Industrial Crops and Products 100 (2017) 146–152

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

Preparation and formation mechanism of size-controlled lignin nanospheres by self-assembly

Fuquan Xiong[a], Yanming Han[a,*], Siqun Wang[a,b], Gaiyun Li[a], Tefu Qin[a], Yuan Chen[a], Fuxiang Chu[a,*]

[a] Research Institute of Wood Industry, Chinese Academy of Forestry, Beijing 100091, China
[b] Center for Renewable Carbon, University of Tennessee, TN 37996-4570, United States

A R T I C L E I N F O

Article history:
Received 19 October 2016
Received in revised form 10 January 2017
Accepted 20 February 2017
Available online 1 March 2017

Keywords:
Enzymatic hydrolysis lignin
Self-assembly
Nanospheres
Formation mechanism

A B S T R A C T

Lignin has recently attracted much attention due to their renewable nature. Here we focused on a simple self-assembly method for fabricating size and shape uniform enzymatic hydrolysis lignin (EHL) nanospheres, without chemical modification of lignin. EHL was dissolved in tetrahydrofuran at different initial concentrations and subsequently self-assembly with adding water under magnetic stirring for fabricating the nanospheres. The self-assembled structure, process parameters and formation mechanism of the nanospheres were investigated by transmission electron microscopy (TEM), scanning electron microscopy (SEM), dynamic light scattering (DLS), fourier transform infrared spectroscopy (FTIR), and UV–vis absorption spectra. Results showed that the nanospheres were formed through a layer-by-layer self-assembly approach from inside to outside based on π–π interactions, which enabled the formation of nanospheres in the size range of 190–590 nm. Increasing the pre-dropping EHL concentration resulted in an increase of the average diameter and yield of the nanospheres. The nanospheres have good stability, and their average diameters had no significant change after 30 days. The chemical structural features of the nanospheres had not produced a significant change in the preparation process. High preparation temperature brought about the formation of the gaps at the surface of the nanospheres due to the effect of volatile speed of solvent. Moreover, the average diameter of the nanospheres decreased with an increase of stirring rate or the dropping speed of water. The proposed EHL nanospheres are eco-friendly, cost-effective and therefore a promising candidate for biomass based carrier.

1. Introduction

Self-assembly based on the spontaneous control of materials through noncovalent interactions, such as hydrogen bonding (Guerlain et al., 2015), van der Waals forces (Wu et al., 2015), electrostatic forces (Zheng et al., 2015) and π–π interactions (Wang et al., 2015), with no external intervention provides an effective method for the application of materials. In recent years, self-assembly as a topic of intense scientific interest has seen an explosive development (Zhang et al., 2012). In order to prepare molecular aggregates with designed properties, geometries and dimensions, various strategies for molecular self-assembly have been employed (Zhang et al., 2012). They may have potential applications in many areas, such as drug delivery (Tyrrell et al., 2010), catalysis (Polshettiwar et al., 2009), medical diagnostics (Sandhu et al., 2010) and sensors (Chen et al., 2013). Amphiphilic polymers composing both hydrophobic and hydrophilic segments possess self-assembly behavior (Guo et al., 2016). Different self-assembly micelle morphologies can be acquired such as spherical micelles, wormlike micelles, and vesicles by a precise control of the environmental conditions (Jain and Bates, 2003). Spherical micelles are suitable to be used as carriers for agents (Qian et al., 2014). Recently, with the rapid energy exhaustion and environmental awareness, increased attention has been paid to the development of spherical micelles obtained from natural renewable resources due to their inherent biodegradability and biocompatibility (Guo et al., 2013; Guo et al., 2016; Lievonen et al., 2016; Qian et al., 2014).

Lignin is an abundant renewable polyaromatic polymer composed of phenylpropanoid units but is not used extensively due to its complex structures. In order to explore the high-value-added application of lignin resources, scientists have made many attempts. Lignin nanoparticles can provide many opportunities for value-added applications of lignin (Nair et al., 2014; Qian et al., 2014). They may have potential applications in UV protection,

* Corresponding authors.
E-mail addresses: hanym@caf.ac.cn (Y. Han), chufuxiang@caf.ac.cn (F. Chu).

http://dx.doi.org/10.1016/j.indcrop.2017.02.025
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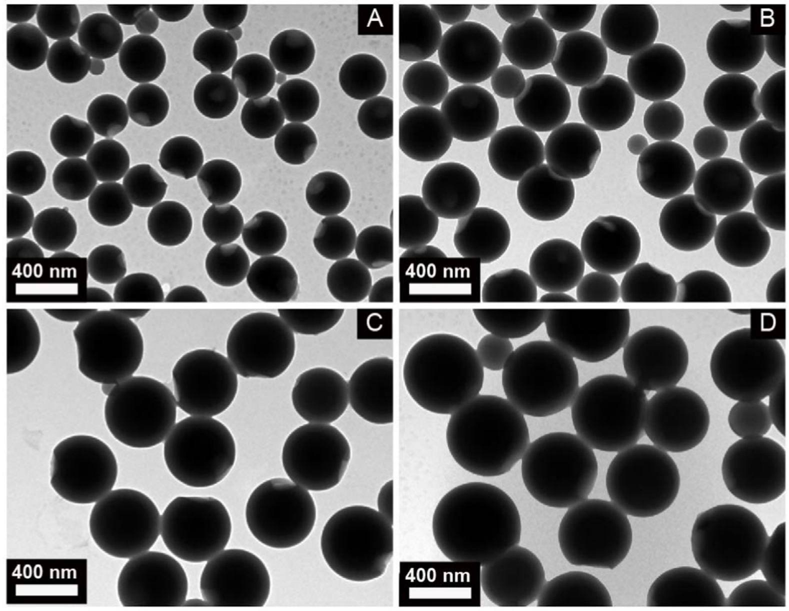

Fig. 1. TEM images of EHL nanospheres obtained at different pre-dropping lignin concentration. Pre-dropping lignin concentration: (A) 0.5 mg/ml, (B) 1 mg/ml, (C) 1.5 mg/ml, (D) 2 mg/ml. The sample used here was prepared at the stirring rate of 600 rpm and at a dropping speed of 4 ml/min.

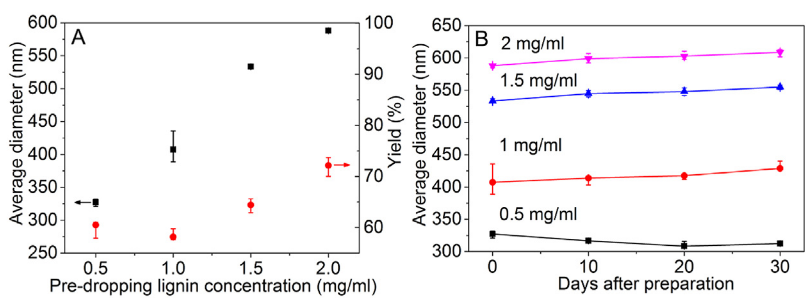

Fig. 2. The yield and size of EHL nanospheres obtained at different pre-dropping lignin concentration (A) and the size change of the nanospheres with time (B). The sample used here was prepared at the stirring rate of 600 rpm and at a dropping speed of 4 ml/min.

antibacterial, nanofiller and biomass based carrier (GÎLCĂ et al., 2011; Richter et al., 2015; Yang et al., 2015; Zimniewska et al., 2008). This suggest that lignin could play a central role as a new inexpensive and renewable starting material used for the praparation of new products (Xiong et al., 2016). In the lignin nanoparticles preparation methods reported so far, the nanoparticles obtained by these methods, i.e., precipitation method (Frangville et al., 2012), mechanical method (Nair et al., 2014) and polyaddition (Yiamsawas et al., 2014), usually possess irregular shape. While spherical lignin nanoparticles can be prepared by self-assembly. Qian et al. (2014) produced uniform colloidal spheres using acetylated lignin via self-assembly. However, this step required environmentally unfriendly chemicals such as acetyl bromide. Lignin exhibit self-assembly behavior in theory because it is a natural amphiphilic polymer composed of hydrophilic hydroxyl groups and hydrophobic aromatic rings (Bartzoka et al., 2016). Lievonen et al. (2016) obtained spherical lignin nanoparticles possessed of compact structure using unmodified lignin through dialysis.

Enzymatic hydrolysis lignin (EHL) reveals better chemical activity, applicability and solubility in ubiquitous organic solvent compared with lignosulfonate or kraft lignin (Han et al., 2016; Jin et al., 2010). However, EHL has not been efficient utilization (Ragauskas et al., 2014). Therefore, the development of value-added EHL-based materials, chemicals or fuels would greatly improve the biorefinery viability through an energy-effective and cost-effective route (Ragauskas et al., 2014). Application of EHL in phenol-formaldehyde resin (Qiao et al., 2015; Zhang et al., 2013), polyurethane foams (Han et al., 2013; Li et al., 2012) and UV-absorbent coatings (Liu et al., 2015; Zong et al., 2016) has been reported in the literature. Moreover, one kind of EHL-based nanoparticle fluorescently labeled by pyrene has been prepared in our recent research, which may have potential applications in nano sensors due to its oxygen-responsive property (Xiong et al., 2016).

Herein this study mainly focused on a simple self-assembly method for fabricating uniform EHL nanospheres through π–π interactions, without the need for chemical modification of lignin. EHL was dissolved in tetrahydrofuran at different initial concentrations and subsequently self-assembly with adding water under magnetic stirring for fabricating the nanospheres. The self-assembled structure and formation mechanism of the nanospheres were investigated by transmission electron microscopy (TEM), scanning electron microscopy (SEM), dynamic light scattering (DLS), fourier transform infrared spectroscopy (FTIR), and UV–vis absorption spectra. Effects of various process parameters on performance of the nanospheres were respectively explored as well.