Hemicellulose-Triggered High-Yield Synthesis of Carbon Dots From Biomass

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1. Determination of cellulose content

1.1 Standard curve of cellulose

Peparation of cellulose standard solution:

Weighed 100 mg of cellulose and added it to a 100 mL volumetric flask. 60-70 mL of 60% H_2SO_4 were added to the volumetric flask under ice bath conditions. The solution kept still for 20-30 mintues. Then diluted it with 60% H_2SO_4 to a final volume of 100 mL. 5 mL of the solution were added to a 50 mL volumetric flask and dilute with 60% H_2SO_4 to a final volume of 50 mL. This solution was the cellulose standard solution.

0, 0.2, 0.4, 0.8, 1.2 and 1.6 mL of cellulose standard solution were put into tubes. Diluted with distilled water to 2 mL and then shake them. Added 0.5 mL of 2% anthrone reagent to each tube and then slowly added 5 mL of concentrated H_2SO_4 along the tubes. The plugs of tubes were plugged and slightly shaken the tubes to catalyze the hydrolysis of ethyl acetate. When there was anthracone flocculent in the tube, shaked the tubes violently to promote anthracone dissolve. The absorbance values of each sample were measured by a spectrophotometer at 620 nm. The standard curve of cellulose was drawn with the absorbance values as the x-coordinate and the cellulose content as the y-coordinate.

1.2 The extraction of sample

0.1g of samples were put into a 25 mL volumetric flask. 15-20 mL of 60% H_2SO_4 were added to the volumetric flask under ice bath conditions. The

solution kept still for 20-30 minutes. Then diluted with 60% H_2SO_4 to a final volume of 25 mL. 5 mL of solution above were put into a 25 mL volumetric flask. Diluted the solution with distilled water to 25 ml and shook under ice bath conditions. The mixture was filtered and filtrate was collected for further use.

1.3 The determination of sample

After the filtrate was diluted to a certain concentration, 1 mL diluent was added to the test tube. 0.5 mL 2% anthrone reagent was added into the tube and then added 5 mL concentrated H_2SO_4. Put the lid on the test tube and let it stand still for 12 minutes. The absorbance value of each sample was measured by a spectrophotometer at 620 nm.

1.4 Calculation of cellulose content

The cellulose content was detected on the standard curve according to the absorbance value of the sample. The cellulose content could be calculated by the following equation: $X=\frac{A \times D}{m} \times 10^{-3}$.

A: cellulose content of sample determined by standard curve of cellulose, ug;

D: is the value of: the volume of the extract (mL)×dilution multiple

m: the weight of sample, g;

X: the cellulose content of sample, mg/g.

2. Determination of hemicellulose content

2.1 The extraction of sample

0.1-0.2 g of samples were added to the centrifuge tubes. 10 mL of calcium nitrate solution were added into the centrifuge tubes and then placed the tubes in a boiling water bath for 5 minutes. After cooling down to room temperature, centrifuged and collected the precipitation. The precipitata flushed with hot water for three times and then 10 mL of 2 M HCl were added to the precipitation. The mixture was placed in a boiling water bath for 45 minutes. After cooling down to room temperature, centrifuged and collected the supernatant. The supernatant was pour into a 25 mL volumetric flask. Added a drop of phenolphthalein to the volumetric flask. Added NaOH to the volumetric flask until the color of solution turned to rose-red. Dilute the solution with distilled water to a final volume of 25 mL. The filtrate was collected for further use.

2.2 Standard curve of glucose

Preparation of DNS reagent: Placed 185 g sodium potassium tartrate in a beaker and added hot water to dissolve it. 6.3 g of 3, 5-dinitrosalicylic acid and 262 mL of 2 M NaOH solution were added into the beaker. Then 5 g of crystalline phenols and 5 g of sodium sulfite were added to the beaker. The solution was transferred to a brown 1 L volumetric flask and diluted with distilled water to a final volume of 1 L.

0, 0.2, 0.4, 0.8, 1.2, 1.6 and 2.0 mL 1mg/mL glucose solution were added into 25 mL tubes. Diluted the solution with distilled water to a final volume of 2 mL. Added 1.5 mL DNS reagent to the tubes. Placed the tubes in a

boiling water bath for 5 minutes and then cooled down by icy water immediately. The solution was diluted with distilled water to a final volume of 25 mL. The absorbance values of each sample were measured by spectrophotometer at 540 nm. The standard curve was drawn with the absorbance values as the x-coordinate and the cellulose content as the y-coordinate.

2.3 The determination of sample

1 mL of filtrate in step ‘2.1 The extraction of sample ’ were put into tubes and diluted with distilled water to 2 mL. 1.5 mL of DNS regent were added to the tubes and then placed the tubes in a boiling water bath for 5 minutes. After cooling down to room temperature, the absorbance values of each sample were measured by a spectrophotometer at 540 nm. The reducing sugar content was detected on the standard curve according to the absorbance value of the sample.

The hemicellulose content could be calculated by the following equation:

$$X=\frac{A}{m}\times 0.9\times 10^{-3};$$

A：the reducing sugar content detected on the standard curve, μg/g；

m：the weight of sample, g;

0.9: conversion factor for converting reducing sugar to hemicellulose;

X：the hemicellulose sugar content, mg/g.

3. Determination of lignin content

3.1 The extraction of sample

0.1 g of samples were added to the centrifuge tubes. 10 mL of 1% HAc solution were added to the tubes and then centrifuged. The precipitation was washed with 5 mL of 1% HAc and then added with a mixture of 3-4 mL ethanol and ethyl ether (*V*:*V*= 1:1). The supernatant was discarded and the precipitation was collected. After the solvent of precipitation was evaporated, 3 mL of 72% H_2SO_4 were added to the precipitation. The mixture was stood still for 16h. 10 mL of distilled water were added to the tubes and then placed the tube in a boiling water bath for 5 minutes. After cooling down to room temperature, 5 mL of distilled water and 0.5 mL of 10% $BaCl_2$ were added to the tubes and then centrifuged. The precipitation was washed twice with distilled water. 10 mL of 10% H_2SO_4 and 10 mL of 0.1 M potassium dichromate solution were added to the tubes. The tubes were placed in a boiling water bath for 15 minutes. The mixture in the tubes was cooled down and saved for further use.

3.2 The determination of sample

The mixture in the tubes was transferred to a beaker. 5 mL of 20% KI solution and 1 mL 0.5% starch solution were added to the beaker. Titrate with 0.2 mol/L sodium thiosulfate until the color of solution became colorless. 10 mL of 10% H_2SO_4 and 10 mL 0.1 M potassium dichromate solution were added to another beaker and the solution was titrate with 0.2 M sodium thiosulfate. This titration sample was used as a control.

3.3 Calculation of cellulose content

The lignin content could be calculated by the equation: $X=\frac{K\times(a-b)}{n\times 48}$

X：the mass fraction of lignin in sample, %;

K: concentration of sodium thiosulfate, M;

a: the volume of sodium thiosulfate consumed by the blank titration sample solution, mL;

b: the volume of sodium thiosulfate consumed by the titration sample solution, mL;

n: the weight of sample, g.

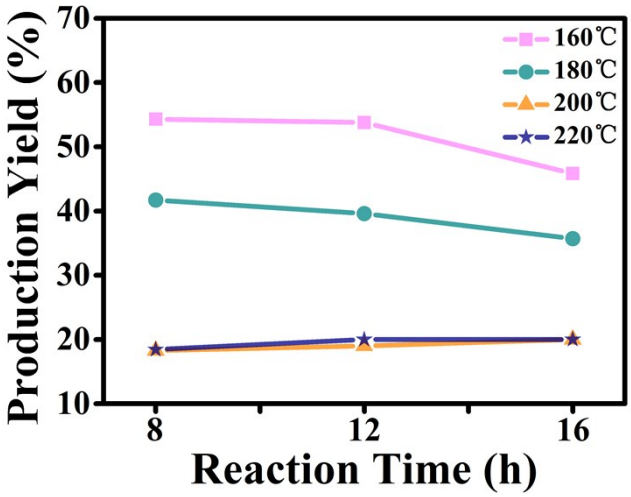

Figure S1 The effect of reaction times and temperatures on the production yield of CC-CDs.

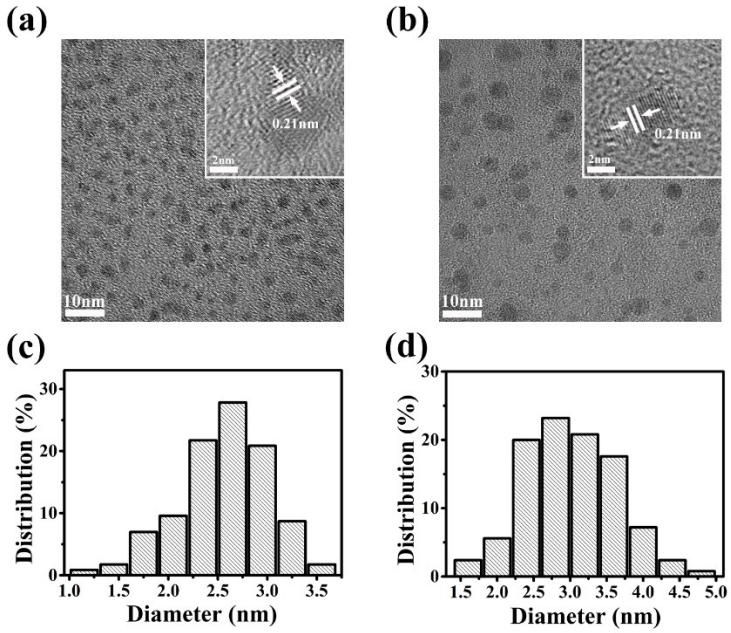

Figure S2 TEM images of (a) CC-CDs-300, (b) CC-CDs-600. Particle size distribution of (c) CC-CDs-300, (d) CC-CDs-600.

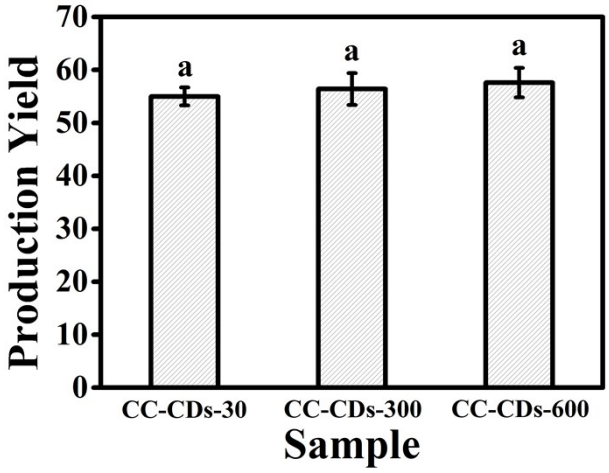

Figure S3 The production yield of CDs prepared from different reaction volumes. The error bars mean the standard deviation of triplicate samples ($P<0.05$). The same letters indicate there is no significant difference.

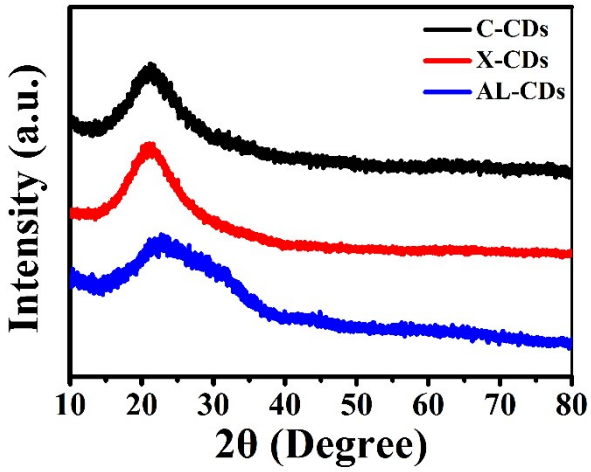

Figure S4 XRD pattern of C-CDs, X-CDs, and AL-CDs.

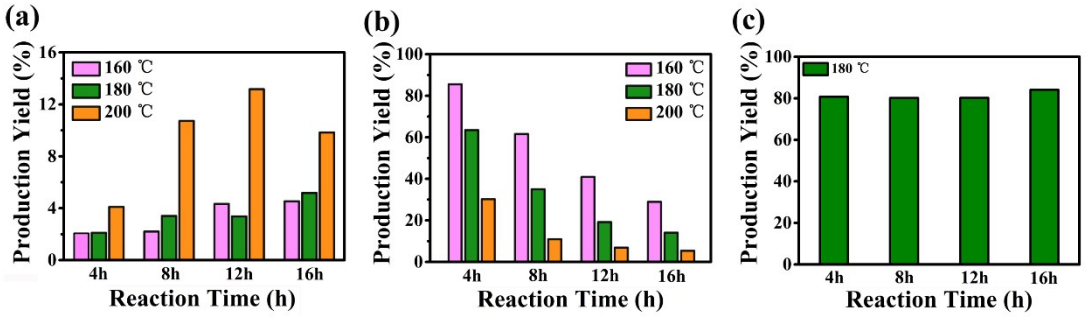

Figure S5 Production yield of (a) C-CDs, (b) X-CDs, (C) AL-CDs at

different reaction conditions.

From Figure S5a, the increase of reaction time or temperature will result in the slight improvement of the production of CDs. In general, C-CDs have a low production yield. This indicates that cellulose is difficult to hydrolyze, which results in the low production yield of C-CDs. As shown in Figure S5b, the production yield of X-CDs decreases when the reaction time is prolonged or the reaction temperature increased. We found that the increase of temperature and reaction time would lead to the formation of more hydrochar. This indicates that xylan is easy to hydrolyze, longer reaction time or higher reaction temperature, will lead to the formation of hydrochar and reduce the production yield of X-CDs.

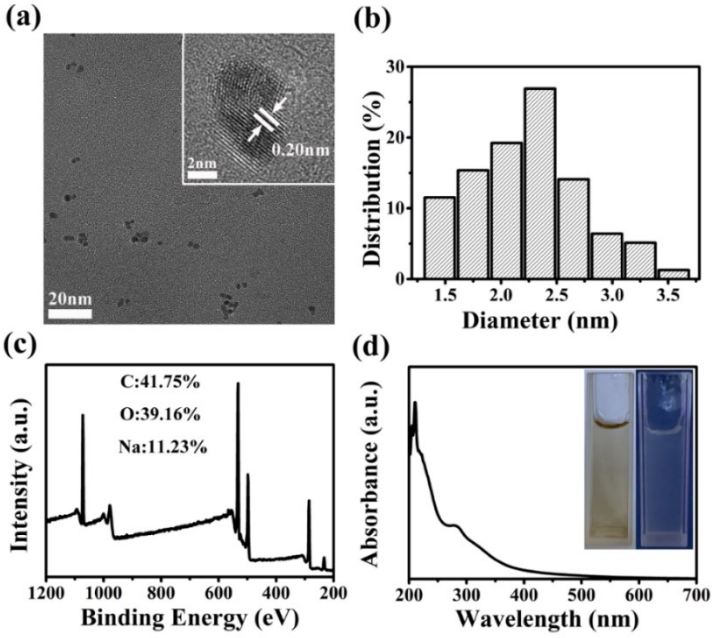

Figure S6 (a) TEM image, (b) particle size distribution, (c) XPS pattern, (d) UV-vis absorption spectrum of CDs prepared from lignin (dealkaline).

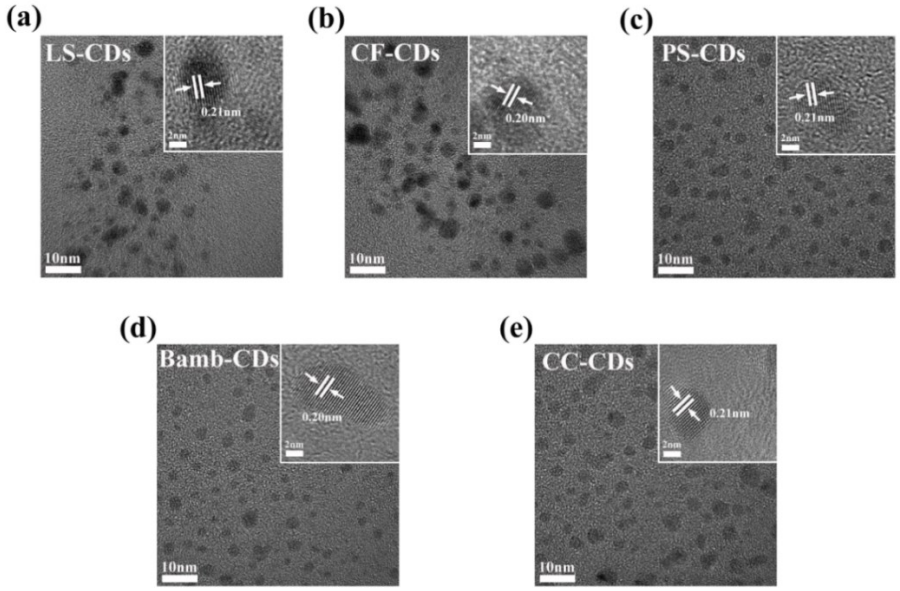

Figure S7 (a) TEM images of (a) LS-CDs, (b) CF-CDs, (c)PS-CDs, (d)Bamb-CDs, (e) CC-CDs.

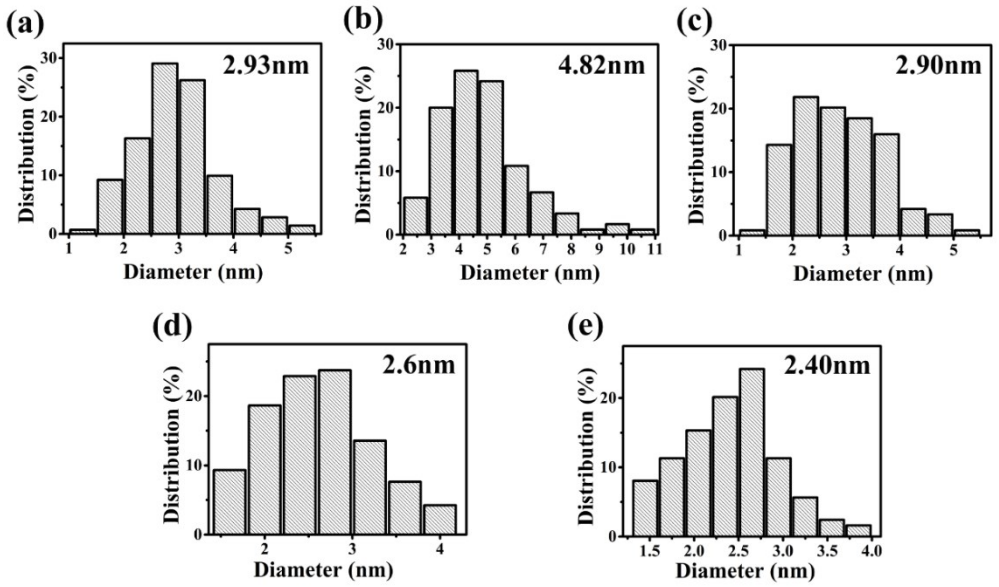

Figure S8 Particle size distribution of (a) LS-CDs, (b) CF-CDs, (c) PS-CDs, (d) Bamb-CDs, (e) CC-CDs. The average particle size of CDs is indicated in the corresponding figure.

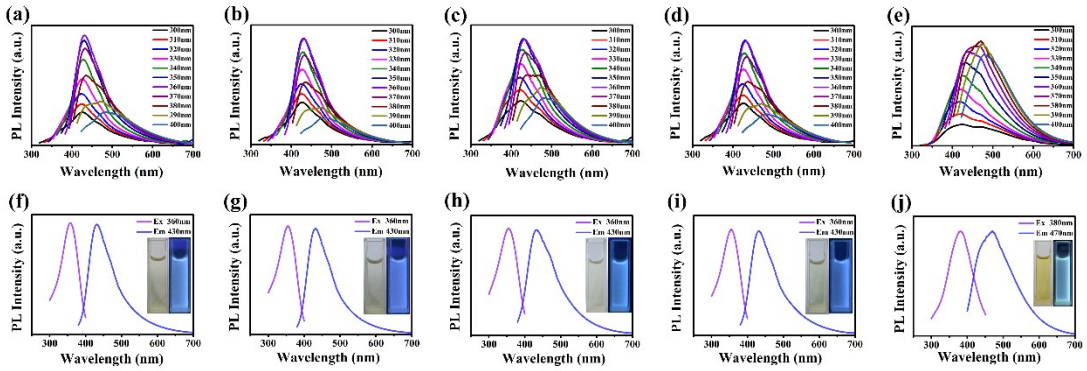

Figure S9 PL emission spectrums obtained from different excitation wavelengths of (a) LS-CDs, (b) CF-CDs, (c) PS-CDs, (d) Bamb-CDs, (e) CC-CDs. PL excitation and PL emission spectrums of (f) LS-CDs, (g) CF-CDs, (h) PS-CDs, (i) Bamb-CDs, (j) CC-CDs.

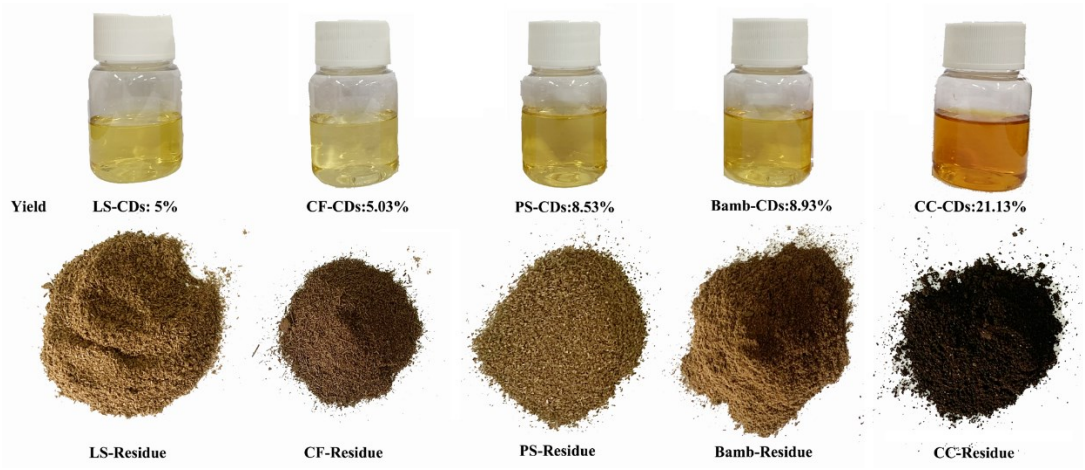

Figure S10 Photograph of CDs and their hydrothermal residues. LS, CF, PS, Bamb, and CC are the abbreviations of linen stalk, coir fibre, peanut shells, bamboo, and corn cob, respectively. Residue means the hydrothermal residues of the corresponding biomass.

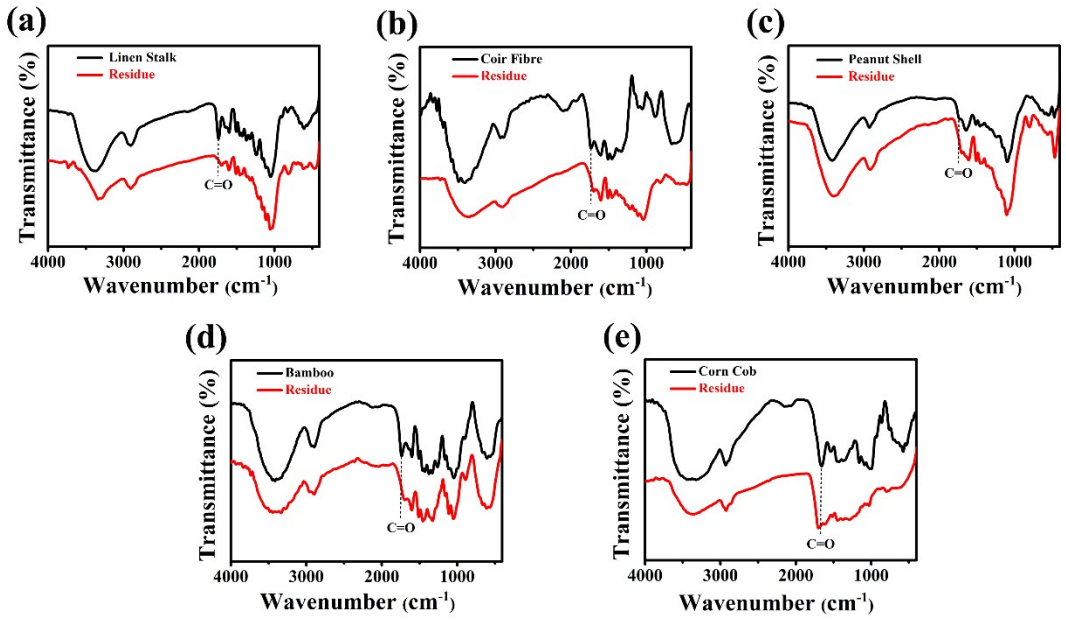

Figure S11 FT-IR spectrums of biomass and their hydrothermal residue. The black dotted line shows the characteristic peaks of stretching vibration of C=O of hemicellulose.

Table S1 Comparsion of production yield of CDs prepared from different biomass

Biomass	Preparation Methods	Particle Size (nm)	Production Yield (%)	Quantum Yield (%)	Reference
bee pollens	hydrothermal	1-2	30	9	[1]
poplar leaves	hydrothermal	3.26	10	10.64	[2]
egg	pyrolysis	2.15	6	8	[3]
coffee grounds	pyrolysis	5±2	12	3.8	[4]
prawn shell	hydrothermal	3	18	9	[5]
chia seed	pyrolysis	2-6	10	4-25	[6]
rice husk	pyrolysis, oxidation	3-6	15	8.1	[7]
durian	hydrothermal	2-6	6.8	79	[8]
linseed	hydrothermal	4-8	7.8	14.2	[9]
gelatin	hydrothermal	1.7	38.6	31.6	[10]
konjac flour	pyrolysis	3.37	3	22	[11]
corn cob	hydrothermal	2.54	55	1.0	This work

Table S2 Components of Biomass and their hydrothermal residue.

	Cellulose (mg/g)	Hemicellulose (mg/g)	Lignin (mg/g)	a (%)	b (%)	c (%)
(1) LS	439.575	187.098	323.4	46.27	19.69	34.04
Residue	317.018	23.214	319.7	-	-	-
(2) CF	408.285	182.75	391.4	41.56	18.6	39.84
Residue	291.433	18.373	253.2	-	-	-
(3) PS	368.6	183.308	322.1	42.17	20.97	36.85
Residue	266.449	17.434	270.8	-	-	-
(4) Bamb	429.648	213.884	349.2	43.28	21.54	35.18
Residue	336.169	42.753	191.6	-	-	-
(5) CC	565.07	386.99	26.9	57.72	39.53	2.75
Residue	124.732	36.311	22.7	-	-	-

LS, CF, PS, Bamb, and CC represent linen stalk, coir fibre, peanut shell, bamboo, and corn cob respectively; Residue means the hydrothermal residue of the corresponding biomass.

a: the mass percentage of cellulose in the three components (cellulose, hemicellulose, lignin) of biomass;

b: the mass percentage of hemicellulose in the three components (cellulose, hemicellulose, lignin) of biomass;

c: the mass percentage of lignin in the three components (cellulose, hemicellulose, lignin) of biomass;

Reference

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