Controllable "Clicked-to-Assembled" Plasmonic Core-Satellite Nanostructures and its Surface-Enhanced Fluorescence in Living Cells

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Synthesis of nanoparticles.

(1) Synthesis of 30 nm, 50 nm and 70 nm GNPs[1].

30 nm GNPs: 150 mL of sodium citrate solution (2.2 mM) was placed in a three-necked flask with vigorous stirring and heated at 130 °C for 15 min. After heated to boiling, 1 mL of $HAuCl_4$ (25 mM) solution was added quickly, the color of the solution changes from yellow to grayish blue. Then after heated for 10 min, the color of the solution changed into pink, indicating the formation of 10 nm Au seeds. Later, 2 mL of $HAuCl_4$ solution (25 mM) were injected slowly at 90 °C twice, and reacted for 30 min each time to obtain 30 nm GNPs.

For the synthesis of 50 nm and 70 nm GNPs, stock solutions of $HAuCl_4$ (25 mM) and sodium citrate (60 mM) were prepared. A solution of 55 mL 30 nm GNPs and 53 mL ultrapure water was mixed with 2 mL of sodium citrate (60 mM) and heated to 90 °C. Then, 3 mL of $HAuCl_4$ solution (25 mM) were injected slowly at 90 °C for three times, and reacted for 30 min each time to obtain 50 nm GNPs. If 9 mL of $HAuCl_4$ solution (25 mM) was added and reacted for 30 min each time, the 70 nm GNPs were prepared. The GNPs were cooled to room temperature and stored at 4 °C for use.

(2) Synthesis of 20 nm GNPs[2]: A total of 95 mL of ultrapure water contained with 1 mL of $HAuCl_4$ (25 mM) was heated to reflux under stirring, and then add 4 mL of trisodium citrate solution (1%, w/w) rapidly. Then stir quickly for 15-20 min. When the color of the solution changes from light red to light purple and finally becomes wine red, continues to react for 15 min at room temperature, keep stirring until the solution cools and stored at 4 °C for use.

(3) Synthesis of 5 nm GNPs[3]: Mix 40 mL of $HAuCl_4$ solution (0.25 mM) with 40 mL of trisodium citrate solution (0.25 mM), then add 1.2 mL of 0.1 M freshly prepared $NaBH_4$ solution to the flask rapidly, stir vigorously for 2 min, and continue to react for 45 min at room temperature. Stored at 4 ^oC for further use.

(4) Synthesis of 15 nm silver nanoparticles (SNPs). SNPs of about 15 nm were prepared by the steps as follows[4]:

Dissolve 0.792 g of β-CD in 98.6 mL of ultrapure water. Then 0.4 mL of $HAuCl_4$ (10 mM) solution was added into it. After 2 min, 1 mL of NaOH (1.0 M) solution was added to adjust the pH of the solution to ~10-12. The mixture was heated to 130 ^oC for 20 min. Later, the solution turned pink, producing a gold species of about 5 nm. After the solution was cooled to room temperature, 3 mL of the solution was diluted with 97 mL of ultrapure water. After 2 min, 1 mL of NaOH (1.0 M) solution was added. After 5 min, 1 mL of $AgNO_3$ (20 mM) solution was added to fully adsorb the silver ions to the surface of the gold seed. After heating at 130 ^oC for 10 min, add 1 mL of trisodium citrate solution (40 nM) and continue heating for 20 min until the solution is yellow, indicating the formation of gold-core silver shell nanoparticles. The solution was naturally cooled to room temperature and stored at 4 ^oC for use.

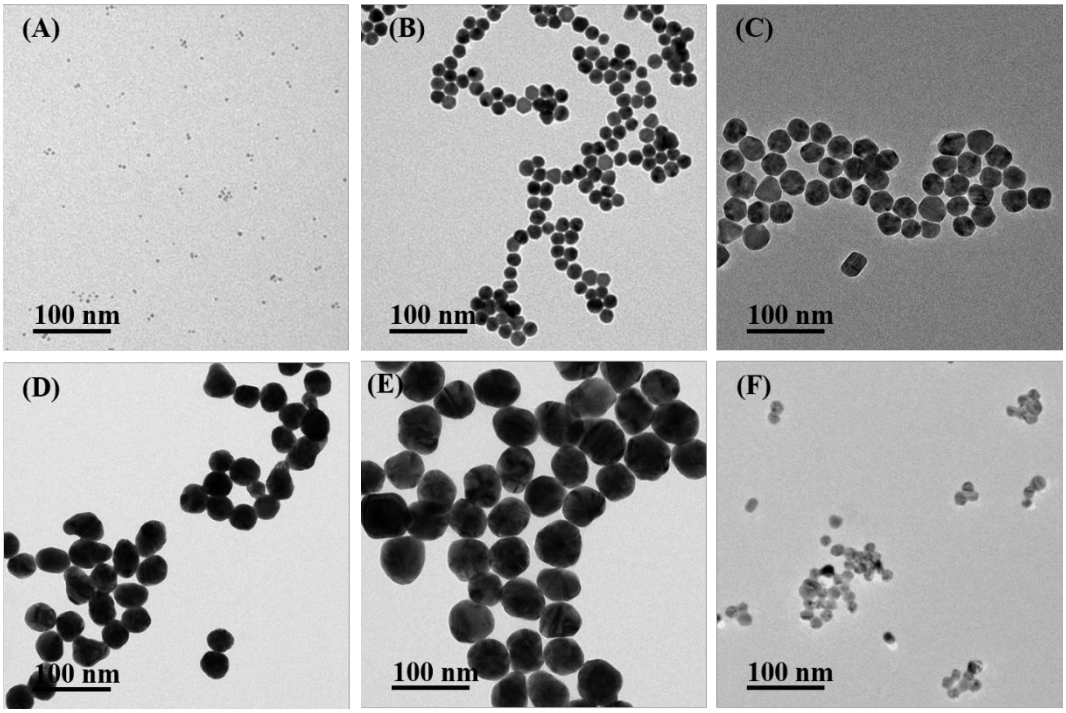

Figure S1. TEM images of (a) 5 nm GNPs, (b) 20 nm GNPs, (c) 30 nm GNPs, (d) 50 nm GNPs, (e) 70 nm GNPs, (f) 15 nm AgNPs

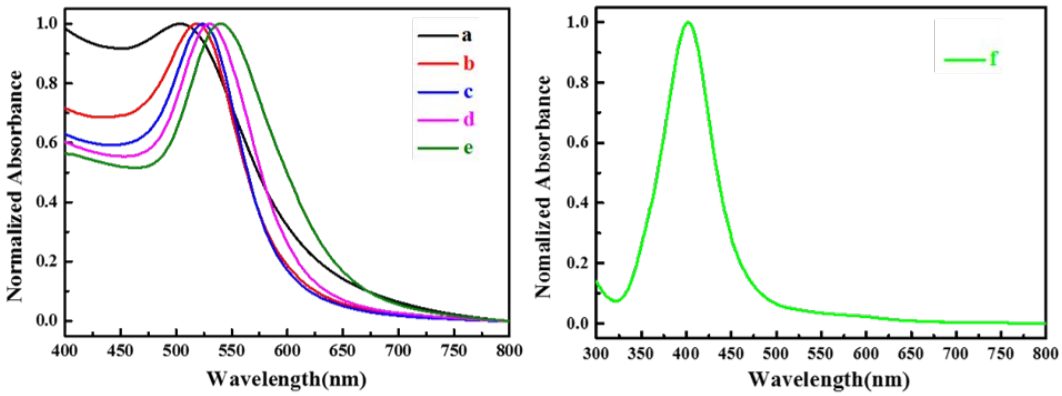

Figure S2. The UV-Vis absorption spectra of (a) 5 nm GNPs, (b)20 nm GNPs, (c)30 nm GNPs, (d)50 nm GNPs, (e)70 nm GNPs, (f)15 nm AgNPs.

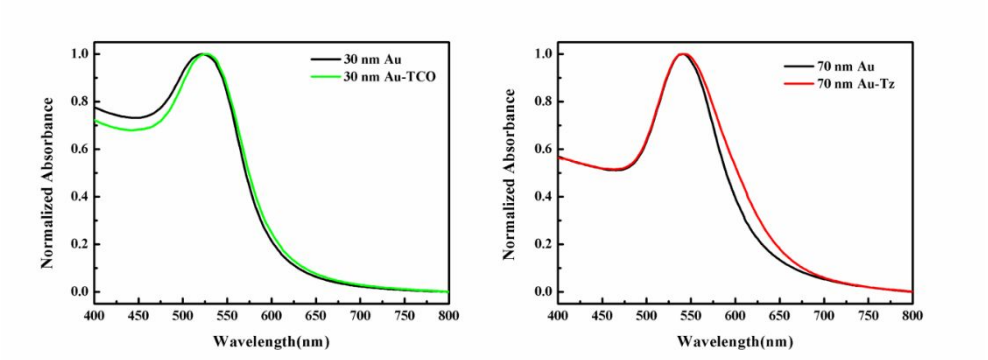

Figure S3. UV-Vis absorption spectrum before and after 30 nm GNPs (Left) and 70 nm GNPs were modified with TCO and Tz (Right).

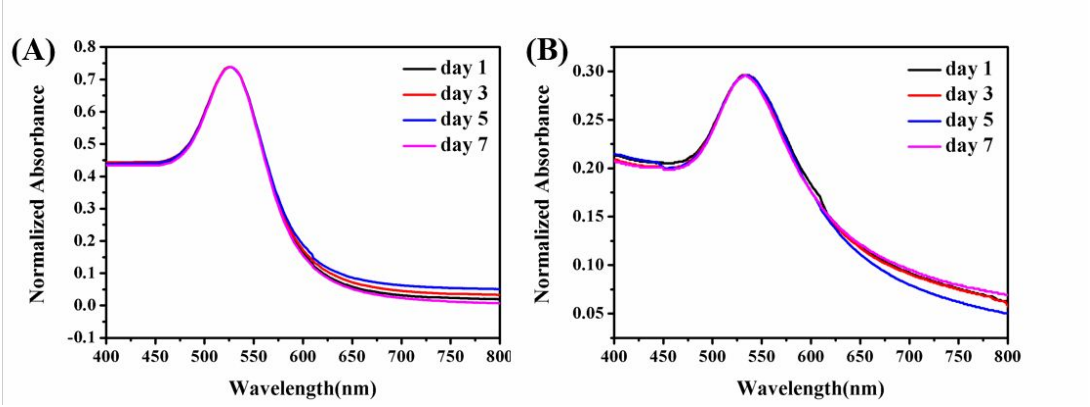

Figure S4. The visible absorption spectra change of TCO-GNPs (A) and Tz-GNPs (B) with different store days.

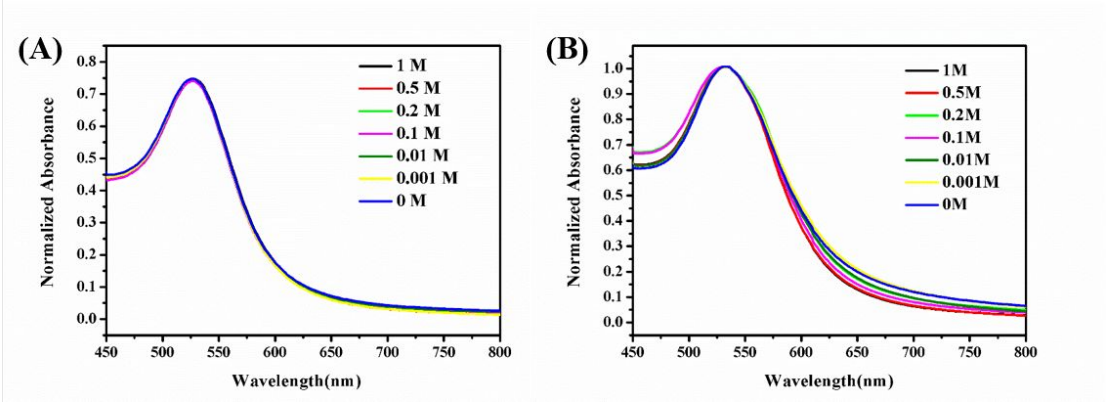

Figure S5． The UV-Vis absorption spectra changes of TCO-GNPs (A) and Tz-GNPs (B) with NaCl concentration.

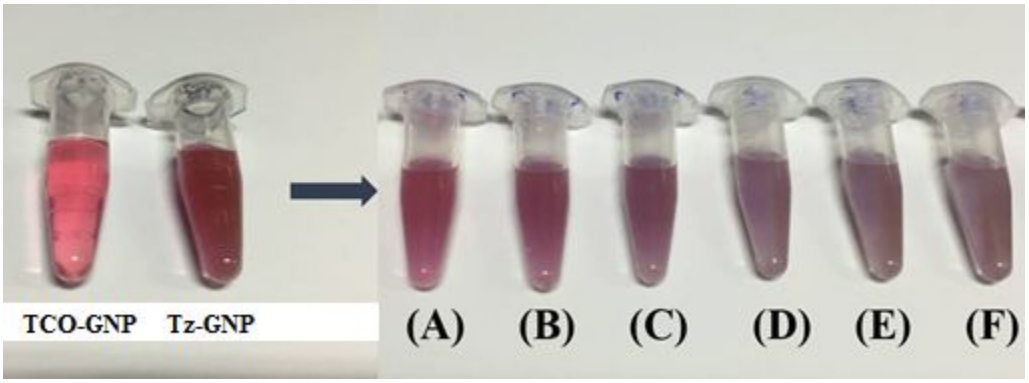

Figure S6. The photograph of CS nanostructure samples assembled with different feeding ratio of satellite (TCO-GNP) to core NPs (Tz-GNP). (A) 1.3, (B) 2.6, (C) 4.1, (D) 5.2, (E) 6.2, (F) 7.8.

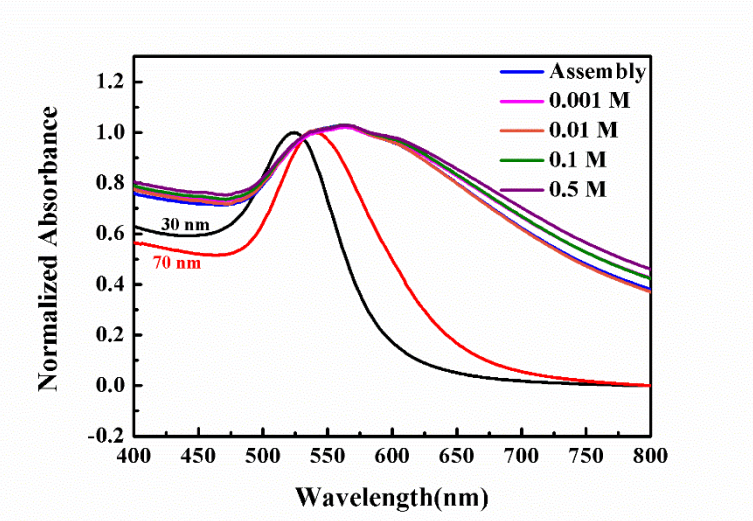

Figure S7. UV-Vis absorption spectrum changes of CS nanostructures in different concentrations of NaCl solution

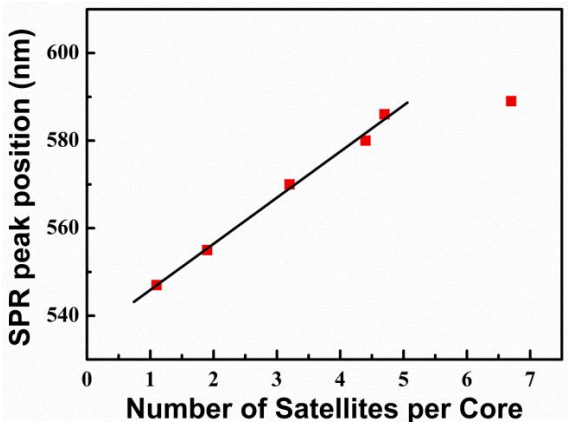

Figure S8. The effect of satellites number on SPR peak position

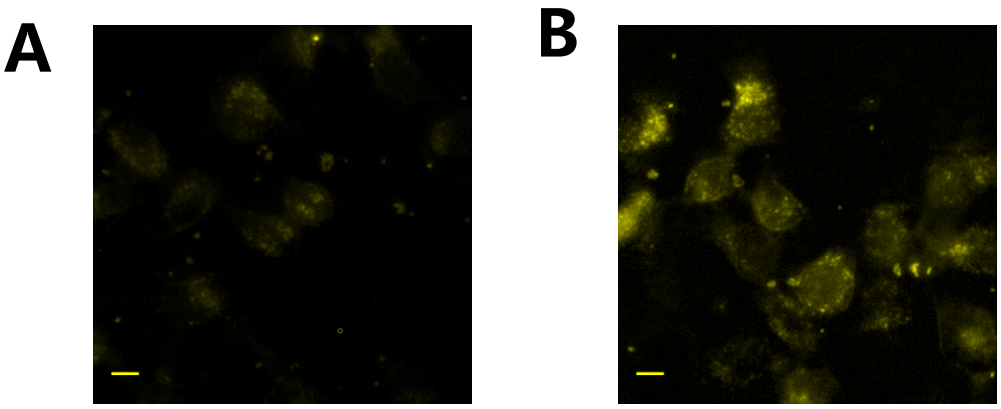

Figure S9. Dark field images of cells incubated with CS nanostructures. The cells were incubated without aptamer (A) or 100 nM aptamer (B). Scale bar is 10 um.

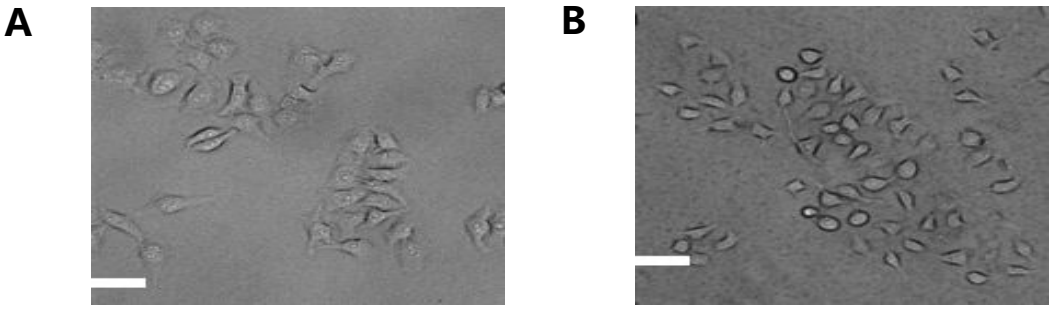

Figure S10. Transmission images of HeLa cells without CS nanostructures (A) or with 30 pM CS nanostructures (B).

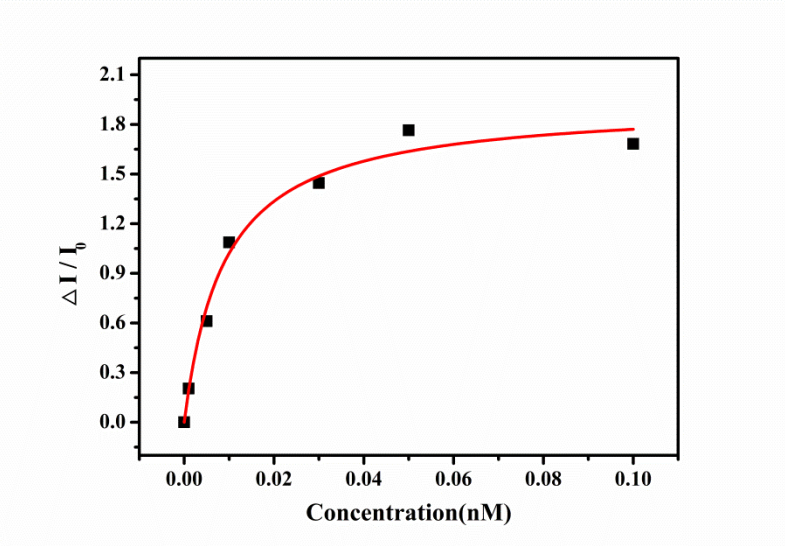

Figure S11. The influence of CS nanostructures on the fluorescence intensity of HeLa cell. $\Delta I=I-I_0$. I_0 and I are the average fluorescence intensity of Hela cell before or after CS nanostructures were incubated with cells.

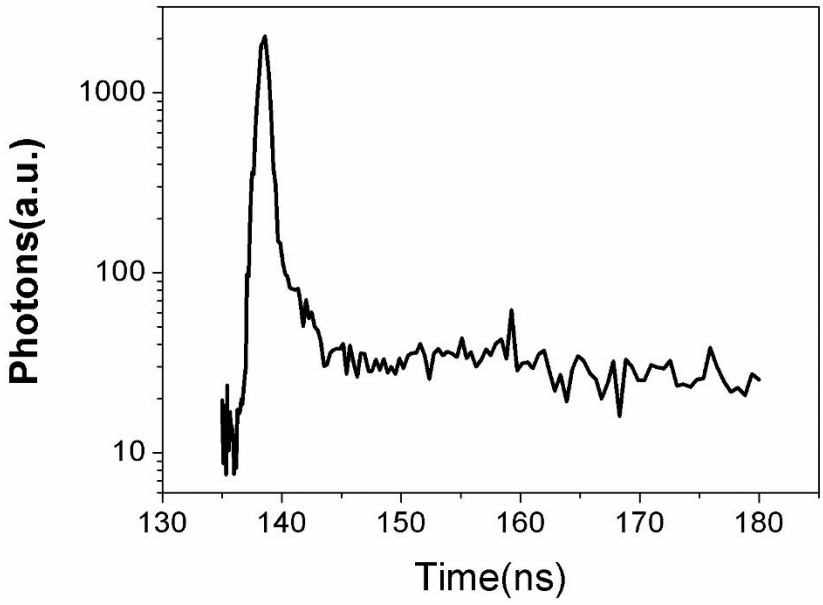

Figure S12. Instrument response function (IRF) of time-resolved fluorescence lifetime

measurement system.

References

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[4] Pande S, Ghosh S K, Praharaj S, et al. Synthesis of Normal and Inverted Gold−Silver Core−Shell Architectures in β-Cyclodextrin and Their Applications in SERS [J]. *The Journal of Physical Chemistry C*, **2007**, 111(29): 10806-10813.