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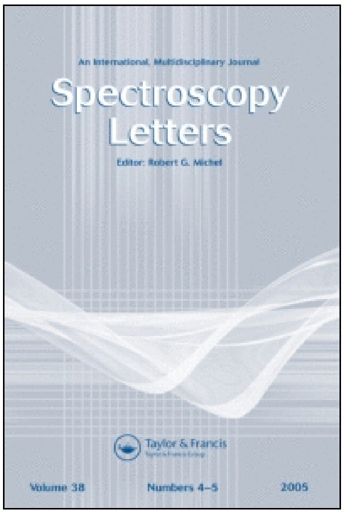

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Surface-Enhanced Raman Spectra of Fulvic and Humic Acids Adsorbed on Copper Electrodes

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SURFACE-ENHANCED RAMAN SPECTRA OF FULVIC AND HUMIC ACIDS ADSORBED ON COPPER ELECTRODES

Key words: Humic acid, fulvic acid, surface-enhanced Raman scattering (SERS), copper electrode

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ABSTRACT

The surface-enhanced Raman scattering of fulvic or humic acid adsorbed on copper electrodes demonstrates a unique resolution-enhanced effect. The effect is due to chemical binding of humic substances on copper surfaces. It is deduced that only a few

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kinds of chemically and geometrically favorable groups or portions such as carboxylic ions and pyridine-substituted rings in the humic aggregates specifically bind onto the copper surfaces while the rest dangles in the solutions. Since the rest are far from the surface and their SERS signals are too weak to be observed, the SERS spectra only characterize the binding groups specifically and therefore they are highly resolved and simple. Such a unique resolution-enhanced effect may be valuable to reveal specific clues regarding the binding groups of humic substances, particularly at low concentrations typically found in aquatic environments.

INTRODUCTION

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Humic substances affect soil weathering and fertility, pH of natural waters, trace metal chemistry and bioavailability, degradation and transport of hydrophobic organic chemicals, formation of disinfection by-products during water treatment, and hetetrophic production in blackwater ecosystems. Accordingly, these substances have attracted extensive attention.

In the past decades, almost all classical and modern techniques and methodological approaches have been used to elucidate the structures of humic substances and characterize their behavior and multiple functions in the environment (Aiken et al., 1985; Hayes et al., 1989; Schnitzer and Khan, 1972). In particular, non-separative, non-destructive, spectroscopic techniques have been playing a vital role in the development of this field at each stage. Our current knowledge about the composition, structures and physical-chemical properties of humic substances has greatly benefited from applications of various spectroscopic techniques such as IR (MacCarthy and Rice, 1985), NMR (Wershaw and Mikita, 1987; Wilson, 1987) and fluorescence spectroscopy (Senesi, 1990). However, due to the extremely high heterogeneity of these mixtures, these spectra are inevitably poorly resolved and overlapped. They can only reveal the total and limited information regarding the composition and structure of humic substances (Hayes et al., 1989; MacCarthy and Rice, 1985; Wershaw and Mikita, 1987; Wilson, 1987). In such a situation, it should be of importance to develop some highly selective and sensitive probes. These probes are not used for the total characterization of humic substances. Instead, they can selectively detect the functional groups or portions in these substances and sensitively reveal the environmental processes they take part in.

When organic species are adsorbed on noble metal surfaces, i.e. copper, silver and gold, their Raman signals are enhanced to 10^3 – 10^7 folds (Chang and Furtak, 1982; Fleischman et al., 1974; Garrell, 1989). The effect is called surface-enhanced Raman scattering (SERS). Due to its sensitivity, surface selectivity and the ability to quench fluorescence, this technology should be very valuable to characterize humic substances at low concentrations typically found in aquatic environments. Unfortunately, the applications of SERS spectroscopy in the study of humic substances and their environmental roles is still in its infancy because the previous researches on silver and gold surfaces reveal very limited information (Liang et al., 1996; Wang et al., 1996; Yang and Zhang, 1996). This paper preliminarily explores the SERS characteristics of humic substances adsorbed on copper electrodes. A unique resolution-enhanced effect is observed and the observation recommends that the SERS spectroscopy based on copper substrates, as an ideal probe described above, might selectively reveal enriched information regarding the specific groups or portions of humic substances in aquatic environments.

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EXPERIMENTAL

Four humic acids from soils, named as Anjo Black, Sanage, Yamamono and Tsubame (Kuwatsuka et al., 1978) were used for the analysis. Other tested samples included a humic acid from ocean water and the fulvic acid from the same source, a fulvic acid from weathered coal and a fulvic acid from peat (Liu and Zheng, 1980). Their elemental composition, spectroscopic characteristics and the degrees of humification were well-characterized (Kuwatsuka et al., 1978; Liu and Zheng, 1980). These purified samples were dissolved in 0.1 M NaOH and the pH values were adjusted back between 7 and 9 by adding 0.1 M HCl.

To activate the copper surface, a strip of copper foil was polished with a fine emery paper and rinsed with deionized water. Then the copper foil was dipped into an electrochemical cell which contained 0.08 M KCl and 0.2 g/L humic samples. The copper foil was activated by oxidation – reduction cycles by continuously changing the electrode potential from – 3.0 V to + 3.0 V and back to – 2.6 V for measurements. A Pt wire was used as the referenced electrode. A similar procedure onto a gold electrode was previously described in more detail (Wang et al., 1996).

The SERS spectra were recorded with a Spex 1404 0.85m double spectrometer equipped with a Photometrics, model Spectra 9000 TM cooled CCD system. The 647.1 nm laser line of Spectra – Physics model 2020 krypton ion laser was used for excitation. Laser power at the electrode surface was reduced to about 10 mW. A detailed description regarding the system was previously reported by Liang et al. (1996).

RESULTS

The SERS spectrum of the fulvic acid from peat (Liu and Zheng, 1980) on a copper electrode is shown in Figure 1.

This spectrum shows a good signal to noise and contains abundant Raman peaks. The combined effect of fluorescence quenching and enormous enhancement of Raman signals can partially account for the observed result. The former effect is due to

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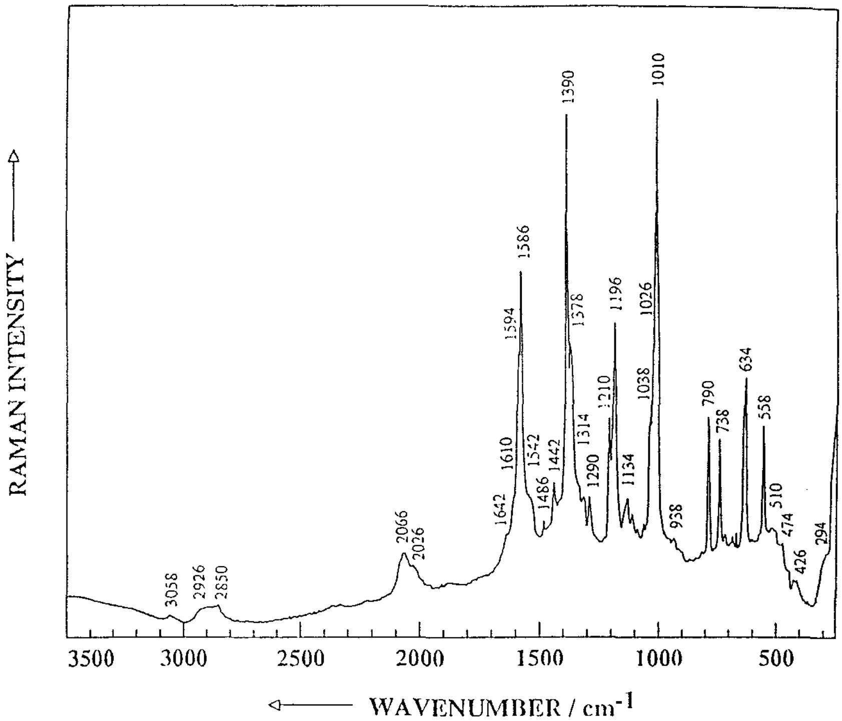

FIGURE 1
SERS spectrum of the fulvic acid from a peat

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nonradiative attenuation channels provided by the presence of the metal while the latter results from the resonance excitation of surface plasmons and charge transfer resonance between the adsorbed species and the metal substrate (Chang and Furtak, 1982; Garrell, 1989). Definite information can be derived from the vibration features of the fulvic acid. The two bands at 1594 and 1586 cm^{-1} are typical for in-plane ring vibration 8a (Mehdi, 1977). Further interesting bands can be found at 738 and 1190 cm^{-1}, which may correspond to in-plane ring vibration 12 and 9a, respectively (Barthemes et al., 1993;

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Dollish et al., 1974). The three bands at 1038, 1026 and 1010 cm^{-1} are assigned to the ring breath mode (Saito, 1993). On the basis of the SERS selective rules (Creighton, 1988), it is postulated that the aromatic rings and/or pyridine-like rings are adsorbed on the electrode surface in a perpendicular orientation. The intensive Raman bands at 1390 and 1378 cm^{-1} were definitely assigned to COO^- symmetric stretching vibrations (Moskovits and Suh, 1984; Moskovits and Suh, 1985; Pagannone et al., 1987). It is certain that the COO^- groups in the fulvic acid chemically bind to the copper surfaces. The bands at 2926 and 2850 cm^{-1} are the symmetric and antisymmetric stretching vibration of aliphatic C-H.

The SERS spectra of the other samples are shown in Figures 2-4.

The SERS spectra of the humic acid and the fulvic acid from ocean water are identical in band positions (Figure 2), showing the same SERS characteristics.

The SERS spectra of humic acids from Sanage 29, Yamamono and Tsubame soils (Figure 3) are very similar to Figures 1-2.

The Raman spectra of the two samples with high degree of humification, i.e. Anjo Black soil humic acid and the fulvic acid from weathered coal of Tulufan (Figure 4) show some differences from the previous spectra, particularly the bands at 1390 cm^{-1} and 1378 cm^{-1}. These bands are much weaker, particularly in spectrum B of Figure 4, showing that very few COO^- groups chemically bind onto the copper surfaces. It results from a high degree of substitutions of aromatic acids in humic substances with a high degree of humification. For example, most aromatic rings in the fulvic acid from weathered coal of Tulufan are substituted with three or four or five carboxylic and phenolic groups (Zhou and Zhang, 1994). When the acids with one or two COO^- groups chemically bind onto SERS substrates via the COO^- groups in a perpendicular fashion, highly substituted acids

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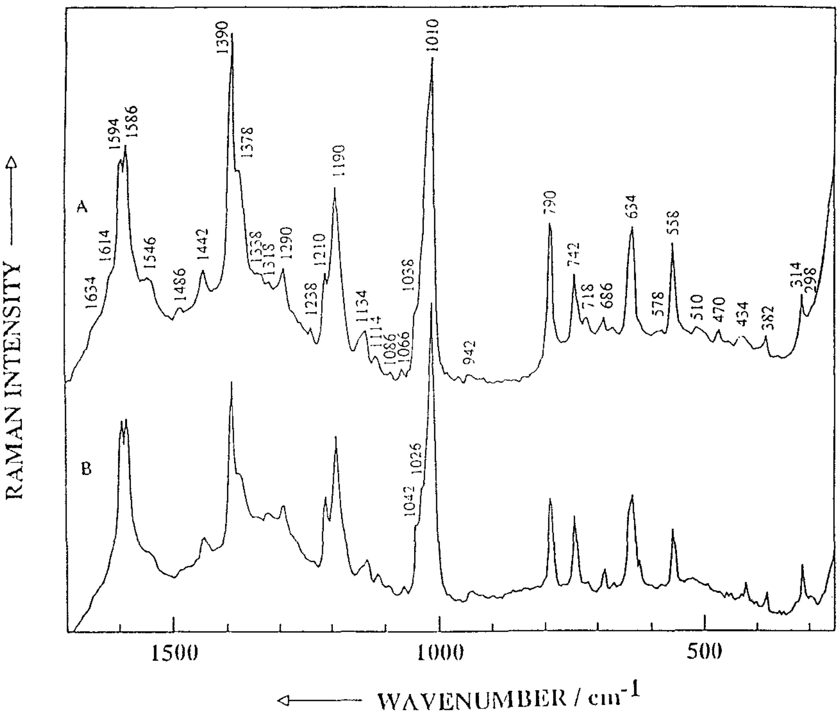

FIGURE 2
SERS spectra of the humic acid (A) and the fulvic acid (B) from ocean water

prefer to flatten on the surfaces via the aromatic rings in a p-π mode. Since the COO$^-$ groups do not directly bind onto the surfaces, their vibrational signals are too weak to be observed.

DISCUSSION

Nature of the Resolution-enhanced Effect

A scientifically based analysis regarding the nature of the resolution-enhanced SERS effect is first from the direct comparison between the SERS spectra and the normal ones.

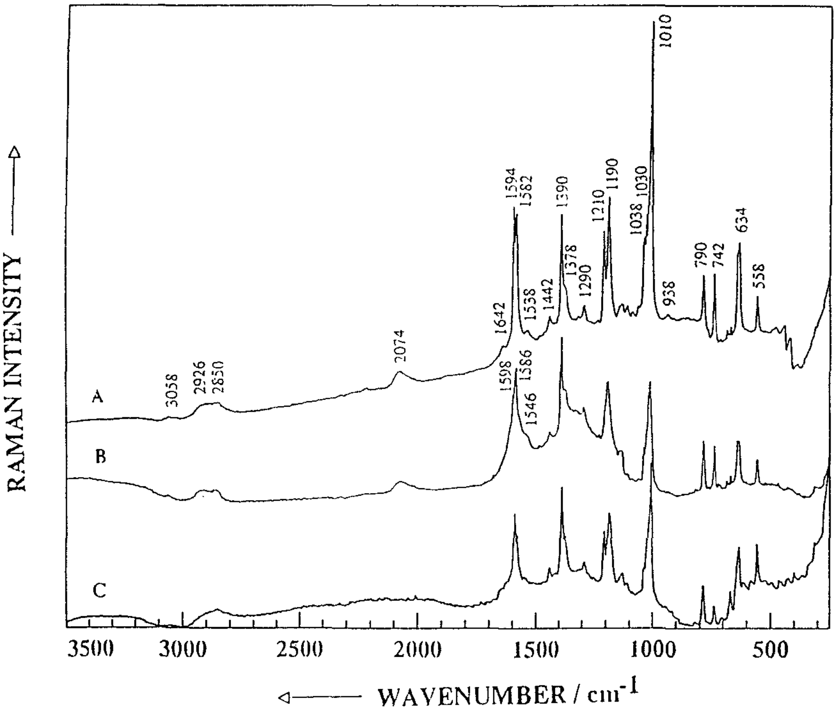

FIGURE 3
SERS spectra of Sanage 29 (A), Yamamono (B) and Tsubame (C) soil humic acids

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In many cases, the surface-enhanced Raman spectra of organic compounds are quite similar to their normal Raman spectra without enhancement (Chang and Furtak, 1982; Garrell, 1989). It is because the organic compounds are mainly adsorbed on the surfaces via physical modes instead of chemical binding (Chang and Furtak, 1982; Garrell, 1989).

Although the problems arising from fluorescence and the deep color of humic substances prevents the detection of the normal Raman signals when visible lasers are used, the normal Raman spectra of humic substances have been successfully measured under near-IR excitation (Yang and Wang, 1997). Two broad D and G bands

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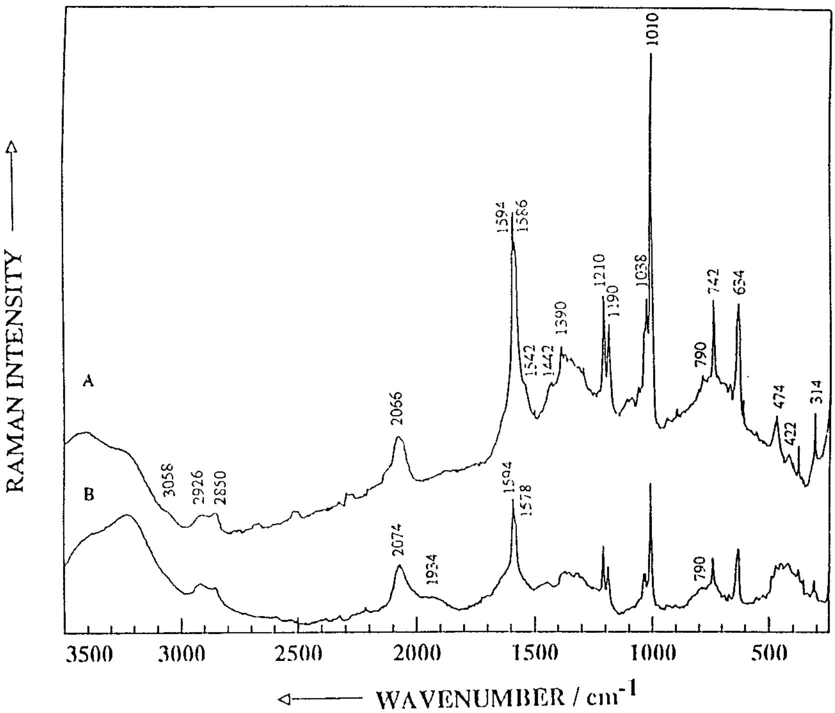

FIGURE 4
SERS spectra of Anjo Black soil humic acid (A) and the fulvic acid from weathered coal of Tulufan (B)

predominate in the spectra and the data reveal that the backbones of humic substances are structurally disordered carbon networks (Yang and Wang, 1997). The SERS spectra of humic substances adsorbed on silver substrates are very similar to the normal spectra (Liang et al., 1996; Yang and Zhang, 1996). It implies that humic substances are physically adsorbed on the silver surfaces and the physically enhanced effect plays a vital role.

However, the SERS spectra of humic substances adsorbed on the copper surfaces are totally different from the normal spectra reported previously (Yang and Wang, 1997). It definitely demonstrates the occurrence of chemical bindings (Chang and Furtak, 1982; Garrell, 1989).

According to Wershaw's micelle model (Wershaw, 1989), humic and fulvic acids behave as aggregates or even micelles, particularly on interfaces. It is quite impossible for the aggregated "pseudo-polymers" to chemically interact with the surfaces via all their groups and/or fragments. Instead, only a few kinds of chemically and geometrically favorable groups in the humic substances bind onto the surfaces, while the rest of the aggregates **dangle** in the solution. On the basis of the SERS selective rule (Creighton, 1988), since the rests are far from the surface, their SERS signals are too weak to be observed. Therefore, the SERS spectra are highly simple and only characterize a few of the specific groups bound onto the surfaces. It is the reason why a unique resolution-enhanced effect is observed herein.

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The Significance of the SERS spectroscopy on Copper Electrodes

SERS spectroscopy on copper substrates should be treated as a spectroscopic probe in the study of humic substances and their environmental roles.

The role of this probe is different from those by IR, NMR, normal Raman and many other physical-chemical approaches. FT-IR-Raman and NMR realistically reveal the average and total information regarding the composition and structure of humic substances. On the other hand, although the SERS spectra are highly resolved, they only reveal specific information regarding the binding groups on the surfaces, which belongs to small portions of humic substances.

In a way, this kind of probe is quite similar to the current fluorescence probes (Senesi, 1990). It may be more useful to use these probes for the investigation of the behavior and the multiple functions of humic substances in aquatic environment, instead of their structural aspects. Of course, it also has potential to deduce the total information regarding the structural and conformation of humic substances by these probes.

SERS spectroscopy is a very sensitive tool. A previous research (Yang and Zhang, 1996) has revealed that humic substances and co-existing organic compounds at low concentrations typically found in aquatic environments can be totally characterized by SERS spectroscopy. When SERS substrates such as copper, silver and gold electrodes are dipped into the aquatic samples, the adsorbed orientation and the competition between humic substances and co-existing organic species on these metal surfaces can be observed. The spectra may reveal on-going environmental processes in the presence of humic substances.

In this preliminary study, it is found that fulvic and humic acids from different sources possess very similar SERS characteristics. The spectra reported herein should be able to be used as references when we further use the SERS probe in the study of natural waters.

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