Electronic Supplementary Information

Fabrication of liquid–liquid self-assembled Ag array on disposable screen-printed electrodes and their application in the identification and analysis of adsorption behavior of organic carboxylates through *in-situ* electrochemical surface-enhanced Raman scattering

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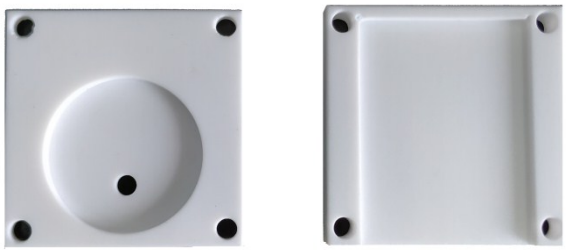


Fig.S1 The specially designed electrochemical cell used in this EC-SERS platform

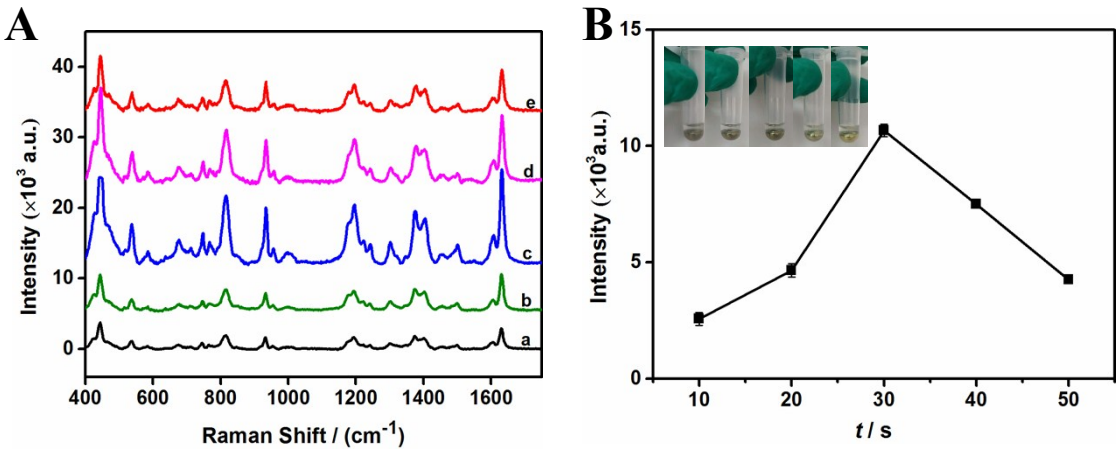


Fig. S2 SERS spectra (a-e) of 10^{-6} mol/L MG solution (A) and corresponding SERS intensity (B) and digital photograph (the inset) on liquid–liquid self-assembled Ag nanoarrays prepared by 10, 20, 30, 40, 50 s vortex mixing time, respectively.

Calculation of Enhancement Factor (EF).

SERS spectra of 2.5 μL of 10^{-2} mol/L MG and 10^{-6} mol/L MG solution on bare SPE and Ag nanoarrays were recorded and the intensity at the peak of 436 cm^{-1} was selected to calculate the EF. The EF for the Ag nanoarray@SPE was estimated according to the following equation:

$$EF = \left(\frac{I_{SERS}}{I_{norm}}\right)\left(\frac{C_{norm}}{C_{SERS}}\right)$$

Where I_{SERS} is the SERS intensity of the MG adsorbed on the Ag nanoarray@SPE; I_{norm} is the normal Raman intensity of the MG on the bare SPE; C_{SERS} is the concentration of the MG irradiated by laser on the Ag nanoarray@SPE; C_{norm} is the concentration of the effective MG irradiated by a laser on the bare SPE. For the SERS peak at 436 cm^{-1}, the ratio of I_{SERS} to I_{norm} was calculated as 20, so EF was about 2×10^5.

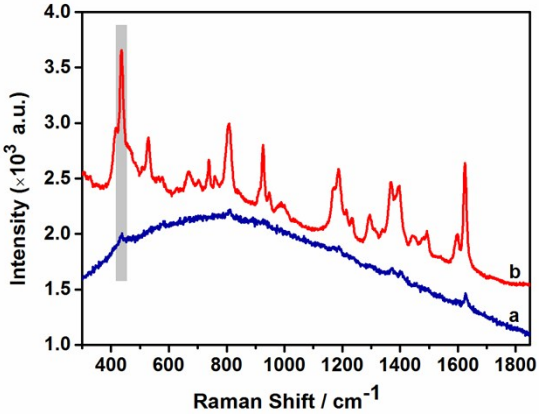


Fig. S3 Normal Raman spectrum of 10^{-2} mol/L MG solution on bare SPE (a) and SERS spectrum of 10^{-6} mol/L MG solution on Ag nanoarray@SPE (b).

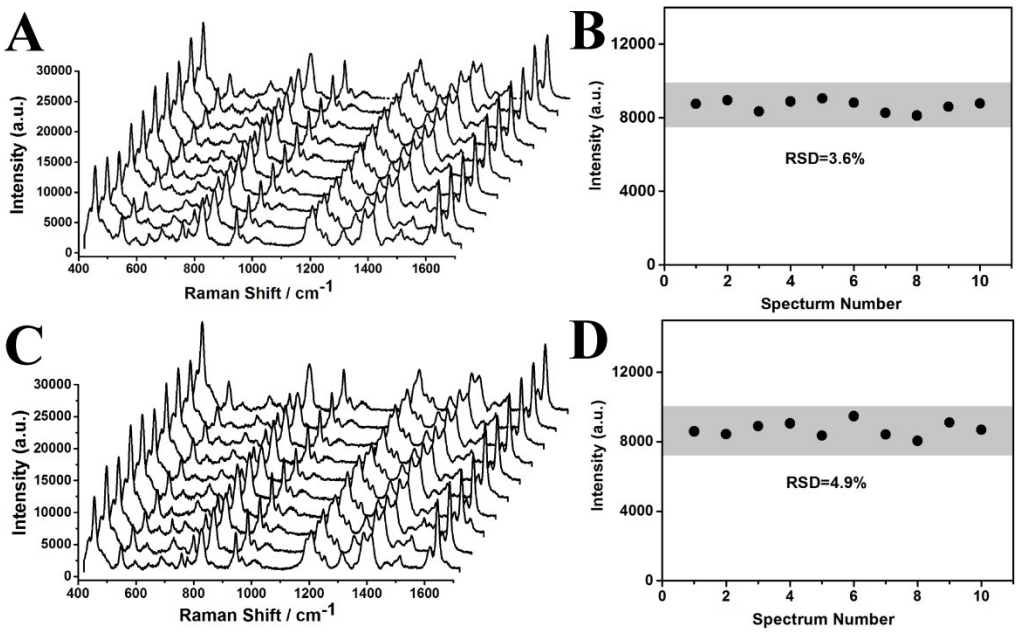


Fig. S4 (A) SERS spectra of 10^{-6} mol/L MG solution collected from 10 randomly selected points on the same Ag nanoarray@SPE. (B) SERS intensity distribution at 1624 cm^{-1}. (C) SERS spectra of 10^{-6} mol/L MG solution collected from 10 randomly selected Ag nanoarray@SPEs. (D) Corresponding SERS intensity distribution at 1624 cm^{-1}.

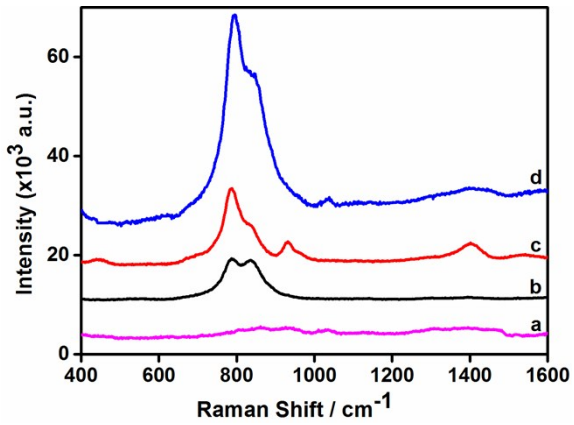
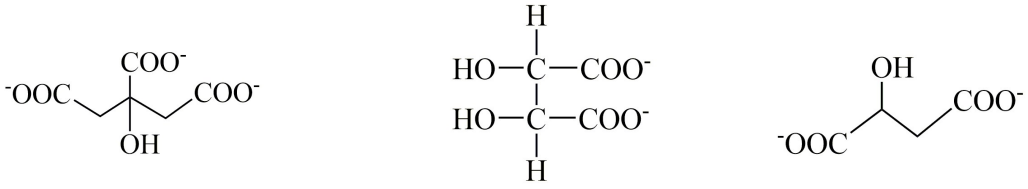


Fig. S5 SERS spectra of background of Ag array@SPEs (a), tartrate (b), malate (c) and citrate (d) at the voltage of 0.100 V.

Table S1 Comparison the developed method for the qualitative analysis of citrate, tartrate and malate with the reported literature

Technology	Analyte	Substrate	Adsorption behavior	reference
SERS	citrate	Ag Nps	NG	42
SERS	tartrate, malate	Ag Nps	tartrate adsorbed vertically and malate parallelly	43
EC-SERS	citrate, tartrate, malate	Ag array@SPE	citrate adsorbed in claw, tartrate parallelly and malate vertically	This work

Note: NG: not given in the literature



Citrate Tartrate Malate

Fig. S6 The chemical structures of citrate, tartrate and malate