Wood Functional Modification Based on Deposition of Nanometer Copper Film by Magnetron Sputtering

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Abstract

It can be helpful for selected applications to improve the functionality of wood by compounding nano-metal materials with wood, endowing the wood surface with certain physical properties, for example, metallicity, electrical conductivity, and hydrophobicity. Therefore, in this study, a thin copper film was deposited on the surface of *Pinus sylvestris* L. var. *mongholica* Litv. veneer by magnetron sputtering. The film was applied at both room temperature and 200°C to obtain nano-copper–wood composites. The physical properties of wood-based nano-metal composites were characterized. The results indicated that the wood veneer metallization had no effect on the crystallization zone of wood; there were still wood cellulose characteristic peaks, but the intensity of the diffraction peak decreased. At the same time, there were characteristic diffraction peaks of copper. The mechanical properties of the wood veneer surface changed greatly; the surface of copper-plated wood veneer had good electrical conductivity and the wettability of the wood surface transformed from hydrophilic to hydrophobic. When the base temperature was 200°C, not only was the sheet resistance of the sample with coating time of 15 minutes about 4.6 times that of the sheet resistance of the sample at room temperature, but also the quality of the copper film on the wood surface was better than that at room temperature. The copper film was mainly composed of small particles with a compact arrangement.

Wood is a natural organic polymeric material, which is a poor electrical conductor and strongly hydrophilic. There are performance problems with wood such as low density, low strength, easy deformation, cracking, decaying, and burning (Li et al. 1995, Wang et al. 2015a). Development and evaluation of a wood–metal composite material has been an evolving area of research in recent years; such a composite can endow wood with metallic properties, changing the physical properties of the wood surface to result in functional improvements. These improvements can result in the expansion of wood applications with the associated added value (Li et al. 1995, Qin et al. 2014). In recent years, the electrolysis plating method has been used to develop a wood composite through the modification of the wood surface. Physical properties such as electrical conductivity, shielding properties, wettability, and weatherability of the wood surface have been studied for these modified materials (Nagasawa et al. 1994, Huang and Zhao 2004, Jia et al. 2011, Qin et al. 2014, Wang et al. 2015b). Based on the mature electroless plating method, multifunctional inorganic nano-composite films with various modifications have also been studied. Some researchers have prepared a hydrophilic antibacterial polyvinylidene fluoride separation membrane by using a new method of polyacrylic acid radiation grafting combined with electroless nickel plating (Shen et al. 2019). However, there are some problems with the electroless plating of wood. First, the method of preparing thin films by electroless plating is a liquid-phase method. It is necessary for the wood substrate to be plated in the plating solution, and the wood surface coating can only be formed after a chemical reaction, which also causes serious damage to the aesthetic and functionality of wood. In addition, the coating conditions, such as the stability of electroless plating solution, the ratio of components in the electroless plating solution, and reaction temperature and time are very demanding, all of which increase the difficulty of obtaining an ideal compact uniform electroless plating (Sun 2013). The method of electroless plating also results in other problems in that the film surface is not smooth, the metal coating on the surface is not dense and is uneven, the coating sheds easily, and the bonding condition between the

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coating and the substrate is poor. Most importantly, there are many process options for the electroless plating of wood, and a large number of chemical agents are used, so a large amount of wastewater and exhaust gas would be produced in an industrial production, which can result in serious harm to the human body and the environment (Xu et al. 2006). More environmentally friendly methods are being used to deposit inorganic nano-film on the wood surface. Currently, the dielectric barrier discharge plasma pretreatment method is being used in some studies to improve the wettability of lignocellulosic raw materials. In research, other scholars used a cold plasma method to spray the zinc–zinc oxide coating on the wood surface to improve the ultraviolet light protection, and also obtained good results (Wallenhorst et al. 2018, Žigon et al. 2018). Wood coatings can also be prepared using polyvinyl acetate–silicone dioxide-based electrospun nanofibers to improve adhesion and scratch resistance, or octadecyltrichlorosilane can be used to effectively improve the dimensional stability, hydrophobicity, and antibacterial properties (Kumar et al. 2016, 2017). Therefore, the pollution-free modification method and the multifunctional composite modification with films are two of the important directions of wood modification.

Magnetron sputtering is a physical vapor deposition. The films prepared by magnetron sputtering are uniform, dense, and consistent. Moreover, the thin films prepared by magnetron sputtering do not easily detach because of the strong adhesion between the films and the substrate. At the same time, this method does not result in pollutants such as waste gas and wastewater. Therefore, the magnetron sputtering method has been widely used in the preparation of various nano-material films (Peng et al. 2014). Magnetron sputtering coating has also gradually begun to be used in wood modification. In the early efforts, some researchers used magnetron sputtering to prepare metallized films on the surface of plywood to study the weather resistance and electromagnetic shielding effect of metallized films. More recently it has been possible to deposit a copper film by magnetron sputtering to prepare wood that has superhydrophobic properties (Chang et al. 2007, Bao et al. 2019). We have used magnetron sputtering to deposit copper films on the surface of wood to investigate the effect of sputtering time on the metallization structure and mechanical properties of wood veneers (Li et al. 2018). In the process of magnetron sputtering coating, the growth of the film on the wood surface is affected by the motion state and growth environment of the sputtering particles. Enhanced physical properties of the metal–wood composites can be obtained by changing the technological parameters, such as target–substrate distance, substrate temperature, sputtering pressure, sputtering power, and basic pressure. It is important to explore the optimum technological parameters of magnetron sputtering to maximize the metal film on the wood surface. Currently there is little research on metallization of wood veneers, and its application in the field of wood modification is immature. *Pinus sylvestris* L. var. *mongholica* Litv. has been used as the substrate veneer, the surface of which was treated with melamine-formaldehyde resin (MF2; Chang et al. 2016). The copper film was deposited on the surface of the *Pinus* veneer by magnetron sputtering to obtain the nano-copper–wood composite in order to achieve various functional improvements in hydrophobic and mechanical properties and, simultaneously, conductivity of the wood surface. This enables the wood modification to overcome the limitation of a single modification, further providing a basis for the research and application of wood-based nano-metal composites, as well as providing some experimental basis for improving the overall properties and performance of wood.

Materials and Methods

The experimental materials

The samples were five side-by-side 15 by 15 by 0.5-mm (longitudinal by tangential by radial) veneer samples taken from a large veneer sample processed from the *Pinus sylvestris* L. var. *mongholica* Litv. core, one of which was the original wood as the control sample and the other four veneers that served as experimental samples. Wood veneers were taken from ovendried wood.

Other materials included 99.99 percent copper target, KH-560 silane coupling agent, MF2, acetone, anhydrous ethanol, distilled water, and metallographic abrasive paper.

Pretreatment of wood veneer

We polished off a thin layer of the wood veneer sample surface with coarse-to-fine metallographic sandpaper (400, 600, 800, 1,500, and 2,000 mesh) and cleaned the sawdust on the surface of the wood veneers in order to make it smooth enough to provide the initial conditions for magnetron sputtering.

We stirred and dissolved the MF2 sealant solution (50% MF2 added first, then 1% KH-560 silane coupling agent added to the solution) to form a uniform milky paste liquid.

We evenly coated the MF2 sealant solution on the polished wood veneer and let it dry naturally.

Preparation of wood-based nano-metal composites

The preparation of a copper film for the wood veneer surface was performed on a JGP450 multitarget magnetron sputtering device. The sputtering material was copper target (purity of 99.99%), which was placed on the direct current sputtering cathode. The substrate was the pretreated wood veneer, which was installed on a sample rack in a vacuum chamber. When the vacuum of the background reached 8.0 by 10^{-4} Pa, argon was injected into the chamber, with the argon gas flow fixed at 20 cm^3/min in standard conditions. The sputtering pressure and power were 5.0 Pa and 100 W, respectively. The coating times were 10 and 15 minutes, respectively. A thin layer of copper was deposited on the surface of wood veneer by magnetron sputtering at room temperature and at 200°C. Experiments were replicated five times, with five samples used in each of the replications. The wood veneer that was copper-plated by magnetron sputtering at different substrate temperatures is shown in Figure 1.

Characterization of physical properties of wood-based nano-metal composites

The wood-based nano-metal composite was characterized by a LabXRD-6100 X-ray diffractometer manufactured by Shimadzu Corporation, and the crystallinity of wood cellulose was calculated by the method developed and described by Segal et al. (Segal et al. 1959, Mwaikambo and Ansell 2002, Jiang et al. 2004, Lv and Zhao 2007). The mechanical properties of the copper-plated wood veneer

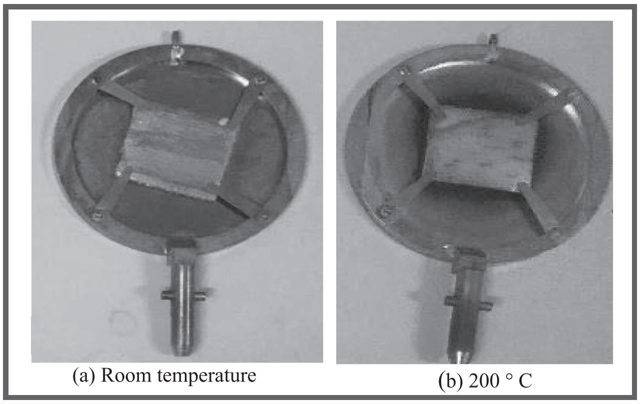


Figure 1.—Wood veneer copper-plated by magnetron sputtering at different substrate temperatures.

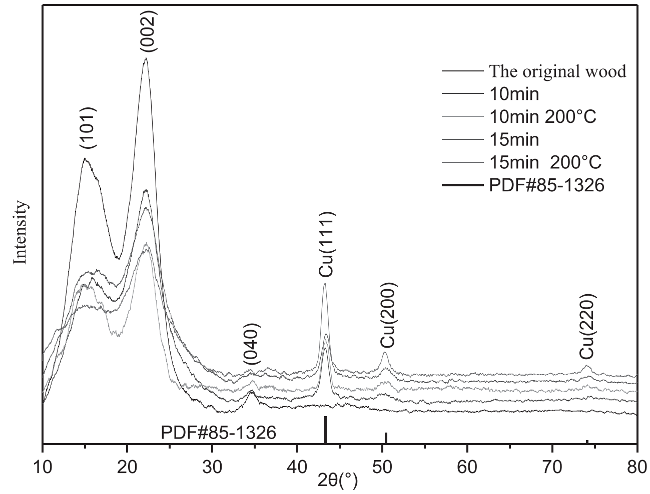


Figure 2.—X-ray diffraction pattern of wood veneer copper-plated by magnetron sputtering.

were characterized by a Nano Indentert-XP nano indenter manufactured by MTS. The mode of loading and unloading was set to a quasi-static constant rate, with a maximum load of 0.5 mN, loading time of 5 seconds, resistance time of 1 second, and Poisson ratio of 0.18. During the test, five points were selected per sample for indentation. We determined elastic modulus and hardness of the nano-indentation using the O&P method (Oliver and Pharr 1992). The testing procedure was completed by computer control. The sheet resistance of the wood veneer surface was measured by the HPS2523 film-coated block resistor tester. Six test points were randomly selected for each sample, of which three points were along the grain and three points across the grain, and the square resistance value of copper-plated wood veneer was thus obtained from the average value. The water contact angle of the surface of the copper-plated wood veneer was measured by a DSA-100S contact-angle measuring instrument produced by Krüss. Three different positions of the sample surface were randomly selected for each measurement, and a single test was completed within 3 seconds. The results were averaged and recorded. The functional group of the copper-plated wood veneer was analyzed by the Thermo Scientific Nicolet iS10 Fourier-transform infrared (FTIR) spectrometer. The instrument was equipped with a multifunctional attenuated total reflection sampling accessory. The acquisition range was set to 500~4,000 cm^{-1}, and the resolution was set to 4 cm^{-1}. The number of sampling times was set to 32, and automatic air suppression was set to remove the influence of the absorption peak caused by carbon dioxide and water in the air. The fluorescent effect of copper-plated wood veneer was characterized by a DXM1200F fluorescence microscope produced by Nikon Corporation. The surface morphology of wood veneer was characterized by a JSM-7500F cold field emission scanning electron microscope.

Results and Analysis

Analysis of wood veneer metallization structure with X-ray diffraction

The X-ray diffraction pattern of wood veneer copper-plated by magnetron sputtering is shown in Figure 2. There are characteristic peaks of three crystal faces (101, 002, and 040) of cellulose in wood. The metallization of wood veneers by magnetron sputtering does not affect the crystallization zone of wood, and the crystal structure of wood cellulose was not damaged. However, the intensity of the characteristic peaks of the three crystalline surfaces was weakened. The relative intensity of the peak of the 002 plane mainly affected the crystallinity of the wood that decreased most with the sputtering time, of which the intensity of the diffraction peak of the sample sputtered at 200°C decreased most. One reason for the decrease was that the depth of X-ray radiation decreased as a function of the growth of copper film on the surface of the wood veneer. Another reason was the absorption and reflection of wood diffraction lines by the copper film, which also resulted in the decrease of the characteristic peak strength of wood cellulose (Nikulin et al. 2000, Xu et al. 2007). In addition, the growth of copper film on the surface of wood veneer reduced the crystallinity of cellulose, and the substrate temperature also affected the quality of the film forming on the wood surface, which further influenced the crystallinity of the wood cellulose. The crystallinity of wood is defined as the weight fraction of crystalline material—crystalline cellulose—in wood (Andersson et al. 2003). In most cases, the cellulose molecular chains of the wood crystalline region were arranged tightly and orderly, and as a result the sealing agent and sputtering of copper atoms could enter the crystalline region. However, the structure in the amorphous zone was loose. Some of the copper atoms of the sealing agent and sputtering entered into the nano-void of the wood and infiltrated the amorphous area of the wood cell wall during the coating treatment. With the increase in thickness of the copper film, the quality of the amorphous area increased and the crystallinity of the wood cellulose decreased (Lv and Zhao 2007). In addition, when heated to 200°C, the crystallinity of cellulose decreased. This may be due to the deacetylation of hemicellulose to form acetic acid, as acetic acid causes partial acid hydrolysis of cellulose at high temperatures, destroying the structure of cellulose. This results in a decrease in the degree of polymerization of cellulose and thus a decrease in crystallinity (Sun and Li 2010).

As can be seen from Figure 2, there were diffraction peaks of Cu (111), Cu (200), and Cu (220) crystal planes of copper near 43.3°, 50.4°, and 74.1°. The intensity of the diffraction peak of the Cu (111) crystal plane of the copper film deposited on the wood veneer surface varied most, indicating that the growth of copper film on the wood surface had a preferred orientation of Cu (111) crystal plane. The structure of metallic copper represents the face-centered cubic lattice structure type. Since the Cu (111) crystal plane has a larger atomic plane density among the three crystal planes of the copper thin film, the surface energy of the crystal plane will be relatively small, which is beneficial to the growth of the Cu (111) crystal plane. The characteristic diffraction peak intensity and shape of the sample were higher and sharper at the substrate temperature of 200°C for both sputtering times (10 and 15 min). This suggests that when the substrate temperature is 200°C, the crystal cell orientation and grain arrangement of copper film deposited on the wood surface are better than at room temperature. At the same time, the copper film also has a better crystalline state than at the room-temperature state.

Load-pressing depth curve from nano-indentation

The load-compaction depth curve of copper-plated wood veneer is shown in Figure 3. During the loading process, elastic deformation and plastic deformation occurred, resulting in a nonlinear loading curve. The unloading curve reflects the elastic recovery process of the sample. The whole process consists of loading, holding, and unloading phases. Figure 3 shows that the load-compression depth curve of the copper film deposited on the wood veneer surface significantly shifted to the left. In the quasi-static constant rate mode of loading and unloading, the maximum load was 0.5 mN, and the loading time was 5 seconds. The loading displacement of the original wood was 684 nm. At room temperature, the load displacement of samples was 126.9 and 107.7 nm for samples with coating times of 10 and 15 minutes, respectively. When sputtering occurred at 200°C, the load displacement of samples was 112.2 and 101.9 nm for coating times of 10 and 15 minutes, respectively. The load displacement of the wood veneer copper-plated by magnetron sputtering decreased by more than 80 percent, indicating that the copper film deposited on the wood veneer surface had a great influence on the load-pressing depth. However, different substrate temperatures had little influence on the load displacement of sputtered samples.

Modulus of elasticity and hardness

Elastic modulus and hardness are important material properties. The magnitude of elastic modulus reflects the resistance to elastic deformation. The elastic modulus and hardness of the copper-plated wood veneer are shown in Figure 4. The average elastic modulus of the original wood was 0.57 GPa and the average hardness was 0.048 GPa. For sputtering at room temperature, the average elastic modulus for a coating time of 10 minutes was 11.69 GPa, an increase of 19.5 times over original wood. The average hardness was 0.667 GPa, an increase of 12.9 times over original wood. The average elastic modulus for the 15-minute coating time was 14.26 GPa, an increase of 24.1 times, and the average hardness was 0.879 GPa, an increase of 17.3 times. For sputtering at 200°C, the average elastic modulus for a 10-minute coating time was 13.16 GPa, an increase of 22.1 times, and the average hardness was 0.834 GPa, an increase of 16.4 times. The average elastic modulus for a 15-minute coating time was 15.52 GPa, an increase of 26.4 times, and the average hardness was 0.902 GPa, an increase of 18.4 times. These results indicated that the growth of the copper film on the surface of the wood veneer can increase the modulus of elasticity and hardness of the wood veneer, and that the mechanical properties such as the modulus of elasticity and hardness were better on samples processed at 200°C compared with those processed at room temperature. The elastic modulus and hardness of metallic copper were 210 times and 44 times greater than those of wood. Depositing a copper film on the surface of the wood veneer increased the elastic modulus and hardness of the wood surface and improved the mechanical properties of the wood surface. In addition, as the substrate temperature increased, the interface diffusion also increased. The deposited film was better, and the surface elastic modulus and hardness were also slightly increased.

Sheet resistance of wood-based nano-metal composites

The sheet resistance of the wood veneer surface was determined by the four-probe method. Table 1 shows the sheet resistance of the copper-plated wood veneer. The original wood is a natural organic polymer material, which is a poor conductor of electricity. No sheet resistance was detected on the original wood veneer surface. When the

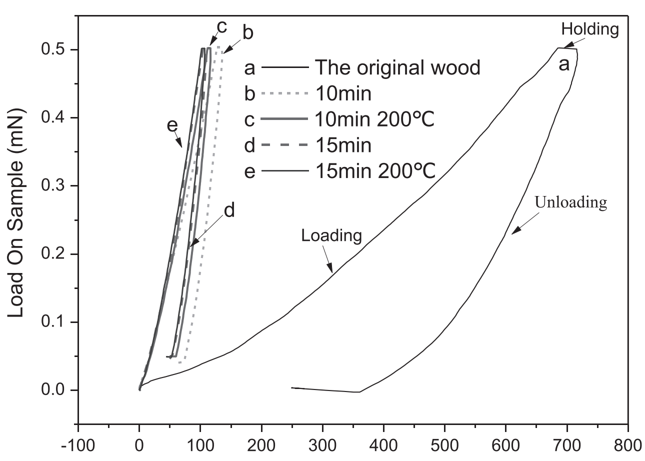


Figure 3.—Load pressure depth curve.

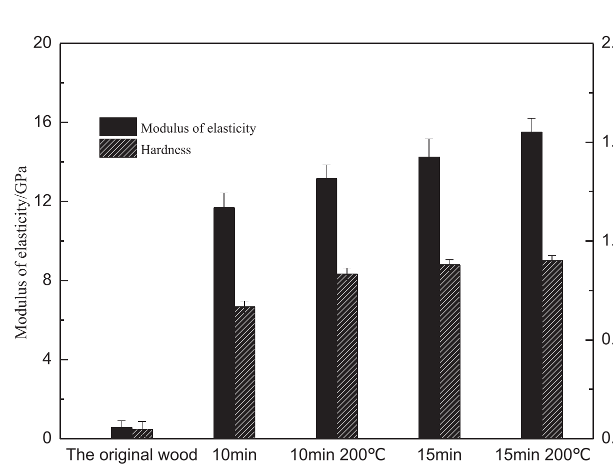


Figure 4.—Modulus of elasticity and hardness.

Table 1.—Sheet resistance of wood-based nano-metal composites.[a]

Sputtering time (min)	Substrate temperature (°C)	Surface of wood veneer treated with sealing agent?	Sputtering air pressure (Pa)	Mean along-line sheet resistance (SD) (mΩ)	Mean transverse sheet resistance (SD) (mΩ)
The original wood	Room temperature	No	—	—	—
Sealant treatment	Room temperature	Yes	5	—	—
10	Room temperature	Yes	5	39.533 (1.4012)	40.403 (1.4001)
10	200	Yes	5	300.660 (1.4916)	304.783 (1.4916)
15	Room temperature	Yes	5	37.337 (1.4554)	39.123 (1.2139)
15	200	Yes	5	178.327 (1.8189)	174.873 (1.2139)

[a] Dash indicates that the value is not applicable or is not detected.

coating time was 10 minutes and sputtering occurred at room temperature, the surface sheet resistance of samples was 40.0 mΩ. When sputtering occurred at 200°C, the surface sheet resistance of samples was 302.7 mΩ, which was 7.57 times greater than that at room temperature. When the coating time was 15 minutes and sputtering occurred at room temperature, the surface sheet resistance of samples was 38.2 mΩ. When sputtering occurred at 200°C, the surface sheet resistance of samples was 176.6 mΩ. The sheet resistance of the sample prepared at 200°C was about 4.6 times that of the room-temperature sample. It can be seen that when sputtering occurred at 200°C, the electrical conductivity of the surface of the copper-plated wood veneer sharply decreased.

These differences occurred for the following reasons: (1) As the base temperature increased, the interface diffusion also increased. The copper layer and the veneer surface diffusion reduced the effective thickness of the copper layer, so the square resistance increased. (2) The increase in the substrate temperature may result in the destruction of sealing strata of the wood veneer, increasing the surface roughness of the wood. The rough interface will cause diffuse scattering of electrons on the copper film surface, resulting in an increase in sheet resistance of the wood surface (Li et al. 2009). (3) The increase in substrate temperature increased the probability of copper oxidation, resulting in a decrease in the conductivity of the film. It can be seen that the formation of crystals in copper films on the surface of wood veneer was determined by the substrate temperature and the energy of copper particles sputtering to the wood veneer. When the sputtering power was constant, the energy of the copper particles reaching the surface of the veneer was also constant, and the crystallinity of the copper film was determined by the substrate temperature of the wood veneer. In addition, after the wood veneer was treated with a sealant, the resistance of the along-the-grain block and the across-the-grain block were not much different, indicating that the veneer surface becomes flat and smooth after sealing treatment, which makes up for the difference in the ductility of the films deposited by magnetron sputtering on the wood surface between the two grain directions.

Wettability

The wettability of the wood veneer surface is expressed by the contact angle of liquid on its surface. When the surface static contact angle is greater than 90°, the specimen surface is considered to have a hydrophobic surface, and conversely, when less than 90°, it is considered to have a hydrophilic surface (Cheng and Gu 2002, Jin et al. 2015, Peng and Zhang 2018). The wettability of the wood veneer copper-plated by magnetron sputtering is shown in Figure 5. The contact angle of untreated original wood was 73.5°, which means that water partially moistens the wood sample of *Pinus sylvestris* L. var. *mongholica* Litv. This is because the wood has a porous structure, and there are a large number of polar functional groups on the wood surface. These functional groups are attracted to water droplets, thereby exhibiting certain wettability. Under room temperature, the contact angle of samples with a coating time of 10 minutes was 106.7°, and 110.7° for samples with a coating time of 15 minutes. Under the condition of sputtering at 200°C, the contact angle of samples with a coating time of 10 minutes was 131.1°, and 136.4° for samples with a coating time of 15 minutes. The reason for this was that the growth of the copper film on the wood veneer surface covers the wood surface, decreasing the porous structure of the wood. A large amount of gas-phase nano-copper particles was sputtered from the target and covered the surface of the wood veneer and entered the pores. The nano-scale film formed by accumulating a large amount of nano-copper particles covering the wood surface. A large number of hydrophilic polar functional groups on the wood surface were covered with a copper film, which improved wood hydrophobicity. The deposition of a copper film on the wood surface by magnetron sputtering can change the wettability of the wood veneer from hydrophilicity to hydrophobicity. The hydrophobicity of the copper-plated wood veneer at 200°C was better than that at room temperature. That is because the increase of substrate temperature may lead to the destruction of the veneer sealing layer, and further increase the roughness of the wood, thereby improving the hydrophobicity.

FTIR map

The FTIR map of copper-plated wood veneer (total reflection sampling) is shown in Figure 6. Because of the strong absorption of infrared wavelengths by the copper film, the intensity of the infrared absorption peak of the wood veneer can be reduced by the growth of the copper film on the wood surface. In the FTIR map of the original wood, the absorption peak near 3,330 cm^{-1} was caused by the stretching vibration of hydroxyl (–OH) on the wood surface. The absorption peak intensity of hydroxyl groups on the surface of metalized wood was reduced compared with the original wood. One of the reasons was that the growth of the nano-copper film covers the hydroxyl on the wood veneer surface. Another reason could be that the nano-copper particles deposited on the wood surface react with hydroxyl on the wood surface to form hydrogen bonds, which causes hydroxyl condensation between the nano-

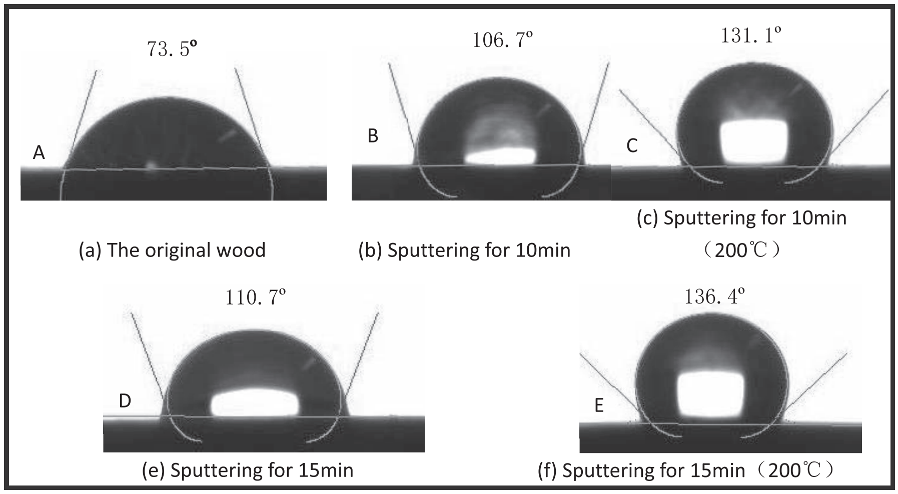


Figure 5.—Wettability of wood-based nano-metal composites.

copper and the wood and which also makes nano-copper particles tightly bond to the wood surface. The absorption peak at 2,922 cm^{-1} was mainly the asymmetric stretching vibration absorption peak of $-CH_3$, which was caused by the stretching vibration of wood C–H, and the absorption peak at 2,850 cm^{-1} was mainly the symmetric stretching vibration of $-CH_2$, both of which were characteristic peaks of organic functional groups. The reason why the strength of the two peaks decreased was that the nano-copper films deposited on the wood surface covered the organic functional groups. The decrease in the intensity of the absorption peak at 1,026 cm^{-1} was attributed to the in-plane bending of aromatic C–H. The copper film deposited on the wood surface completely covered a large number of polar functional groups on the wood veneer surface, resulting in the decrease in the intensity of the absorption peak of the metallized wood veneer (Wang et al. 2011). The hydroxyl groups on the surface of polymers such as cellulose contained in wood can provide nucleation and film-forming substrates for inorganic nanoparticles. These studies provided a theoretical basis for the formation of wood surface films (Schmalzl and Evans 2003, Ding et al. 2009). Moreover, there were unsaturated bonds (including residual bonds and suspended bonds) and free hydroxyl groups on the surface of sputtered nanometer copper particles after they leave the target material. All of these create conditions for the chemical binding of nanoparticles and wood. In addition, the surface of the wood has a physical adsorption effect on the nano-copper particles, that is, the van der Waals force between the nano-copper particles and the wood polymer (Roy et al. 2010, Wang et al. 2018). The combination of the nano-copper particles and the wood surface was the result of physical adsorption (van der Waals force) and chemisorption (chemical bond; Yuan et al. 2012).

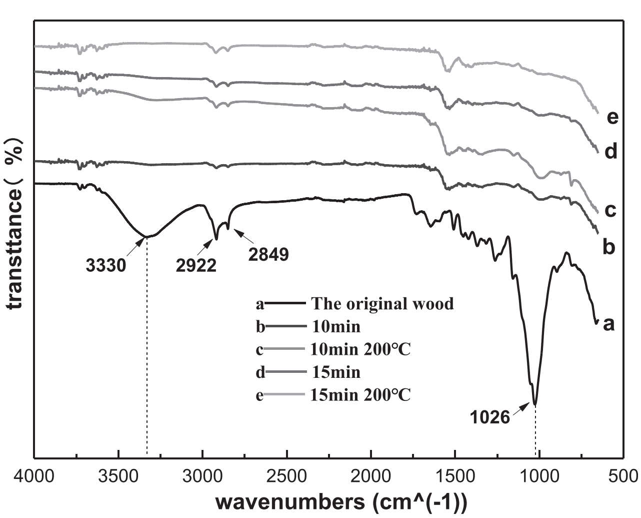


Figure 6.—Fourier-transform infrared map of copper-plated wood veneer.

From Figure 6, it can be seen that the absorption peak was slightly offset from the short wave at 200°C relative to room temperature sputtering, but there was almost no difference in the intensity of the absorption peak. According to the Burstein-Moss effect hypothesis (Moon et al. 2006), the filling of the conduction band brings about the increase of electron carriers, which further ensures that the fermi level inside the conduction band moves upward as donor concentration increases. Thus, the optical band gap increases at 200°C compared with room temperature and the absorption peak shifts to the shorter wavelength at 200°C.

Micromorphology

Fluorescence effect of wood-based nano-metal composites.—Some substances may emit radiation transitions and emit longer wavelengths of light (fluorescence) under the irradiation of shorter wavelength light (excitation light). Under ultraviolet light irradiation, the wood can produce natural fluorescence, which the copper film cannot. Therefore, the growth of copper film on wood veneer by magnetron sputtering can be judged according to the fluorescence effect. Although a small number of impurities on the film surface may cause fluorescence, this does not substantially affect the characterization of the growth of the wood veneer film by the fluorescent probe technique. As shown in Figure 7, the original wood could produce light blue fluorescence under ultraviolet excitation light. The sealing treatment does not affect the fluorescence effect of wood, and the whole veneer surface still shows light blue

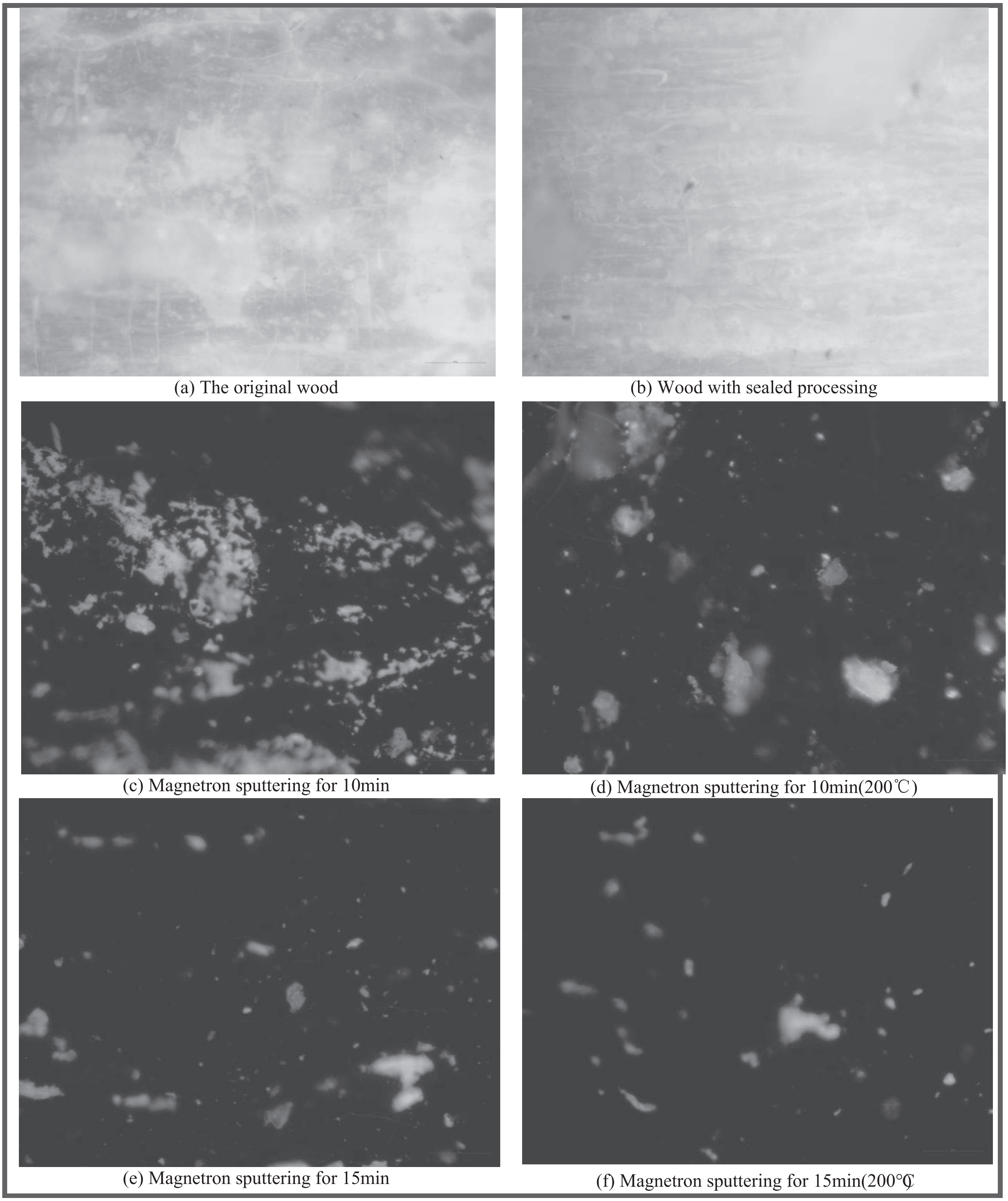
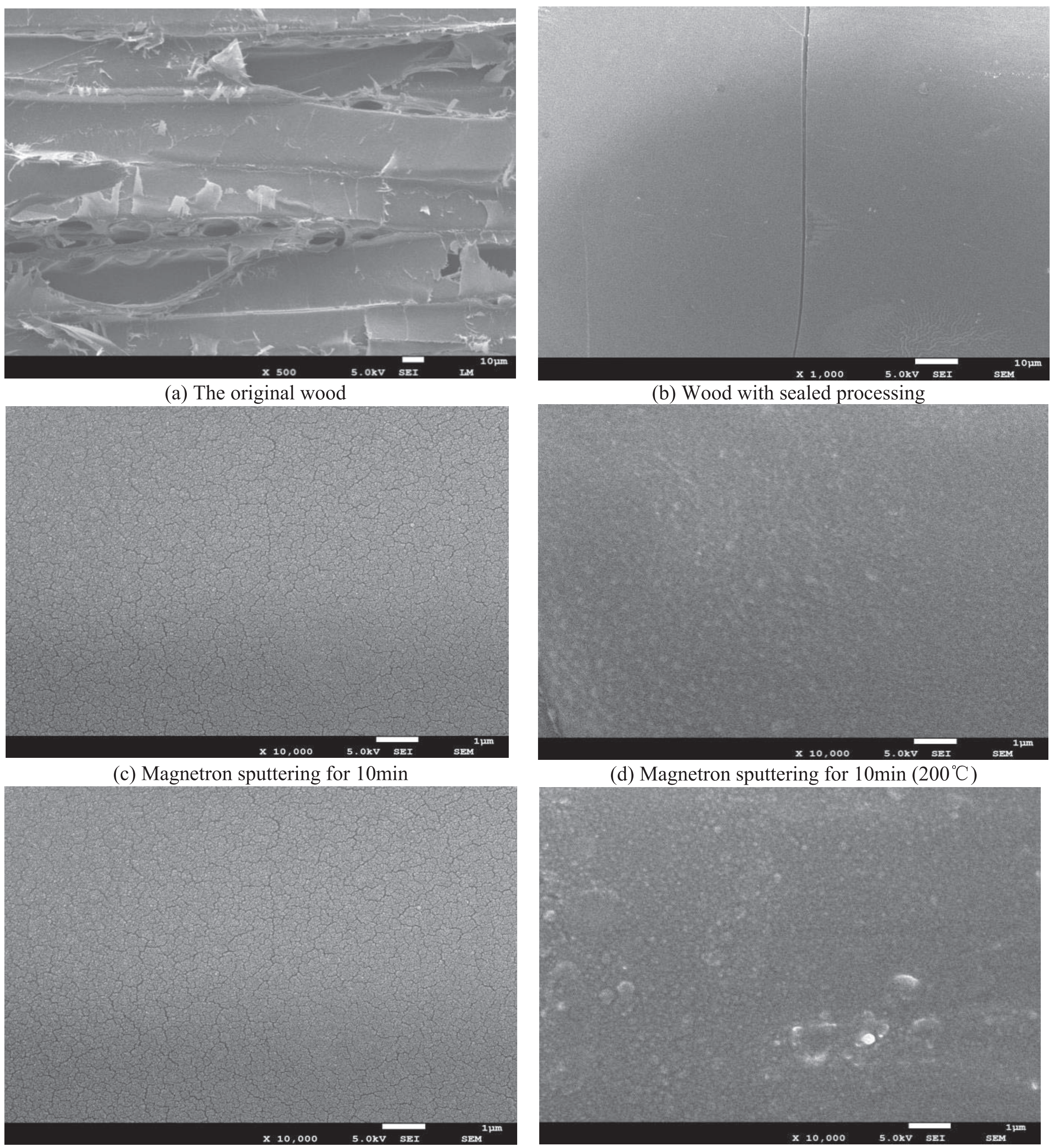


Figure 7.—Fluorescence effect of wood-based nano-metal composite (200 times).

fluorescence. Most of the samples prepared by magnetron sputtering for 10 and 15 minutes formed black regions that did not produce fluorescence, and only a part of wood veneer surface could produce a faint light blue fluorescence. Additionally, the region where fluorescence could be produced became smaller and the fluorescence intensity was weaker at 200°C. The film growth was denser and more uniform at 200°C, and the copper film was able to completely cover the wood surface by magnetron sputtering. The fluorescence generation in some regions may be caused by impurities that can produce fluorescence on the surface; another reason may be a crack on the surface caused by the poor quality of copper film deposited on the surface of the wood.

Analysis of microscopic morphology by scanning electron microscopy.—Scanning electron microscopy images of the wood-based nano-metal composite are shown in Figure 8. The original wood was a porous material with a complex surface structure (Fig. 8a). Its fibers, pores, ducts, and parenchyma cells are clearly visible, and its surface is rough and uneven, which was not conducive to the growth of copper films. Therefore, the wood veneer was sanded with metallographic sandpaper to make the wood surface smooth enough to create preliminary conditions for the growth of



(a) The original wood
(b) Wood with sealed processing
(c) Magnetron sputtering for 10min
(d) Magnetron sputtering for 10min (200℃)
(e) Magnetron sputtering for 15min
(f) Magnetron sputtering for 15min (200℃)

Figure 8.—Scanning electron microscopy images of wood veneer copper-plated by magnetron sputtering.

copper film by magnetron sputtering. After the sealing treatment, the surface of the wood veneer was smooth, thus suitable for the growth of copper film and providing favorable conditions for the construction of wood-based nano-metal composite by magnetron sputtering (Fig. 8b). When the substrate was at room temperature, although the copper thin film deposited on the surface of wood veneer was uniform, compact and smooth, it cracked on the film surface (Figs. 8c and 8d). However, when the substrate temperature was 200°C, the copper film was mainly composed of small particles and could also be presented as nanoparticles. The weight gain rate of the copper film was 0.032 percent. Having less roughness, the copper film was uniform, dense, flat, wand free of cracks, and could almost be integrated into a single film, which guaranteed a copper film of superior physical properties (Figs. 8e and 8f).

Conclusions and Discussion

In this study, copper film was deposited on the surface of *Pinus sylvestris* L. var. *mongholica* Litv. veneers by magnetron sputtering at room temperature and 200°C to produce a composite of nano-metal copper and wood. The physical properties of wood-based nano-metal composites were then characterized. From the structural characterization results obtained using X-ray diffraction, it can be seen that there were still characteristic diffraction peaks of cellulose in wood, and there were also characteristic diffraction peaks of three crystal planes of copper. The deposition of nano-copper films on the wood surface not only improved the strength and mechanical properties of the wood surface but also increased the electrical conductivity. Moreover, the deposition of copper films on the wood surface can modulate the porous structure of the wood by filling the pores. A large number of hydrophilic polar functional groups on the wood surface were covered by the copper film, which changed the wettability of the wood surface from hydrophilic to hydrophobic. Therefore, the preparation of copper films on the wood veneer surface by magnetron sputtering can combine the nano-copper and wood and improve their mechanical and conductive properties, and the wettability of the wood surface, which results in the overall improvement of wood properties.

Magnetron sputtering has a strict requirement for substrate materials; wood is a porous material with complex surface structure, a rough and uneven surface, and surface impurities such as gum, filler, and ash, which is very unfavorable to the growth of copper thin films. However, a small amount of MF2 sealant solution that is evenly applied to the polished wood veneer to make the wood surface flatter and smoother thereby creates a good base condition for the deposition of copper films on the wood surface. It is also necessary to find other environmentally friendly methods for wood surface treatment to prepare the environmentally friendly wood-based nano-metal composites by magnetron sputtering.

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