Supporting Information

[SERS detection of the antioxidant BHA]

As shown in Fig. S1(A), a preliminary SERS assay for BHA was performed and the detection limit was found to be in the range of 1-10 mg. And the SERS intensity diminished at BHA detection solution concentrations above 500 mg/L. Therefore, the concentration range of the solution in the SERS sensitivity assay was limited to the range of 100 mg/L. The detection performance of AgNT substrate was explored through the analysis of trace amounts of BHA. As shown in Fig. S1(B), the characteristic peaks of BHA could be detected at 692 and 910 cm^{-1}. These two peaks gradually diminished with the decrease of BHA concentration. In this detection, faint characteristic peaks could still be observed at a BHA concentration of 10 mg/L. At a concentration of 5 mg/L, the detection signals were all background signals. The SERS intensities of BHA at 692 and 910 cm^{-1} showed a good linearly correlation with concentration in the concentration range of 10 mg/L to 100 mg/L, as in Fig. S1(C). The linear equations were $I_{692} = 12.71+0.70C_{BHA}$, $I_{910} = 8.10+0.62C_{BHA}$ with correlation coefficients of 0.99 for both, respectively. The LOD of BHA was determined to be 10 mg/L according to the 3σ principle.
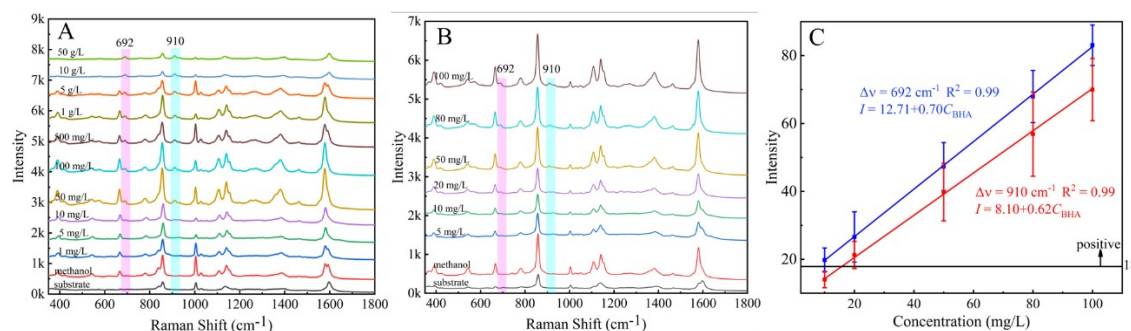

Fig. S1 (A) SERS spectra of AgNT substrates for the detection of different concentrations of BHA solutions. (B) The intensity of the corresponding characteristic peaks at 692 cm^{-1} and 910 cm^{-1}.

[Vibration assignment of Raman characteristic peaks of BHA and BHT]

The vibration mode assignments of BHA and BHT are shown in Table S1 of the Supporting Information. The characteristic peaks of BHA are distributed at 577 cm^{-1}, 692 cm^{-1}, 751 cm^{-1}, 910 cm^{-1} and 1596 cm^{-1}. The most typical peaks of BHA appear in the spectral regions near 692 cm^{-1} and 910 cm^{-1}, which are caused by in-plane ring deformation and C-O stretching & C-C stretching & in-plane ring breathing, respectively, while other characteristic peaks, such as 577 cm^{-1}, 751 cm^{-1}, and 1596 cm^{-1} are caused by C-O rocking, C-O stretching and C-O stretching & in-plane ring deformation.

The characteristic peaks of BHT are mainly distributed at 556 cm^{-1}, 775 cm^{-1}, 811 cm^{-1}, 930 cm^{-1} and 1596 cm^{-1}. The most typical peaks of BHT appear around 460

cm^{-1} and 556 cm^{-1}, which are caused by in-plane ring deformation and C-C stretching between the benzene ring and -C(CH$_3$)$_3$ respectively.

Table S1 Vibrational assignments of the theoretical Raman, solid Raman and experimental SERS spectra of BHA, BHT.

Abbreviation of chemical name	Theoretical Raman	Experimental SERS	Vibrational modes
BHA	586	577	C-O rocking
	704	692	In-plane ring deformation
	756	751	C-O stretching
	915	910	C-O stretching & C-C stretching & In-plane ring breathing
	935	932	C-C stretching & C-H wagging
	1220	1199	C-H wagging & C-C stretching
	1619	1596	C-O stretching & In-plane ring deformation & C-H rocking & O-H rocking
BHT	473	460	In-plane ring deformation
	556	556	C-C stretching & C-C rocking
	777	777	C-O stretching & C-C stretching & In-plane ring deformation
	811	811	C-O stretching & In-plane ring breathing
	924	931	C-C stretching & C-H wagging
	1047	1005	C-H wagging & C-C wagging
	1619	1596	In-plane ring deformation & C-C stretching & C-H rocking & O-H rocking

【SERS adsorption site】

The theoretical and practical Raman spectra of BHA and BHT are shown in Fig.S2(A). The DFT calculations were used to assign vibrations to the experimental Raman and SERS results. The theoretical Raman spectra calculated by DFT have similar characteristic to the SERS spectra. By analyzing the vibration assignments of BHA and BHT, the most typical characteristic peaks of BHA were confirmed at 692 cm^{-1} and 910 cm^{-1}. The most typical peaks of BHT are 460 cm^{-1} and 556 cm^{-1}.
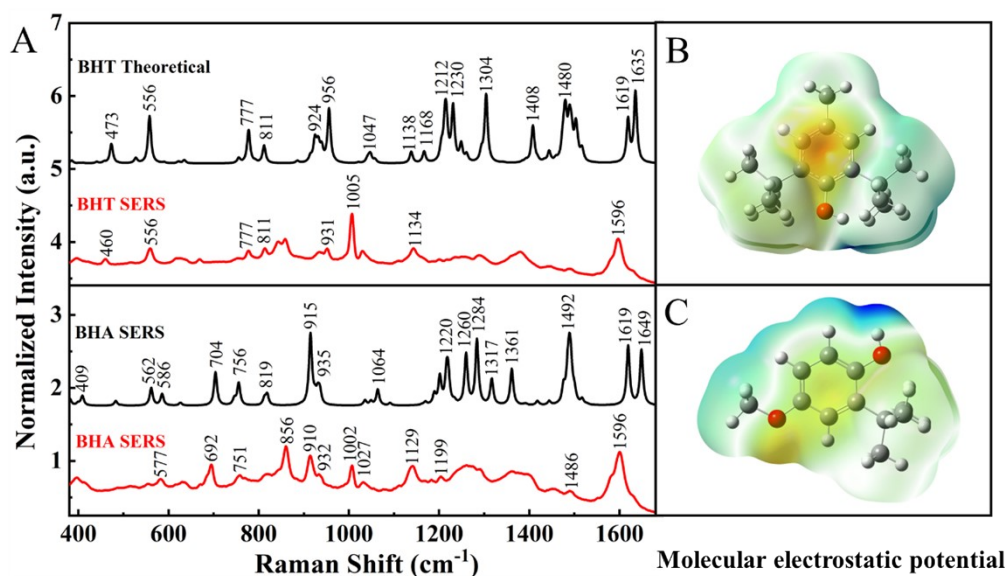
Fig. S2 (A) Theoretical Raman and SERS spectra of BHA and BHT. (B) The molecular electrostatic potential map of BHT. (C) The molecular electrostatic potential map of BHA.

Through the analysis of theoretical Raman and SERS spectra, it is found that there is a significant difference between SERS and theoretical Raman spectra of BHA due to the interaction between molecules and silver surface. Within a molecule, the vibrational spectra generated by atoms closer to the surface of SERS substrate will be more strongly affected. The wavenumber difference between Raman spectrum and SERS spectrum band is not more than 5 cm^{-1}, indicating that molecular end is connected to metal surface[1]. When the ring interacts directly with the metal, the breathing mode with a larger bandwidth in SERS range is red-shifted by about 10 cm^{-1}.[2]

The Raman characteristic peak of BHA at 704 cm^{-1} is 692 cm^{-1} in SERS, blue-shifted by 14 cm^{-1}, and its corresponding vibration mode is in-plane ring deformation. The Raman peak 915 cm^{-1} is blue-shifted by 5 cm^{-1} to 910 cm^{-1} in SERS, and its corresponding vibration mode is C-O stretching & C-C stretching & in-plane. This suggests that BHA may interact with the benzene ring and the silver surface through ether bonds, and the ether bond is the adsorption site of BHA and the metal surface in the reported literature.[3]

The most obvious Raman characteristic peak of BHT is 473 cm^{-1}, which is 460 cm^{-1} in SERS, with a blue shift of 13 cm^{-1}. Its vibration mode is in-plane ring deformation, and the Raman peak is 556 cm^{-1}. Raman and SERS There is no displacement in C-C stretching, and the corresponding vibration is C-C stretching & C-C rocking. These indicate that BHT may be adsorbed on the silver surface by hydroxyl groups and benzene ring on the molecule, and the benzene ring of BHA has a strong interaction with metal surface. It has also been reported that BHT in colloidal gold particles may be connected to a metal surface by hydroxyl group[4]. From the electrostatic potential distribution, both hydroxyl and methyl groups may be connected to the metal surface to generate SERS signals. Unfortunately, electrostatic potential analysis showed that more BHT tended to be adsorbed horizontally, while

lying down adsorption of BHT could not generate a tremendously SERS signal

In this article, we only analyzed the phenomenon of BHA. Since BHT has the same phenomena, we have performed extra analysis in the supporting information.

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2.   Y. S. Mary, P. J. Jojo, C. Van Alsenoy, M. Kaur, M. S. Siddegowda, H. S. Yathirajan, H. I. Nogueira and S. M. Cruz, *Spectrochim Acta A Mol Biomol Spectrosc*, 2014, **120**, 370-380.

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4.   Y.-Y. Sun, Y.-F. Xie, H.-Y. Wang, H. Qian and W.-R. Yao, *Applied Surface Science*, 2012, **261**, 431-435.