Highly Thermally Conductive Composite Films Based on Nanofibrillated Cellulose in Situ Coated with a Small Amount of Silver Nanoparticles

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Supporting Information

ABSTRACT: In this paper, a freestanding flexible nanofibrillated cellulose (NFC)/silver (Ag) composite film with high thermal conductivity (TC) was prepared using the NFC that was in situ coated with a small amount of Ag nanoparticles through mussel-inspired chemistry of dopamine. The results demonstrated that Ag nanoparticles were homogeneously coated on the surface of NFC nanofibers and their incorporation had little influence on the film-forming ability of NFC. The NFC decorated with Ag nanoparticles could easily form thermally conductive pathways in the composite films, and the resultant films containing only 2.0 vol % of Ag showed a high in-plane TC value of 6.0 W/(m·K), which was 4 times that of pure NFC film. Moreover, the composite films exhibited relatively high strength and flexibility. The highly thermally conductive NFC/Ag composite films possess potential applications as lateral heat spreaders in flexible electronic equipment.

KEYWORDS: nanofibrillated cellulose, silver nanoparticles, chemistry of dopamine, composite film, in-plane thermal conductivity

1. INTRODUCTION

As modern electronic devices continue to develop toward higher integration, miniaturization, and higher performance, thermal management materials (TMMs) with high thermal conductivity (TC) have become important in the electronic field, which can efficiently remove redundant heat generated by high-power integrated circuits.1 Polymers are regarded as suitable matrixes of TMMs due to their ease of processing, low weight, and low cost.2 Unfortunately, most of these polymers have inherent low TCs, which cannot meet the demands for fast heat conduction. A conventional method to enhance TCs of polymers is to blend them with high-TC fillers, for example, carbon materials,3–8 ceramic,8–15 or metallic particles.15–22 Silver (Ag) nanoparticles exhibit the largest TC (∼430 W/(m·K)) among all of the metals and have received great attentions of researchers.17,19,20 For example, Yu et al. incorporated Ag nanoparticles into polystyrene (PS) matrix and prepared PS/Ag composite with a high TC of 140 W/(m·K) at 70 vol % Ag loading, which was comparable with one-third of the value of pure Ag.19 Huang et al. obtained poly(vinylidene fluoride)/Ag composite with a TC of 6.5 W/(m·K) at 20 vol % Ag.20 However, as a zero-dimensional (0D) filler, its intrinsic low aspect ratio as well as poor compatibility with polymers make it difficult to form effective thermally conductive pathways in the composites prepared by traditional melting or solution mixing methods. To achieve high TC, very high Ag loadings are usually needed, which inevitably brings a series of problems, such as high costs, processing inconvenience, and deterioration of mechanical properties.20,23 Therefore, it still remains a great challenge to obtain polymer materials with high TC using small addition of Ag nanoparticles.

One-dimensional (1D) nanofibrillated cellulose (NFC), a new, biobased, and highly crystalline nanofiber, exhibited remarkable high strength and stiffness.24,25 Moreover, it can easily construct a continuous network to form a freestanding flexible film via cast drying or vacuum filtration methods.26 Therefore, NFC has attracted increasing attention as a suitable matrix to prepare composite films. Up to now, NFC-based composites with high TC have been manufactured by incorporating various high-TC fillers, for example, boron nitride, graphene, etc.27–30 Recently, Song et al. proposed a strategy to improve the TC of NFC composites by adding 0D nanodiamond (ND).31 They found that ND nanoparticles dispersed in NFC suspension tended to gather on the surface of nanofibers during the formation process of composite films. Especially, it was found that when ND nanoparticles were uniformly dispersed on the surface of NFC nanofibers, a small
amount of ND could lead to dramatic improvement of TCs of the resulting NFC/ND composite films. Because of ND’s inherent high TC (~2000 W/(m-K)), the in-plane TC of composite film containing 0.5 wt % ND reached 9.82 W/(m-K). Inspired by this study, it was reasonable to suppose that if thermally conductive 0D nanoparticles were beforehand anchored on the surface of NFC via chemical methods, the possible filler agglomeration during the physical mixing process due to the significant mismatch in polarity and density between NFC matrix and filler would be avoidable, which was beneficial to utilize smaller amount of nanoparticles to achieve high TC. However, to the best of our knowledge, there are no attempts concerning a strategy to fabricate highly thermally conductive NFC-based composite films using nanoparticle-precoated nanofibers.

In this work, we synthesized a series of Ag-decorated NFCs through mussel-inspired chemistry of dopamine (DA) and then prepared NFC/Ag composite films via a facile vacuum filtration technique. DA has been found to be spontaneously polymerized into polydopamine (PDA) in alkaline aqueous solution and formed biocompatible coatings on almost all kinds of substrates.52–56 Recently, many studies also confirmed that the PDA layer could behave as a reducing agent to reduce metal ions into metal nanoparticles.52,57–60 Combined with its robust adhesion property and reducing ability, various metal nanoparticle-coated hybrids, such as Ag-coated boron nitride nanosheet (BNNS),37 gold-coated tobacco mosaic virus,38 and nanoparticle-coated hybrids, such as Ag-coated boron nitride nanosheets (BNNS),39 have been synthesized. In this work, we found that Ag nanoparticles could be homogeneously in situ coated on the surface of NFC nanofibers via chemistry of DA and the Ag nanoparticle coating had little influence on the film-forming ability of NFC. The Ag-decorated NFC could form effective thermally conductive pathways at low loading of Ag nanoparticles, and the obtained film showed a high in-plane TC value of 6.0 W/(m-K) at only 2.0 vol % of Ag, which was 4 times that of pure NFC film. The highly thermally conductive NFC/Ag composite films possessed potential applications as TMMs in portable electronic devices.

2. EXPERIMENTAL DETAILS

2.1. Materials. NFC aqueous dispersions with a concentration of 1.5 wt % were purchased from Tianjin Woodfiber Cellulose Co. Ltd., China. 3,4-Dihydroxyphenethylamine hydrochloride (DA·HCl) and silver nitrate (AgNO₃) were purchased from Sigma-Aldrich Co. Ltd. Tris–Cl solution (10 mM, pH 8.5) was prepared from tris-(hydroxymethyl)aminomethane and hydrochloric acid, which were obtained from Shanghai Sinopharm Co. Ltd. All chemicals were used without further purification.

2.2. Preparation of NFC/Ag Composite Films. The NFC/Ag composite films were prepared by in situ deposition of Ag nanoparticles on the NFC via the DA chemistry and then vacuum filtration. In brief, 10 g of NFC aqueous dispersions were diluted into 90 g of Tris–Cl solution to obtain a homogenous NFC–Tris mixture with a concentration of 0.15 wt % under vigorous stirring (10 000 rpm). Then, 0.15 g of DA·HCl was added and the resulting mixture was stirred for 8 h at room temperature. After centrifugation and washing with deionized water for three times to remove free PDA, the PDA-coated NFC was dispersed in 100 mL of water. AgNO₃ (10 mL, 0.1 M) solution was dropwise added into the above dispersion and stirred for 6 h in the dark to get NFC/Ag suspension. The suspension was vacuum filtered on a cellulose acetate filter membrane with a pore size of 0.22 μm to obtain the NFC/Ag composite films with thickness of 50 ± 5 μm. The films with different Ag loadings were prepared by controlling the addition of AgNO₃ solution and denoted as Agₓ, in which x was the volume fraction of Ag nanoparticles. The x values were determined by the weight fractions of Ag, which was obtained from the thermogravimetric analysis (TGA) curves of composite films. For comparison, pure NFC and only PDA-coated NFC films were also prepared under the identical procedure.

2.3. Characterization. Transmission electron microscopy (TEM) images were acquired using a Tecnai G2 20 TWIN transmission electron microscope (FEI). Scanning electron microscopy (SEM) images were captured using an Ultra S5 field-emission scanning electron microscope (Zeiss, Germany). X-ray diffraction (XRD) patterns were recorded on an Xpert diffractometer (PANalytical, Netherlands) using Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) was conducted with an Escalab 250XI electron spectrometer (Thermo Fisher Scientific) with monochromatic 150 W Al Kα radiation. Thermal diffusivities (α) of all samples were measured using a LFA 467 NanoFlash laser flash apparatus (NETZSCH, Germany). The composite films were cut into round disks with a diameter of 25.0 mm and square disks with a length of 10.0 mm for in-plane and through-plane thermal diffusivities measurements, respectively. The average of at least three measurements was calculated as final results. The TC was calculated using TC = α × ρ × Cp, where ρ is the density of composite papers according to ρ = m/V in which m and V are the mass and volume of the samples, respectively, and Cp is the specific heat capacity obtained by differential scanning calorimetry (Mettler-Toledo, Switzerland) through the sapphire method.11 The detailed results are listed in Table S2. The tensile properties of composite films were evaluated at room temperature using a CMT-6503 universal testing machine (SANS, China) with a speed of 2 mm/min. The electrical resistivity of NFC film was measured by a digital high-resistance meter (Taiou Electronic Co., China) and that of Agₓ composite films was tested by a four-probe tester (Suzhou Jingge Electronic Co., China).

3. RESULTS AND DISCUSSION

3.1. Preparation and Characterizations of NFC/Ag Composite Films. NFC/Ag composite films were prepared through sequential three steps using NFC as a starting material, as shown in Figure 1. First, DA·HCl was added into a dispersion of NFC in Tris–Cl solution (pH 8.5) to produce the dark-black dispersion of PDA-coated NFC. Second, AgNO₃ solution was incorporated into the aqueous dispersion of PDA–NFC to prepare the Ag nanoparticle-coated NFC suspension through reduction of Ag⁺. Finally, NFC/Ag composite films were fabricated using the above Ag

![Figure 1. Preparation process of NFC/Ag composite films.](Image)
Because the as-received NFC underwent a TEMPO oxidation process, an abundance of ionized carboxyl groups was grafted on the surface of NFC. It can stably disperse in the Tris−Cl aqueous solution and a transparent suspension was obtained, as shown in Figure 1. The TEM observations revealed the characteristic structure of NFC with a diameter of ∼50 nm and length of a few micrometers (Figure 2a). After the incorporation of DA·HCl and stirring for 8 h, the transparent NFC solution changed into dark-black, which may be attributed to the fact that the DA molecules self-polymerized in the alkaline solution and deposited on the surface of NFC to produce an adherent PDA layer coating on the NFC. According to previous studies, the formation process of PDA underwent complex redox reaction as well as the generation of a series of intermediates and its superior adhesion properties stemmed from the peculiar coexistence of inherent specific structural features (e.g., planar indole units, amino group, carboxylic acid group, catechol or quinone functions, and indolic/catecholic π-systems). On further dropwise adding of AgNO₃ solution, owing to that the catechol moieties presence of the PDA layer could reduce Ag⁺ into Ag atoms, the dark-black suspension turned into yellow without adding any external reducing agent after keeping in the dark for 6 h. According to previous report, the amino and hydroxyl groups of the PDA layer on the surface of NFC acted as anchors for Ag nanoparticles via the atom-by-atom growth with continuous growth.
reduction of Ag⁺ and finally NFC nanofibers were in situ coated with Ag nanoparticles. The SEM image of NFC/Ag suspension (Figure 2b) and its corresponding energy dispersive spectroscopy (EDS) elemental maps of Ag element (Figure 2d) clearly showed that Ag nanoparticles were homogeneously anchored on the surface of NFC entanglements. By sequential centrifugation and washing, free PDA particles were removed and the PDA only existed on the surface of NFC nanofibers. Therefore, no free Ag nanoparticles can be seen in the SEM image of NFC/Ag suspension (Figure 2b). The high-magnification TEM image (Figure 2c) indicated that Ag nanoparticles on the nanofibers were nearly spherical and discrete, with a relatively uniform size (∼30 nm). The homogeneous distribution of Ag nanoparticles coated on the surface of NFC was helpful for the ultimate dispersion of Ag nanoparticles in the NFC/Ag composite films.

Using the above NFC/Ag suspension, we prepared NFC/Ag composite films via a facile vacuum filtration technique. It is found that a small amount of Ag nanoparticle coating had little influence on the film-forming ability and the obtained composite films were intact and freestanding. By controlling the addition of AgNO₃ solution, a series of composite films with different Ag loadings were fabricated and denoted as Agₓ, in which x was the volume fraction of Ag nanoparticles. From TGA results of composite films (Figure S1), we calculated the x values (Table S1) and they were 0.8, 1.4, and 2.0% corresponding to samples Ag0.8, Ag1.4, and Ag2.0, respectively. As shown in Figure 3a, the composite films showed a brown yellow color and the color changed into slightly deeper with the content of Ag nanoparticles.

To explore the structural features of composite films, XRD and XPS patterns of NFC and sample Ag2.0 were comparatively studied. Figure 3b shows the XRD curves of NFC and Ag2.0 composite film. For NFC film, two peaks at 2θ values of 14.5 and 22.6° could be observed on its XRD pattern, which corresponded to the (110) and (200) diffraction planes of NFC, respectively. On the XRD pattern of Ag2.0 film, besides two characteristic peaks of NFC, another two peaks at ∼38.1 and 44.4° could be also obviously seen, which are assigned to the (111) and (200) diffraction planes of Ag crystals, respectively. These results confirmed the Ag nanoparticles coating on the surface of NFC nanofibers, which was in accord with the SEM and TEM observations. The XPS spectra (Figure 3c) showed that only the O and C elements existed on the surface of NFC, whereas Ag elements also existed on the surface of NFC/Ag composite films, which further demonstrated that Ag nanoparticles were in situ coated on the surface of NFC. On the basis of above results, we can conclude that the surface of NFC was decorated with Ag nanoparticles by mussel-inspired chemistry of DA and freestanding NFC/Ag composite films were fabricated via a facile vacuum filtration process.

The SEM images of surface and cross sections of NFC and NFC/Ag composite films were employed to investigate the morphology, as shown in Figure 4. For pure NFC film, its surface was smooth (Figure 4a) and the layer structures...
composed of in-plane oriented NFC nanofibers could be clearly observed (Figure 4b). The well-ordered structure has been derived from layer-by-layer self-assembly of NFC nanofibers during the film-forming process. For the NFC/Ag composite film, its surface image (Figure 4c) showed that Ag nanoparticles were uniformly distributed on the surface and no agglomerates were found, which was benefited from the fact that Ag nanoparticles were coated on the surface of NFC nanofibers in advance. Compared to that of NFC film, NFC/Ag composite film had a relatively loose hierarchical structure (Figure 4d), which may be in relation that the interactions between NFC nanofibers were weakened by the presence of Ag nanoparticles coating.

3.2. Thermal Conductivities of NFC/Ag Composite Films. For next-generation portable and collapsible electronic devices, anisotropic conductive papery films with high in-plane TCs are highly needed, which can dissipate heat from the hot regions along the in-plane direction to prevent neighboring components from being influenced.\textsuperscript{33} For pure NFC film, its in-plane TC was 1.5 W/(m·K), which was higher than that of conventional polymers. This might be ascribed to its own high crystalline structure as well as good alignment of NFC in the film, which were both beneficial for phonon conduction.\textsuperscript{32} For NFC/Ag composite films, their in-plane TCs had obvious enhancement compared to that of NFC film. From Figure 5a, it was found that the TC values increased significantly with the loadings of Ag nanoparticle coating. When the contents of Ag nanoparticles were 0.8, 1.4, and 2.0%, the in-plane TCs of composite films were 2.8, 4.2, and 6.0 W/(m·K), which were 1.9, 2.8, and 4.0 times that of pure NFC film, respectively.

To quantitatively characterize the efficiency of Ag nanoparticles in the composite films, we calculated the TC enhancement per vol % Ag nanoparticles (η) using\( \eta = \frac{TC_{\text{land}} - TC_{\text{Ag}}}{V_f \times TC_{\text{Ag}}} \times 100\% \), where TC and TC\textunderscore Ag are the thermal conductivities of the composites and pure NFC film, respectively, and \( V_f \) is the volume fraction of Ag nanoparticles in composites. The η values were 112, 128, and 150% corresponding to sample Ag0.8, Ag1.4, and Ag2.0, respectively. We compared in-plane TC and η values for sample Ag2.0 with the reported η values for polymer composites with low loadings of various fillers (\( \leq 5 \) vol %). As listed in Table 1, it was found that TC and η values were at high levels at the same filler contents. Such an enhancement in composite films was supposed to benefit from the Ag nanoparticle coating. The 1D nanofibers coated with 0D Ag nanoparticles formed the hierarchical composite films via layer-by-layer assembly. At every layer, the continuous network composed of NFC nanofibers decorated with Ag nanoparticles could easily form thermally conductive pathways (Figure 5b) and therefore the heat dissipated easily along the in-plane direction. Besides in-plane TCs, through-plane TCs of NFC/Ag composite films were also measured (Table S2). It can be found that through-plane TC values also increased with the loadings of Ag nanoparticles. The through-plane TC of Ag2.0 reached 0.8 W/(m·K), which was 3.2 times that of pure NFC film (0.25 W/(m·K)). The less enhancement along the through-plane direction compared to that of in-plane direction might be ascribed to a looser hierarchical structure in the composite films, which was bad for heat transport.

We tested mechanical properties of composite films, and typical stress–strain curves of NFC and Ag2.0 films are depicted in Figure 6. It can be seen that pure NFC film had a high tensile strength (110.4 MPa) and elongation at break (5.1%), which was related to the existence of strong hydrogen and ionic bonding between NFC nanofibers.\textsuperscript{50} Compared with pure NFC film, NFC/Ag composite films might possess decreased mechanical properties, which was due to that the interactions between nanofibers were weakened by the Ag nanoparticle coating. As shown in Figure 6, although that mechanical property of Ag2.0 was inferior to pure NFC film, due to that the loading of Ag nanoparticles was small, the sample Ag2.0 still showed a relatively high tensile strength (55.0 MPa) and elongation at break (2.4%). Moreover, we found that the composite films exhibited good flexibility, as shown in Figure 6 (inset). The relatively high strength and excellent flexibility were helpful for the NFC/Ag composite films to be applied in the flexible electronic devices. We also measured the surface electrical resistivities of NFC and Agx films (as shown in Figure S2). The results found that pure NFC film exhibited electrical insulation of 8.0 × 10\textsuperscript{14} Ω cm, which was in accord with previous study.\textsuperscript{61} As Ag nanoparticle was a good electrically conductive filler, a small amount of the Ag nanoparticle coating led the electrical resistivity of composite film to significantly decrease. For example, Ag2.0 possessed a low resistivity value of 2.7 × 10\textsuperscript{3} Ω cm. Therefore,
the prepared Agx composite films were favorable for thermal management applications where electrical insulation was not strictly required.

To demonstrate the potential application of NFC/Ag composite films as a TMM in electronic devices, the sample Ag2.0 was utilized as the substrate of a light-emitting diode (LED) chip (Figure 7a). Surface temperature variations of NFC and Ag2.0 at the edge and close to the chip with the working time were recorded. As shown in Figure 7b, compared with NFC film, Ag2.0 showed a faster heating rate at the edge. After 300 s, the edge temperature of Ag2.0 increased to 30.6 °C, whereas that of NFC film only increased to 28.1 °C. In contrast, the NFC film showed a higher surface temperature of 49.0 °C than that of Ag2.0 (40.5 °C) at the position close to the chip. Both results confirmed a better heat dissipation ability of Ag2.0 than that of pure NFC film. On the basis of the above results, freestanding flexible NFC/Ag composite films with high TC and strength had great potential for thermal management applications.

**4. CONCLUSIONS**

In summary, we prepared NFC/Ag composite films with high TC at low loadings of Ag nanoparticles using NFC as a starting material via the chemistry of DA and then vacuum filtration. The structure characterizations showed that Ag nanoparticles were homogeneously in situ coated on the surface of NFC nanofibers. A small amount of the Ag nanoparticle coating had little influence on the film-forming ability of NFC, and the freestanding NFC/Ag composite films were obtained via a facile vacuum filtration technique. In the prepared composite films, the continuous Ag-decorated NFC nanofiber structure could easily form thermally conductive pathways along the in-plane orientation and therefore their in-plane TCs improved significantly at low loadings of Ag. Moreover, the NFC/Ag composite films exhibited relatively high strength and excellent flexibility. However, the incorporation of Ag nanoparticles led composite films to possess inferior electrical insulation and the PDA coating inevitably bereaved of film transparency. Therefore, our prepared flexible NFC/Ag composite films with high TCs can serve as a lateral heat spreader in the thermal management applications where electrical insulation or film transparency were not strictly required.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b07249.

- TGA curves of composite films (Figure S1); surface electrical resistivities of NFC and composite films (Figure S2); weight and volume fractions of Ag in the NFC/Ag composite films (Table S1); the density (ρ), specific heat capacity (Cp), thermal diffusivities (α), and the calculated thermal conductivities (TCs) of NFC and composite films (Table S2) (PDF)

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The manuscript was written through contributions of all authors.

**Notes**

The authors declare no competing financial interest.

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**REFERENCES**


(18) Li, X.; Park, W.; Chen, Y. P.; Ruan, X. Effect of Particle Size and Aggregation on Thermal Conductivity of Metal-Polymer Nanocomposite. J. Heat Transfer 2017, 139, No. 024401.
(26) Liimatainen, H.; Ezekiel, N.; Sliz, R.; Ohenjoa, K.; Sirvio, J. A.; Berglund, L.; Hormi, O.; Niinimäki, J. High-Strength Nanocellulose-


