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In Situ Measurement and Monitoring of Diphenyl Disulfide in Ethanol Solution by SERS

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Shiwei Wu[a], Yu Liu[a], Jing Wang[a], Caiqing Ma[a], Yao Zhang[a,*], Lixin Xia[a,*]

Abstract. Diphenyl disulfide (DPDS) finds a wide range of applications in organic synthesis, polymer manufacture, and other fields. The structure of the DPDS molecule makes it amenable to monitor by Raman spectroscopy. Studying the fate of DPDS in the course of chemical reactions is of great significance for delineating mechanisms. In this work, the normal Raman and surface-enhanced Raman spectroscopy (SERS) signals of DPDS in ethanol solution have been characterized. In ethanol solution, the Raman signals of DPDS are completely obscured by the solvent signal. However, after irradiation for more than 10 s, a characteristic peak of DPDS appears at ν=2544 cm^{-1} (in both normal Raman and SERS), and a further peak at ν=1582 cm^{-1} appears in the SERS spectrum. Hence, in situ measurement and monitoring of DPDS in ethanol solution by SERS is feasible. It would allow us to reveal the micro mechanisms of chemical reactions, determine kinetic characteristics, estimate reasonable reaction end points, improve reaction selectivity, assess the quality and yield of the product, and so on.

1. Introduction

Diaryl disulfides are bioactive electrophilic reagents. They are important intermediates for the synthesis of other organic sulfides, important organic reagents, and are widely used in organic synthesis, polymer manufacture, and other fields [1-3]. As such, monitoring of their fate in the course of chemical reactions is of great significance.

Real-time monitoring technology can be applied to effectively detect pertinent changes in parameters during chemical processes [4]. In recent years, the widespread use of real-time monitoring technology has included spectroscopic methods [5], chromatography, and chromatography coupled with spectral detection [6-7]. At present, gas chromatography is the most commonly used real-time on-line analysis technology [8]. However, quantitative chromatographic analysis has certain stringent requirements in terms of volatility, thermal stability, and chemical stability of the tested samples [9]. Spectroscopic technologies have the advantages of high sensitivity and specificity. Spectroscopic monitoring technology can be divided into five main methods: UV/Vis spectrophotometry [10], infrared spectroscopy [11], Raman spectroscopy [12], nuclear magnetic resonance (NMR) [13], and mass spectrometry [14].

Among these methods, Raman spectroscopic detection has high sensitivity, rapid throughput, small sample weight, ease of sample preparation, no interference from fluorescence, remote transmission [15-16], high resolution, high frequency accuracy, and is non-destructive [17]. Because of the symmetrical structures of diaryl disulfides (-S-S-), they are not amenable to infrared detection, but are Raman-active.

Diphenyl disulfide (DPDS), the simplest diaryl disulfide, is widely used in pharmaceutical, chemical, and other fields as an intermediate [18-20]. It was thus selected for this study to assess the feasibility of applying surface-enhanced Raman spectroscopy (SERS) for its real-time monitoring.

2. Experimental

All Silver nitrate (>99.95%), trisodium citrate (99%), diphenyl disulfide was obtained from Shanghai Chemical Reagent Co. Ltd (China), and absolute ethanol were purchased from Tianjin Damao Chemical Reagent Co. Ltd (China). All aqueous solutions were prepared using 18 MΩ high purity water.

Nanosized silver particles were obtained by citric acid reduction of a silver nitrate solution (1.00 mmol L^{-1}). The silver nitrate solution 10 mL was heated to boiling and combined with 1 wt.% sodium citrate solution (10 mL). Boiling was kept for 1 h, and then the mixture was stirred until cool. Aliquots of a suspension of Ag NPs were mixed with DPDS solutions of different concentrations in a 1:1 (v/v) ratio, and the supernatant was collected after shaken with an oscillator for 24 hours to record the spectrum. A 10^{-3} mol L^{-1} solution was sealed in a capillary for Raman characterization with an incident laser of 638 nm. All Raman spectra were recorded on a Renishaw inVia spectrometer, and absorption spectra were recorded on an Optizen 2120UV spectrophotometer.

Samples were directly examined under a microscope. For powder samples, the laser was directly focused on the surface thereof, whereas for liquid samples, it was focused on the interior of the capillary. The excitation wavelength was 638 nm, with a slit width of 50 μm and a 50× objective lens. The laser power was about 1–2 mW, and Raman scattered signals were acquired in the spectral range 100–2500 cm^{-1}, with a spatial resolution of 1 μm and a spectral resolution of 1 cm^{-1}.

UV/Vis absorption spectra were recorded over the range 400–1100 nm from Ag NPs sol, a solution of DPDS, and a 1:1 mixture of Ag NPs and DPDS, each in ethanol.

Department of Chemistry, Liaoning University, Shenyang 110036, P. R. China.
lixinxia@lnu.edu.cn, zhangyao@lnu.edu.cn

3. Results and discussion

The In UV/Vis absorption spectra, metal nanoparticles give rise to a surface plasmon resonance absorption peak corresponding to the specific properties of the interband transition [21]. The size and shape of the metal particles and the condensed state exert an influence on this peak [22]. Moreover, the size distribution of metal particles affects the shape of the absorption lines. With a more uniform particle size distribution, the shape of the spectral line should be more symmetrical and narrower. From Figure 1, it can be clearly seen that the Ag NP sol (black line) gave rise to a strong absorption peak at around 450 nm. The full-width at half-maximum of this peak was narrow, indicating a uniform particle size distribution of the silver sol. This was consistent with the experimental particle size distribution shown in Figure 2.

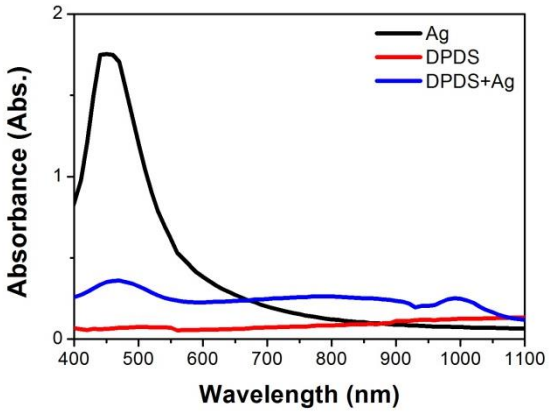

Figure 1: Absorption spectra of Ag NPs sol, a solution of DPDS, and a 1:1 mixture of Ag NPs and DPDS, each in ethanol, from 400 to 1100 nm.

From Figure 1, Ag NPs sol (black line) and the 1:1 mixture of Ag NPs and DPDS in ethanol (blue line) showed maxima at 450 and 464 nm, respectively. This red-shift was indicative of interaction between the Ag NPs and DPDS, presumably through electronic dipole-dipole interaction and a plasma coupling effect. The spectrum of the 1:1 mixture of Ag NPs and DPDS also featured a new signal at 1000 nm [23].

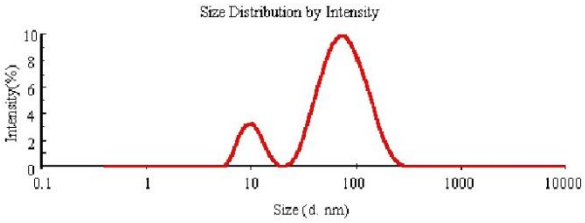

Figure 2: Size distribution by intensity of Ag NPs sol.

Because DPDS is insoluble in water, we chose the commonly used anhydrous ethanol as solvent. To investigate the influence of solvent on the Raman spectrum of DPDS, spectra were measured under different power.

From Figure 3, for a 10^{-3} M solution of DPDS in ethanol, with 638 nm excitation for a relatively short time (10 s), the Raman peaks of DPDS were almost entirely concealed by the solvent peaks.

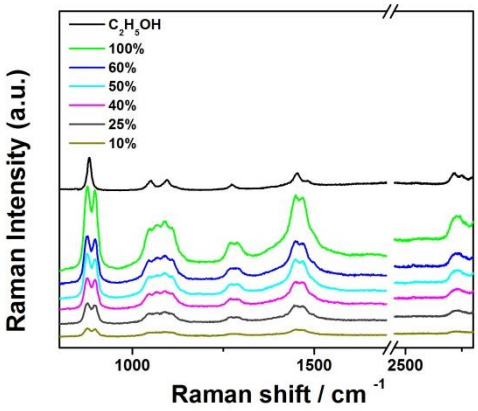

Figure 3: Raman spectra of ethanol and a 10^{-3} M solution of DPDS in ethanol acquired with excitation at 638 nm at different powers for a duration of 10 s.

In order to study the effect of silver sol on Raman signal, after adding nano-silver sol, we have made the SERS test similar to the above. From Fig. 4, it can be concluded that the SERS spectra obtained in the short time (10 s) after the addition of nano-silver sol are the characteristic peaks of ethanol for 10^{-3} M DPDS ethanol solution. The characteristic peaks of the DPDS itself are almost entirely obscured by the characteristic peaks of the solvent.

This result was incompatible with our aim of applying Raman spectroscopy for the real-time monitoring of DPDS in chemical processes. Although calculation software can be applied to exclude background peaks due to the reaction medium, we sought more direct in situ data so as to reduce any interference from calculations and to speed up the real-time monitoring. Therefore, we conducted further experiments.

Figure 5 shows the Raman spectrum of DPDS powder and SERS spectra of a 10^{-3} M solution of DPDS in ethanol excited at 638 nm for durations of 10–60 s at a power of 10%. It can be seen that, with increasing excitation time, peaks at 1582 and 2544 cm^{-1} developed in the spectrum of the solution, corresponding to those seen for the powder sample.

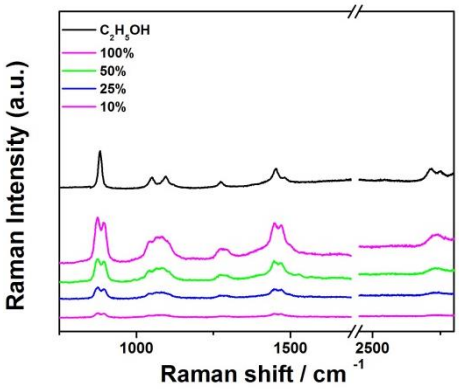

Figure 4: SERS spectra of ethanol and a 10^{-3} M solution of DPDS in ethanol acquired with excitation at 638 nm at different powers for a duration of 10 s.

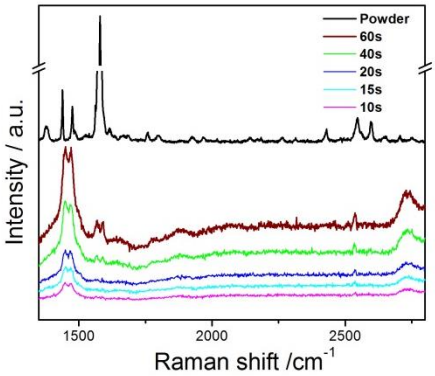

Figure 5: Raman spectrum of DPDS powder and SERS spectra of a 10^{-3} M solution of DPDS in ethanol acquired by excitation at 638 nm at a power of 10% for durations of 10–60 s as indicated.

Raman intensities are affected by the polarizability of the molecule [24-25], with the intensities of the first j normal modes being related to molecular polarizability as follows [26]:

$$I_j \propto I_0 \frac{(\nu_0 - \nu_j)^4}{\nu_j} (\partial\alpha/\partial Q_j)^2$$

Where vj are the first j normal modes of the frequency, I0 is the excitation laser intensity, α is the molecular polarizability, and Qj is a normal coordinate corresponding to the jth normal module.

From the above formula that Raman intensity is proportional to the molecular polarizability. In our experiment, the polarizability of DPDS (26.76 10^{-24} cm^3) is larger than that of ethanol (5.09 10^{-24} cm^3). Hence, with increasing excitation time, polarizability exerted an increasing influence on the intensity of the Raman peaks. Therefore, with the increasing excitation time, the characteristic peaks of DPDS emerged from the ethanol solvent peaks and gradually intensified.

To assess the SERS enhancement effect, we measured normal Raman spectra in the absence of Ag NPs under otherwise identical conditions. From Figure 6 that, with increasing excitation time, the peak at ν=1582 cm^{-1} did not appear in the spectra of the ethanolic DPDS solution. The second peak at ν=2544 cm^{-1} started to appear after an excitation time of 20 s, albeit only weakly.

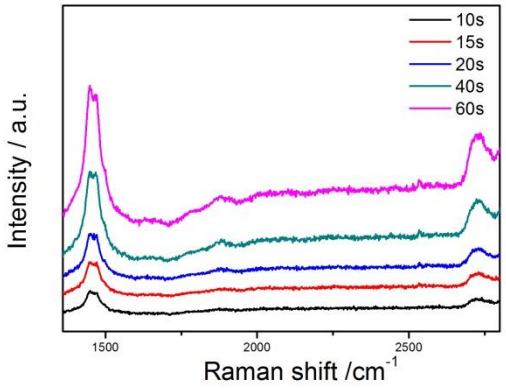

Figure 6: Normal Raman spectra of a 10^{-3} M solution of DPDS in ethanol acquired by excitation at 638 nm at a power of 10% for durations of 10–60 s as indicated.

Comparing the normal Raman and SERS spectra, obtained after excitation times longer than 10 s, highlights the advantage of adding Ag NPs. Thus, in the SERS spectra, the DPDS peaks at both 1582 and 2544 cm^{-1} were discernible, whereas the former could not be discerned in the normal Raman spectra.

In summary, SERS enables the measurement and monitoring of DPDS in a relatively short period of time through its signals at ν=1582 and 2544 cm^{-1}.

4. Conclusions

In this work, the normal Raman and SERS signals of DPDS in ethanol solution have been characterized. The following conclusions have been drawn:

1. The main Raman peak from a solution of DPDS in ethanol is that of the solvent

2. SERS spectra shows considerable signal enhancement compared with the normal Raman spectra.

3. After an irradiation time of more than 10 s, a characteristic peak of DPDS appears at 2544 cm^{-1} (in both the normal Raman and SERS, but more strongly in the latter), which intensifies with increasing excitation time.

4. With the increasing excitation time, the second characteristic peak of DPDS at ν=1582 cm^{-1} emerges and intensifies in the SERS spectra, but is not so prominent in the normal Raman spectra.

Thus, the characteristic peaks at ν=1582 and 2544 cm^{-1} may be used for SERS monitoring of ethanolic solutions of DPDS. This method has the advantages of high sensitivity, short test times, small sample weight, simple sample preparation, and is non-destructive.

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