

## Supporting Information

### Shell-Isolated Nanoparticle-Enhanced Luminescence of Metallic Nanoclusters for Sensitive Surface Analysis

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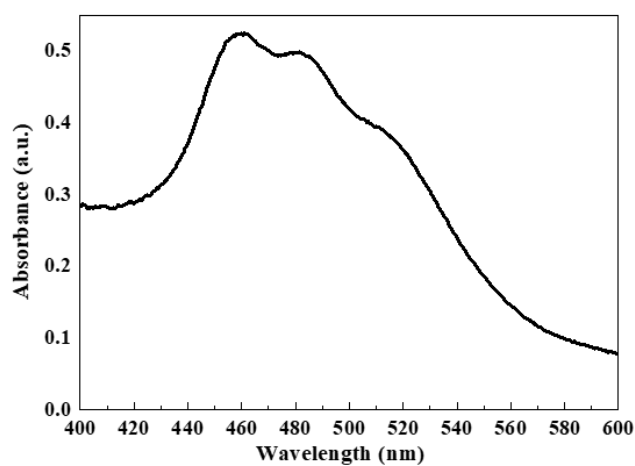
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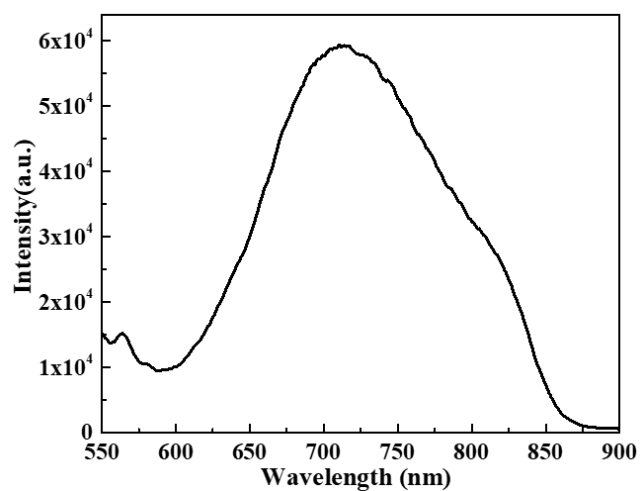
The details of calculation processes of the 3D-FDTD method

**Table S1.** Oligonucleotides sequences used in this work

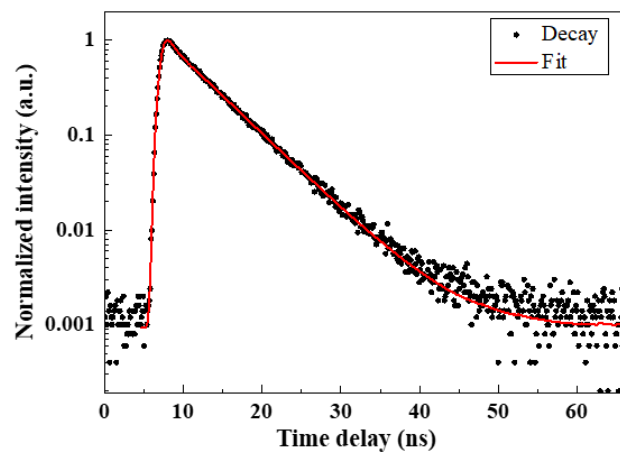
Name	Sequences: 5'-3'
DNA1:	SH-ATTCGCTACGAAT
DNA-Ag NCs	ACCCGAACCTGGGCTACCACCCTTAATCCCCATCGTAGCG
Ag NC-MBs	ACCCGAACCTGGGCTACCACCCTTAATCCCCTT AGTTACATTCTCCAGTTGATTAAAGGTGGTAGC-SH
Target	AATCAACTGGGAGAATGTA ACT



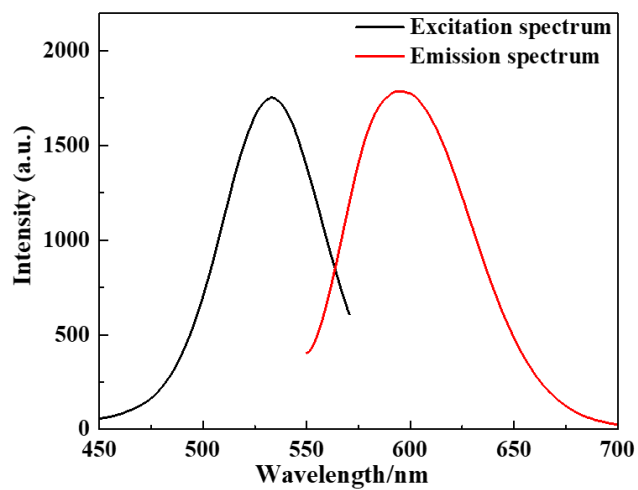
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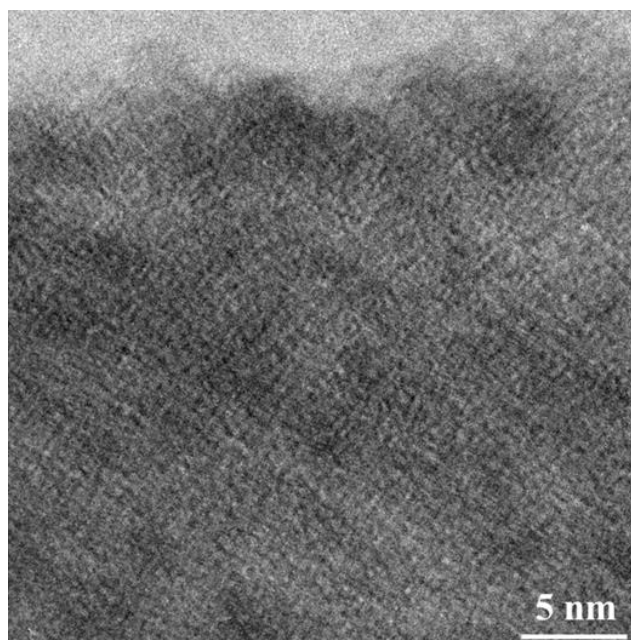
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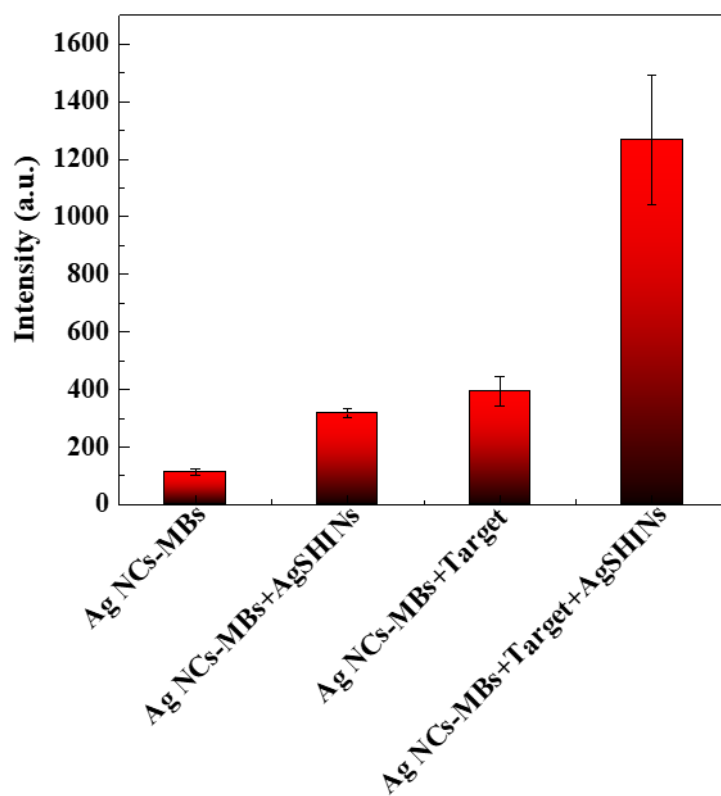
**Figure S3.** The decay curves of Au<sub>7</sub>Ag<sub>8</sub> NCs on a quartz substrate



**Figure S4.** Excitation and emission spectra of DNA-Ag NCs



**Figure S5.** TEM images of DNA-Ag NCs



**Figure S6.** Fluorescence signal of the proposed sensing platform under different experimental conditions. Error bars indicate one standard deviation which propagated errors from three independent experiments

**3D-FDTD Calculation Details for Ag SHINs Enhancement Mechanism.** To simplify the model, a  $2 \times 2$  Ag SHINs array was used to model the silica shell. Geometric parameters were derived from experimental measurements, thus, the nanogap between Ag SHINs was assumed to be 8 nm. Perfectly matched layer boundary conditions were adopted for all the calculations, and the calculation times were set as 1,000 fs to ensure convergence. Frequency-dependent optical constants for bulk Ag were taken from the literature.<sup>1</sup> The silica shell and spacer layer were modeled as dielectrics with an index of refraction of  $n = 1.4$ . The normal illumination mode was used where the electric field amplitude of the p-polarized plane waves was 1.0 V/m. The calculation parameters and processes of the three-dimensional finite-difference time-domain (3D-FDTD) were:

A point electric dipole source was used to model the excited molecule that behaves as an oscillating electric dipole. The enhancement decay rate can be inferred from the following relationship:

$$\frac{\gamma}{\gamma_0} = \frac{P}{P_0} ,$$

Where  $\gamma$  and  $P$  are the decay rate and radiation power in the presence of the SHINs layer configuration, respectively. Subscript 0 denotes that the molecule is in free space. In our calculations, two monitor boxes were set to collect data on the total and radiated power of the electric dipole in the system, and thus finally calculate the radiative ( $\gamma_r/\gamma_{r,0}$ ) and nonradiative ( $\gamma_{nr}/\gamma_{nr,0}$ ) decay enhancement.

Fluorescence enhancement arises mainly from comprehensive contributions of excitation and emission processes. A localized plasmonic field can generate large excitation enhancement ( $|M|^2 = |E_L/E_0|^2$ , where  $E_L$  and  $E_0$  are local and incident electric field, respectively) and radiative decay rates. The emission enhancement embodies the change in the quantum yield of molecules in the nanogap exposed to the SHINs layer configuration. To simulate the incoherent emission process of molecules, only one-point electric dipole was used in each simulation step, while the location of the dipole was varied on a discrete  $70 \times 70$  grid. The quantum yield (QY) can be defined as:

$$QY = \frac{\gamma_r/\gamma_{r,0}}{\gamma_r/\gamma_{r,0} + \gamma_{nr}/\gamma_{nr,0}} .$$

Therefore, we can define the fluorescence (EF) as:

$$EF = |M|^2 * Q .$$

Further calculation details for this method can be found in these papers.<sup>2-4</sup>

## References

- (1) Johnson, P. B; Christy, R. W. Phys. Rev. B **1972**, 6 (12): 4370-4379.
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- (4) Liaw, J. W.; Chen, J. H.; Chen, C. S; Kuo, M. K. Opt. Express **2009**, 17 (16):13532-40.