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Studies of the Adsorption Behaviours of Reactive Brilliant Blue K-NR on Silver by Surface-Enhanced Raman Scattering

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The adsorption behaviours of reactive brilliant blue K-NR adsorbed on silver mirror were studied using the surface-enhanced Raman scattering. The adsorptive mechanisms of reactive brilliant blue K-NR were discussed. The results indicated that silver could greatly enhance Raman scattering responses. The surface-enhance Raman scattering intensity of reactive brilliant blue K-NR varied its and blue K-NR concentration was adsorbed on silver mirror through electrostatic force and van der Waals force.

Key Words: Surface-Enhanced Raman scattering, Silver mirror, Reactive brilliant blue K-NR, Adsorption.

INTRODUCTION

It has been found that the technique of surface-enhanced Raman scattering (SERS) spectroscopy is a powerful technique for studying adsorption behaviour[1,2] and has been widely in past[3,4]. Among the substrates employed in surface-enhanced Raman scattering, silver is the most widely used, particularly colloidal silver and silver electrode[5-8].

Reactive brilliant blue KN-R is anthraquinone dye widely used in textile, printing and dyeing industries. A large amount of reactive brilliant blue KN-R, which is a difficult-decomposing organic compound, is discharged into environment. Researchers paid attention to remove the brilliant blue KN-R for its high solubility, difficult decolourization and high toxicity[9].

There are several reports on the studies of absorption behaviours of many kinds of dyes on silver[10-13]. To our best of knowledge, there is so far no report on the studies of absorption behaviours of reactive brilliant blue K-NR on silver using surface-enhanced Raman scattering.

In this paper, adsorption behaviour and the mechanism of the reactive brilliant blue K-NR (Fig. 1) on silver mirror is described.

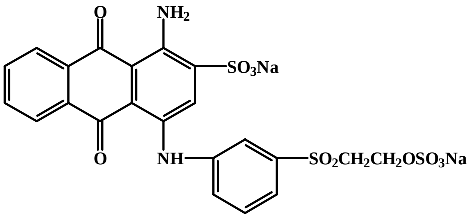

Fig. 1. Reactive brilliant blue K-NR

EXPERIMENTAL

Reactive brilliant blue K-NR was purchased from Aldrich and used without further purification. All the other reagents were purchased from other commercial sources. All the solutions were prepared with deionized water. The surface-enhanced Raman scattering measurements were performed on Jobin-Yvon U-1000 Micro Raman spectroscopy with exciting wavelength at 632 nm.

Preparation of silver mirror[14]

Solution A: 5.0 g $AgNO_3$ was dissolved in 10.0 mL distilled water, then $NH_3 \cdot H_2O$ of 6 mol/L was dropwise added continuously at swirling till the precipitation was dissolved again. Three drops of 0.8 mol/L NaOH was added and the black precipitation appeared again. Then add 6 mol/L $NH_3 \cdot H_2O$ (about 3-4 drops) just to let the precipitate disappear.

Solution B: To 1.3 g grape sugar were dissolved in 25 mL distilled water in a 100 mL beaker, then a drop of 65 % nitric acid and 25 mL 95 % ethanol were brought into it, which was the deoxidizing agent.

To decontaminate the glass: The surface of the glass should be smooth, which was washed by 10 % NaOH then with water and hydrochloric acid (1:1) and finally with distilled water before dipping in distilled water.

Plating silver: A solution of 2:1 solution A and B was added while shaking into a beaker in which a piece of pretreatment glass lied there, then left it for standing till the glass was covered with shine sliver, put it out immediately and washed by distilled water and dipped in distilled water.

Measuring procedure: (i) The solid of active brilliant blue K-NR on a glass block was measured directly by Raman spectroscopic technique. (ii) In a 1 mm capillary, 10^{-3} mol/L active brilliant blue K-NR was measured by Raman spectroscopic technique. (iii) After the silver mirror was dipped and left for standing 3 h in aqueous solution of reactive brilliant blue K-NR with the concentration of 10^{-3}, 10^{-5}, 10^{-7}, 10^{-8}, 10^{-10} mol L^{-1}, Raman spectroscopic measurement was performed.

RESULTS AND DISCUSSION

Fig. 2 shows the Raman spectra of reactive brilliant blue K-NR in solid, being absorbed on silver mirror and solution of 10^{-3} mol/L. As shown in Fig. 2, Raman signals could not be identified clearly for reactive brilliant blue K-NR in solid due to its fluorescence as shown in Fig. 2a and in aqueous solution, its Raman responses were very weak (Fig. 2c), while after being absorbed on silver, they showed strong and well-resolved Raman spectroscopic peaks (Fig. 2b). The silver produced significantly enhancing effect on the Raman responses of reactive brilliant blue K-NR by quenching its fluorescence.

As shown in Fig. 2a and b, the peak positions of the two spectra are nearly same which implies that reactive brilliant blue K-NR was mainly adsorbed physically on the surface of silver through electrostatic force and van der Waals forces.

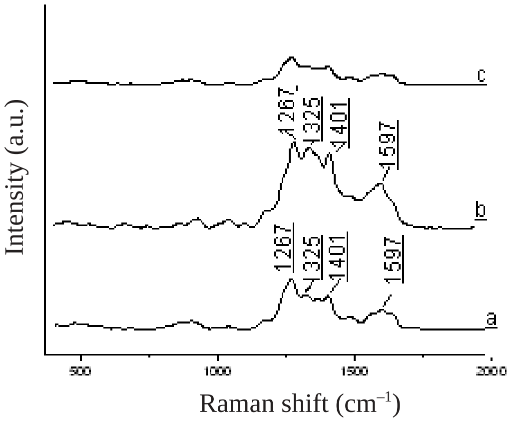

Fig. 2. (a) The normal Raman spectra of reactive brilliant blue K-NR in the solid state
(b) The SERS spectra of reactive brilliant blue K-NR of 10^{-3} mol/L
(c) The normal Raman spectra of reactive brilliant blue K-NR of 10^{-3} mol/L

In Fig. 2b, the peak at 1267 cm^{-1} is assigned to the breathing vibration of anthracene whereas the peaks at 1325 and 1401cm^{-1} are attributed to the flex vibrations of C-C bond and the peaks at 1597 cm^{-1} are originated from the flex vibrations of C=C of benzene[15].

As shown in Fig. 2b and 1c, It is noteworthy that the peak height at 1325, 1401 and 1597 cm^{-1} increased significantly, further more, sulfur atom and nitrogen atom are absorbed more easily for their coordinate characters. which indicates that the anthracene and C-C bond and benzene motif was perpendicularly adsorbed on the surface of silver as shown on Fig. 3[16].

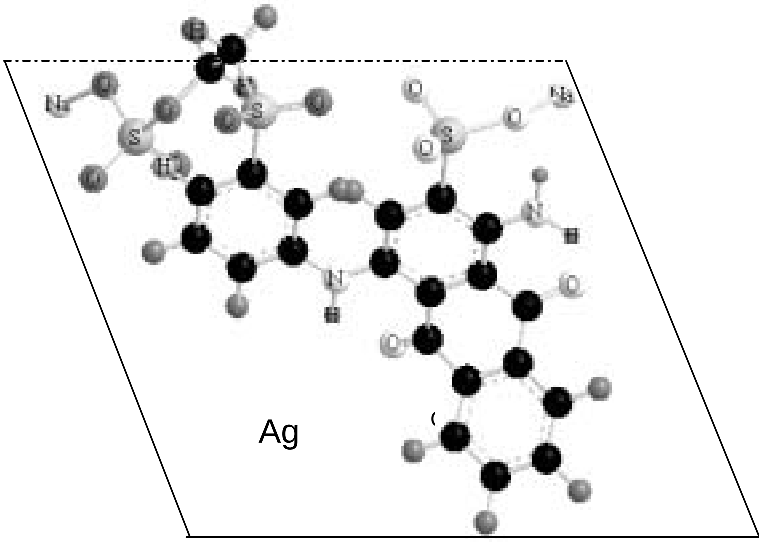

Fig. 3. Speculation of adsorption for reactive brilliant blue K-NR on silver mirror

Fig. 4 showed the Raman spectra of reactive brilliant blue K-NR with the concentration of 10^{-3}, 10^{-5}, 10^{-7}, 10^{-8}, 10^{-10} mol L^{-1} adsorbed on silver mirror. The relationship of Raman intensity to reactive brilliant blue K-NR concentration are shown in Fig. 5. It is clear that silver mirror can produced significantly enhancing effect on the Raman responses of 10^{-3}-10^{-8} mol/L and the effect between 10^{-3}-10^{-6} mol/L is not much differ. Furthermore, the intensity of 10^{-3} mol/L reactive brilliant blue K-NR slightly moved down, whereas the response of reactive brilliant blue K-NR between 10^{-8}-10^{-10} mol/L changed significantly. The results fit the theory of rare solution effect. In other words, molecules in rare solution arrange easier than in thick solution[15].

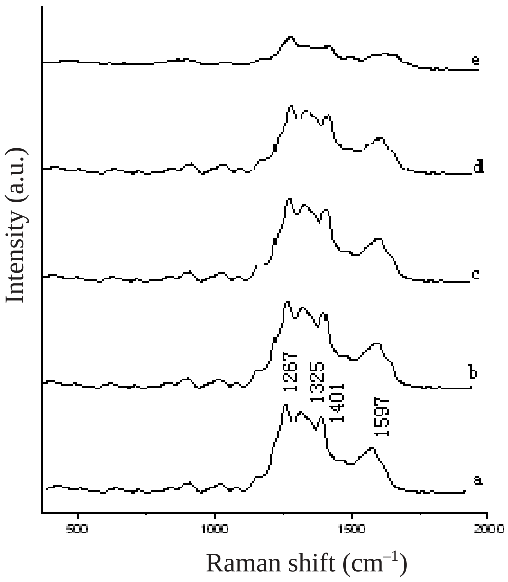

Fig. 4. Surface-enhanced Raman scattering spectra of reactive brilliant blue K-NR with the concentration of 10^{-3}, 10^{-5}, 10^{-7}, 10^{-8}, 10^{-10} mol L^{-1} (a, b, c, d, e)

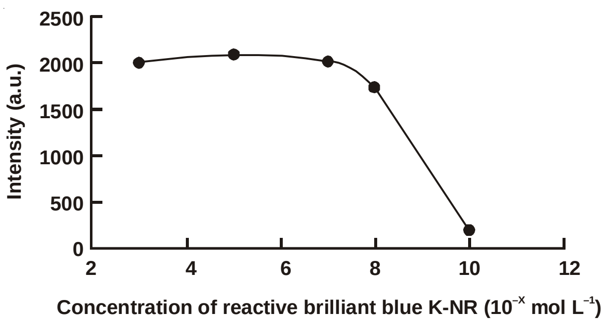

Fig. 5. Relationship of Raman intensity to reactive blue K-NR concentration

Conclusion

The results shown above suggested that silver could greatly enhance Raman scattering responses and quench fluorescence. The reactive brilliant blue K-NR was adsorbed on silver mirror through electrostatic force and van der Waals force and the varied regulations of surface-enhanced Raman scattering intensity with reactive blue K-NR concentration were fit with the theory of rare solution effect. The present studies also suggested that surface-enhanced Raman scattering find wide applications in identifying trace organic substrates, for example, in environmental monitoring, dye industry and water quality control.

REFERENCES

1. M. Fleischmann, P.J. Hendra and A.J. Mcquillan, *Chem. Lett.*, **26**, 163 (1974).
2. D. Wu and Y. Fang, *J. Colloid Interf. Sci.*, **265**, 234 (2003).
3. D.L. Jeanmaire and R.P.V. Duyne, *J. Electroanal. Chem.*, **84**, 1 (1977).
4. M.G. Albrecht and J.A. Creighton, *J. Am. Chem. Soc.*, **99**, 5215 (1977).
5. R.L. Paul, A.J. McQuillan, P.J. Hendra and M. Fleischmann, *J. Electroanal. Chem.*, **66**, 248 (1975).
6. C.S. Allen, G.C. Schatz and R.P. Van Duyne, *Chem. Phys. Lett.*, **75**, 201 (1980).
7. S. Sunchez-Cortes and J.V. Garcia-Ramos, *J. Raman Spectrosc.*, **21**, 679 (1990).
8. J. Wang and P. Zhang, *J. Phys. Chem.*, **92**, 942 (1988).
9. X.J. Dong and Z. Chen, *J. Environ. Sci.*, **15**, 377 (2003).
10. Z.M. Li, N. Zhang and F.T. Li, *Appl. Surf. Sci.*, **253**, 2870 (2006).
11. A. Kudelski, *Chem. Phys. Lett.*, **14**, 271 (2005).
12. Z. Wang, Z.M. Li and F.T. Li, *J. Spectro. Lab. (China)*, **22**, 638 (2005).
13. Z.M. Li, F.T. Li, B.R. Zhang and Z. Wang, *J. Instru. Anal. (China)*, **25**, 38 (2006).
14. Z.M. Li, F.T. Li and Z. Wang, *J. Zheng Zhou University (China)*, **36**, 71 (2004).
15. Z.Y. Zhu, R.A. Gu and T.H. Lu, Applications of Raman Spectroscopy in Chemistry, Northeast University Press, Shengyang, China, p. 77 (1998).
16. M. Moskovits and J.S. Suh, *J. Am. Chem. Soc.*, **107**, 6826 (1985).

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