Self-assembled dynamics of silver nanoparticles and self-assembled dynamics of 1,4-benzenedithiol adsorbed on silver nanoparticles: Surface-enhanced Raman scattering study

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\textbf{Abstract}

Self-assembled dynamics of silver nanoparticles and self-assembled dynamics of 1,4-benzenedithiol (1,4-BDT) adsorbed on silver nanoparticles were investigated experimentally with surface-enhanced Raman scattering (SERS) and theoretically with density functional theory (DFT) and finite difference time domain (FDTD) method. The absorption spectroscopy of 1,4-BDT in silver sol at different time intervals was measured, which give the indirect evidence of self-assembled dynamics of silver nanoparticles and self-assembled dynamics of 1,4-benzenedithiol (1,4-BDT) adsorbed on silver nanoparticles. To obtain the direct evidence of self-assembled dynamics of silver nanoparticles and self-assembled dynamics of 1,4-benzenedithiol (1,4-BDT) adsorbed on silver nanoparticles, the SERS of 1,4-BDT were measured experimentally and investigated theoretically. The appearances of S–S stretching band (revealing the formation of multilayers of 1,4-BDT), and strongly enhanced S–C stretching, C–C ring stretching vibrational modes clearly show self-assembled dynamics of 1,4-BDT.

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1. Introduction

Since its discovery, surface-enhanced Raman scattering (SERS) has been developed as a powerful tool for analyzing vibrational structure [1–5]. SERS of 1,4-benzenedithiol (1,4-BDT, see Fig. 1) adsorbed on metal nanoparticles has been greatly investigated experimentally and theoretically [6–10]. The SERS studies showed that only monolayer of 1,4-BDT was assembled on silver nanoparticles, while the S–S stretching vibration appeared at \( \sim 536 \text{ cm}^{-1} \), when the 1,4-BDT was adsorbed on gold nanoparticles (revealing the formation of multilayers of 1,4-BDT) [6,7]. They considered that the monolayer was assembled on the silver surface with a flat orientation by forming two Ag–S bonds [7]. Is it true? What is the nature?

In this paper, self-assembled dynamics of silver nanoparticles and self-assembled dynamics of 1,4-BDT adsorbed on silver nanoparticles were investigated experimentally and theoretically. We measured the absorption of 1,4-BDT adsorbed on silver nanoparticles at different time intervals. Secondly, we measured the SERS of 1,4-BDT adsorbed on silver nanoparticles at different time intervals. At the early stage, the SERS of 1,4-BDT is consistent with the results shown in Ref. [7]; with the increase of the time, the evidence for the aggregation of silver nanoparticles and the formation of multilayers of 1,4-BDT as well as the help of the simulation of SERS was obtained directly.

2. Experimental

The SERS active silver colloid was prepared by citrate reduction of AgNO\(_3\) [11]. AgNO\(_3\) (90 mg) was dissolved in 650 ml of quartz-distilled water. 500 ml of this solution was brought to boiling and then a solution of 1% sodium citrate (10 ml) was added. 30 min later the remaining 150 ml AgNO\(_3\) solution was added 3 times every 15 min. The solution was kept on boiling about 1.5 h. The final Ag particle concentration was estimated to be \( \sim 35 \text{ pM} \) with an average diameter size around 100 nm [11(b)].

\( 10^{-2} \) to \( 10^{-3} \text{ M} \) ethanol solution of 1,4-benzenedithiol was added dropwise into 5 ml Ag sol solution, and the final concentrations are \( 10^{-3} \) and \( 10^{-4} \text{ M} \), respectively. The newly produced 1,4-benzenedithiol in aqueous silver at concentration of \( 10^{-3} \text{ M} \) was diluted fivefold by distilled water and was measured for absorption spectrum immediately with Optic Spectrometer (Ocean Optics Inc., Model HR2000). The absorption spectra were measured in the time intervals of 40 min, 2 h, 5 h and 17 h. The light was turn off between two measurements.
The solution of 1,4-benzenedithiol in aqueous silver at concentration of $10^{-4}$ M was introduced into capillary sample cells for SERS measurement. SERS spectra were recorded immediately after laser irradiating on the samples. The Raman spectra were measured in the intervals of 0, 5 and 120 min. The laser was irradiated on the samples during the whole measurement process. SERRS spectra were recorded by the Renishaw inVia Raman system equipped with an integral microscope (LEICA, DMLM). The 514.5 nm radiation from a 25 mW air-cooled argon ion laser (Laser Physics, Model 25s-514) was used as the excitation sources. In our Raman experiment, the laser power irradiated on the SERS sample was 2 mW with 5× objective. The appropriate holographic notch filter was set in the spectroscopy. The holographic grating (1800 grooves/mm) and the slit allowed the spectra resolution to be 1 cm$^{-1}$. The spectrometer repeatability is ±0.2 cm$^{-1}$. Raman scattering was detected using a peltier cooled CCD detector (576 × 384 pixels). Data acquisition time used in the experiment was 10 s.

3. Theoretical

Absolute off resonance Raman intensities can be calculated as the differential Raman scattering cross-section. For Stokes scattering with an experimental setup of a 90° scattering angle and perpendicular planar-polarized light, the cross-section is written as [12]

$$\frac{d\sigma}{d\Omega} = \frac{\pi^2}{\varepsilon_0^2} (\omega_{in} - \omega_p)^4 \frac{h}{8\pi^2c\omega_p} S_p \frac{1}{45[1 - \exp(-hc\omega_p/k_BT)]}$$  \hspace{1cm} (1)

where $\omega_{in}$ and $\omega_p$ are the frequency of the incident light and of the $p$th vibrational mode, respectively, and $S_p$ is the Raman scatter-

Fig. 1. Chemical structure of 1,4-benzenedithiol (1,4-BDT).

Fig. 2. The absorption spectroscopy of 1,4-BDT adsorbed on silver nanoparticles at different time intervals.

Fig. 3. (a) The experimental SERS spectra, (b) the simulated normal Raman spectra of 1,4-BDT monomer and dimer, (c) the simulated normal Raman spectra of 1,4-BDT monomer with the vibrational modes, and (d) the simulated normal Raman spectra of 1,4-BDT dimer with the vibrational modes.
The electromagnetic enhancements (|M|) of two Ag nanoparticles (D = 100 nm) with a distance of 2 nm (a) and 1 nm (b) at incident lights of 514.5 nm. The color bars of |M| were shown at the right of the pictures. The enhancements of SERS intensities, approximated as the fourth power of the field enhancement factor |M|, are |M|^4. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

\[ S_p = 45 \left( \frac{\partial \sigma_p}{\partial Q_p} \right)^2 + 7 \left( \frac{\partial \gamma_p}{\partial Q_p} \right)^2 \]  

which is a pure molecular property and independent of experimental setup. \( \sigma_p \) and \( \gamma_p \) are the isotropic and anisotropic polarizabilities, respectively. In this paper, the ground-state geometry of 1,4-BDT (Fig. 1) was optimized with density functional theory (DFT) [13], B3LYP functional [14], basis sets of 6-31G(d). With the optimized geometry of 1,4-BDT, \( S_p \) was directly calculated by Gaussian 03 suite [15].

The electromagnetic enhancements at the incident light of 514.5 nm were calculated with the finite difference time domain (FDTD) method [16]. In the calculations, the coupling effects [6] of two nanoparticles (diameter 100 nm) with a distance of 2 and 1 nm were considered, for example. The molecules are assumed to be located in the center between particles, where the large enhancement can be obtained. The electromagnetic enhancements of SERS can be estimated by

\[ G_{EM} = |M|^4 = \frac{E_i^4}{E_i} \]  

where \( E_i \) and \( E_i \) are the local and incident fields.

4. Results and discussion

4.1. Self-assembled dynamics of silver nanoparticles

The experimental absorption spectra of 1,4-BDT in silver sol were measured at different time intervals (see Fig. 2). It can be found that with the increase of the time, the 500 nm peak at 0 min gradually red shifted to 535 nm after 17 h, which is the experimental evidence for the aggregates of silver nanoparticles. With the aggregation of silver nanoparticles, the distance between the nanocrystals decreases, the coupled plasmon resonance shifted to the red.

To further confirm it, the SERS of 1,4-BDT adsorbed on silver nanoparticle at different time intervals (Fig. 3(a)). At the early stage, the SERS of 1,4-BDT is consistent with the results shown in Ref. [7]; with the increase of the time, the SERS intensity increases as the interparticle distance between the silver aggregates decreases with a constant dye concentration.

With the aggregates of silver nanoparticles, the distance between the nanocrystals decreases, and the enhanced electromagnetic field increases between the particles. The dominant part of the enhancement factor is due to an increase of the local electric field between silver particles. The molecules are assumed to be located in the center between particles, where the large enhancement can be obtained. Considering the coupling effect from two Ag nanoparticles with the distance of 2 and 1 nm, and the electromagnetic enhancements of SERS (\( G_{EM} = |M|^4 \)) at 514.5 nm in the center between two particles are \( G_{EM} = 7.16 \times 10^7 \) and \( G_{EM} = 2.16 \times 10^9 \) (see Fig. 4).

4.2. Self-assembled dynamics 1,4-benzenedithiol adsorbed on silver nanoparticles

The energy dependence for oligomers can be predicted by exciton theory [17],

\[ E_l = E_0 + 2 \beta \cos \left( \frac{\pi l}{N + 1} \right) \]  

Fig. 5. The experimental and theoretical normal Raman spectra of 1,4-BDT powder.
where \( l = 1, 2, \ldots, N \) (\( N \) is the unit of monomer), \( E_0 \) is the energy of excited state of each unit and \( \beta \) is the interaction strength between nearest-neighbor units. According to Eq. (4), with the increase of the numbers of monomers, the absorption of multilayers of 1,4-BDT will be red shifted, which reveal the formation of multilayers of 1,4-BDT. To obtain detailed answer, the SERS of 1,4-BDT adsorbed on silver nanoparticles at different intervals was measured, and the vibrational modes were assigned theoretically.

Before SERS measurement, the Raman spectroscopy of 1,4-BDT powder was measured experimentally (Fig. 5(a)) and calculated theoretically (Fig. 5(b)), and vibration modes with strong intensity were assigned (Fig. 6). The Raman intensities in the range of 400–600 cm\(^{-1}\) vanished.

To obtain direct evidence of self-assembled dynamics of 1,4-BDT adsorbed on silver nanoparticles, the SERS of 1,4-BDT was measured experimentally at different time intervals, and analyzed theoretically. At the early stage, the SERS of 1,4-BDT is consistent with the results shown in Ref. [7]; with the increase of the time, the appearances of S–S stretching band reveals the formation of multilayers of 1,4-BDT. The strongly enhanced S–C stretching and C–C ring stretching vibrational modes in SERS measurement, also show that the formation of multilayers of 1,4-BDT, which result from the coupling effect of the symmetric vibrations between two monomers (see Figs. 3(b) and 7 below analysis).

As shown in Fig. 3(a), the vibrational modes \( v_3 \) and \( v_4 \) are absent at the early time intervals; with the increase of the time, the intensities of these two vibrational modes were strongly enhanced. These are the direct evidence for the formation of multilayers of 1,4-BDT, which can be confirmed by the theoretical calculations of Raman spectra of 1,4-BDT monomer and dimer connected with S–S bond (see Fig. 7). For the 1,4-BDT monomer, these two vibrational modes are absent (see Fig. 3(c)); while they are appeared for the Raman of 1,4-BDT dimer connected with S–S bond (see Fig. 3(d)). The vibrational mode at 480 cm\(^{-1}\) in Fig. 3(a) is the S–S stretching mode, which can be supported by the vibrational mode at 450 cm\(^{-1}\) in Fig. 3(b). The difference between the experimental and theoretical results is from the ignorance of silver sol in the calculations. In our theoretical calculations, the scaling factor is not consid-
Fig. 7. The vibrational modes for the normal Raman spectrum of 1,4-BDT dimer.

![Vibrational Modes](image)

Fig. 8. The models of 1,4-benzenedithiol adsorbed on silver surface (a) flat and (b) certain angle with one S–Ag bond.

symmetric S–C stretching. The ratio of SERS intensity for symmetric S–C stretching over that for asymmetric S–C stretching is 5.11.

For the vibrational modes $v_{\text{S}}$, with the increase of time intervals, the SERS intensities were strongly enhanced, which result from the coupling effect of the symmetric C–C stretching vibrations between two monomers. For the vibrational modes $v_{\text{C}}$, there are two almost degenerate vibrations, one is the symmetric C–C ring stretching, the other is asymmetric C–C ring stretching. The rate of SERS intensity for symmetric C–C stretching over that for asymmetric C–C stretching is 1.73. So, the strongly enhanced SERS intensity for C–C stretching is contributed from the coupling of dimeric symmetric C–C ring stretching and as well as the coupling of dimeric asymmetric C–C ring stretching.

The enhancement of SERS intensities for $v_{\text{C}}$ and $v_{\text{D}}$ with the increase of the time intervals can be interpreted by comparing Fig. 3(c) with Fig. 3(d). When $t=0$ min, the intensities of $v_{\text{C}}$ and $v_{\text{D}}$ are weak, with the increase of the experimental times $t=5$ and 120 min, the intensities of these two normal modes are gradually enhanced. The calculated intensities of $v_{\text{C}}$ is weak and there is no $v_{\text{D}}$ for monomer; while for dimer, the calculated intensities of $v_{\text{C}}$ is stronger than that of monomer, and the $v_{\text{D}}$ appears. So, the self-assembly of molecule can be confirmed with the time-dependent SERS spectroscopy.

So, the self-assembled 1,4-benzenedithiol adsorbed on silver nanoparticles revealed that the 1,4-benzenedithiol is not flatly adsorbed on silver nanoparticles. If the 1,4-benzenedithiol is flatly adsorbed on silver nanoparticles by two S–Ag bonds (see Fig. 8(a)), the self-assembled 1,4-benzenedithiol by S–S bond cannot be formed. The 1,4-benzenedithiol stand on silver nanoparticles with one S–Ag bond with certain angle (see Fig. 8(b)), then the second S of the first 1,4-benzenedithiol is bonded to the second S of 1,4-benzenedithiol.

5. Conclusion

The evidence for self-assembled dynamics of silver nanoparticles and 1,4-benzenedithiol (1,4-BDT) adsorbed on silver nanoparticles was obtained with the experimental absorption
spectra and SERS spectra at different time intervals as well as with the theoretical simulations. Experimentally, the vibrational modes $v_a$ and $v_d$ are absent at the early time interval; with the increase of the time, the intensities of these two vibrational modes were strongly enhanced. This is the direct evidence for the formation of multilayers of 1,4-BDT, which have been confirmed by the theoretical calculations of Raman spectra of 1,4-BDT monomer and dimer connected with S–S bond. For the 1,4-BDT monomer, these two vibrational modes are absent; while they are appeared for the Raman of 1,4-BDT dimer connected with S–S bond. The experimental vibrational mode at 480 cm$^{-1}$ is the S–S stretching mode, which can be supported by the calculated vibrational mode at 450 cm$^{-1}$. The 1,4-benzenedithiol stands on silver nanoparticles with one S–Ag bond with certain angle, not flatly adsorbed on silver nanoparticle.

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References