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表面增强拉曼光谱研究自组装单分子层在化学接触和纳米隔绝下的分子振动活性变化

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摘要: 为确定表面增强拉曼光谱中某些有争议的弱振动模式是来自高阶的影响还是分子基团对称性变化的影响, 本文以 1,4-苯二硫醇作为探针分子提供了一种实验验证的框架方法. 光谱实验显示, 观测到的有争议的弱振动模式并不是来自高阶的影响, 而是分子基团对称性变化所致. 我们的实验框架方法很容易拓展开来, 如用于研究其它波长激光激发的类似体系或有机分子搭接的分子结.

关键词: 表面增强拉曼光谱; 高阶影响; 对称性变化; 1,4-苯二硫醇; 银纳米颗粒

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Vibrational Activity Change of Self-Assembled Monolayers upon Chemical Attachment and Nanoscale Block Revealed by Surface Enhanced Raman Spectroscopy

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Abstract: The origin of weak ambiguous vibrational modes in surface enhanced Raman scattering (SERS), i.e., from the high-order effect or symmetry change using 1,4-benzenedithiol (BDT) as a probe, is investigated. Weak ambiguous vibrational modes are caused by symmetry change rather than high-order effect. The experimental method can be extended, e.g., to similar systems excited by lasers with different wavelengths, or microelectronic junctions bridged by organic molecules.

Key Words: Surface-enhanced raman scattering; High-order effect; Symmetry change; 1,4-Benzenedithiol; Silver nanoparticle

1 Introduction

The rapid development of the nanotechnology today is deep-

ly rooted in its ability of integrating with other research areas within physics, chemistry, biology, and materials science, etc.

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One of the mostly studied nanoscale materials is the metal nanoparticle (MNP) due to its broad applications in catalysis, photovoltaics, microelectronics, biological diagnostics, and therapeutics, etc.¹⁻⁴ It is well recognized that MNPs can provide multiple functional properties related to optics, magnetism, and thermotics. For example, in order to serve as a biosensor, the surfaces of MNP need to be functionalized with specific molecular groups, such as fluorescence or vibrational chromophores. It is thus of great importance to characterize the spectroscopic activity or sensitivity of the corresponding molecular groups attached to the surfaces of MNPs. One of the commonly used characterization techniques is surface enhanced Raman scattering (SERS) which can provide the huge enhanced vibrational signals.^{5,6} Excellent work has been done to illustrate this issue and successfully increase the detection resolution.⁷⁻⁹ However, with respect to SERS itself, there still remains certain fundamental questions, one of which is, whether the high-order effect can contribute to the observed vibrational signals during a SERS process.¹⁰⁻¹⁵ As discussed in previous literature,^{11,12} the quadrupole polarizability may operate significantly comparable to the normal electric dipole polarizability which can make normal inactive vibrational modes to be active when a field gradient exists near the metal surface. In a SERS study on 1,4-benzenedithiol (BDT) adsorbed on silver colloids,^{13,14} the appearance of some weak ungerade vibrations were attributed to either the quadrupole effect or the reduced symmetry associated with the flat adsorption geometry of BDT on the Ag surface. Given the assignment uncertainty of such vibrational modes, in this paper, we used 1,4-benzenedithiol as probe molecules and prepared samples of BDT in several distinct geometries. Via the SERS measurement for such BDT samples, we can easily recognize the origin of some usually ambiguous weak vibrational modes. In addition, our experimental method presented in this paper provides an easy framework which can be applied to study the metal-organic hybrid materials in the nanoscale.

2 Experimental

Basically we had nine BDT samples binding in different geometries and/or chemical states, six of which were sequentially bulk BDT (bBDT), BDT dithiolate, BDT adsorbed onto the silver (Ag) nanoparticles (BDT-AgNP), oligomer BDT adsorbed onto the Ag nanoparticles (*n*BDT-AgNP) (*n*=5-7), self-assembled monolayer of BDT on the gold (Au) substrate (BDT-Au), Ag nanoparticles-capped self-assembled monolayer of BDT on the gold substrate (AgNP-BDT-Au), Ag nanoparticles-capped self-assembled monolayer of oligomer BDT on the gold substrate (AgNP-*n*BDT-Au). The remaining two samples were nearly the same as those of AgNP-BDT-Au and AgNP-*n*BDT-Au; the only difference was that we sandwiched a thin layer of polymethylmethacrylate (PMMA) between the Ag nanoparticles and the self-assembled monolayer of BDT or *n*BDT on Au to prevent the formation of Ag-S bonds (AgNP-PMMA-BDT-Au and AgNP-PMMA-*n*BDT-Au). So the S-H bonds at the

end BDT towards AgNP still existed. The simplified schematics of the nine samples for SERS measurement are shown in Fig.1.

Preparation of AgNP was following the reported method¹⁶ with necessary modification. 17 mg of silver nitrate (AgNO₃) was dissolved in 100 mL of water and heated to boiling. 2 mL of 1% (g · mL⁻¹) sodium citrate-water solution was added with stirring. The mixture was kept on boiling for ~30 min. The solution containing AgNP in greenish yellow was obtained and then stabilized for 2 h. The obtained AgNP was of a nearly spherical shape with an average diameter of 60 nm (there was a diameter distribution of the AgNP, mostly ranging from 40 to 80 nm) under the scanning electron microscope (JSM-5610, JEOL), as shown in Fig.2. BDT (99%, GC, Sigma-Aldrich) was dissolved in ethanol and then added into the AgNP solution to prepare a BDT-AgNP solution with a concentration of 0.4 mg · mL⁻¹. BDT dithiolate solution was prepared by adding BDT-ethanol solution into 6 mol · L⁻¹ sodium hydroxide (NaOH)-water solution. Oligomer BDT (*n*BDT) was prepared by adding 1,3-dibromo-5,5-dimethylhydantoin (DBDMH) into the BDT-ethanol solution with stirring for more than 1.5 h.¹⁷ *n*BDT-AgNP was prepared in the same way as BDT-AgNP was prepared. The Au substrates were prepared by sputtering 100-nm layers of Au onto the clean glass slides using an ion sputter coater (JS-1600, Beijing Hetongchuangye Technology Co., Ltd.). Before that, a 10-nm layer of nickel (Ni) was sputtered onto the glass slides to promote the adhesion between Au and glass slides. The Au substrates were immersed into the BDT and *n*BDT solutions respectively to form self-assembled monolayers (SAM) of BDT (BDT-Au) and *n*BDT on top. The AgNP solutions were then casting onto the SAM-capped Au substrates to make AgNP-BDT-Au and AgNP-*n*BDT-Au samples. The AgNP-PMMA-BDT-Au and AgNP-PMMA-*n*BDT-Au samples were prepared by spin coating a thin layer of PMMA (2-4 nm thick measured by an EP3-SW ellipsometer, Nanofilm Technologie, GmbH) onto the SAM-capped Au substrates and then casting the AgNP solutions on top. The solid samples including AgNP-BDT-Au, AgNP-*n*BDT-Au, AgNP-PMMA-BDT-Au,

Fig.1 Schematics of the nine samples studied in this paper

A: bBDT; B: BDT dithiolate; C: BDT-AgNP; D: *n*BDT-AgNP; E: AgNP-BDT-Au; F: AgNP-PMMA-BDT-Au; G: AgNP-*n*BDT-Au; H: AgNP-PMMA-*n*BDT-Au; I: BDT-Au. For simplification, only single molecules of BDT or *n*BDT were plotted since no ambiguity could arise.

Fig.2 SEM image of the as-prepared AgNP

and AgNP-PMMA-*n*BDT-Au were dried at 40 °C under the vacuum oven for overnight.

3 Results and discussion

Fig.3 showed the Raman spectra of bBDT, BDT dithiolate, SERS spectra of BDT-Ag and *n*BDT-Ag in the range of 300 to 1600 cm^{-1} where the fingerprint vibrational modes can serve as the characterization bands of the benzene ring.^{18,19} Table 1 listed the assignment of the observed vibrational modes.^{14,15,18,19} For bBDT, with considering the two S—H bonds, its symmetry becomes C_s and thus all the vibrational modes should theoretically be active (Fig.3(a)). For BDT dithiolate, its high symmetry of D_{2h} must make certain active bands under the C_s symmetry inactive. Indeed, in the Raman spectra of BDT dithiolate, the 16b, 20a, 6b, and 3 modes disappeared compared to that of bBDT, which is consistent with our anticipation (Fig.3(b)). Besides, the bandwidths of BDT dithiolate were broader than those of bBDT, indicating the inhomogeneity under ionization and solvation in the basic solution. In the SERS spectrum of BDT-AgNP (Fig.3(c)), similar to what has been reported,^{14,15} several minor vibrational modes were observed including the 16b, 20a, 18a, and 19a modes. A flat adsorption geometry of BDT dianion on Ag which holds the C_{2v} symmetry has been proposed to be responsible for appearance of such minor vibra-

Fig.3 Raman spectra of (a) bBDT, (b) BDT dithiolate, (c) BDT-AgNP, and (d) *n*BDT-AgNP

The spectra in the figure A were offset and the spectra in the figure B were rescaled and offset for clarity. The bands in dashed circles indicate those ambiguous bands with assignment uncertainty.

tional modes.^{14,15} In Table 1, we can see, if the BDT dianion was considered to belong to the C_{2v} symmetry rather than the D_{2h} symmetry, the vibrational modes of 16b, 20a, 18a, and 19a were Raman-active and this was consistent with the observed spectra in Fig.3. An alternative explanation was also given that the high-order effect related to the quadrupole polarizability could cause such vibrational modes when the field gradient was present in the vicinity of the Ag surface.^{11,12} Since we prepared oligomer-BDT (*n*BDT with $n=5-7$), it could provide useful information when the S—H group in the vicinity of Ag surface was replaced by the S—S bond. Indeed, in the SERS spectrum of *n*BDT-AgNP (Fig.3(d)), the vibrational modes of 16b, 20a, 18a, and 19a modes did not appear. If the high-order effect did have the unnegligible contribution to the SERS process, such vibrational modes should be clearly observed not only in the SERS spectrum of BDT-AgNP but also in that of *n*BDT-AgNP since such modes are not involved in the S—H vibration. It is thus questionable to attribute such observed un-

Table 1 Assignment of vibrational modes of 1,4-benzenedithiol (BDT)^{14,15,18,19}

Peak center/ cm^{-1}	Vibrational mode	Assignment of C_{2v}		Assignment of C_{2h}	
		symmetry species	Raman activity	symmetry species	Raman activity
~1574	8a	A_1	$\alpha_{xz}, \alpha_{yz}, \alpha_{zz}$	A_g	$\alpha_{xz}, \alpha_{yz}, \alpha_{zz}$
~1468	19a	A_1	$\alpha_{xz}, \alpha_{yz}, \alpha_{zz}$	B_{1u}	inactive
~1305	3	B_2	α_{yz}	B_{3g}	α_{yz}
~1186	9a	A_1	$\alpha_{xz}, \alpha_{yz}, \alpha_{zz}$	A_g	$\alpha_{xz}, \alpha_{yz}, \alpha_{zz}$
~1093+1058	1(Fermi)	A_1	$\alpha_{xz}, \alpha_{yz}, \alpha_{zz}$	A_g	$\alpha_{xz}, \alpha_{yz}, \alpha_{zz}$
~1009	18a	A_1	$\alpha_{xz}, \alpha_{yz}, \alpha_{zz}$	B_{1u}	inactive
~945	5	B_1	α_{zz}	B_{2g}	α_{zz}
~913	$\beta(\text{CSH})^*$	—	—	—	—
~740	7a	A_1	$\alpha_{xz}, \alpha_{yz}, \alpha_{zz}$	A_g	$\alpha_{xz}, \alpha_{yz}, \alpha_{zz}$
~632	6b	B_2	α_{yz}	B_{3g}	α_{yz}
~541	20a	A_1	$\alpha_{xz}, \alpha_{yz}, \alpha_{zz}$	B_{1u}	inactive
~521	16b	B_1	α_{zz}	B_{3u}	inactive
~338	6a	A_1	$\alpha_{xz}, \alpha_{yz}, \alpha_{zz}$	A_g	$\alpha_{xz}, \alpha_{yz}, \alpha_{zz}$

* β : bending

Fig.4 Images of FDTD calculation result

Side views showing EM field distribution contours of a 60 nm Ag nanoparticle on a perfectly smooth Au substrate in the xz plane and in the yz plane.

Top view showing EM field distribution contour in the plane between the Ag nanoparticle and the smooth Ag surface, where the probe molecules (BDT) would locate. The incident light had a wavelength of 1064 nm and a polarization as shown.

gerade vibrational modes of BDT-AgNP to the high-order effect or the flat geometry. The more authentic reason is still the symmetry difference between BDT dithiolate and BDT-AgNP.

In order to gain the further evidence related to the origin of the observed ungerade vibrational modes, we prepared the geometrically sandwiched samples of AgNP-BDT-Au, AgNP-*n*BDT-Au, AgNP-PMMA-BDT-Au, and AgNP-PMMA-*n*BDT-Au and collected their SERS spectra. As we know, for such samples, the SERS signals should come from the gap area between AgNP and Au where the coupling between the localized surface plasmon of AgNP and the surface polariton of the underneath Au were existing.²⁰ The finite-difference time-domain (FDTD) simulation result shown in Fig.4 suggested that the gap between AgNP and the Au substrate was the most intense area with respect to the distributed field. It is therefore that the vibrational modes in the SERS spectra shown in Fig.5 were all from the SAM of BDT at the gap area. As a comparison, the Raman spectrum of only a SAM of BDT on top of the Au substrate was also collected, as shown in Fig.5(a). Indeed, without the AgNP cap, there was no detectable vibrational signal at all, again suggesting the observed vibrational signals were coming from the gap area between AgNP and the Au substrate.

It is pretty clear from Fig.5 that when AgNP was directly deposited onto SAM of BDT, no ungerade vibrational modes were observed (AgNP-BDT-Au (Fig.5(b)) and AgNP-*n*BDT-Au (Fig.5(c))); when a blocked PMMA layer was placed between AgNP and SAM of BDT, the ungerade vibrational modes including 16b, 20a, and 18a appeared again (AgNP-

PMMA-BDT-Au (Fig.5(d)) and AgNP-PMMA-*n*BDT-Au (Fig.5(e))). Due to the relatively high noise-to-signal ratio, the 19a mode in SERS spectra of AgNP-PMMA-BDT-Au and AgNP-PMMA-*n*BDT-Au could hardly be identified. But this would not affect our judgment. Since in this case, the field gradient at the gap area (along the surface normal, from the AgNP to the Au substrate) was definitely not as significant as that in the vicinity of Ag surface (BDT-AgNP), the appearance of such vibrational modes can not be attributed to the quadrupole

Fig.5 Raman spectra of (a) BDT-Au, (b) AgNP-BDT-Au, (c) AgNP-*n*BDT-Au, (d) AgNP-PMMA-BDT-Au, and (e) AgNP-PMMA-*n*BDT-Au

The spectra in the figure A were offset and the SERS spectra in the figure B were rescaled and offset for clarity. The bands in dashed circles indicate those ambiguous bands with assignment uncertainty.

polarizability effect. Such vibrational modes can only arise from the reduced symmetry due to the protection of the PMMA layer to the end S—H bond of BDT and *n*BDT towards AgNP.

4 Conclusions

In this paper, an experimental framework was worked out to illustrate the origin of certain ambiguous vibrational modes in the SERS spectra. Concerning the BDT molecules prepared in different geometries/states for the SERS measurement excited by the 1064 nm laser, no vibrational signals originated from the high-order effect were detected in the SERS spectra. The observed change of the vibrational signals was proved to be attributed to the symmetry change of the BDT molecules *via* chemical attachment and/or nano block. Although currently we can not make judgment whether the same conclusion can be drawn for the previous studies, our experimental framework can be feasibly transferred to study similar systems. We also believe that the experimental methodology provided in this paper can be generalized and applied to study other nanoscale hybrid materials, for instance microelectronic junctions, when using SERS as a characterization technique.

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