Metal Coordination Bonds Crosslinked Polydopamine/Cellulose Nanofibril Composite Aerogels with Significantly Improved Thermal Stability, Flame Resistance, and Thermal Insulation Properties

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Abstract

Cellulose nanofibril (CNF) aerogels have attracted great interests in recent years due to the low cost, sustainability and biocompatibility of raw CNFs. However, the poor thermal stability and flammable feature of CNF aerogels have limited their wider applications. In this paper, polydopamine/CNF composite aerogels with good comprehensive properties are fabricated by modification of CNF with polydopamine and metal coordination bonds crosslinking. The microstructure and properties of composite aerogels are thoroughly characterized by a variety of tests. It is found that the microstructure of aerogels are more regular and the compressive strength of aerogels are enhanced by the incorporation of polydopamine and Fe^{3+} crosslinking. Importantly, the thermal stability and flame resistance of aerogels are significantly improved, which permit the application of composite aerogels in high-temperature thermal insulation. In addition, the reversible characteristic of metal coordination bonds allows the water induced healing of fractured composite aerogels. This study is expected to provide information for future development of green and high-performance aerogels.

Introduction

Aerogels have attracted great interests in recent years because of their advantages of ultralight weight, ultrahigh porosity, and large surface area, which hold great promising in diverse applications of catalyst, thermal/electrical insulation, adsorbent of wastes, compressible sensor, and so on (Ziegler et al. 2017; Ding et al. 2019; Hu et al. 2019; Shao et al. 2020). However, traditional silica aerogels are commonly characterized by fragility despite their good thermal and electrical properties, which significantly limits their application where mechanical robustness is needed. Therefore, many kinds of robust aerogels constructed from inorganic nanomaterials, such as silica nanofiber (Wang et al. 2020), carbon nanotube (Ozden et al. 2017), graphene oxide (Oh et al. 2021), or MXene (Deng et al. 2019), and organic polymers, such as polyimide (Cashman et al. 2020), polyamide (Williams et al. 2014), poly(vinyl alcohol) (Ma et al. 2017), or polyurethane (Donthula et al. 2017), have been developed recently. All of these aerogels have their own advantages in terms of mechanical, thermal, or electrical properties. However, these aerogels are more or less suffered from problems of cost, complicated processing, suspicious biocompatibility, environmental issues, and so on. As such, many researchers have focused on developing new aerogels with low cost, renewability, safety, easy access and good comprehensive properties.

One of the most frequently investigated aerogels that meet most of the above-mentioned requirements are cellulose nanofibril (CNF) aerogels (Yang et al. 2019; Ahankari et al. 2021; Chen et al. 2021). CNF is typically produced by high-energy homogenization of wood pulp, in which process the delamination or fibrillation of CNF is often assisted by TEMPO oxidation or other chemical treatments (Isogai et al. 2011). Although CNF possesses lower crystallinity and inherent mechanical properties than its cellulose nanocrystal (CNC) counterpart, CNF has much higher aspect ratio (> 200) than CNC. Thus, CNF is able to form physically entangled network at much lower concentration than CNC, which is very promising to lower the density of aerogels. In addition, the chemical treatment of CNF during production endows CNF with rich surface chemistries that could facilitate the further crosslinking of CNF aerogels to enhance

their mechanical performance. For instance, Hsieh et al. crosslinked the CNF aerogel by reacting diisocyanate with the surface hydroxyl function of CNFs, the covalently crosslinked CNF aerogel was then applied in oil absorption (Jiang et al. ; Guo et al. (2018) employed carboxyl compound to crosslink CNF aerogel with the aim of improving its mechanical properties. Therefore, the high aspect ratio and polar surface characteristics of CNFs offer great potential for design of ultralight weight yet robust aerogel. Probably the biggest weakness of CNF aerogels is their poor thermal stability and flammability, which hampers the practical applications of CNF aerogels (Zhao et al. 2021). Incorporating inorganic nanomaterials, such as zinc borate (Cheng et al. 2020), black phosphorus nanosheets (Du et al. 2020), graphene (Guo et al. 2019), and montmorillonite (Wang et al. 2019), to construct composite aerogels is a common strategy to improve the thermal performance of CNF aerogels. However, the presence of these inorganic materials also gives rise to economic, environment, and even safety concerns as that of inorganic aerogels. Therefore, it is still a challenge to fabricate CNF aerogels with good comprehensive properties in a facile and green way.

On the other hand, dopamine is an important biological molecule that present in animals. Since the discovery that dopamine can self-polymerize in alkaline or oxidative conditions that mimic mussel-adhesive proteins (Lee et al. 2007), polydopamine has attracted more and more attentions. The excellent adhesive properties, good biocompatibility and antioxidant properties of polydopamine have encouraged researchers to exploit polydopamine in various biological and surface coating applications (Ryu et al. 2018; Lee et al. 2020; Zhang et al. 2021). Recently, polydopamine has been incorporated into polymer composites to enhance the mechanical, thermal, antioxidant, and UV-shielding properties (Xiong et al. 2014; Xiong et al. 2016; Wang et al. 2017; Fang et al. 2020). In addition, the use of polydopamine as coating or filler to improve the flame retarding property of polymer foam or composites has also been demonstrated due to its good radical scavenging ability (Fang et al. 2020; Cho et al. 2015; Yang et al. 2020). Meanwhile, polydopamine could strongly coordinate with many transition metal ions, such as Fe^{3+} , Zn^{2+} , Cu^{2+} , Ni^{2+} , etc (Wang et al. 2020). These coordination bonds have inspired the design and synthesis of novel bio-mimetic materials with high strength and toughness (Wan et al. 2017; Chen et al. 2019). These works highlight the promising applications of polydopamine in composite materials. However, the combination of polydopamine and CNF in constructing composite aerogel has rarely been reported, and the influence of polydopamine on the thermal and other properties is still to be exploit.

Herein, we report a green and facile approach for the fabrication of polydopamine/CNF composite aerogel (PCA). The dopamine was first in-situ polymerized in CNF suspension, then the polydopamine coated CNF was crosslinked by Fe^{3+} , the PCAs were finally obtained by freeze-drying of the crosslinked hydrogel. The morphology and properties of PCAs were thoroughly investigated. It was found that the mechanical, thermal, and flame retarding properties of CNF aerogels were significantly enhanced by such design. The application of PCAs in high-temperature thermal insulation application was also evaluated. Interestingly, the PCAs show water induced healing capability due to the reversible characteristic of metal coordination bonds.

Experimental Section

Materials

Aqueous dispersion of TEMPO-oxidized CNFs (1.15 wt%) was purchased from Tianjin Wood Spirit Biotechnology Co., Ltd, China. Dopamine hydrochloride, ammonium persulfate ((NH₄)₂S₂O₈) and ferric chloride were purchased from Sinopharm Chemical Reagent Co., Ltd (SCRC). All reagents were used as received and deionized water was used for all experiments.

Synthesis of polydopamine/CNF composite aerogels (PCAs).

In a typical synthesis of PCAs, required amount of dopamine was first added into the aqueous dispersion of CNF. Then (NH₄)₂S₂O₈ (the weight of (NH₄)₂S₂O₈ was 50 % of the weight of dopamine) was added into the mixture and stirred for 3 h in ambient condition. After completion of the polymerization of dopamine, the polydopamine modified CNF was filtered and washed by deionized water for 3 times to remove the impurities. The polydopamine modified CNF was re-dispersed in water with concentration of 2 wt%, and Fe³⁺ was then added to crosslink the polydopamine modified CNF. The obtained crosslinked hydrogel was finally freeze-dried to afford PCAs. The weight ratio of CNF: dopamine was set as 1: 0.1, 1: 0.2, 1: 0.3, 1:0.4, and 1: 0.5, and the resultant PCA was denoted as PCA1, PCA2, PCA3, PCA4 and PCA5, respectively. Pure CNF aerogel prepared by direct freeze-drying of dispersion of CNF was also used for comparison.

Characterizations

Transmission electron microscopy (TEM) images were recorded by JEOL2100F at a voltage of 200 kV. TEM equipped with a high-angle annular dark-field (HAADF) detector was used for the characterization of Fe³⁺ crosslinked sample. Scanning electron microscopy (SEM) images were obtained by FEI SIRION field emission scanning electron microscope. The bulk density of aerogels were obtained from the mass and the volume of regular specimens. The information of porosity, pore size, and surface area of aerogels were obtained by an automated mercury porosimeter (AutoPore IV 9510, Micromeritics, America). The compressive test of aerogels was carried out on an electronic universal testing machine (MTS C44-104) at room temperature with cubic shaped samples. Thermal stability was evaluated on a TA instrument (TG 209 F1, Netzsch) under nitrogen from 30 to 700°C at a rate of 10°C/min. The Limiting oxygen index (LOI) value was obtained by a HC-2 oxygen index meter (Jiangning Analysis Instrument Co., China) according to ASTM D 2863. Thermal conductivity of aerogels were measured using laser thermal conductivity meter (NETZSCH LFA 457) at room temperature. Thermal images were obtained using a thermal image camera (FL-IR A400).

Results And Discussion

Preparation and structures of PCAs.

The synthetic process of PCAs was illustrated in Fig. 1a, dopamine was first in-situ polymerized onto surface of CNF due to the adhesive property of polydopamine, which has been frequently applied for surface modification of various kinds of nanomaterials (Yue et al. 2013; Liu et al. 2013). Then Fe^{3+} was introduced into the mixture to crosslink the polydopamine modified CNFs due to the strong coordination bonds between catechol groups in polydopamine and metal ions. Note that the residual carboxyl groups in TEMPO oxidized CNF could also form coordination bonds with Fe^{3+} , which was also beneficial to the crosslinking of

PCAs (Zou and Chen 2020). However, it is very difficult to identify the contribution of different polar groups on crosslinking of PCAs because of the complex surface chemistry of both polydopamine and CNFs. Thus, the addition amount of Fe^{3+} was set on the basis of total amount of dopamine and CNF. For PCA4, it was found that the optimal Fe^{3+} content was 20 wt%, as the shrinkage of PCA4 was smallest at this weight ratio. Therefore, for the following of this study, the weight content of Fe^{3+} crosslinker was fixed at 20 wt%. Figure 1b shows that with the addition of dopamine and oxidant, the aqueous dispersion of CNF immediately changed from white to pink as the oxidation polymerization of dopamine occurred. The dispersion become dark brown after 3 h of reaction, suggesting the proceeding of polymerization of polydopamine. When Fe^{3+} was added into the dispersion of modified CNF, the dispersion was gelated due to the formation of coordination bonds between metal ions and polar surface groups. The brownish PCAs were finally obtained by freeze-drying of the hydrogels.

The TEM image of pristine CNFs is shown in Fig. 2a. The diameter of CNFs are in the range of 10 to 50 nm with some bundles, and the length of CNFs are as long as tens of micrometers, indicating the high aspect ratio of CNF. After polymerization with dopamine, the high aspect ratio of CNF is preserved, and some small particles are adhered on the surface of CNFs, which are attributed to the polydopamine (Fig. 2b). Figure 2c shows the HAADF-TEM image of Fe^{3+} crosslinked polydopamine modified CNFs. It can be seen that the stripe shaped modified CNFs are crosslinked into sheet-like networks. The EDX-mapping images (Fig. 2d-2f) of crosslinked CNFs present the even distribution of N and Fe elements in the crosslinked network, demonstrating the successful surface modification of CNFs by polydopamine and the homogenous crosslinking points in PCAs.

The microstructure of pure CNF aerogels and PCAs were investigated by SEM characterizations (Fig. 3). All images exhibit typical porous structure of aerogels. However, the porous structure of CNF aerogel is relatively dense as compared to those of PCAs, which we attribute to the high shrinkage of CNF aerogel because there are only physical entanglement or weak van der Waals force among CNFs. With the incorporation of polydopamine, the porous structure of PCAs are more significant with thin sheets interconnected fibrous filaments. The sheets presented in PCAs are attributed to the crosslinked CNF networks or some CNF agglomerates squeezed by ice crystals during freezing step. In addition, it seems that the pore size of PCAs increased with increasing amount of polydopamine. For example, the pores in PCA4 are more regular than PCA1, PCA2, and PCA3 with size about 200 ~ 300 μm , suggesting more polydopamine could provide more crosslinking to maintain the microporous structure of aerogels.

However, the microstructure of PCA5 is not as uniform as that of PCA4 probably due to the uneven distribution of excess polydopamine.

More precise structure parameters, including the density, porosity, average pore size, and surface area of CNF aerogel and PCAs, are compared in Fig. 4 and listed in Table 1. The density of CNF aerogel is about 34.1 mg/cm^3 , which is similar to previous reported CNF aerogels (Yang and Cranston 2014; Wang et al. 2018). The density gradually increases from 41.1 mg/cm^3 of PCA1 to 47.5 mg/cm^3 of PCA5 because of the addition of polydopamine and Fe^{3+} , despite the smaller shrinkage of PCAs as compared to CNF. The porosity of CNF aerogel is also increased with the addition of polydopamine. For example, the porosity of CNF aerogel increases from 94.6 % to 96.6 % in PCA4. This increase is also attributed to the efficient crosslinking of CNF that suppresses the aggregation of CNF and shrinkage of aerogels. As such, the average pore size obviously increases from $163.4 \text{ }\mu\text{m}$ in CNF aerogel to 200.6, 220.1, 224.4, 226.9, and $232.0 \text{ }\mu\text{m}$ in PCA1, PCA2, PCA3, PCA4, and PCA5, respectively. In addition, the surface area of PCAs are in the range of 210.6 to $220.1 \text{ m}^2/\text{g}$, which are also higher than that of CNF aerogel ($193.8 \text{ m}^2/\text{g}$) and similar to other reported crosslinked CNF aerogels (Jiang et al. 2017). The increased porosity and pore size in PCAs are advantageous for thermal insulation application because of more entrapped air inside aerogels.

Table 1
Structure parameters and properties of CNF aerogel and PCAs.

	Density (mg/cm^3)	Porosity (%)	Average pore size (μm)	Surface area (m^2/g)	Compressive strength at 70 % strain (kPa)	T_d ($^{\circ}\text{C}$)	LOI (%)	λ ($\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$)
CNF Aerogel	34.1	94.6	163.4	193.8	43.3 ± 5.8	276.2	18.7	0.042
PCA1	41.1	93.5	200.6	210.6	56.7 ± 4.7	317.1	24.5	0.034
PCA2	43.4	95.7	220.1	217.2	61.8 ± 8.3	341.5	26.3	0.035
PCA3	44.7	95.6	224.4	214.7	104.5 ± 9.2	342.4	28.7	0.031
PCA4	45.2	96.6	226.9	220.1	107.7 ± 10.1	333.7	29.2	0.033
PCA5	47.5	95.9	232.0	218.8	105.8 ± 13.5	345.3	33.1	0.037

Mechanical, thermal and flame retarding properties of PCAs

The mechanical properties of CNF aerogel and PCAs were evaluated by compressive test, as shown in Fig. 5. The CNF aerogel shows typical compressive behavior of soft aerogels. That is, a slowly increased stress in response to deformation at lower strain range, and a fast increasing stress response at large strain. At 70 % strain, the compressive strength of CNF aerogel is 43.3 kPa. It is found that the stress response of PCAs are faster than that of CNF aerogel, indicating the hardening of CNF aerogel by the

reinforcement of polydopamine and crosslinking. As a result, the compressive strength of PCAs are all improved, and the compressive strength at 70 % of PCA4 is obviously increased to 107.7 kPa, corresponding to about 2.5 times that of pure CNF aerogel, demonstrating the good reinforcement effect of our strategy.

The thermal stabilities of CNF aerogel and PCAs were investigated by TGA. Figure 6 shows the TGA and derivative thermogravimetric (DTG) curves. CNF aerogel exhibits a minor decomposition at about 231.3°C, which is attributed to the decomposition of labile side functional groups on CNF. The maximum decomposition temperature (T_d) of CNF aerogel appears at 276.2°C, corresponding to the pyrolysis of CNF backbone. The functionalization of CNF by polydopamine and crosslinking by Fe^{3+} have significantly improved the thermal stability of aerogels. As shown in Fig. 6b, the first minor decomposition peak in CNF is almost disappeared, and the T_d of PCA2 to PCA5 are in the range of 333.7 ~ 345.3°C. Such improved T_d are even more pronounced than some inorganic nanomaterials reinforced CNF aerogels (Guo et al. 2019; Wang et al. 2019). The superior thermal stability of PCAs are attributed to 1) the CNF was coated by polydopamine by in-situ polymerization and the polydopamine acted as physical barrier to retard the decomposition of CNF, and 2) the free radical scavenging ability of polydopamine could eliminate the radicals generated by the breaking of C–C bonds, and block chain-scission depolymerization (Fang et al. 2020; Cho et al. 2015; Yang et al. 2020). The improved thermal stability of PCAs is beneficial to their thermal applications.

We have also evaluated the flame retardancy of PCAs because of the flame retarding property of polydopamine. As presented in Fig. 7a, pure CNF was easily ignited because of its flammable feature, and it was completely burned after removal from flame. In sharp contrast, the PCA4 immediately self-extinguished after removal from flame, visually proving the good flame retardancy of our PCAs. The LOI test was conducted to more quantitatively evaluate the flame resistance of PCAs, as compared in Fig. 7b. Pure CNF aerogel owns low LOI value of 18.7 %. The PCAs possess much higher LOI value even with low content of polydopamine and Fe^{3+} crosslinking. For example, PCA1 has LOI value of 24.5%, and as the polydopamine content was reached 30 wt%, the PCA3 become nonflammable with LOI value of 28.7 %, and the LOI value further increases to 29.2 and 33.1 in PCA4 and PCA5. The scavenging of free radical by polydopamine, thus suppressing fuel supply during combustion is also thought to be the main reason for this enhanced flame resistance of PCAs (Fang et al. 2020; Cho et al. 2015; Yang et al. 2020). Additionally, the catalysis effect of Fe^{3+} on polymer materials during combustion could also contribute to the flame retardancy of PCAs (Zhang et al. 2018; Zhang et

al. 2020), because the more efficient formation of char could act as physical barrier to retard the combustion.

Thermal insulation application of PCAs

The improved thermal stability of PCAs permits their safer operation in some thermal application such as thermal insulation. We first determined their thermal conductivity (λ), as shown in Fig. 8a. The λ of CNF

aerogel is about $0.042 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, which is slightly higher than some previously reported cellulose aerogel due to the higher density of our CNF aerogel (Gupta et al. 2018; Zhang et al. 2021). The λ of our PCAs are in the range of $0.031 \sim 0.037 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, which are generally lower than that of CNF aerogel probably because of the higher porosity and uniform microstructure of PCAs. Then we evaluated the thermal insulation performance of PCAs by using an electric heating platform placed with aerogels (the thickness of all aerogels are about 1 cm), as illustrated in the inset of Fig. 8b. The stabilized temperature of the surface of CNF aerogel and PCAs as a function of platform temperature are compared in Fig. 8b. It is found that when the temperature of heating platform was 100 and 150°C, the temperature of CNF aerogel and PCAs are in the range of 36 ~ 43 and 60 ~ 68°C, indicating similar insulation performance of all the aerogels. However, when the temperature of heating platform was elevated to 200 and 250°C, the temperature of CNF aerogel were increased to 88 and 134°C. While the temperature of PCAs were in the range of 67 ~ 76 and 80 ~ 91°C, respectively, demonstrating the good thermal insulation properties of PCAs even at high temperature. The inferior performance of CNF aerogel is attributed to the deterioration of microstructure or degradation of CNF aerogel because of their inferior thermal stability.

Water induced healing of PCAs

Because of the dynamic nature of metal coordination bonds, we are curious about if the PCAs were able to repair damages. In a preliminary experiment, we cut the CNF aerogel and PCA4 into two halves, and then a drop of water was dropped onto the fracture surfaces, the two halves were then pressed by hand. It is found that the CNF aerogel could not heal by this operation, while the two pieces of PCA4 were firmly adhered together. We attributed the water induced healing of PCA4 to the reversible crosslinking of metal coordination bonds (Xia et al. 2016; Chen et al. 2018). In contrast, the CNF aerogel was mainly formed by physical entanglement, thus could not be healed due to the lack of bonding between two fracture surfaces. Nevertheless, further works are needed to give deep insight into the healing behavior of this kind of dynamic crosslinked CNF aerogels.

Conclusions

This paper reported the synthesis of polydopamine/CNF composite aerogels. The microstructure of PCAs are more regular than pure CNF aerogel, and the porosity, average pore size, and surface area of PCAs are higher than those of CNF aerogel due to efficient crosslinking of PCAs. The compressive strength of PCAs are largely increased due to the reinforcement of polydopamine and Fe^{3+} crosslinking, while the thermal stability and flame resistance of PCAs are significantly improved due to the free radical scavenging ability of polydopamine and catalytic effect of Fe^{3+} on char formation during combustion. The T_d and LOI value of CNF aerogel increase from 276.2°C and 18.7 % to 345.3°C and 33.1 % in PCA5, such great reinforcement effect is even higher than many inorganic materials reinforced CNF aerogels. The better performance of PCAs in high-temperature thermal insulation applications is also demonstrated. This paper is expect to provide a facile and green approach for CNF aerogels with good comprehensive properties.

Declarations

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Informed Consent

Informed consent was obtained from all individual participants included in the study.

Conflict of interest

The authors declare that they have no conflict of interest

Human and animal rights

This article does not contain any studies with human participants or animals performed by any of the authors

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Figures

Figure 1

(a) Schematic illustration of the fabrication process of PCAs. (b) Photographs of the fabrication process of PCAs.

Figure 2

(a) TEM image of CNFs. (b) TEM image of polydopamine modified CNFs. (c) HAADF-TEM image of Fe³⁺ crosslinked polydopamine modified CNFs. (d-f) Distribution of O, N, and Fe element in Fe³⁺ crosslinked polydopamine modified CNFs.

Figure 3

SEM images of (a) pure CNF aerogel, (b) PCA1, (c) PCA2, (d) PCA3, (e) PCA4, and (f) PCA5.

Figure 4

(a) Comparison of the density and porosity of CNF aerogel and PCAs. (b) Comparison of the average pore size and surface area of CNF aerogel and PCAs.

Figure 5

(a) Typical compressive stress-strain curves of CNF aerogel and PCAs. (b) Comparison of the compressive strength at 70 % strain of CNF aerogel and PCAs.

Figure 6

TGA (a) and DTG (b) curves of CNF aerogel and PCAs.

Figure 7

(a) Photographs of the burning of CNF aerogel. (b) Photographs of the burning of PCA4. (c) Comparison of the LOI of CNF aerogel and PCAs.

Figure 8

(a) Thermal conductivity of CNF aerogel and PCAs. (b) Thermal insulation performance of CNF aerogel and PCAs. Inset: Thermal image of heating platform with PCAs.

Figure 9

The water induced healing test of CNF aerogel and PCA4.

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