Electromagnetic-shielding, Wood-based Material Created Using a Novel Electroless Copper Plating Process

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A copper coating was deposited on *Fraxinus mandshurica* veneers to create an EMI-shielding, wood-based material *via* a simple electroless copper plating process. The wood veneers were pretreated in a $NaBH_4$ solution. The wood veneers treated with $NaBH_4$ were immersed in a plating bath in which copper coating was successfully initiated. The coatings were characterized by SEM-EDS, XPS, and XRD. The metal deposition, surface resistivity, and the effectiveness of electromagnetic shielding were measured. The morphology of the coating was uniform, compact, and continuous. The grain of the wood was preserved on the plated wood veneer, which had a copper-like color. But the samples were less glossy compared to those from Pd activation. EDS, XPS, and XRD results indicated that the coating consisted of Cu^0 with a crystalline structure. The surface resistivity and copper deposition were 0.399 Ω/cm^2 and 31.98 g/m^2 when the veneer was pretreated with a 3 g/L $NaBH_4$ solution for 10 min and plated for 25 min at 60 °C. The plated veneers exhibited good electromagnetic shielding effectiveness of over 40 dB in frequencies ranging from 10 MHz to 1.5 GHz.

Keywords: Electroless copper plating; Fraxinus mandshurica veneers; $NaBH_4$ pretreatment; Coating characterization; Electromagnetic shielding

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INTRODUCTION

Electroless plating is the preferred technique for depositing metal coatings on various insulating substrates due to its outstanding deposition characteristics, such as simplicity of operation, uniformity on complicated shapes, and low cost. Conductive wood-based composites made *via* electroless plating have been paid greater attention in the last 20 years (Nagasawa *et al.* 1989, 1990, 1991a, 1991b, 1992, 1999; Huang and Zhao 2004; Wang *et al.* 2006a,b, 2007, 2008; Sun and Wang 2008). Insulating materials such as wood, polymers, glass, *etc.* should be catalyzed by activators prior to the plating process. Activation is the key step that introduces catalytic sites onto the surface of the substrates for initiating the electroless plating. Palladium colloid is a mixed $SnCl_2/PdCl_2$ solution used as a conventional and commercial catalyst. However, its stability is poor and it can only be absorbed on the substrate surface *via* physical interaction, which easily leads to the self-decomposition of the plating solution. Therefore, palladium ion was used as an alternative to palladium colloid. Palladium ion is very stable in solution and it is not readily adsorbed directly onto the substrate surface, which requires Pd(0) activation for the initiation of plating. Therefore, electroless plating was realized by the introduction of amino groups that can form strong complexes with palladium ions. Aminosilane and

chitosan were used to form a bridge with amino groups to connect the wood surface and palladium ions, and electroless nickel plating was successfully carried out on the modified surface (Liu and Wang 2010; Wang and Liu 2011). The biggest weakness of activation processes involving palladium is that the cost of palladium is extremely high and can significantly increase the total expenses of the plating process. Therefore, it is necessary to develop a Pd-free activation process that is feasible, low-cost, and can obtain uniform coating with good properties.

In the past few years, some attention has been focused on Pd-free activation processes. In order to avoid the use of Pd and to decrease the cost, many attempts have been made to employ Ni activation; two methods have been widely investigated. In one method, Ni^0 is produced on the substrate from absorbed Ni^{2+} by thermal treatment at high temperatures (Li *et al.* 2006; Li and An 2008; Tang *et al.* 2008, 2009; Yan *et al.* 2013); in the other, Ni^{2+} on the surface of the substrate is reduced to Ni^0 by sodium borohydride ($NaBH_4$) in two separate steps (Gao and Huang 2007). Both of these processes are relatively complicated. In our previous work, a simple process was developed to deposit nickel coating on wood surfaces to make an electro-conductive composite (Li *et al.* 2011; Wang *et al.* 2011a).

In this work, a simple electroless plating process was employed to plate copper coating on wood veneer for electromagnetic interference (EMI) shielding without $PdCl_2$-$SnCl_2$ colloid activation. In the process, wood veneers were pretreated with sodium borohydride ($NaBH_4$) and suspended in air for 1 min, then directly submersed in the copper plating solution. The activation and copper plating processes were combined and completed in one bath. It is a very simple, feasible, and low-cost method. The effects of $NaBH_4$ treating time, pH of the plating solution, and plating time on the deposition were investigated, as well as the surface resistivity. The coating on the wood veneer was characterized by scanning electron microscopy (SEM-EDAX) and X-ray diffraction (XRD), and the electromagnetic shielding performance of plated veneers was also measured.

EXPERIMENTAL

Materials

The substrates used in this study were *Fraxinus mandshurica* veneers of thickness 0.6 mm. They were polished with 120-mesh emery paper to remove fine fibers and dust. The veneers were cut into squares 5 × 5 cm in size (Wang *et al.* 2008).

Glyoxylic acid was of industrial grade and purchased from a factory. All other chemicals were of analytical grade.

Activation and Plating

Firstly, specimens were dipped in a $NaBH_4$ solution containing 5 g/L sodium hydroxide (NaOH) for a specified time at room temperature. Next, the samples were hung in the air to provide time for the $NaBH_4$ to diffuse into the pores for about 1 min. Then the specimens were put into the plating bath. The composition of the electroless bath and the operating conditions are listed in Table 1. The pH of the bath was adjusted using NaOH.

Table 1. Composition and Conditions of Electroless Copper Plating

Chemicals	Content (g/L)
$CuSO_4$•$5H_2O$	18
$NiSO_4$ • $6H_2O$	0.5
$EDTANa_2$•2 H_2O	39
Glyoxylic	8.5
2, 2'-dipyridyl	0.008
Potassium ferrocyanide	0.011
Temperature	60 °C

Surface Characterization

The surface morphology and elemental composition of the coatings were characterized by scanning electron microscopy (SEM) (Quanta 200) and an X-ray energy dispersive spectrometer (EDS). Specimens were directly observed without gold spraying. XPS was used for chemical state analysis of the copper coating. XPS signals were recorded with a K-Alpha XPS analyzer (ThermoFisher Scientific Company) using an Al K_α source. Additionally, the phase structure of the coating was clarified by X-ray diffraction (XRD, Rigaku D/max 2200 diffractometer) using Cu K_α radiation generator settings of 40 kv and 30 mA.

Measurement of Metal Deposition

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

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

where S is the surface area of the sample (m^2).

Measurement of Electrical and Magnetic Shielding Performance

The surface resistivity of the metallized wood veneers was evaluated using the designated method according to the Chinese national military standard GJB2604-96. The shielding effectiveness of the plated veneers was measured using the method outlined in Chinese industrial standard SJ20524-95. The specific measurement method and calculation formula can be seen in Wang *et al.* (2005). As shown in Fig. 1, an Angilent E4402B spectrum analyzer and a standard butt coaxial cable line with flange were used to detect the generation of incidence electromagnetic waves and the transmission of electromagnetic waves.

Fig. 1. The instrument for measuring electromagnetic shielding effectiveness

RESULTS AND DISCUSSION

Effect of $NaBH_4$ Treating Time

Wood veneers were pretreated with $NaBH_4$ alkaline solution, in which $NaBH_4$ and NaOH were loaded onto the surface of the wood veneer. When the pretreated veneer was immersed in the copper plating solution, Cu^{2+} and Ni^{2+} ions were reduced to form Cu^0 and Ni^0. Then, Ni^0 catalyzed the further plating reactions and brought about a substitution reaction with Cu(II) ions in the plating solution. In the initial stage, the deposition depends the amount of Cu^0 and Ni^0. Therefore, the $NaBH_4$ treating time is the key factor in the process. The greater the amount of $NaBH_4$ loaded on the veneer, the greater the amounts of Cu^0 and Ni^0 created.

The effects of $NaBH_4$ treating time on the deposition and surface resistivity of the plated veneers are shown in Fig. 2. Deposition increased from 29.4 g/m^2 to 33.5 g/m^2, and the surface resistivity decreased from 0.45 Ω/cm^2 to 0.24 Ω/cm^2 with an increase in treatment time from 6 min to 10 min. Any further increase of treating time led to the opposite trend because part of the $NaBH_4$ was exhausted by the reaction with some components in wood, especially under alkaline conditions.

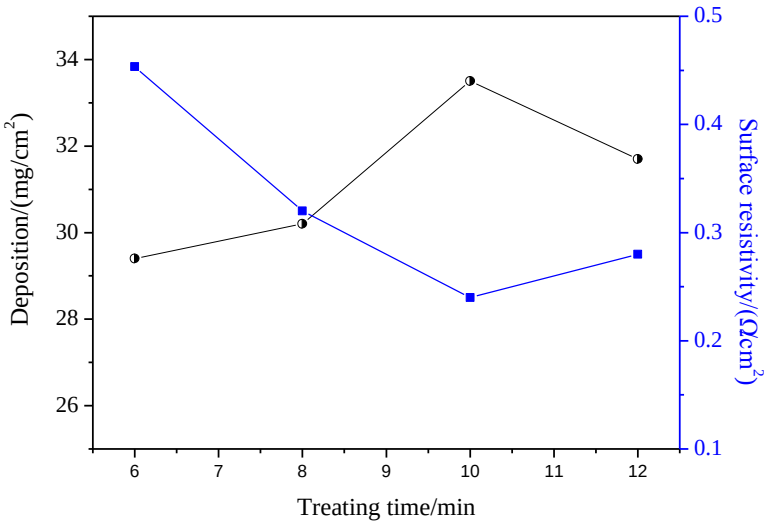

Fig. 2. The effects of $NaBH_4$ treating time on the deposition and surface resistivity of the plated veneers (pH of the plating solution 12.25, plating time 30 min)

Effect of pH of Plating Solution

The pH of the plating solution played an important role in the coating deposition. The effect of the pH value on copper deposition is shown in Fig. 3. The deposition increased from 20.8 g/m^2 to 34.8 g/m^2, and the surface resistivity decreased from 1.99 Ω/cm^2 to 0.08 Ω/cm^2 with an increase of pH from 11.75 to 12.25. Above a pH value of 12.25, the deposition decreased and the surface resistivity increased. The oxidation-reduction reaction between Cu^{2+} ions and glyoxylic acid required alkaline conditions. The initial increase of the deposition to 12.25 was due to the effect of OH^- ions as reactants in the total reaction, as represented by Eq. 2:

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

The decrease in the deposition at pH values over 12.25 was attributed to the consumption of glyoxylic acid by the diproportionation reaction shown in Eq. 3.

$$2CHOCOOH + 2OH^- \rightarrow 2C_2O_4^{2-} + H_2O + 2\,HOCH_2COOH \quad (3)$$

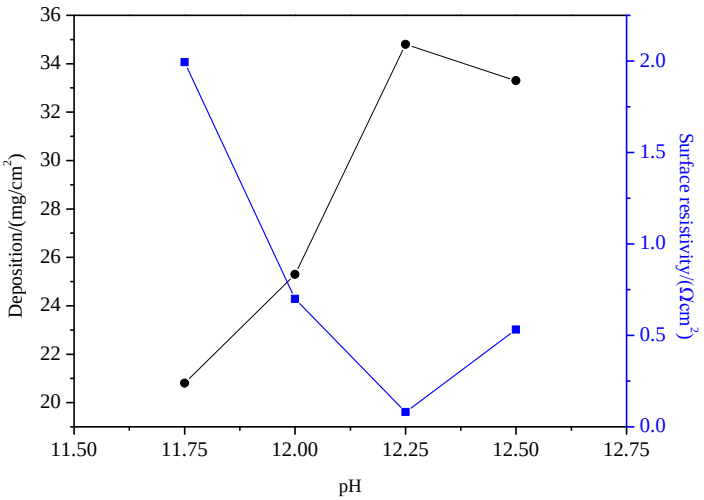

Fig. 3. The relationship between the pH of the plating solution and the deposition and surface resistivity of the plated veneers

Effects of Plating Time

It is well known that the plating time is a key factor in deposition by electroless plating at a constant bath temperature. During the plating stage, more of the Cu^{2+} in the bath can be reduced to Cu and deposited on the substrate if the time is increased. Figure 4 shows the effect of plating time on metal deposition and surface resistivity from pretreatment in 2 g/L and 3 g/L of $NaBH_4$.

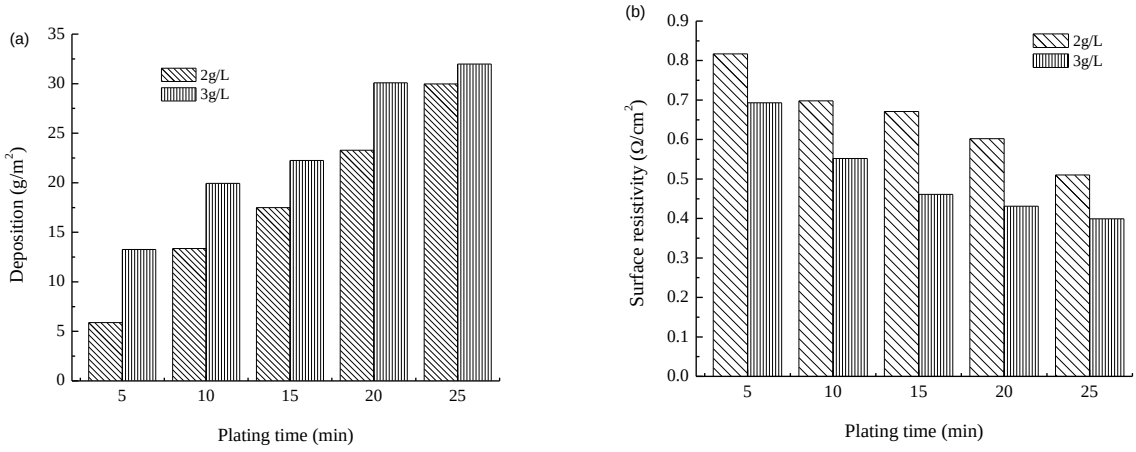

Fig. 4. The effects of plating time on (a) the deposition and (b) surface resistivity of the plated veneers

It can be seen in Fig. 4 that the metal deposition increased with plating time. From plating times of 5 min to 20 min, the deposition gradually increased from 13.26 g/m^2 to 30.09 g/m^2 and the surface resistivity accordingly decreased from 0.693 Ω/cm^2 to 0.399 Ω/cm^2 after pretreatment in 3 g/L of $NaBH_4$. Any further increase of plating time led to only small changes in deposition and surface resistivity. However, the deposition after pretreatment in 2 g/L of $NaBH_4$ increased from 5.89 g/m^2 to 29.97 g/m^2, and the surface resistivity accordingly decreased from 0.817 Ω/cm^2 to 0.510 Ω/cm^2 from 5 min to 25 min. It was found that the deposition from pretreatment in 3 g/L of $NaBH_4$ was higher than pretreatment in 2 g/L of $NaBH_4$. The veneers pretreated in solutions of higher concentration could load more $NaBH_4$, which reduced more Cu^{2+} and Ni^{2+} ions to Cu^0 and Ni^0 in the initial plating stage. More Cu^0 and Ni^0 catalyzed and accelerated the subsequent plating process. Therefore, pretreatment in 3 g/L of $NaBH_4$ gave better plating results.

SEM-EDS Analysis

It can be seen in Fig. 5(a) that the surface was compactly and entirely covered by the coating.

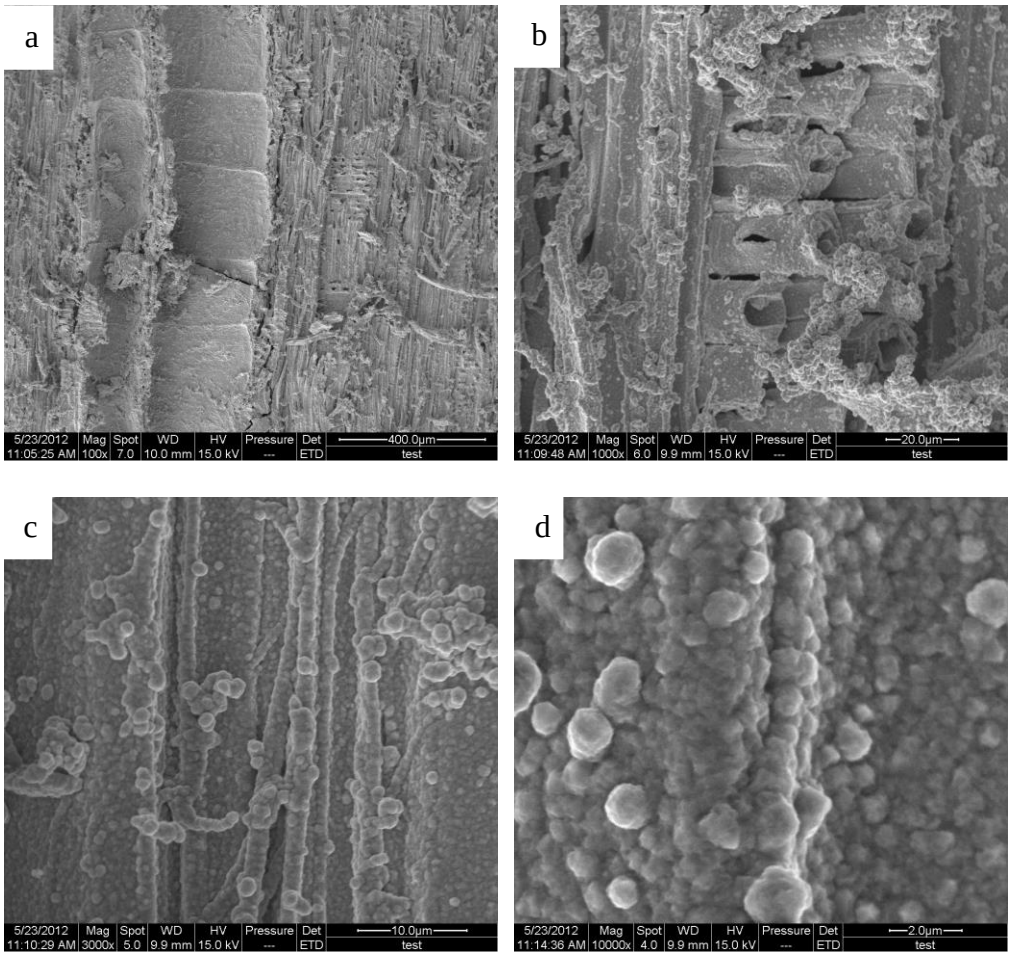

Fig. 5. Morphology of plated *Fraxinus mandshurica* veneers (a) overall surface 100×; (b) xylem ray; (c) inner wall of vessel; (d) pits with high magnification

Pores in the surface of the plated wood veneers can still be clearly observed in Fig. 5(b, c), especially xylem ray and vessel structures. Therefore, the natural grain was preserved on the surface of plated wood, although the color changed to the brown-red of copper metal, which endowed the wood's surface with a metallic feeling, as shown in Fig. 6. Based on the photograph at high magnification in Fig. 5(d), it was found that the coating was composed of small cells, whose diameters were around 0.7 to 1.0 μm. These cells were deposited compactly so that the coating was smooth and continuous. However, the metallic luster was not as bright as the coating obtained using the copper plating process based on Pd activation (Wang *et al.* 2011b).

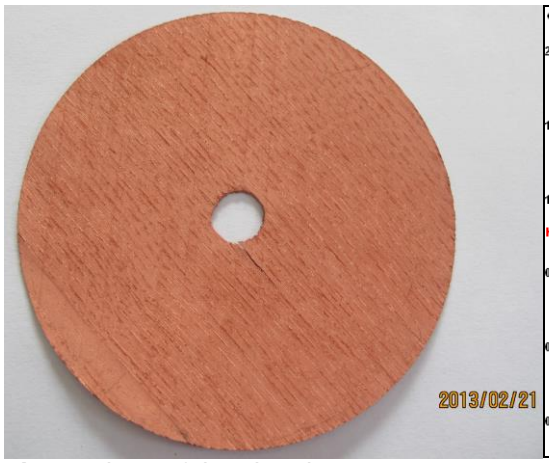

Fig. 6. Photo of the plated veneer

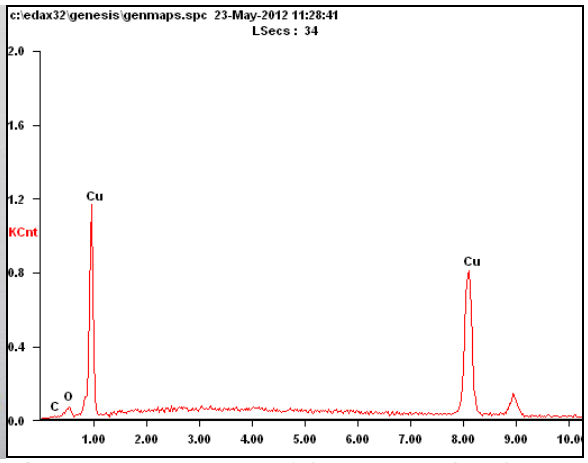

Fig. 7. EDS spectrum of the copper-plated veneer

Figure 7 shows the EDS results for plated *Fraxinus mandshurica* veneer. The spectrum indicates that the coating was composed of Cu and a little C and O. It is possible that some contamination and oxygen were absorbed in the pores, or CuO and Cu_2O were formed, which should be clearly explained by XPS analysis. Nickel was not detected, which indicated that no Ni deposition occurred. This circumstance can be attributed to the substitution reaction with Cu^{2+} ions in the plating solution. The following elemental percentages were determined from the analysis: Cu: 95.8%; C: 2.4%; O: 1.8%.

XPS Analysis of the Coating

XPS analysis was used to provide 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. 8, which indicates that only copper and some O and C were detected. The peaks at 932.28 eV, 123.08 eV, and 76.08 eV were attributed to Cu2p, Cu3s, and Cu3p, respectively. In order to reveal the nature of the coating, it was etched by argon ion sputter for 30 seconds to remove contaminants on the surface. In the XPS wide spectrum of the etched surface, the peaks of C and O disappeared. Moreover, there were two shoulder peaks at 934.06 eV and 954.04 eV in the XPS high-resolution scan of Cu2p (Fig. 9a), which indicated that some Cu(II) was still present. Furthermore, the shoulder peaks at 934.06 eV and 954.04 eV in the XPS high-resolution scan of $Cu2p_{3/2}$ and $Cu2p_{1/2}$ (Fig. 9b) also disappeared. The results indicated that Cu in the coating existed as metallic copper (Lu 2010). Cu(II) had been reduced to Cu^0 in the plating process. In fact, O, C, and Cu(II) were detected, which indicated either that there were contaminants from the plating solution or that surface oxidization had taken place on the copper coating.

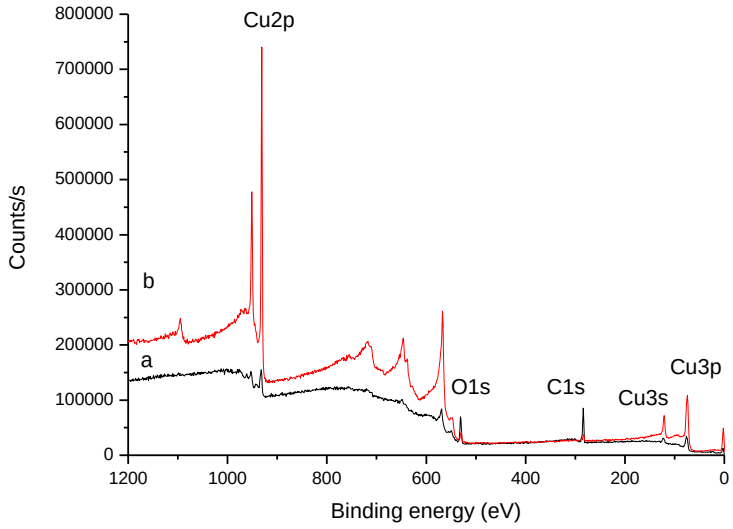

Fig. 8. XPS spectrum of copper coating on *Fraxinus mandshurica* veneer (a) surface and (b) etched

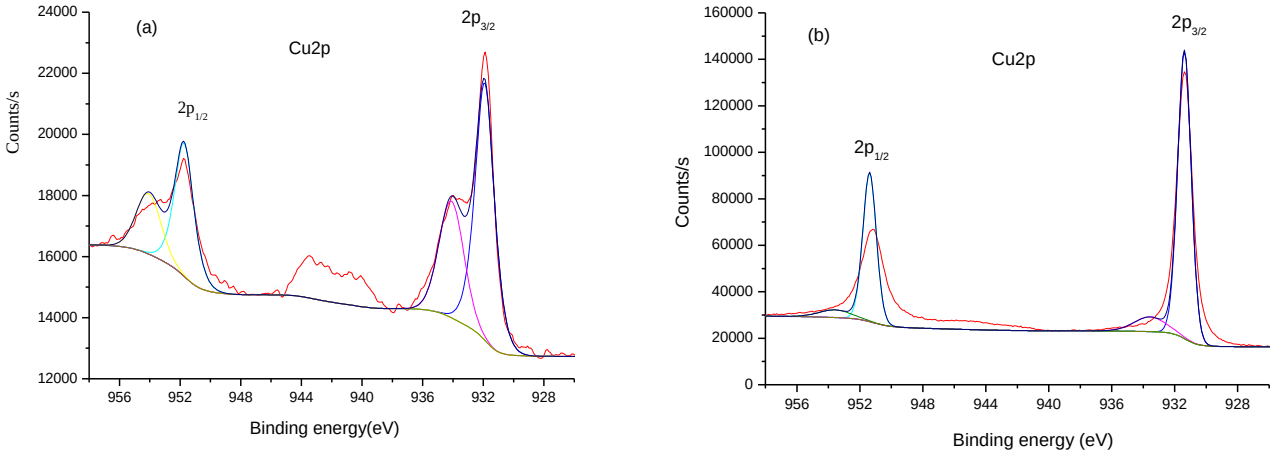

Fig. 9. High-resolution XPS spectra of Cu2p of the coating (a) surface and (b) etched

XRD Analysis

The 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 *Fraxinus mandshurica* veneer. The peaks at 2θ = 43.08°, 50.12°, 74.04°, and 89.76° were attributed to Cu (111), Cu (200), Cu (220), and Cu (311), respectively, which is indicative of 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 cellulose in wood in Fig. 10(b) were obviously weaker. These results indicated that the wood surface was entirely covered with a continuous and compact coating. In addition, no peaks from impurities or copper oxide occurred. XRD and XPS analyses indicated that either none or an extremely small amount of copper oxide was mixed in the coating.

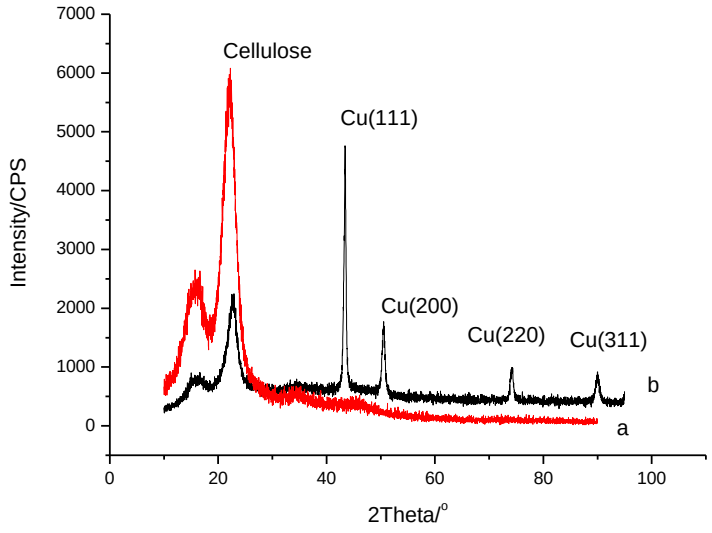

Fig. 10. XRD patterns of *Fraxinus mandshurica* veneer (a) before and (b) after being plated with copper coating

Electromagnetic Shielding Performance

The electromagnetic shielding results for the pristine and for the plated *Fraxinus mandshurica* veneers 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 deposition of 31.98 g/m^2, surface resistivity of 0.399 Ω/cm^2 and shielding effectiveness higher than 40 dB for frequencies ranging from 10 MHz to 1.5 GHz. The copper-plated veneer had shielding effectiveness and could be utilized in some anti-EMI applications. In comparison with Pd activation, the performance of the plated veneers from this simple method was a bit weak (Wang *et al.* 2011b).

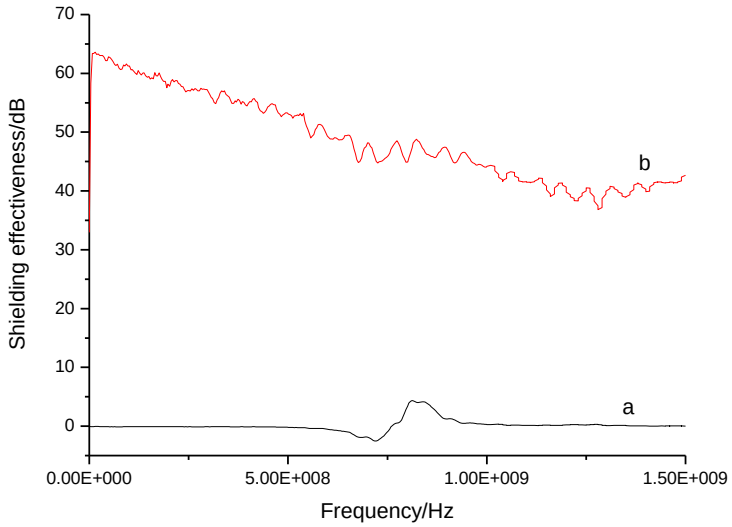

Fig. 11. Electromagnetic shielding effectiveness of *Fraxinus mandshurica* veneers (a) before and (b) after copper plating

CONCLUSIONS

1. Copper coating was successfully deposited on *Fraxinus mandshurica* veneers using a simple electroless copper plating process.
2. The wood veneers were pretreated in $NaBH_4$ solution. Pretreatment in 3 g/L $NaBH_4$ solution for 10 min at room temperature resulted in a good coating. The optimal pH value of the plating solution was 12.25.
3. The hue of the coated veneer is that of freshly polished copper. But relative to brightness, the coated veneer is darker. SEM observation and XRD analysis showed that the coatings plated on the *Fraxinus mandshurica* veneers were continuous, compact, and crystalline. The naturally beautiful grain can be clearly seen on the surface of plated veneers.
4. The EDS and XPS results indicated that copper in the coating existed as Cu^0 with some contaminants on the surface of the coatings.
5. The electromagnetic shielding effectiveness of the plated veneers was higher than 40 dB in the frequency range from 10 MHz to 1.5 GHz.
6. The performance of the plated veneers from this simple process was a little weak in comparison with those from the process based on Pd activation.

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