Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Supporting Information

Sustainable Carbon Quantum Dots from Forestry and Agricultural Biomass with Amplified Photoluminescence by Simple NH_4OH Passivation

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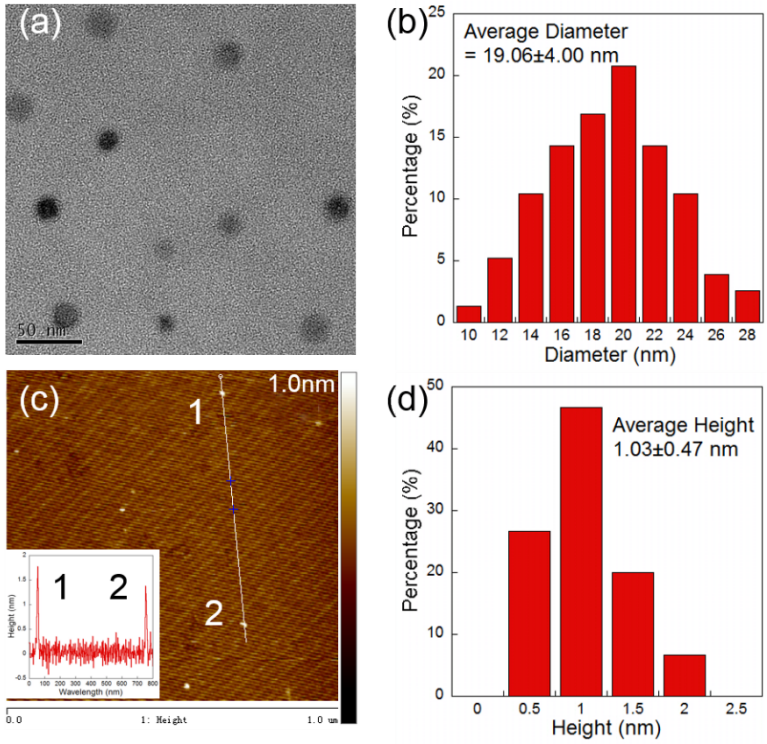

Fig. S1 (a) A HRTEM image of BCDs. (b) The statistic diameter from HRTEM analysis. (c) An AFM image of BCDs with height of section from AFM analysis. (d) Statistic height distribution from AFM analysis.

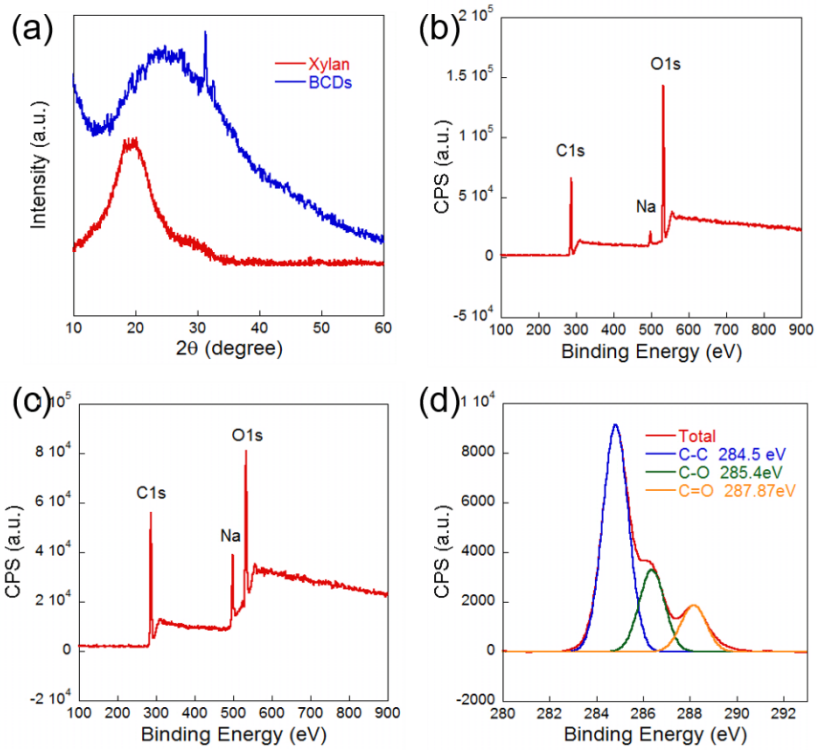

Fig. S2 (a) The XRD patterns of xylan and BCD. (b) The XPS spectrum of xylan. (c) The XPS spectrum of BCDs. (d) The C1s signals of BCDs.

Table.S1 The elemental composition of the CDs form XPS analysis				
Sample	C%	N%	O%	C/O
Xylan	58.63	-	41.37	1.42
NCDs	71.68	6.37	21.95	3.27
BCDs	72.70	-	27.30	2.66

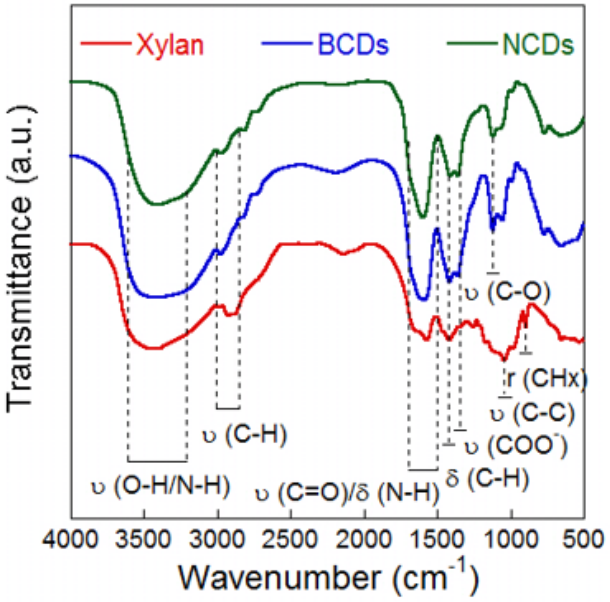

Fig. S3 FTIR spectra of the CDs. Decomposition of sugar chains and furanose rings can be observed, and –OH/C=O/N-H bonds strengthen.

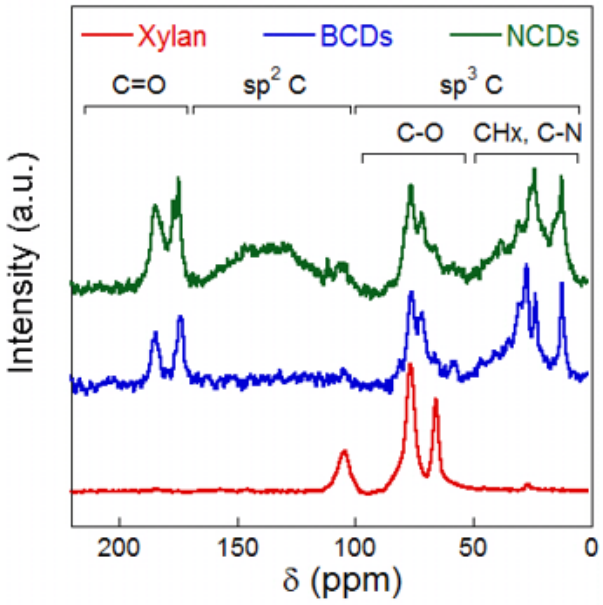

Fig. S4^{13}C NMR spectra of the CDs. Obvious C=O, CH_x/C-N signals can be observed.

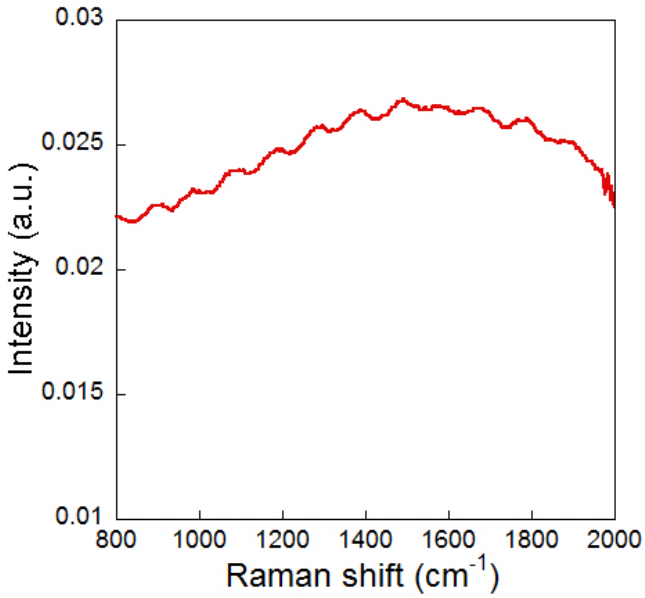

Fig. S5 Raman spectrum of NCDs. D band at 1350 cm^{-1} and G band at 1598cm^{-1}were unobservable. Strong fluorescence background would disturb the Raman signals[1].

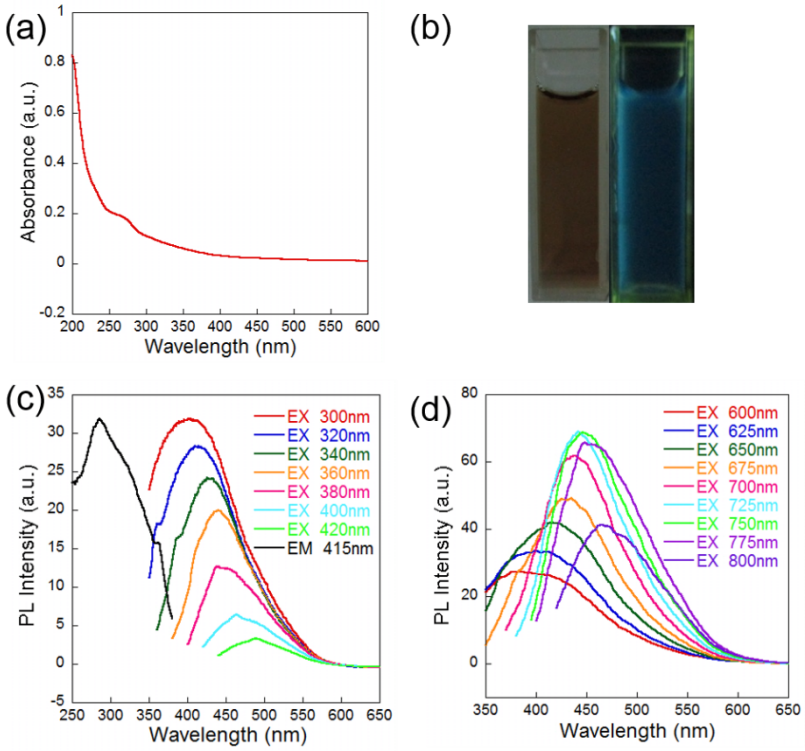

Fig. S6 (a) Absorbance spectrum of BCDs. (b) The images of BCDs under daylight and UV lamp radiation. (b) Fluorescence spectra. (c) Up-conversion PL spectra.

QY measurements: The quantum yields (QYs) of CDs were measured with the equation[2] (2):

$$QY = QY_R \frac{I A_R n^2}{I_R A n_R^2}$$

Quinine sulfate in 0.1 M sulfuric acid solution (literature QY=54% at 360 nm excitation) was selected to be a reference. In the equation, I is the calculated integrated emission intensity of the sample, A is the optical absorbance at the corresponding excitation wavelength and n is the refractive index of the solvent. The subscript R refers to the reference fluorescein. For aqueous solution, $n/n_R=1$. All the QYs were calculated in a concentration of 0.1 mg/mL.

Table. S2 The PL properties of the CDs in different conditions				
Starting materials	Dispersants/ Passivation agents	Max. Em (Ex)	Solvents	QYs (360 nm)
Quinine sulfate	-	-	0.1M H_2SO_4	54% (known)
Xylan (BCDs)	2% NaOH	415 nm (300nm)	Water	2.06%
Xylan	0.1% NH_4OH	408 nm (320nm)	Water	3.22%
Xylan	0.25% NH_4OH	396 nm (320nm)	Water	5.54%
Xylan	0.5% NH_4OH	402 nm (320nm)	Water	9.44%
Xylan	1.0% NH_4OH	404nm (320nm)	Water	11.50%
Xylan	1.5% NH_4OH	405nm (320nm)	Water	10.11%
Xylan (NCDs)	2.0% NH_4OH	403nm (320nm)	Water	13.00%
Xylan	2.0% NH_4OH	394nm (320nm)	Methanol	6.59%
Xylan	2.0% NH_4OH	378nm (300nm)	Ethanol	7.91%
Xylan	2.0% NH_4OH	389nm (320nm)	DMF	10.39%
Xylan	2.0% NH_4OH	415 nm (320nm)	DMSO	8.23%
Xylan	5.0% NH_4OH	406 nm (320nm)	Water	11.65%
Xylan	12.5% NH_4OH	405 nm (320nm)	Water	14.15%
Xylan	25.0% NH_4OH	414 nm (320nm)	Water	16.18%
Xylan	2% EDA	447 nm (380nm)	Water	7.48%
Xylan	2% TTDDA	445nm (380nm)	Water	7.26%
Chitosan	2% Acetic acid	401nm (320nm)	Water	12.99%
HEC	Water	427nm (340nm)	Water	3.42%
Starch soluble	Water	429 nm (340nm)	Water	1.42%
β-cyclodextrin	Water	427nm (340nm)	Water	1.11%

Average lifetime determination: The average lifetime of CDs was determined by following equation[3] (1):

$$\tau_{av} = \tau_1 a_1 + \tau_2 a_2 + \tau_3 a_3$$

Here, τ_1, τ_2, τ_3 were the first, second and third component of the decay time of CDs, and a_1, a_2, a_3 were the corresponding relative weights of these components, respectively.

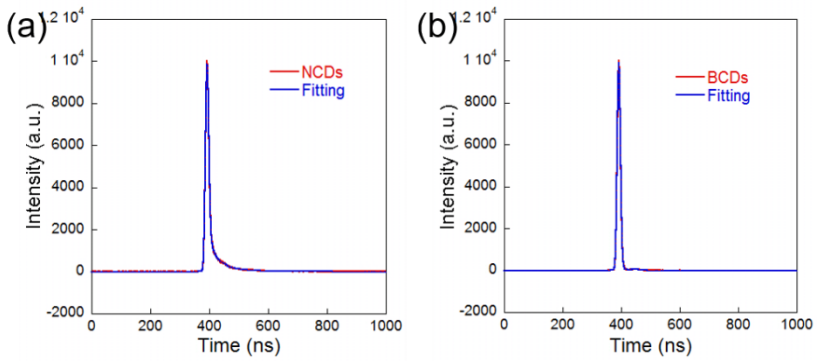

Fig. S7 (a) Fluorescence decaycurve of NCDs. (b) Fluorescence decay curve of BCDs.

Table. S3 TCSPC data for the CDs

Sample	τ_1 (ns)	a_1	τ_2 (ns)	a_2	τ_3 (ns)	a_3	τ_{av} (ns)	CHISQ
NCDs	0.8734	0.1609	1.747	0.6747	3.4936	0.1644	1.8934	1.2127
BCDs	0.0771	0.9905	0.3085	0.0095	-	-	0.0793	0.9061

Table. S4 The PL properties of NCDs in different pH values at 320 nm excitation

pH	Emission	QY
NCDs (~6)	403nm	10.62%
2.5	407 nm	8.83%
4	403 nm	10.55%
5	402 nm	9.10%
6	402nm	9.76%
7	404 nm	8.61%
8	406 nm	7.78%
9.5	409 nm	7.55%
11	412 nm	8.08%
13	387 nm	4.38%

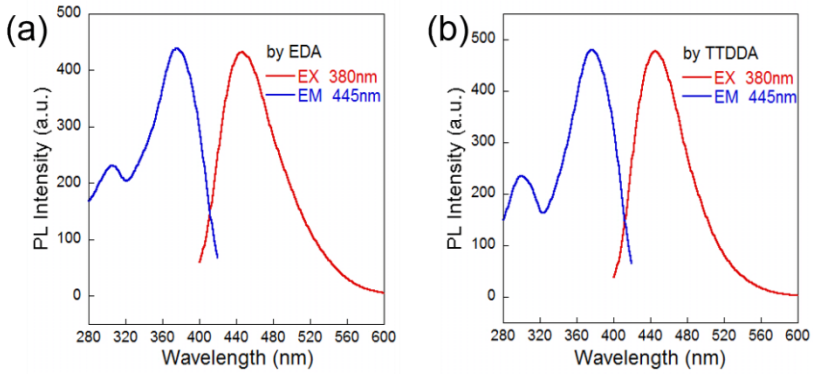

Fig. S8(a) Fluorescence spectra of the CDs doped by EDA. (b) The fluorescence spectra of the CDs passivated by TTDDA. Both of these CDs have maximum emission at 445 nm when excited at 380 nm.

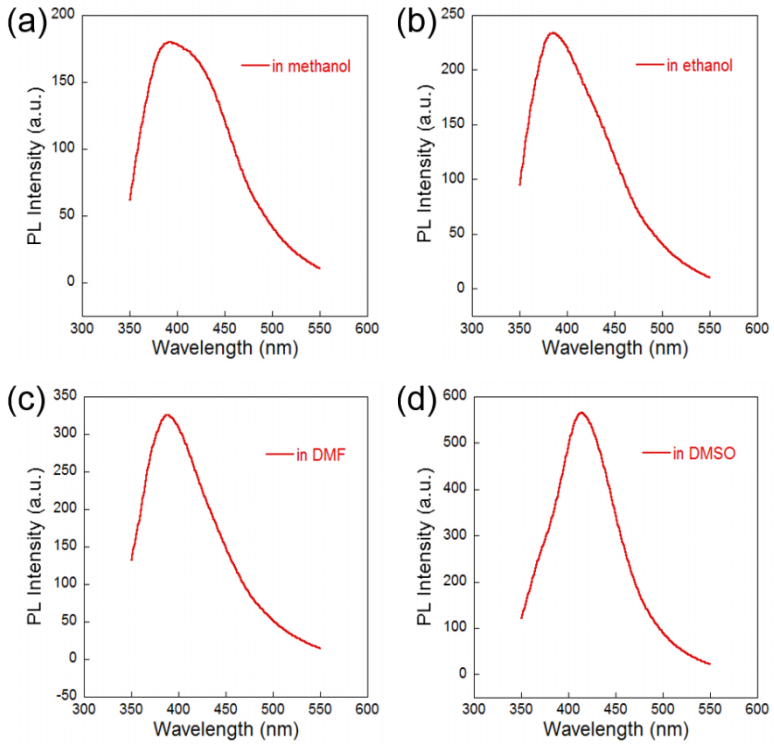

Fig. S9 (a) Fluorescence spectrum of NCDs in methanol at 320 nm excitation. (b) In ethanol. (c) In DMF. (d) In DMSO. The emission peaks of NCDs in methanol, ethanol and DMF slightly blue shift, while red shift can be seen in DMSO.

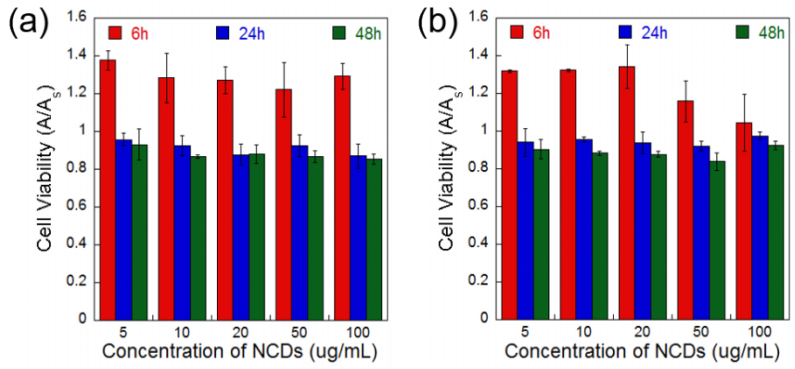

Fig. S10(a) Cytotoxity evaluation results of NCDs. (b) Cytotoxity evaluation results of BCDs. No significant toxicity can be evaluated with CCK-8 test with at least 85% cell viability even in high concentration.

Energy gap measurements: The HOMO and LUMO levels of NCDs were calculated with ferrocene curves as reference by the equation (3):

$$HOMO = -[E^{ox} - E(Fc/Fc^{+}) + 4.8]eV$$

$$LUMO = -[E^{red} - E(Fc/Fc^{+}) + 4.8]eV$$

$$E(LUMO) = E(HOMO) + E_g$$

Here, E^{ox} and E^{red} are the onset of oxidation and reduction potential, and $E(Fc/Fc^{+})$ is the onset of the oxidation potential of ferrocene/ferrocenium (HOMO level -4.8 eV)[4]. The E^{ox} and the $E(Fc/Fc^{+})$ were determined to be 0.67 eV and 0.47 eV, respectively. The corresponding HOMO level was -5.0 eV. However, the LUMO level could not be directly obtained in CVs. The Energy gap (E_g) was calculated by the onset of absorbance spectrum. The E_g was determined to be 3.2 eV, so the LUMO level was calculated as -1.8 eV.

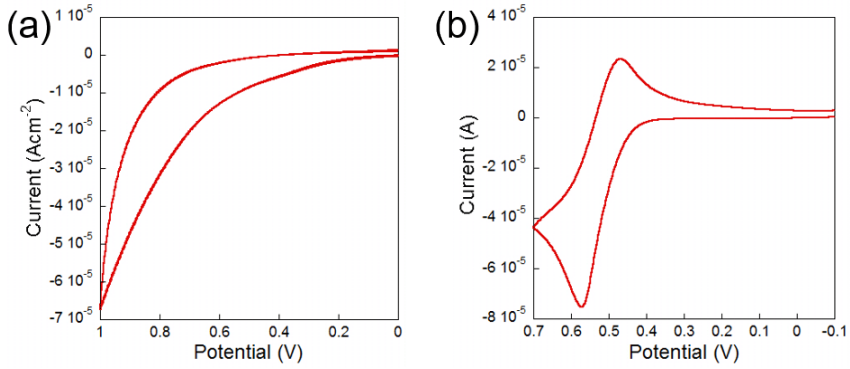

Fig. S11(a) An oxidation scanning of NCDs. (b) An oxidation scanning of Fc/Fc+.

Reference:

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4. S. O. Jung, Q. Zhao, J.-W. Park, S. O. Kim, Y.-H. Kim, H.-Y. Oh, J. Kim, S.-K. Kwon and Y. Kang, *Org. Electron.s*, 2009, **10**, 1066-1073.