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Near-IR surface-enhanced Raman spectrum of lignin†

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Compacted powders of commercially available nano- and microparticles of silver were used to successfully induce the surface-enhanced Raman scattering (SERS) effect in spruce milled-wood lignin (MWL). For the two silver particle sizes used in this investigation, the spectra were mostly similar. Some general characteristics of the lignin SERS spectrum are described. The SERS technique was found to be sensitive for detecting lignin. Significant spectral changes were present between the SERS and normal Raman spectra of MWL. The SERS spectrum was assigned on the basis of literature-reported vibrational assignments of lignin and its models. Based on significant changes in Raman features, we propose that the lignin is strongly adsorbed on silver. To determine whether SERS of lignin can be obtained directly from wood without its isolation, Wiley-milled spruce wood (WMW) adsorbed on silver was studied. The results indicated that not only the surface-enhancement effect was successfully induced in the WMW, but that its spectrum was similar to MWL SERS. Moreover, for WMW, no signals from the carbohydrate components were observed, and therefore, lignin was detected selectively. This nano- and microparticle-based molecularly specific method is expected to make a significant contribution in identifying and investigating lignin in various lignin-containing materials. Published in 2009 by John Wiley & Sons, Ltd.

Keywords: surface-enhanced Raman scattering (SERS); lignin; cellulose; wood; silver; nano; micro; benzoic acid; muconic acid

Introduction

Wood and other lignocellulosics (agricultural residues, grasses, water plants, and other plant substances) are heterogeneous natural polymer composites with large variations in physical and chemical properties. These natural materials are composed of cellulose, lignin, and hemicelluloses. After cellulose, lignin is the second most abundant organic material on earth. Compared with cellulose and hemicelluloses, both of which have regular chemical structures, the structures of lignins are highly irregular[1,2] (Fig. 1 illustrates the molecular structure of softwood lignin). Because of this irregularity, the structures of lignins have proven to be difficult to study even in their native states. The same holds true for other modified states of lignins, such as wood pulp where residual lignin poses a similar characterization problem.[3] Because of their high molecular weight and complex structure, lignin polymers cannot be isolated without some structural modification. Lack of detailed information on lignin structures has hindered progress in a number of science and technology fields. Areas as diverse as lignin biosynthesis, plant cell wall lignification, forage digestibility, delignification in pulping and bleaching, biodegradation of agro materials, genetic modification of plants, and biomass utilization (e.g. biofuels) are likely to benefit from an improved understanding of lignins at the molecular level.

Over the years, numerous techniques have been applied to studying lignins.[4,5] Whereas a large number of the techniques can be applied to studying isolated lignins in the solution state, with nuclear magnetic resonance spectroscopy being the most useful, only a few yield information when lignin is present in the solid state – either isolated or in its native environment. Usually, isolated lignin represents only a small part of its total amount in the sample.[6] Both Raman and infrared (IR) spectroscopies are capable of analyzing samples in the solid state. Compared to IR, Raman investigations of lignins are relatively recent.[7–19] In the early days, with excitation in the visible range, it was difficult to obtain Raman spectra of acceptable quality for lignin/lignocellulosics because of fluorescence. Sampling methods that minimized the fluorescence contribution[4,7,8] helped in alleviating this problem. However, with longer wavelength excitation at 1064 nm where absorption of lignin is significantly reduced, good-quality FT-Raman spectra were obtained.[10,12,15] More recently, resonance Raman studies of highly fluorescent lignins have been successfully carried out using UV laser excitations.[13,16,18] Although good progress has been made so far, Raman spectroscopy has further potential for obtaining much more informative data on lignins.

Surface-enhanced Raman scattering (SERS) is a special phenomenon within the field of Raman spectroscopy and involves generation of enhanced Raman signal (by as much as 10^8) from analyte molecules adsorbed on roughened metal surfaces (usually nanoparticles of silver and gold).[20–22] The SERS technique, attributed to large electromagnetic fields near nanostructured metallic surfaces[23] (usually of silver and gold) and short-range chemical effect,[24] has the capability to detect a single molecule[25–27] and provide information on molecular structure. Several types of metal surfaces have been used in SERS applications: e.g. sols,[28] electrodes,[29,30] evaporated[31] and chemically deposited[32,33] films, compacted powders,[34,35] metallic nanoparticle arrays,[36] and nanofabricated substrates.[37] Although some enhancement in SERS is due to chemical contribution[24,38] (electronic interaction between the metal and the adsorbate), the main reason why SERS produces extraordinary enhancements is surface plasmons – the electromagnetic property of nanostructures. The

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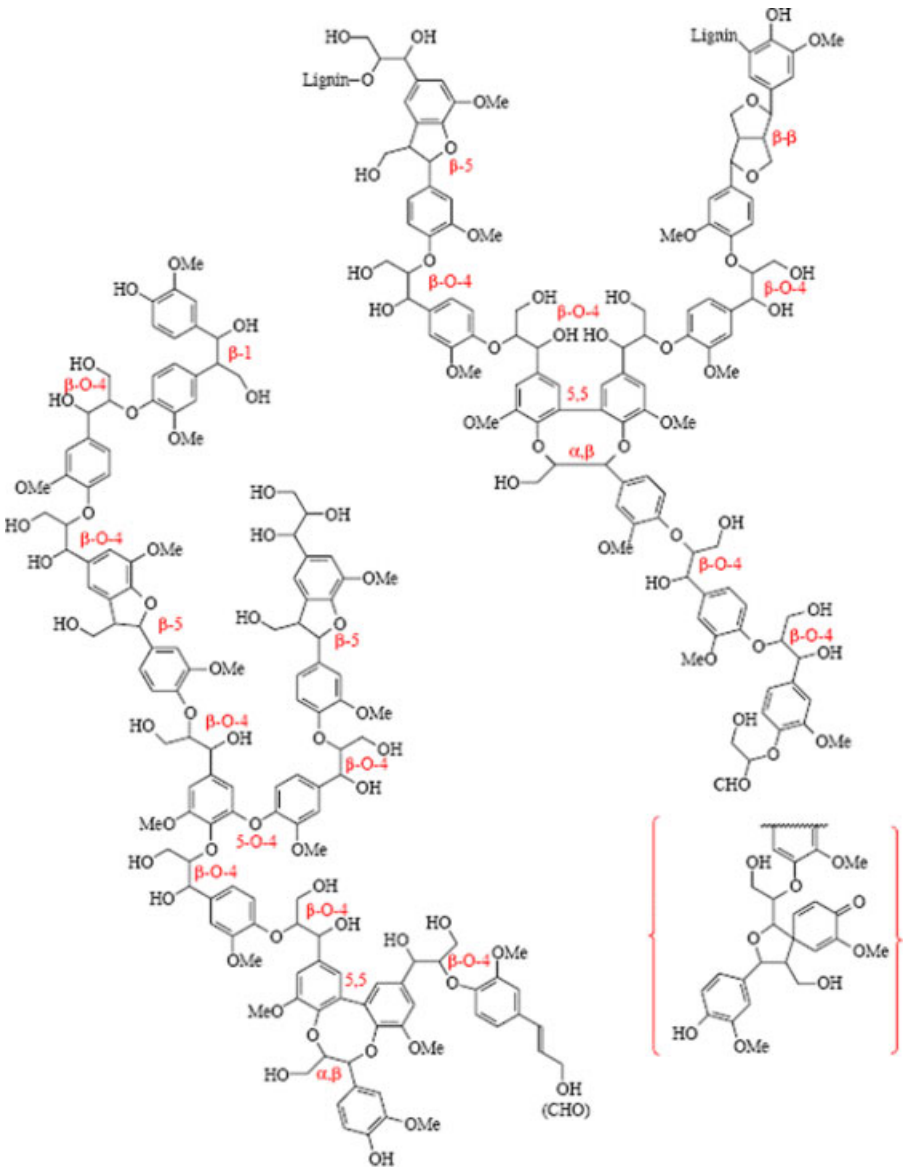

Figure 1. Representation of the molecular structure of softwood lignin. Although the lignin polymer is not a regular polymer with a particular constitutional repeat unit, the phenyl propane (C_9) unit is considered a skeleton unit linked to other C_9 units in 3D. The structure shown here incorporates the recently discovered dibenzodioxocin and spirodienone units in lignin.[2] Interunit linkages in lignin are annotated. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

magnitude of the chemical enhancement SERS factor usually does not exceed 10[23,24] and can be rationalized in terms of change in the Raman polarizability tensor of the molecule due to the formation of the complex between silver and the molecule. SERS using near-IR excitation at 1064 nm has been demonstrated[39–41] and is expected to arise from aggregates of silver particles and near-IR localized plasmon resonances detected in fractals. Recent advances have made SERS a versatile technique having diverse fields of application not only in analytical science but also in forensic science, biomedicine, environmental monitoring, and artwork conservation. Detailed SERS characterizations of various materials such as single-wall carbon nanotubes, polymers, and self-assembled layers have been carried out. An additional advantage of SERS when applied to the study of fluorescent materials is that it effectively overcomes the fluorescence problem.

In our laboratory, earlier efforts to induce SERS in wood and its component polymers (cellulose, hemicellulose, and lignin) have not been successful. In the case of wood, such attempts consisted of precipitating silver in the cell wall and applying gold and/or silver coating, using a sputter coater, to 30-μm sections of wood. The cell wall components cellulose, hemicellulose, and lignin silver sols prepared using the literature-based methods[42–44] failed to bring about the surface enhancement effect. Nevertheless, when commercially obtained larger size particles of silver were used, the SERS effect was induced in the samples of milled-wood lignin (MWL) and Wiley-milled spruce wood (WMW), indicating that these materials were spontaneously adsorbed onto interacting metallic silver particle surfaces. In this paper, results of applying SERS to study lignin and wood using commercially available Ag particles are presented.

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Experimental

Black spruce wood was used with previously described procedures to obtain samples of WMW and MWL.[10] The isolated MWL represented ~15% of the total lignin present in WMW.[10] As described in Ref. [10], WMW was extracted overnight by acetone/water (9 : 1) solvent mixture and filtered. The extraction process was repeated four additional times.

Silver particles (average sizes, 100–150 nm and 2–3.5 μm; purity, >99 and 99.9 + %, respectively), benzoic acid (≥99.5%), and *t,t*-muconic acids (98%) were purchased from Sigma–Aldrich, Milwaukee, WI. Ethanol (200% proof) was from Aaper Alcohol and Chemical Company, Shelbyville, KY. Cellulose powder CC31 was purchased from Whatman Ltd., Maidstone, Kent, England.

For benzoic and muconic acids, SERS sample preparation involved adding 50 μl of 8×10^{-3} M ethanol solution to 15 mg of Ag particles and vigorously mixing them together using a spatula. Additionally, in the case of muconic acid, various Ag : acid dilutions in the range of 100 : 1 to 1 020 000 : 1 were prepared and analyzed using 2–3.5-μm Ag powder. For MWL, WMW, and Whatman CC31 cellulose, the samples were prepared by mixing, in the presence of ethanol, a small amount (a few milligrams) of the solid sample with 15–20 mg Ag substrate. If needed for dispersion, a few drops of ethanol were further added. Once the mixture was completely dry, it was sampled in an 'aluminum well,' a Raman sampling accessory. Various dilutions of Ag : MWL samples were also prepared in a similar manner. A MWL solution (0.0281 M) was made by dissolving 5.2 mg lignin in 1 ml of dioxane : water (9 : 1). Further dilutions were made as needed.

A Bruker RFS-100 near-IR FT-Raman spectrometer (Bruker Instruments Inc., Billerica, MA) was used to obtain the spectra. The instrument has been described previously.[10] For most acquisitions, samples were pressed into the 'Al wells' and spectra were acquired using 600 mW of unfocused laser power; 1024 scans were accumulated for each spectrum. Raman spectrum of WMW was obtained by pressing it into a pellet. Bruker's OPUS software was used to find the peak positions and manipulate spectra. For display purposes, some spectra were shifted on the intensity scale (*y*-axis). The spectral data were not processed in any manner.

Transmission IR spectrum on MWL, as KBr pellet, was recorded on a Galaxy 5000 spectrometer (Mattson Instruments, Middleton, WI). Scanning electron micrographs (SEMs) of Ag substrates and WMW were obtained. For this purpose, samples were gold-coated using a sputter coater, examined, and photographed with a Zeiss EVO 40 SEM (Carl Zeiss MicroImaging, Inc., Thornwood, NY).

Results and Discussion

Target compounds

Benzoic and muconic acids were used as target molecules to evaluate the SERS suitability of commercially obtained Ag substrates. Muconic acid was chosen because these kinds of structures are one type of byproduct in oxidized lignin.[45] In our laboratory, both these compounds produced good SERS spectra using commercial Ag particles (Figs 2 and 3). For either acid under identical experimental conditions, no Raman signal was detected from the ethanol solution. Spectra of neat solid samples are included in the figures for comparison purposes.

Benzoic acid is known to be SERS active,[46] and this behavior is supported by the SERS spectrum in Fig. 2(c), which was produced using the commercially obtained 100–150 nm Ag particles. This

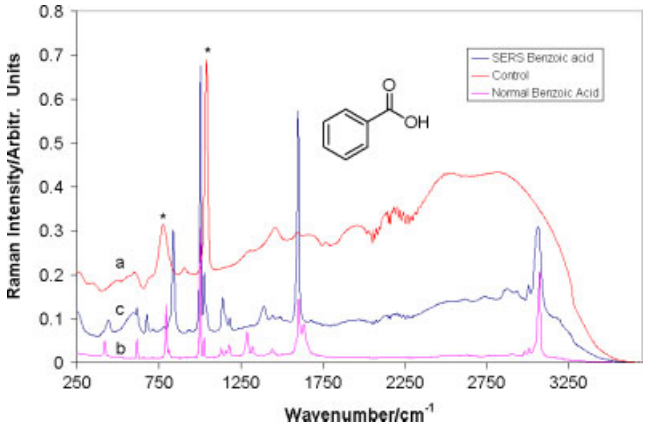

Figure 2. Near-IR spectra of (a) 100–150-nm Ag particles, (b) solid benzoic acid, and (c) Ag : benzoic acid. In (a) silver substrate, bands are marked with an *. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

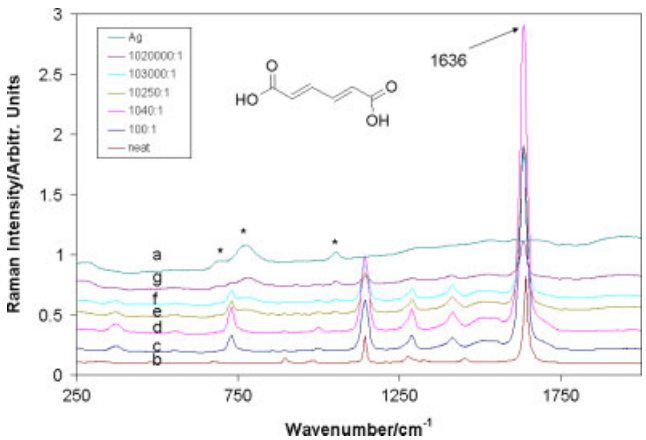

Figure 3. Near-IR SERS spectra of *t,t*-muconic acid at various Ag : acid dilutions: (a) Ag 2–3.5 μm, (b) neat acid, (c) 100 : 1, (d) 1040 : 1, (e) 10 250 : 1, (f) 103 000 : 1, and (g) 1 020 000 : 1. Peaks due to Ag particles are marked with an * in spectrum (a). This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

behavior was also seen for the muconic acid SERS spectra shown in Fig. 3 where less expensive 2–3.5 μm Ag particles were used. In our investigation, we observed that both the 100–150 nm and 2–3.5 μm Ag particles gave equally good SERS spectra with either target compound.

Commercially obtained Ag particles clearly produced the SERS enhancement for both benzoic and muconic acids. The enhancement factor calculated for the muconic acid spectra showed that the band at 1636 cm^{-1} was enhanced by 10^6, a value similar to other SERS enhancement factors reported in the literature.[20,21,47] Also noteworthy is that at higher Ag : acid dilutions, peaks due to Ag are more prominently seen in Fig. 3.

Milled-wood lignin

When a sample of MWL thoroughly mixed in presence of ethanol with the silver particles was analyzed, the Raman spectrum of the MWL was found to be surface-enhanced (Fig. 4(b)) when compared to the normal near-IR FT-Raman spectrum of MWL[10] (Fig. 4(a)). As expected in SERS,[21,48] C–H stretches were weak and the normal Raman selection rules seem to have been relaxed (modes usually

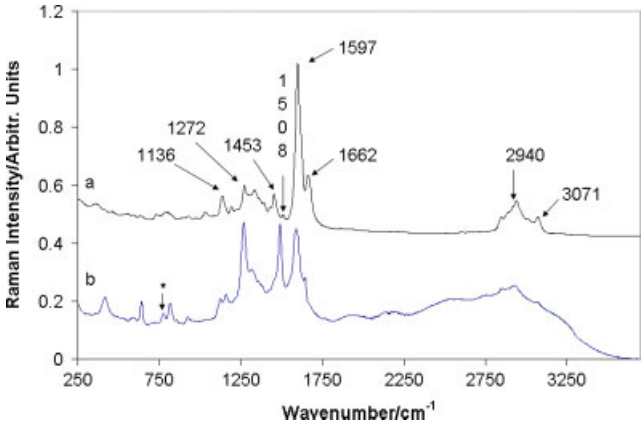

Figure 4. Near-IR spectra of spruce MWL (a) normal and (b) surface-enhanced (Ag : MWL = 4.36). Spectra have been vertically offset for improved visualization. In the lignin SERS spectrum, most enhanced bands were present between 250 and 1800 cm^{-1}. * indicates Ag peak. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

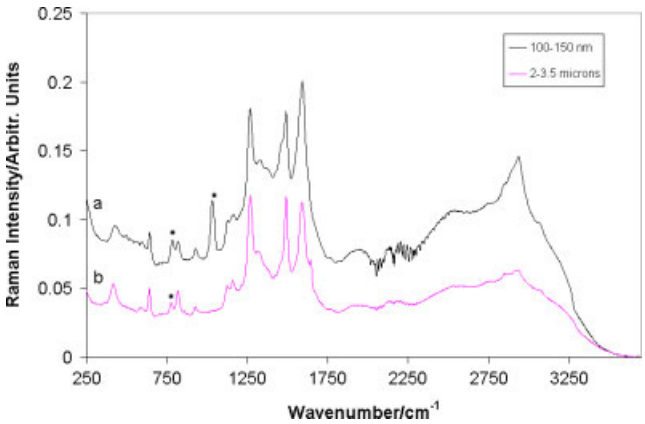

Figure 5. MWL SERS spectra obtained with different Ag substrates: (a) 100–150-nm particles, (b) 2–3.5 μm particles. * indicates Ag peak. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

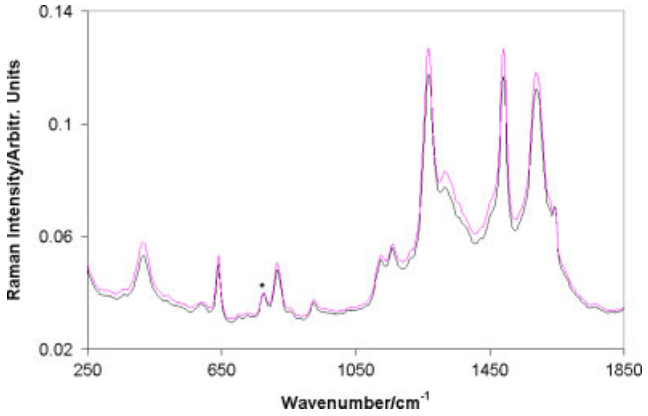

Figure 6. Reproducibility of MWL SERS spectrum. * indicates 2–3.5-μm Ag peak. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

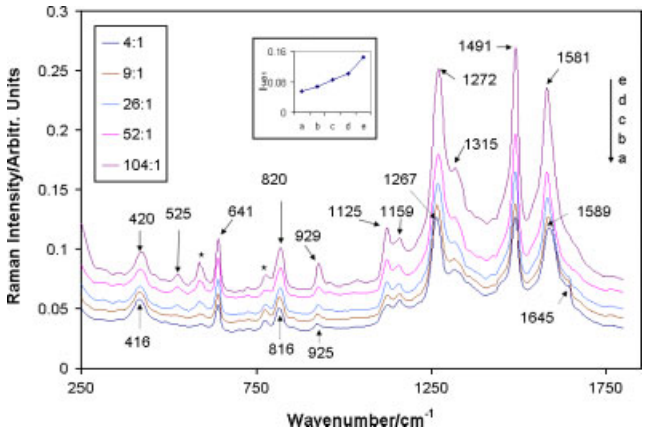

Figure 7. MWL SERS spectra obtained with different Ag : MWL dilutions: (a) 4 : 1, (b) 9 : 1, (c) 26 : 1, (d) 52 : 1, and (e) 104 : 1. Spectra were obtained using 2–3.5-μm Ag particles. * indicates Ag peak. The inset shows the Raman peak intensities of the MWL's 1491 cm^{-1} SERS band at different Ag : MWL dilutions. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

not seen in Raman are detected). A number of peaks in the normal Raman became stronger and were found to have shifted in frequency (Table 1). The latter suggested the likelihood of silver–lignin complex formation. The nature of the mixing solvent did not influence the SERS spectrum in any manner. The vibrational frequencies, band intensities, and MWL SERS assignments are given in Table 1. The assignments are tentative and based on the literature.[11,49–54] Further refinements of the assignments are expected to result from the SERS studies of lignin models that are ongoing in our laboratory.

Next, the effect of sizes and morphologies of two Ag substrates was studied. In the field of SERS, Ag particle/colloid size has been reported to influence the SERS spectrum.[22] This results from the ways in which the different size and shape nanostructures interact with light and enhance local electric fields. The spectra in Fig. 5, acquired using 100–150-nm and 2–3.5-μm Ag particles, suggest that between the two types of Ag powders used, only a small effect on the spectrum could be seen. Most of the SERS signals were present in both the spectra.

Reproducibility of the SERS spectrum was evident from the replicate measurement on the same sample (Fig. 6). Based on Fig. 6, the extent of the variability clearly was low. This implied that SERS features and Ag particle surfaces were stable and did not change with time. This also confirmed that lignin did not undergo any chemical modification under the sampling conditions used in this study.

To investigate the effect the Ag : MWL dilution on the SERS spectrum, spectra were obtained at a number of dilutions. Concentration-dependent spectra are shown in Fig. 7. There were no drastic changes in most SERS signals as the MWL concentration was reduced in several steps by a factor of 26. However, with increased dilution, not only the underlying background and the Ag bands increased slightly in intensity, but several SERS signals also showed change. The peak profile of the 1589 cm^{-1} band experienced the most modification. The band shifted to 1581 cm^{-1} and became considerably less broad (full width at half-maximum or FWHM changed from 39 to 31 cm^{-1}). Other prominent changes were a decline leading to disappearance of features at 1645 and 1628 cm^{-1}, and enhancement of peak intensities of 1491 (inset in Fig. 7), 1267, 960, 641, 587, and 525 cm^{-1}.

For better comparison, between-spectra changes relative to the peak intensity at 641 cm^{-1} were assessed. This band was chosen

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Table 1. Comparison of SERS, normal Raman, and IR band positions (250–1700 cm^{-1})

Band ID	SERS, spruce MWL (Ag : MWL = 4.36)	Normal Raman spruce MWL[10]	SERS, WMW (Ag : WMW = 1)	Normal Raman, WMW	IR, spruce MWL	MWL SERS Assignment,[11,49–54] tentative
1	1645 m	1662 s	–	1659 m[a]	1667 sh	C═C coniferyl alcohol + C═O coniferaldehyde
2	1628 w, sh	1621 sh	–	1620 sh	–	C═C coniferaldehyde
3	1589 vs	1597 vs	1584 vs	1600 vs	1600s	Aromatic ring stretch, symmetric
4	1546 w, sh	–	1548 w, sh	–	–	Aromatic ring stretch
5	1491 vs	1508 vw	1490 vs	1508 vw	1513 vs	Aromatic ring stretch, asymmetric
6	–	–	–	–	1466 s	–
7	–	1453 m	–	1456 m[b]	1458 sh	–
8	1449 br, sh	–	–	–	–	CH3 bending in OCH3
9	1426 vw	1430 w	–	1425 sh	1428 m	CH3 bend + ring stretch
10	–	1392 sh	–	–	–	–
11	1380 w, sh	–	–	1377 m[b]	1375 w	CH3 bend + ring stretch
12	1357 w, sh	1363 sh	1360 vw, sh	1367 sh	–	CH3 deformation in OCH3
13	1336 w, sh	1334 m	1325 m	1338 m[b]	1331 sh	Aromatic ring breathing + C-O stretch
14	1315 m	–	–	–	–	Aliphatic O-H bend
15	–	1298 sh	–	1307 w	–	–
16	1267 vs	1272 m	1263 vs	1272 m	1270 vs	C-OH + C-O(in OCH3) stretch
17	–	1226 vw	–	–	1226 m	–
18	1212 w, sh	–	1216 w	–	–	C-O (in OCH3) stretch
19	–	1192 w	–	1191 w	–	–
20	1159w, br	–	1165 m	–	–	Aromatic CH in plane bending
21	–	–	–	1152 sh[b]	–	–
22	–	1136 m	–	–	1142 s	–
23	1125 m	–	1124 m	1124 s[c]	–	C-O stretch (in CHOH)
24	–	–	1114 sh	–	–	–
25	–	1089 w	–	1096 s[c]	1085 w	–
26	–	–	–	1061 w[b]	–	–
27	–	1033 w	1031 m	1039 sh[b]	1035 s	–
28	1003 vw	–	–	1000 vw[b]	–	O-CH3 stretch
29	–	975 vw	–	973 sh[b]	–	–
30	925 m	928 vw	925 w	927 sh	914 vw	Aromatic CH twisting
31	884 vw	895 vw	–	899 m[b]	–	Aromatic CH deformation
32	–	–	–	–	878 sh	–
33	855 m	–	–	–	863 w	Aromatic CH deformation
34	816 s	–	816 m-s	803 w	823 w	Aromatic CH twisting
35	–	787 w	781 w	785 w	784 vw	–
36	775 m-s	–	–	767 sh	–	Aromatic ring breathing
37	–	–	–	–	742 vw	–
38	727 w	731 w	728 vw	731 w	–	Aromatic ring twisting
39	702 w	–	–	–	–	Ring deformation
40	641 s	637 vw	641 s	635 vw	–	Ring deformation
41	–	–	–	621 vw	–	–
42	587 m	588 vw	589 m	596 w	–	CO rocking (in CHO) + other modes
43	–	557 vw	–	562 w	–	–
44	–	534 vw	526 w, sh	520 m[b]	–	–
45	488 vw	491 vw	492 w	493 w[d]	–	Aromatic ring deformation + other modes
46	–	457 vw	–	459 m[b]	–	–
47	–	–	–	436 vw	–	–
48	416 s	–	419 s	–	–	Aromatic ring deformation + other modes
49	–	384 w	–	380 m[b]	–	–
50	–	361 w	–	350 sh[b]	–	–

[a] Band intensities are relative to other peaks in the spectrum.
[b] Cellulose band.[10]
[c] Band assigned to cellulose, xylan, and glucomannan.[10]

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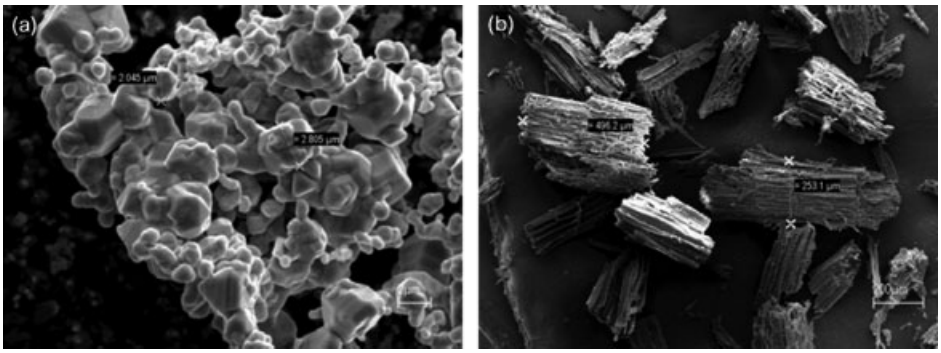

Figure 8. Scanning electron micrographs (SEMs) of (a) aggregated silver particles (2–3.5 μm particles, scale bar 2 μm); (b) Wiley-milled wood (scale bar 200 μm). Particle sizes in both cases were widely distributed.

because it was free of overlapping bands and its profile seems to remain unchanged upon dilution. Relative band intensities at 1159, 856, and 416 cm^{-1} declined, whereas the only place it increased was at 1491 cm^{-1}. The band intensities at 1267 and 775 cm^{-1} oscillated, first declining and then increasing with dilution. Of the prominent SERS peaks, the ones at 1491 and 641 cm^{-1} did not shift in position, whereas those at 1267, 925, 816, and 416 cm^{-1} shifted to 1272, 929, 820, and 420 cm^{-1}, respectively. An upward shift of approximately 4 cm^{-1} was detected. The reasons behind these spectral changes are presently unknown but are likely associated with both the lignin–Ag interactions and the local nature of chemical enhancement mechanisms.[24,54] Besides, coverage of the Ag particle surface will play a role as well.

At a higher concentration, not all sample layers are in direct contact with the Ag surface and therefore contribute differently to SERS. This, for example, can explain why at higher MWL concentration, the contributions at 1645 and 1628 cm^{-1} are detected; these bands are not enhanced in SERS but are noticeable when lignin is present in layers not in direct contact with the Ag surface. Several bands showing changes upon dilution were associated with aromatic ring modes (Table 1); therefore, it is likely that π-electrons were involved in the adsorption of lignin on Ag surfaces. This is likely to influence the modification of some spectral peaks more than the others. Further experiments using dissolved MWL were carried out to determine the sensitivity of the SERS method. Spectra recorded from the samples of 0.5 g/l MWL solution on the Ag substrates indicated that as little as 10 μg of lignin could be detected using SERS.

Spectral characteristics

To determine how the spectral features in MWL SERS spectrum (Fig. 4(b)) were different from those of normal Raman (Fig. 4(a)), the two spectra were compared (Table 1). Table 1 lists, in the region 250–1700 cm^{-1}, the MWL band positions in SERS, normal Raman (near-IR), and FT-IR. A number of observations can be made. For the SERS spectrum, band positions are from the spectrum obtained at the Ag : MWL ratio of 4.36. The composite coniferaldehyde C═O and ethylenic C═C band is shifted from 1662 to 1645 cm^{-1} (Table 1, band ID 1). A shift of 17 cm^{-1} is significant and suggests the existence of an altered chemical environment around these groups. One of the strongest bands in the spectra corresponds to the aromatic ring stretch mode, observed at 1597 and 1589 cm^{-1} for normal and SERS, respectively (Table 1, band ID 3). A lowering of frequency by 8 cm^{-1} in SERS is noted for this mode.

Additionally, in the SERS spectrum considerable change of intensity for many bands can be noted from Fig. 4 and Table 1. The very weak 1508 cm^{-1} band present in the normal spectrum of lignin (Table 1, band ID 5, column 3) seems to have shifted in SERS to a very strong 1491 cm^{-1} band, and in IR corresponds to the band at 1513 cm^{-1}. Another lignin SERS band belonging to this category that has a strong IR intensity is the band at 1267 cm^{-1} (Table 1, band ID 16, column 2), although its frequency shifted by a lesser amount (5 cm^{-1}, Table 1, columns 2 and 3) in SERS. Other strong lignin SERS bands were present at 816, 641, and 416 cm^{-1}. These were bands that had no corresponding peak in normal Raman and IR spectra of MWL and therefore are new. Nevertheless, these bands have been observed in the SERS spectra of thiophenol,[55] vanillic acid,[53] and variously substituted monomeric lignin model compounds (authors' unpublished results).

From these studies, it is clear that these modes belong to the aromatic ring in lignin. Comparing normal Raman and SERS MWL spectra, it is interesting to note that a number of bands have lowered frequencies and enhanced relative intensities, indicating that these bands are sensitive to the complexation of lignin with the Ag particles.

Wiley milled wood

Because isolation procedures modify lignin chemically to some degree[56,57] it is of great interest to develop methods that are capable of studying lignin in its native environment. Therefore, it would be advantageous if the SERS of lignin and other wood components could be obtained *in situ*. For this purpose, SERS samples of WMW were prepared and analyzed. SEM images of WMW and Ag particles (2–3.5 μm) are shown in Fig. 8. Clearly, in both cases, the micrographs showed that the particle sizes were widely distributed.

Normal (peak positions annotated) and SERS spectra of the WMW are shown in Fig. 9(a) and (b), respectively. The latter is very similar to the SERS spectrum of MWL (Fig. 9(c)). Nevertheless, a detailed comparison (Table 1, columns 2 and 4) of the two spectra indicated some minor differences. For example, in the MWL spectrum, the subtle features at 1645, 1628, and 1450–1380 cm^{-1} were different. But these differences disappeared in the higher Ag : MWL ratio spectrum (see above and Fig. 7(e)), indicating that the dissimilarities were concentration dependent. The only extra features present in the WMW SERS were a stronger peak at 1216 cm^{-1} and a shoulder at 1114 cm^{-1}, which may have something to do with the undisturbed structure of lignin in wood. Compared to MWL, lignin in WMW is not degraded and is therefore representative of whole wood lignin.[58,59]

The majority of bands in the WMW SERS spectrum belonged to lignin, but surprisingly no features in the carbohydrate regions

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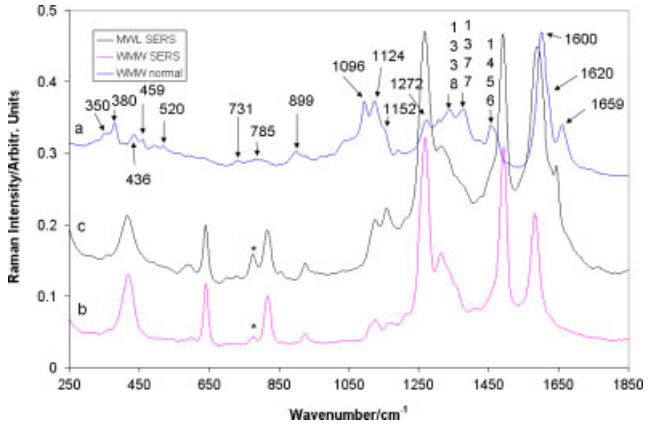

Figure 9. Raman spectra of (a) Wiley-milled wood, normal; (b) Wiley-milled wood, SERS (Ag : wood ratio 1.07); and (c) MWL, SERS (Ag : MWL ratio 4.36). In (b) and (c) * indicates Ag peak. Most peaks in the SERS spectra of wood and lignin are same, indicating that cellulose contributions were not detected. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

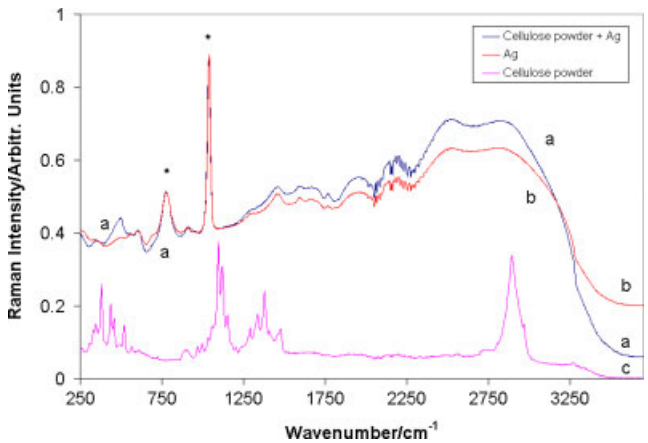

Figure 10. Raman spectra of (a) sample containing cellulose and silver, (b) silver, and (c) cellulose powder Whatman CC31. In (a) and (b) * indicates Ag peak (783 and 1040 cm^{-1}). No SERS features of cellulose were detected. This figure is available in colour online at www.interscience.wiley.com/journal/jrs.

were detected. This implied that SERS can be used to selectively investigate lignin in a multicomponent lignocellulose sample. This was found to be the case when samples of kraft pulp (another type of lignocellulose) were studied using the SERS technique.[60]

To find out whether indeed cellulose would not produce a SERS spectrum under these conditions, a Ag-adsorbed cellulose sample (Whatman CC31) was analyzed (Fig. 10). As expected, only bands caused by the Ag substrate were detected and no Raman signal from cellulose was seen. This supported the above-mentioned observation that peaks seen in the SERS spectrum of WMW (Fig. 9(b)) are due to lignin. Inability of the cellulose molecule to produce SERS may have to do with a lack of lone pair or π electrons because molecules with the latter trait are known to show the strongest SERS (e.g. carboxylic acids and phenols). Moreover, lack of such electrons is likely to be responsible for cellulose's inability to experience chemical enhancement because of adsorption on the rough silver surfaces.

Conclusions

Using commercially available Ag particles, SERS spectra of MWL and WMW were obtained. Characteristics of lignin SERS spectrum were discussed. Based on the relative changes in Raman intensities and wavenumbers, it appears that the lignin and silver are involved in complex formation. In the WMW SERS spectrum, lignin was selectively detected in presence of carbohydrate polymers, and no cellulose features were detected. Based on the initial examination, the SERS technique seems to be a useful method for selectively investigating lignin in unmodified state in the native environment of various lignocellulose biomaterials.

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