Physicochemical Properties of Nanocellulose Isolated from Cotton Stalk Waste

Ming Li,* Beihai He, Yiyi Chen, and Lihong Zhao*

ABSTRACT: In recent years, nanocellulose has become an attractive and high-value-added product. The cotton stalk is a waste product with a high cellulose content. Therefore, nanocellulose can be isolated from the cotton stalk. Properties of nanocellulose are affected by its nanoscale. In this study, the characteristics of cellulose in nanoscale were investigated. A series of cotton stalk nanocelluloses were prepared by sulfuric acid hydrolysis to study their physicochemical properties and the differences of nanocelluloses on different nanoscales. The obtained nanocelluloses were analyzed by atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TA), and X-ray diffractometry (XRD). From the morphology analysis, the mean length and width of nanocelluloses were decreased to 90.5 and 7.0 nm, respectively. From the FTIR analysis, with the particle size decreasing, hydrogen bonds were broken and recombined. Acid hydrolysis mainly acted on intramolecular hydrogen bonds of cellulose macromolecules, especially on O(3)H···O(5) bonds. The crystal arrangement model of nanocellulose was investigated. From the TA analysis, the thermal property was decreased with a reduction of nanocellulose particle size. The CrI of the cotton stalk nanocellulose was the highest at up to 87.10%. The differences of cotton stalk nanocelluloses give significant changes to physicochemical behaviors at the nanoscale. The research would provide a theoretical basis for the future application of nanocelluloses.

1. INTRODUCTION

Environmental problems have resulted in a growing interest in renewable resources and biodegradable polymers. Lignocellulosic biomass becomes increasingly significant. Lignocellulosic biomass is a renewable carbon resource on earth, and interests have increased for producing cellulosic and nanocellulosic materials. Lignocellulosic biomass includes woods, agricultural byproducts, dedicated energy crops, and grass. Of the many agricultural wastes, the cotton stalk is one of the most abundant agricultural residues in cotton-producing countries such as the United States, China, India, etc. Cotton stalk was once known as a semi-wood fiber raw material, and its major components are cellulose, hemicellulose, and lignin. Compared to other raw agricultural wastes, cotton stalk fiber is more advantageous. In practice, cellulose could be converted and processed into nanocellulose, pulps, cellulose acetate, dissolving pulp, mannitol, microcrystalline cellulose, furfural, cellulose ethanol, and so on. To increase the revenue from the cotton stalk and maximize cellulose utilization, producing a high-value-added product is considered a significant choice.

Nanocellulose is an attractive and high-value-added product that has a broad range of applications from an industrial, technological, and academic perspective. It has unique characteristics such as high tensile strength, mechanical robustness, low weight, high surface area, biodegradability, hydrophilicity, and tunable optical properties. Nanocellulose is usually used as a reinforcing agent. For example, the tensile strength of polyvinyl alcohol films increased with low filler nanocellulose loadings. And it proved that nanocellulose could not only build a reinforcing network but also support the hierarchical 3D conductive network in a natural rubber matrix. Furthermore, nanocellulose could improve the characteristics of poly(lactic acid) and poly-3-hydroxybutyrate-co-3-hydroxyvalerate. Nanocellulose extraction techniques include mechanical extraction, electrospinning technique, acid hydrolysis, TEMPO, etc. Among several methods for producing nanocellulose, acid hydrolysis is the most well-known method. Earlier studies about nanocellulose mainly focused on the technology of extraction, separation, and manufacturing methods, and little was found in the literature on the typical physicochemical differences of cotton stalk cellulose in nanoscale. The direct evidence of the relationship...
between hydrogen bonding interactions and property enhancement of cellulose nanocrystal-based bionanocomposites had been proven. The formation of hydrogen bonds and nanosized cellulose was the main factor that contributed to the final properties of biocomposites. Various nanocelluloses of different sizes could be blended with biomaterials to reinforce the physicochemical characterizations. Particle size affects the bioactivity, hydrophilicity, and mechanical properties of bioactive glass-reinforced polycaprolactone composites. The size of nanocellulose affects its physicochemical properties, and it is needed for users to distinguish the appropriate products. Investigation of cellulose supramolecular structure changes and different physicochemical properties is significant.

There are few works of literature that reveal the nanocellulose properties isolated from cotton stalk and characterization of nanocellulose in nanoscale. Therefore, this study aims to obtain nanocellulose from the cotton stalk and assess the physicochemical properties of nanocellulose. In this work, nanocellulose was isolated from cotton stalk by sulfuric acid. Physicochemical properties of different sizes of nanocellulose were analyzed by AFM, TA, FTIR, and XRD.

2. RESULTS AND DISCUSSION

2.1. AFM Analysis. When pulps are treated with sulfuric acid, the most accessible part (amorphous region) of the fiber hydrolyzes first. It digests rapidly upon contact with the acid. The glycosidic bond between cellulosic chains breaks down, and cellulosic chains shorten. AFM, a widely used method for analyzing the surface of cellulose, is adopted for analyzing the shape and size of nanocellulose samples. The AFM observations are shown in Figure 1. The lengths of NC-1, NC-2, and NC-3 are ~200, ~500, and ~1 μm, and their mean lengths are 90, 229, and 644 nm, respectively. The mean widths of NC-1, NC-2, and CN-3 are 7.0, 12.1, and 19.2 nm, respectively (as shown in Table 1). The NC-1, NC-2, and NC-3 samples have rod-like shapes and smooth surfaces. From the AFM analysis, the particle size of NC samples can be controlled by the acid and reaction time. As the reaction time increased, the samples showed an outward trend of being hydrolyzed by the acid. Therefore, the longer the reaction time of acid hydrolysis was, the smaller the sample size became.

2.2. FTIR Analysis. The FTIR spectra of NC-1, NC-2, and NC-3 samples are given in Figure 2. The absorption bands and their assigned functional groups are shown in Table 2. Compared with prior literature, the FTIR spectrum of NC-3 is similar to microcrystalline cellulose.

As shown in Table 2, the broad peaks in the range of 3500–3300 cm⁻¹ are attributed to −OH stretching and intermolecular hydrogen bonding. The peaks around 1640–1650 cm⁻¹ are assigned to −OH stretching. It is indicative of the absorption of water by cellulose. The peaks located at 1460–1410 cm⁻¹ are due to −CH₂ vibration and C–H stretching. And these peaks are assigned to the crystallinity of cellulose. The fitted reduction of peaks in the region of 1167–1160, 1112–1114, 1064–1073, and 1032–1036 cm⁻¹ is shown in Figure 3. The crucial process of isolating nanocellulose is to open the H-bonded structure and break the glycosidic linkage. As a result, the curves observed from the 1200–1000 cm⁻¹ region of the FTIR spectrum are shaped differently. As shown in Figure 3, the results showed that in the range of 1167–1032 cm⁻¹, the absorption peak decreased with the decrease of nanocellulose particle size. And acid mainly attacks the −OH and C–O–C groups. The band around 1160 cm⁻¹ is assigned to the C–O–C glycosidic ether band. As shown in Figure 3, the intensity of peaks was decreased with the decreasing size in CN-1 and CN-2. It reveals that the peaks in the range of 1167–1032 cm⁻¹ are typically amorphous regions or degradable crystalline regions. And it could be degraded in the acid hydrolysis of cotton stalk cellulose process to obtain nanocellulose. The peaks at 900–896 cm⁻¹ are attributed to C–O–C vibration.

The hydrogen bond has a considerable influence on the properties of nanocellulose. The parameters of various hydrogen bonds that appeared at wavenumbers of 3800–3000 cm⁻¹ are shown in Table 3. The intramolecular hydrogen bonds for O(3)H···O(5) and O(2)H···O(6) are located at 3455–3410 and 3375–3340 cm⁻¹. And the intermolecular hydrogen bond O(6)H···O(3′) is located at 3310–3230 cm⁻¹.

In this study, the FTIR fitted peaks located at 3540–3510 and 3340–3390 cm⁻¹ represent the intramolecular hydrogen bonds for O(2)H···O(6) and O(3)H···O(5), respectively. The intermolecular hydrogen bonds for O(6)H···O(3′) are located at 3114–3230 cm⁻¹. As shown in Table 3, the contents of hydrogen bonds are changed obviously due to the different particle sizes. For example, the contents of O(2)H···O(6) for NC-1 and NC-2 are increased by 6.59 and 5.59% compared with NC-3, respectively. And the contents of O(3)H···O(5) bonds are decreased by about 8–10%. The intermolecular

Table 1. Particle Size of Nanocellulose Isolated from Cotton Stalk

| Sample | Average Length (nm) | Average Width (nm) | Ratio |
|--------|---------------------|--------------------|-------|
| NC-1   | 90.5                | 7.0                | 12.9  |
| NC-2   | 270.4               | 12.1               | 22.3  |
| NC-3   | 664.9               | 19.2               | 34.6  |
hydrogen bonds are increased by 1.69 and 4.34% compared with NC-3, respectively. It also indicates that the O(2)H...O(6) bonds are easier to form. And the O(3)H...O(5) bonds are partially fractured during an acid attack. The intramolecular hydrogen bonds for O(6)H...O(3') are more stable during acid hydrolysis. A possible examination is that the cellulose structure becomes relatively loose due to the acid attack, so the cellulose chains get together to form new intermolecular hydrogen bonds. And the result also indicates that the acid hydrolysis mainly acted on O(3)H...O(5) bonds. In addition, the bond energy of hydrogen bonds almost increases with the hydrolysis mainly acted on O(3)H...O(5) bonds. And the result also indicates that the acid cellulose chains get together to form new intermolecular structure becomes relatively loose due to the acid attack, so the acid hydrolysis. A possible examination is that the cellulose

| bands (cm\textsuperscript{-1}) | assigned functional groups of cellulose |
|-------------------------------|---------------------------------------|
| 3600–3300                     | –OH stretching                        |
| 2900–2905                     | C–H stretching vibration\textsuperscript{26} |
| 1640–1650                     | –OH stretching\textsuperscript{31}     |
| 1460–1410                     | –CH\textsubscript{2} vibration; C–H stretching\textsuperscript{22} |
| 1167–1160                     | –OH bonding; C–O–C stretching\textsuperscript{31} |
| 1112–1114                     | C–O stretching                        |
| 1064–1073                     | C–O stretching; C–O–C symmetric bonding\textsuperscript{32} |
| 1032–1036                     | C–O/C–C stretching\textsuperscript{33} |
| 900–896                       | C–O–C vibration\textsuperscript{34}; C–H rocking vibration\textsuperscript{29} |

due to the dehydration of absorbed water.\textsuperscript{30} A sharp reduction of mass is observed in the second stage (141–400 °C). In this stage, the cellulose chain and chemical bonds such as C–C, C–O, and C–H are broken, leading to the dehydration, depolymerization, and decomposition of cellulose. In the last phase (400–500 °C), the solid residues form. As seen from Figure 4 and Table 4, nanocellulose samples show noticeable differences in thermal performance. The onset decomposition temperature of NC-1 is 179.1 °C, which is lower than NC-2 and NC-3 and different from earlier research (245 °C)\textsuperscript{15} according to its dimensions. Furthermore, NC-1 also presents lower decomposition temperature at T\textsubscript{\text{onset}} and T\textsubscript{\text{max}} when compared to NC-2 and NC-3. Interestingly, the T\textsubscript{\text{onset}} for CN-1 is the highest at up to 377.3 °C. For NC-2, its thermal performance is between NC-1 and NC-3. The NC-2 sample obtained two DTG peaks during 200–300 °C. It is a prominent feature that distinguished it from the other two samples. NC-3 showed the typical character of microcrystalline cellulose in thermal properties. T\textsubscript{\text{onset}} of NC-3 is 288.9 °C, which is similar to microcrystalline cellulose from roselle fibers\textsuperscript{34} and soybean hulls.\textsuperscript{27} T\textsubscript{\text{max}} of NC-3 is 311.7 °C, which is the lowest among all samples and is close to oil palm microcrystalline cellulose.\textsuperscript{29} A close inspection of the DTG curves also presents that the degradation peak temperature of NC-3 occurred at 306.2 °C (T\textsubscript{\text{max}}). It was reported that the first stage of degradation of cotton stalk nanocellulose occurred at a temperature of 235 °C, which was similar to CN-2 in this study.\textsuperscript{12} It is reported that the crystal size might affect the onset decomposition and degradation temperature.\textsuperscript{31} In this study, the results confirm this conclusion. In addition, the residual weight of NC-2 is higher than that of NC-1 and NC-3. The results also prove that cellulose crystal size affects its thermal properties. The thermodynamic property follows the sequence NC-1 < NC-2 < NC-3. Overall, the comprehensive thermal property is decreased with a reduction of nanocellulose particle size.

2.4. Nanocellulose Crystal Model. The smaller the scale of cotton stalk nanocellulose is, the more accurate it is to show the arrangement model of the cotton-stalk-based nanocellulose chain. In this paper, CN-1 is selected as the typical sample to analyze the nanocellulose chain arrangement model of cotton.
Figure 3. Part of fitted curves of FTIR spectra of samples: (a) NC-1, (b) NC-2, and (c) NC-3.

Table 3. Parameters for Hydrogen Bonds in the Nanocelluloses

|      | fitted peak | hydrogen bond   | $r^2$   | wavenumber (cm$^{-1}$) | content (%) | bond energy (kJ/mol) | bond length (Å) |
|------|-------------|-----------------|---------|------------------------|-------------|---------------------|-----------------|
| NC-1 | i           | O(6)H···O(3$'$) | 0.9742  | 3114.1                 | 20.34       | 2.19                | 2.71            |
|      | ii          | O(3)H···O(5)    |         | 3340.0                 | 38.88       | 1.27                | 2.76            |
|      | iii         | O(2)H···O(6)    |         | 3535.0                 | 40.78       | 0.47                | 2.80            |
| NC-2 | i           | O(6)H···O(3$'$) | 0.9893  | 3199.2                 | 22.97       | 1.84                | 2.73            |
|      | ii          | O(3)H···O(5)    |         | 3381.1                 | 37.25       | 1.10                | 2.77            |
|      | iii         | O(2)H···O(6)    |         | 3539.1                 | 39.78       | 0.45                | 2.80            |
| NC-3 | i           | O(6)H···O(3$'$) | 0.9970  | 3210.5                 | 18.65       | 1.80                | 2.73            |
|      | ii          | O(3)H···O(5)    |         | 3359.6                 | 47.17       | 1.19                | 2.76            |
|      | iii         | O(2)H···O(6)    |         | 3512.1                 | 34.19       | 0.56                | 2.80            |
The X-ray diffraction pattern and peak separation of CN-1 sample are shown in Figure 5.

There are three reflections: a shoulder with two reflections in the region 2θ = 14 to 17° (10 and 110 planes) and one peak at 2θ = 22.46° (002 plane). The values of CrI, L, and d-spacing of CN-1 are shown in Table 5.

The CrI of nanocellulose was different for various raw materials. The CrI of the sweet lime was 89.6%, and that of the CN-1 sample obtained from the cotton stalk was up to 87.10%. The high CrI (%) was the similarity between this study’s nanocellulose and other cotton stalks’ nanocellulose (86.3%) in sulfuric acid extraction. The differences between the nanocellulose of this study and other industrial textile cotton waste nanocelluloses were mainly attributed to the fact that the raw materials were taken from different parts of the cotton plant. It was reported that there were morphological differences for nanocellulose isolated from cotton and cotton stalk. The d-spacing of the CN-1 is substantially the same as that of the textile cotton waste, date palm, the eucalyptus wood pulp, and the plum seed shells. The crystal model of cotton-stalk-based nanocellulose is shown in Table 5, as follows: L (the crystallite size) in 1̅0, 110, and 002 planes was 4.25, 4.26, and 4.30 nm; d-spacing was 0.60, 0.53, and 0.40 nm, respectively. It could help understand the cotton stalk nanocellulose, providing a basis for further application and designing nanocellulose-based materials from the molecular scale.

3. CONCLUSIONS

In this paper, nanocellulose was isolated from cotton stalk by acid hydrolysis and was characterized by FTIR, AFM, XRD, and TA. The results showed that nanocellulose had rod-like shapes and a smooth surface. The acid hydrolysis acted on the internal chemical bonds of cellulose macromolecules, especially for O(3)H···O(5) bonds. With the particle size decreasing, hydrogen bonds broke and recombined. The nanocellulose size affected thermal properties. Compared with all samples, the comprehensive thermal property was decreased with a reduction of nanocellulose particle size. The CrI of nanocellulose obtained from the cotton stalk was up to 87.10%. The

Table 4. Thermal Property Parameters of Nanocellulose Samples

| samples     | T onset (°C) | T10  (°C) | T50  (°C) | T max1 (°C) | T max2 (°C) | residual weight (%) |
|-------------|--------------|-----------|-----------|-------------|-------------|---------------------|
| NC-1        | 179.1        | 185.7     | 377.3     | 187.3       |             | 33.5                |
| NC-2        | 198.0        | 217.5     | 369.5     | 225.7       | 289.6       | 40.2                |
| NC-3        | 288.9        | 274.1     | 311.7     | 306.2       |             | 26.4                |

“TGA onset decomposition temperature. bTGA temperature at 10% weight loss. cTGA temperature at 50% weight loss. dDTG maximum temperature. eTGA charred residue weight at 550 °C.

Figure 4. Typical TGA (a) and DTG (b) curves of nanocellulose samples.

Table 5. Parameters of the Crystal Model of Nanocelluloses from Various Resources

| sample                               | CrI (%) | L (nm) | d-spacing (nm) | r^2 |
|--------------------------------------|---------|--------|----------------|-----|
|                                      |         | 10     | 110            | 200 |     |
|                                      |         | 10     | 110            | 200 |     |
| CN-1                                 | 87.10   | 4.25   | 4.26           | 4.30| 0.60 | 0.53 | 0.40 | 0.98 |
| industrial textile cotton waste      | 81      | 5.51   | 5.18           | 6.57| 0.60 | 0.54 | 0.40 |       |
| date palm                            | 83      | 2.98   | 3.01           | 4.35| 0.60 | 0.53 | 0.39 |       |
| sweet lime pulp                      | 89.6    | 4.25   | 4.26           | 4.30| 0.60 | 0.53 | 0.40 |       |
| eucalyptus wood pulp                 | 56      | 2.98   | 3.01           | 4.35| 0.60 | 0.53 | 0.39 |       |
| plum seed shells                     | 54.0    | 4.25   | 4.26           | 4.30| 0.60 | 0.53 | 0.40 |       |
crystal model of the cotton-stalk-based nanocellulose was shown as follows: \( l \) in 10, 110, and 002 planes was 4.25, 4.26, and 4.30 nm; \( d \)-spacing was 0.60, 0.53, and 0.40 nm, respectively. This study will guide further research work in the field of nanocellulose isolated from the cotton stalk.

4. MATERIALS AND METHODS

4.1. Materials. The raw cotton stalk was collected from the Changji Hui Autonomous Prefecture (Xinjiang, China), and its chemical composition is shown in Table 6. Sulfuric acid and hydrogen peroxide (30%) were purchased from the Guangzhou Chemical Reagent Factory (Guangzhou, China). Stabilized chlorine dioxide was brought from the Huashi Pharmaceutical Company (Weifang, China). Sodium sulfide, sodium hydroxide, and sodium carbonate were purchased from Tianjin Yongda Chemical Reagent Co., Ltd., China. All of the other chemicals were from commercial sources.

4.2. Preparation of Nanocellulose. The cotton stalk pulps were cooked and bleached in the laboratory. The Kraft cooking process was completed in a laboratory digester under the following conditions: 23% active alkali, 25% sulfidity, a solid-to-liquid ratio of 1:15 (w/v), a temperature of 160 °C, and a duration of 3 h. The pulp obtained was then washed and screened. Stabilized chlorine dioxide was used to bleach cotton stalk pulp four times at pH 3 to 4 ranging from 95 to 100 °C for 1 h and then washed with distilled water until neutral pH. MCC (microcrystalline cellulose) was isolated under the cooking process was completed in a laboratory digester under following conditions: 1.5 mol/L HCl, 90 °C, 60 min, and a solid-to-liquid ratio of 1:10 (w/v). The acid hydrolysis was performed at 50 °C using 15 mL of H\(_2\)SO\(_4\) (65 wt %) for each gram of MCC to prepare different sizes of nanocellulose samples marked as NC-1, NC-2, and NC-3 by acid hydrolysis within different hydrolysis reaction times (40, 50, and 60 min), respectively. The main process after the acid reaction was as follows: (1) A 10-fold amount of cold distilled water was added to terminate the acid hydrolysis process. (2) The obtained suspension was allowed to stand for 10 h to separate the layers, and the lower layer of the liquid was taken to dialyze against water for 4 days until the constant pH was neutral. (3) The samples were collected, homogenized, concentrated, and stored at 4 °C.

4.3. Characterization. The chemical structure changes with nanocellulose size were analyzed using FTIR. The FTIR spectra of NC-1, NC-2, and NC-3 samples were acquired using 32 scans with a Vector 33 spectrometer (Bruker, Ettlingen, Germany) in the range of 400 to 4000 cm\(^{-1}\). The dried samples were mixed with potassium bromide (Kermel, Tianjin, China) and pressed. Deconvolution of the spectra (3600–3000 and 1200–1000 cm\(^{-1}\)) was performed by the Peakfit software (Systat Software, San Jose, USA) in conjunction with the Gaussian distribution function. After deconvolution, bond energies (E) and bond lengths (R) of different hydrogen bond models were calculated using eqs 1 and 2, respectively.

\[
E_H = \frac{v_0 - v}{kT}
\]

(1)

where \( v_0 \) was the standard free hydroxyl (−OH) frequency (3650 cm\(^{-1}\)), \( v \) was the sample hydroxyl (−OH) frequency, and \( k \) was constant (3.82 × 10\(^{-3}\) kJ\(^{-1}\)).

\[
\Delta v = v_0 - v
\]

(2)

where \( v_0 \) was the stretch vibration frequencies of hydroxyl at 3600 cm\(^{-1}\) and \( v \) was the sample hydroxyl (−OH) frequency.

The crystallinity index (CrI) was analyzed using a D8 ADVANCE X-ray diffractometer (XRD, Bruker Corporation, Ettlingen, Germany) with Cu K\(\alpha\) radiation (\( \lambda = 1.54 \) A) at 40 mA and 40 kV. The scattering angle (2\( \theta \)) range and step width were 5 to 60° and 0.02°, respectively. The CrI was calculated using eq 3.

\[
\text{CrI} = \left( \frac{I_{002} - I_{am}}{I_{002}} \right) \times 100\%
\]

(3)

where \( I_{002} \) was the peak intensity of the (002) lattice plane at a 2\( \theta \) of 22.5° and \( I_{am} \) was the peak intensity of the amorphous domain at a 2\( \theta \) of 18.5°. The d-spacings were calculated by Bragg’s equation, and the crystallite size was calculated from the Scherrer equation (eq 4).

\[
L = \frac{k\lambda}{\beta \cos \theta}
\]

(4)

where \( L \) was the crystallite size (nm), \( k \) was 0.94, \( \lambda \) was 0.15418 nm (X-ray wavelength), \( \beta \) was the full width at half-maximum of the lattice plane reflection (FWHM) in radian, and \( \theta \) was the corresponding Bragg angle (reflection angle).

A TA Instruments Q500 thermogravimetric analyzer (New Castle, USA) was used to characterize the thermal stability of the samples. Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) were conducted in a nitrogen flow and at a constant heating rate of 10 K/min from 30 to 550 °C. The morphological characterization was obtained by AFM (PicoForce, Veeco, USA). Samples were diluted to 0.001 wt %, dropped on the washed mica tablets with a pipette, and measured after drying. And a suitable area was selected for scanning. All AFM images collected had a 512 × 512 pixel size.

**AUTHOR INFORMATION**

**Corresponding Authors**

Ming Li – Printing & Packaging of China National Light Industry, Key Laboratory of Printing & Packaging Materials and Technology of Shandong Province, School of Light Industry Science and Engineering, Qili University of Technology (Shandong Academy of Sciences), Ji’nan City, Shandong Province 250353, P.R. China; State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou S10640, P.R. China; orcid.org/0000-0002-4092-8423; Email: mingliscut@hotmail.com

Lihong Zhao – State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou S10640, P.R. China; Phone: +86-020-87117770; Email: zhaolh@scut.edu.cn
Authors

Beihai He — State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, P.R. China
Yi Yi Chen — Hubei Province Fibre Inspection Bureau, Wuhan 430000, P.R. China

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acsomega.1c02568

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Notes

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