

## Electronic supplementary information

### **Synchronous and rapid preparation of lignin nanoparticles and carbon quantum dots from natural lignocellulose**

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## Methods

### 1. Materials and reagents

The rice straw, obtained from Shandong, China, was ground into powder and air-dried as the feedstock. The ethanol and hydrochloric acid (HCl, 37 wt%) were purchased from Sinopharm Chemical Reagent Co., Ltd (Beijing, China).

### 2. Synchronous preparation of LNPs and CQDs

7 g of air-dried rice straw were mixed with 70 ml of ethanol–water solution (65:35, v/v) contained 0.5 wt% HCl. The mixture was transferred into a KDB-III and statically treated at 400W of microwave irradiation in microwave digestion system (Galanz P70F20L-DG, China) for 10 min. Ten-fold volume of water was added and filtered through multi-layer gauze, then the colloidal solution was obtained. The colloidal solution was separated by a high-speed centrifuge (Multi-purpose, High Speed Centrifuge, 1580R, Gene Company Limited) with the relative centrifugal force of 24000 g. After separation, the precipitate was the LNPs and the supernatant liquor was the CQDs. The residues were collected and thoroughly washed with de-ionized water, and subsequently dried at 50°C. The dissolved lignin in this strategy was also collected as control. Moreover, the holocellulose (removed all the lignin fraction according to the literature<sup>1</sup>), alkali lignin, and the compounds released by acidolysis (including xylose, arabinose, galactose, glucose, etc.) were also treated under microwave irradiation as the process mentioned above.

### 2. Characterization of colloidal solution and rice straw residue

Tyndall effect was employed to confirmed the formation of the colloidal solution.

Transmission electron micrograph (TEM, JEOL, JEM-2100F, Japan) was used to characterize the morphology of the colloidal solution. Meanwhile, solid gold-coated rice straw residues were observed under a scanning electron microscope (SEM, JSM-IT300LA, JEOL, Japan).

### 4. Characterization of LNPs

The LNPs were observed under TEM and Helios NanoLab (Helios Nanolab G3 UC, FBI, U.S.A). Then a 1760X Fourier Transform Infrared (FTIR) spectrometer (PerkinElmer, Shanghai, China), X-ray photo-electron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher Scientific), and X-ray diffraction (XRD, Bruker D8 Advance) were employed to analyzed the structure of the LNPs. Moreover, two-dimensional heteronuclear single quantum coherence (HSQC)–nuclear magnetic resonance (NMR) and <sup>31</sup>P NMR spectra of the LNPs were performed in a Bruker Avance 400 MHz spectrometer (Bruker GmbH, Karlsruhe, Germany).

To evaluate the stability of LNPs, the particle size and zeta potential of the LNPs dispersion at pH 2 to 12 were measured via a Malvern Zetasizer Nano-ZS ZEN3600 Instrument (Malvern, United Kingdom). Each sample was measured three times. Thermal degradation ( $T_d$ ) behavior of the samples were analyzed by TG-DSC STA 449 F3 Jupiter (Netzsch, Germany).

Besides, FTIR and UV–vis spectroscopy (U-4100, Hitachi, Japan) analysis were employed to further explore the formation mechanism of the LNPs. The alkali lignin and the dissolved lignin were characterized as control.

### 5. Characterization of CQDs.

The CQDs were observed under TEM and high-resolution TEM. Then FTIR spectrometer,

XPS and Raman spectra (Renishaw Raman system model 1000 spectrometer with radiation at 633 nm) were employed to analyze the structure of the CQDs. Photoluminescence (PL) spectra were performed using a fluorescence spectrophotometer (Edinburgh FLsp920 transient, USA).

To explore the formation mechanism of the CQDs, the high-performance liquid chromatography (HPLC) system (Agilent 1200, China) with the refractive index (RI) detector (Agilent G1362A, China) and GC QP2010 MS (Shimadzu, Kyoto, Japan) were employed to determine the compounds produced by the acidolysis.

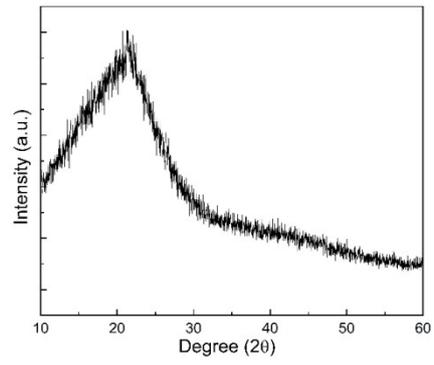


Fig. S1 XRD patterns of the LNPs

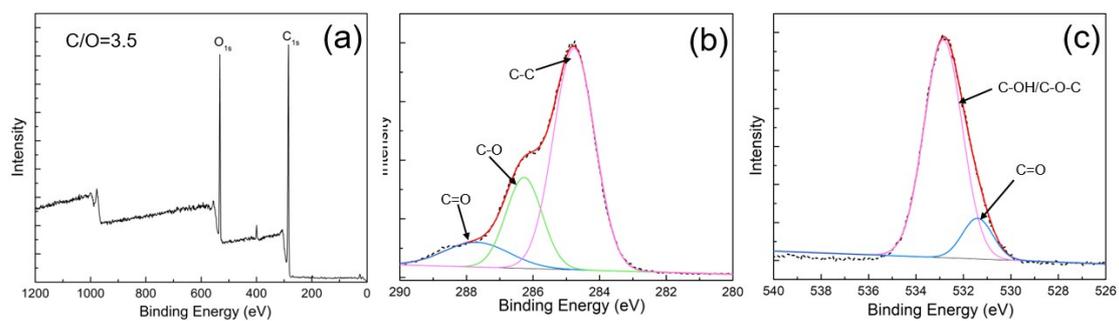


Fig. S2 (a) XPS spectrum of LNPs; (b) high-resolution C 1s peaks of the LNPs; (c): high-resolution O 1s peaks of the LNPs.

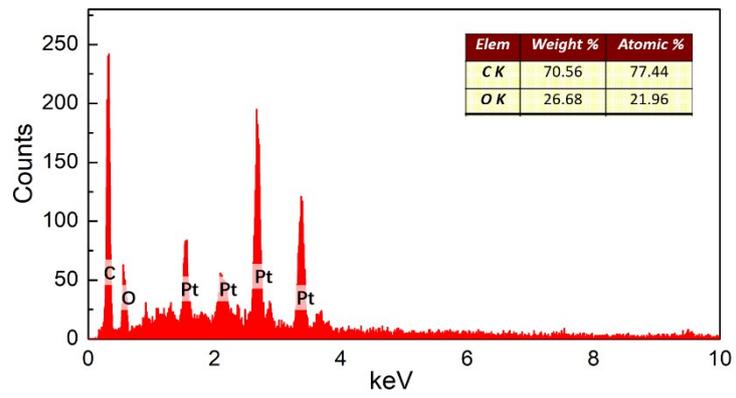


Fig. S3 EDS image of LNPs (obtained by SEM-EDS).

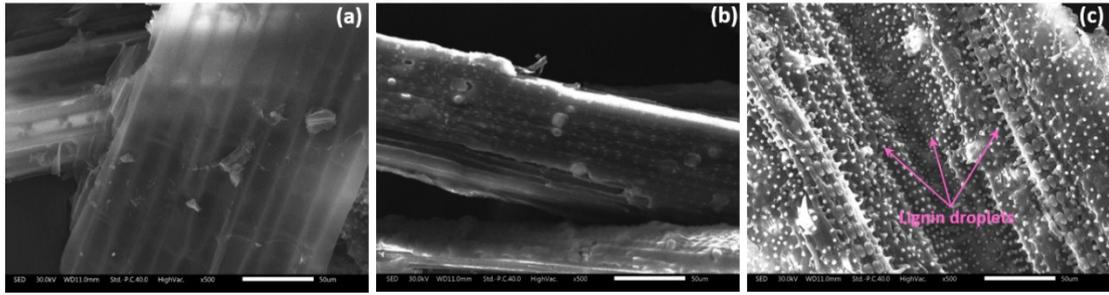


Fig. S4 SEM images of the rice straw residue, (a) untreated rice straw (b) treated rice straw residue after as-synchronous preparation (ethanol-water, 0.5 wt% HCl microwave-assist) (c) treated rice straw residue after the control group (0.5 wt% HCl, microwave-assist)

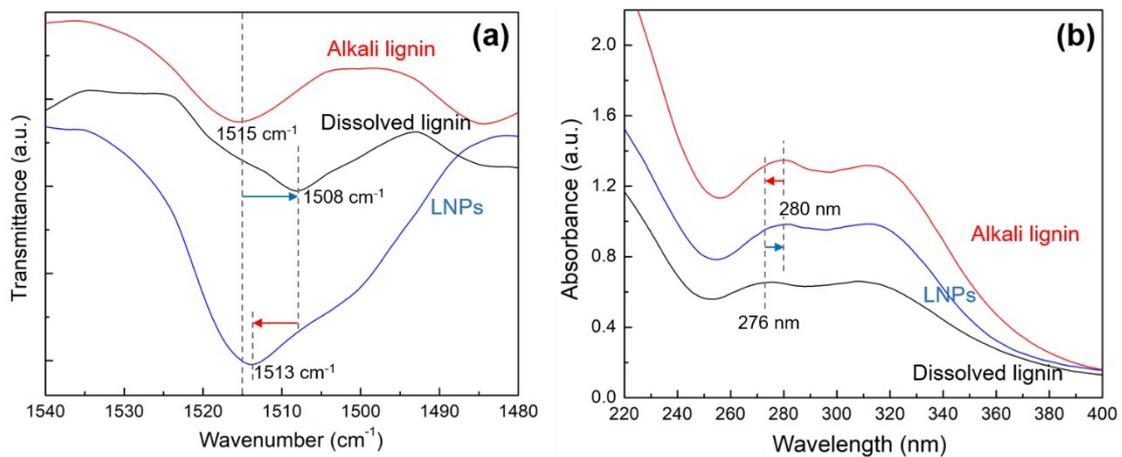


Fig. S5 (a) FTIR spectra of alkali lignin, dissolved lignin and LNPs. (b) UV-vis absorption spectra of alkali lignin, dissolved lignin and LNPs.

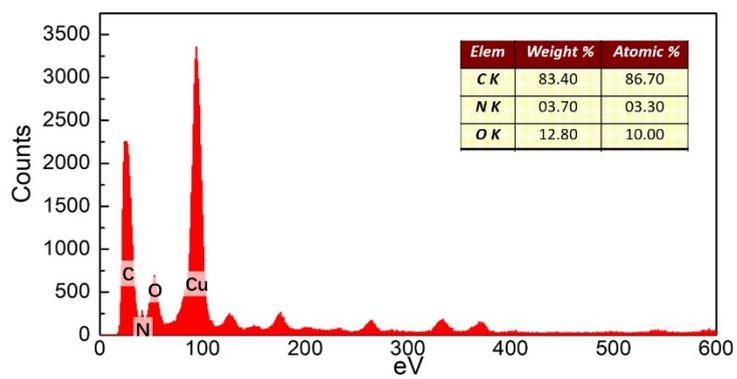


Fig. S6 EDS image of CQDs (obtained by TEM-EDS, and the carbon content is inaccurate in EDS analysis due to the existence of carbon membrane)

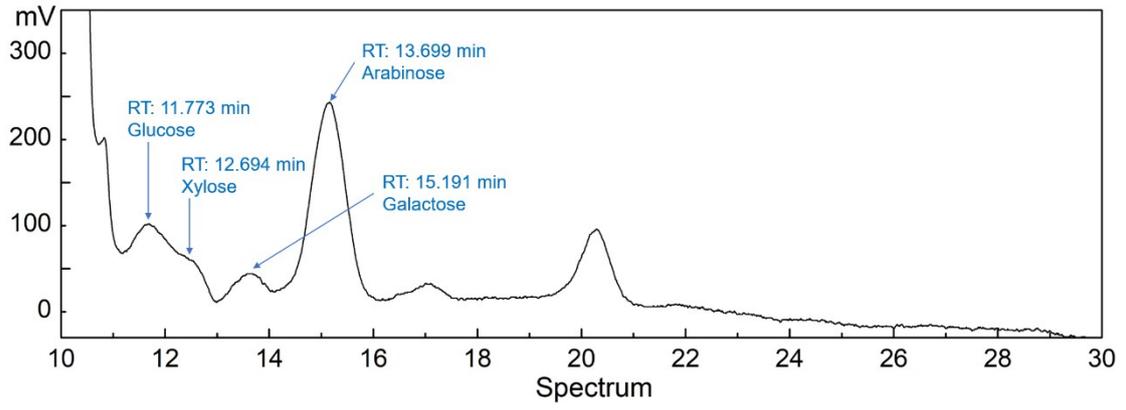


Fig. S7 Chromatogram of the liquor (obtained by HPLC).

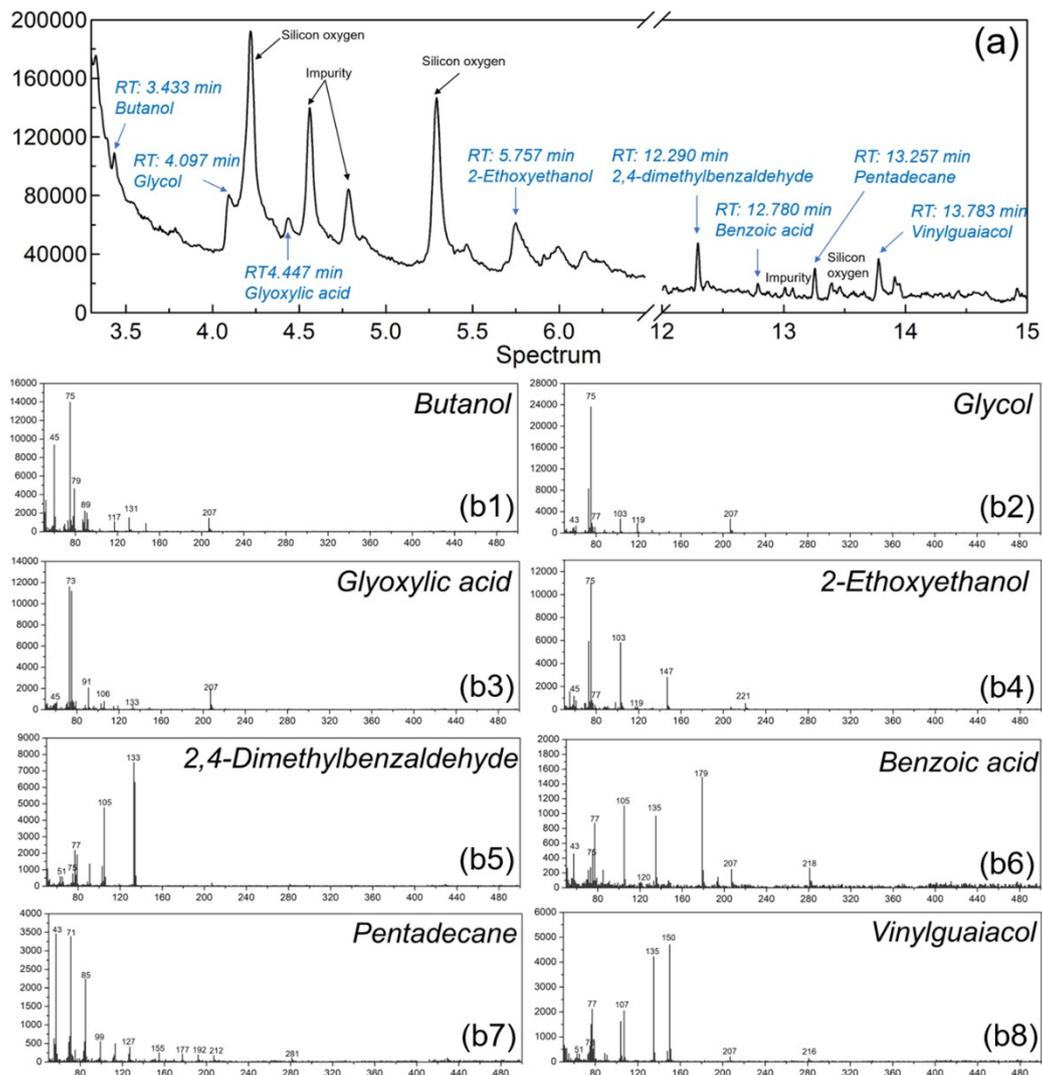


Fig. S8 (a) TIC of TMS derivatives of compounds extracted with ethyl acetate from the liquor, (b1-8) the mass spectrum of the compounds.

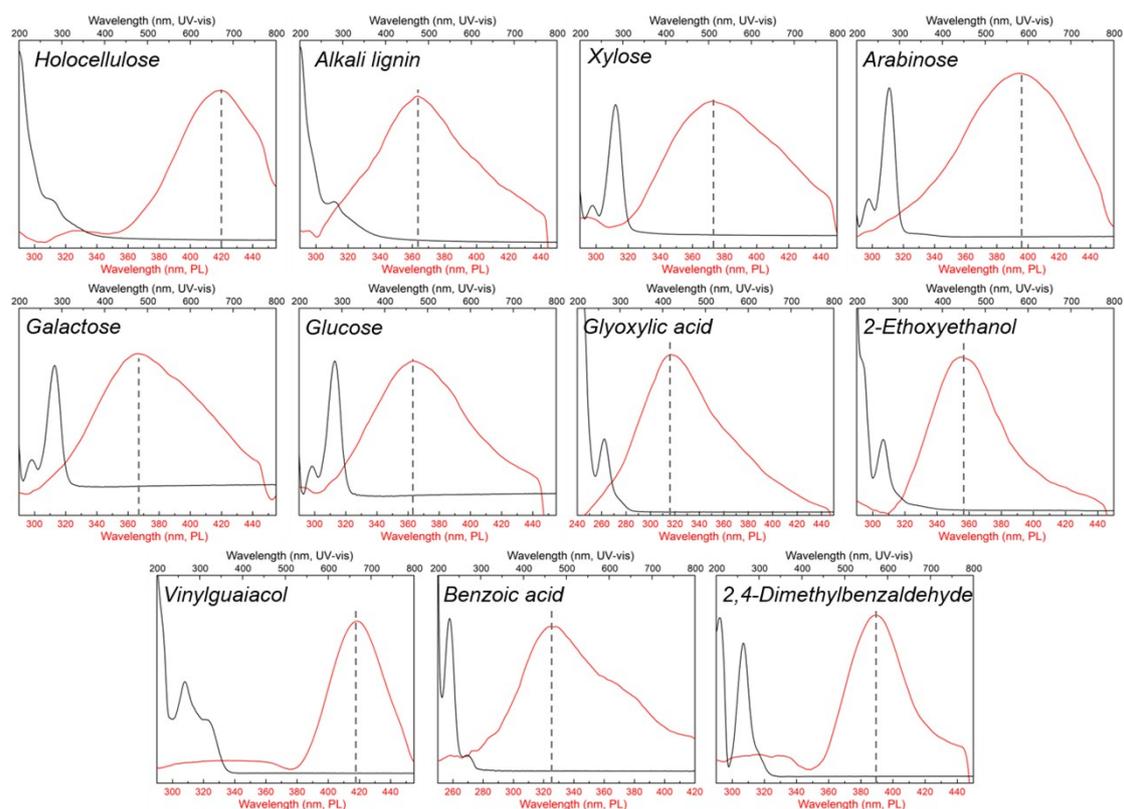


Fig.S9 UV-vis absorption and PL spectra of the CQDs obtained from treated samples: holocellulose, alkali lignin, xylose, arabinose, galactose, glucose, glyoxylic acid, 2-ethoxyethanol, vinylguaiacol, benzoic acid, and 2,4-dimethylbenzaldehyde at the excitation wavelength of 480 nm.

## Reference

1. S. Y. Ding, Y. S. Liu, Y. Zeng, M. E. Himmel, J. O. Baker and E. A. Bayer, *Science*, 2012, **338**, 1055-1060.