Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Improving revenue of lignin conversion into carbon dots by prior amino modification

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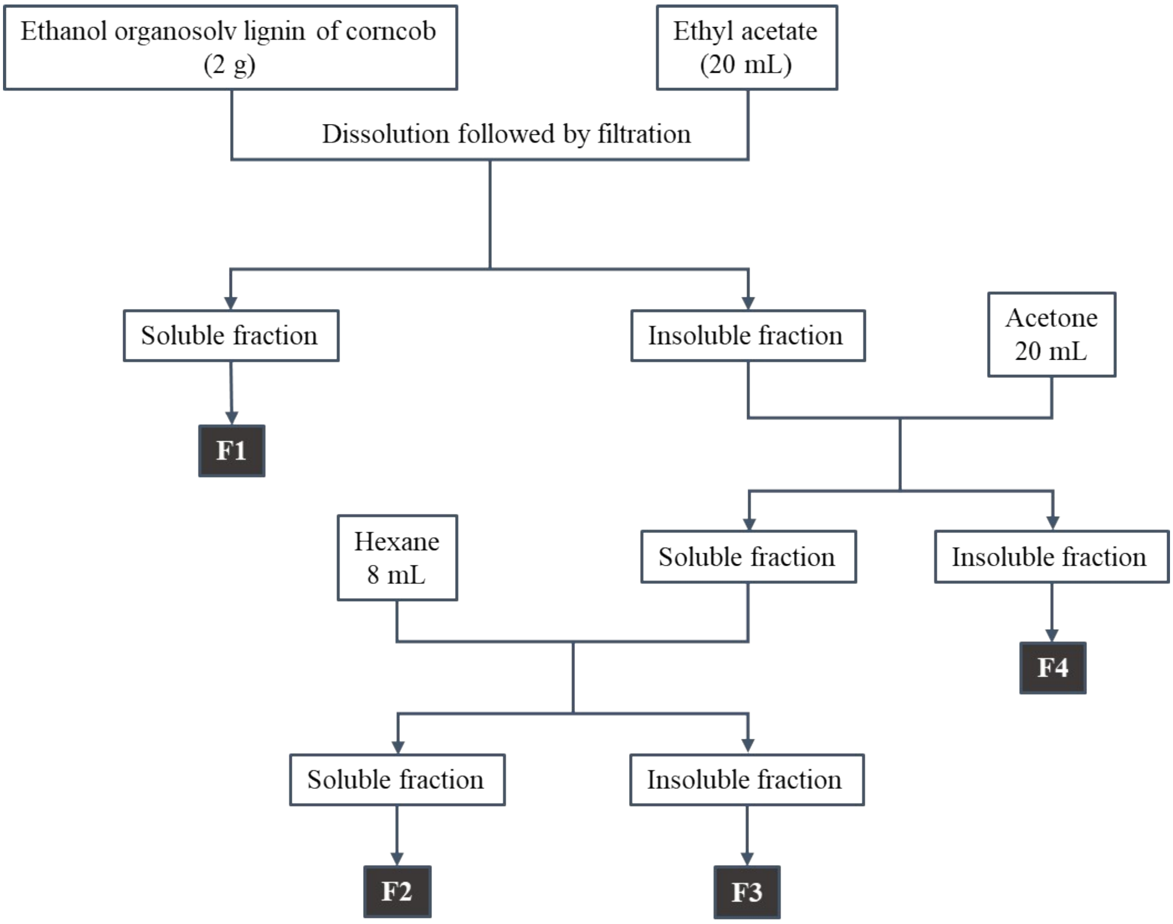
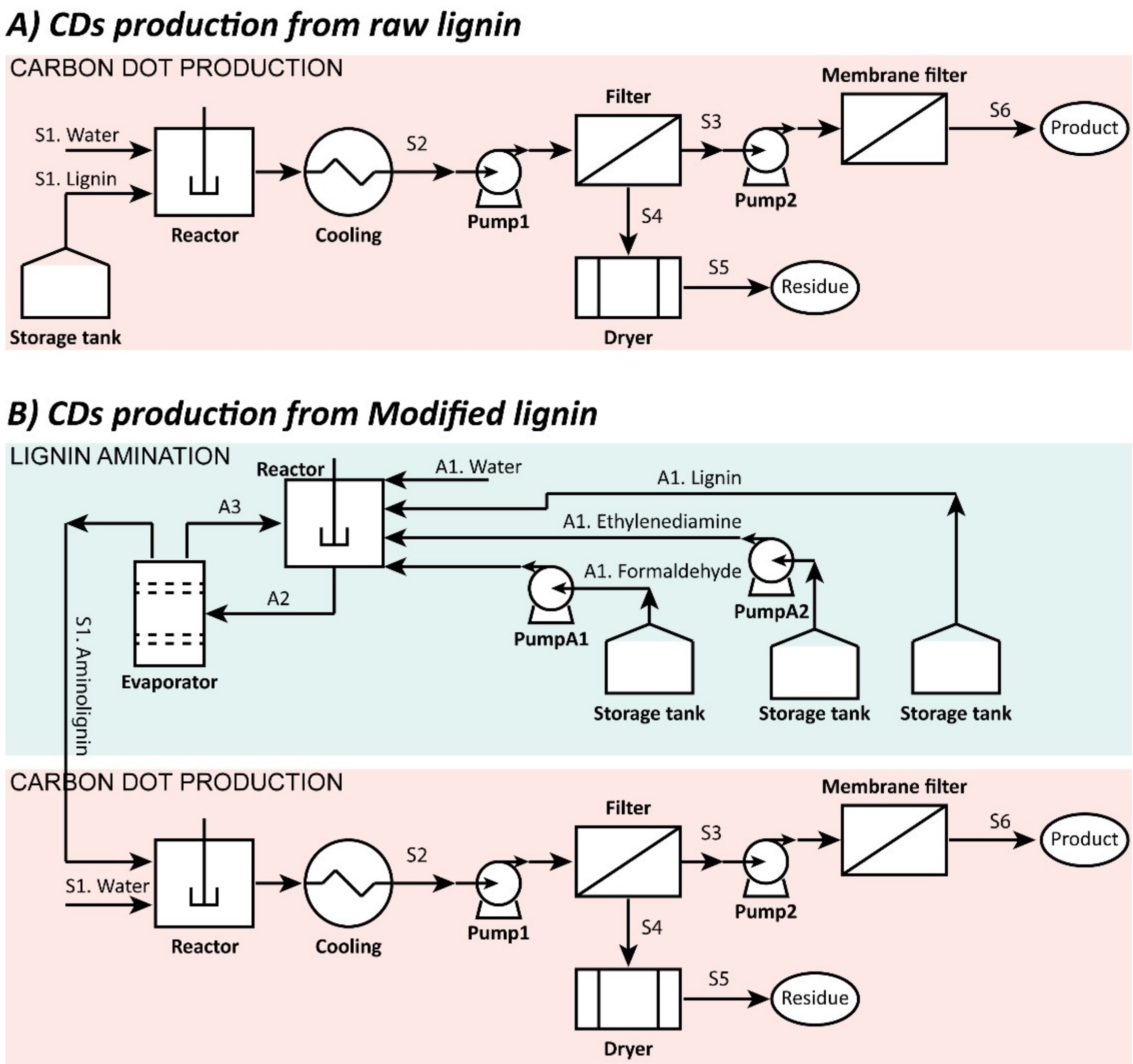
Section Schemes



Scheme S1 Fractionation of ethanol organosolv lignin of corncob



Scheme S2. Process diagram of industrial-scale carbon dots production from raw lignin, and modified lignin.

Section Figures

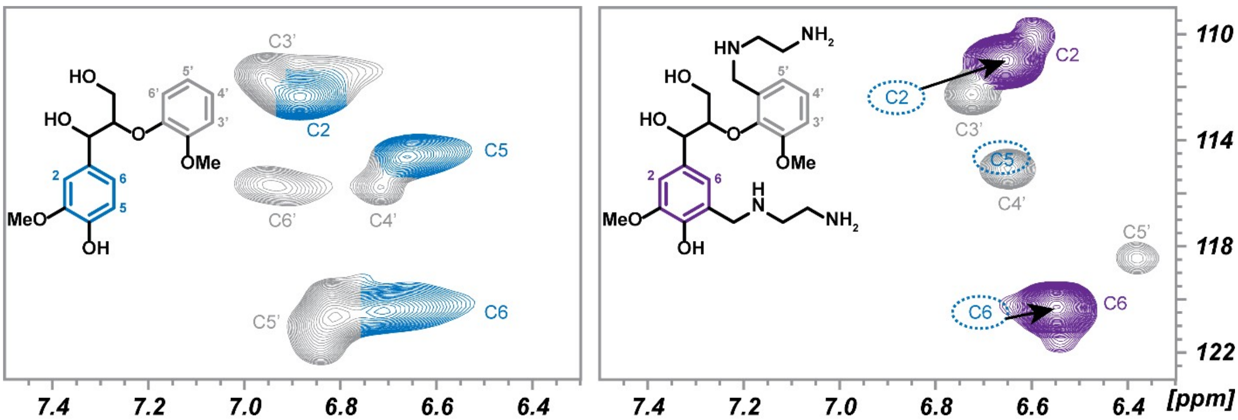


Fig. S1 The HSQC NMR of lignin model compound of the β-O-4 dimer, and the modified β-O-4 dimer by Mannich reactions with ethylenediamine. The reaction between β-O-4 dimer and ethylenediamine was performed by mixing the β-O-4 dimer (0.55 mmol), formaldehyde (1.1 mmol), and ethylenediamine (1.1 mmol) at room temperature for 24 h. Then the isolation was performed by extraction with ethyl acetate, then evaporation, and vacuum dried at 50 ^{o}C.

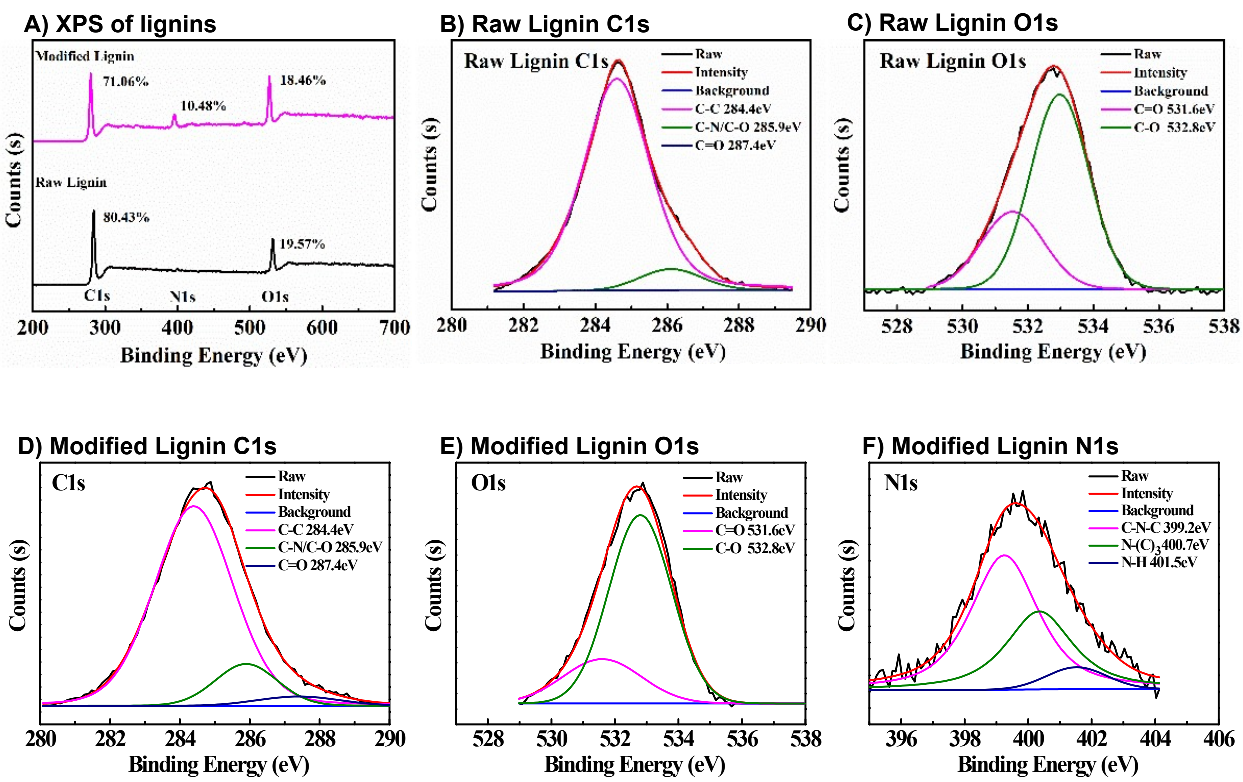


Fig. S2 XPS studies of the raw lignin and modified lignin by Mannich reaction. The results indicated nitrogen was covalently bonded onto lignin.

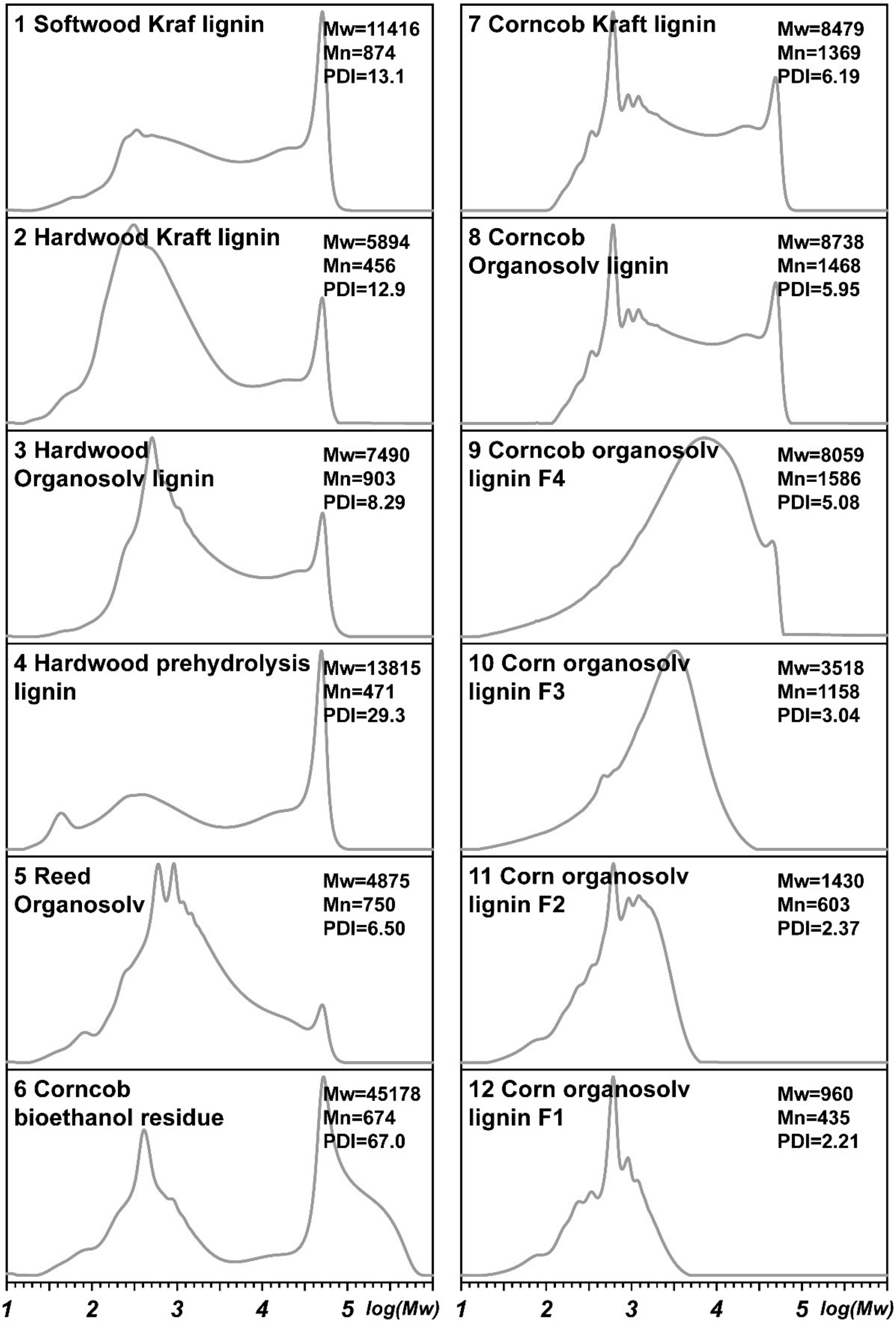


Fig. S3 Molecular weight of lignin by GPC study.

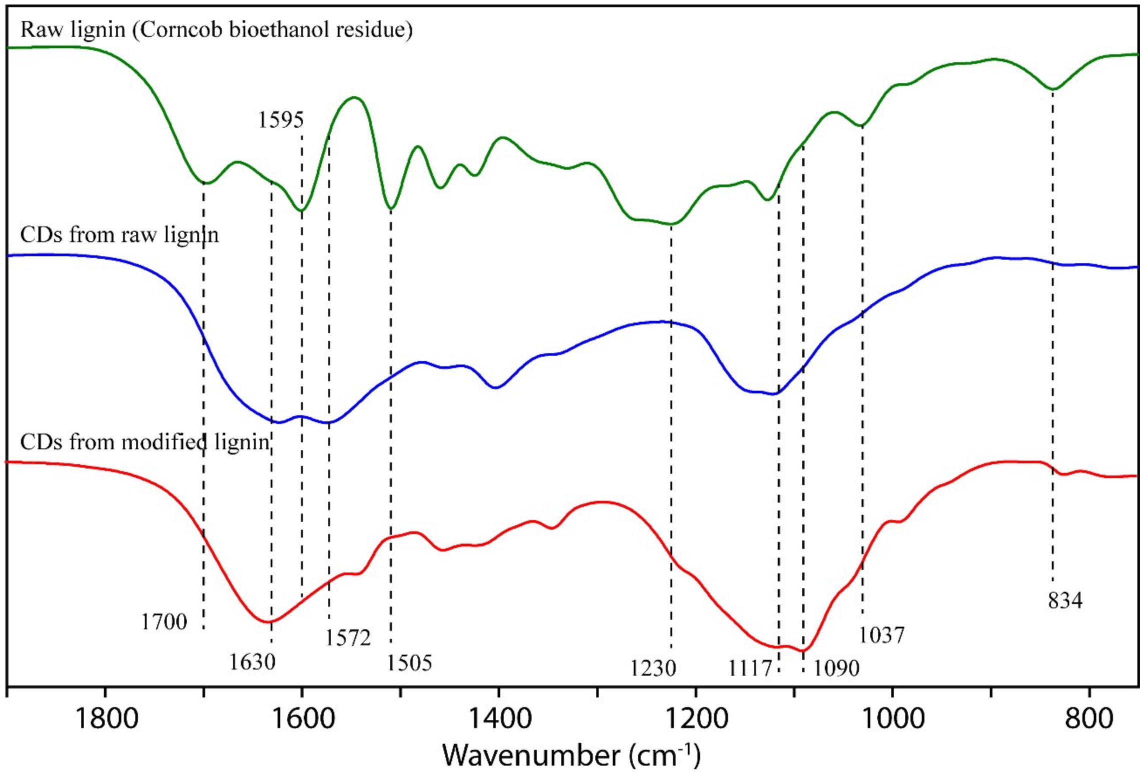


Fig. S4 FTIR spectra of lignin and CDs.

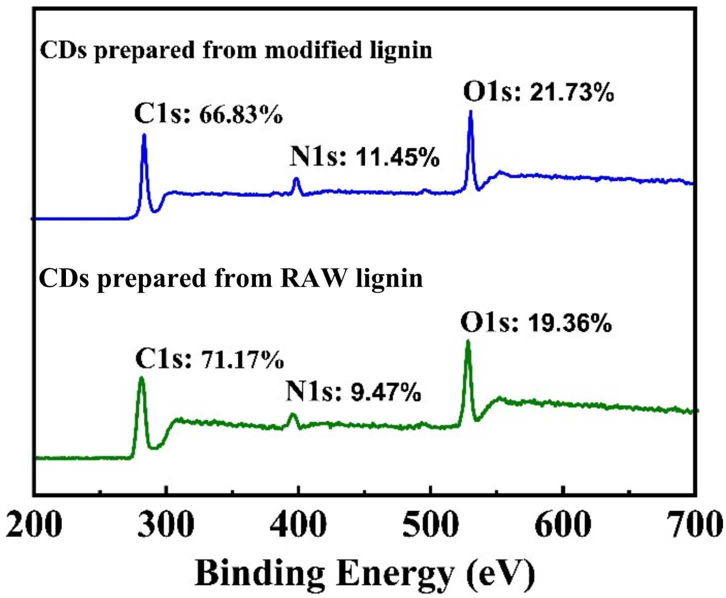


Fig. S5 XPS result of as-prepared CDs

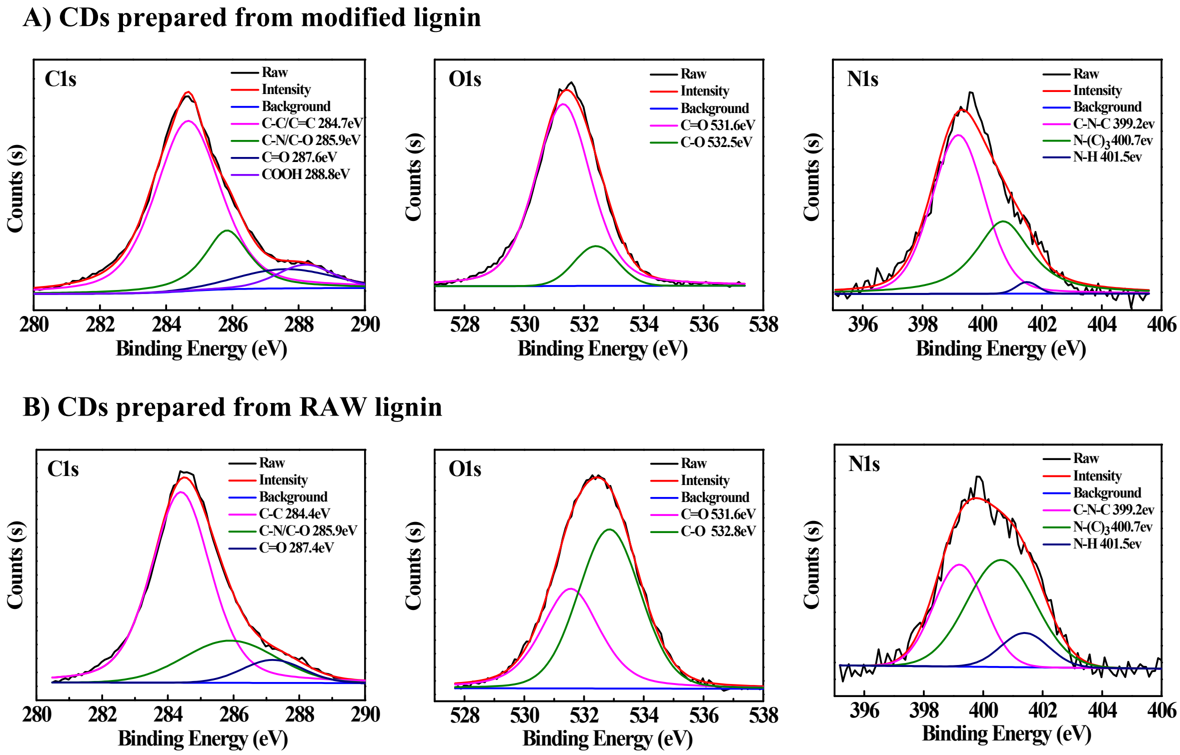


Fig. S6 Deconvolution of the XPS peaks of CDs.

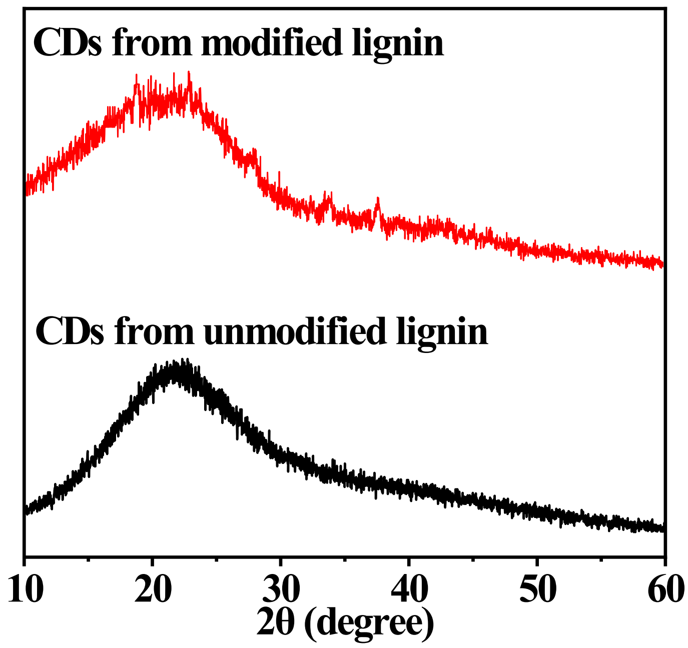


Fig. S7 XRD patterns of CDs.

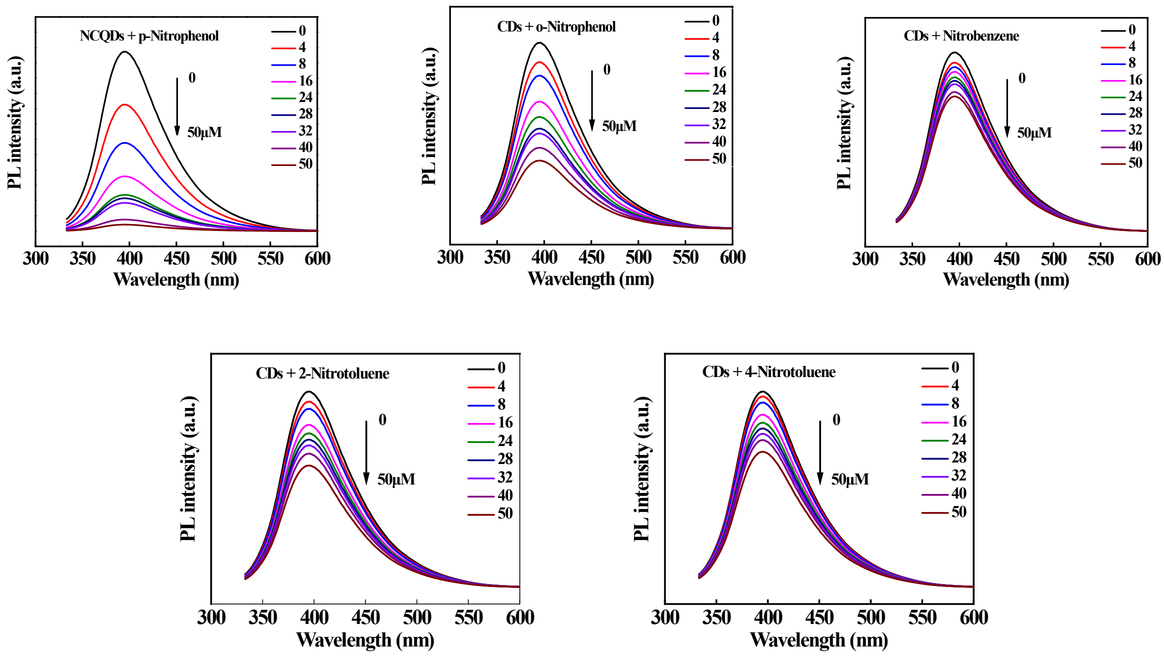


Fig. S8 Photoluminescence spectra of CDs solutions with different concentrations of nitroaromatic compounds

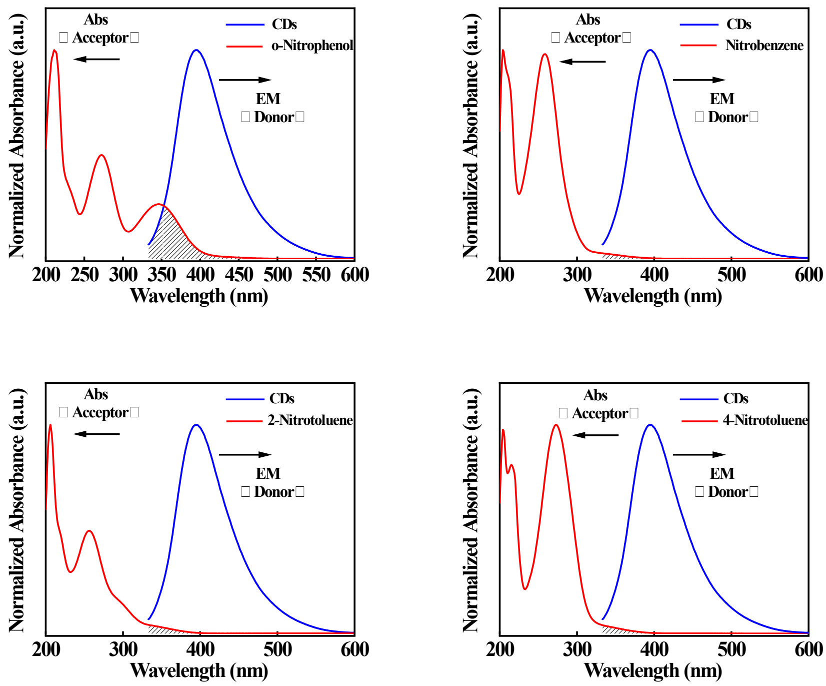


Fig. S9 The overlapped absorption spectrum of nitroaromatic compounds and fluorescence emission spectrum of CDs

Section Tables

Table S1 The yield and QY of CDs by previous reports.

Lignin source	Method	Synthetic methods	Yield /%	QY /%	Ref
Alkali lignin/Citric acid (0.1g/7g)	Bottom up	Hydrothermal method with ethylenediamine	--	43	[1]
Alkali lignin	Bottom up	1. HNO3 treatment 2. hydrothermal method	21	22	[2]
Lignin	Bottom up	Oxidative hydrothermal with H_2O_2	0.8-12.06	--	[3]
Alkali lignin (TCI)	Bottom up	0.1 g Lignin+0.6ml EDA+9.4 H_2O	82.4	<17	[4]
Biorefinery residue	Bottom up	Ethanol solvothermal method	--	1.68-2.47	[5]
Pre-hydrolyzed lignin	Bottom up	0.075 g Lignin + 3 g sulfuric acid + 10 mL H2O	--	2.7-13.5%	[6]
Alkali Lignin	Top-Down	1. Carbonization with DES 2. Ball mill	--	7.95	[7]
Lignin amines	Top-Down	1. Carbonization 2. Ball mill	--	8.1	[8]
Alkali lignin	Bottom up	Hydrothermal with ammonia water	--	1.49-14.24	[9]
Alkali lignin	Bottom up	1. Hydrothermal 2. 30ml H2SO4+HNO3	--	17.3	[10]
Sodium lignosulfonate/Citric acid	Bottom up	Hydrothermal with 10 mg/mL NaOH solution	--	23.3	[11]
Alkali lignin	top-down	1. Carbonization 2. Oxidation H2SO4:HNO3 = 3:1, v/v	6-7	8.1-13.0	[12]
Lignosulfonate	Bottom up	Microwave irradiation method	2.39-5.02	31.27	[13]
Lignin corncob/Citric acid (0.1g/2.1g)	Bottom up	Hydrothermal with EDA	--	43.9	[14]
Lignin	Top-down	1. Hydrothermal method 2. NaOH/O2 oxidation	42.5	10.0	[15]

Table S2 The yield and QY of CDs derived from biomass other than lignin

Carbon source	Method	Synthetic methods	Yield	QY	Ref
Lignocellulose residue	Bottom up	Solid acid catalyzed DMF solvothermal method	--	2.7	[16]
Pine wood	Bottom up	Hydrothermal	--	4.69	[17]
Hemicellulose	Top-down	1. Hydrothermal carbonization 2. NaOH/O2 oxidation	16.9-29.1	2.8-16.6	[15]
Cellulose	Top-down	1. Hydrothermal carbonization 2. NaOH/O2 oxidation	34.0	13.4	[15]
Chitosan	Top-down	1. Hydrothermal carbonization 2. NaOH/O2 oxidation	33.5	11.5	[15]
Cabbage	Bottom up	hydrothermal	7.067	16.5	[18]
Cellulose (MCC)	Bottom up	1. Dissolved with NaOH/Urea 2. Hydrothermal treatment of the cellulose NaOH/Urea solution	<6	<11	[19]
Cellulose	Bottom up	Microware assisted hydrothermal method	--	6.20	[20]
Protein	Bottom up	Microware assisted hydrothermal method	--	6.81	[20]
Peanut shell	Bottom up	Microware assisted hydrothermal method	--	2.83	[20]
Cotton stalk	Bottom up	Microware assisted hydrothermal method	--	2.95	[20]
Soymeal	Bottom up	Microware assisted hydrothermal method	--	4.92	[20]
Tannic acid	Bottom up	Microwave-assisted hydrothermal method with 25% ammonia solution	--	2.1-19.15	[21]

Table S3 DFRC results, and phenolic hydroxyl content by potentiometric titration of lignins

Lignins	G units μmol/g	S units μmol/g	Total (S+G) μmol/g	S/G	Phenolic -OH mmol/g
Corncob bioethanol residue	23.0±1.0	27.4±0.6	50.3±1.6	1.19	1.29
Hardwood prehydrolysis lignin	5.09±0.09	13.8±0.4	18.8±0.3	2.70	1.53
Softwood Kraft lignin	40.9±1.3	0	40.9±1.3	0	1.50
Hardwood Kraft lignin	35.8±0.6	23.1±5.0	58.9±5.6	0.64	1.88
Hardwood organosolv lignin	159±3	158±2	317±5	0.99	1.47
Reed organosolv lignin	78.0±1.4	60.5±2.8	138±4	0.78	1.62
Corncob Kraft lignin	15.7±0.7	18.8±1.7	34.5±2.4	1.20	1.03
Corncob organosolv lignin	16.4±0.9	15.2±1.1	31.6±2.0	0.92	1.76
Corncob organosolv lignin F1	3.11±0.34	17.1±2.3	20.2±2.7	5.49	2.23
Corncob organosolv lignin F4	10.1±4.4	11.2±3.8	21.3±8.2	1.12	1.28
Corncob organosolv lignin F3	11.2±0.3	10.1±0.9	21.3±0.6	0.90	1.65
Corncob organosolv lignin F2	6.68±1.02	9.99±1.15	16.7±2.2	1.50	1.96

Table S4 Nitrogen content and water solubility of modified lignin, and the yield and QY of resultant

Samples	Nitrogen Content Wt%		Solubility pH 7 g/L		Solubility at pH 5 g/L		QY %	Yield wt%
	Raw lignin	Modified lignin	Raw lignin	Modified lignin	Raw lignin	Modified lignin		
Softwood Kraft lignin	0.47	9.72	0.65	4.70	0.27	4.99	19.13	50.2
Hardwood Kraft lignin	0.46	9.27	0.08	9.63	0.27	9.04	12.39	64.6
Hardwood organosolv lignin	0.43	9.44	0.69	9.32	0.32	9.01	11.69	61.5
Hardwood prehydrolysis lignin	0.59	9.71	0.52	10.26	0.35	10.10	13.89	64.4
5 Reed solvent lignin L6	0.56	10.05	0.81	6.70	0.30	6.98	20.10	53.5
Corncob bioethanol residue	1.11	12.26	0.50	6.22	0.43	7.37	36.42	68.3
Corncob Kraft lignin	0.62	12.17	0.21	6.27	0.11	7.11	36.82	72.3
Corncob organosolv lignin	0.58	12.33	0.85	7.98	0.62	9.29	32.88	67.6
Corncob organosolv lignin F4	0.37	11.85	0.65	4.70	0.22	7.26	35.22	55.3
Corncob organosolv lignin F3	0.57	11.43	0.52	10.26	0.34	7.70	30.30	66.1
Corncob organosolv lignin F2	0.72	10.75	0.69	9.32	0.40	9.62	21.67	63.9
Corncob organosolv lignin F1	0.45	10.28	0.08	9.63	0.43	9.07	21.81	71.7

Table S5 Estimation of Total product cost & minimum product selling prices of carbon dots production from **RAW lignin**

Total Product Cost & Minimum Product Selling Prices		
Items	Cost* (UDS/t)	Descriptions
I. Total Operation Cost	**10817**	
A. Direct Production Costs	8794	
1. Raw Materials	2568	
Lignin	2551	
Water	17	
2. Operating Labor	1728	10% Total Product Cost
3. Direct Supervisory	346	20% Operating Labor
4. Utilities	2593	15% Total Product Cost
5. Maintenance and Repairs	904	3% Fixed-Capital Investment
6. Operating Supplies	136	15% Maintenance and Repairs
7. Laboratory Charges	173	10% Operating Labor
8. Patents and Royalties	346	2% Total Product Cost
B. Fixed Charges	813	
1. Local Taxes	602	2% Fixed-Capital Investment
2. Insurance	211	0.5% Fixed-Capital Investment
C. Plant-Overhead Costs	1210	70% Operating Labor
II. Depreciation	3012	10% Fixed-Capital Investment
III. General Expenses	3456	
A. Administrative Costs	519	3% Total Product Cost
B. Distribution Costs	1296	7.5% Total Product Cost
C. R&D Costs	864	5% Total Product Cost
D. Financing	778	4.5% Total Product Cost
IV. Total Product Cost	17285	
V. Minimum Product Selling Prices	**26488**	
A. Residue Value	920	
B. Income Tax	3037	30% Gross Earning
C. Return On Investment	7087	20% Total Capital Investment
D. Gross Earning	9204	

Notes: * The cost to produce one ton carbon dots.

Table S6 Estimation of Total product cost & minimum product selling prices of carbon dots production from **MODIFIED lignin**

Total Product Cost & Minimum Product Selling Prices		
Items	Cost* (UDS/t)	Descriptions
I. Total Operation Cost	**5984**	
A. Direct Production Costs	4963	
1. Raw Materials	1716	
Lignin	208	
Ethylenediamine	1274	
Formaldehyde	230	
Water	4.3	
2. Operating Labor	922	10% Total Product Cost
3. Direct Supervisory	184	20% Operating Labor
4. Utilities	1383	15% Total Product Cost
5. Maintenance and Repairs	418	3% Fixed-Capital Investment
6. Operating Supplies	63	15% Maintenance and Repairs
7. Laboratory Charges	92	10% Operating Labor
8. Patents and Royalties	184	2% Total Product Cost
B. Fixed Charges	375	
1. Local Taxes	278	2% Fixed-Capital Investment
2. Insurance	97	0.5% Fixed-Capital Investment
C. Plant-Overhead Costs	645	70% Operating Labor
II. Depreciation	1392	10% Fixed-Capital Investment
III. General Expenses	1844	
A. Administrative Costs	277	3% Total Product Cost
B. Distribution Costs	692	7.5% Total Product Cost
C. R&D Costs	461	5% Total Product Cost
D. Financing	415	4.5% Total Product Cost
IV. Total Product Cost	9220	
V. Minimum Product Selling Prices	**13854**	
A. Residue Value	47	
B. Income Tax	1404	30% Gross Earning
C. Return On Investment	3276	20% Total Capital Investment
D. Gross Earning	4633	

Notes: * The cost to produce one ton carbon dots.

Table S7 Mass balance of carbon dots production from **RAW lignin**

Stream	Description	Solid	water	Total
S1 Lignin	Dried raw lignin	1.02	0.00	1.02
S1 Water	Water added	0.00	25.5	25.5
S2	Products to filter	1.02	25.5	26.5
S3	Filtered carbon dots solution	0.100	23.7	23.8
S4	Wet residue	0.920	1.84	2.76
S5	Dried residue	0.920	0.102	1.02
S6	Purified carbon dots	0.100	0.300	0.400

Table S8 Mass balance of carbon dots production from **MODIFIED lignin**

Stream	Description	Solid	Solvent	Total
A1. Water	Feed	0.000	0.147	0.147
A1. Lignin	Feed	0.0834	0.0000	0.0834
A1. Ethylenediamine	Feed	0.0425	0.0000	0.0425
A1. Formaldehyde	Feed	0.0212	0.0361	0.0574
A2	Modified lignin slurry	0.147	0.333	0.481
A3. Ethylenediamine	Recovered ethylenediamine	0.0109	0.0000	0.0109
A3. Formaldehyde	Recovered formaldehyde	0.00545	0.00000	0.00545
A3. Water	Recovered water	0.000	0.186	0.186
S1 Lignin	Modified lignin	0.147	0.147	0.294
S1 Water	Water added	0.000	3.53	3.53
S2	Products to filter	0.147	3.53	3.68
S3	Filtered carbon dots solution	0.100	3.44	3.54
S4	Wet residue	0.0471	0.0941	0.141
S5	Dried residue	0.0471	0.0052	0.0523
S6	Purified carbon dots	0.100	0.300	0.400

Table S9 Estimation of capital investment cost of carbon dots production from **RAW lignin**

Capital Investment Cost		
Items	Cost (USD)	Descriptions
I. Direct Costs	21487288	
A. Equipment Installation	16068754	
1. Purchased Equipment	4671150	
2. Installation	1868460	40% Purchased Equipment
3. Instrumentation and Controls	840806.9	18% Purchased Equipment
4. Piping	2102017	45% Purchased Equipment
5. Electrical	1167787	25% Purchased Equipment
B. Buildings, Process and Auxiliary	1868460	40% Purchased Equipment
C. Service Facilities and Yard Improvements	3269805	70% Purchased Equipment
D. Land	280269	6% Purchased Equipment
II. Indirect Costs	7677294	
A. Engineering and Supervision	2410313	15% Direct Costs
B. Construction Expense and Contractor’s Fee	2892376	18% Direct Costs
C. Contingency	2374605	10% Fixed-Capital Investment
III. Fixed-Capital Investment	23746048	Direct Costs + Indirect Costs
IV. Working Capital	4190479	15% Total Capital Investment
V. Total Capital Investment	27936527	

Table S10 Estimation of capital investment cost of carbon dots production from **MODIFIED lignin**

Capital Investment Cost		
Items	Cost (USD)	Descriptions
I. Direct Costs	7428407	
A. Equipment Installation	4923479	
1. Purchased Equipment	2159421	
2. Installation	863768	40% Purchased Equipment
3. Instrumentation and Controls	388696	18% Purchased Equipment
4. Piping	971739	45% Purchased Equipment
5. Electrical	539855	25% Purchased Equipment
B. Buildings, Process and Auxiliary	863768	40% Purchased Equipment
C. Service Facilities and Yard Improvements	1511594	70% Purchased Equipment
D. Land	129565	6% Purchased Equipment
II. Indirect Costs	3549128	
A. Engineering and Supervision	1114261	15% Direct Costs
B. Construction Expense and Contractor’s Fee	1337113	18% Direct Costs
C. Contingency	1097753	10% Fixed-Capital Investment
III. Fixed-Capital Investment	10977534	Direct Costs + Indirect Costs
IV. Working Capital	1937212	15% Total Capital Investment
V. Total Capital Investment	12914746	

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