Supporting information for

Bimetallic plasmonic Au@Ag nanocuboids for rapid and sensitive detection of Phthalate plasticizers with label-free Surface-enhanced Raman Spectroscopy

Xiaoyan Hu[a], Xinru Wang[a], Zipan Ge[a], Le Zhang[a], Yaru Zhou[c], Jingya Li[d], Linfeng Bu[e], Hengan Wu[e], Pan Li[f*], Weiping Xu[a,b*]

a. Department of Pharmacy, Anhui University of Chinese Medicine, Anhui, Hefei, 230038, China.

b. The First Affiliated Hospital of USTC, Anhui Provincial Hospital, Anhui, Hefei, 230001, China.

c. School of Chemistry and Chemical Engineering, Hefei University of Technology, Anhui, Hefei, 230009, China.

d. Department of Biological Physics, University of Science and Technology of China, Anhui, Hefei, 230027, China.

e. CAS Key Laboratory of Mechanical Behavior and Design of Materials, Department of Modern Mechanics, CAS Center for Excellence in Complex System Mechanics, University of Science and Technology of China, Hefei 230027, China.

*f.*Center of medical physics and technology, Hefei institutes of physical science, CAS, Hefei 2300 21, China

Correspondence to: Weiping Xu （weipingx@ustc.edu.cn） and Pan Li (lipan2011@iim.ac.cn)

Simulations of Electromagnetic Field Distribution.

To investigate the electromagnetic field distribution of plasmonic bimetallic (Au@Ag) core-shell nanocuboid, we perform three-dimensional finite-difference time-domain (FDTD) simulations using a commercially available software FDTD solution. Perfectly matched layer (PML) adsorbing boundary conditions are imposed on all directions of the simulation domain to simulate infinite space and adsorb all ejection waves. The size of the simulation domain was 1000 nm × 1000 nm × 1000 nm. Au@Ag core-shell nanocuboid is placed at the center of the simulation domain. The size of Au core is 23 nm in diameter and 78 nm in length. The Au core is embedded into the Ag shell. Four different sizes for Ag shell are used: 80 nm × 26 nm × 26 nm, 82 nm × 37 nm × 37 nm, 84 nm × 47 nm × 47 nm, and 88 nm × 59 nm × 59 nm, respectively. The material parameters are used based on the material database in FDTD solution program. The refractive indexes of Au and Ag are set based on the corresponding built-in materials of Au-Palik and Ag-Palik, respectively. Au@Ag core-shell nanocuboid is immersed into water (surrounding medium). The refractive index for water is 1.33. The precision of element meshing is 0.1 nm. In the meshing of simulation model, to decrease the interpolation error, the max element size of surrounding air field was limited to lower than one-sixth wavelength, and the max element size of Au@Ag nanocuboid was smaller than the skin depth of corresponding wavelength. The laser (TFSF source) wavelength was 633 nm and the angle of incidence was 30º. The polarization angle is 90º.

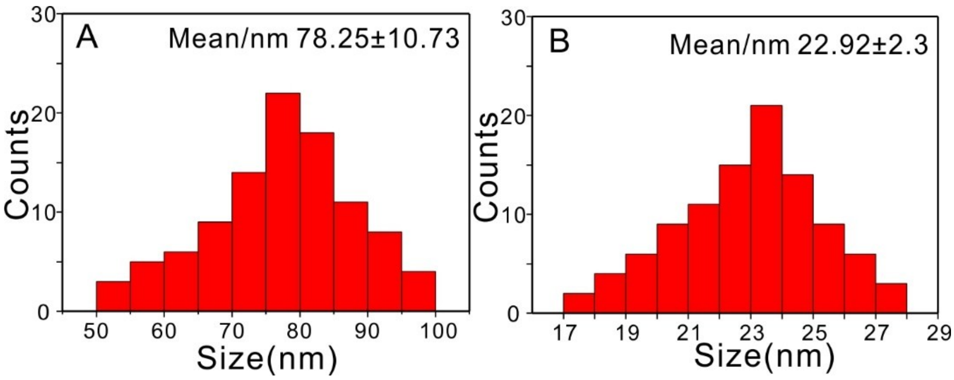

Fig. S1: The (A) length and (B)diameter distribution of the Au NRs.

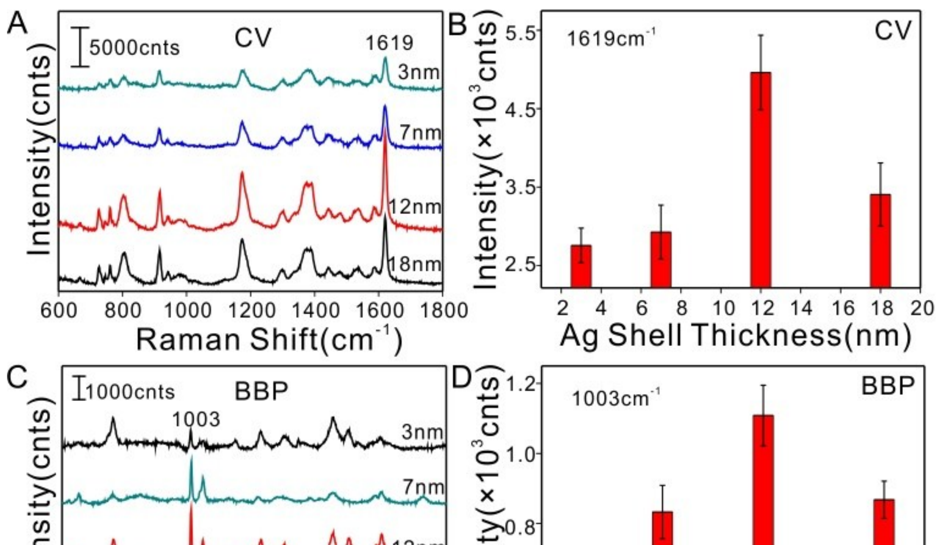

Fig. S2: SERS detection of CV (10^{-6} M) and BBP (10^{-5} M). (A) The serial of SERS spectra of 10^{-6}

M CV of Au@Ag NCs with different shell thickness. (B) The Raman intensity of 10^{-6} M CV at 1619 cm^{-1} varying with different shell thickness of Au@Ag NCs. (C-D) The serial of SERS spectra and the Raman intensity at 1003 cm^{-1} of 10^{-5} M BBP of Au@Ag NCs with different shell thickness, respectively.

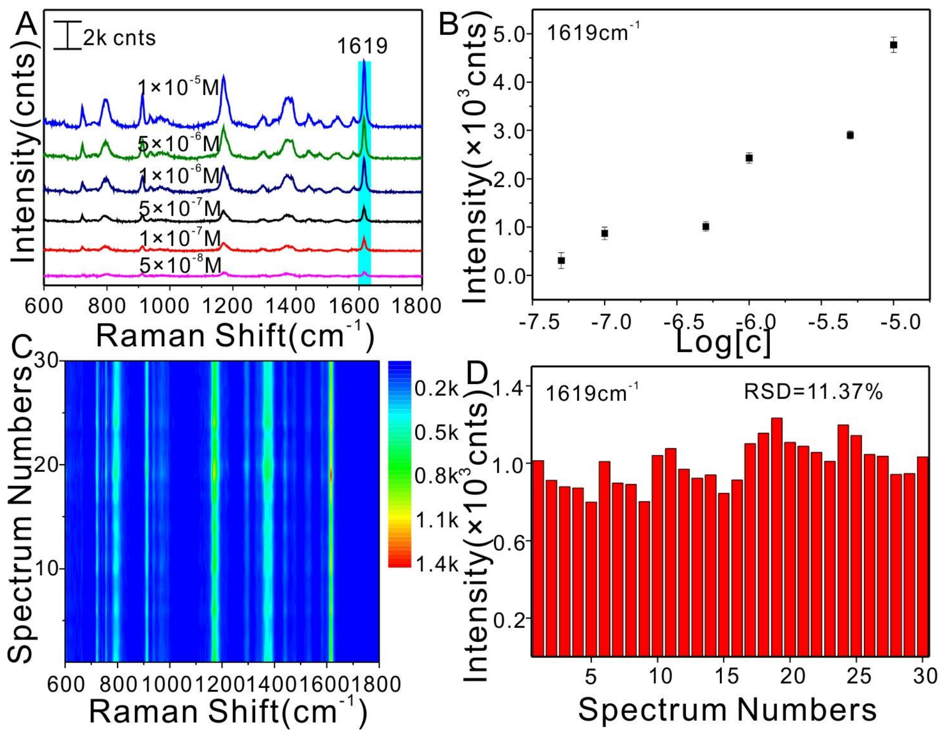

Fig. S3: SERS sensitivity and reproducibility of Au NRs with CV. (A) The SERS spectra of different concentration of CV: 1×10^{-5}, 5×10^{-6}, 1×10^{-6}, 5×10^{-7}, 1×10^{-7}, 5×10^{-8} M. (B) The plots of SERS intensities versus the different logarithm of concentration at peak value of 1619 cm^{-1}. (C) 2D presentation of 30 spectra randomly collected from 30 spots with 10^{-6} M CV. (D) Histogram of the SERS intensity at 1619 cm^{-1} from 30 spectra in Fig.S3C (the RSD is 11.37%).

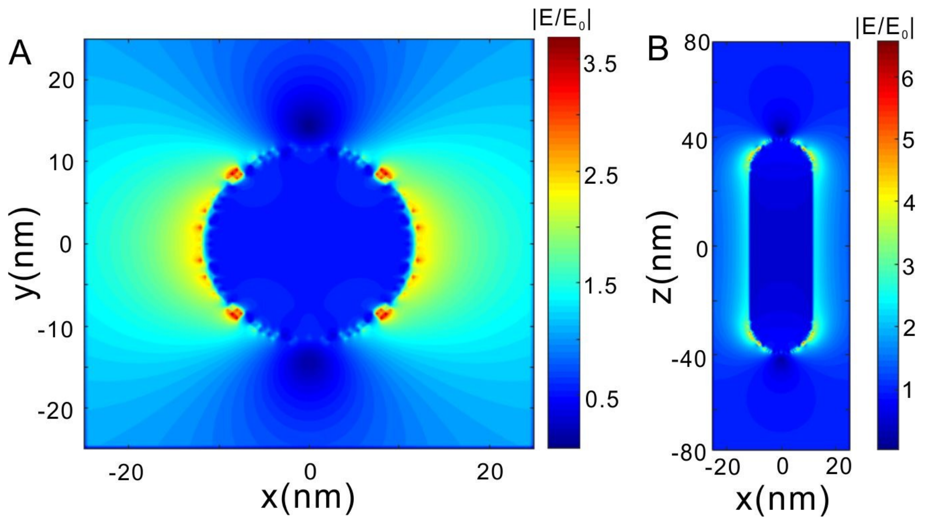

Fig. S4: The electric field distribution by FDTD simulations of Au NR with x-y view (A) and x-z view (B).

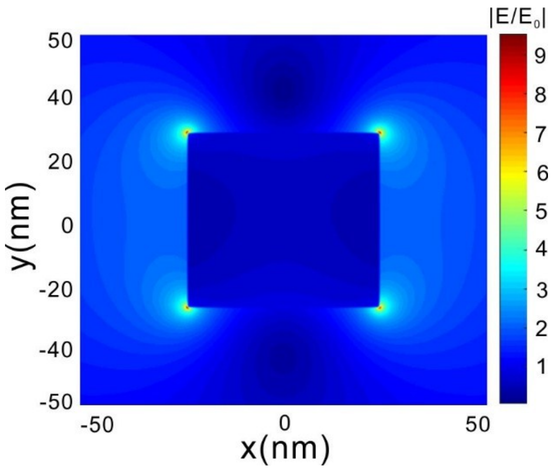

Fig. S5: The electric field distribution by FDTD simulations of Ag NC with x-y view.

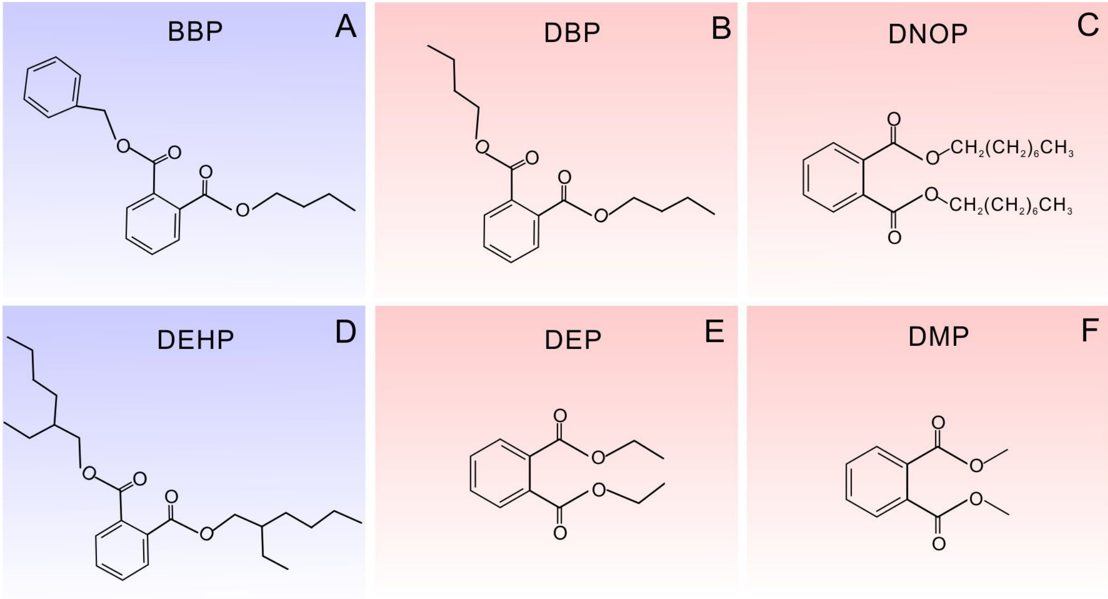

Fig. S6: The chemical structure of six PAEs: (A) BBP, (B) DBP, (C) DNOP, (D) DEHP, (E) DEP, (F) DMP.

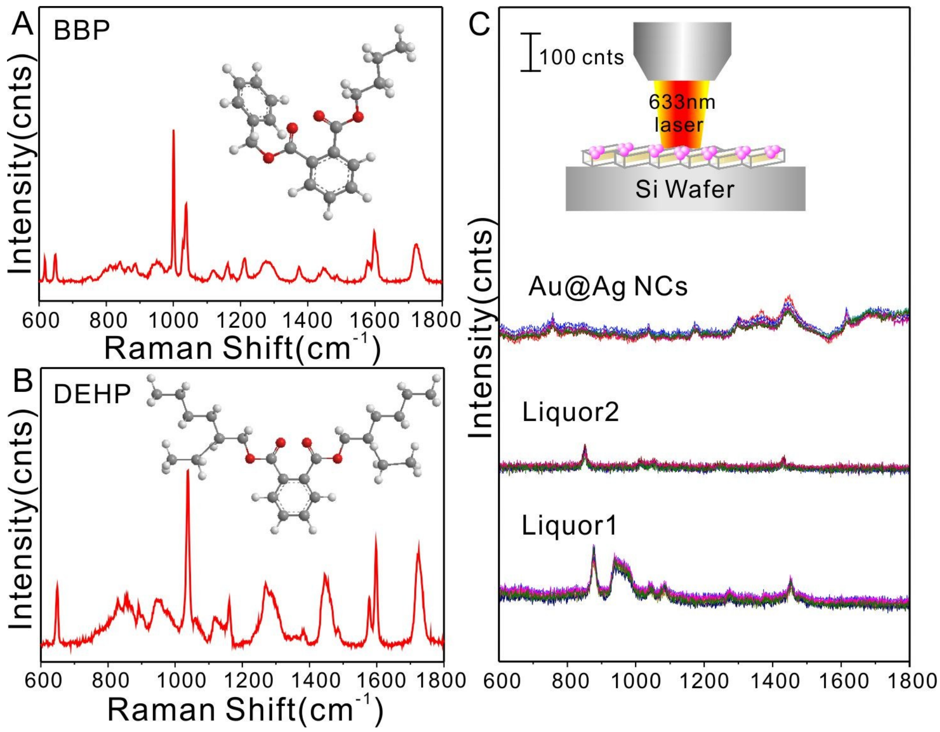

Fig. S7: The SERS spectra of (A) BBP, (B) DEHP, (C) the blank substrate and the liquor. The ball-stick models of BBP and DEHP are shown in the inset of (A), (B), respectively.

Calculation of the enhancement factor (EF) of Au@Ag NCs for various PAEs and PAEs in liquor

(1) The enhancement factor of a single Au@Ag NC was estimated using the following equation[1]:

$$EF = (I_{surface}/N_{surface}) / (I_{solution}/N_{solution})$$

where $I_{surface}$ and $N_{surface}$ are the Raman intensity probed from the Au@Ag NCs mixed with BBP (10^{-6} M) and numbers of BBP (10^{-6} M) molecules absorbed on the Au@Ag NCs. $I_{solution}$ and $N_{solution}$ are the Raman intensity probed from BBP and the numbers of BBP molecules in the focus of the laser beam.

The Raman intensity $I_{surface}$ was 2035 cnts at the peak of 1003 cm^{-1} (Fig. S8A2), and the $I_{solution}$ was measured to be 175 cnts (Fig. S8A1). While the $N_{surface}$ was estimated using the following equation:

$$N_{surface} = n_{surface} \times 6.02\times10^{23} = c_{surface}\, v_{surface} \times 6.02\times10^{23}$$

$$N_{solution} = n_{solution} \times 6.02\times10^{23} = c_{solution}\, v_{solution} \times 6.02\times10^{23}$$

In this article, both the $v_{surface}$ and $v_{solution}$ are 2 μL, ensuring that the analytes are within the focus of the laser beam and the experimental conditions are the same. So the EF can be estimated as:

$$EF = (I_{surface}/N_{surface}) / (I_{solution}/N_{solution}) = (I_{surface}/\ c_{surface}) / (I_{solution}/\ c_{solution})$$

The purchased Butyl benzyl phthalate (BBP) has a density of 1.116 g/mL and a concentration of 98%. So the $c_{solution}$ = n/v = (m/M) / (m/ρ) =3.49 mol/L. So,

$$EF = (2035 \text{ cnts} / 10^{-6} \text{ M}) / (175 \text{ cnts} / 3.49 \text{ M}) = 4.06\times10^{7}$$

(2) Here, we also used the above equation to obtain the EF of Au@Ag NCs for diethylhexyl phthalate (DEHP, 10^{-6} M). The Raman intensity $I_{surface}$ was 2869 cnts at the peak of 1001 cm^{-1} (Fig. S8B2), and the $I_{solution}$ was measured to be 217 cnts (Fig.

S8B1). The purchased DEHP has a density of 0.985 g/mL and a concentration of 99%. So the $c_{solution}$ = n/v = (m/M) / (m/ρ) = 2.50 mol/L. So,

$$EF = (2869\ cnts / 10^{-6}\ M) / (217\ cnts / 2.50\ M) = 3.31\times10^{7}$$

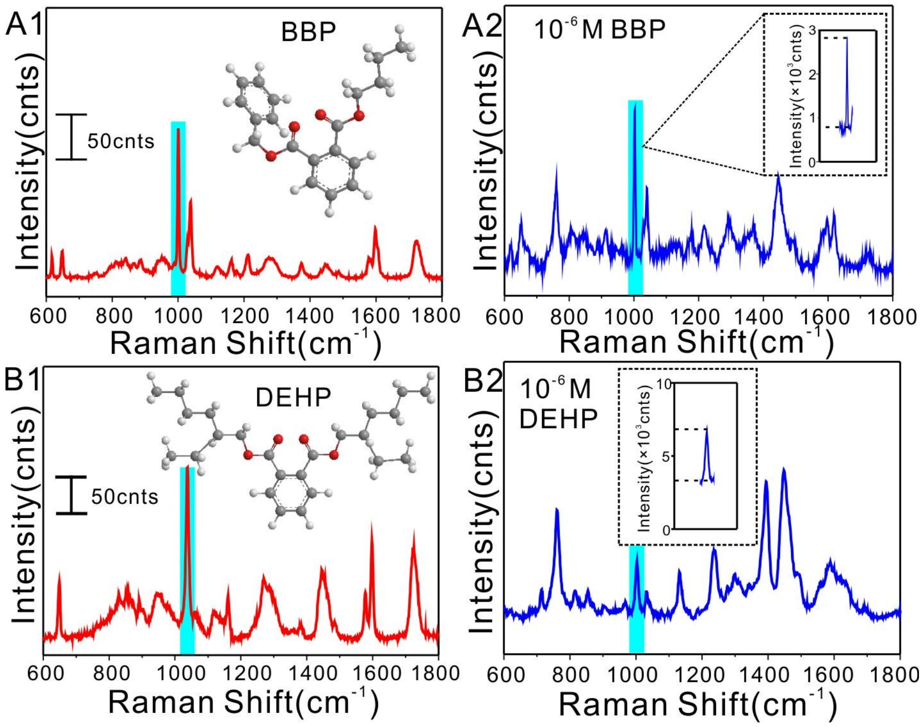

Fig.S8: The SERS spectra of (A1) BBP, (B1) DEHP. The SERS spectra of (A2) 10^{-6} M BBP, (B2) 10^{-6} M DEHP.

(3) The alcohol concentration of liquor1 purchased from the supermarket is 48%. And the survey results show that the density of ethanol is 0.789 g/mL, and the density of water is 1.0 g/mL. So,

$$\rho_{liquor1} = (m_{water} + m_{alcohol}) / V = (\rho_{water}\times V_{water}+\rho_{alcohol}\times V_{alcohol}) / V$$

$$= (\rho_{water}\times 0.52V+\rho_{alcohol}\times 0.48V) / V = 0.52\times 1\ g/mL + 0.48\times 0.789\ g/mL = 0.899\ g/mL$$

$$c_{liquor1} = m_{alcohol} / m_{liquor1} = (\rho_{alcohol}\times V_{alcohol}) / (\rho_{liquor1}\times V)$$

$$= (\rho_{alcohol}\times 0.48V) / (\rho_{liquor1}\times V) = (0.48\times 0.789) / 0.899 = 0.421\ g/g = 4.21\times10^{5}\ mg/kg$$

The Raman intensity $I_{surface}$ was 1278 cnts at the peak of 1001 cm^{-1} (Fig. S9A2), and the $I_{solution}$ was measured to be 49 cnts (Fig. S9A1). So,

$$EF = (1278 \text{ cnts} / 1.3 \text{ mg/kg}) / (49 \text{ cnts} / 4.21\times10^{5} \text{ mg/kg}) = 8.45\times10^{6}$$

(4) The alcohol concentration of liquor1 purchased from the supermarket is 52%. And the survey results show that the density of ethanol is 0.789 g/mL, and the density of water is 1.0 g/mL. so,

$$\rho_{liquor2} = (m_{water} + m_{alcohol}) / V = (\rho_{water}\times V_{water}+\rho_{alcohol}\times V_{alcohol}) / V$$

$$= (\rho_{water}\times 0.48V+\rho_{alcohol}\times 0.52V) / V = 0.48\times1 \text{ g/mL} + 0.52\times0.789 \text{ g/mL} = 0.896 \text{ g/mL}$$

$$c_{liquor1} = m_{alcohol} / m_{liquor1} = (\rho_{alcohol}\times V_{alcohol}) / (\rho_{liquor1}\times V)$$

$$= (\rho_{alcohol}\times 0.52V) / (\rho_{liquor1}\times V) = (0.52\times0.789) / 0.896 = 0.457 \text{ g/g} = 4.57\times10^{5} \text{ mg/kg}$$

The Raman intensity $I_{surface}$ was 6587 cnts at the peak of 1001 cm^{-1} (Fig. S9B2), and the $I_{solution}$ was measured to be 24 cnts (Fig. S9B1). So,

$$EF = (6587 \text{ cnts} / 1.3 \text{ mg/kg}) / (24 \text{ cnts} / 4.57\times10^{5} \text{ mg/kg}) = 9.65\times10^{7}$$

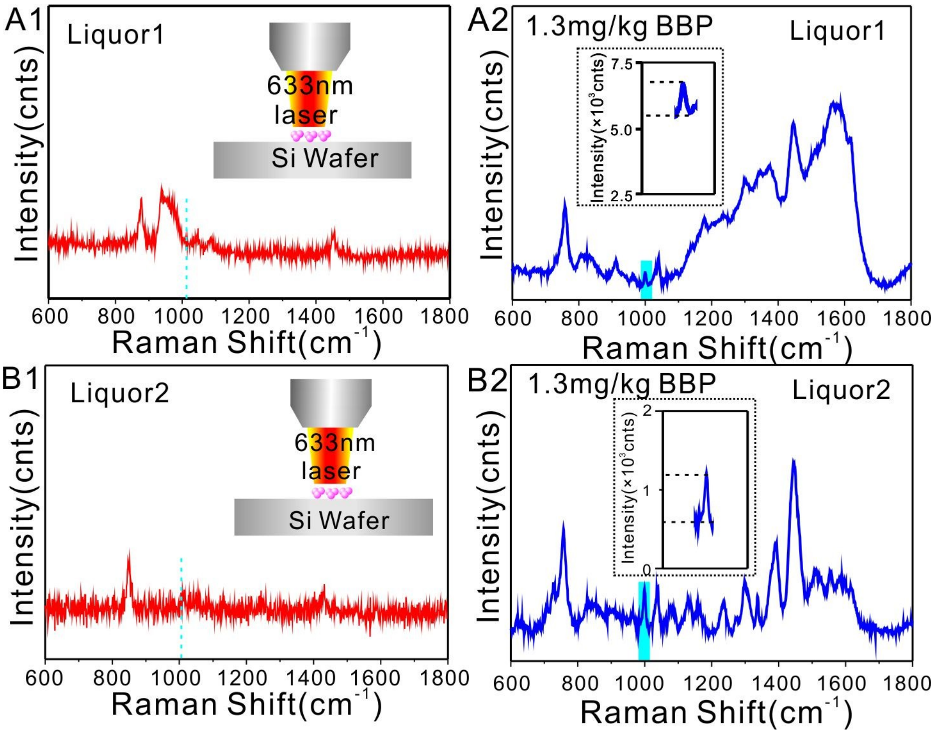

Fig.S9: The SERS spectra of (A1) liquor1 (B1) liquor2. The SERS spectra of (A2) 1.3 mg/kg BBP in liquor1 and (B2) 1.3 mg/kg BBP in liquor2.

REFERENCES

[1] Liu K , Bai Y , Zhang L , et al. Porous Au-Ag Nanospheres with High-Density and Highly Accessible Hotspots for SERS Analysis[J]. Nano Letters, 2016, 16, 3675-3681.