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Microstructure Defines the Electroconductive and Mechanical Performance of Plant-derived Renewable Carbon Fiber

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Plant-derived lignin polymer has been sought after as a low-cost carbon fiber (CF) precursor, but the underlying mechanisms defining CF performances are still elusive. This study revealed that both electroconductive and mechanical performances of lignin-based CF were synergistically improved by enhancing microstructures through modifying lignin chemistry, which paved a pathway to holistically improve lignin CF quality.

As the second most abundant biopolymer from plant and a major byproduct from paper industry and lignocellulosic biorefinery, 150 to 300 million tons of lignin could be generated annually,¹ representing an immense renewable source for chemicals and materials. Lignin has been extensively sought after as an alternative precursor of polyacrylonitrile (PAN) for renewable and low-cost carbon fiber, due to its prevalent abundance, high carbon content, and low market price (Figure S1).^[1] Despite extensive studies on mechanical properties, few studies investigated the functional properties of lignin carbon fibers for other applications, including its usage as an electrical conductor. Electrically conductive carbon fibers could be broadly used for energy storage applications, including as carbonaceous electrodes in lithium-ion batteries^[2] and as supercapacitors.^[3] It is therefore important to explore different functionalities of lignin-based carbon fibers and to reveal the fundamental mechanisms defining their properties. Nevertheless, the research on electrical conductive performance of lignin carbon fiber is still lacking, probably due to the challenges in the formation of uniform microstructures from the heterogeneous lignin polymers. Lignin heterogeneity will lead to molecular defects such as entanglements, voids and polymer chain ends, preventing the formation of quality crystallite structures.^[4] Such microstructures could be well formed in carbon fibers made from homogeneous precursors like PAN^[5] and their composite with carbon nanotubes (CNT).^[6] We therefore hypothesized that the microstructure of lignin

carbon fiber impacts on the electroconductive and mechanical performances. In order to understand the mechanisms, it is critical to achieve three aspects of fundamental understandings. First, electrical conductivity of lignin carbon fiber needs to be investigated. Second, how microstructure will impact electroconductive and mechanical properties of the resultant lignin carbon fibers needs to be elucidated. Third, the underlying relationship among lignin chemistry, carbon fiber microstructure, mechanical properties, and electrical conductivity needs to be revealed so that both electrical and mechanical properties can be synergistically improved.

In order to achieve these understandings, we adapted fractionation technologies to derive lignin polymer with different chemical characteristics to tailor microstructure formation, electrical and mechanical performances. The most abundant industrial Kraft lignin has been used in the study. Based on lignin chemistry, we have developed a series of novel fractionation methods to derive lignin precursors with improved molecular uniformity.^[7] These fractionation techniques include: 1) biological fractionation using enzyme-mediator system, which partly solubilized the lower molecular weight lignin into water-soluble fraction and derived a water-insoluble lignin fraction;^[1, 8] 2) physical fractionation using dialysis tubes according to lignin molecular weight;^[8] 3) chemical fractionation by tuning lignin hydroxyl groups (-OH) and hydrogen bonding with acidic precipitation.^[9] Among these methods, only biological fractionation using laccase-mediator system simultaneously increased lignin β -O-4 linkage, reduced -OH, and increased lignin molecular uniformity, all of which could improve crystallite carbon and microstructure of carbon fibers. We hereby used the laccase-mediator system to derive lignin fractions with different chemical features to reveal the relationship among lignin chemistry, microstructure and carbon fiber performances. More importantly, low temperature physics of the resultant carbon fibers were investigated to further reveal the mechanisms for microstructure properties and defects. With laccase-mediator fractionation, the water-soluble and water-insoluble fractions were used for carbon fiber manufacturing along with the raw Kraft lignin and pure PAN polymer as the controls. All lignin samples were mixed with PAN at a weight ratio of 50% to 50% for spinning dopes. We for the first time demonstrated the electrical conductivity of lignin-based renewable carbon fibers

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and the synergistic improvement of such electroconductivity with mechanical performances. The underlying mechanism as revealed lay in the enhancement of microstructures such as crystallite content and size in carbon fibers. Modification in lignin chemistry through fractionation accounted for the enhanced microstructures and the synergistically improved carbon fiber performances. The low temperature physics experiment further suggested that amorphous structure accounts for the lower electroconductivity, verifying the discovery in the microstructure.

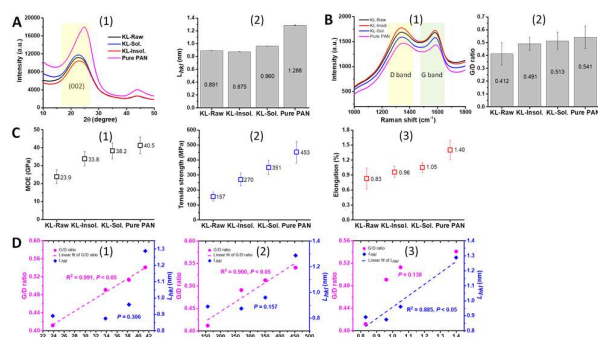


Figure 1. Microstructures as characterized by XRD (A) and Raman spectroscopy (B), and mechanical properties (C) and their linear correlation with crystallite structures (D). A1 and A2 are XRD diffractograms and L_{hkl} , respectively; B1 and B2 are Raman spectra and G/D ratio, respectively; C1 to C3 are MOE, tensile strength, and elongation, respectively; D1 to D3 are linear correlations of mechanical properties to both G/D ratio and L_{hkl} , respectively.

Lignin-based carbon fibers were prepared by a wet-spinning set-up (Figure S6A) followed by thermostabilization and carbonization. The microstructures of lignin-based carbon fiber were analyzed by both X-ray diffraction (XRD) and Raman microscopy. As shown in Figure 1A1, significant intensity associated with diffraction from (002) planes was observed around 2θ of 23.5° in XRD diffractograms.^[10] The crystallite size was calculated from this (002) peak by Scherrer's equation,^[1, 8-9] which showed significant increase in crystallite size (L_{hkl}) for carbon fibers made of water-soluble lignin (0.960 nm) as compared to that of raw Kraft lignin (0.891 nm) (Figure 1A2). Improvement in overall crystallinity was also observed in the G/D ratio of graphite band (G band, 1588 cm^{-1}) and disordered band (D band, 1355 cm^{-1}) in Raman microscopy (Figure 1B1).^[1, 8] As shown in Figure 1B2, G/D ratio for carbon fiber made of water-soluble lignin (0.513) was much higher than that of raw Kraft lignin (0.412). While the crystallite size of the carbon fibers made from water-insoluble lignin/PAN (L_{hkl} 0.875 nm) was similar to that of raw lignin/PAN (L_{hkl} 0.891 nm, Figure 1A2), the crystallinity for carbon fibers from water-insoluble lignin/PAN (G/D ratio 0.491) remained higher than that from raw lignin/PAN (G/D ratio 0.412, Figure 1B2). Overall, these observations supported the hypothesis that lignin fractionation increased crystallinity and crystallite grain size, in particular for water-soluble lignin-based carbon fiber. With the enhanced microstructures, mechanical properties of carbon fibers from enzyme-mediator fractionated lignin were significantly improved. The modulus of elasticity (MOE), tensile strength, and elongation were obtained from the stress-strain

test. As shown in Figure 1C1-1C3, all three mechanical properties, MOE, tensile strength and elongation were increased from 23.9 GPa, 157 MPa and 0.83 % for carbon fiber made of raw Kraft lignin/PAN to 33.6 GPa, 270 MPa and 0.96 % for carbon fiber made of water-insoluble lignin/PAN, and further increased to 38.2 GPa, 351 MPa and 1.05 % for carbon fiber made of water-soluble lignin/PAN, respectively. To further understand how microstructures in carbon fiber could enhance the mechanical properties, correlation analysis was carried out to reveal the relationship between each mechanical property with the crystallite content and size. As shown in Figure 1D1 and 1D2, both MOE ($R^2 = 0.991$, $p < 0.05$) and tensile strength ($R^2 = 0.900$, $p < 0.05$) highly correlated with the crystallite content as reflected by the G/D ratio. Nevertheless, neither MOE nor tensile strength showed significant correlation with the crystallite size of L_{hkl} , as the P value was 0.306 for MOE and 0.157 for tensile strength. For elongation, high correlation with crystallite size (L_{hkl} , $R^2 = 0.885$, $p < 0.05$) was found, yet not with crystallite content (G/D ratio, $p = 0.138$). These data suggested that the improved MOE and tensile strength of carbon fibers could be attributed to the formation of more crystallite in carbon fibers with the enzymatically fractionated lignin as the precursor. In addition, the enhanced elongation could result from the improved crystallite size. The crystallite in lignin-based carbon fiber was primarily the turbostratic carbon, which formed the microstructure in carbon fiber with more or less-bent SP^2 -hybridized crystallite carbon layers.^[1, 10b] As shown in the results, the improvements in the content and size of this turbostratic microstructure have improved various aspects of mechanical properties of the lignin-based carbon fibers. The improved carbon fiber microstructure by lignin fractionation could also increase the electrical conductivity. The electrical conductivity of carbon fibers was measured using a multimeter after fixing the fibers on cover glasses with silver paint (Figure S7). When measuring at room temperature, the electrical conductivity increased 1.12-fold for water-insoluble lignin-based carbon fiber (10725 S/m) and 1.48-fold for water-soluble lignin-based carbon fiber (14096 S/m) as compared to that of raw Kraft lignin-based carbon fiber (9553 S/m), respectively (Figure 2A). Further analysis revealed a high correlation coefficient between electrical conductivity and mechanic performance. As shown in Figure 2B1, both tensile strength ($R^2 = 0.910$, $p < 0.05$) and elongation ($R^2 = 0.907$, $p < 0.05$) had very good linear correlation with electrical conductivity, even though the correlation was not significant between electrical conductivity and MOE ($p = 0.109$). In fact, abundant and well-aligned crystallite carbons at the microstructural level are important for the performance of multi-functional carbon fibers, as such structure could resist fiber deformation under loading and enhance electron transportation along the fiber, thereby rendering carbon fibers superior with mechanical strength and electrical conductivity.^[1, 5a, 5b, 8, 11] Considering that crystallite content and size both impacted mechanical properties, we were expecting to identify the correlation between the microstructures and electrical conductivity. However, p values

of correlation for both G/D ratio ($p = 0.125$) and L_{hkl} ($p = 0.070$) with conductivity were higher than 0.05 (Figure 2B2), which indicated that the electrical conductivity might not linearly correlated with the crystallite content and size. This could be due to the impact of electrical conductivity from other features of fiber microstructure such as orientation of highly anisotropic carbon crystallites and distribution of conductive crystallites in a less conductive amorphous matrix.^[3b, 10b, 12] Even though the p value was not significant at 0.05, the trend is still clear that improved crystallite content and size in these lignin-based carbon fibers correlated with better conductivity. In addition, the electrical conductivity of lignin carbon fiber did not change when its microstructure kept constant even after lignin esterification, as reported by Chatterjee et al.^[13] Considering the correlation between tensile strength and elongation and conductivity, the results highlighted that the mechanical and electrical properties of carbon fibers could be improved synergistically by enhancing turbostratic content.

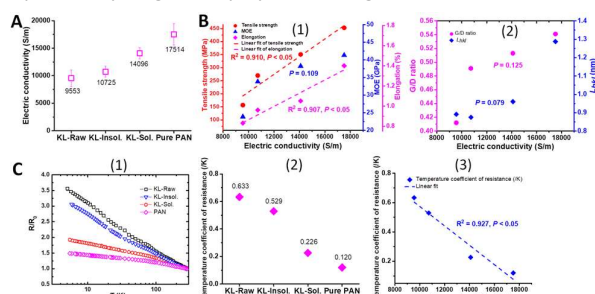


Figure 2. Electroconductivity (A), the correlation relationships between carbon fiber properties (B), and temperature dependence of normalized electrical resistance (R/R_0) of carbon fibers from 300K (room temperature) to 4.2K (C). B1 and B2 are correlations between electroconductivity and mechanical properties, and electroconductivity and crystallite structures, respectively. C1 to C3 are R/R_0 against logarithmic temperature, temperature coefficient of resistance (α), and the linear correlation between α and electroconductivity, respectively. R_0 is resistance at 300K that used as the base of normalized resistance.

In order to further understand the mechanism of electrical transport in lignin-derived carbon fibers, the temperature-dependent resistance (R) of different carbon fibers was measured from 300 K to 4.2 K. The normalized temperature-dependent resistance (Figure 2C1) follows simple logarithmic temperature dependence over a broad temperature range as below,

$$R(T)/R(300\text{ K}) = \beta - \alpha \ln T \quad (\text{Equation-1})$$

where β is the intercept, α is the temperature coefficient of resistance ($/K$) and T is temperature (K), suggesting a single transport mechanism across this temperature range.

The resistance of all carbon fibers increased as the temperature decreased, indicating the semiconducting electrical transport, rather than metallic behavior.^[14] Similar logarithmic temperature dependence has been observed in the electrical conductivity of a number of disordered low-dimensional systems.^[14-15] One proposed mechanism for such behavior was weak localization due to coherent electron backscattering.^[15a] However, the relative increase in resistance in our carbon fibers at 4.2 K relative to 300 K (256.0 %, 205.7 %, 92.4 % and 48.8 % for raw Kraft lignin/PAN, water-insoluble

lignin/PAN, water-soluble lignin/PAN and pure PAN, respectively) were too large to be accounted for by weak localization.^[12] An alternative mechanism proposed in systems with magnetic impurities was the Kondo effect.^[15b] However, this mechanism can be excluded since carbon fibers in our study had only trace amount of magnetic impurities (data not shown). A more likely explanation for negative logarithmic temperature dependence of electrical resistance is associated with the microstructure of our carbon fibers.^[16] Carbon fibers can be modeled as network of small graphite crystallites embedded in a matrix of disordered amorphous carbon.^[17] In this amorphous region, atoms and molecules can have a number of nearly degenerate configurational states separated by low-energy barriers, similar to those found in amorphous alloys.^[14] These low-energy barriers could form two-level states from which conduction electrons will scatter, resulting in logarithmic temperature dependence in the resistance.^[14, 18] In support of this hypothesis, the temperature coefficient of resistance (α) was significantly reduced from raw Kraft lignin/PAN carbon fiber ($\alpha = 0.633$) to water-soluble lignin/PAN carbon fiber ($\alpha = 0.226$), as could be expected if grain sizes and overall crystallinity increase, and the role of electrical transport through amorphous regions lessens (Figure 2C2). Moreover, the electroconductivity had a linear negative correlation with α ($R^2 = 0.927$, $p < 0.05$, Figure 2C3), which is consistent with the proposed hypothesis, as a decrease in the amorphous component would be anticipated both to increase overall electroconductivity and to decrease the observed temperature-dependence due to electron transfer through that amorphous region. Overall, the discovery clearly indicated that the improvement of electroconductivity in lignin-based carbon fibers heavily depends on the increases in content and size of crystallite structures as well as the reduction of amorphous regions.

The enhancement of microstructures and both electrical and mechanical performances of the lignin-based carbon fibers actually lies in the improvement of precursor chemistry, where the heterogeneity of the lignin polymer with diverse chemical linkages, functional groups, molecular weight and polydispersity (Figure S1f) could hinder the microstructures formation in carbonization and graphitization of lignin carbon fibers, resulting in low mechanical strength, poor electrical conductivity, and limited application.^[18, 19] We have revealed before that enzyme-mediator fractionation decreased lignin – OH, increased β -O-4 linkage, and improved molecular uniformity, which could enhance the mechanical properties of lignin-based carbon fiber.^[1] In this study, the electrical conductivity of carbon fibers was synergistically improved with the mechanical properties through modifying lignin chemistry. The improved lignin heterogeneity could enhance the intermolecular interactions between lignin and PAN and improve the molecular alignment/orientation to reduce the defects of polymer entanglements, voids and chain ends in fibers, which further enhances the formation of crystallite microstructure during carbonization.^[1, 4a, 20] Such enhanced microstructures as characterized by XRD and Raman spectroscopy synergistically improved the electrical

conductivity and mechanical performances of lignin-based carbon fibers. Additionally, we further analyzed the changes of -OH in different lignin interunitary linkages to understand the fundamental mechanisms of how laccase-mediator reduced lignin heterogeneity. ^{31}P NMR is a powerful tool to analyze the existence of lignin -OH and thereby to demonstrate the reaction mechanism.^[21] Under the laccase-mediator system, lignin could go through benzylic hydrogen abstraction, phenolic hydrogen abstractions, lignin degradation, and/or repolymerization.^[22] As shown in Figure S2, the aliphatic -OH (Alk-OH) in lignin was significantly decreased after laccase-mediator treatment, indicating that lignin with the phenolic end groups (phenolic lignin) underwent the benzylic hydrogen abstractions with the conversion of Alk-OH on C_{α} position into carbonyl groups (Figure S2H-a). Meanwhile, the aromatic -OH (Ar-OH) was also significantly decreased in laccase-mediator fractionated lignin (Figure S2C). This decrement in Ar-OH could be rendered by the phenolic hydrogen abstractions followed by the C_1 - C_{α} aryl-alkyl cleavage, which could yield p -quinones products (Figure S2H-b). The loss of small oxidized molecules like p -quinones could reduce the Ar-OH in both water-soluble and water-insoluble lignin fractions.^[22c] In addition, the content of β -5 linkage in the water-soluble lignin was found to be increased by laccase-mediator treatment,^[1] and we further found that the Ar-OH content in β -5 linkage was decreased in ^{31}P NMR analysis (Figure S2D). All these data indicated that the repolymerization of β -5 by oxidative coupling could occur in water-soluble lignin. The reduced Ar-OH content in β -5 could be rendered by the re-aromatization that forms α -O-4 links. The removal of the water-soluble lignin could leave water-insoluble lignin with higher β -O-4 profile as compared with raw lignin. Overall, all these reactions under the laccase-mediator system have concurrently reduced Kraft lignin heterogeneity, which could reduce the molecular defects involving polymer entanglements, voids and chain ends,^[1, 4a, 20] resulting in enhanced microstructure in carbon fiber and synergistically improved the electroconductive and mechanical properties. In summary, renewable carbon fiber with improved electrical conductivity and mechanical performance has been fabricated from Kraft lignin. The study has for the first time revealed that electrical conductivity of lignin-based carbon fiber can be enhanced by modifying lignin chemistry with enzyme-mediator fractionation. Moreover, such electrical conductivity was found to correlate to the mechanic properties of carbon fibers and can be synergistically improved with the mechanical properties. The underlying mechanism as revealed by XRD and Raman spectroscopy suggested that the enhancement of microstructures such as crystallite content and size accounted for the synergistic improvement in electrical conductivity and mechanical performance. This study thus demonstrated the fundamental relationship between lignin chemistry, carbon fiber microstructure and its properties of lignin-based carbon fiber. Such synergistic improvement in carbon fiber mechanical and electroconductive properties by enhancing microstructure through regulating lignin heterogeneity enabled the multiple functions of the lignin-based carbon fibers, which could therefore open new avenues for their applications like

carbonaceous electrode materials in energy storage devices. The fundamental study of the underlying mechanism could further guide the development of processing technologies to tailor lignin chemistry for superior carbon fibers and thus profoundly impact renewable lignin carbon fiber production.

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Conflicts of interest

The authors declare no competing financial interests.

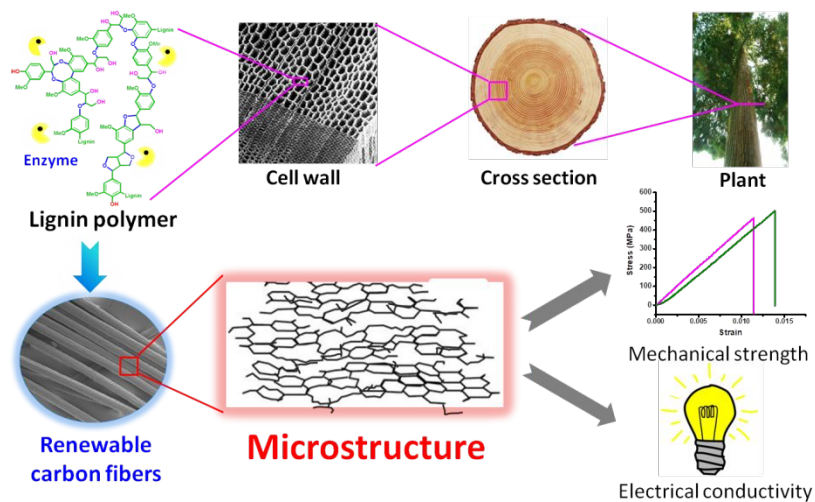
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Plant-derived lignin polymer has been enzymatically fractionated to tune its chemistry for making renewable carbon fiber, both electrical conductivity and mechanical properties of which were found to be defined by the formed microstructures.