STUDY OF ADSORPTIVE BEHAVIOR OF A SERIES OF N-AMINOBENZOIC ACIDS ON SILVER NANO-PARTICLES BY SERS

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Abstract: Surface-enhanced Raman scattering (SERS) spectra of a series of n-aminobenzoic acids (n-ABA, n=P, M and O) adsorbed on the silver nano-particles were studied, respectively, in the silver colloidal solution and on the dried silver-coated filter paper. Significant changes were found from two SERS spectra of PABA but MABA or OABA. The probable reasons are given.

SERS technology is a powerful utility in studying the surface characteristic of the substrates and the surface configuration of the adsorbates. Thus, it is fairly significant with the SERS technology to detect the adsorptive behavior of the molecules with representative configuration, to acquire the factors influencing the molecules’ adsorptive behavior and to grasp the general adsorptive law of representative molecules adsorbed on the surfaces of silver nano-particles. In our former study [1], it has been found that the SERS spectrum of p-hydroxybenzoic acids adsorbed on the silver nano-particles in colloidal solution is fairly different from that on dried filter paper. In our study now, the similar methods are employed and significant changes are also found in two SERS spectra of PABA but MABA or OABA, which is derived from the different adsorptive behavior of the same molecules on the different substrate. The SERS spectra of PABA, MABA and OABA on two substrates are respectively shown in Fig.1~3 and the vibrational mode assignments refer to references [2~8].

From Fig.1 it can be seen obviously that two SERS spectra of PABA are different. In Fig.1(b), the appearance of the middle broad peak at 1378 cm\(^{-1}\) belonged to \(\tilde{v}_s(CO_2)\) and the strong peak at 858 cm\(^{-1}\) ascribed to \(\tilde{v}_s(CO_2)\) suggest that the carboxyls of PABA molecules interact directly with the silver surface and the bond of C-CO\(_2\) is perpendicular to it. The strong enhancement of 1537 cm\(^{-1}\) peak ascribed to \(\tilde{v}(CC)\) of benzene, 1144 cm\(^{-1}\) peak attributed to \(\tilde{\alpha}(C-H)\) and 411 cm\(^{-1}\) peak of benzene in-plane breathing all indicate that the plane of benzene ring is perpendicular to the silver surface. So PABA molecules in silver colloid stand perpendicularly on the silver surface through carboxyls. While in Fig.1(c), the strong enhancement of 1453 cm\(^{-1}\) peak and the significant redshift of 1602 cm\(^{-1}\) which are all ascribed to \(\tilde{v}(CC)\) indicate that the benzene rings probably participate the interaction between PABA molecules and silver surfaces. The relatively weakening of 1370 cm\(^{-1}\) peak of \(\tilde{v}_s(CO_2)\) and 858 cm\(^{-1}\) peak of \(\tilde{v}_s(CO_2)\) shows that the carboxyls of PABA molecules still interact with silver surface but the bond of C-CO\(_2\) is not perpendicular to it. The appearance of broad peak at 980 cm\(^{-1}\), which is probably derived from the interaction of amino group with silver surface, and the relatively broadened and redshifted peak at 1137 cm\(^{-1}\) which is attributed to both \(\tilde{\alpha}(C-H)\) and \(\tilde{\delta}(NH_2)\) indicate that the amino groups of PABA molecules interact directly with the silver surface. So PABA molecules on silver-coated filter paper are probably lie flat on the silver surface through carboxyl and amino groups.

From Fig.2 we can see that two SERS spectra of
MABA molecules on two substrates are very similar except the background in high wavelength due to the filter paper. The appearance of peak at 1381 cm\(^{-1}\) assigned to \(\nu_s(\text{COO}^-)\) and the absence of peak near 850 cm\(^{-1}\) assigned to \(\nu_a(\text{CO}_2)\) indicate that carboxyls interact directly with silver surface but C-CO\(_2\) bond is not perpendicular to the silver surface. The strong enhancement of 1000 cm\(^{-1}\) peak attributed to benzene breathing suggests that the plane of benzene is perpendicular to silver surface. The broad peak at 519 cm\(^{-1}\) corresponding to \(\delta(\text{NH}_2)\) shows that the amino groups probably adsorb directly on silver surface. So MABA molecules probably adsorb on the surface of silver nano-particles by side through carboxyl and amino groups on two substrates.

From Fig.3 we can see that two SERS spectra of OABA molecules on two substrates are very similar except the relatively intensity of a few peaks. In Fig.3(b), 1392 cm\(^{-1}\) peak of \(\nu_a(\text{CO}_2)\) and 853 cm\(^{-1}\) peak of \(\nu_a(\text{CO}_2)\) indicate OABA molecules also adsorb on silver surface through carboxyls. The appearance of other out-of-plane mode peaks show that OABA molecules probably tilt on silver. The relatively intensities of 1611, 1582, 1392, 853 and 850 cm\(^{-1}\) peaks in Fig.3(b) are different from those in Fig.3(c), which are probably due to the different orientations of OABA molecules. So OABA molecules tilt on silver surface through carboxyls and in silver colloid its plane tends to be perpendicular to silver surface but on silver-coated filter paper tends to be parallel.

In conclusion, significant changes were found from two SERS spectra thus the molecules’ adsorptive behavior of PABA but MABA or OABA, suggesting that the surface characteristic of the substrate and the surface configuration of the adsorbate could exert a great influence on the adsorptive behavior.

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**References:**