Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Surface-enhanced Raman spectroscopy Detection of Organic Molecules and *in situ* Monitoring of Organic Reactions by Ion-induced Silver Nanoparticle Clusters

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TABLE OF CONTENT

S1. Experimental method

Ag@ IACNPs preparation

The Ag@IACNPs was prepared based on our previous work. Briefly, 5 mL of sodium citrate-reduced silver sol was centrifuged (5500 rpm, 10 min, 15 ° C), after the removal of the supernatant, 15 μL of the centrifuged silver sol was mixed with 15 μL of potassium iodide solution (1 mM) at room temperature for 30 minutes. Then, add 1 μL of the mixture sample and 2 μL of Ca^{2+} (0.01 M $CaCl_2 \cdot 2H_2O$) one after another. The SERS test instrument is made by WITec alpha 300R. (Germany). The laser wavelength is 532 nm, the scan time is 30 s, and each test is accumulated once.

Sample preparation for SERS

Organic small molecule

Organic samples (AR grade) were purchased from Chongqing Chuandong Chemical (Group) Co., Ltd. We dissolve 10 μL of pure sample in the mixture of 30 μL pure water and 100 μL acetone, and then add 1 μL mixture sample and 2 μL of Ca^{2+} (0.01 M $CaCl_2 \cdot 2H_2O$) one after another to AgIACNPs. After that, the mixture was shaken well for SERS detection. The aggregation of nanoparticles does not increase in a linear relationship.

Monitoring organic reactions

Organic samples (AR grade) were purchased from Chongqing Chuandong Chemical (Group) Co., Ltd. After the reaction started, 20 μL reaction solution was added into 30 μL pure water to quench the reaction. Shake the mixture well, and then, add 1 μL of the mixture sample and 2 μL of Ca^{2+} (0.01 M $CaCl_2 \cdot 2H_2O$) one after another.

S2. TEM images of Ag@IACNPs

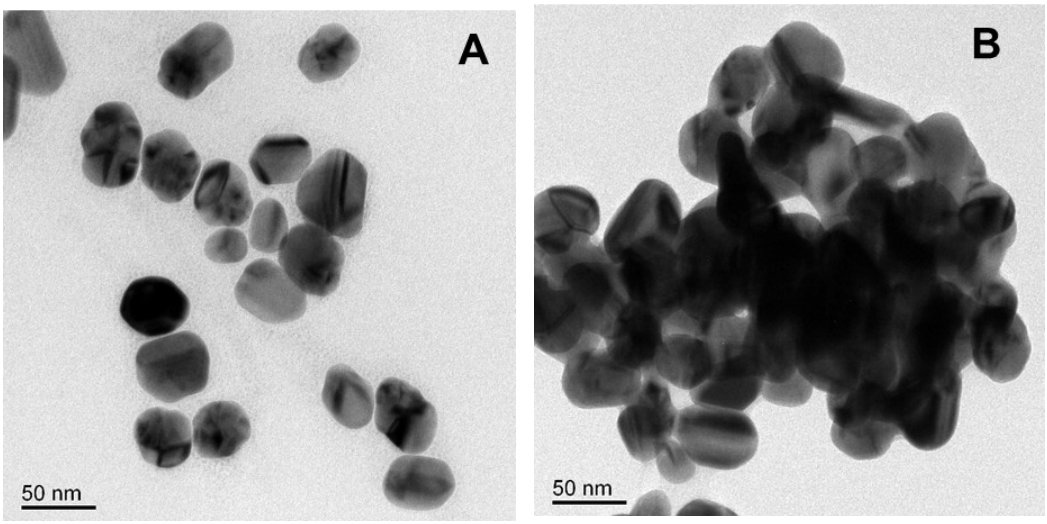

Figure S1. (A) Transmission electron microscopy (TEM) image of the nanoparticles (Ag@IA). (B) TEM image of nanoparticles after introducing Ca^{2+} ions in the above system (Ag@IACNPs).

S3. DLS spectra of Ag@IACNPs

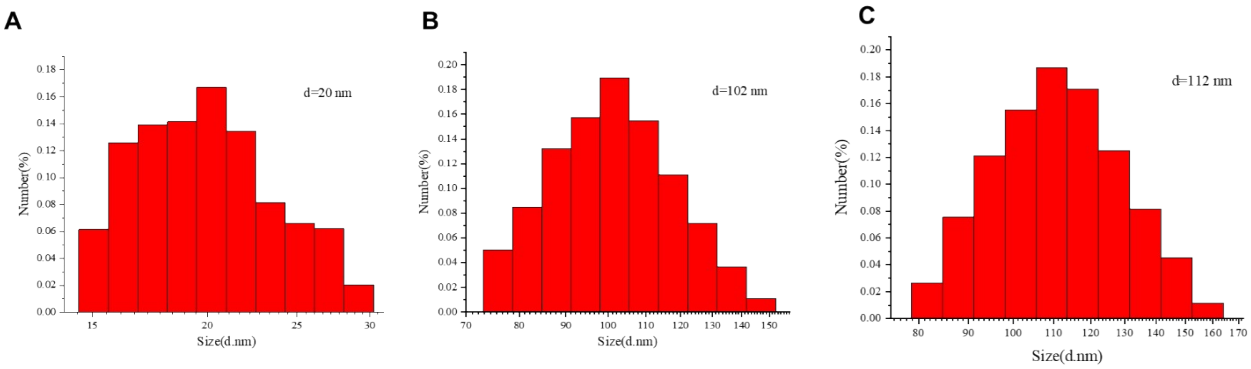

Figure S2. (A) DLS data of the nanoparticles after adding potassium iodide solution to replace citrate ions (Ag@I). (B) DLS data of the nanoparticles after adding Ca^{2+} ions to the Ag@I nanoparticles to induce aggregation. (C) DLS data of the nanoparticles after adding Ca^{2+} ions and organic molecules.

S4. SERS spectra reproducibility

The relative standard deviation (RSD) of the predominant peaks of ethyl phenylpropiolate at 2208, 2236 and 1709cm^{-1} in Figure S3 below are calculated as follows:

$$RSD = \frac{StD}{\bar{x}} \times 100\%$$

where StD is the standard deviation and x is the average value of the Raman peak intensities of the 15 spectra.

Table S1. RSD calculation of the SERS peaks of ethyl phenylpropiolate

Raman peak (cm^{-1})	StD (counts)	$\bar{x}$ (counts)	RSD (%)
2208	434.01157	4369.96921	9.93
2236	356.17294	3006.80055	11.84
1709	309.18691	2307.68787	13.39

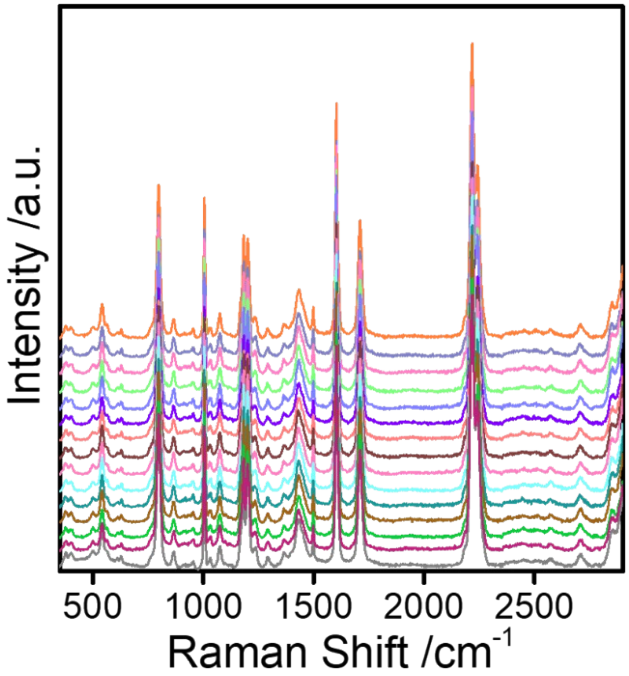

Figure S3. 15 sets of random SERS signals obtained by 5 mM ethyl phenylpropiolate in the presence of the enhanced substrate Ag@IACNPs.

S5. Raman spectra of acetone using various substrate

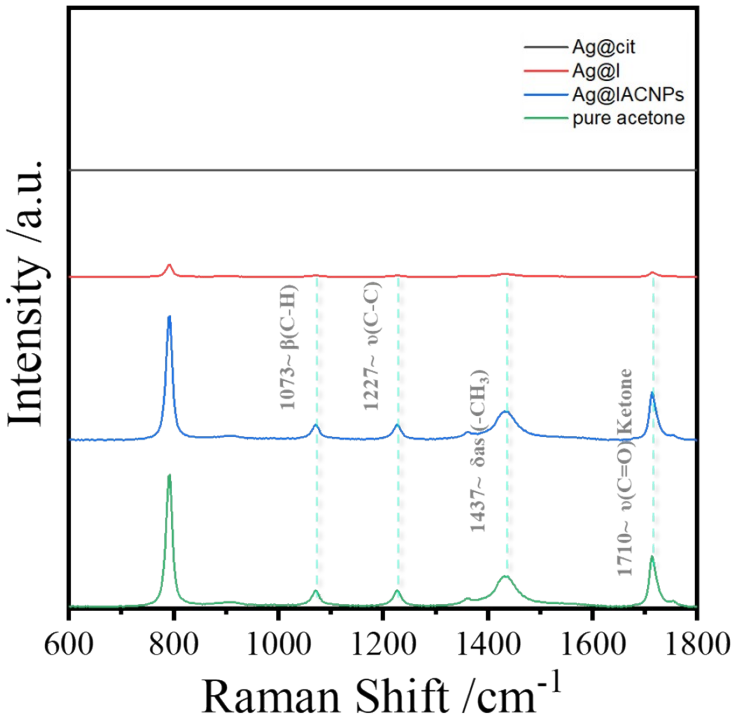

Figure S4. Raman spectra of acetone using substrate of Ag@IACNPs (blue line), Ag@I (red line), Ag@cit (black line) and Raman spectra of pure acetone (green line).

S6. SERS spectra of esterification reaction monitoring

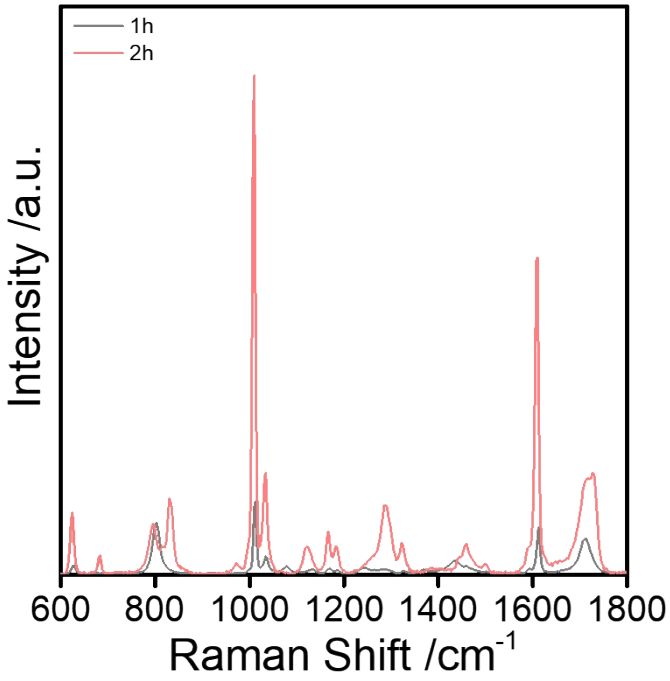

Figure S5. The SERS spectra of esterification reaction monitoring obtained by current method at different times.

S7. The limit of detection use AgIACNPs substrate

Table S2. LOD calculation of the SERS peak of ethyl phenylpropiolate

Raman peak (cm^{-1})	Y-intercept value	standard errors of the Y-intercept	LOD (mol/L)
2208	151.53946	±128.7516	3.97×10^{-5}

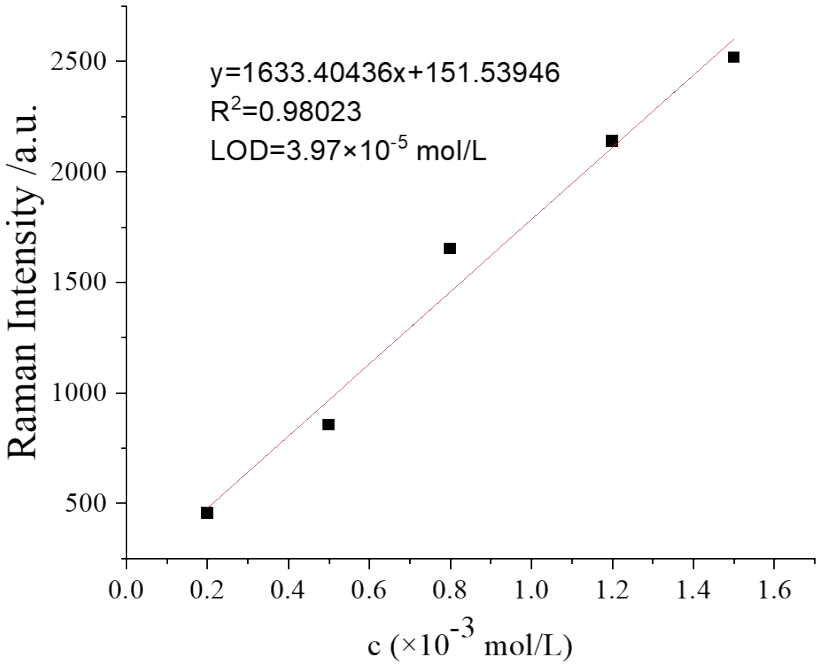

Figure S6. The calibration curve of the concentration of ethyl phenylpropiolate at 2208cm^{-1} versus the Raman intensity.

S8. Enhancement factor (EF) calculation

The EF is calculated by the following formula:

$$EF = \frac{I_{SERS}/(\mu_M \mu_S A_M)}{I_{RS}/(C_{RS} H_{eff})}$$

where I_{RS} is the Raman intensity of the analyte molecules under non-SERS conditions and I_{SERS} the intensity under SERS conditions. C_{RS} [μm^{-3}] is the volume density of the molecules used for the non-SERS measurement, H_{eff} [μm] is the effective height of the scattering volume of the objective, μ_M [μm^{-2}] is the surface density of the individual Ag@IACNPs producing the enhancement, and μ_S [μm^{-2}] is the surface density of molecules on the metal. A_M [μm^2] is the surface area of one Ag@IACNPs. Because we are testing in a capillary tube, the cross-sectional area and volume of the test are the same. The simplified formula can be obtained: $EF=(I_{SERS}/\mu_M)/(I_{RS}/C_{RS})$.

$EF_{2208} = (39325.727/3.05\times10^{-7}) / (8.1499/6.0563\times10^{-5}) = 9.58\times10^{5}$

S9. The Raman peak assign to Organic molecules

Table S3. The bands and their assignment appeared in the SERS spectra of Organic molecules

Molecular name	Raman Shift/cm^{-1}	Assignment	Ref.
Acetone	1710~	υ(C=O) Ketone	
	1437~	δas ($-CH_3$)	[2,3]
	1227~	υ(C-C)	
	1073~	β(C-H)	
Cyclohexane	1350~, 1450~	δ($-CH_2$) Cyclane	
		υ($-CH_2$) Cyclane	
	1007~	δ(ring)	
Ethanol	1457~	δas($-CH_3$)	
	1280~	β(O-H)	
	1101~, 1056~	υ(C-O)	[2,3]
	887~	γ(H-O)	
Toluene	1600~	δ(ring)	
	1371~	δ($-CH_3$)	
	1215~, 1030~, 1003~	β(C-H)	[1]
	798~	β(C-H) Benzene ring monosubstitution	
Benzaldehyde	2742~	υ(C-H) Aldehyde hydrogen	
	1602~	δ(ring)	
	1145~, 1029~, 1003~	β(C-H)	
	847~	γ(C-H) benzene ring monosubstitution	
	650~	γ_{ring}(C-H)	
AceticAcid	1692~	υ(C=O) Carboxylic acid	
	1486~	β(O-H)	
	941~	ω(C-H)	
		ω(O-H)	
Ethyl phenylpropargylate	2236~, 2208~	υ(C≡C)	
	1709~	υ(C=O) Esters	
	1616~, 1497~, 1450~	δ_{bk}(ring)	
	1201~, 1181~	υ(C-O-C)	
	1029~, 1006~	δ(C-H)	
	761~	γ(C-H) Benzene ring monosubstitution	
Triazole	1726~	υ(C=O)	
	1532~	υ(N=N)	
	1587~, 1477~, 1455~	δ(ring) Vibration of benzene ring skeleton	
	1269~, 1176~	υ(C-O-C)	

	1003~	δ(C-H)	
	841~	γ(C-H) Benzene ring monosubstitution	
Methyl benzoate	1723~, 1681~	υ(C=O) Esters and ketones	
	1603~, 1501~, 1445~	δ(ring)	
	1131~, 1109~, 1011~	β(C-H)	
	847~	γ(C-H) Benzene ring monosubstitution	
	721~, 685~	γ_{ring}(C-H)	
Methanol	1463~	δas (-CH_3)	
	1372~	β(O-H)	
	1026~	υ(C-O)	[4]
	843~	γ(H-O)	

Note: υ = stretch, δ = deformation, β = in-plane bending vibration, γ = external bending vibration, ω = out of plane sway vibration, bk = backbone.

S10. References

1. Q. Q. Chen, R. N. Hou, Y. Z. Zhu, X. T. Wang, H. Zhang, Y. J. Zhang, L. Zhang, Z.Q. Tian, and J. F. Li, *Anal. Chem.*, 2021, **93**, 7188−7195.
2. C. L. Wong, U.S. Dinish, M. S. Schmidt, M. Olivo, *Anal. Chim. Acta*, 2014, **844**, 54-60.
3. J. H. Fu, Z. Zhong, D. Xie, Y. J. Guo, D. X. Kong, Z. X. Zhao, Z. X. Zhao, M. Li, *Angew. Chem.*, 2020, **59**, 20489-20498.
4. X. Chen, M. M. Liang, J. Xu, H. L. Sun, C. Wang, J. Wei, H. Zhang, W. M. Yang, Z. L. Yang and J. J. Sun, *Nanoscale*, 2020, **12**, 5341-5346.