Study of Substitution Effect of Anthraquinone by SERS Spectroscopy

Chul Jae Lee, Jae Soo Kang, Yong-Tae Park,[†] Karim Mohammad Rezaul, and Mu Sang Lee[*]

Department of Chemistry Education, Kyungpook National University, Daegu 702-701, Korea
[†]Department of Chemistry, Kyungpook National University, Daegu 702-701, Korea
Received March 30, 2004

In the present study, we carried out comparative research on the anthraquinones Raman spectrum and on the anthraquinones derivative 1,4-diamino-anthraquinone focusing on change in its intermediate in terms of pH and change in the substituent. WE use the SERS method and employ a silver sol prepared by Creighton *et al.*'s method. From the analysis of the UV spectrum of the mixture solution of 1,4-diamino-anthraquinone and silver sol, we could see that the 1,4-diamino-anthraquinone physically adsorbs silver sol. In terms of the adsorbing orientation, the adsorption of the nitrogen atom in the amino group is perpendicular to the surface of silver sol according to the surface selection rule. From the structure of the 1,4-diamino-anthraquinone intermediate according to the change of pH, we could see that the C=O bond is strengthened in the acidic state and weakened in the neutral and the alkaline state because of the resonance effect of the amines.

Key Words : SERS spectroscopy, Anthraquinone, Substitution effect

Introduction

Surface enhanced Raman scattering (SERS), a type of Raman scattering that occurs when the molecule is adsorbed or located within hundreds of nanometers to the surface of a certain metal whose surface is roughly processed, is a phenomena in which the intensity of the Raman scattering is enhanced by 10^4-10^6 times of the ordinary Raman intensity. It is quite useful in the research of the adsorbing method or the surface chemical reaction of molecules that are adsorbed to the roughened surfaces of metals.[1-3] Ever since the SERS phenomena was first reported, many research papers have been issued on the theories, the applications and the phenomenal expansions of SERS.[4-11] Generally, quinone plays a very important role in the movement of electrons in bacteria photosynthesis. These days, quinone is being utilized because of its coordinating capability to heavy metals and its conductive property when synthesized into a polymer. In anthraquinone derivatives research, SERS studies by Isao Taniguchi using a self-assembled monolayer (SAM) as silver and gold electrodes have been reported,[12] and recently research by V. Ramakrishnan using a silver sol was reported.[13] In the present work, we study the adsorbing property of anthraquinone derivative 1,4-diamino-anthraquinone to silver sol, and compare research findings using the SERS method on the effects on the substituent, the change of the intermediate, and the adsorbing orientation according to the pH based on previous reports.

Experimental Section

Analytical-reagent grade anthraquinone and 1,4-diamino-anthraquinone were purchased from Sigma Co. and used without further purification. All procedures were accomplished with sonication. The solutions were prepared with water that had been distilled three times.

The aqueous silver sol used in these experiments had been prepared by reduction of $AgNO_3$ with excess $NaBH_4$ at room temperature as described in Creighton *et al.*'s method.[14]

Briefly, a 5.0×10^{-4} M aqueous solution of 1,4-diamino-anthraquinone was mixed with the silver sol in the volume ratio of 1 : 10. A 0.1 mL of 1.0 M KCl solution was added to the silver sol to prolong the silver colloid activity.

The Raman instrument was equipped with a SPEX 1403 scanning double monochromator, an RCA C31034 PMT detector, and SPEX DM 3000R software. A coherent Innova 90-5 argon ion laser (514.5 nm) was used as the excitation source. The laser power and the spectral slit widths used were 100 mW and 600 μm, respectively. The Raman in situ measurements were performed in the conventional way for samples with observation orientation perpendicular to the laser. UV-visible absorption spectra were measured using a Shimadzu UV-360 pc instrument. An image of the Scanning electron microscope(SEM) was obtained with a Hitachi H-710.

The pH of the solutions was adjusted by injecting the necessary amounts of reagent grade H_2SO_4 and NaOH solutions.

Results and Discussion

We studied anthraquinone in order to find the characteristic of the Raman spectrum of the substituted anthraquinone. The structure of anthraquinone is D_{2h}-symmetry as shown in Figure 2(a). Table 1 shows the analysis of the vibration mode of the Raman spectrum of anthraquinone shown in Figure 1. The normal-mode calculations of anthraquinone were performed with the program package Hyper-Chem (release 7.0). The program uses the PM3 hamiltonian for the calculation of ground-state energies. The stretching vibration of C=O appears at 1668 cm^{-1}, that of C=C at 1598

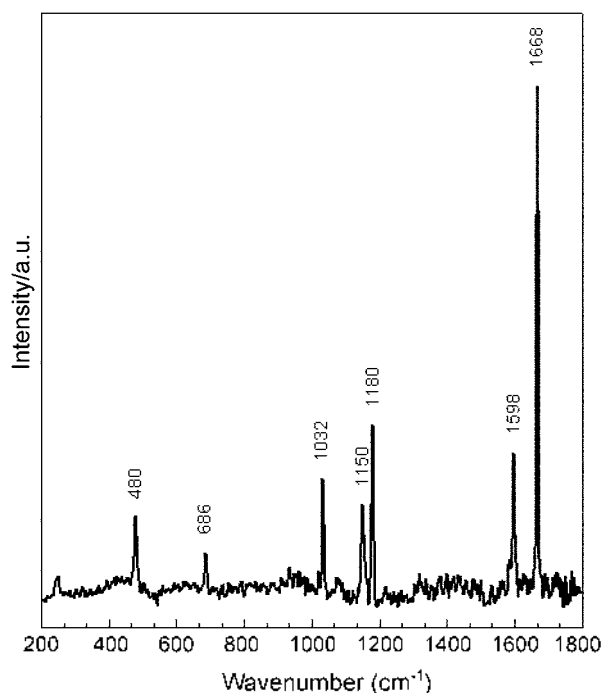[*]Corresponding Author. e-mail: mslee@mail.knu.ac.kr

Figure 1. Raman spectrum of anthraquinone.

Table 1. Normal mode analysis of anthraquinone

Observed wavenumber (cm^{-1})	Calculated wavenumber (cm^{-1})	Mode	Assignment
1668	1950	A$_{1g}$	ν(C=O)
1598	1793	A$_{1g}$	ν(C=C)
1180	1356	A$_{1g}$	ν(C-C)
1150	1328	A$_{1g}$	ν(C-C)
1032	1168	A$_{1g}$	δ(C-H)
686	750	A$_{1g}$	Skelectal deformation
480	519	A$_{1g}$	Skelectal deformation

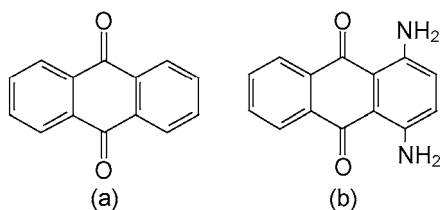ν = stretching, δ = deformation

Figure 2. Structure of (a) anthraquinone and (b) 1,4-diamino-anthraquinone.

cm^{-1}, and that of C-C at 1180 cm^{-1} and 1150 cm^{-1}. Skeletal deformation appears at 686 cm^{-1} and 480 cm^{-1}.

Figure 3 shows the UV absorption spectra of 1,4-diamino-anthraquinone, the silver sol and their mixture, which is obtained to find the adsorbing property of 1,4-diamino-anthraquinone. The UV-VIS spectrum of silver sol is showed in Figure 3(a) has a maximum at 393 nm, which is an absorption band of plasmon resonance. As for this
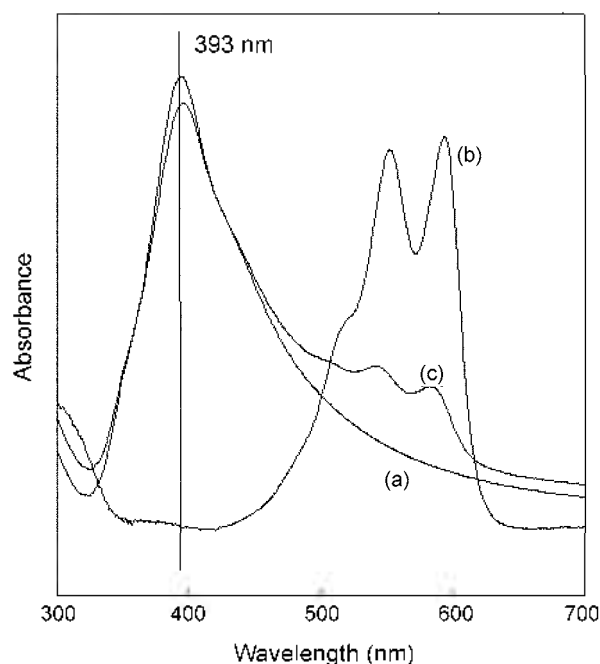

Figure 3. Absorption spectra of (a) silver sol, (b) 1,4-diamino-anthraquinone (5.0 × 10^{-4} M) in aqueous solution, and (c) mixture of sol and 0.1 mM 1,4-diamino-anthraquinone in the volume ratio of 20 : 1.
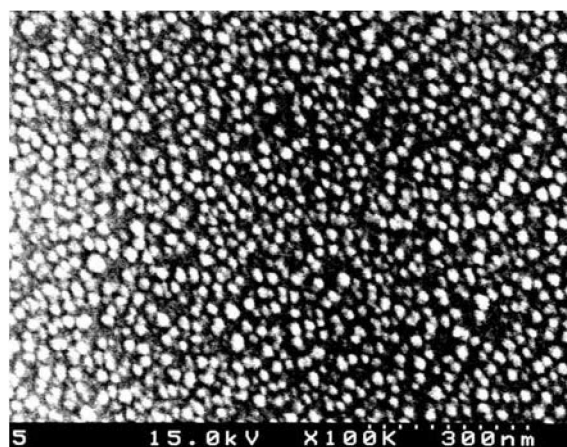

Figure 4. Scanning electron microscope (SEM) image of silver sol.

absorption band, the sizes of the particles are not homogeneous if the full width at half maximum (FWHM) is wide but they are homogeneous if it is narrow. Also, it has been reported that the sizes of the particles are small if this band shifts to a shorter wavelength, and large if it shifts to a longer wavelength.[15]

In the case of silver sol used in this experiment, the FWHM is about 85 nm. Figure 4 shows the Scanning electron microscope (SEM) image of silver colloid, which demonstrates that silver particles are almost uniform in size, with an estimated average diameter of 30 nm. In the case of 1,4-diamino-anthraquinone, we found two unique charactristic bands between 550-600 nm as shown in Figure 3(b). If the chemical adsorption is strong in the interaction between
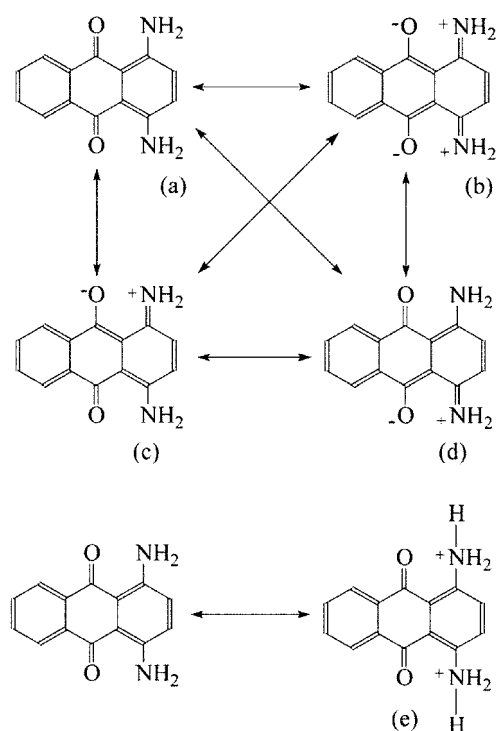
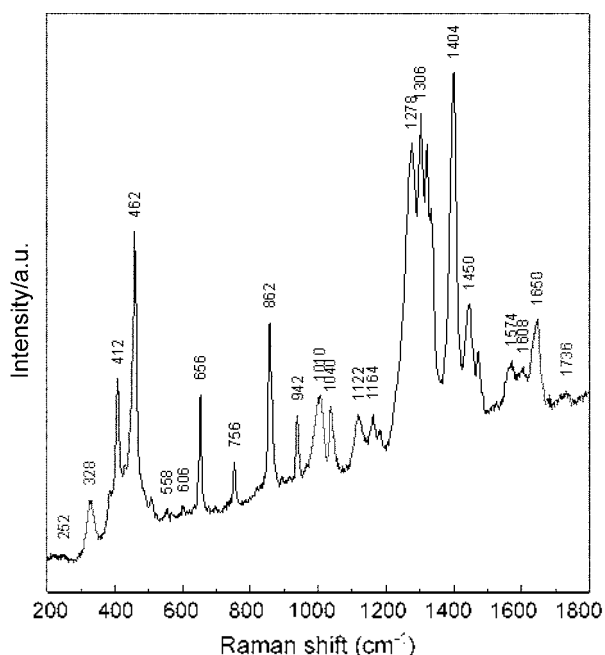**Figure 5.** Resonance form of 1,4-diamino-anthraquinone as pH condition.

Figure 7. SERS spectrum of 5.0×10^{-4} M 1,4-diamino-anthraquinone in pH=7.0.

Figure 6. SERS spectrum of 5.0×10^{-4} M 1,4-diamino-anthraquinone in pH=1.0.

Figure 8. SERS spectrum of 5.0×10^{-4} M 1,4-diamino-anthraquinone in pH=13.0.

the silver sol and the sample, the FWHM of the silver sol widens and shifts to a longer wavelength. When the adsorption is closer to the physical adsorption, the change in the FWHM and its location is not observed in the UV absorption spectrum of the silver sol. The UV absorption spectrum of the sample shows a wider FWHM and shifts to a shorter
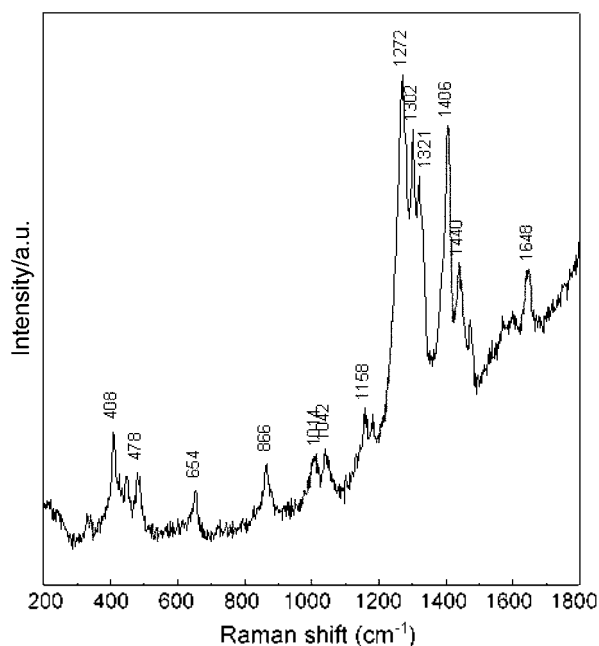
wavelength in the case of chemical adsorption. As for physical adsorption, the UV absorption spectrum of the sample rarely shows any change in the FWHM and its locations.[16] As shown in Figure 3(c), the change in the location and the FWHM of the UV absorption spectrum did not observe the adsorption of 1,4-diamino-anthraquinone on the silver sol. This is because the 1,4-diamino-anthraquinone is physically adsorbed on the silver sol. Figure 5 shows the resonance structure according to the pH change of the 1,4-

Table 2. Assignment of 1,4-diamino-anthraquinone

SERS Spectra			Assignment
pH=13.0	pH=7.0	pH=1.0	
1644(m)	1648(m)	1650(m)	v_s(C=O)
1596(w)			v(C=C)
1566(vw)	1474(vw)		v(C=C)
1444(m)	1440(m)	1450(m)	v(C=C)
1406(vs)	1406(s)	1404(vs)	v(C=C) + v(C-N)
1322(w)	1321(w)	1323(w)	v(C=C) + v(C-N)
1302(w)	1302(m)	1306(m)	v(C=C) + v(C-N)
1272(s)	1272(s)	1278(s)	v(C=C) + v(C-N)
1162(m)	1158(w)	1164(w)	v(C=C)

s = strong, m = medium, w = weak, v = very, V = stretching

diamino-anthraquinone, and Figure 6, 7, and 8 show their SERS spectra respectively. Compared to the anthraquinone, the bands in the vicinity of 400 cm^{-1} and 1300 cm^{-1} appear much different. These two regions can be attributed to amines, and the vibration modes according to each property are shown in Table 2. In Table 2, the vibrational assignments of the 1,4-diamino-anthraquinone in the SERS spectra are summarized with reference to the literature.[12,13]

The stretching vibration of carbonyl appears at 1668 cm^{-1} in the case of anthraquinone, and at 1650 cm^{-1} in the case of 1,4-diamino-anthraquinone. The reason the wavenumber of carbonyl is red-shifted like this is that the resonance effect of the two amines weakens the double-bond of the carbonyl. The carbonyl band, therefore is red-shifted. In terms of the location change of carbonyl according to the pH effect, the 1,4-diamino-anthraquinone has the structure shown in Figure 5(e) in acid solutions and does not show resonance effects because the positively charged nitrogen is unable to push the unshared electron pair to the phenyl. In the case of alkaline solutions, it has resonance structures as shown in Figure 5(a), 5(b), 5(c) and 5(d). As a result, the double-bond of C=O weakens and the v(C=O) band is red-shifted.

In Figure 8, more SERS peaks appear at about 1500-1300 cm^{-1} than in the case of anthraquinone shown in Figure 1. As the structural difference of these two substances is two amines, the band in this area can be assigned to the characteristic band of the amines. The band that appears near 1450 cm^{-1} is assigned to a stretching vibration of C=C and the orientation of the C=C vibration is directed to the z-axis. The band near 1400 cm^{-1} is the combined vibration mode of C-N stretching and C=C stretching. Also, in the case of Figure 6, the bands at 1278 cm^{-1}, 1306 cm^{-1}, and 1323 cm^{-1} are attributed to the C-N stretching vibration more than anything else, and a large enhancement of these band shows that N is adsorbed to the silver sol by the surface selection rule.[17-19] It also shows that these modes are all adsorbed in the orientation of the z-axis, perpendicular to the silver sol. As seen in the case of anthraquinone near 400 cm^{-1}, the band originated from the skeletal vibrations of the functional groups that are attached to the phenyl ring that appear at about 408 cm^{-1} in neutral and alkaline solutions and at 462
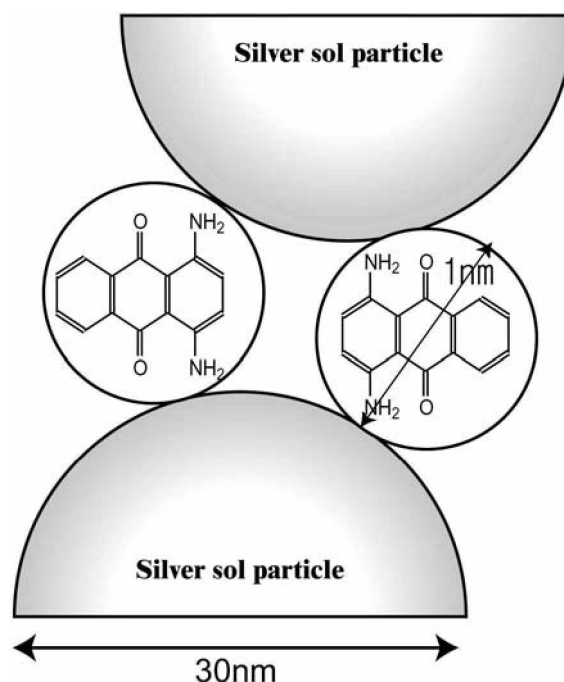

Figure 9. Schematic model for the adsorption geometry of 1,4-diamino-anthraquinone on a colloidal silver surface.

cm^{-1} in acid solutions. This shows that the amines exist in the form of a positive ion in acid and in the form of a neutron in alkaline, according to the pH. Orientation of the 1,4-diamino-anthraquinone, therefore is perpendicular to the silver sol in the method of physical adsorption, as shown in Figure 9.

Conclusion

Anthraquinone has D_{2h}-symmetry, and we observed its Raman spectrum in that its A_{1g} mode appears characteristically strong. In the SERS spectrum of 1,4-diamino-anthraquinone according to the pH, the bands in the vicinity of 400 cm^{-1} and 1300 cm^{-1} appear much different compared to those of the anthraquinone, and it can be seen that these are the characteristic bands of the amines, the substituents. Also, in the case of C=O stretching vibration, the resonance effect of the two amines weakens the double-bond of carbonyl and causes the band to red-shift. It can be seen that the method of adsorption was in the form of physical adsorption, and the adsorption orientation was perpendicular to the surface of the silver sol.

References

1. Garrell, R. L. *Anal. Chem.* **1989**, *61*, 401.
2. *Surface Enhanced Raman Scattering*; Chang, R. K., Furtak, T. E., Eds.; Plenum: New York, 1982.
3. Fleischman, M.; Hendra, P. J.; McQuillan, A. J. *Chem. Phys. Lett.* **1974**, *26*, 163.

4. Abe, H.; Mansel, K.; Schultze, W.; Moskovits, M.; Dilella, D. P. *J. Chem. Phys.* **1981**, *74*, 792.

5. Chen, C. Y.; Burstein, E. *Phys. Rev. Lett.* **1980**, *45*, 1287.

6. Kim, M. S.; Kang, J. S.; Park, S. B.; Lee, M. S. *Bull. Korean Chem. Soc.* **2003**, *24*, 633.

7. Kang, J. S.; Lee, C. S.; Kim, M. S.; Lee, M. S. *Bull. Korean Chem. Soc.* **2003**, *24*, 1599.

8. Ruppin, R. *J. Chem. Phys.* **1982**, *76*, 1681.

9. Ohtaka, K.; Inonue, M. *Phys. Rev.* **1982**, *B25*, 677.

10. Kerker, M.; Blatchford, C. G. *Phys. Rev.* **1982**, *B26*, 4052.

11. Gersten, J. I.; Nitzan, A. *J. Chem. Phys.* **1981**, *75*, 1139.

12. Nishiyama, K.; Tahara, S.; Uchida, Y.; Tanoue, S.; Taniguchi, I. *J.*

13. Umadevi, M.; Ramakrishnan, V. *Spectrochimica Acta Part A* **2002**, *58*, 2941.

14. Creighton, J. A.; Blatchford, C. G.; Albrecht, M. G. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 790.

15. Rivas, L.; Sanchez-Cortes, S.; Garcia-Ramos, J. V.; Morcillo, G. *Langmuir* **2000**, *16*, 9722.

16. Anderson, M. R.; Evans, D. H. *J. Electroanl. Chem.* **1988**, *167*, 6612.

17. Moskovits, M. *Rev. Mod. Phys.* **1985**, *57*, 783.

18. Moskovits, M.; Suh, J. S. *J. Phys. Chem.* **1984**, *88*, 5526.

19. Moskovits, M.; Suh, J. S. *J. Phys. Chem.* **1988**, *92*, 6327.

Electroanal. Chem. **1999**, *478*, 83.