Electronic Supplementary Material (ESI) for Analyst.

Ag-Decorated Polymer Chip for the Determination of the Respective Concentrations of TTD and Hg^{2+} by Surface-Enhanced Raman Scattering

Bo Yang[a], Ye Wang[a], Sila Jin[b], Shuang Guo[b], Eungyeong Park[b], Jin Y. Shin[c], Weiyu Zhang[a,*], Young Mee Jung[b,*]

[a]*School of Pharmaceutical Sciences, Changchun University of Chinese Medicine, Changchun 130117, P.R. China*

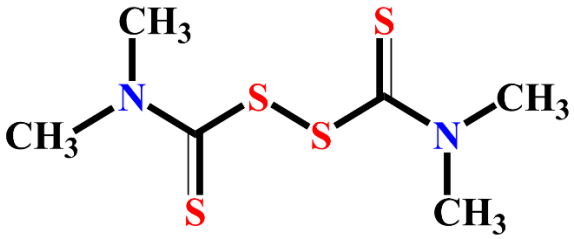
[b] *Department of Chemistry, Institute for Molecular Science and Fusion Technology, Kangwon National University, Chunchon 24341, Korea*

[c] *Department of Chemistry & Environmental Science, Medgar Evers College-The City University of New York, Brooklyn, NY, 11225, USA*

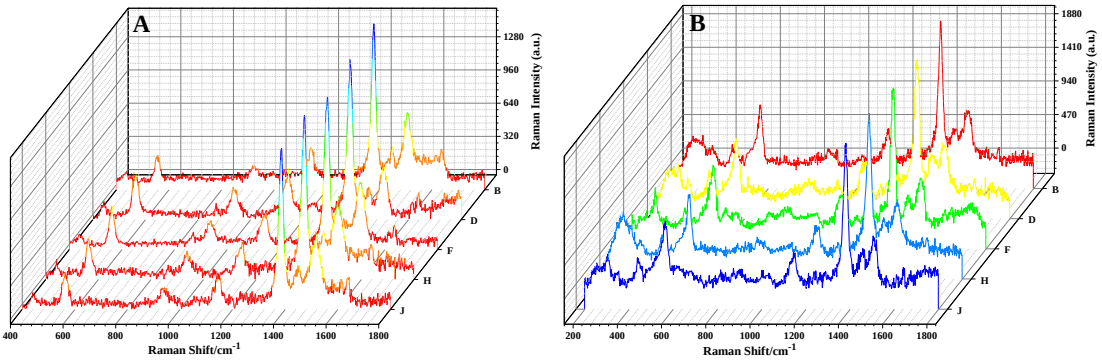
*To whom correspondence should be addressed.

E-mail: weiyuzhang2003@126.com (W. Zhang); ymjung@kangwon.ac.kr (Y.M. Jung)

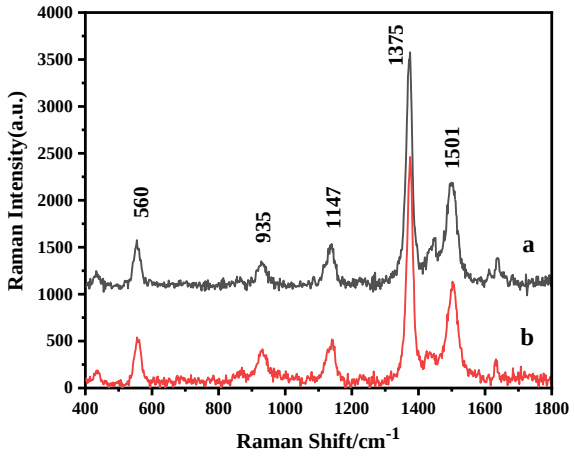
SI_Figure 1. Optical images of Ag-decorated polymer films with different soaking time from 0 to 5 h (from left to right are 0, 1, 2, 3, 4, and 5 h).



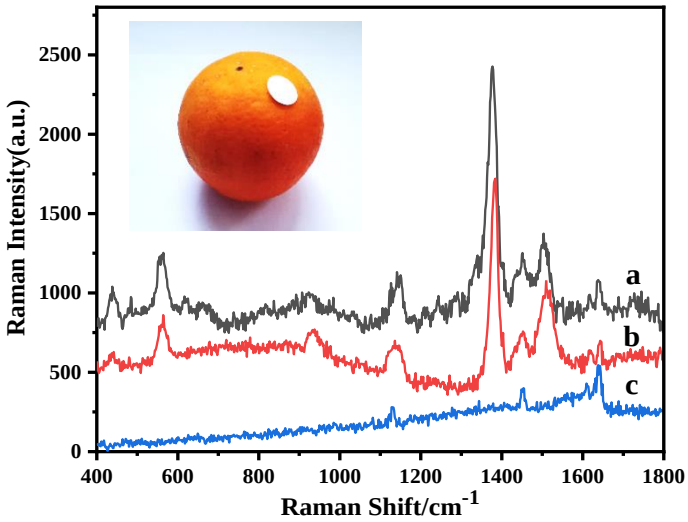
SI_Figure 2. The chemical structure of TTD.



SI_Figure 3. Reproducibility of SERS spectra of (A) TTD (1.0×10^{-5} M) and (B) TTD with of Hg^{2+} (1.0×10^{-7} M). The RSD for TTD and Hg^{2+} are 3.41% and 1.35%, respectively.



SI_Figure 4. SERS spectra of (a) TTD and (b) TTD with additives of Chlordimeform, Vamidothion, and Trichlorphon adsorbed on the Ag-decorated polymer. The concentration of TTD and additives are 1.0×10^{-4} M and 1.0×10^{-3} M, respectively. The frequency used pesticides (Chlordimeform, Vamidothion, and Trichlorphon) were used to check the selectivity for the TTD. Due to the weak adsorption force on the surface on the Ag and small Raman scattering cross section, the obtained SERS bands are assigned to the TTD. Thus, the proposed substrate is sensitive to TTD determination.



SI_Figure 5. SERS spectra of (a) TTD on the orange peel by touching method and (b) TTD on the orange peel and (c) flesh by pretreatment method based on the Chinese National Standard (GB23200.121). Herein, the TTD (10^{-5} mol/L) was sprayed on an orange surface. The insert is photo of TTD sprayed on an orange surface. We found that we could not obtain the SERS signal from the orange flesh. And the SERS intensity of TTD in the orange peel after pretreatment was decreased compared to the touch method. This is possible due to the molecular loss during the sample

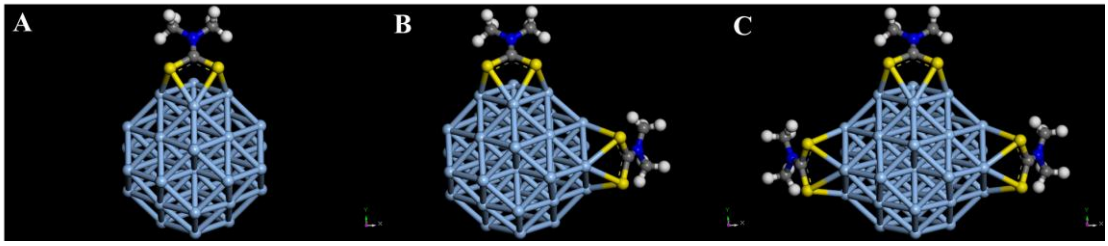
pretreatment.

DFT calculation.

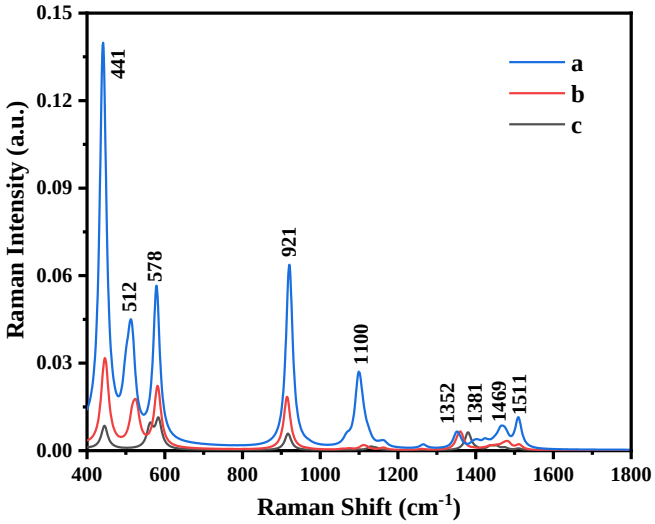
The DFT calculation was carried out using DMol3 package. A double-numeric polarized basis set and all electron for the core-treatment were selected. For the numerical integration, the system was set as the open-shell (spin unrestricted) structure. The general gradient approximation with the Perdew-Burke-Ernzerh function (GGA-PBE) was applied for the electronic structure. The convergence tolerances of energy, maximum force and maximum displacement for structural optimization were 1.0×10^{-5} Ha, 0.002 Ha/Å and 0.005 Å, respectively. The self-consistent field (SCF) density convergence tolerance was 1×10^{-6}. The adsorption energy (E_{ads}) was calculated according to the following equation:

$$E_{ads} = E_{A+Ag} — E_{Ag} — n*E_A$$

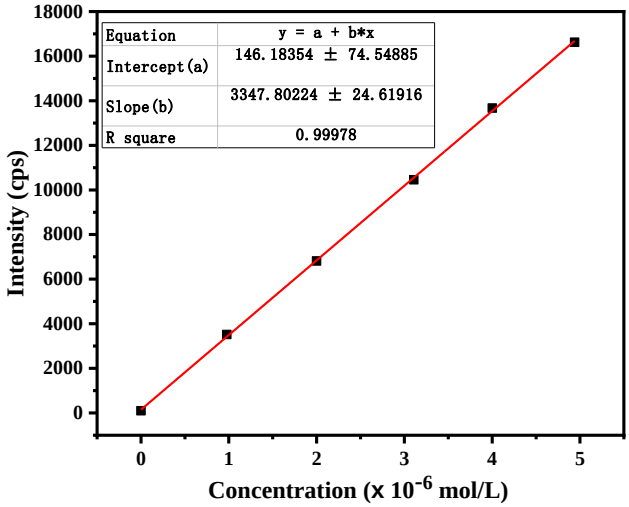
Where, E_{A+Ag} was the energy of the adsorption system; E_A and E_{Ag} were the energies of the isolated molecule and Ag cluster, respectively; the n was the number of adsorbed molecules.



SI_Figure 6. The optimal structural model of TTD adsorbed on the Ag cluster. The adsorbed number of dimethyl residues of TTD are (A) one, (B) two, and (C) three. For the optimal structural model, the bond order of two S-Ag bond of each S is about 0.6, and the bond order of the C-S is 1.4, which fully conforms to the characteristics of S-C-S resonance. Therefore, this calculation result is reliable.



SI_Figure 7. The theoretical Raman spectra of (a) three, (b) two, and (c) one dimethyl residues of TTD molecule adsorbed on the Ag cluster based on DFT method (DMol3 package). With the decrease of the dimethyl residues of TTD molecule, the band at 1352 cm^{-1} was shifted to 1381 cm^{-1}. These results are in good agreement with the fact that the SERS band at around 1375 cm^{-1} shifts to 1386 cm^{-1} with increase of the Hg^{2+} concentrations, which induces the S-Ag to break, decreasing the number of the dimethyl residues.



SI_Figure 8. ICP-MS standard curve between intensity and concentrations of Hg^{2+}.

Calculation of the enhancement factor (EF) for Ag-decorated polymer.

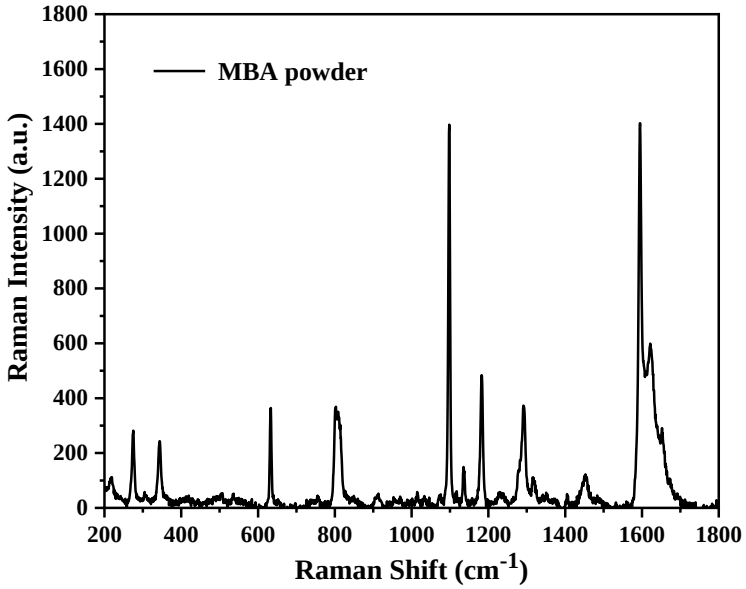
For the Ag-decorated polymer SERS-active substrate, the main contribution is from the Ag aggregation, which induce the strong electromagnetic field contribution. Therefore, the enhancement factor (EF) of the proposed SERS substrate was evaluated by the following relationship:

$$EF = (I_{SERS}/I_{NR})(N_{NR}/N_{SERS})$$

Where I_{SERS} and I_{NR} are the SERS intensity of 4-MBA on Ag-decorated polymer film (self-assemble time is 4 h) and normal Raman scattering intensity of solid sample of 4-MBA (SI_Figure 9), respectively. N_{SERS} and N_{NR} are the number of 4-MBA molecule adsorbed on Ag-decorated polymer film and bulk molecule to obtain corresponding SERS and normal Raman spectra, respectively. Herein, the laser spot is 1 μm in diameter and the penetration depth is 17 μm of the focused laser beam are used, and the density of 4-MBA is 1.345 g/cm^{-3}, thus the number of 4-MBA molecule is 7.01×10^{10}. N_{SERS} is evaluated according to the Orendorff et al method.[1]

$$N_{SERS} = N_d A_{laser} A_N / \sigma$$

Herein, N_d is the density of Ag aggregation, A_{laser} is the area of the laser focal spot, A_N is the Ag aggregation's footprint area, and σ is the surface area occupied by the adsorbed molecule. N_d and A_N were obtained from the SEM images. A_{laser} is the area of laser spot (1 μm), and σ is 0.20 nm^2/molecule for MBA.[1] In case of full coverage of 4-MBA molecules on Ag-decorated polymer film, then the EF for the band located at 1584 cm^{-1} is about 1.05×10^6.



SI_Figure 9. Raman spectra of MBA powder based on 532 nm laser excitation.

Table S1. Comparison of the different SERS active materials

Materials	EF	LOD (M)	Ref.
PMMA-Ag nanocomposite films	10^4	10^{-9}	2
Ag-TiO_2 hybrid nanoparticles	10^5	10^{-9}	3
Ag-Fe_3O_4 nanocomposites	10^6	10^{-10}	4
PVP-protected silver nanocubes films	10^6	10^{-8}	5
Au-Ag dealloyed substrate	10^6	10^{-9}	6
AgNC-grafted PAN nanofiber	10^7-10^8	10^{-9}	7
Ag-decorated polymer chip	10^6	10^{-10}	this work

References:

1. C. J. Orendorff, A. Gole, T. K. Sau, and C. J. Murphy, *Anal. Chem.*, 2005, **77**, 3261-3266.
2. K. B. Bhavitha, A. K. Nair, H. Mariya, J. Jose, A. Mayeen, M. S. Kala, A. Saha, S. Thomas, O. S. Oluwafemi and N. Kalarikkal, *New J. Chem.*, 2018, **42**, 15750-15761.
3. L. B. Yang, Q. Q. Sang, J. Du, M. Yang, X. L. Li, Y. Shen, X. X. Han, X. Jiang and B. Zhao, *Phys. Chem. Chem. Phys.*, 2018, **20**, 15149-15157.
4. S. Zhu, C. Fan, J. Wang, J. He, E. Liang and M. Chao, *J. Colloid Interf. Sci.*, 2015, **438**, 116-121.
5. S. Zhu, C. Fan, J. Wang, J. He and E. Liang, *Appl. Phys. A*, 2014, **117**, 1075–1083.
6. U. Waiwijit, C. Chananonnawathorn, P. Eimchai, T. Bora, G.L. Hornyak and N. Nuntawong, *Appl. Surf. Sci.*, 2020, **530**, 147171.
7. P. Jia, J. Qu, B. Cao, Y. Liu, C. Luo, J. An and K. Pan, *Analyst*, 2015, **140**, 5190-5197.