ELECTROLESS COPPER PLATING ON *FRAXINUS MANDSHURICA* VENEER USING GLYOXYLIC ACID AS REDUCING AGENT

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Copper coating was deposited on *Fraxinus mandshurica* veneers for preparing EMI shielding composite by electroless plating using glyoxylic acid as reducing agent in the solution. XPS and SEM were used to analyze the activation process. It was found that a continuous chitosan membrane was loaded on the wood surface. XPS results showed that Pd(II) ions were chemically adsorbed on a chitosan membrane on the wood surface through an N-Pd σ coordination bond. After reduction, part of Pd(II) absorbed formed very little Pd(0) particles on the chitosan-treated wood surface. The activated wood veneers were immersed into a plating bath in which copper film was successfully initiated. The coatings were characterized by SEM-EDS, XPS, and XRD. The metal deposition, surface resistivity, and electromagnetic shielding effectiveness were measured. The morphology of the coating was uniform, compact, and continuous. The wood grains were preserved on the plated wood veneer, which had a copper-like color and sheen. EDS, XPS, and XRD results indicated that the coating consisted of Cu^0 with crystalline structure. The surface resistivity and copper deposition reached 175.14 $m\Omega \cdot cm^{-2}$ and 21.66 g/m^2 when the veneer was pretreated with 0.8 % chitosan for 8 min and plated for 30 min at 55 ^oC. The plated veneers exhibited good electromagnetic shielding effectiveness of over 60 dB in frequency ranging from10 MHz to 1.5 GHz.

Keywords: Electroless copper plating; Fraxinus Mandshurica veneers; Pd (Ⅱ) activation; Chitosan pretreatment; Electromagnetic shielding

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INTRODUCTION

Wood-based conductive composites have received increasing attention for many years (Nagasawa et al. 1989, 1990, 1991a, 1991b, 1992, 1999; Huang et al. 2004; Wang et al. 2006 a, 2006 b, 2007; Sun et al. 2008). Electroless plating is an effective method for preparing wood-based conductive composites. Nickel has been widely used in the plating process in some areas. However, nickel has a lower electrical conductivity than copper. Copper plating on wood has been investigated by using formaldehyde as the reducing agent in the plating solution (Shang et al. 2008). In the plating process, formaldehyde can easily escape from the solution and seriously pollute the environment (Masato et al. 2005; Tang et al 2009). Subsequently, hypophosphite has been used as reducing agent in copper plating to avoid the pollution from formaldehyde. However, the copper coating obtained

using this approach was a mixture containing elemental phosphorus and it had a dark appearance (Wang et al 2008). Copper plating using glyoxylic acid as reducing agent is an environment-friendly process in which there is no toxic gas diffusion. Moreover, the coating looks like copper metal and has good conductivity.

Non-metallic materials need to be activated before electroless plating. Colloidal palladium is the commercial and essentially universal agent used in the activation process. However, the palladium colloid adheres to the surface only via weak physical absorption, which often makes some of the activator slide into the plating solution, resulting in the decomposition of the plating bath. In order to improve the controllability of the activating process, stable Pd(II) was used as activator. Wood can only absorb a very small amount of Pd(II), which is not enough to initiate the plating process. Aminosilane-modified wood was successfully activated and plated with nickel coating, because aminosilane contains a nitrogen atom with an isolated electron pair, which can chemically absorb Pd(II). However, aminosilane requires 5 to 7 hours to age before forming a membrane. Also, the process is complicated.

Chitosan is a very abundant biopolymer, and the molecule contains abundant amine groups that offer strong affinity for metal ions (Guibal et al. 2005; Renbutsu et al. 2008; Pillai et al. 2009; Rani et al. 2010). Moreover, it has the merits of non-toxicity, good film forming, and easy operation. Several researchers have utilized chitosan for pretreatment of fabric or ABS plastic in electroless nickel plating (Tang et al 2008; Yu 2011). In our laboratory, chitosan-modified wood was successfully used to deposit nickel coatings with good properties. In the present work, we developed an activation process to prepare electroless copper-plated wood veneers using chitosan pretreatment with glyoxylic acid as the reducing agent in the plating solution. In this process, a very thin chitosan membrane on the wood surface was used to chemically absorb Pd(II) via a hydrogen bond and an N–Pd σ coordination bond. The metal deposition, surface resistance, and electromagnetic shielding effectiveness of the copper-coated wood veneer were measured, and the effects of chitosan pretreatment in the activation process were also evaluated. The coating on wood veneer was characterized by scanning electron microscopy (SEM-EDAX), X-ray photo electron spectroscopy (XPS), and X-ray diffraction (XRD).

EXPERIMENTAL

Materials

The substrates used were *Fraxinus mandshurica* veneers as described previously (Liu et al. 2010). Chitosan was obtained from Jinan Haidebei Marline Bioengineering Company Limited. Palladium chloride ($PdCl_2$, >99.5 %) was obtained from Shenyang Jinke Reagent Factory. Glyoxylic acid was of industrial grade and purchased from factory. All other chemicals were of analytical grade.

Pretreatment of Wood Veneer

Fraxinus mandshurica veneers were polished with 120-mesh emery paper to remove wood dust, then, cut into samples. The shape and size of samples can be seen in

the article by Wang (2008).

The samples were immersed in a solution containing 0.8% wt/vol chitosan and 1% wt/vol acetic acid for a certain time at room temperature, then dried with hot air after being picked out of the solution and removal of the excess chitosan solution. The surface was modified with a thin chitosan membrane.

The chitosan-modified sample was dipped into a solution of palladium chloride ($PdCl_2$•$2H_2O$ 0.2g/L, HCl 15mL/L) at 40 ^oC for 7 min, rinsed, and then reduced in sodium hypophosphite solution of 2 g/L for 8 min. Thus, Pd(0) formed on the surface of chitosan-modified wood.

Electroless Copper Plating of Wood Veneer

The sample loaded with Pd(0) was put into the copper plating solution, and copper coating quickly deposited on the surface. The composition of the electroless bath and the operating conditions are listed in Table 1. Distilled water was used to prepare the solutions. NaOH was used to adjust the pH of the plating solution. After plating, the samples were carefully rinsed with distilled water and dried in an oven at around 103 ^oC to constant weight.

Table 1. Composition and Operation Conditions of Electroless Copper Plating

Chemical	Concentration(g/L)
$CuSO4•5H_2O$	20
$EDTANa_2•2\ H_2O$	40
Glyoxylic	10.5
2, 2'-dipyridyl	0.01
Potassium ferrocyanide	0.01
pH	12
T	55 ^oC

Measurement of Metal Deposition

The wood veneers were dried at 103±2 ^oC to constant weight (G_0). The copper-coated veneers were also dried to constant weight (G_1), and the metal deposition was calculated as,

$$\text{Metal deposition } (g/m^2) = (G_1 - G_0)/0.005 \quad (1)$$

where 0.005 is the total area of the sample (m^2).

Measurement of Surface Resistance and Shielding Effectiveness

The procedures used for measurement of surface resistance and shielding effectiveness was given by Li (2010).

Characterization Methods

For each step of the activation process, the surface morphology and elemental compositions of the coatings were characterized by scanning electron microscopy (SEM), using a Quanta 200 device equipped with EDAX. Specimens were directly observed without spraying gold. XPS was used for chemical state analysis of the activation process and the copper coating. XPS signals were recorded with a K-Alpha XPS Analyzer

(ThermoFisher Scientific Company) using an Al K_α source. In addition, the phase structure of the coating was investigated by X-ray diffraction (XRD, Rigaku D/max2200 diffractometer) using a Cu K_α radiation generator operated at 1200W(40 kV×30 mA).

RESULTS AND DISCUSSION

Effects of Chitosan Pretreatment

Wood can't be electrolessly plated without an activation process. However, the wood surface can't directly absorb enough Pd(Ⅱ) as activator. Here, chitosan was used as a bridge connecting with wood surface and Pd(Ⅱ). So, chitosan pretreatment is a key step for wood plating by using Pd(Ⅱ) as activator. As shown in Fig. 1, the copper deposition increased from 17.64 g/m^2 to 21.66 g/m^2 with increasing time of chitosan treatment from 2 min to 8 min. Conversely, the surface resistivity of the plated sample decreased from 180.77 mΩ/cm^2 to 175.14 mΩ/cm^2. Then, prolonging treating time didn't lead to significant changes in surface resistivity and copper deposition. As it is known, sufficient chitosan can make it absorb the necessary amount of Pd(Ⅱ), which is critical for initiating the plating process. With the increase of treating time, the amount of chitosan loaded on the wood surface increases. Saturation is reached at a treating time of about 8 min. Further prolonging the treatment time can't increase the amount of chitosan loaded. Therefore, an ideal plating effect could be achieved when the chitosan pretreatment time was 8 min.

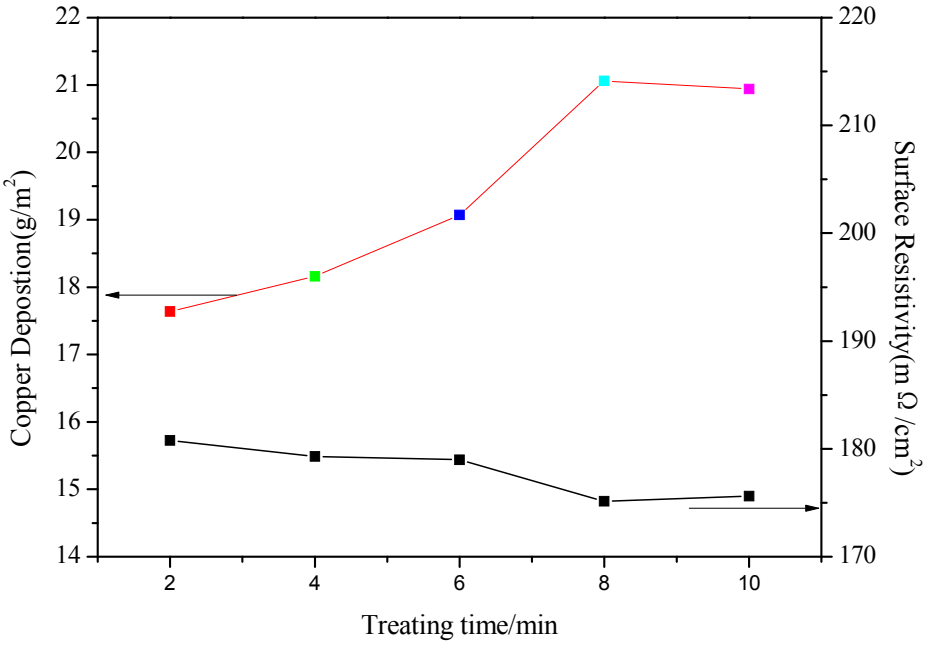

Fig. 1. The effects of chitosan treating time on the copper plating (plating time 30 min at 55 °C)

XPS and Surface Morphology Analysis of the Activation

Figure 2 shows a wide scan XPS spectrum of a chitosan-treated wood veneer. C, O, and N elements were detected. Their atomic percentages are listed in Table 2: the N element is attributed to chitosan, whereas C and O come from both wood veneer and chitosan. The peak at 398.6 eV in Fig. 3 is attributed to N1s in the amino group of chitosan on the treated wood. This indicates that chitosan was successfully loaded on the wood surface through hydrogen bonds, with the amino group oriented outwards. Moreover, part of the N1s peak shifted from 398.6 eV to 401 eV after Pd(Ⅱ) absorption, which indicates that part of the amino groups were bonded to Pd(Ⅱ) via an N-Pd σ coordination bond and some were still free. XPS spectra of Pd 3d of wood-chitosan-Pd(II) and the reduction product are shown in Fig. 4. Part of the Pd 3d peaks shifted from 341.8 eV and 336.4 eV to 340.5 eV and 335.1 eV, respectively. Peaks at 340.5 eV and 335.1 eV are close to the characteristic binding energy of Pd(0) (Lim et al 2001). It is concluded that the absorbed Pd(II) was partly reduced to Pd(0) by NaH_2PO_2.

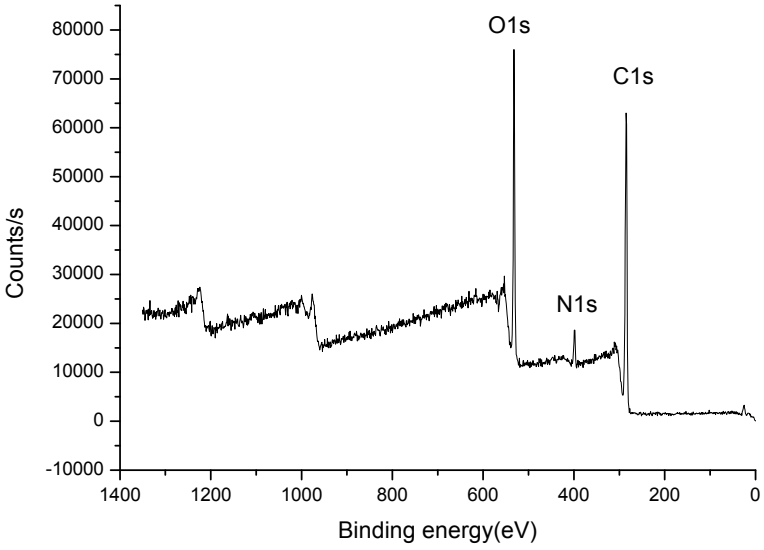

Fig. 2. XPS survey spectrum of chitosan-treated wood veneer

Table 2. Atomic Percent of Elements on Chitosan-treated Wood Veneer as Measured by XPS

Element	Content(%)
C	68.90
O	26.26
N	4.84

It can be observed in Fig.5 (a) that the wood surface was covered with a chitosan membrane. In particular, the apertures were choked up. After absorbing Pd(Ⅱ), the chitosan membrane became thinner and some of the choked apertures began to show in

Fig. 5 (b) because a small part of chitosan dissolved in acid $PdCl_2$ solution during the absorption process.

Figure 5 (c) is an SEM photograph with 60000 magnification, in which Pd(0) particle was not found. If the magnification was increased, the chitosan membrane should be ruptured under higher electric voltage. XPS results showed the existence of Pd(0). Those indicate that the Pd(0) particle from partly reduced Pd(II) is extremely small but very effective for the initiation of copper plating.

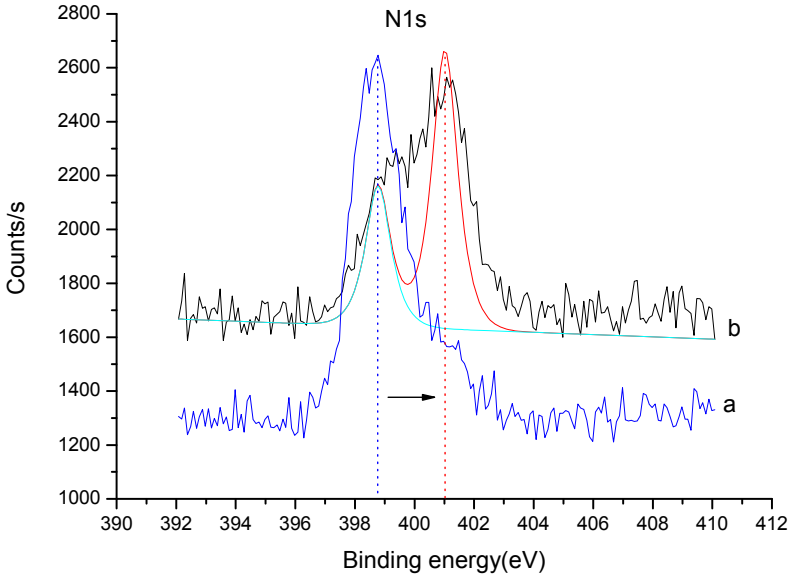

Fig. 3. XPS spectra of N1s in (a) wood-chitosan, and (b) wood-chitosan-Pd(II)

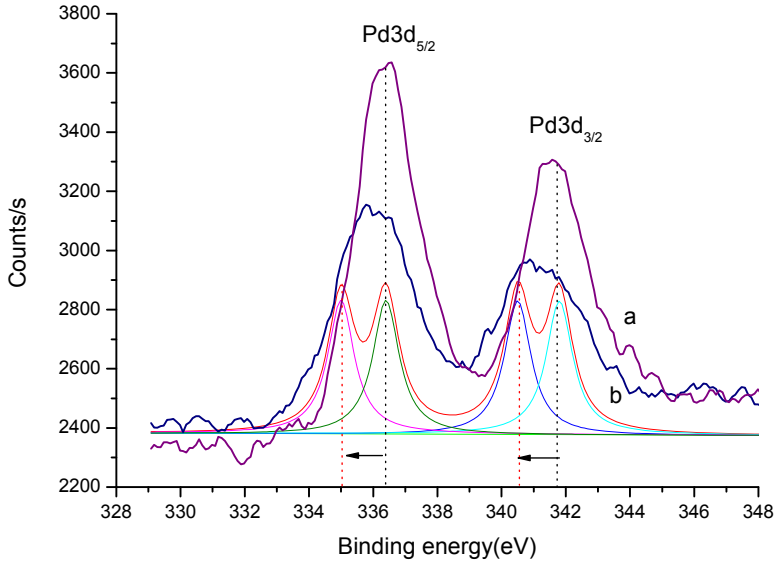

Fig. 4. XPS spectra of Pd 3d in (a) wood-chitosan-Pd(Ⅱ), and (b) reduction product of wood-chitosan-Pd(II)

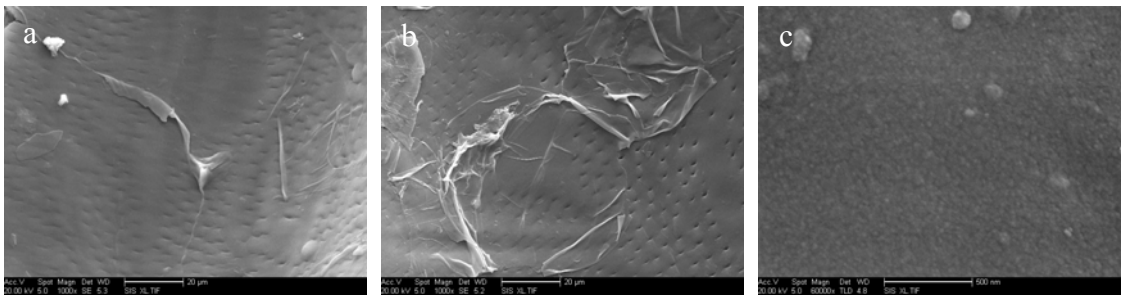

Fig. 5. Surface morphology of (a) wood-chitosan, (b) wood-chitosan-Pd(II), and (c) wood-chitosan-Pd(0)

SEM-EDAX Analysis of the Coating

It can be seen in Fig. 6 (a) that the surface was uniformly and entirely covered by the coating. Pores in the surface of plated wood veneers are still clearly apparent, especially xylem ray and vessel structures in Fig. 6 (b and c). Therefore, natural and beautiful grain had been preserved on the surface of plated wood, although the color had changed to the bright brown-red of copper metal, which endowed wood surface with a metallic sheen, as shown in Fig. 7.

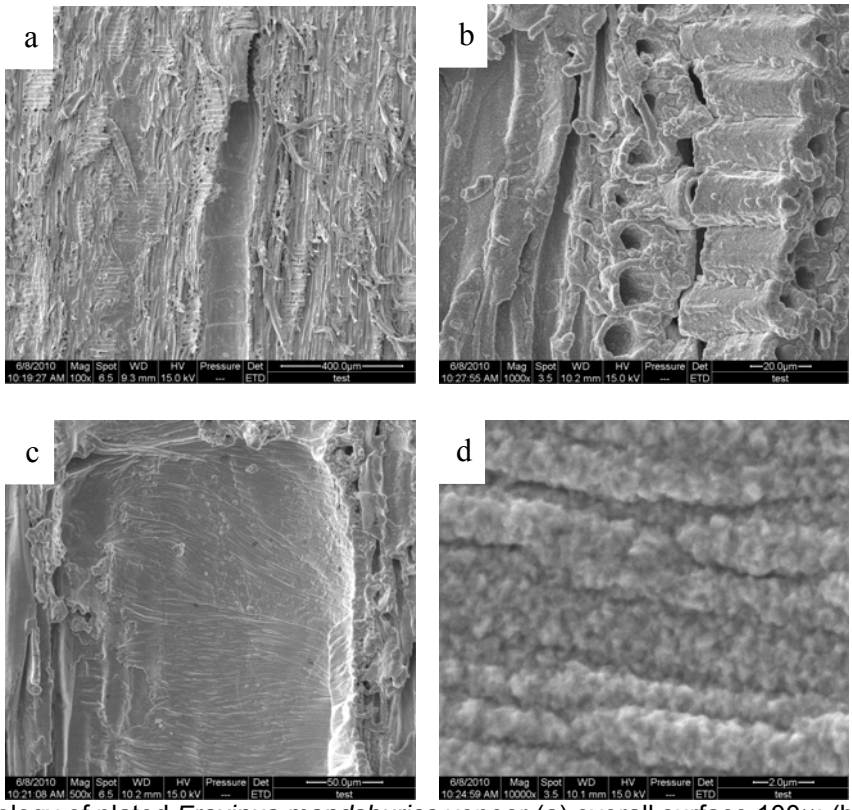

Fig. 6. Morphology of plated *Fraxinus mandshurica* veneer (a) overall surface 100×; (b) xylem ray; (c) inner wall of vessel; (d) pits with high magnification

Based on the photograph of high magnification in Fig. 6 (d), we found that the coating was composed of small cells, whose diameters were around 0.5 μm. These cells

had been deposited together compactly, and there were no clear dividing lines between them, so that the coating was extremely smooth and continuous. It was better than the coating obtained by using sodium hypophosphite as reducing agent (Wang 2008).

Fig. 7. Photo of the plated *Fraxinus mandshurica* wood

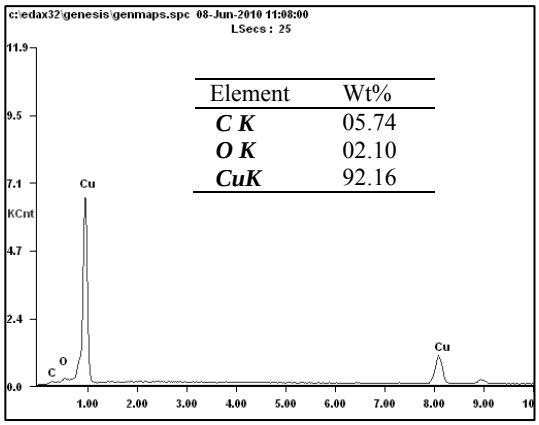

Fig. 8. EDS spectrum of the plated *Fraxinus mandshurica* veneer

Figure 8 shows the EDS results for the plated *Fraxinus mandshurica* veneer. It indicates that the coating was composed of Cu element, and little C and O. It is possible that a little contamination and oxygen were absorbed in the pores, or CuO and Cu_2O formed, which should be clearly explained by XPS analysis. N and Pd elements were not detected, which indicates X-ray did not penetrate the coating because N and Pd are at the bottom of the copper coating. Therefore, C and O are surely not from the wood surface.

XPS Analysis of the Coating

XPS analysis was employed to offer further information about the chemical state of the copper coating. A typical XPS wide spectrum of the surface of the plated veneer is shown in Fig. 9, which indicates that only copper element with some O and C was detected. The peaks at 932.08 eV, 123.08 eV, and 77.08 eV are attributed to Cu2p, Cu 3s, and Cu 3p, respectively. However, there is a shoulder peak at 934.38 eV in the XPS high-resolution scan of Cu2p (Fig. 9 A), which indicates that Cu(II) was present. In order to reveal the nature of the coating, it was etched by argon ion sputter for 30 seconds to remove the contaminant on the surface. In the XPS wide spectrum of etched surface, peaks of C and O disappeared. Furthermore, the shoulder peak at 934.38 eV in the XPS high-resolution scan of Cu2p (Fig.9 B) disappeared, too. The results indicate that Cu element in the coating existed as metallic copper (Lu 2010). Cu^{2+} had been reduced to Cu^0 in the plating process, as written below:

$$CuEDTA^{2-} + CHOCOOH + 4OH^- \rightarrow Cu\downarrow + 2C_2O_4^{2-} + 2H_2O + H_2\uparrow + EDTA^{4-}$$

The fact that O, C, and Cu(II) were detected indicates that the contaminants really were absorbed on the surface of the plated veneer (Wang et al 2002). Because plated wood veneer is still porous, it easily absorbs the components from the plating solution. On the other hand, the surface oxidization of copper coating is possible, too.

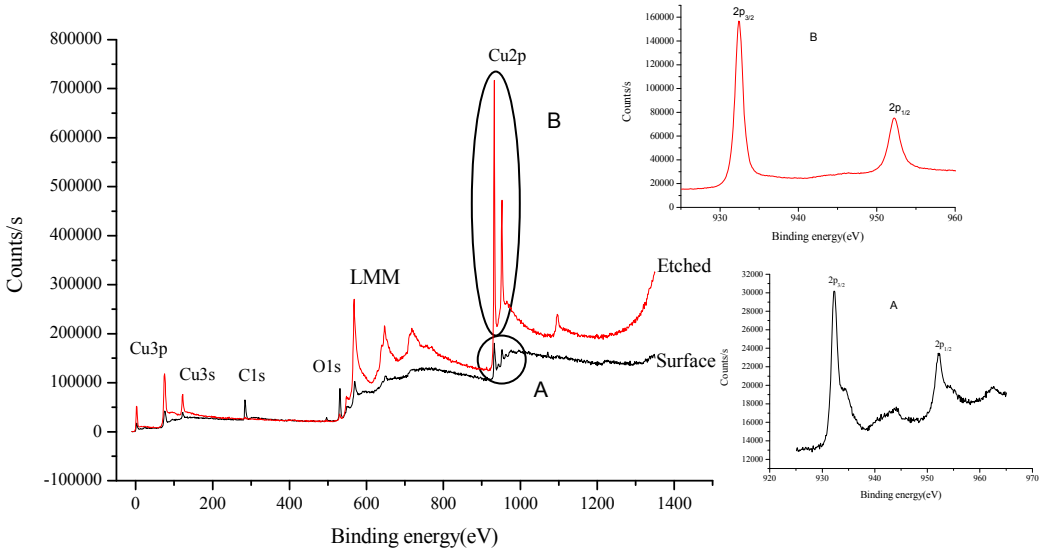

Fig. 9. XPS spectrum of copper coating on *Fraxinus mandshurica* veneer

XRD Analysis

XRD spectra for *Fraxinus mandshurica* veneer before and after plating are shown in Fig. 10. The strong diffraction peaks at 2θ= 16.11° and 22.45° are characteristic peaks of cellulose in wood. The peaks at 2θ= 43.43°, 50.55°, 74.21°, and 90.11° are attributed to Cu (111), Cu (200), Cu (220), and Cu (311), respectively, which indicates the face-centered cubic phase of copper (JCPDS: 04-0836), and the crystalline nature of the copper coating. Compared with Fig. 10 (a), the characteristic peaks of wood in Fig. 10 (b) became distinctly weaker. This result indicates that a continuous and compact coating covered the wood surface entirely. In addition, no peaks of impurity and copper oxide were present. It is indicated by XRD and XPS analysis that the coating consisted mainly of metallic copper with an extremely small amount of copper oxide.

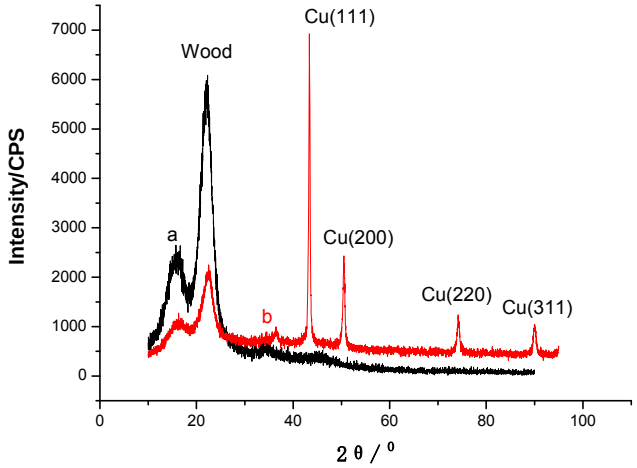

Fig. 10. XRD patterns of (a) pristine *Fraxinus mandshurica* veneer and (b) *Fraxinus mandshurica* veneer plated with copper coating

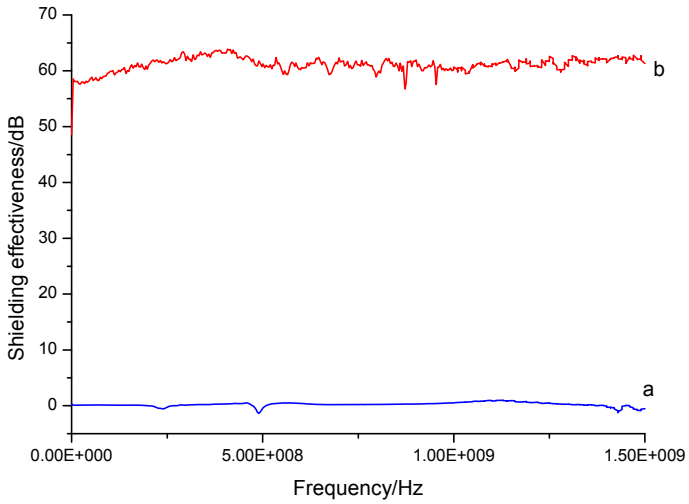

Fig. 11. Electromagnetic shielding effectiveness of *Fraxinus mandshurica* veneers (a) before and (b) after copper plating

The electromagnetic shielding results of the pristine and plated *Fraxinus mandshurica* veneer are shown in Fig. 11. The shielding effectiveness of the pristine veneer fluctuated around 0 dB; therefore, it had no shielding performance at all. The plated veneers had an average surface resistivity of 176.45 mΩ/cm^2 and shielding effectiveness higher than 60 dB in frequencies ranging from 10 MHz to1.5 GHz, which indicates the plated veneer had a better shielding effectiveness and can be utilized in some anti-EMI applications.

CONCLUSIONS

1. Copper coating was successfully deposited on *Fraxinus mandshurica* veneer modified with chitosan by using Pd^{2+} as activator and glyoxylic acid as reducing agent in plating solution.
2. The activation process including chitosan pretreatment, Pd(II) absorption, and Pd(0) formation is very important for the whole plating process. The surface resistivity and copper deposition reached 175.14 mΩ·cm^{-2} and 21.66 g/m^2 when the veneer was pretreated with 0.8 % chitosan for 8 min and plated for 30 min at 55 ^{o}C.
3. The color of the coated veneer was copper-bright. SEM analysis showed the coatings plated on the *Fraxinus mandshurica* veneers to be very smooth, continuous, compact, and also crystalline. The natural and beautiful grain could be clearly seen on the surface of plated veneers.
4. The EDS and XPS results indicate that Cu element in the coating existed as Cu^0 with some contaminants and very little copper oxide on the surface of the coating.
5. The electromagnetic shielding effectiveness of the plated veneers was higher than 60 dB in the frequency range from 10 MHz to 1.5 GHz.

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