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

Supporting Information—

Dual photoluminescence centers from inorganic-salt-functionalized carbon dots for ratiometric pH sensing

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1. Experimental section

1.1 Sample synthesis

Synthesis of S1:

Anthracite was used without further treatment and obtained from Yangquan Coal Industry, China. A four-station horizontal planetary mill was used for reducing the size of coal. The initial powder, 1 g anthracite and 20 mL H2O were loaded in a poly(tetrafluoroethylene) (Teflon)-lined milling vial with 25 ceramic balls, which are composed of 8 large balls with a diameter of 10 mm and 17 small balls with a diameter of 6 mm. The vial was then fixed in the planetary ball-mill machine, and agitated at 400 rpm for 5 h. The resultant product was dried at 60 ℃ in vacuum oven. 200 mg ultrafine powder was dispersed in 10 mL H_2O by ultrasonication and then mixed with 20 mL of 30% hydrogen peroxide (H_2O_2) solution. The obtained mixture was heated at 80 ℃ in the atmosphere. After reacting for 10 min under vigorous stirring conditions, another 5 mL of 30% H_2O_2 solution was added. This process was repeated four times within 40 min. The total volume of H_2O_2 added in the reaction system was 40 mL. The reaction time reached 3 h after which the experiment was stopped. The final product was obtained by removing unreacted coal via centrifugation at 3500 rpm.

Synthesis of S2 and S3:

Firstly, 50 or 100 mg of DAP was added in 10 mL of S1 solution and then mixed with 10 mL absolute ethanol. Secondly, the resultant solution was transferred into 50 mL Teflon-lined stainless autoclave and then heated at 200 ℃ for 10 h under solovthermal condition. Finally, after cooling to room temperature, the sample containing D-CDs was obtained and named as S2. Similarly, 100 mg of DAP was added in 10 mL of S1 solution and mixed with 10 mL absolute ethanol, then following the process of the S2 to obtain sample S3.

Synthesis of S4—S10:

The S4 and S5 were prepared at different temperatures following the same recipe and process as for S3 (the samples prepared at 150℃ and 250℃, respectively).

The S6 and S7 were prepared by replacing DAP with disodium phosphate (DSP) or ammonium nitrate (NH_4NO_3) and followed the same approach for S3.

The S8 were prepared following almost the same recipe and process as for S3 but worked with water instead of S1 solution.

The S9 were fabricated by simply replacing ethanol with water and followed the same approach for S3.

The S10 were prepared following the same recipe and processes as for S3 except for without adding DAP.

1.2 Characterizations

The resulting solution was dropped onto copper grids covered with an amorphous carbon film for transmission electron microscopy (TEM) observation using an FEI Tecnai G2 F20 microscope with a field-emission gun operating at 200 kV. X-ray photoelectron spectroscopy (XPS) data of all samples was collected by a Kratos AXIS 165 mutitechnique electron spectrometer having an Al Ka X-ray source for determining the composition and chemical bonding configurations. The infrared spectra were obtained on a Thermo Nicolet 260 FT-IR spectrophotometer. Fluorescence spectroscopy and absorption were conducted with a Hitachi F4500 fluorescence spectrophotometer and a Shimadzu UV-2550 UV-vis spectrometer, respectively. All fluorescence spectra were acquired with a 1 cm × 1 cm cuvette, and the excitation and emission monochromator slit width in the fluorophotometer were kept at 5 nm. Time-resolved PL lifetime measurements were carried out using a time-correlated single-photon counting（TCSPC）lifetime spectroscopy system.

1.3 Measurement of pH sensing

For pH sensing, deionized water and different concentrations of NaOH or HCl solution were injected in each sample vial containing 1.5 mL of as-prepared S3. The total solution volume in each vial is 2.0 mL. After vigorous stirring for 1 h, the pH values of samples were recorded and then measured their PL with fluorescence spectrophotometer under the same conditions.

1.4 Electrochemical measurements

The sample electrodes for electrochemical analysis were prepared by drop-casting sample suspensions onto ITO glass (Bio-logic, SP 120, France). We subjected the sample electrodes to electrochemical analysis in 1 M HCl, Na_2SO_4 and NaOH solution with a Pt foil counter and an Ag/AgCl reference. A linear potential scan (5 mV/s) was conducted to determine the HOMO and LUMO of the D-CDs.

2. Supporting Results

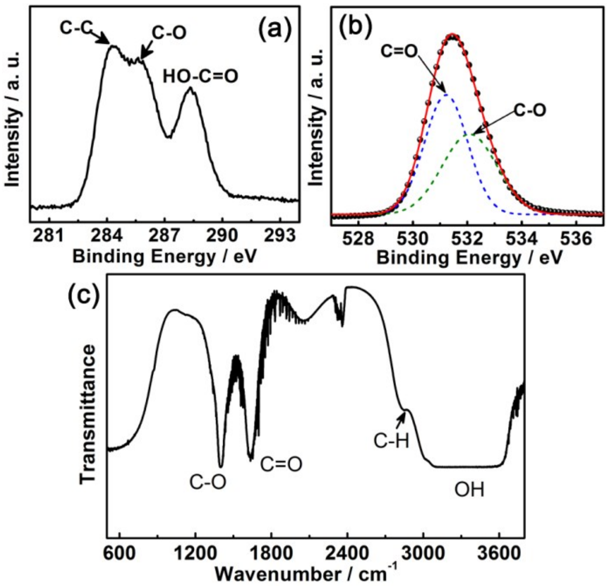


Figure S1 Chemical composition characterization of S1. (a) high-resolution XPS C1s spectrum; (b) high-resolution XPS O1s spectrum; (c) FTIR spectrum.

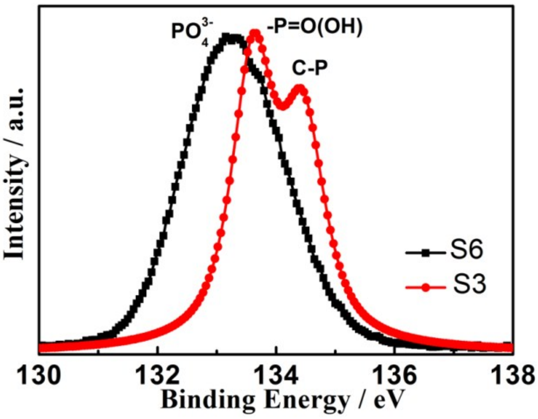


Figure S2 Comparison of XPS P2p spectra from samples S3 and S6.

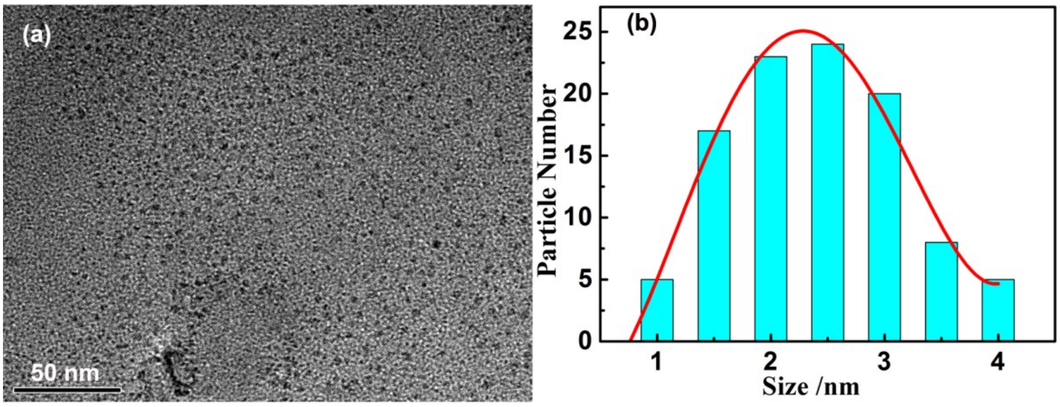


Figure S3 TEM image (a) and size distribution (b) of S9

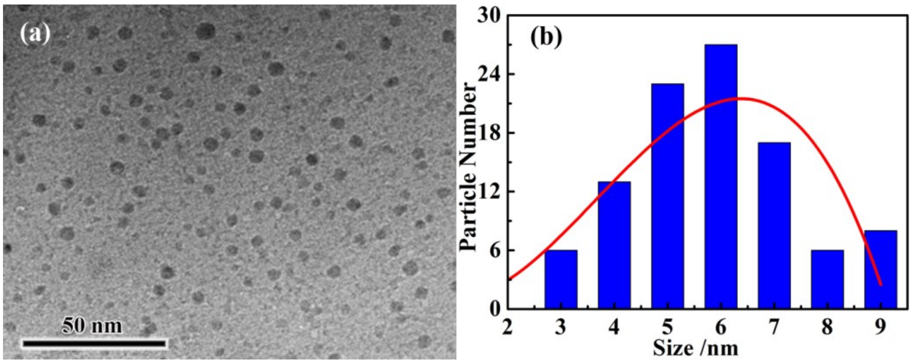


Figure S4 (a) TEM image of S10; (b) The corresponding size distribution of CDs from S10.

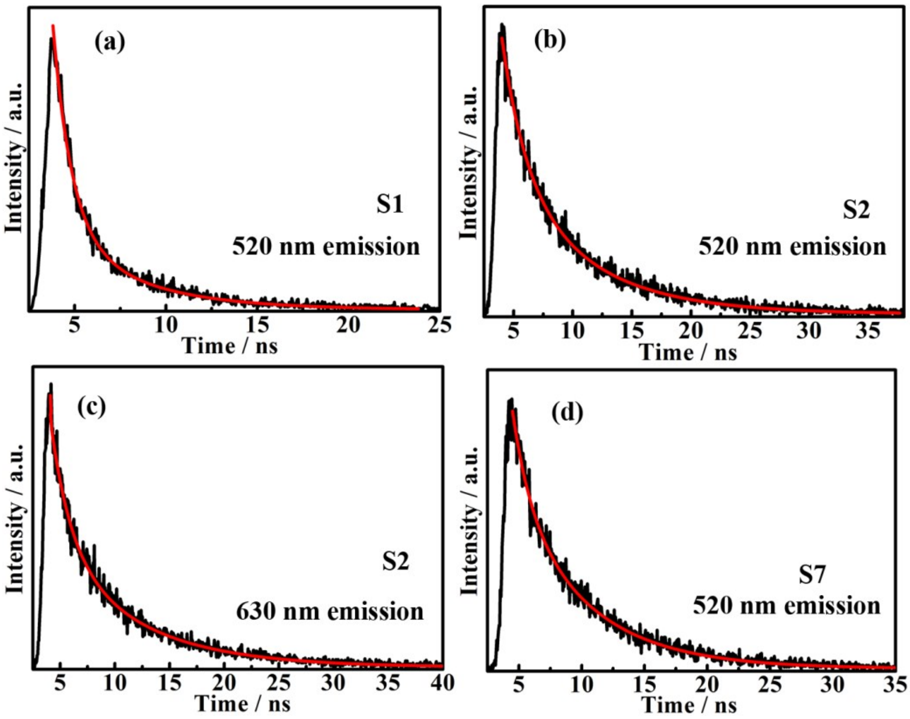
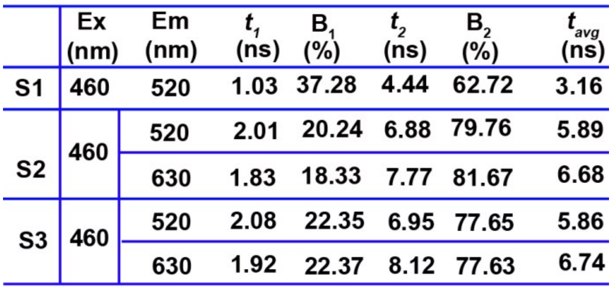


Figure S5 PL decay spectra and fitted curves for S1, S2 and S7

Table S1 Fluorescence lifetimes of S1-S3 under excitation at 460 nm



	Ex (nm)	Em (nm)	t_1 (ns)	B_1 (%)	t_2 (ns)	B_2 (%)	t_{avg} (ns)
S1	460	520	1.03	37.28	4.44	62.72	3.16
S2	460	520	2.01	20.24	6.88	79.76	5.89
		630	1.83	18.33	7.77	81.67	6.68
S3	460	520	2.08	22.35	6.95	77.65	5.86
		630	1.92	22.37	8.12	77.63	6.74

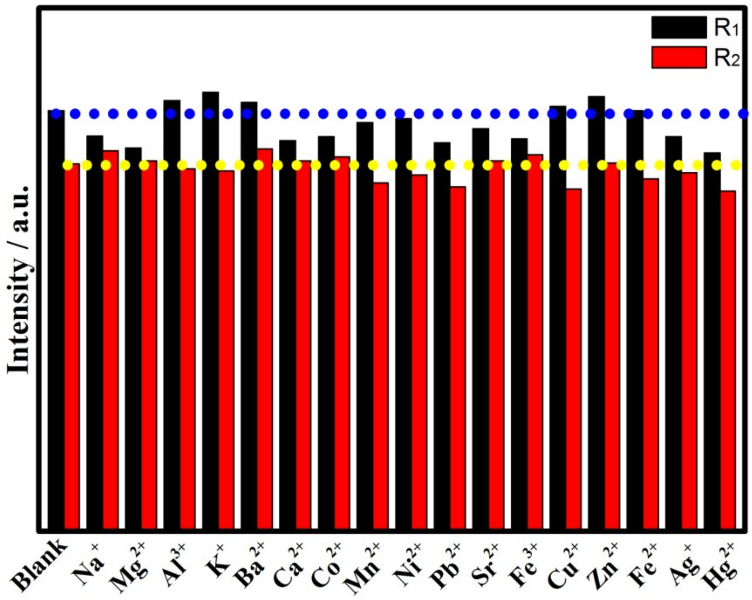


Figure S6 The intensity changes of R1 and R2 emissions in the presence of 17 kinds of metal ions (10 mM) at excitation with 520 nm wavelength

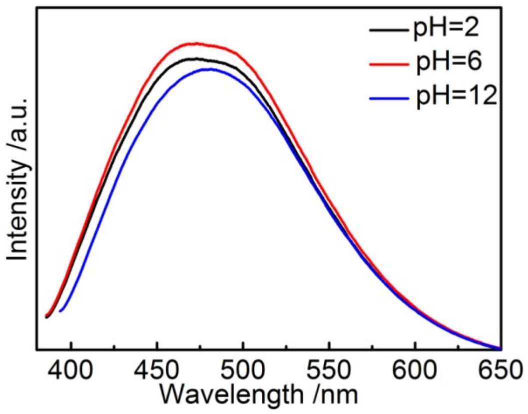


Figure S7 The effects of pH value on the PL of S1 excited at 360 nm.

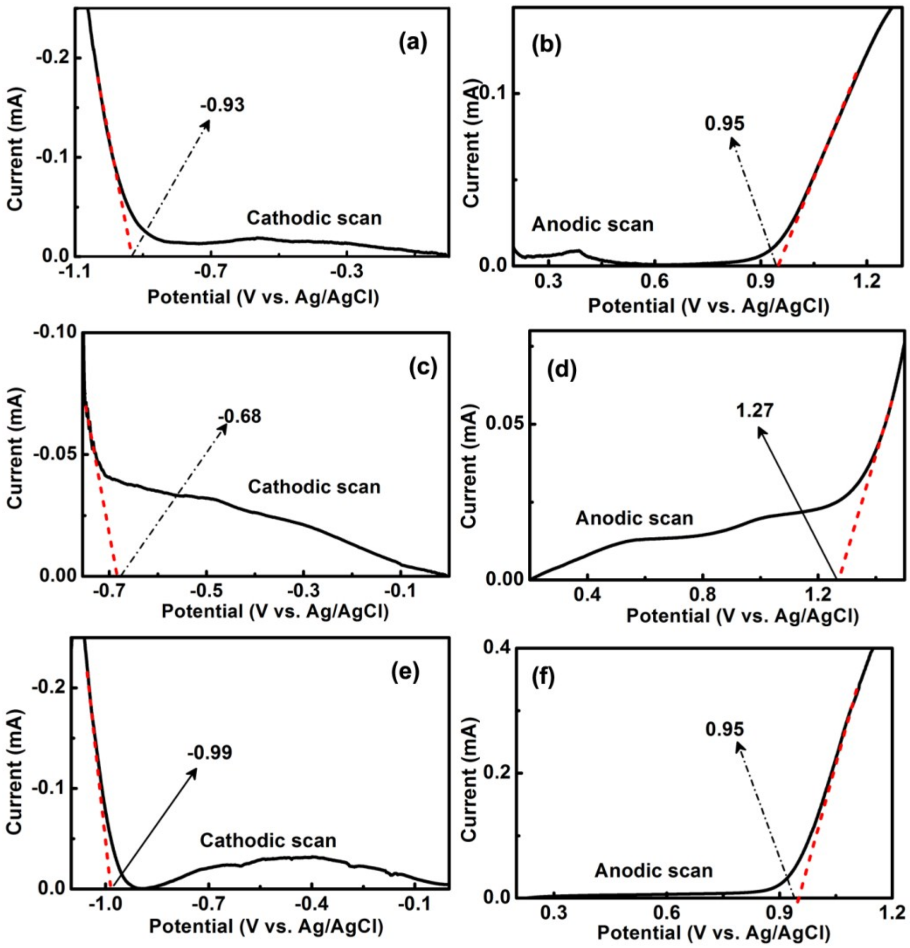


Figure S8 Cathodic and anodic scan for determining the LUMO and HOMO of D-CDs at neutral (a, b), acidic (c, d), and alkali (e, f) mediums

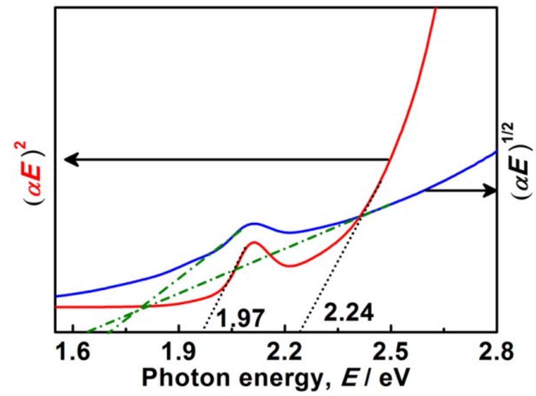


Figure S9 Plots of $(\alpha E)^2$ and $(\alpha E)^{1/2}$ against photon energy (E) for the S3, where α is the absorbance.