Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Preparation of solvent-free starch-based carbon dots for the selective detection of Ru^{3+} ions

Menglin Chen[a,b], Can Liu[c*], Jichao Zhai[c], Yulong An[c], Yan Li[c], Yunwu Zheng[c], Hao Tian[d], Rui Shi[b], Xiahong He[b] and Xu Lin[a,b*]

[a]Yunnan Key Laboratory of Wood Adhesives and Glued Products National Joint Engineering Research Center for Highly-Efficient Utilization of Forest Biomass Resources, Southwest Forestry University, 300 Bailong Road, Kunming 650224, Yunnan Province, China
[b]Key Laboratory for Forest Resources Conservation and Utilization in the Southwest Mountains of China, Ministry of Education; Southwest Forestry University, Kunming, China
[c]National Joint Engineering Research Center for Highly-Efficient Utilization Technology of Forestry Resources, Chin; Southwest Forestry University, Kunming, China
[d]Agro-products Processing Research Institute, Yunnan Academy of Agricultural Sciences, Kunming, China
E-mail: linxunefu@126.com

Materials and Methods

Materials

Ethanol (99.7%) was provided by Shanghai Titan Science Co., Ltd. (Shanghai, China). Starch was obtained from Sinopharm Chemical Reagent Co. $AlCl_3$, $CaCl_2$, $CuCl_2$, $FeCl_3$, LiCl, $MgCl_2$, $MnCl_2$, $ZnCl_2$, $RuCl_3$, $IrCl_3$ and $NiCl_2 \cdot 6H_2O$ were purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents were used as received without further purification unless otherwise specified, and eionised (DI) water is used throughout the study.

Methods

Transmission electron microscopy (TEM) images by FEI TECANI G2 F20 running at an accelerating voltage of 200 kV. UV-Visible spectra were obtained with a Shimadzu UV-2600 spectrometer. Using a Shimadzu fluorescence spectrophotometer RF-6000, the CDs fluorescence intensity was detected. Fourier transform infrared (FT-IR) spectra obtained by the KBr Pellet technique on the Nicolet iS5 spectrometer (Waltham, MA, USA) at Thermal Sciences in the primary transmission mode, and 8 scans at a resolution of 1 cm^{-1} were accumulated to obtain one spectrum. X-ray photoelectron spectroscopy (XPS) was characterised primarily by using a K-Alpha spectrometer and a single X-ray source Al Kα excitation (1486.6 eV). Binding energy calibration for C1s at 284.8 eV. Use HORIBA Scientific LabRAM HR Evolutio for Raman analysis. The X-ray diffractometer was a D8 Advance X-ray diffractometer from Bruker, Germany, with a scanning wavelength of 0.02°. The XRD test conditions were as follows: Cu-Kα-ray source, tube voltage 40 kV, tube current 40 mA, 2θ angle range 5-90°, scanning rate 2°/min. The sample is pyrolyzed by using the model (Japanese Science, thermo plus EV_2/ thermo mass photo) Thermogravimetry-Mass Spectrometer (TG-MS) Analyze the experiment, cellulose and lignin warming rate of 10°C/min. The quantum yields (QYs) of the carbon dots obtained were determined using the relative method. In particular, the use of quinine sulphate (QY = 55% in 0.1 M H_2SO_4) as a calibrator was chosen as a reference for the blue emission in the emission range 400-480 nm. Each experiment was performed three times in parallel to obtain the mean fluorescence measurement of QY was collected with a Shimadzu fluorescence spectrophotometer RF-6000.

Synthesis of CDs

First, 1.0 g of starch was placed in separate 50 ml crucibles, heated in a muffle furnace at different temperatures for 6 hours, and then cooled naturally to room temperature. The biomass-derived carbon black was ground and placed in a beaker containing 100 ml of ethanol and sonicated in a sonicator for 15 minutes to obtain a sample that fluoresced bright blue. This suspension is filtered to remove the carbon residue to give a solution containing carbon dots. The solution was collected carefully and then purified with a silica column chromatography using ethanol as eluents. The process was repeated three times to remove excess impurities. The final products were dried and collected under vacuum environment and dissolved in ethanol. For comparison with the solvothermal method, starch (1.0 g) was dissolved in 10 ml of ethanol, and the solution was transferred to an autoclave lined with polytetrafluoroethylene. The sample was heated in a muffle furnace at 180°C for 6 hours, cooled naturally to room temperature in an autoclave, the reaction material removed and impurities filtered to obtain a brown solution. This was then filtered through a 0.22-μm filter membrane. The solution was collected carefully and then purified with a silica column chromatography using ethanol as eluents. The process was repeated three times to remove excess impurities. The final product was dried and collected under vacuum and dissolved in ethanol to obtain blue carbon dots (CDs-Hydro) for the control group.

Fluorescence detection of ten metal ions

In a typical assay, ten metal ion solutions (Al^{3+}, Ca^{2+}, Cu^{2+}, Fe^{3+}, Li^{+}, Mg^{2+}, Mn^{2+}, Zn^{2+}, Ru^{3+}, lr^{3+}, Ni^{2+}) were prepared at a concentration of 1000μM. To assess the selectivity of carbon dots for different metal ions, a concentration of 1000 μM of different metal ions (e. g. Al^{3+}, Ca^{2+}, Cu^{2+}, Fe^{3+}, Li^{+}, Mg^{2+}, Mn^{2+}, Zn^{2+}, Ru^{3+}, lr^{3+}, Ni^{2+}), 45uL of different metal ion solutions with specific concentrations were added to 5uL of carbon point aqueous solution and sonicated for 15 minutes and the fluorescence emission spectra were recorded at the same excitation light of 320nm. A series of metal ion solutions (pH = 7.0) at concentrations of 0, 20, 50, 100, 200, 400, 600, 800 and 1000 μM were prepared in the metal ion solution (pH = 7.0) and added to the carbon dot solution in the same manner and all measurements were carried out three times.

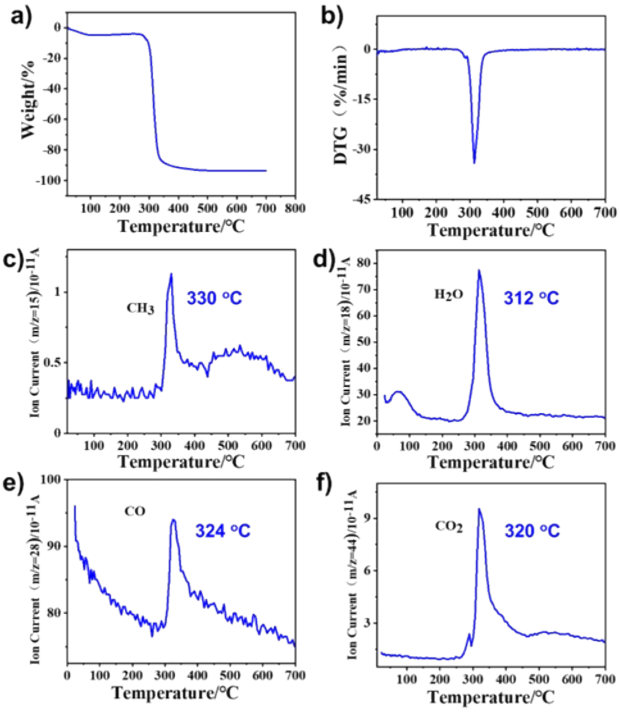

Fig. S1 a, b) TG/DTG curve of starch. c-f) The evolutions of gaseous product for the starch at 10 °C min^{-1} .

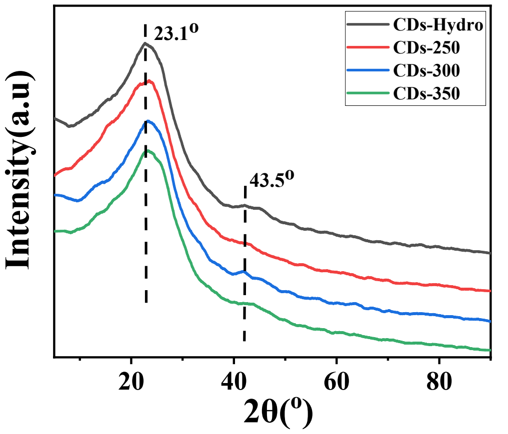

Fig. S2 XRD pattern of CDs- Hydro and CDs-250-300.

Tab.S1 Elemental proportions and chemical bonds in starch-based CDs

	CDs-Hydro	CDs-250	CDS-300	CDS-350
C 1s	79.8%	79.2%	81.6%	80.3%
O 1s	20.2%	20.8%	18.4%	19.7%
C=C/C-C	76.4%	84.1%	85.2%	84.1%
C-O	16.6%	11.2%	6.8%	13.0%
C=O	7.0%	4.7%	8.0%	2.9%