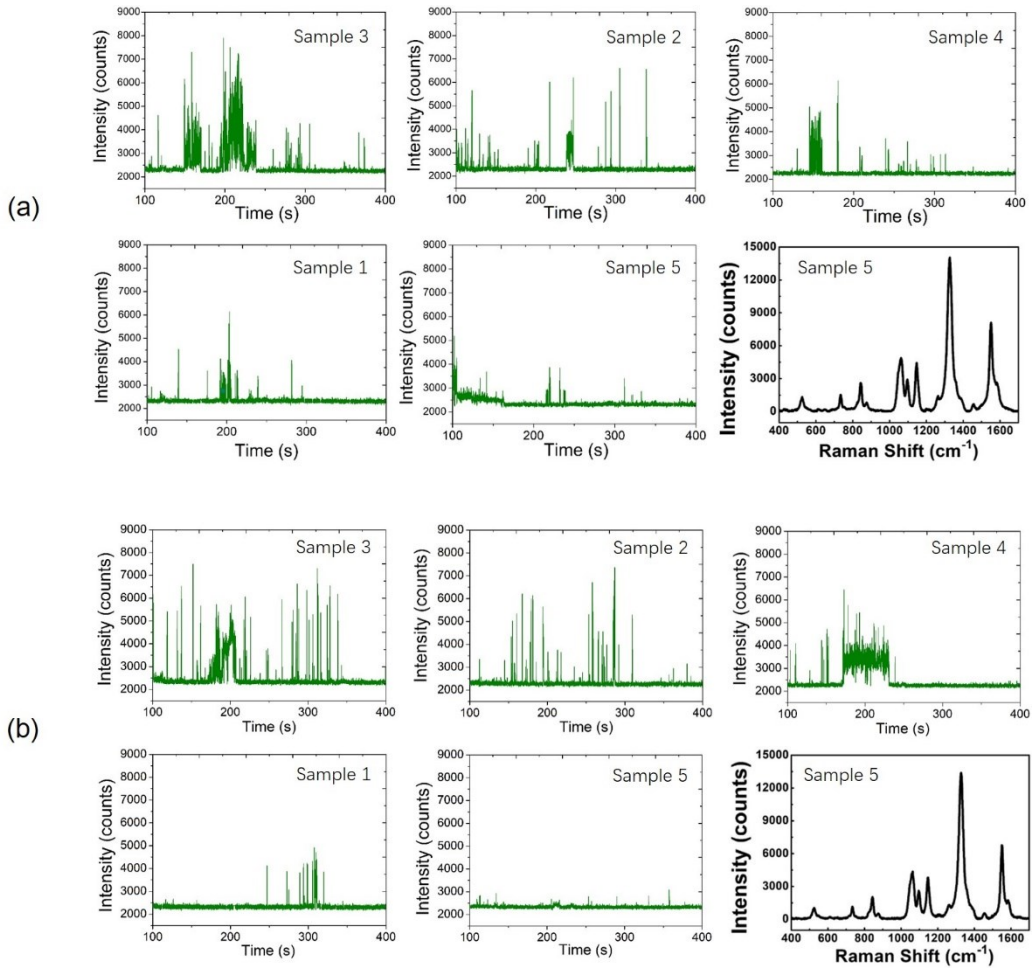

Figure S4. Fluorescence blinking and SERS performances of another two batches of samples.

Calculation of the enhancement of SERS and SEF was performed with FDTD Solutions

For SERS, the simulation setting is as follows:

Material model : Ag/Au –Johnson and Christy

Size: Ag NR radius ends: 0.00625, radius 0.00625, z span: 0.038; (μm)

Ag NR radius ends: 0.00425, radius: 0.00425, z span: 0.034

Background index: 1.33

Mesh accuracy: 0.0001 (μm)

Source: TFSFSource wavelength 0.633 (μm)

To better excite the SPR, the excitation light was set to be polarized along the long axis of the Ag NR. The calculated electromagnetic (EM) field is shown in Figure R3. Obvious EM enhancement is observed around the tips of the Ag NRs. The enhancement of SERS at the tips, which is proportional to the fourth power of the EM enhancement, is thus estimated to be 5.76×10^6.

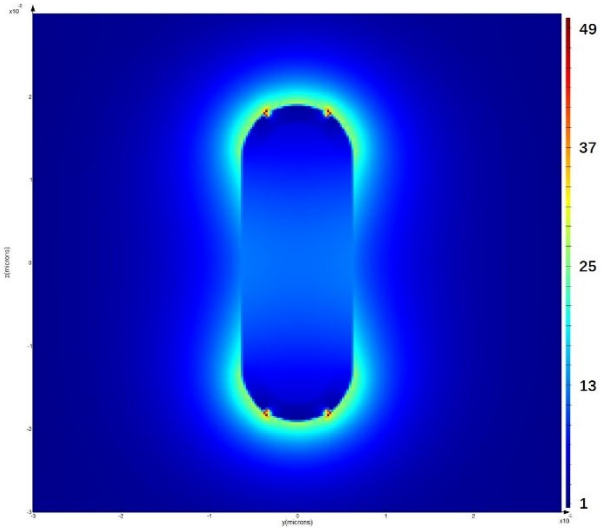

Figure S5. Calculated electromagnetic field distribution on the Ag NR surface. The color coded scale bar on the right represent the field enhancement factor.

The enhancement of SEF was calculated according to the following formula reported previously (*Japanese Journal of Applied Physics*, 2005, 44, 6833–6837).

$$E_{SEF} = {E_{EM}}^2 \times \frac{Q_{SEF}}{Q_0}$$

Here, E_{SEF} represents the enhancement of SEF, which is the ratio of the fluorescence intensity of the dye near the Ag NR to that without Ag NR. E_{EM} represents the enhancement of local electric field amplitude at the excitation wavelength. Q_{SEF} is the quantum efficiency (QE) of the fluorophore in the presence of the Ag NR. Q_0 is the QE of the fluorophore in the absence of the Ag NR. For A647, Q_0 is 0.33. E_{EM} and Q_{SEF} were obtained via simulation. The simulation setup is as follows:

Material model : Ag/Au –Johnson and Christy

Size: Ag NR radius ends: 0.00625, radius 0.00625, z span: 0.038; (μm)

Ag NR radius ends: 0.00425, radius: 0.00425, z span: 0.034

Background index: 1.33

Mesh accuracy: 0.0001 (μm)

Source: TFSFSource wavelength 0.642 (μm)

Dipole position: 0.02052, 0.02356, 0.0266, 0.02964, 0.0327 (μm)

Dipole wavelength: 0.665 (μm)

Dipole polarization: phase 0, theta 90, phi 0. (degree)

Analysis group: quantum_efficiency

The simulation results are presented in Table R1.

Table S1. Simulation of the SEF enhancement.

	Thickness of PEs (nm)	**E_{EM}**	**Q_{SEF}**	**E_{SEF}**
Sample 1	1.52	19.08	0.00096	1.06
Sample 2	4.56	7.619	0.083	14.60
Sample 3	7.60	5.196	0.482	39.43
Sample 4	10.64	3.234	0.806	25.54
Sample 5	13.70		0.945	

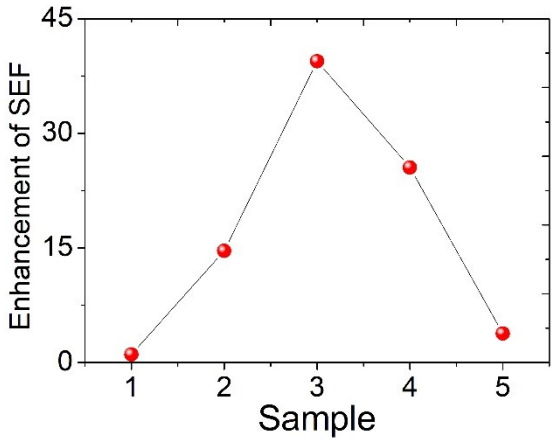

Figure S6. Calculated enhancement of SEF for different samples.

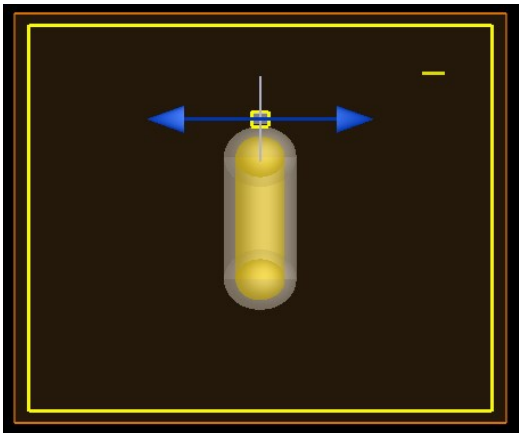

Figure S7. Representative view of the Ag NRs and dipole molecule in the xy plane while calculating QE.