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A rapid and reversible pH control process for the formation and dissociation of lignin nanoparticles

Jiayun Xu,[a,b] Hao Zhou,[a] Yong Zheng,[a] Chenyu Li,[c] Lin Dai,*[a] Chunlin Xu,[b] and Chuanling Si*[a]

[a] J. Xu, H. Zhou, Y. Zheng, Prof. Dr. L. Dai, Prof. Dr. C. Si
School of Light Industry Science and Engineering
Tianjin University of Science and Technology
No. 9 at 13th Avenue, TEDA, Tianjin 300457, China
E-mail: dailin@tust.edu.cn, sichli@tust.edu.cn

[b] J. Xu, Prof. Dr. Chunlin Xu
Research Group of Wood and Paper Chemistry
Laboratory of Natural Materials Technology
Åbo Akademi University
Turku FI-20500, Finland

[c] Dr. Chenyu Li
Department of Environment and Health
Tianjin Institute of Environmental and Operational Medicine
No. 1 at Dali road, Tianjin 300050, China

Abstract: As a new and green type of nanomaterials, lignin nanoparticles (LNPs) have been considered as high-value renewable materials for application in many fields. However, the industrialization of LNPs faces many challenges, such as high manufacturing costs and small-scale production. Here, we provide a simple but rapid and reversible approach for the fabrication of LNPs *via* switching pH environments. The LNPs were regularly shaped in the acetonitrile/water system and their size appeared to be very homogeneous. The alternation of forming and dissolving of LNPs can be repeated many times simply by adding the acid and alkaline solutions alternately. There was little difference in the molecular structures between the original and regenerated LNPs. In addition, the consumption of solvents for LNPs production was only 200 mL g^{-1}, which was reduced by more than 10 times than conventional solvent exchange methods. The concentration of LNPs in the solution also improved to 5.0 g L^{-1}. This study not only provides a new, simple, and effective strategy for the fabrication of LNPs but also paves the way towards their real green production and application.

Introduction

Lignin is the most abundant natural aromatic feedstock. The valorization of lignin for materials has drawn immense attention in biorefineries.[1] In the past decade, the development of lignin micro- and nanoparticles (LNPs) not only cleverly avoid the heterogeneity of lignin, but also endows it with a variety of properties of nanomaterials,[2] which greatly expands the application of lignin in many fields including composites,[3] carrier,[4] surfactants in Pickering emulsions,[5] and catalysts,[6] etc.

A green, simple, and controllable method is a goal of the fabrication of lignin nanoparticles. In recent years, several methods have been developed for preparing LNPs, using different chemical, physical and biological approaches including acid precipitation,[7] solvent exchange,[2b] self-assembly,[8] ultrasonication,[9] polymerization,[10] biological methods,[11] etc. Among these methods, the solvent exchange method has been applied extensively because of its implementing easily and good repeatability, generating the lignin nanoparticles regularly and uniformly.[12] Ma et al. applied the ethanol/water solvent exchange system to prepare the LNPs with the concentration of 0.4 g L^{-1}.[12a] Wang et al. prepared LNPs with the maximum concentration of 0.4 g L^{-1} by tetrahydrofuran/water solvent exchange system.[13] However, the high consumption of solvents and the low concentration of product significantly increased the costs of the production and limited the application of LNPs. Although spray drying and a few cosolvent approaches can prepared the LNPs with higher concentrations,[5b, 14] the uniformity, stability, and regenerability of LNPs also limited their large-scale applications. Several strategies have been investigated to enhance the stability of LNPs.[15] However, it is worth noting that few studies reported the simple and quickly regenerating approach of lignin nanoparticles which could be essential for green materials. Thus, to achieve real green production and application, it is necessary and challenging to develop a rapid and reversible approach with a high yield of LNPs.

In the process of traditional alkaline pulping, β-O-4' linkages in the lignin molecules break and some C-C bonds form. The acid-base nature is limited to phenolic hydroxyls and minor amount of carboxylic acid groups present and formed during the pulping. The acid and alkali recovery can realize the precipitation of lignin along with the reversible protonation and ionization. Moreover, acid solutions have higher surface tension than pure water. For the theory of colloid chemistry, the difference in the values of surface tension between solvent and non-solvent could affect the formation of LNPs. Enlighted by the unique solubility of industrial lignin and the forming conditions of LNPs, we first report a simple but rapid and reversible approach for the fabrication of LNPs *via* switching pH values. Acetonitrile and water were chosen as the solvent and non-solvent of lignin, respectively. The chemical and micro-structures of all the lignin and its nano-products were investigated systematically by Fourier transform infrared spectroscopy (FT-IR), gel permeation chromatography (GPC), nuclear magnetic resonance (2D HSQC and ^{31}P NMR), and scanning electron microscope (SEM).

Results and Discussion

The objective of this study was to realize the rapid and reversible fabrication of LNPs by switching pH environments. In this work, the original LNPs were first prepared from KL in

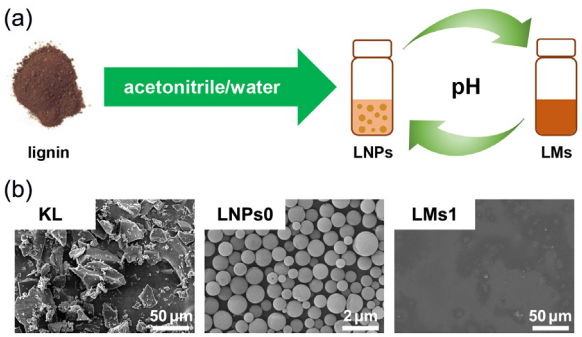

Figure 1. (a) Schematic illustration of the preparation of LNPs and LMs in acetonitrile/water binary solvent. (b) SEM images of KL, LNPs0, and LMs1.

acetonitrile/water binary solvent and named LNPs0. The preparation route and SEM of the samples are shown in Figure 1. The formation of LNPs is known to be influenced by interfacial tension of both solvent and non-solvent. With the addition of acid and alkaline, the surface tension of non-solvent water increases. The solvents with higher surface tension could facilitate the formation of LNPs in electrolyte-containing aqueous anti-solutions of lignin.[16] In this work, acetonitrile was used as the solvent of lignin, which has higher surface tension (29 dyn cm^{-1}) than other common solvents of lignin, such as tetrahydrofuran (26.4 dyn cm^{-1}) and ethanol (22.27 dyn cm^{-1}).

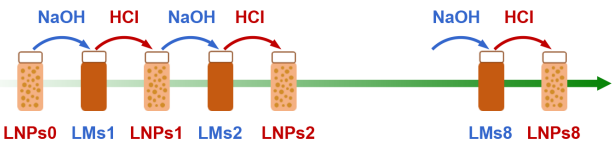

Figure 2. Schematic of the alternation of forming and dissolving of LNPs.

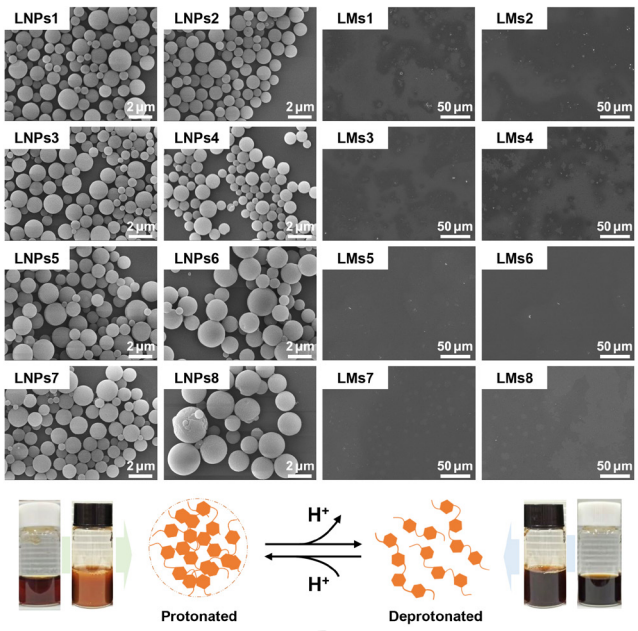

Figure 3. SEM images of regenerated LNPs (left, after adding HCl) and dissolved LMs (right, after adding NaOH).

Here, the consumption of solvents for LNPs production was only 200 mL g^{-1}, which was reduced by more than 10 times than conventional solvent exchange methods. The concentration of LNPs in the solution also improved to 5.0 g L^{-1}. The lower consumption of solvents and higher content of lignin in process streams would significantly reduce the cost of production of LNPs, energy consumption, and environmental burdens.

The LNPs can be dissolved and regenerated by adding NaOH and HCl solutions, respectively. The dissolving and forming processes can be repeated many times (8 times in this work). The samples after adding acid were named LNPs and numbered from 1 to 8. The samples after adding alkaline were named LMs and numbered from 1 to 8 (Figure 2). The LNPs were regularly shaped in acetonitrile/water solvents and their size appeared to be very homogeneous (Figure 3). When adding the alkaline solution, the LNPs were disappeared. This phenomenon is consistent with previous studies.[17] It is worth noting that, when the environment of the solution switched to acid again, the LNPs regenerated with a perfect sphere. The alternation of forming and dissolving of LNPs can be repeated many times simply by adding the acid and alkaline solutions alternately. Compared with LNPs0, there was little change in the morphology of LNPs8 except for slightly increased sizes. This is quite different from what is usually desired result of being stable at different pH environment.[8a]

Recyclability is an important metric for materials based on biorefinery. The LNPs could be rapidly regenerated to the original spherical shape upon switch pH, suggesting the excellent reversibility and controllability of the LNPs fabrication (Figure 3). Although some previous studies introduced that the high stability of LNPs at different pH environments can be beneficial for their retention and large-scale production,[6b, 15b, 18] the rapid and reversible fabrication of LNPs opens a new route for lignin valorization.

To investigate the chemical structure variation in the alternation cycle, the functional groups, molecular weights, and substructures of lignins were comprehensively analyzed. FTIR spectra of all the samples are shown in Figure 4. Obviously, the FTIR spectra of all samples were basically changed with the addition of acid or alkaline. The signal at 1710 cm^{-1} was attributed to the stretching of unconjugated carbonyl and

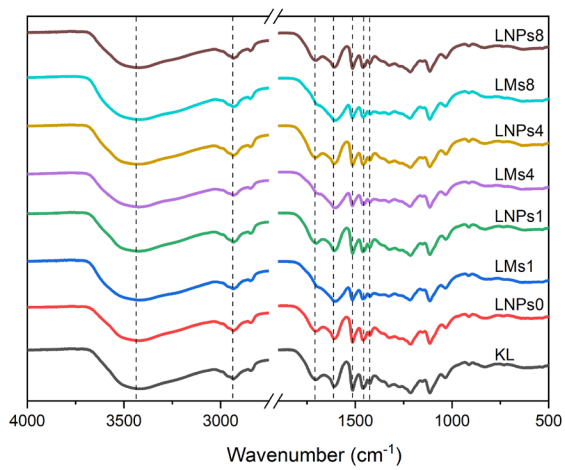

Figure 4. FTIR spectra of KL, original LNPs, regenerated LNPs, and dissolved LMs.

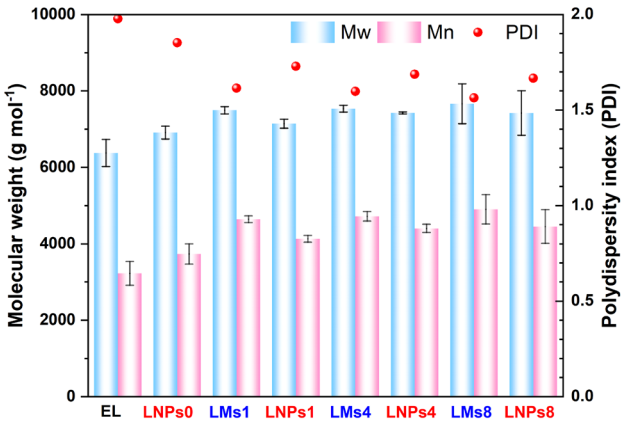

Figure 5. Quantitative molecular-weight results including weight-average molecular weight (M_w), number-average molecular weight (M_n), and polydispersity index (PDI).

conjugated ester bonds, indicating that the reversible esterification reaction happened with the addition of acid or alkaline.[19] The assignments at 1600, 1510, and 1425 cm^{-1} are relative intensities of the bands for aromatic skeleton vibration in lignin which were rather similar in LNPs and LMs, indicating a similar core structure of the lignins.[20]

Figure 5 shows the quantitative weight-average molecular weight (M_w), number-average molecular weight (M_n), and polydispersity index (PDI) of the lignins, which varied periodically with the pH environment. Under the alkaline environment, the lignins showed narrow distributions of molecular weights, which could be attributed to the ionization of lignin and higher solubilities. When the environment of the solution switch to neutral or acid, the protonation of lignin led to a decrease of its solubility, resulting in the relatively broad molecular-weight distribution.[17, 21]

The subunit structures of the lignins were analyzed by two-dimensional heteronuclear single-quantum coherence nuclear magnetic resonance (2D HSQC NMR) (Figure 6).[22] The aliphatic C-O region and side-chain region are displayed at δC/δH 50−90/2.5−5.0 and δC/δH 100−130/5.8−7.8, respectively. There was little difference in the 2D HSQC NMR spectra. All the samples after adding acid or alkaline showed almost the same spectra in the both aliphatic C-O and side-chain region, owing to the variations of lignin in the acetonitrile/water system by protonation/ionization alone. The S/G ratios of samples were plotted along with the switching pH during this process. Compared with LNPs, LMs had relatively lower S/G ratios, which can be contributed to the dissolution of LNPs. Higher S/G ratios are beneficial to the aggregation of LNPs.[12a]

^{31}P NMR spectra of phosphorylated lignins were used to determine the changing of hydroxyl groups (Figure 7).[23] Aliphatic hydroxyl, phenolic hydroxyl, and carboxyl groups were commonly formed intermolecular hydrogen bonds and π−π interactions which will affect the formation of LNPs.[24] Here, the

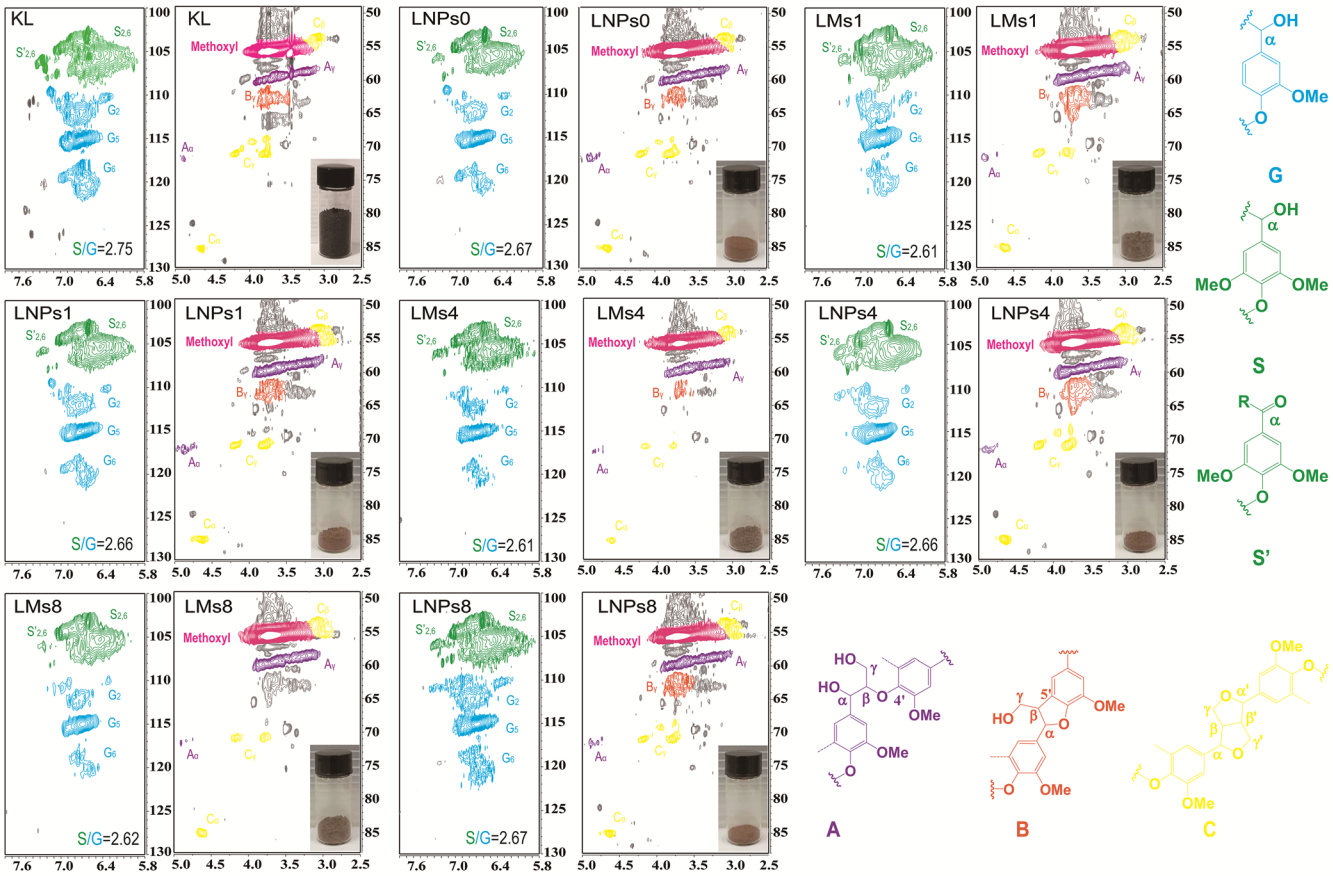

Figure 6. Main substructures of lignin identified in the 2D HSQC NMR spectra: (A) β-aryl ether (β-O-4); (B) phenylcoumaran (β-5); (C) resinol (β−β) linkages; (S) syringyl; (S') oxidized syringyl; and (G) guaiacyl.

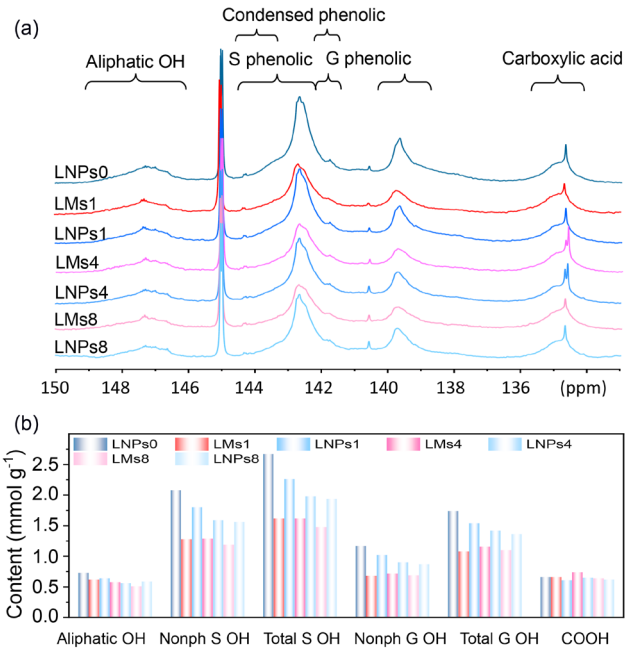

Figure 7. (a) Quantitative ^{31}P NMR spectra, (b) content of hydroxyl (-OH) and carboxyl groups (-COOH) of LNPs and LMs.

contents of phenolic hydroxyl groups of LNPs were higher than those of LMs samples.[8a] While the contents of carboxyl group had no obvious. The low content of phenolic hydroxyl groups weakens the intermolecular hydrogen bond, leading to the dissolution of lignin. With the increase of regeneration times, the content of phenolic hydroxyl groups of LNPs decreased, which could be due to the rapid processes and small amount of dissolution of lignin in the solutions.

Figure 8 compares the UV-Vis transmission and absorbance of LNPs and LMs in the wavelength range from 200 to 800 nm. In the visible spectrum region, the transmittances of all the LMs samples were higher than those of LNPs samples. Moreover, after multiple cycles, LMs had almost the same transmittance of visible light. LMs showed the obvious higher UV-shielding properties in the wavelength range of 200 to 320 nm that covered all ranges of UVB. Compared to LNPs, the relatively higher UV-shielding properties are possibly a result of the higher phenolic group.[25] The formation of LNPs can achieve the reduction of not only the color of lignin[26] but also their transmittances of visible light. Applying these properties, the fabricated LNPs can be considered as antiglare glass, while LMs are ideal raw materials for food packaging, solar panel protection, and sunscreens as UV-shielding material.[27] Moreover, some smart applications can be proposed by this rapid and reversible pH control process, such as LNPs-containing switchable glasses (Figure 8d).

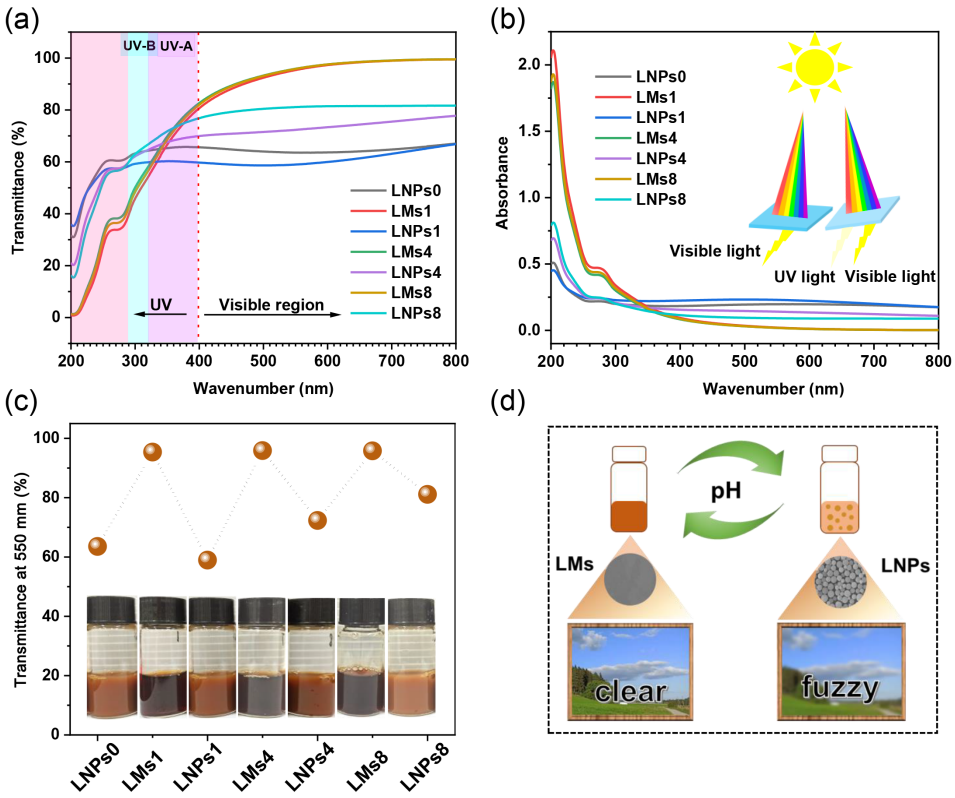

Figure 8. UV-Vis curves of LNPs and LMs. (a) Transmittance. (b)Absorbance. (c) Transmittance of samples at 550 nm. (d) Optical change of LNPs and LMs.

Conclusion

In summary, we have reported an unprecedented but simple, rapid, and reversible approach for the fabrication of LNPs. In the acid and neutral acetonitrile/water system, the LNPs with regular spherical shape showed good properties of dissolution and regeneration, respectively. This procedure can be rapidly repeated many times simply by adding the acid and alkaline solutions alternately without destroying the molecular structures of lignin. We believe that this method will provide guidance for more smart applications by rational design and preparation. Moreover, the consumption of solvents and the concentration of LNPs decreased (more than 10-folds) and increased (more than 10-folds), respectively. LNPs have promising applications in blending plastics, hydrogels, and some other green materials. This work provide an effective method for the scale-up, low-cost, and real green production and regeneration of LNPs and lignin valorization.

Experimental Section

Materials

Kraft lignin (KL) was provided by Shandong Sun Paper Industry Joint Stock Co, Ltd. (Jining, China). Acetonitrile (CH_3CN, chromatographic grade), sodium hydroxide (NaOH), hydrochloric acid (HCl), and other reagents were provided by Jindong Tianzheng Precision Chemical Reagent Factory (Tianjin, China) and directly used without further purification.

Preparation of LNPs

150 mg KL sample was dissolved in 30 mL of A solution (CH_3CN/H_2O, v/v = 2/1) by ultrasonic treatment (180 W, 1 min). The resulting LNPs sample was named LNPs0. Then, 600 μL NaOH (1.0 M) was added to the above solution by ultrasound (180 W, 1 min) to dissolve the LNPs. The resulted molecular solution of lignin was named LMs1. The regenerated LNPs (LNPs1) can be easily obtained by adding HCl (600 μL, 1.0 M) to the solution by ultrasonic treatment (180 W, 1 min). The above cycle was repeated 8 times. The samples after adding acid were named LNPs and numbered from 1 to 8. The samples after adding alkaline were named LMs and numbered from 1 to 8. All the acetonitrile and water were recovered and reused.

Characterization

The microstructures of the samples were detected by scanning electron microscope (SEM), The samples were prepared by dropping the diluted and dispersed solution onto a Silicon wafer at room temperature. After air-drying, the samples were then coated with platinum prior to SEM analysis (JSM-IT300LV, JEOM) at an accelerating voltage of 10.0 kV. The lignin sample was dissolved in 0.1% NaOH and diluted with tris-acetate buffer (20 mmol L^{-1}, pH 7.4), then analyzed for molecular weight distribution using gel permeation chromatography (GPC) on a high-performance liquid chromatograph (LC) system (Agilent 1200, USA) as described previously[28]. The GPC system was equipped with a TSK G3000 PWxl column and a UV-Vis detector at 280 nm for detecting lignin with polyethylene glycol as standards. The GPC was operated at 25°C using tris-acetate buffer as eluent at a flow rate of 0.5 mL min^{-1}. Absorbance spectra of the samples after dialysis were recorded by using an ultraviolet-visible (UV-Vis) spectrophotometer (UV-6100, MAPADA). Absorbance within a 200 to 800 nm spectral range was measured at 1 nm spectral resolution. The baseline during the experiment was made using only DI water as a reference.

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Keywords: lignin • nanoparticles • formation • dissociation • green production

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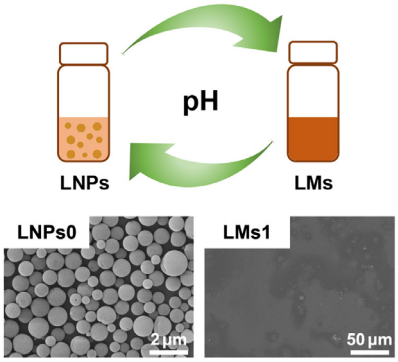

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