

# Temperature-Induced Effect on Surface-Enhanced Raman Scattering of *p,m*-Hydroxybenzoic Acid on Silver Nanoparticles

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The authors discuss temperature-induced effects on surface-enhanced Raman scattering of PHBA and MHBA adsorbed on silver colloidal particles.

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Surface-enhanced Raman scattering (SERS) has been an important part of surface and interface science since Fleischmann first discovered it in 1974 (1). Wide applications of SERS in colloid systems have significant value in industry and scientific research. However, according to many factors involved, its enhancement mechanisms are not yet very well understood.

SERS is sensitive enough for in situ study of the orientation of molecules adsorbed on the substrate and probing interfacial phenomena. Under different environments, such as under a variety of temperatures or pH values, molecules adsorb on metal particles in distinct ways (2–5). SERS could be used to probe the adsorbed-state changes for just such properties.

*p*-Hydroxybenzoic acid (PHBA) is a favorable molecule to study the adsorption state because of its simple structure and specific characteristics in adsorption. It has both carboxyl group and hydroxyl group elements, which are con-

trapuntal, and it is possible for both to adsorb to the nanoparticles. Because it has been widely studied and its spectra are well known (6, 7), we chose PHBA

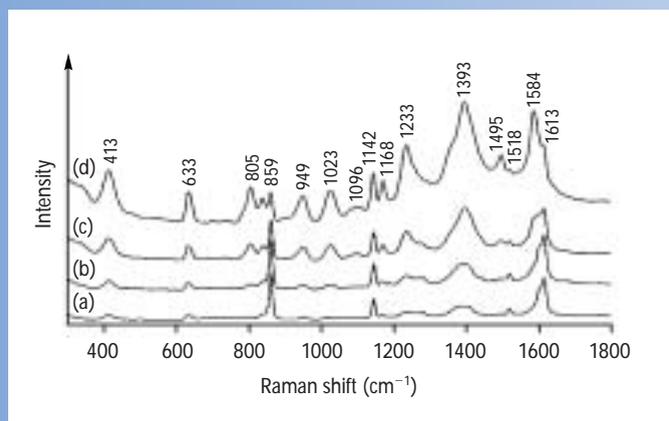
to study the transformation of adsorption modes induced by environment changes. The SERS of *m*-hydroxybenzoic acid (MHBA) can reveal more about the change of PHBA from indirect sources.

It is known that temperature is an important factor influencing surface adsorption and reaction. However, few temperature-induced effects have been reported. In this article, we examine the SERS spectra of the mixed solution of aqueous PHBA and silver colloid, which was extracted during the heating process at different temperatures. After heating treatment of the sample, we found that a number of new peaks occurred in the SERS spectrum. We analyzed the possible factors inducing the changes in the spectra and presumed that the changes of SERS spectra were caused by transformation of the adsorbed state of PHBA on the nanoparticles.

## Experimental

**Preparation of silver colloid.** Silver colloid was prepared according to Lee and Meisel's method (8). We dissolved 90 mg of silver nitrate in 500 mL of deionized water and heated the solution to boiling. Then 10 mL of a 1% aqueous solution of trisodium citrate was added into the boiling silver nitrate solution drop by drop, accompanied by vigorous stirring. The mixed solution was kept boiling for a further 10 min. Finally, a green-gray silver colloid was obtained, which was stable for several days to weeks.

**Instrumentation.** The Raman spectra were obtained by the RFS100/S Bruker (Bruker Optics, Billerica, MA) NIR-FT spectrophotometer. The exciting laser wavelength was 1064 nm. Resolution was  $4\text{ cm}^{-1}$ , and  $180^\circ$  geometry was employed. The output laser power, which induced no change of the adsorbate-substrate system, was 200 mW.



**Figure 1.** SERS of PHBA in silver solution at (a) room temperature and after cooling from (b) 70 °C, (c) 90 °C, and (d) 100 °C.

All samples were extracted from the mixed solution of aqueous PHBA and silver colloid at different temperatures during the process of heating to boiling and then cooled down to room temperature to record the Raman spectra. The case of MHBA was similar.

**Results.** The spectrum of PHBA in the silver colloid at room temperature (about 20 °C) is shown in Figure 1a, and the spectra of the mixed solution cooling down from 70 °C, 90 °C, and 100 °C to room temperature are presented in Figures 1b, 1c, and 1d. From these spectra, we found that the higher the temperature, the greater the change in spectra. The greatest change took place in the spectrum after the sample was heated to boiling. Some new bands occurred at 805  $\text{cm}^{-1}$ , 836  $\text{cm}^{-1}$ , 949  $\text{cm}^{-1}$ , 1023  $\text{cm}^{-1}$ , 1168  $\text{cm}^{-1}$ , 1495  $\text{cm}^{-1}$ , and 1584  $\text{cm}^{-1}$ . Some weak bands at 413  $\text{cm}^{-1}$ , 632  $\text{cm}^{-1}$ , 1233  $\text{cm}^{-1}$ , and 1393  $\text{cm}^{-1}$  were enhanced notably, among which the band at 1393  $\text{cm}^{-1}$  became the strongest in Figure 1d, and the other bands such as 859  $\text{cm}^{-1}$  and 1279  $\text{cm}^{-1}$  weakened. All the observed bands are listed in Table I. The possible assignments were acquired through comparing Raman, infrared (IR) SERS spectra, and data from references 6 and 7.

The spectra of MHBA before and after heating are shown in Figure 2. And there is no novel result except the increased intensity after heating.

**Discussion.** Figure 1 shows that the heating significantly influenced the

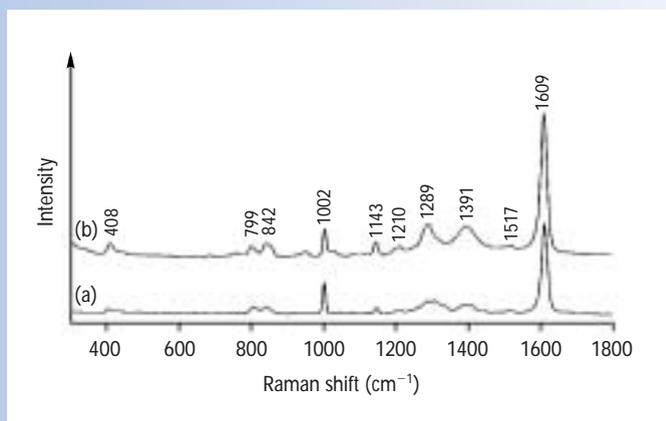
spectra. The SERS spectrum of PHBA in silver colloids after cooling down from boiling to room temperature differed notably from the spectrum of the unheated. There were some possible reasons for the changes in the spectra of PHBA:

- structural decomposition of PHBA
- chemical change of the silver colloids
- adsorbed PHBA formed a special surface complex
- change of the adsorbed state.

To confirm the changes weren't due to structural decomposition of PHBA, we subjected solid PHBA powder to a temperature of 100 °C for more than 2 h. The Raman and IR spectra of the heated solid powder were the same as those of the unheated. Moreover, the aqueous solution of PHBA (10<sup>-2</sup> M) cooled down from boiling was added into the silver colloid and a spectrum was recorded that was also the same as that of PHBA unheated in the silver colloid. This spectrum indicated that the structural decomposition didn't take place and PHBA was still stable at temperatures as high as 100 °C.

The changes in the spectra weren't attributed to chemical changes of silver colloid because it was prepared by boiling and possessed high thermal stability.

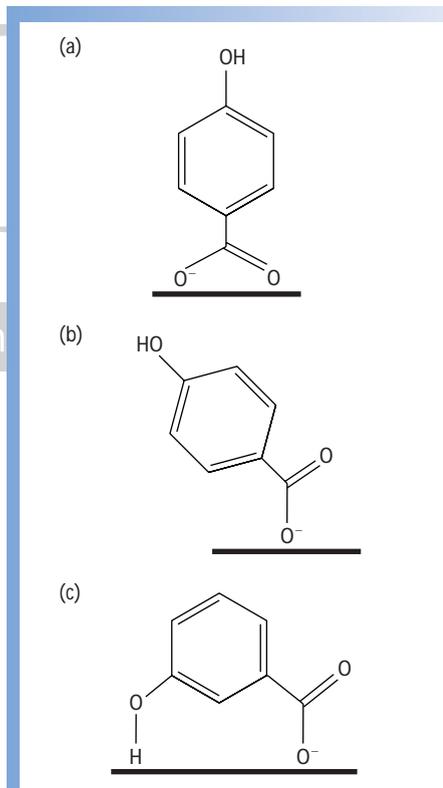
As for the third possibility — that is, a surface complex — the authors of reference 2 also proved that the SERS spectra of the heated para-substituted benzoic acids in silver colloid were caused by other sources rather than by a surface chemical reaction. They



**Figure 2.** SERS of MHBA in silver solution at (a) room temperature and (b) after cooling from 100 °C.

recorded the UV spectra of the benzoate ion and the adsorbed-desorbed benzoate ion on the silver mirror surface. Because both spectra were identical, the authors confirmed that the SERS spectrum for the heated sample must be caused by other sources rather than a surface chemical reaction.

We ruled out three of the possible reasons mentioned earlier and inferred



**Figure 3.** Schematic diagrams showing the adsorption of PHBA at (a) room temperature, and (b) after heating, and (c) the adsorption of MHBA.

**Table I. Raman frequency assignments for solid PHBA powder and SERS frequency assignments for aqueous PHBA (0.01 M) in heated silver solution.**

| Raman of Solid PHBA (cm <sup>-1</sup> ) | SERS of PHBA unheated (cm <sup>-1</sup> ) | SERS of PHBA heated (cm <sup>-1</sup> ) | Band assignment                           |
|---|---|---|---|
| 390                                     | 415                                       | 413                                     | In-plane ring deformation                 |
| 639                                     | 633                                       | 633                                     | C=O out-plane bending                     |
| 695                                     | 698                                       |   |   |
| 762                                     |   |   |   |
| 774                                     |   |   |   |
|   |   | 805                                     | Ring breathing vibration                  |
| 841                                     | 840                                       | 836                                     | Ring breathing vibration                  |
| 856                                     | 862                                       | 859                                     | C-COO <sup>-</sup> stretching             |
|   |   | 949                                     | C-H out-plane bending                     |
|   |   | 1023                                    | C-H in-plane bending                      |
| 1131                                    | 1145                                      | 1142                                    | C-H in-plane bending                      |
| 1165                                    |   | 1168                                    | C-H in-plane bending                      |
| 1221                                    |   | 1233                                    | C-OH bending                              |
| 1265                                    |   |   | C-H stretching                            |
| 1287                                    | 1280                                      |   | C-OH stretching                           |
| 1314                                    |   |   | CC stretching of benzene                  |
|   | 1392                                      | 1393                                    | COO <sup>-</sup> symmetric stretching     |
| 1441                                    |   |   | In-plane ring deformation                 |
|   |   | 1495                                    | In-plane ring deformation                 |
|   | 1518                                      | 1518                                    | In-plane ring deformation                 |
|   |   | 1584                                    | COO <sup>-</sup> antisymmetric stretching |
| 1600                                    | 1600                                      | 1600                                    | CC stretching of benzene                  |
| 1611                                    | 1614                                      | 1613                                    | CC stretching of benzene                  |

that the changes in the spectra were caused by the transformation of the adsorbed state of PHBA at silver surface due to the temperature-induced effect.

The FT-Raman spectrum of solid PHBA did not show any  $\nu(\text{C}=\text{O})$  band from an acid group. It was probably due to the formation of PHBA dimer in the crystalline network (9,10), which was formed by carboxyl groups involving H bonds and was broken in solution. The presence of a relatively strong  $\nu_s(\text{COO}^-)$  band at  $1392\text{ cm}^{-1}$  (see Figure 1a) indicated a dissociation of carboxylic acid on adsorption, while the relative weakness of the bands in the  $1200\text{--}1300\text{ cm}^{-1}$  region, corresponding to phenol moiety (hydroxyl group), suggested that the molecules were attached to the silver surface through the carboxyl group. Figure 1a shows strong bands attributed to the benzene ring at  $1614\text{ cm}^{-1}$ , which corresponds to the in-plane C-C stretching mode of benzene, and at  $1145\text{ cm}^{-1}$ , which was due to the in-plane C-H bending motions.

The band at  $860\text{ cm}^{-1}$  was also enhanced, which may be assigned to C-COO<sup>-</sup> stretching possibly coupled to the ring breathing mode of benzene. The strong intensity of in-plane modes in the SERS of PHBA suggested the perpendicular orientation of this molecule in relation to the surface (7). The suggested bonding configuration is shown in Figure 3a. In addition, the hydroxyl group of PHBA contained a lone pair of electrons and tended to adsorb to silver particles through charge transfer. The system of silver colloid was in dynamic equilibrium and there were more than one kind of possible adsorption modes. As a result, while the mass of molecules adsorbed through the carboxyl group, some might adsorb through the hydroxyl group.

Based on these discussions, we analyzed the adsorbed state of PHBA in silver colloids after cooling down from boiling. Comparing Figure 1d with 1a, we found that the bands at  $1393\text{ cm}^{-1}$  and  $1584\text{ cm}^{-1}$ , due to COO<sup>-</sup> symmet-

ric and antisymmetric stretching vibration, respectively, were enhanced significantly and became the strongest peaks in Figure 1d. The peak at  $859\text{ cm}^{-1}$  decreased, which was assigned to C-COO<sup>-</sup> stretching vibration, possibly coupling with benzene breathing. The band at  $1279\text{ cm}^{-1}$  corresponding to phenol moiety weakened, accompanying the rise of a peak at  $1233\text{ cm}^{-1}$  due to C-OH bending mode. According to the SERS selection rules (11,12) and on the basis of spectral changes and with the result in (2), we proposed that the geometry of PHBA chemisorbed on the surface of silver was as shown in Figure 3b. The carboxyl group bond (C-O<sup>-</sup>) was perpendicular to the metal surface in another mode and the  $1393\text{ cm}^{-1}$  band was enhanced extraordinarily. The  $1393\text{ cm}^{-1}$  was broadened, corroborating the interaction between

the carboxyl group and the silver surface. The peak at  $859\text{ cm}^{-1}$  assigned to C-COO<sup>-</sup> stretching vibration weakened because the bond of C-COO<sup>-</sup> could not be perpendicular to the surface of metal in latter mode. The band of  $1279\text{ cm}^{-1}$  due to C-OH stretching vibration weakened for the same reason. The  $1168\text{ cm}^{-1}$  band was enhanced for the C-H bending mode, and was possibly perpendicular to the surface. The band at  $633\text{ cm}^{-1}$  due to the C=O bending mode was also notably enhanced. Given the nature of dynamic equilibrium of the colloid, there were possibly other adsorbed modes, which were not dominating.

We speculated that the adsorbed state changed from bonding by the carboxyl group (two oxygen atoms) to bonding by the electron of the carboxyl group (electrovalent bond) because the relatively stable double layer was destroyed in varying degrees by the heating treatment. In the silver colloid, nanoparticles tended to adsorb negative ions so

that the nanoparticles were surrounded by a layer of negative ions, which in turn were surrounded by a diffusive layer of positive ions, thus forming a diffusive double layer. The colloid was a thermodynamically unstable system in nature and it could be stable for days to weeks because the double layer prevented silver particles from collision or aggregation with each other. This double layer was formed in the course of silver colloid preparation, so the negative ions adsorbed on the surface of silver particles came from  $\text{NO}_3^-$  and  $(\text{cit})^{3-}$  and so on. When an aqueous solution of PHBA was added into silver colloid, the metal sites were mainly occupied by  $\text{NO}_3^-$  and  $(\text{cit})^{3-}$ . So the sites occupied by  $-\text{COO}^-$  and  $-\text{OH}$  were few, which led to the competition between  $-\text{COO}^-$  and  $-\text{OH}$ . As a result, the PHBA molecules tended to adsorb to the silver nanoparticles by carboxyl group.

As the temperature went up, the negative ions broke away from the metal surface and the relatively stable double layer was destroyed in varying degrees. After the heating ceased, the temperature decreased and a vast amount of negative ions, including PHBA, would seek dynamic equilibrium to reconstruct a new diffusive double layer. PHBA adsorbed to the silver by the carboxyl group electron makes more molecules adsorb, but the heat treatment may destroy the bond between  $\text{C}=\text{O}$  and silver and cause the  $\text{C}=\text{O}$  to break away from the substrate surface.

As for MHBA, heating seemed not to induce the tremendous change on the adsorption mode. This resistance to change may result from the relative steadiness of the adsorbed state through both the carboxyl group and the phenol of MHBA. The intensity of Figure 2b is twice that of Figure 2a, which possibly is caused by damage to the double layers for heating and the increased amount of adsorbed MHBA.

In addition, Figure 2b also demonstrates that the  $1393\text{ cm}^{-1}$  band may be strong when the  $\text{COO}^-$  was connected to the silver surface by the electron of the carboxyl group, which was the same as the case of PHBA after heating.

## Conclusion

The variation of temperature influenced SERS of PHBA in a silver system occurs mainly because the heating treatment destroyed the bond between  $\text{C}=\text{O}$  and silver and destroyed the double layer formed in the course of silver colloid preparation. The heating treatment brought about the transformation of the adsorbed state of PHBA on the silver particle surface. As the temperature increased, the adsorbed state of the PHBA molecules on the metal surface changed from bonding through the carboxyl group to bonding through the carboxyl group electron.

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