ELECTROLESS NICKEL DEPOSITION ON *FRAXINUS MANDSHURICA* VENEER MODIFIED WITH APTHS FOR EMI SHIELDING

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Electroless nickel deposition was carried out on *Fraxinus mandshurica* veneers for EMI shielding under a new activation process. In the process, Pd(II) was absorbed on the surface of veneers modified with γ-aminopropyltrihydroxysilane (APTHS) obtained from the hydrolysis of γ-aminopropyltriethoxysilane (APTES). After the reduction, electroless plating was successfully initiated, and Ni-P coating was deposited on the veneers. The activation process and resulting coating were characterized by XPS, SEM-EDS, and XRD. The metal deposition, surface resistivity, and electromagnetic shielding effectiveness were measured. XPS analysis proved that Pd(II) was bonded to the amino group of APTHS and reduced to Pd(0). The coating was continuous, uniform, and compact. It consisted of 97.4 wt% nickel and 2.6 wt% phosphorus. XRD analysis showed that the coating was crystalline, which was related to the low phosphorus content. The plated *Fraxinus mandshurica* veneers exhibit good electro-conductivity with surface resistivity of $0.21\Omega \cdot cm^{-2}$ and higher electromagnetic shielding effectiveness of over 50dB in frequencies from 10 MHz to 1.5 GHz.

INTRODUCTION

Wood is a natural renewable biomass material with some notable properties such as high ratio of strength to weight, humidity control, and heat and sound insulation. However, unmodified wood has no ability to shield against electromagnetic radiation or signals. In order to improve electrical performance of wood, an electroless plating technique has been used by many researchers to coat a metal layer such as nickel or copper on its surface (Nagasawa et al. 1989, 1990, 1991, 1992, 1999; Wang et al. 2006, 2007, 2008; Huang and Zhao 2004). However, for non-metallic materials such as glasses, mica, silicon, and plastics, the key to electroless plating is an activation process. For many years, palladium colloid has been employed as an effective activator. Two approaches have been mostly used to obtain a palladium activation layer. One is the "two-step" method (Deonath and Rohatgi 1981), by which the substrate to be coated is immersed successively in $SnCl_2$ (sensitization) and $PdCl_2$ (activation) solutions. Another is the "one-step" process using $PdCl_2$-$SnCl_2$ colloidal solution (Garg and Jonghe 1993). Unfortunately, adhesion between the palladium colloid and the substrate is a physical

interaction in both cases mentioned above. As a result, in the subsequent plating process, a small amount of palladium particles may drop off from the substrate and cause self-decomposition of the plating solution (Stremsdoerfer et al. 1993). A third approach has been to make $PdCl_2$ directly absorbed on the surface of the substrate (Harizanov et al. 1998; Li et al. 2010). However, it is very difficult for untreated wood veneer to absorb enough Pd(II) without chemical bonding.

Organosilanes are useful coupling agents and have been used to promote adhesion between organic polymers and a wide variety of substrates in industry for many years (Mittal 1992). The organosilanes of most interest are hybrid organic-inorganic compounds with the general formula $X_3Si(OH)_nY$, where Y is an organofunctional group, X is a hydrolysable group, and n is typically in the range of 0 to 3. The organofunctional groups are chosen to be compatible with a subsequently applied polymer or paint, while the hydrolysable groups are present to form silanol groups for bonding to the substrate.

Recently, some organosilanes have been used by investigators in electroless plating of non-metallic materials with surface hydroxyl groups (Xu et al. 2002; Dai et al. 2006). Cellulose, lignin, and hemicellulose in wood have plenty of hydroxyl groups. So, it was possible that such organosilanes can be used in electroless plating of wood.

Here we developed a new activation process to prepare electroless nickel-plated wood veneers for electromagnetic interference (EMI) shielding, in which APTHS was supposed to form a self-assembled monolayer (SAM) (Huang et al. 2006; Sugimura et al. 2002; An et al. 2007) on the surface of veneers, which linked wood and the palladium activator firmly through a Si-O-C bond and a N-Pd σ coordination bond. In our work, the metal deposition, surface resistivity, and electromagnetic shielding effectiveness of the metallized wood veneer were measured, and the APTHS pretreatment in activation process is also discussed. X-ray photoelectron spectroscopy (XPS) was applied for surface analysis of wood veneer in activation process. The coating on wood veneer was characterized by scanning electron microscopy (SEM-EDS) and X-ray diffraction (XRD).

EXPERIMENTAL

Materials

The substrates used were *Fraxinus mandshurica* veneers, for which the size was the same as described earlier (Li et al. 2010). APTES($(C_2H_5O)_3Si(CH_2)_3NH_2$), 97+%) was purchased from Nanjing Youhao Auxiliary Chemical Co., Ltd. Palladium Chloride ($PdCl_2$, 99.5+%) was from Shenyang Jinke Reagent Factory. Sodium hypophosphite was from Tianjin Fengchuan Chemical Reagent Co., Ltd. All the other chemicals were of analytical grade.

Preparation of Nickel-Plated Wood Veneers

The proposed mechanism of the plating process is shown in Fig. 1. First, APTES was dissolved in ethanol and water solution with certain volume ratios, then they were aged for some hours in order that APTES was inverted into APTHS. After that, wood veneers were immersed into the APTES solution for 10 minutes so as to self-assemble a monolayer of APTHS on the surface of the substrate. After air-drying ($70\,^{\circ}C$, 5 minutes),

the treated wood veneers were dipped in $PdCl_2$ aqueous solution (0.2 g/L $PdCl_2$, 15 mL 37%HCl) for 10 minutes at room temperature and then washed by distilled water for the purpose of removing any free Pd(II) ions. This step resulted in the Pd(II) ions being complexed with the amino groups, as indicated in Fig. 1. The Pd(II) ions were then reduced to Pd(0) by soaking in NaH_2PO_2 aqueous solution($2g·L^{-1}$) at 40^oC. Finally, the activated wood veneers were coated through the autocatalytic reaction in the nickel solution for 20 minutes at 70 ^oC. The compositions of the plating solution are listed in Table 1.
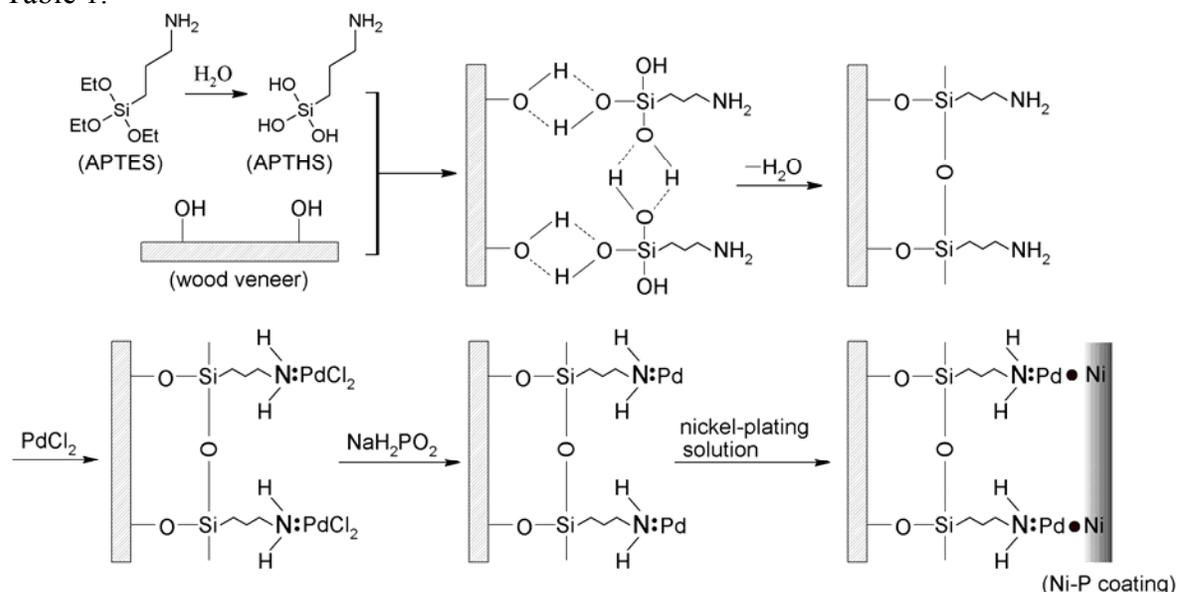
Figure. 1. The proposed mechanism of the plating process

Table 1. Composition of Nickel-Plating Solution

Chemicals	Content $(g·L^{-1})$
$NiSO_4·6H_2O$	25-35
$NaH_2PO_2·H_2O$	25-35
Complexing agent	15-25
Buffering agent	30
Thiourea	0.002
pH	8.5

Measurement of Metal Deposition

The raw wood veneers were dried at $103±2°C$ to constant weight and weighed (the weight here is denoted with G_0). Accordingly, those that had been nickel-coated were also dried to constant weight and weighed with a mark G_1. The metal deposition was calculated as follows:

$$Metal\ deposition\ (\%) = (G_1 - G_0)/G_0 \times 100\% \tag{1}$$

Measurement of Surface Resistivity and Shielding Effectiveness

Here we measured the surface resistance of the metallized wood veneers through the YD2511A-type smart low direct-current (DC) resistance tester, according to Chinese National Military Standard GJB2604-96. The detailed calculation was presented in our previous literature (Li et al. 2010).

The shielding effectiveness (SE) of the metallized wood veneers was measured by using Angilent E4402B spectrum analyzer and standard butt coaxial cable line with a flange based on Chinese industrial standard SJ20524-95. The SE value was calculated as follows:

$$SE(\text{dB}) = -10 \times \lg\left(P_{out} / P_{in}\right) \tag{2}$$

where P_{out} is the incident power and P_{in} is the transmitted power.

Characterization Methods

In this study, XPS was employed for surface analysis of the activation process of the wood veneers, which focused on the elements of palladium and the nitrogen in APTHS molecules. XPS signals were recorded by a K-Alpha XPS Analyzer (Thermofisher Scientific Company) using Al Kα source. The X-ray beam was operated at 6 mA, and the pass energy was set at 50 eV. The pressure in the analysis chamber was 1.0×10^{-8} mbar.

The surface morphology and element compositions of the coatings were characterized by SEM-EDS (Quanta 200). Specimens were not sprayed with gold prior to analysis. Additionally, the phase structure of the coating was clarified by XRD (Rigaku D/max2200 diffractometer) using a Cu Kα radiation generator operated at a power of 1200W (40 kV×30 mA).

RESULTS AND DISCUSSION

Effect of Pretreatment in APTES Solution

With the goal of obtaining an effective palladium activation layer, wood veneers were treated in APTES solutions with two different volume ratios (APTES/H_2O/ C_2H_5OH), which were 1.5/3/95.5 and 1.5/6/92.5, respectively. In the solution, the water induced stepwise hydrolysis of APTES to form APTHS, which promotes the APTES adsorption onto the OH-rich wood surface through hydrogen bonding. The results from Fig. 2 indicate that the metal deposition of coated veneers increased rapidly to a maximum first and then decreased slightly, when the APTES solutions were aged from 0h to 24 h. This is attributed to the fact that the hydrolysis of the APTES requires sufficient time. Therefore, if aging time is too short, the number of silanol groups will not be enough to bond with the hydroxyl groups on the surface of the wood veneers; conversely, the process can lead to little self-condensation, by which OH groups are exhausted and then unable to take part in subsequent reactions. However, the metal deposition was higher in the condition of the APTES solution containing 6 mL water than that of 3 mL water. The reason is that the appropriate increase of the water will accelerate

the hydrolysis of the APTES. Table 2 shows the surface resistivity of the coated veneers pretreated in the 1.5/3/95.5 and 1.5/6/92.5 APTES solutions. With aging time increasing from 0 h to 5 h, the surface resistivity of plated veneers decreased, then changed little for both low and high water content. The surface resistivity was practically the same after 24 h aging time. Because the content of APTHS in 1.5/3/95.5 APTES solution was close to that in 1.5/6/92.5 APTES solution, the veneers treated in the two solutions yielded similar results. Compared with Fig. 2, the surface resistivity and the metal deposition were negatively correlated; that is, the greater the amount of metal deposition, the smaller the surface resistivity. Because the structure of wood is anisotropic, the plated veneers were also anisotropic in their electrical conductivity; the surface resistivity parallel to the fiber direction was not equal to that across the fiber direction. So, here we calculated the average of the surface resistivities for both directions. The minimum mean surface resistivity reached about $0.21\ \Omega\cdot cm^{-2}$, while the metal deposition was about 69%, when the wood veneers were pretreated in 1.5/6/92.5 APTES solution aged for 5 h.
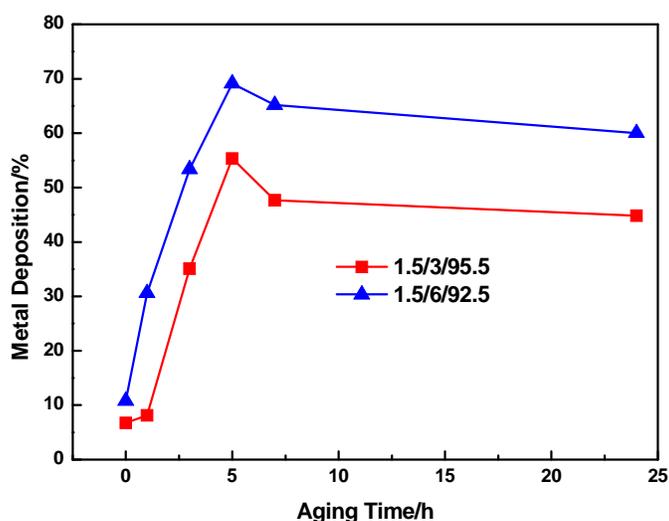
Figure. 2. Influence on metal deposition by APTES solutions

Table 2. Influence of Aging Time of APTES Solutions on Surface Resistivity

Aging Time (h)	Surface Resistivity ($\Omega\cdot cm^{-2}$)	
	1.5/3/95.5	1.5/6/92.5
0	No value (not fully coated)	No value (not fully coated)
1	No value (not fully coated)	26.11×10^{3}
3	7.69	0.39
5	0.39	0.21
7	0.44	0.39
24	0.37	0.33

XPS Analysis of the Activation Process

In this study, palladium activation was key to the subsequent electroless nickel-plating process. Through trace analysis, we found the N1s signal with two peaks centered at 398.49 eV and 400.51 eV(Fig. 3a), respectively. The former is attributed to the free amino group and the latter to a protonated amino group (Kowalczyk et al. 1996;

Bierbaum et al. 1995). These results indicated that the APTHS was successfully bonded on the wood surface and that the amnio group was directed outward. After being adsorbed with palladium(II), the peak of N1s shifted from 398.49 eV (Fig. 3a) to 400.87 eV (Fig. 3b), which means that the amino group was bonded with palladium chloride in the form of N-Pd σ coordination bond. Then, palladium(II) was reduced to Pd(0) by NaH_2PO_2, which can be confirmed by the displacement of Pd3d XPS spectra shown in Fig. 4. The peak of $Pd3d_{5/2}$ was shifted from 337.37 eV (Fig. 4a) to 335.05 eV (Fig. 4b) which is close to the characteristic peak of Pd(0) (334.9 eV) (Wagner et al. 1978).

This activation process can be highly effective for increasing the shielding effectiveness of the nickel-plated wood veneers, as will be shown below.
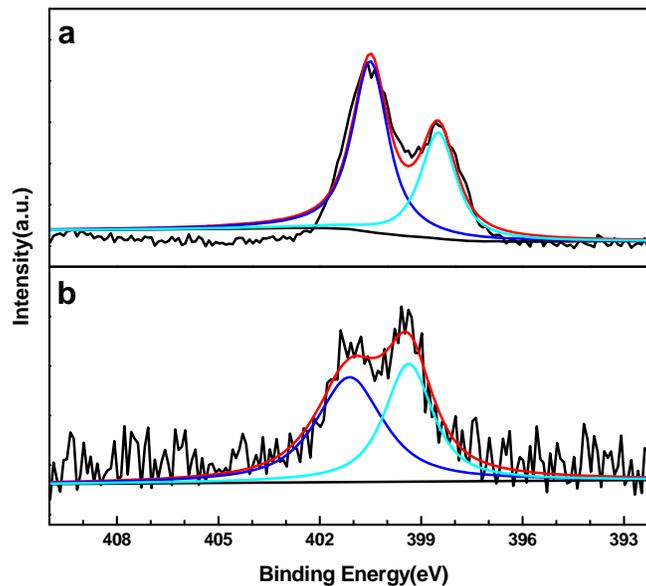
Figure. 3. XPS spectra of N1s in (a) wood/APTHS, and (b) wood/APTHS/$PdCl_2$
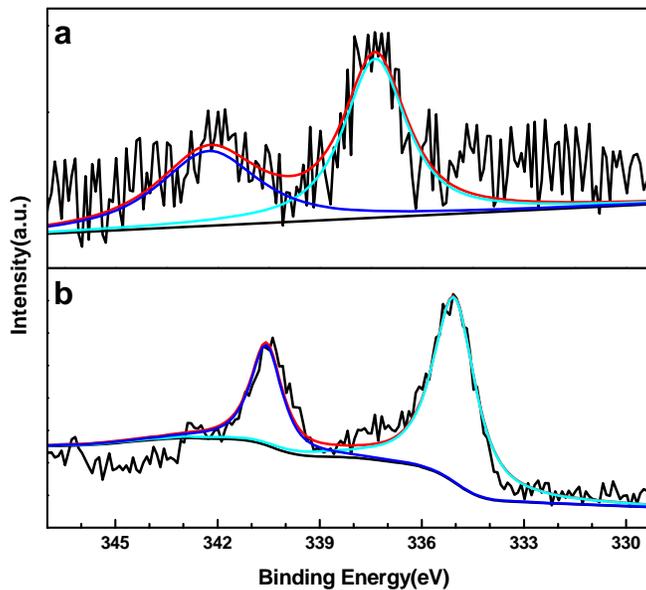
Figure. 4. XPS spectra of Pd3d in (a) wood/APTHS/$PdCl_2$, and (b) wood/APTHS/Pd

Surface Morphology and Phase Structure of the Coating

Figure 5 shows SEM photographs of the unplated and plated wood veneers.
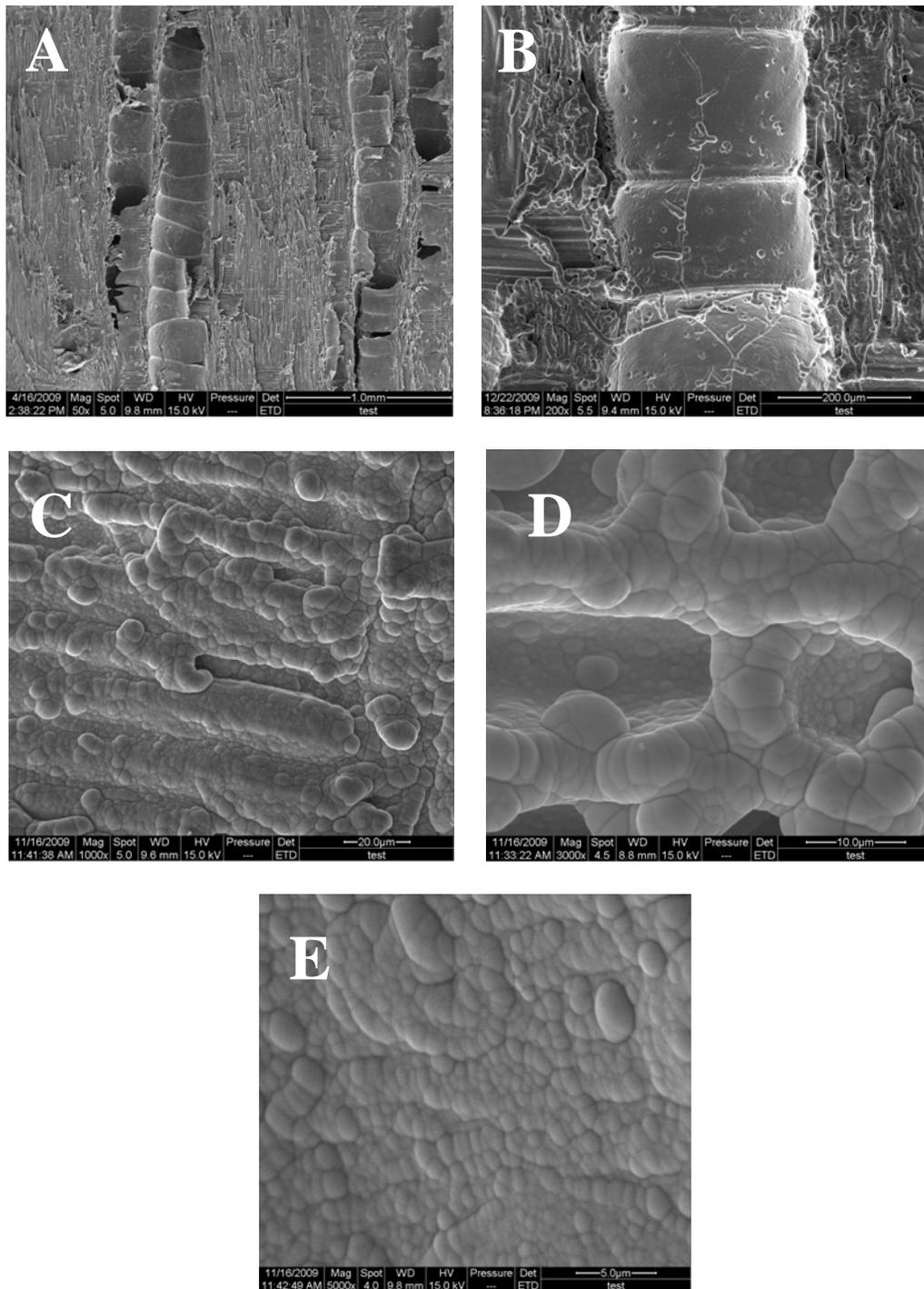
Figure. 5. SEM photographs of the unplated and plated *Fraxinus mandshurica* veneers. A. The surface of the unplated veneer. ×50. B. The surface of the plated veneer. ×300. C. The plated xylem ray structure. ×1,000. D. The plated xylem parenchyma. ×3,000. E. Enlarged area of the plated internal wall of the pipe. ×5,000.

Figure 5A shows that the unplated veneer had a porous surface with complicated structures. It can be seen that the whole wood surface including the pores was covered by a metal coating, which shows obvious metallic sheen (Fig. 5, B and C). We also found that the metal coating was uniform and continuous at high magnification (Fig. 5, D and E).

Figure 6 displays EDS spectra of the plated wood veneer. Peaks for nitrogen and silicon are from APTHS, and carbon and oxygen are from both APTES and wood veneer. As shown, the existence of palladium indicates that palladium activator was obtained. Although chloride was also found, its content was very low, which indicates that very little chloride anions in plating solution were absorbed on the coating. Peaks for nickel and phosphorus are attributed to the coating, and their contents were 97.4 wt% and 2.6 wt%, respectively. At the beginning of the electroless plating process, catalyzed by palladium, Ni^{2+} is reduced rapidly to Ni^0, which in return catalyzes the subsequent Ni-P co-deposition. The process can be written as:

$$Ni^{2+} + 2H_2PO_2^- + 2H_2O \rightarrow Ni\downarrow + 2H_2PO_3^- + 2H^+ + H_2\uparrow \qquad (3)$$

$$3H_2PO_2^- + 2H^+ \rightarrow 2P\downarrow + H_2\,PO_3^- + 3H_2O \qquad (4)$$
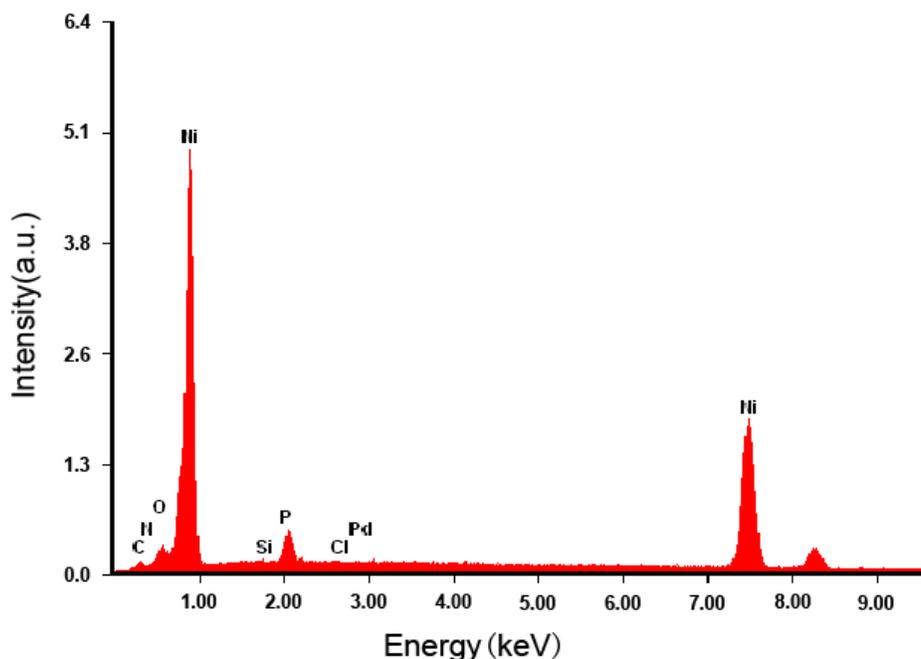
Figure. 6. EDS spectra of the plated *Fraxinus mandshurica* veneer

Figure 7 shows the XRD patterns of the wood veneer before and after plating. As indicated, the strong peak at $2\theta=22^o$ (Fig. 7, a trace) is a characteristic peak of cellulose (JCPDS: 03-0289) in uncoated wood veneer. Peaks at $2\theta=44.66^o$, 51.50^o, and 76.48^o (Fig. 7, b trace) are attributed to Ni(111), Ni(200), and Ni(220), which corresponds to a face-centered cubic phase of nickel (JCPDS: 04-0850) and a crystalline nature of the coating. This result is mainly related to lower P content and largely attributed to slight distortion of crystallinity of nickel caused by phosphorus atoms. Additionally, the characteristic

peak of cellulose at 2θ=22° in trace b has a small intensity related to the same peak in trace a and the nickel peak, which means that the veneer was entirely and compactly covered by Ni-P coating with a thickness of at least micron-size.
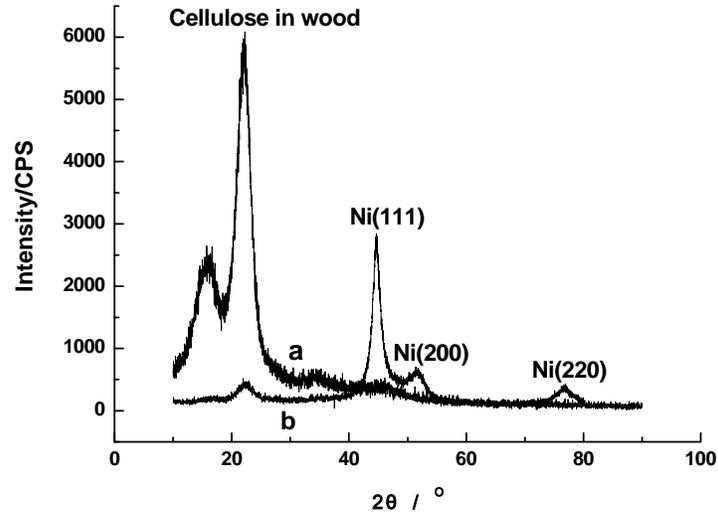
Figure. 7. XRD patterns of (a) the unplated veneer and (b) the plated veneer

Shielding Effectiveness Performance of the Nickel-Plated Wood Veneers

As shown in Fig. 8, the electromagnetic shielding effectiveness of the plated wood veneer was higher than 50 dB in frequencies from 10MHz to1.5GHz. The raw *Fraxinus mandshurica* veneer, with surface resistivity of more than 10^{10} Ω·cm^{-2}, had no shielding performance. Therefore, the plated wood veneer had a good shielding effectiveness and was judged to be suitable for use in areas of anti-EMI.
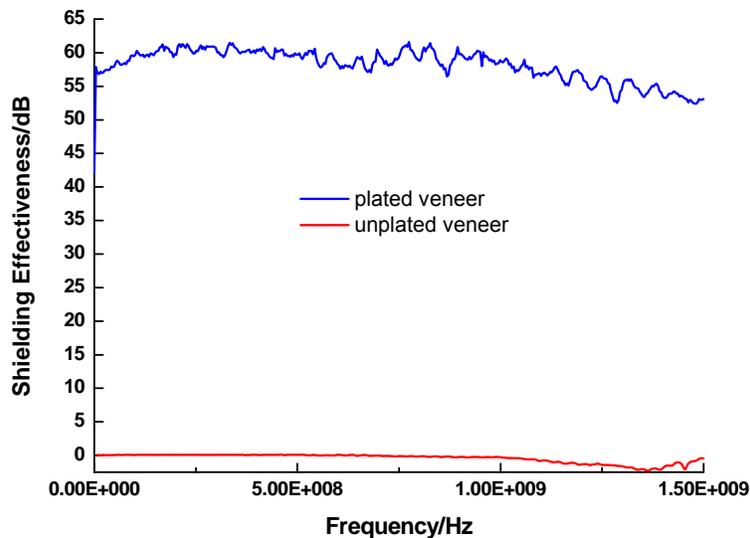
Figure. 8. Electromagnetic shielding effectiveness of the unplated and plated veneers

CONCLUSIONS

1. Electroless plating was successfully initiated, and Ni-P coating was deposited on wood veneer modified with APTHS using Pd(II) as activator.
2. Performances of metal deposition and surface resistivity of the plated *Fraxinus mandshurica* veneer pretreated in 1.5/6/92.5 APTES solution were better than those in 1.5/3/95.5 APTES solution. The surface resistivity was 0.21 $\Omega \cdot cm^{-2}$, which shows high conductivity.
3. The coating plated on the *Fraxinus mandshurica* veneers was crystalline and had a relative low phosphorus content of 2.6 wt.%.
4. The electromagnetic shielding effectiveness of the plated *Fraxinus mandshurica* veneers was higher than 50 dB in the frequency range from 10 MHz to1.5 GHz.

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REFERENCES CITED

An Y. Q., Chen M., Xue Q. J., and Liu W. M. (2007). "Preparation and self-assembly of carboxylic acid-functionalized silica," *J. Colloid Interface Sci.* 311, 507-513.

Bierbaum, K., Kinzler, M., Wöll, Ch., Grunze, M., Hähner, G., Heid, S., and Effenberger, F. (1995). "A near edge X-ray absorption fine structure spectroscopy and X-ray photoelectron spectroscopy study of the film properties of assembled monolayers of organosilanes on oxidized Si(100)," *Langmuir* 11, 512-518.

Dai, H. B., Li, H. X., and Wang, F. H. (2006). "Electroless Ni–P coating preparation of conductive mica powder by a modified activation process," *Appl. Sur. Sci.* 253, 2474-2480.

Deonath, and Rohatgi P. K. (1981). "Cast aluminium alloy composites containing copper-coated ground mica particles," *J. Mater. Sci.* 16, 1599-1606.

Garg A. K., and De Jonghe, L. C. (1993). "Metal-coated colloidal particles," *J. Mater. Sci.* 28, 3427-3432.

Harizanov, O. A., Stefchev, P. L., and Iossifova, A. (1998). "Metal coated alumina powder for metalloceramics," *Mater. Lett.* 33(5-6), 297-299.

Huang, J. T., and Zhao, G. J. (2004). "Electroless plating of wood," *J. Beijing For. Univ.* 26(3), 88-92.

Huang, Y., Shi, K., and Liao, Z. J. (2006). "The best silane coupling agent for pretreating conductive glass fiber," *J. Northwestern Polytech. Uni.* 24(5), 624-628.

Kowalczyk, D., Slomkowski, S., Chehimi Mohamed, M., and Delamar, M. (1996). "Adsorption of aminopropyltriethoxy silane on quartz: An XPS and contact angle

measurements study," *Int. J. Adhesion and Adhesives* 16, 227-232.

Li, J., Wang, L. J., and Liu, H. B. (2010). "A new process for preparing conducting wood veneers by electroless nickel plating," *Sur. Coat. Technol.* 204, 1200-1205.

Mittal, K. L. (ed.). (1992). *Silanes and Other Coupling Agents*, VSP, the Netherlands.

Nagasawa, C., and Kumagai, Y. (1989). "Electromagnetic shielding particle boards with nickel-plated wood particle," *J. Wood Sci.* 35(12), 1092-1099.

Nagasawa, C., Kumagai, Y., and Urabe, K. (1990). "Electromagnetic shielding effectiveness particleboard containing nickel-metallized wood particles in the core layer," *J. Wood Sci.* 36(7), 531-537.

Nagasawa, C., Kumagai, Y., and Urabe, K. (1991a). "Electro-conductivity and electro-magnetic shielding effectiveness of nickel-plated veneer," *J. Wood Sci.* 37(2), 158-163.

Nagasawa, C., Umehara, H., and Koshizaki, N. (1991b). "Effects of wood species on electroconductivity and electromagnetic shielding properties of electrolessly plated sliced veneer with nickel," *J. Wood Sci.* 40(10), 1092-1099.

Nagasawa, C., Kumagai, Y., Koshizaki, N., and Kanbe, T. (1992). "Changes in electromagnetic shielding properties of particle boards made of nickel-plated wood particles formed by various pre-treatment processes," *J. Wood Sci.* 38(3), 256-263.

Nagasawa, C., Kumagai, Y., Urabe, K., and Shinagawa, S. (1999). "Electromagnetic shielding particle board with nickel-plated wood particles," *J. Porous Mater.* 6(3), 247-254.

Stremsdoerfer, G., Wang, Y., Nguyen, D., Clechet, P., and Martin, J. R. (1993). "Electroless Ni as a Refractory Ohmic Contact for n-InP," *J. Electrochem. Soc.* 140(7), 2022-2028.

Sugimura, H., Hozumi, A., Kameyama, T., and Takai, O. (2002). "Organosilane self-assembled monolayers formed at the vapour/solid interface," *Surf. Interface Anal.* 34, 550-554.

Wang, L. J., Li, J., and Liu, Y. X. (2006). "Preparation of electromagnetic shielding wood-metal composite by electroless nickel plating," *Journal of Forestry Research* 17(1), 53-56.

Wang, L. J., and Li, J. (2007). "Electroless deposition of Ni-Cu-P alloy on *Fraxinus mandshurica* veneer," *Sci. Silv. Sin.*11, 89-92.

Wang, L. J., Li, J., and Liu, Y. X. (2008). "Study on preparation of electromagnetic shielding composite by electroless copper plating on *Fraxinus mandshurica* veneer," *J. Mater. Eng.* 4, 56-60.

Wagner, C. D., Riggs, W. M., Davis, L. E., Moulder, J. F., and Muilenberg, G. E. (eds.), (1978). *Handbook of X ray Photoelectron Spectroscopy*, Perkin-Elmer Corporation, Minnesota, USA.

Xu, L. N., Xu, H. F., and Zhou, Ch. K., (2002). "Study on a new activation method for initiating electroless plating on aluminum powders based on SAMs bonded palladium," *Acta phys.-chim. Sin.* 18(3), 284-288.