Supporting Information

Driving multicolor lignin-based carbon quantum dots into selective metal-ion recognition and photocatalytic antibiotic decomposition

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S1. Materials and Methods

S1.1. Raw materials

Technical lignin is kindly provided by a pulp and papermaking factory in Hubei province, China. Herein, the concise pathway of recovering industrial lignin are given as below: the corncob biomass was hydrothermally dilute sulfuric acid treated to dissociate hemicelluloses followed by the second-step extraction with aqueous sodium hydroxide; thereafter, the alkaline filtrate was regulated using sulfuric acid into acidic environment with a pH value of ~ 2 for detaching the precipitated lignin as the crude feedstock. Throughout the whole experiment, the chemicals are of analytic grade (*e.g.*, organic solvents and mineral acids) and the constant resistivity of deionized water are controlled to approximately 18 MΩ·cm.

S1.2. Acid-mediated fabrication of multicolor fluorescent lignin carbon dots

First, Alkali lignin of 10 g was dispersed in 50 mL of ultrapure water. Second, the concentrated nitric acid of 30 mL was dropped into the mixed solution slowly under continuous stirring to control the reaction temperature. After ultrasonic treatment at room temperature for 5 h, the resulting suspension was diluted and then filtrated through a 0.22 μm filter membrane. Third, the as-prepared samples were exhaustively rinsed by deionized water to recover the HNO_3-treated lignin. A range of organic acids, mainly including folic acid, ethylene diamine tetraacetic acid (EDTA), histidine, and phytic acid (see in Table S1) were chosen to perform the acid-assisted procedure of preparing multicolor CQDs, which determined the unique fluorescence behavior of CQDs ranging from the blue to yellow. During a typical process, the HNO_3-oxidized lignin of 1 g was uniformly dissolved in 100 mL

ethanol with the presence of individual solid acid (~2 g) or liquid acid (~2 mL). Using a 150 mL Teflon-lined stainless steel autoclave, the resultant mixture was solvothermally reacted at 200 °C for 8 h. Specifically, the solvothermal preparation of lignin carbon nanodots which labelled as the selected FCQDs, ECQDs, and HCQDs was conducted with the addition of folic acid, EDTA, and histidine respectively. To eliminate the unreacted lignin oligomers, the products of corresponding CQDs were filtrated through the organic membranes and then dialyzed with the molecular weight cut-off 3000 Da for 24 h. Finally, the physicochemical properties of lignin-to-CQDs and their fluorescent sensing capabilities are gauged *via* an array of advanced instruments.

Fe-CQDs were synthesized *via* an extended one-pot hydrothermal process using HCQDs as the precursor. Firstly, 300 mg HCQDs and 150 mg $FeCl_3$ were dissolved in 30 mL ultrapure water. Then, the mixed solution was transferred to a 100 mL Teflon-lined autoclave and kept at 120 °C for 12 h. The product was further filtered (0.22 μm aqueous filter membranes) and dialyzed with a dialysis bag (1000 Da) for 6 h after cooling down to room temperature. Ultimately, the brown powder was got through a freeze-dried method.

S2. Analytic methods

S2.1. Structural characterization of lignin

The weight average (M_w) and number-average (M_n) molecular weights of the technical lignin were determined by gel permeation chromatography (GPC) with an ultraviolet (UV) detector at 280 nm wavelength. The column used was a PL-gel 10 mm mixed-B 7.5 mm *i.d.* column, which was calibrated with PL polystyrene standards. Initially, four milligrams of lignin was dissolved in 2 mL

of tetrahydrofuran (THF), and then filtered through a 0.22 μm organic membrane before injection. Lignin/THF solution of 20 μL was injected by automatic sampler equipped with GPC. The analytical column was operated at ambient temperature and eluted with THF at a flow rate of 1.0 mL min^{-1}.

The NMR spectra were acquired on a Bruker Avance 400 MHz spectrometer fitted with a 5 mm gradient probe with inverse geometry (proton coils closest to the sample). The each lignin preparation of 25 mg was dissolved in 0.5 mL of DMSO-d_6 respectively. The central solvent peak at δC/δH 39.5/2.49 was used as an internal reference. The standard Bruker implementations of one- and two-dimensional (gradient-selected, ^{1}H-detected HSQC) NMR experiments were used for structural characterization and assignment authentication. For 2D-HSQC spectra, the Bruker pulse program "hsqcetgpsi" was used and the parameters used is listed as below: the number of collected complex points was 1 K for the ^{1}H dimension with d_1 (2 s), number of scanning is 64, and 256 time increments were always recorded.

The ^{31}P NMR spectra were acquired at 25 °C on a Bruker AVIII 400 MHz spectrometer after the reaction of lignin with 2-chloro-1,3,2 dioxaphospholanyl chlorides. Lignin of 20 mg was dissolved in 500 μL of anhydrous pyridine and deuterated chloroform (1.6:1, *v*/*v*) under stirring. This was followed by the addition 100 μL of cyclohexanol (10.85 mg mL^{-1} in anhydrous pyridine and deuterated chloroform 1.6:1, *v*/*v*) as an internal standard and 100 μL of chromium(III) acetylacetonate solution (5 mg/mL in anhydrous pyridine and deuterated chloroform 1.6:1, *v*/*v*) as a relaxation reagent. The mixture was reacted with 100 μL of phosphitylating reagent (2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, TMDP) for 20 min and then transferred into a 5 mm NMR tube for the subsequent NMR analysis. The standard ^{31}P NMR experiment was selected from

Bruker Program Library and the parameters used were listed as follows: the 30° pulse angle, 2 s relaxation delay (d_1), 64 K data points, and 1024 scans. The content of hydroxyl groups in lignin was determined *via* integration of the following spectral regions: aliphatic hydroxyls (149.0–146.0 ppm), condensed syringyl (CS) phenolic hydroxyls (144.5–143.2 ppm), syringyl (S) phenolic hydroxyls (143.2–142.17 ppm), condensed guaiacyl (CG) phenolic hydroxyls (142.17–141.42 ppm), guaiacyl (G) phenolic hydroxyls (140.17–138.79 ppm), *p*-hydroxyphenyl (H) phenolic hydroxyls (138.4–137.1 ppm), and carboxylic acids (135.5–134.2 ppm).

S2.2. Structural characterization, fluorescent sensing, and photocatalytic antibiotic degradation of lignin-derived carbon quantum dots

PL measurements of all liquid CQDs dispersions were performed at room temperature using a commercial spectrometer (Horiba JobinYvon Nanolog-3 spectrofluorometer) equipped with an InGaAs NIR detector and a 20 nm bandpass for both emission and excitation. The PL spectra obtained were scaled according to the measured excitation power. The UV–vis absorbance spectra of all materials were captured using a Shimadzu UV-2450 spectrophotometer with a matched pair of 1 cm path length quartz cuvettes. The corresponding solvents were used as baseline reference for every spectral measurement. Dynamic light scattering (DLS) instrument was recorded in solution phase at room temperature to determine the average particle size and zeta potential of CQDs. Background correction was conducted before sample measurement. A high-resolution transmission electron microscope (HRTEM, Tecnai G2 F20 S-TWIN, FEI Company, USA) that operated at an accelerating voltage of 200 kV was used to characterize the morphologies of the selected CQDs. Elemental and functional groups analyses were made on an ESCALAB 250 X-ray photoelectron spectrometer (XPS)

and the Fourier transform infrared FTIR-8400S spectrometer (Tyoto, Japan) respectively. The Raman spectra were tested by a laser confocal micro-Raman spectrometer with 780 nm diode lasers.

In a typical metal-ion sensing assay, the lignin-based carbon quantum dots (CQDs) powder was dispersed in ultrapure water as a stock solution, and then 2 mL stock solution of CQDs was mixed with specific metal-ion solution. After 5 min of incubation, the PL emission spectra of the complex probe were recorded with an excitation wavelength of 400 nm at room temperature. Different concentrations of metal ions (*e.g.*, Fe^{3+}, Ag^{+}, Cu^{2+} and Co^{3+}) ranging from 0 to 500 μM were prepared in deionized water. Fluorescence readings were recorded using PL spectra, in which percent fluorescence quenching was calculated using the following equation:

$$\%Quenching = \frac{F_0 - F}{F_0} \times 100$$

Where F_0 represents the fluorescence intensity of CQDs in water (control) and F defines the quenching fluorescence of CQDs after the addition of metal ions with the maximum concentration of 500 μM.

The photocatalytic experiment was conducted under visible light irradiation, and the light source was simulated by a 150 W tungsten halogen lamp equipped with a light filter (≥400 nm). Typically, a 10 mL aqueous solution including 0.10 g/L Fe-CQDs, 0.05 g/L tetracycline and 0.2 g/L peroxydisulfate (PDS) was added to a 15 mL quartz reactor and magnetically stirred at 300 r/min. The reaction solution firstly reacted in dark for 30 min to achieve an adsorption–desorption equilibrium at room temperature (25 ±1 °C). In the above reaction system, active species trapping experiments were investigated by adding diverse scavengers before reaction such as 0.5 M TBA for

•OH, 1.2 M MeOH for •OH and $SO_4^{\bullet-}$, 5 mM *L*-histidine for $^1O_2$, and 2 mM BQ for $\bullet O_2^-$. All experiments were repeated 3 times under the same conditions to determine the standard deviations, and the results are expressed as the average values.

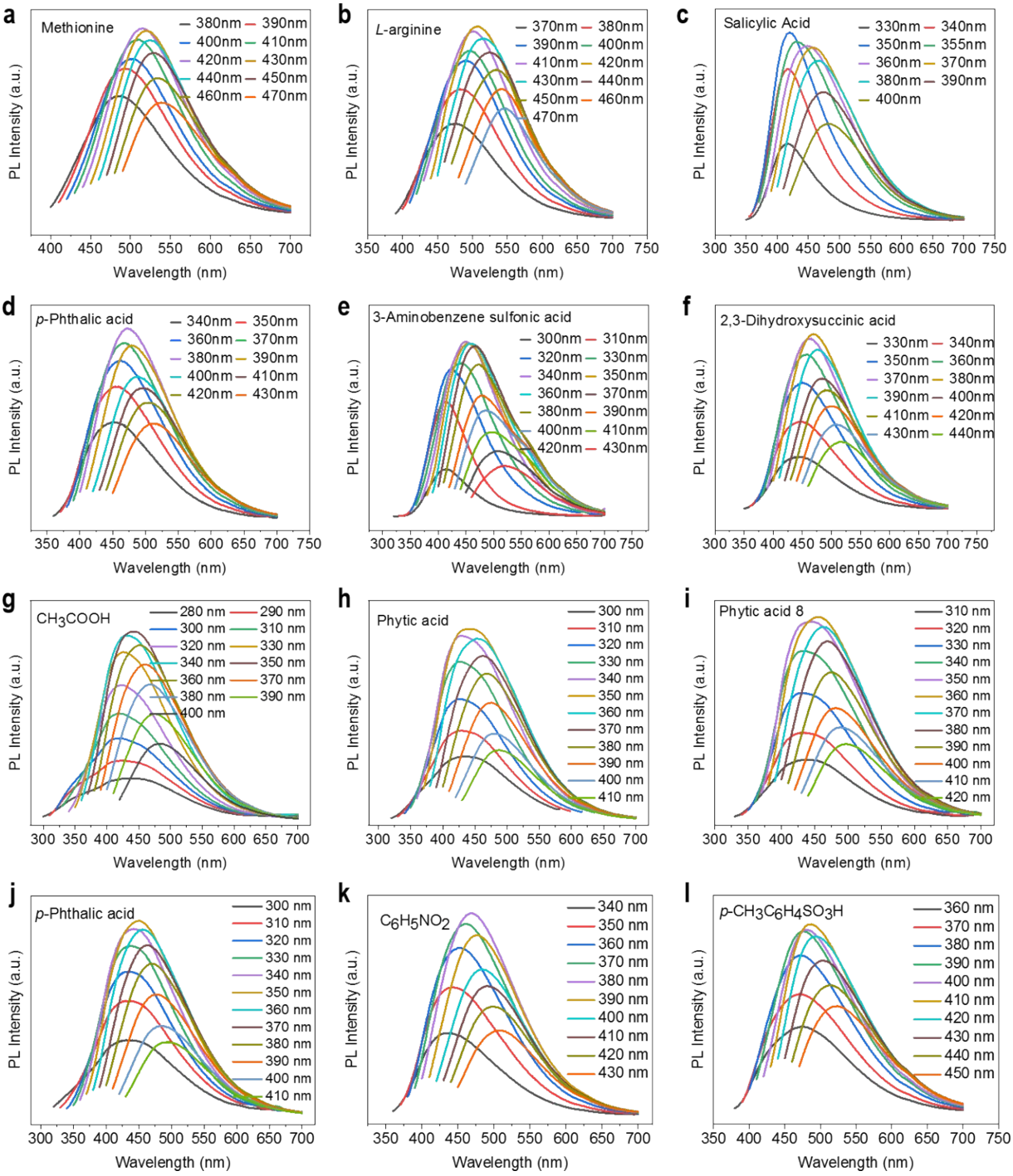

Figure S1. Emission spectra of lignin-based carbon quantum dots (CQDs) that can be tuned by using the acid-medicated solvothermal processing of (**a**) methionine, (**b**) *L*-arginine, (**c**) salicylic acid, (**d**) *p*-phthalic acid, (**e**) orthanilic acid, (**f**) succinic acid, (**g**) acetic acid, (**h**) phytic acid, (**i**) phytic acid 8-1, (**j**) *p*-phthalic acid 1-1, (**k**) nicotinic acid, (**l**) *p*-toluenesulfonic acid TsOH, at the excitation wavelengths of 290−470 nm with an interval of 10 nm.

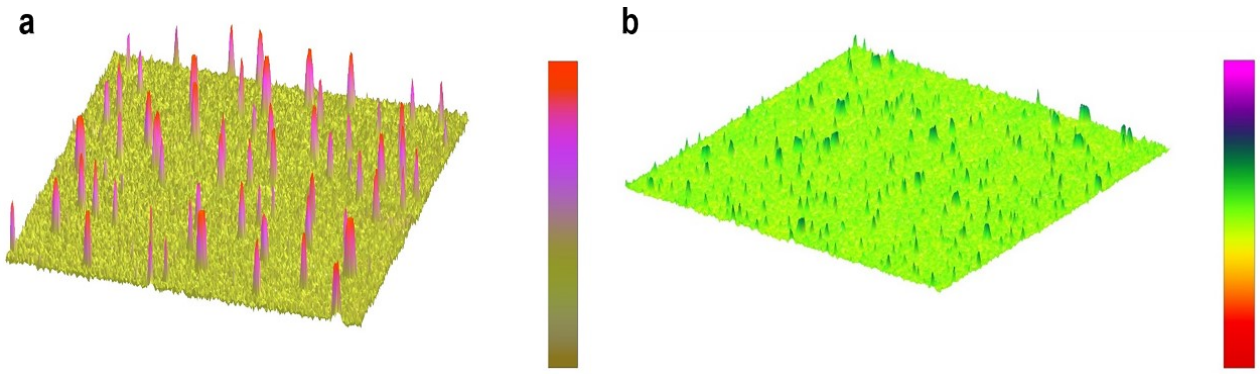

Figure S2. Three dimensional (3D) AFM images and corresponding height patterns of (**a**) FCQDs and (**b**) HCQDs derived from technical lignin.

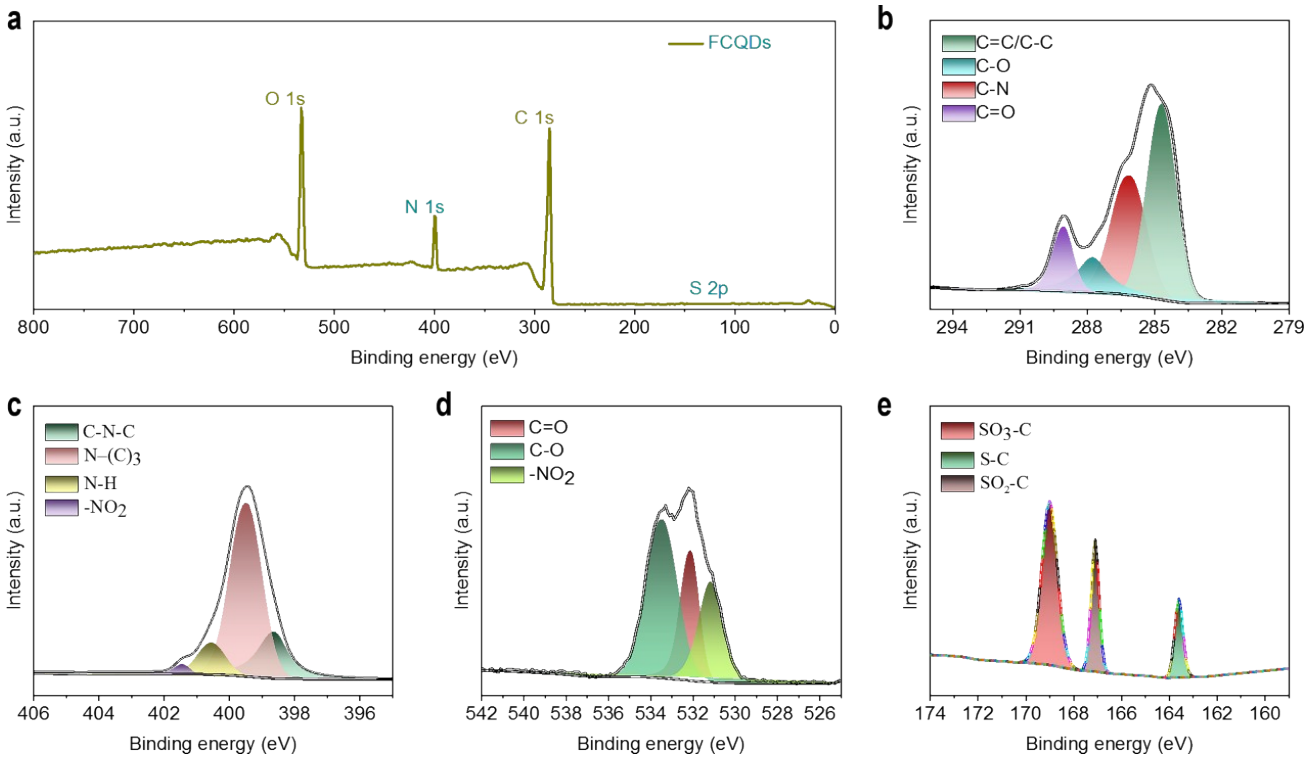

Figure S3. Full XPS survey scan (**a**), high-resolution XPS C 1s (**b**), N 1s (**c**), O 1s (**d**) and S 2p (**e**) spectra of the selected FCQDs.

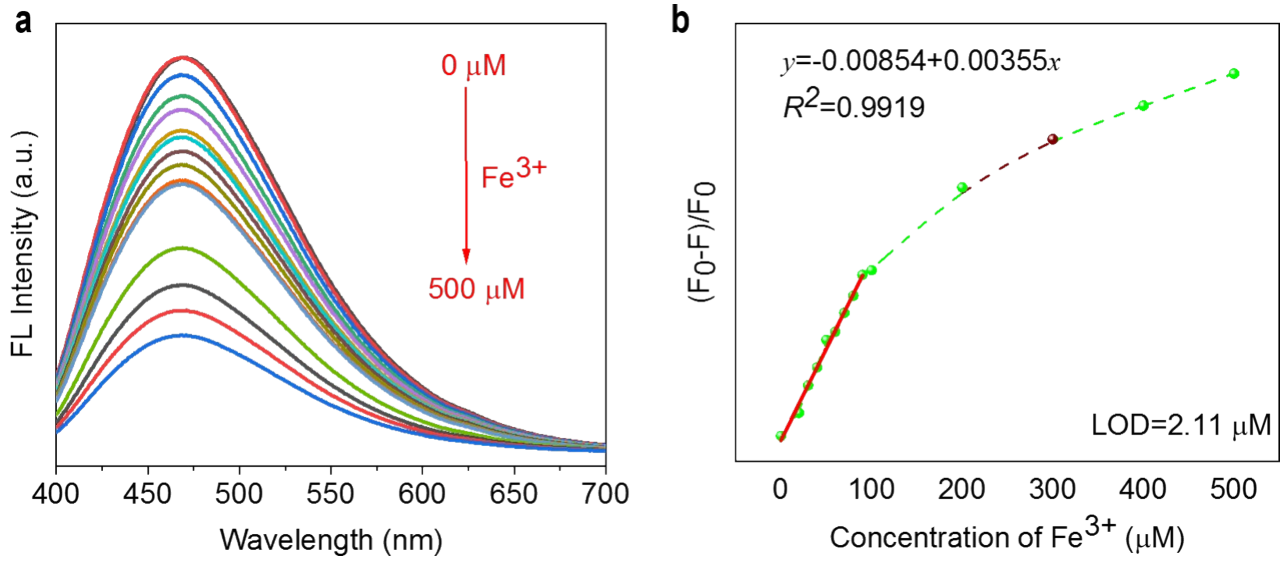

Figure S4. Relative changes in ECQDs fluorescence intensity upon adding different concentrations (0−500 μM) of Fe^{3+} (**a**), as well as, the corresponding fitting plot (**b**) of $(F_0-F)/F_0$ versus concentration of Fe^{3+} and the calculated limit of detection (LOD).

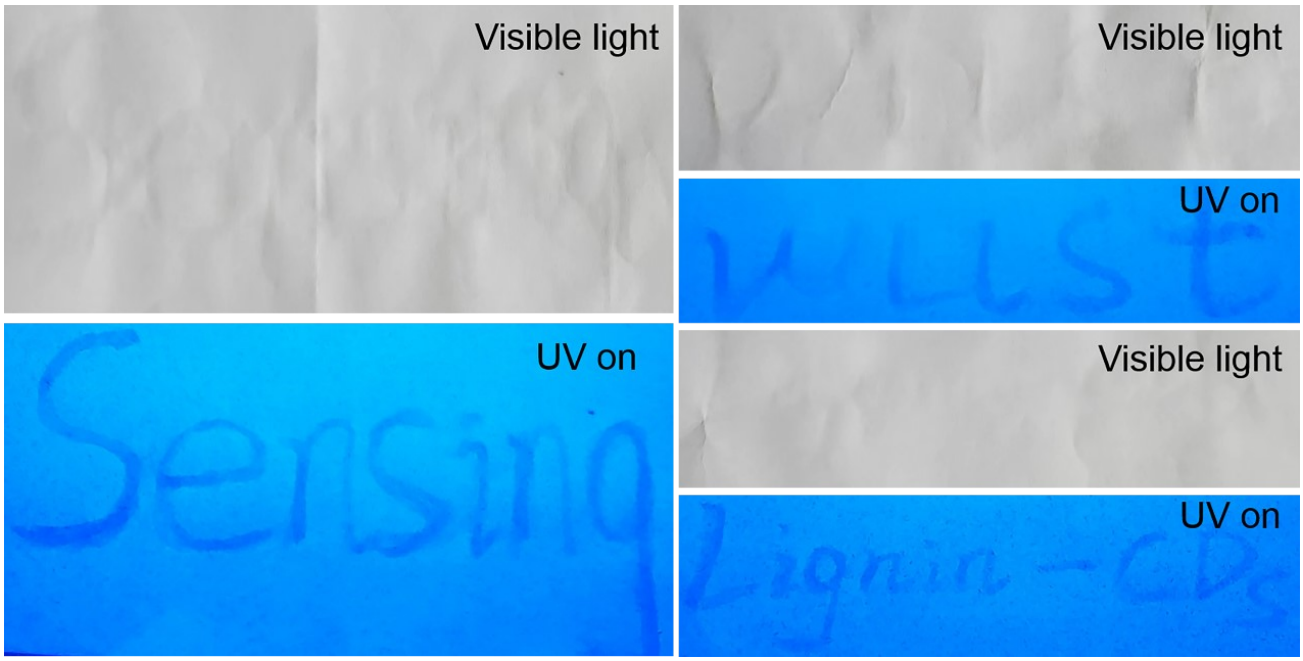

Figure S5. Anti-counterfeiting application of the as-prepared HCQDs. The letters “sensing”, “wust”, and “Lignin-CDs” directly written on the filter paper in visible light and under UV light of 365 nm, respectively.

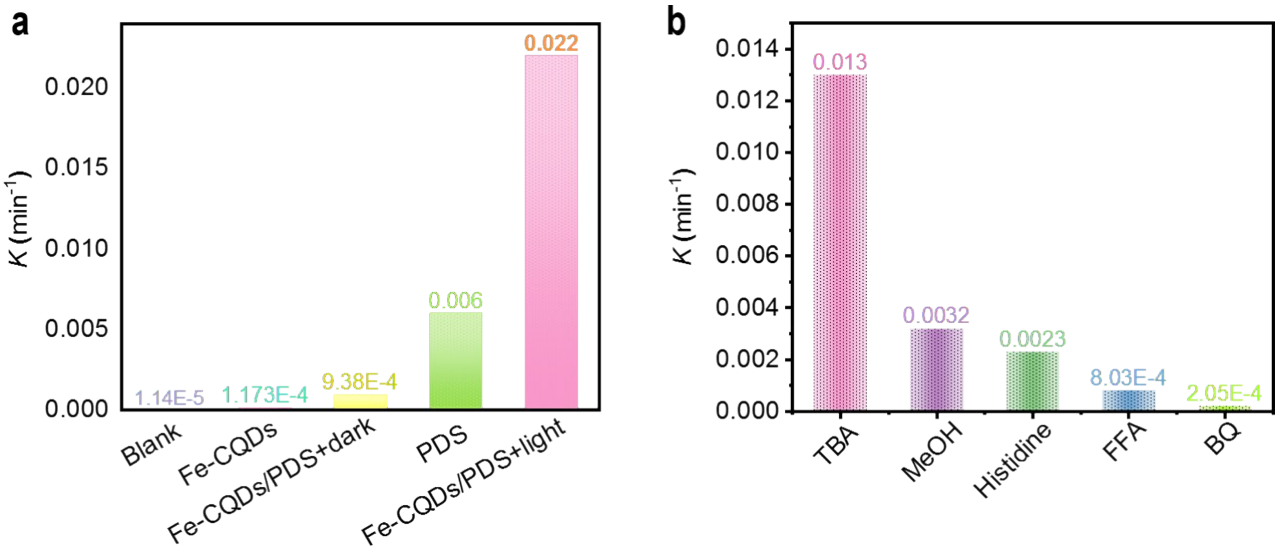

Figure S6. *Pseudo*-first-order kinetic rate constants (k, min^{-1}) of the various catalytic degradation systems within 50 mg L^{-1} TC (*i.e.*, blank, Fe-CQDs, Fe-CQDs/PDS+dark, only PDS, and Fe-CQDs/PDS+light) and the relevant radical-quenching tests (TBA, tertbutyl alcohol; MeOH, methanol; FFA, furfuryl alcohol; BQ, *p*-benzoquinone).

Table S1. The excitation and emission wavelengths of lignin-derived CQDs with diversified acid enegineering systems.

Entry[a]	*Ex* (nm)[b]	*Em* (nm)[c]	Stokes shift (nm)
Methionine	420	515	95
Arginine	420	509	89
Histidine	430	520	90
Tartaric acid	380	469	89
p-phthalic acid	380	472	92
Phytic acid 8-1	360	456	96
p-phthalic acid 1-1	350	451	99
Boric acid 1-1	370	468	98
Boric acid	380	476	96
Bicotinic acid	380	468	88
TsOH	410	487	77
EDTA	380	471	91
Orthanilic acid	350	449	99
Salicylic acid	340	420	80
Acetic acid	350	442	92
Phytic acid 4-1	350	439	89
Folic acid	370	449	79

[a] TsOH: *p*-toluenesulfonic acid; EDTA: ethylene diamine tetraacetic acid; Phytic acid 8-1 or 4:1: the mixture of lignin and phytic acid with a solid-to-liquid ratio of 1:8 or 1:4 g/mL; *p*-phthalic acid 1-1 or boric acid 1-1: the mixture of 1g lignin with 1 g *p*-phthalic acid or boric acid;

[b] *Ex*: excitation wavelength.

[c] *Em*: emission wavelength.