Electronic Supplementary Information

A new plasmonic Pickering emulsion based SERS sensor for in situ reaction monitoring and kinetic study

Lei Ouyang[a,b] *Dingyi Li,*[a] *Lihua Zhu,* [*,a] *Wenwen Yang,*[b] *Heqing Tang*[*,b]

[a] School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, P. R. China

[b] Key Laboratory of Catalysis and Materials Science of the State Ethnic Affairs Commission and Ministry of Education, College of Resources and Environmental Science, South Central University for Nationalities, Wuhan 430074, P. R. China.

*Corresponding Authors: Professor Lihua Zhu, E-mail: lhzhu63@mail.hust.edu.cn; Professor Heqing Tang, E-mail: tangheqing@mail.scuec.edu.cn, hqtang62@aliyun.com).

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S1. Synthesis of CD-Ag NPs and citrate-Ag NPs

In a typical process, 5 mL of β-CD solution (0.01M) was added to 32.5 mL of water, to which 2 mL of NaOH (0.1 M) was added under stirring, giving pH around 12. After the solution was heated to 60 ˚C, 0.5 mL of $AgNO_3$ solution (0.1 M) was poured in under stirring. The solution immediately became blackish brown color. The solution was further reacted for 1 h under stirring at 60 ˚C, and it turned to yellow, indicating the formation of CD-Ag NPs. The resultant yellow solution was centrifuged at 12000 rpm for 5 min, and the residue was washed with water 2 times. Finally, the CD-Ag NPs were re-dispersed in water. Citrate-Ag NPs were synthesized using sodium citrate as the reducing agent in accordance with established procedures.[1] Silver nitrate (19 mg) was dissolved in water (100 mL) and heated to boiling. Then, sodium citrate (2 mL of 1% solution) was added dropwise into the solution, after keep boiling further for 30 min; the obtained colloid was cooled to room temperature for use.

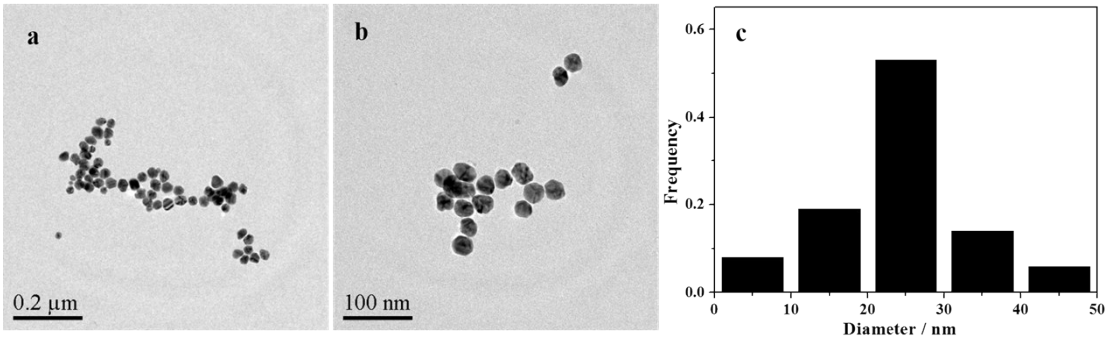

Fig. S1 TEM images of the synthesized CD-Ag NPs and its size distribution. The size distribution based on the statistical results of more than 100 particles from TEM images.

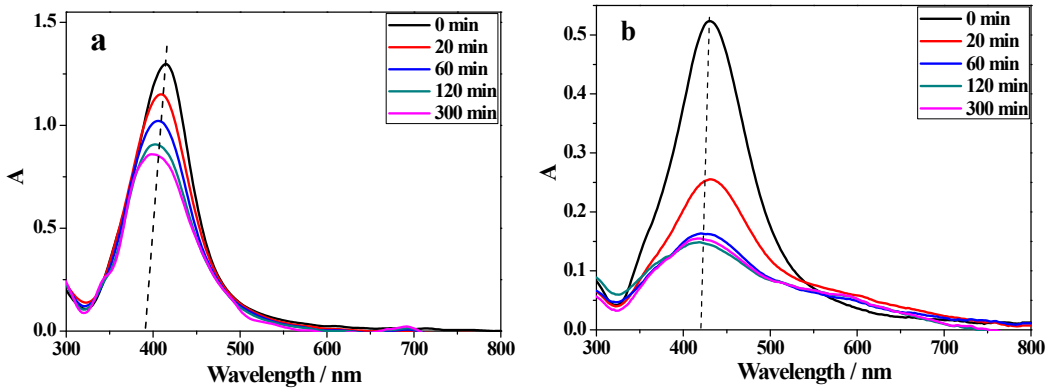

Fig. S2. UV-vis spectra monitored during the process of modifying HS-CD onto (a) CD-Ag NPs and (b) citrate-Ag NPs.

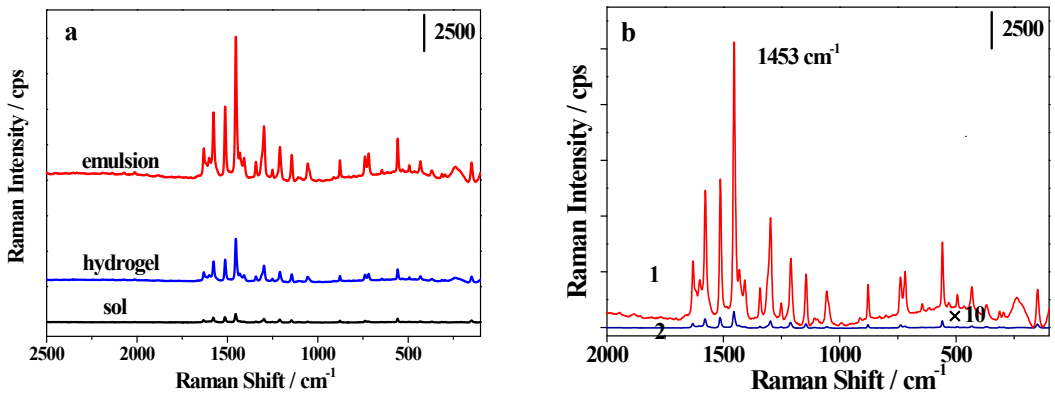

Figure S3. (a) A simple comparison between the SERS performances of the CD-S-Ag emulsion, CD-S-Ag sol and CD-S-Ag hydrogel with 1,10-phenthrpline (10 mg L^{-1}) as the SERS probe. (b) SERS and Raman spectrum for enhancement factor calculation. 1 SERS spectrum of 10 mg L^{-1} 1,10-phenthrpline with CD-S-Ag emulsions as substrate, 2 Raman spectrum of 1 mol L^{-1} 1,10-phenthrpline.

Enhancement Factor (EF) was calculated by using the standard formula, [2]

$$EF=(I_{SERS}/ C_{SERS})* (C_{NR}/I_{NR})$$

where I_{SERS} and I_{NR} are the intensity at the chosen wavenumber in obtained SERS and normal Raman spectrum, respectively. C_{SERS} and C_{NR} are the concentration of analytes used for SERS and normal Raman scattering measurements, respectively. The most intense peak (1453 cm^{-1}) was considered for EF calculation,

$$EF=(9611/5.6\times 10^{-5})*(1/57.45)$$

The EF was calculated to about 3.0×10^{6}.

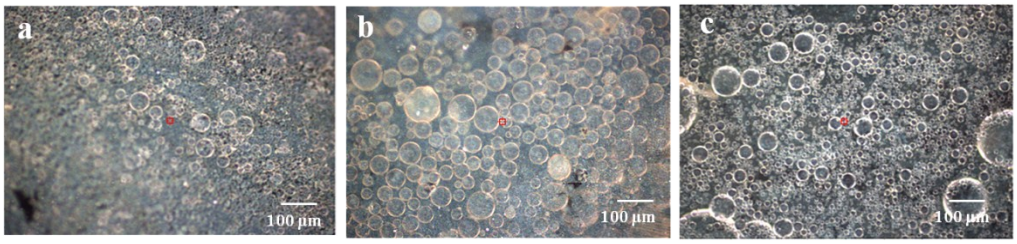

Fig. S4. Optical microscopic images of the CD-S-Ag NPs emulsion platforms modified with different CD-SH concentrations by tuning the molar ratio of Ag and HS-CD at different ratios of (a) 2:1, (b) 1:1, and (c) 0.5:1.

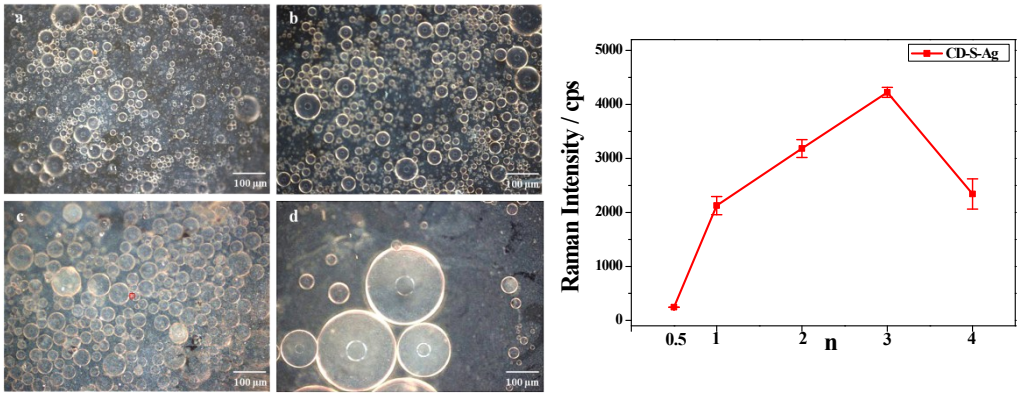

Fig. S5. Optical microscopic images of CD-S-Ag NPs emulsions with different NPs amounts of (a) *n*=0.5, (b) *n*=1, (c) *n*=3, and (d) *n*=4. Here *n* presented the concentrated times of CD-S-Ag particles. (e) Effects of the used NPs amount (*n* value) on the SERS intensity of 10 mg L^{-1} 1,10-phenthrpline at 1453 cm^{-1} observed on the emulsion platform.

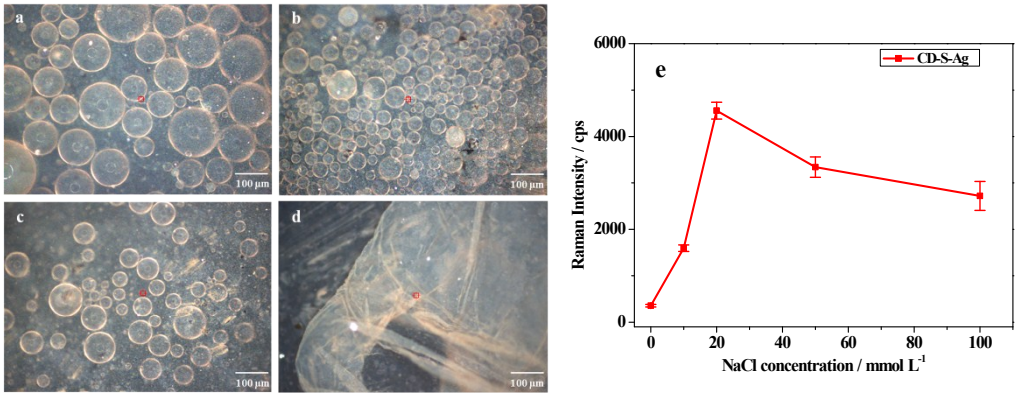

Fig. S6. Optical microscopic images of CD-S-Ag NPs emulsion platforms obtained with addition of different NaCl amounts of (a) 10mM, (b) 20mM, (c) 50mM, and (d) 100mM. (e) Effects of the used NaCl concentration on the SERS intensity of 10 mg L^{-1} 1,10-phenthrpline at 1453 cm^{-1} observed on the emulsion platform.

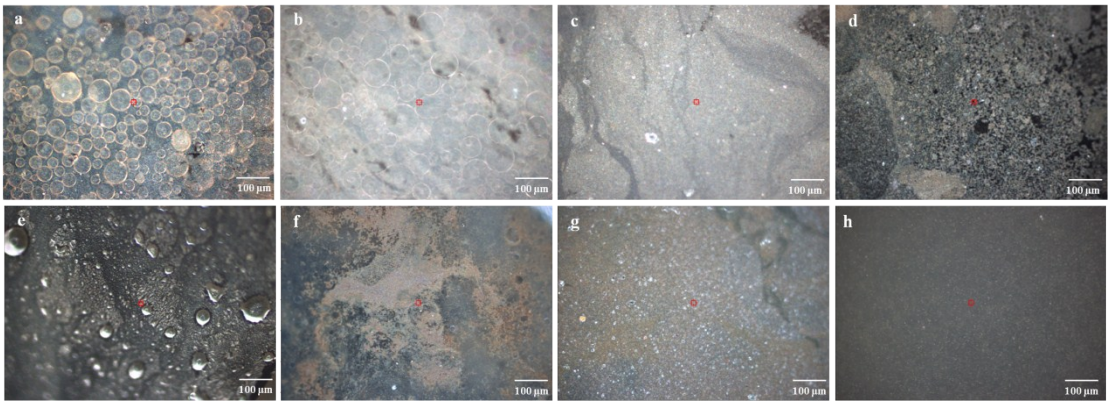

Fig. S7. Optical microscopic images of CD-S-Ag NPs emulsions obtained with different organic solvents of paraffin, toluene, dichloroethane, hexane, carbon tetrachloride, heptane and octane (in the order from a to g). (h) Optical microscopic image of CD-S-Ag sol without emulsification was given as a control.

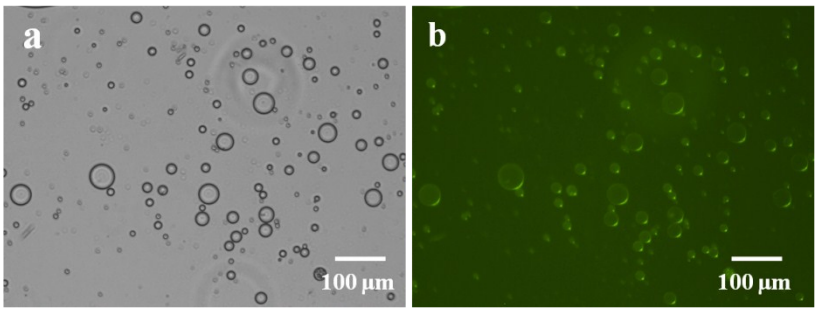

Fig. S8. (a) Optical microscopic images of the CD-S-Ag NPs emulsions. (b) Fluorescence images of CD-S-Ag emulsions in which the CD-S-Ag NPs were pre-modified with RhB (0.5 μg L^{-1}).

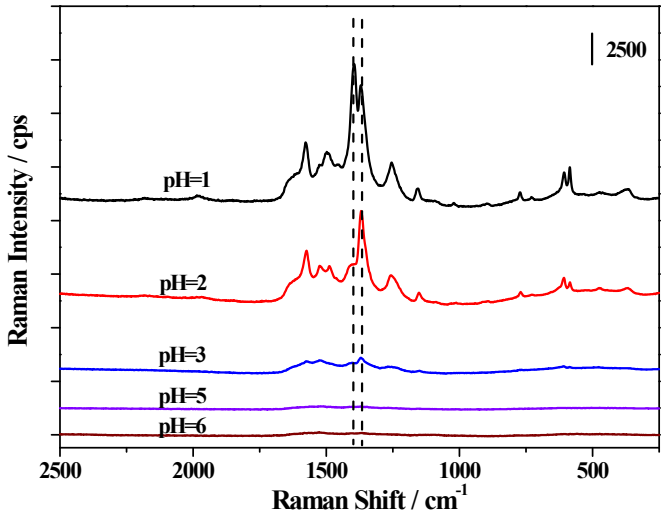

Fig. S9. SERS spectra of OPD after emulsified with water at different pH values.

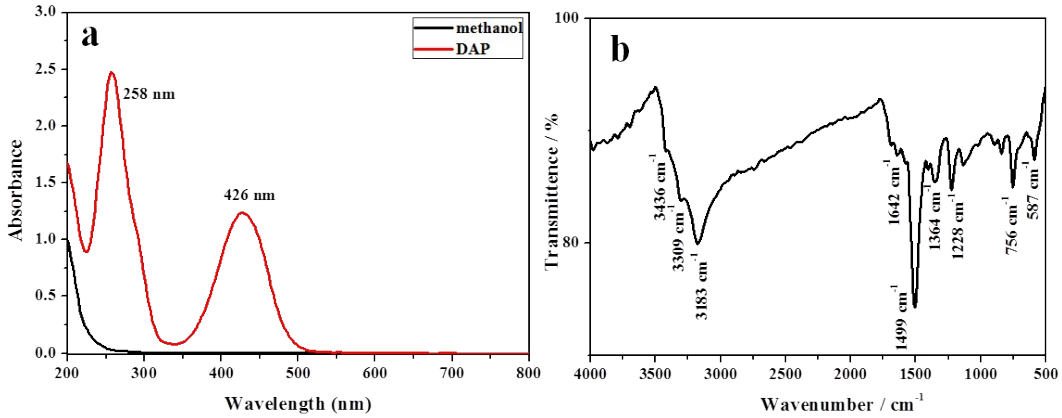

Fig. S10. (a) UV-vis absorption spectra of synthesized DAP. (b) IR spectra of synthesized DAP.

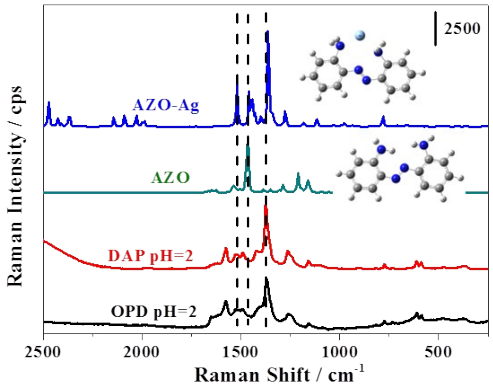

Fig. S11. Comparison of SERS spectra of DAP and OPD with Raman spectra of AZO and AZO-Ag complex at pH=2. A similar intense peak was observed at 1369 cm^{-1} in the cases of both AZO-Ag and OPD, but intense peaks occurred at 1513 and 1455 cm^{-1} for ZAO-Ag unlike OPD.

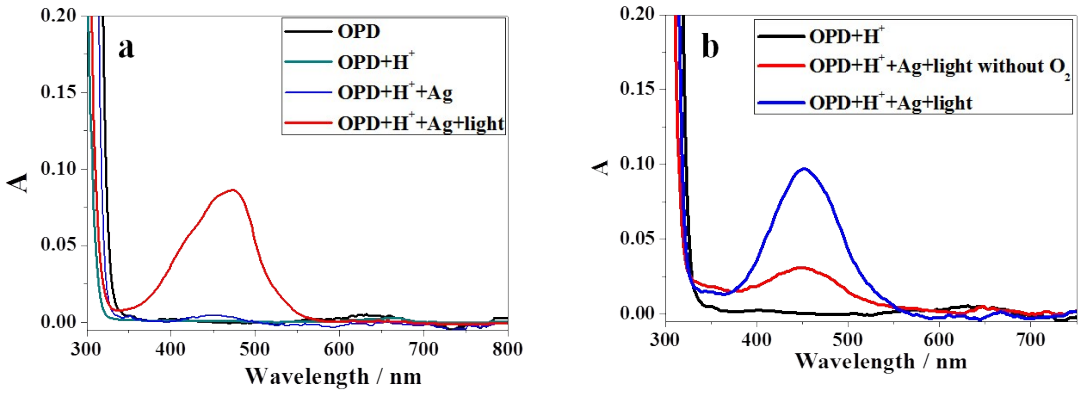

Fig. S12. The effect of light and oxygen on the reaction of OPD from UV-vis absorption spectra. (a) UV-vis absorption spectra of the reaction solution with or without light. (b) UV-vis absorption spectra with or without O_2 for the reaction. When the experiment was carried out without visible light or O_2, such a reaction proceeded quite slowly and even was hindered.

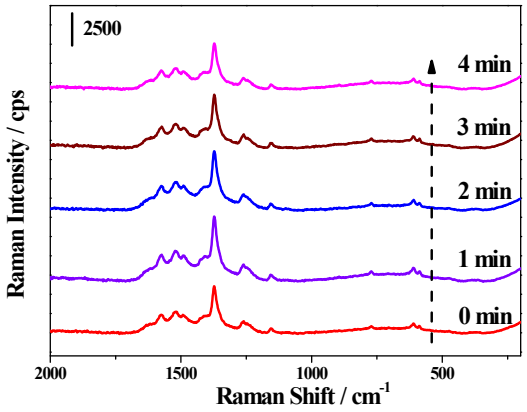

Fig. S13. Effect of detecting time (i.e., reaction time) on the SERS spectra of synthesized DAP. The results demonstrated that DAP itself on the emulsion platform was stable.

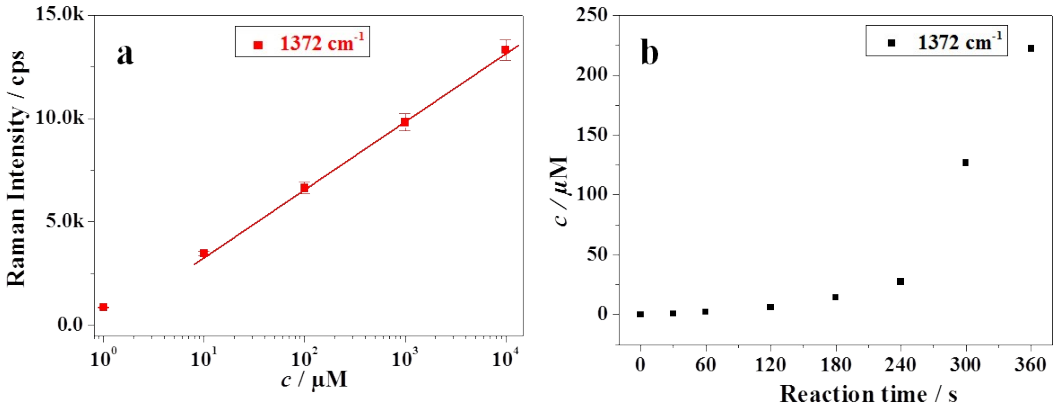

Fig. S14. (a) Plot of the SERS intensity at 1372 cm^{-1} versus the logarithm of concentrations of DAP, The linear range from 10 μM to 10 mM could be obtained with a good correlation coefficient of 0.997. (b) Plot of concentration of DAP versus the reaction time revaluated by the linear equation in (a).

Reference

[1] P. C. Lee and D. Meise, *J. Phys. Chem.* 1982, **86**, 3391.

[2] I. Chakraborty, S. Bag, U. Landman, and T. Pradeep, *J. Phys. Chem. Lett.* 2013, **4**, 2769.