Article

Polymer-Assisted Metal Deposited Wood-Based Composites with Antibacterial and Conductive Properties

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Abstract: Compressible metallic porous materials (CMPMs) have great potential for development in the energy and environmental fields. However, the scale-up preparation of CMPMs with stable metal layers, excellent elasticity, and multifunctionality remains exceedingly challenging. In this study, we designed a novel strategy with the aid of polymer-assisted metal deposition to synthesize metallic porous wood (Ni-PW) with a hierarchical cellular structure and excellent elasticity. Our approach can produce highly compressible MPW using intrinsically porous delignified wood with only 15.16% strain loss under a large compressive strain of 40% after 1000 loading-unloading cycles and 129.4 µm of the average porous size of the Ni-PW measured by mercury injection method. The resulting Ni-PW displays excellent antibacterial properties for Escherichia coli (E. coli) and Staphylococcus aureus (S. aureus) and electric conductivity (Resistance < 7 ty), which renders great potential in energy and environmental applications. This research provides a new insight into the fabrication of CMPMs in a cost-effective (~56.5 ¥ m⁻²) and scalable way.

Keywords: wood; metallic coating; composites; antibacterial property; electrical conductivity

1. Introduction

Compressible metallic porous materials (CMPMs) with large surface areas, high porosity, and superior conductivity have received widespread attention from researchers [1,2], especially in the fields of energy conversion and storage and antibacterial treatments [3–9]. Metallic materials with porous structures allow for rapid access by electrons, molecules, and solutions, which substantially increases material utilization and resultant multifunctionality. Metal nanomaterials, such as nickel, silver, and gold nanoparticles, have been widely demonstrated as effective uses for antibacterial coating and antibacterial treatment, but their high cost is the major obstacle for large-scale applications [10–13]. Therefore, a tremendous amount of research has been done to seek alternative cost-effective approaches to synthesize multifunctional CMPMs in order to accelerate their practical applications. Until recently, one of the most promising strategies has been to integrate metal particles into highly porous matrices, such as porous silica, graphene nanoshell, metal-organic framework, polymer, and hydrogel [14–18]; however, most synthesis methods of the metallic porous materials reported require tough and tedious steps, which limits their feasibility of large-scale production.

Directly deposited metal coating on a target host surface via physical vapor deposition (PVD), electroplating, electroless deposition (ELD), etc., is regarded as a facile way to acquire homogeneous metallic porous materials [19–22]. PVD is the most widely used surface metallization technique for forming a conductive and conformal thin metal layer and reliable barrier layers that protect against metal particle diffusion prior to metal depositing, but expensive equipment, harsh environments, and sophisticated steps are required. The “shadow effect” of this method also deeply affects the metal deposition of the porous matrices. Electroplating is a popular method to synthesize metallic porous materials.
in laboratories and factories due to the low cost and ease of operation. Nevertheless, it is only applicable to conductive substrates. Conversely, ELD is another economic and facile approach to creating metal coating, but can be carried out on both conductive and non-conductive substrates. ELD, essentially, is an autocatalytic redox process in which the metal particles are chemically reduced and deposited on any catalyst preloaded substrates, including flexible polymeric ones such as polyurethane (PU), poly(ethylene terephthalate) (PET), yarn, paper, carbon fibers, etc [21–25]; however, most of these substrates are not porous and exhibit single performance under incompressible resilience. It is a big challenge to construct metallic porous materials endowed with superior antibacterial and conductive properties without compromising the intrinsic compressibility of the substrates.

Herein, we propose a facile and scalable approach for preparing durable compressive metallic porous wood (Ni-PW) via the ELD process. The resultant Ni-PW is demonstrably antibacterial and conductive. In our research, polyethyleneimine (PEI), a functional polymer with abundant amino groups, is first cross-linked onto the PW, which forms a uniform surface for metal ion adsorption through chelation. Reliable nickel (Ni)-coated PW can be obtained after depositing a metal layer on the surface of PEI-PW by an aqueous ELD process. We found that the as-obtained Ni-PW can significantly facilitate the mass transfer and show multifunctional properties. In addition to being remarkably antibacterial against *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*), the Ni-PW is also proven to be highly conductive and compressible, which are the ideal properties for elasticity-responsive conductive materials.

2. Materials and Methods

2.1. Materials and Chemicals

Basswood was purchased from Decci Co., Ltd. (Dongguan, China) PEI (M. W. 70,000, 50 wt.% in water), Ni$_2$SO$_4$·6H$_2$O, and dimethylamine borane (DMAB) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China) AgNO$_3$ was purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). Glutaraldehyde (25 wt.% in water) was obtained from Tianjin Fuchen Chemical Reagent Co., Ltd (Tianjin, China). All other chemicals were of analytical grade.

2.2. Preparation of PW Substrates

The procedure of preparing PW was based on our previous work [26–28]. First, the wood was cut into specific sizes and these blocks were immersed for 10 h in boiling deionized (DI) water (1 L) containing NaOH (99.99 g) and Na$_2$SO$_3$ (56.82 g); next, the blocks were soaked in boiling H$_2$O$_2$ until completely white. The white ones were washed with DI water to remove residual chemicals. Finally, the wet blocks were frozen at $-18^\circ$C several times and subsequently freeze-dried. To make the oxidized wood, 0.5 g dry wooden blocks were submerged in 50 mL DI water with a pH of 10 adjusted with 1 M NaOH. About 5 mM NaClO was introduced to initiate the oxidation process. During the reaction, a pH meter was used to monitor the pH of the solution and a pH (approximately 10) was maintained by adding 1 M HCl. The reaction was stopped after 2.5 h by adding 1 M HCl to adjust the pH to neutral. From there, the mixture was poured out and the blocks were washed with 1 M HCl. The wet blocks were rinsed with DI water until the pH was above 5. Finally, the PW was frozen at $-18^\circ$C several times and subsequently freeze-dried for further PEI grafting.

2.3. Preparation of PEI Grafted on PW Substrates

A certain amount of dry PW was put into a 100 mL beaker, and 4 wt.% of PEI solution dissolved with methanol was added until it completely swamped the white. The PW suspension was put in a water bath of 35 $^\circ$C for 24 h and the PW was squeezed lightly at intervals. After the immersion, the solution was poured and the wet PW was rinsed several times by DI water to remove uncombined PEI. Subsequently, the wet PW was immersed by 4 wt.% of glutaraldehyde solution and squeezed lightly for 1 h at room temperature.
Finally, the PEI grafted PW was washed thoroughly with DI water to remove uncombined glutaraldehyde and then freeze-dried for further ELD performing.

2.4. Preparation of Metallic PW (Ni-PW)

The dried PEI-PW was immersed into a 5 mM AgNO$_3$ solution and dissolved in a 50 g mixture solution of ethanol and ethylene glycol in a ratio of 2:1 by weight and extruded continuously for 1 h. Later, the samples were rinsed with DI water several times to remove the residues. Finally, the Ag$^+$-supported PW was immersed into the Ni ELD bath for different intervals and the target Ni-deposited PW was obtained. The specific experiment was as follows: the ELD of Ni was conducted in a plating bath, which is composed of a 1:1 mixture of pre-prepared solution A and B, and the pH was adjusted to 10 with an ammonia solution. Among these, solution A contains 20 g L$^{-1}$ Ni$_2$SO$_4$·6H$_2$O, 33 g L$^{-1}$ sodium citrate, and 14 g L$^{-1}$ sodium hypophosphite in DI water; solution B contains 3 g L$^{-1}$ DMAB reductant in DI water. The ELD process was conducted at room temperature and after Ni ELD the sample was washed thoroughly with DI water and fully freeze-dried.

2.5. Antibacterial Test

The antibacterial activities of the Ni-PW against *S. aureus* and *E. coli* were evaluated through modified Kirby–Bauer and turbidity assays methods.

2.6. Conductive Test

The resistance of the Ni-PW was measured using a multimeter. In addition, the resistance variation of such modified wood under cyclic compression was determined by a self-designed compression apparatus.

3. Results and Discussion

3.1. The Fabrication of Metallic Porous Woods

Wood, a renewable and natural carbon resource, contains approximately 45% cellulose and is the preferred raw material for low environmental and human health safety risks; it can also be chemically modified for use in traditional and advanced materials fields [29–32]. Porous-wood (PW), composed of cellulose by a “top-down” approach from natural wood [33], is an ideal substrate for fabricating conductive material through ELD due to its excellent porous structure and mechanical properties. We developed the CMPWs based on three criteria: (1) the growth direction of wood fiber must not be destroyed and the whole volume structure of the original wood must be preserved; (2) the metal layers must be firmly adhered to the surface of the wood fiber; and (3) the cellular architecture and porous structure of the metal-coated wood must not collapse during a continuous compression–relaxation process. Polymer-assisted metal deposition (PAMD), a modified ELD method, can enormously increase bonding between the metal layer and the substrate as well as the mechanical strength of the deposited conductive surface. Instead of a catalyst layer, long functional polymer chains are immobilized firmly on the catalyst preloaded substrate before the chemical deposition of metal particles [34,35]. Although PAMD is considered to be one of the most effective methods of preparing CMPWs, choosing an appropriate polymerization reaction can significantly facilitate the fabrication process and enhance the efficiency and reproducibility. For example, an inert atmosphere is a necessity for some polymerization processes such as surface initiated-atom transfer radical polymerization (SI-ATRP), and it usually takes several hours to complete on the PW [36]; however, the commercial polymer PEI can be grafted firmly onto the surface of PW by simple cross-linking.

As shown in Figure 1, Ni-PW with metal coating was successfully prepared via PAMD. In this specific experiment, readily available, pre-washed wood was delignified and bleached completely. Functional polymers were then immobilized onto the treated wood surface through a cross-linking reaction with numerous amine groups on cellulose.
As a proof-of-concept, PEI and glutaraldehyde were chosen as the functional polymer and cross-linking agents, respectively. The cross-linking reaction occurs between amino groups on the PEI and hydroxyls on the PW in the presence of glutaraldehyde, which forms a functional branched polymer coated on PW. The PEI-grafted PW was then immersed into an AgNO$_3$ aqueous solution, where silver ions were adsorbed onto the secondary amine groups of the copolymer layer through ion exchange [37,38]. Finally, Ni-coated PW were obtained after immersing the catalyst-loaded samples into ELD baths of Ni for a certain amount of time. The detailed data of surface morphology (SEM images), chemical composition (FTIR, XPS spectra and EDS images), crystal structure (XRD spectra), thermal behaviors (TGA spectra), pore size and distribution (mercury intrusion method), and cyclic compression release tests of the as-prepared Ni-PW were based on our recent work [39].

Figure 1. Schematic illustration of the PAMD strategy for the synthesis of the Ni-coated wood.

3.2. The Antibacterial Properties of the Ni-PW

It is well known that nanometallic materials (such as nickel) exhibit outstanding antibacterial activities [40–42]. The as-prepared Ni-PW with active Ni nanoparticles and unique porous structure is expected to possess superior antibacterial properties [39]. In this study, Gram-positive \textit{S. aureus} and Gram-negative \textit{E. coli} were used as bacterial models to investigate the antibacterial activities of the as-made Ni-PW.

The antibacterial activities of the modified woods were first assessed by calculating the growth inhibition of the bacteria on LB agar mediums through a modified Kirby–Bauer method. In the disk diffusion antimicrobial tests, a certain amount of \textit{S. aureus} and \textit{E. coli} were inoculated on the mediums, respectively, before various samples with equal quality were placed uniformly. Subsequently, the mediums were cultured for several days at 37 °C, and the antibacterial properties were investigated via measuring the inhibition zones. Surprisingly, no inhibition zone was observed for the original PW and the PEI modified PW against \textit{S. aureus} or \textit{E. coli}, even after 7 days of bacterial culture (Figure 2); however, the Ni-PW exhibited obvious inhibition zones for the two bacteria (Figure 3). The prominent antibacterial activity of Ni-PW can be mainly attributed to two factors: the hierarchical porous structure of the raw wood, which can provide enough space for the bacteriostatic areas, and phosphorous-containing lipopolysaccharides of \textit{E. coli} and teichoic acids of \textit{S. aureus} on the outer bacterial surface, which are susceptible to nanoparticles [43]. Hence, when the enhanced dispersion stability of the metal layer in the fiber substrate significantly increases the contact site between the Ni-layer and the bacteria, the bacterial cell wall is further destroyed and the bacteria are killed.

In addition, the turbidity assays were also used to investigate the antibacterial abilities of Ni-PW against \textit{S. aureus} and \textit{E. coli}. Two bacteria were cultured in the LB liquid mediums at 37 °C for 24 h in the presence of various samples, and the change in turbidity was shown in Figure 4. By our observation, all groups became more turbid after 24 h cultivation except
the Ni-PW, which verifies our finding that the growth of bacteria was effectively inhibited in the medium containing the Ni-PW, which shows its excellent antibacterial activity.

**Figure 2.** Inhibition zone test of the as-made Ni-PW (a), PEI-PW (b), and PW (c) against *E. coli* and *S. aureus*.

**Figure 3.** The detailed antibacterial area of the inhibition zone test for the as-made Ni-PW against *E. coli* and *S. aureus*. 
To study the antibacterial activities of the samples quantitatively, the survival rate of *S. aureus* and *E. coli* was determined in the liquid medium after 24 h cultivation. The bacterial survival was observed by the optical density at 600 nm (OD$_{600}$), and the survival rate was calculated by the equation: Survival (%) = $A/B \times 100\%$ (where $A$ and $B$ are the OD$_{600}$ values in the group and control groups after 24 h cultivation, respectively). As displayed in Figure 5, the survival rates of the control group containing PW and PEI-PW are over 90% regardless of *S. aureus* or *E. coli* after 24 h cultivation, whereas the survival rates of groups containing Ni-PW are below 10%, which is remarkably lower than those of the control groups. These results reconfirm the conspicuous antibacterial properties of the as-prepared Ni-based wood against *S. aureus* and *E. coli*, which is in accordance with the result of the disk diffusion assays.
3.3. The Electrical Conductivity of the Ni-PW

Three-dimensional (3D) compressible conductors with excellent electrical conductivity can expand the scope of applications within the new fields of robotic skins, camera eyes, and pressure detection [44,45]. In addition to the excellent conductivity offered by the coated metal, the original PW also possesses a spongy porous structure with a high surface area that facilitates electron transfer. More notably, the as-prepared Ni-PW still exhibited superior elasticity after 1000 loading-unloading cycles [39]. These characteristics endow the as-prepared Ni-PW with outstanding electrical conductivity.

To evaluate the electrical conductivity of the Ni-PW, we first tested the resistance of the stationary fresh Ni-PW in the air, and the initial resistance was recorded as ~6.7 Ω, indicating that the presence of electron transfer within the material; however, the resistance of the Ni-PW was found to increase to 11.3 Ω (by ~68%) after it was stored in the air for 3 days, and then remained stable for the following 30 days (Figure 6). This increase in resistance is due to the formation of metallic oxide films on the surface of the Ni-based material in a humid environment and can be addressed via electrochemical deposition, self-assembly, physical encapsulation, and other metal-capped methods that have been applied in the electronic industry.

![Figure 6. The resistance vs. storage time of the Ni-PW. The inset shows the Ni-PW stored for a month.](image)

Notably, the Ni-PW simultaneously displayed remarkable compressibility and superior electrical conductivity [36]. The same resistance measured above was conducted on the metal-coated wood under mechanical compression-relaxation cycles. Interestingly, the conductive woods showed higher resistance (~7.9 Ω) in the original state and lower resistance (~1.1 Ω) under a compression strain of 60%. As shown in Figure 7, the curve of the normalized electrical resistances, $(R/R_0)$-compressive strain, could be well fitted to a similar profile under a 60% compression strain, where $R_0$ and $R$ were the resistance of the sample before and after compressing, respectively. Since the conductivity of a material depends heavily on the contact resistance between the fibers, the more closely the fibers contact—or the larger the contact area between the fibers is—the more superior the conductivity is. When the compression strain was higher than 40%, the contact area between fibers did not increase remarkably, thus the $R/R_0$ dropped slowly (Figure 7a). Moreover, the symmetry of the unloading and loading curves indicated the rapid recovery of the Ni-PW in compression cycles. The $R/R_0$ of the Ni-PW returned to the original state is ~1.1, almost the same as the initial value ($R/R_0 = 1$). This negligible change in $R/R_0$ is the result of the excellent compression capacity and fatigue resistance of the as-made Ni-PW. The resistance durability of the Ni-PW was tested under compression strains varying from 0 to 40% for 1000 compression cycles. As shown in Figure 7b, the $R/R_0$ of the as-prepared Ni-PW...
recovered to the original state is ~1.15, indicating that such material still held superior elasticity even after 1000 compression cycles. In addition, the $R/R_1$ ($R_1$ is the resistance in the first cycle with a different compression strain) increased to ~1.2, 1.4, 1.6, 2.4, and 2 at the compression strain of 0%, 10%, 20%, 30%, and 40%, respectively, after 1000 cycles (Figure 8). This increase in resistance was due to the accumulation of microcracks appearing on the metal layer upon compression cycling.

Figure 7. Normalized resistances of Ni-PW at different compression strain for the (a) first and (b) 1000th cycles. The insets in panel (a) show the brightness increases of blue LED on compression of the Ni-PW.

Figure 8. Fatigue tests of compressibility for Ni-PW.

A 3-V circuit with the as-made Ni-PW as the electronic pressure sensor was fabricated to display its elasticity-dependent electrical conductivity. A blue light-emitting diode (LED) was lit when connected to the Ni-PW, and its luminance fluctuated as the sensor was compressed and relaxed (insets in Figure 7 and Supplementary Video S1). Moreover, the as-prepared Ni-PW was used as electrical substrate to drive an LED display with four letters, "S C A U", on a 3-V circuit (Figure 9). Finally, this compression-resilience was applied to adjust the motor speed and the power the fan rotation and ball movement (Figure 10 and Supplementary Video S2). All demonstrations strongly support the application of Ni-PW as flexible electronic pressure sensors in various fields.
Figure 9. Digital images of the electronic circuit. The as-made Ni-PW was used as electrical substrate for powering a display with the letters “S C A U”.

Figure 10. Digital images of electronic circuits. The as-made Ni-PW was used as electronic pressure sensor for blowing up a white ball by driving a pink fan.

4. Conclusions

In summary, we have developed an environmentally friendly and economical path for the production of Ni-PW with a stable structure and outstanding antibacterial and conductive properties. Ni-PW possesses a hierarchical cellular structure, and the size and shape of the materials are highly controllable. Based on the remarkable cyclic compressibility of the PW and the unique multi-functionality of the metals, the as-prepared Ni-PW demonstrates prominent antibacterial abilities against *S. aureus* and *E. coli*, as well as superior electrical conductivity. In light of these advantages, we believe that Ni-PW has promising prospects in multiple fields such as developing antibacterial agents, dampers, pressure sensors, and flexible wearable electronics.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/coatings12081161/s1, Video S1: A blue light-emitting diode; Video S2: Motor, fan and ball.

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