

Supplementary Material

for

Controllable Preparation of Long Wavelength Carbon Dots and its

Application in Fluorescence Detection

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Experimental section

Materials.

P-aminobenzenesulfonic acid (SA), o-phenyldiamine (*o*PD), ethanol absolute (EtOH), L-Cysteine (L-cys), NaOH, C₂H₆O, ethyl acetate (EAC), CaCl₂, KCl, Na₂SO₄, Mg(NO₃)₂ · 6H₂O, Zn(NO₃)₂ · 6H₂O, FeCl₂ · 4H₂O, CuSO₄, BaCl₂ · 2H₂O, MnSO₄ · H₂O, Pb(NO₃)₂, CoNO₃ · 6H₂O, AgNO₃, Al(NO₃)₃ · 9H₂O, Cr(NO₃)₃ · 9H₂O, Fe(NO₃)₃ · 9H₂O were purchased from Sinopharm Chemical Reagent Co., Ltd. Concentrated hydrochloric acid (96%) and Concentrated sulfuric acid (98%) were purchased from Shanghai meiruier Chemical Technology Co., Ltd. All chemical reagents were used as received without further purification. All solutions were prepared and diluted by Deionized (DI) water.

Instruments and Apparatus.

All spectral data were measured by Integrated steady-state transient fluorescence spectrometer FS5 (Edinburgh, UK), Shimadzu UV-VIS-NIR 3600 spectrophotometer, Fourier transform infrared spectrometer (FT-IR, Nicolet-IS50 spectrometer) and X-ray photoelectron spectrometer (ESCALAB250Xi, USA). The morphologies of all CDs were measured by Transmission electron microscopy (TEM, JEM-2100 (HR)) at an accelerating voltage of 200 kV.

Preparation CDs (Multicolor CDs and Red CDs).

Blue-green fluorescent CDs (b/bg-CDs)

b-CDs ^[1]: The crude product was obtained by dissolving 0.5 g of SA in 60 mL deionized water and hydrothermal reaction at 200 °C for 5 hours and cooling to room temperature. The large insoluble particles were removed by filtration, and the resulting brown liquid was freeze-dried to obtain b-CDs powder.

bg-CDs ^[2]: 0.5 g of SA was dissolved in a mixture of 60 mL deionized water and absolute ethanol. The subsequent operation was the same as the preparation method of b-CDs, and bg-CDs powder was finally obtained for use. A series of bg-CDs were obtained by changing the volume ratio of water to ethanol in the solvent (1:1).

bg-CDs of control group: Dissolve 0.5 g of SA in 60 mL hydrochloric acid or sulfuric acid solution (pH=1), the following procedure is the same as bg-CDs.

Yellow-green fluorescent CDs (yg-CDs)

yg-CDs: A certain molar ratio (1: 1, 1: 2, 1: 3, 3:1, 3:2,) of SA and *o*PD were mixed in water and ethanol, stirred by ultrasound for 30 minutes, then put into the reaction kettle, and reacted by solvothermal at 200°C for 8 hours. After cooling to room temperature, the insoluble large particles were removed by filtration three times, and the yg-CDs powder was finally obtained by rotary evaporation. Another group of yg-CDs powder was obtained by dissolving SA and *o*PD at a molar ratio of 1:1 in 50 mL mixtures of water and ethanol (1:4, 2:3, 3:2, 4:1) at different volume ratios.

y-CDs ^[3]: A certain mass of *o*PD was dissolved in water or ethanol and solvothermal reaction was performed at 200°C for 8 hours. After cooling to room temperature, the insoluble large particles were removed by filtration three times and the y-CDs powder was obtained after drying.

Red fluorescent CDs (r-CDs)

r-CDs: A certain molar ratio (1:1, 1:2, 1:3, 2:1, 2:3, 3:1, 5:2) of SA and *o*PD were dissolved in 50 mL deionized water and placed in a reaction kettle at 200°C for 10 hours. After cooling to room temperature, black solid was obtained by filtration. The solid was cleaned and filtered in sodium hydroxide solution and deionized water for several times, and the final black solid was dried as r-CDs powder.

r-CDs of control group: The SA and *o*PD with a molar ratio of 1:1 were mixed and dissolved in hydrochloric acid or sulfuric acid solution with pH=1. The subsequent operation was the same as r-CDs, and the CDs powder was

finally obtained.

Acid-assisted preparation of red fluorescent CDs: Inspired by the reported acid-assisted synthesis of red fluorescent CDs by phenylenediamine [4-5], r-CDs was synthesized by acid-assisted *o*PD. A certain mass of *o*PD was dissolved in 50 mL of hydrochloric acid (0.1 mol/L, 0.2 mol/L, 0.4 mol/L) with a certain concentration, and then the mixed solution was placed in a 100 mL polytetrafluoron reactor and reacted in a vacuum drying oven at 200°C for 10 hours. After cooling, the liner was removed. The crude product was filtered by 0.22 μ m organic filter membrane to obtain black solid, which was repeatedly cleaned and filtered by NaOH solution, and then the solid was cleaned by a mixture of ethanol and ethyl acetate, and finally the black solid was obtained. After drying, it was r-CDs-H powder. When H₂SO₄ was used as the reaction solvent, r-CDs-S was obtained.

Fluorescence stability of Red CDs.

In order to explore the influence of external environmental factors on the luminescence performance of r-CDs, r-CDs-H was selected as a representative, and the same amount of r-CDs-H was dissolved in ethanol, acidic, neutral and basic aqueous solutions, and the fluorescence emission spectrum of r-CDs-H in these solutions was recorded.

In order to further explore the properties and differences of CDs prepared in this experiment, their salt resistance and metal ion resistance were studied by testing their fluorescence spectra. CDs dissolved in different concentrations of NaCl solution (0-0.1 mol/L) were tested for fluorescence spectrum (λ_{ex} =365 nm), and the test results were recorded. The fluorescence spectrum (λ_{ex} =365 nm) was measured after the same amount of CDs solution was mixed with 1 mmol/L metal ion solution, and the test results were recorded.

RESULTS AND DISCUSSION

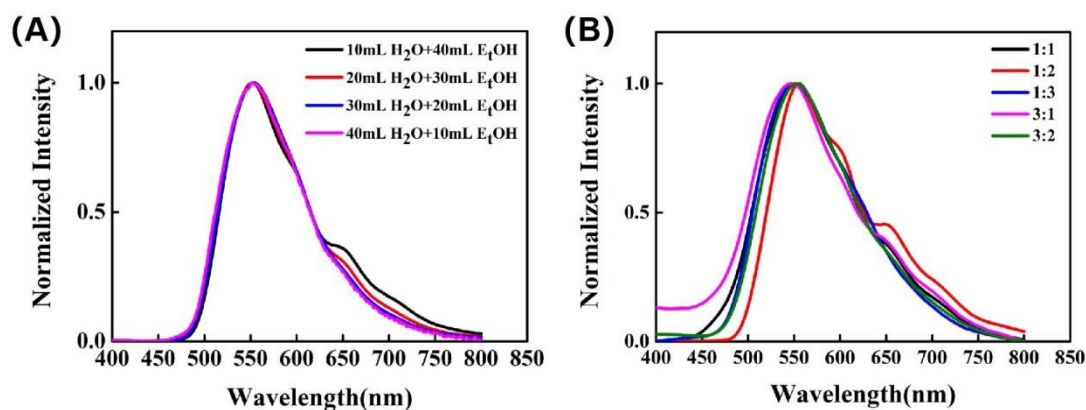


Figure S1. Normalized fluorescence emission spectra of yg-CDs in ethanol solution (λ_{ex} =380 nm): (A) different ratios of reaction solvents; (B) different ratios of precursors

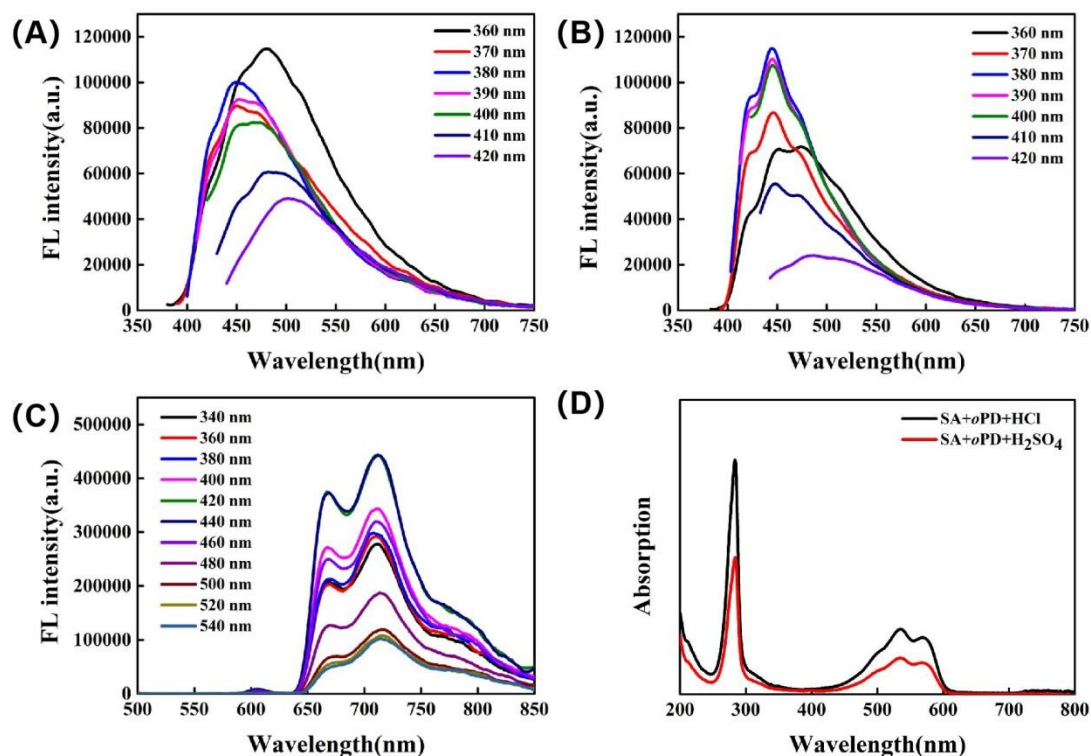


Figure S2. (A) Fluorescence emission spectra of CDs prepared by SA in H_2SO_4 (pH=1); (B) Fluorescence emission spectra of CDs prepared by SA in HCl (pH=1); (C) Fluorescence emission spectra of CDs prepared by SA and *o*PD in HCl (pH=1) in ethanol solution; (D) UV-vis absorption spectra of CDs prepared with H_2SO_4 or HCl (pH=1) for SA and *o*PD in ethanol, respectively

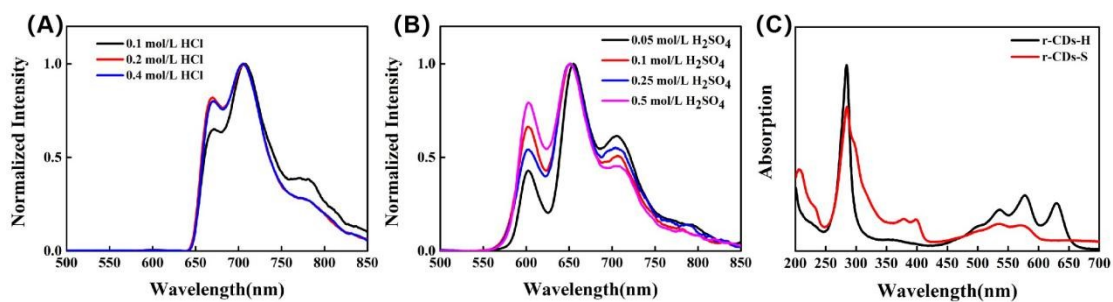


Figure S3. (A) Normalized fluorescence emission spectra of r-CDs-H prepared with different concentrations of HCl in ethanol ($\lambda_{\text{ex}}=365$ nm); (B) Normalized fluorescence emission spectra of r-CDs-S prepared with different concentrations of H_2SO_4 in ethanol ($\lambda_{\text{ex}}=365$ nm); (C) UV-vis absorption spectra of r-CDs-H and H_2SO_4 in ethanol solution, respectively

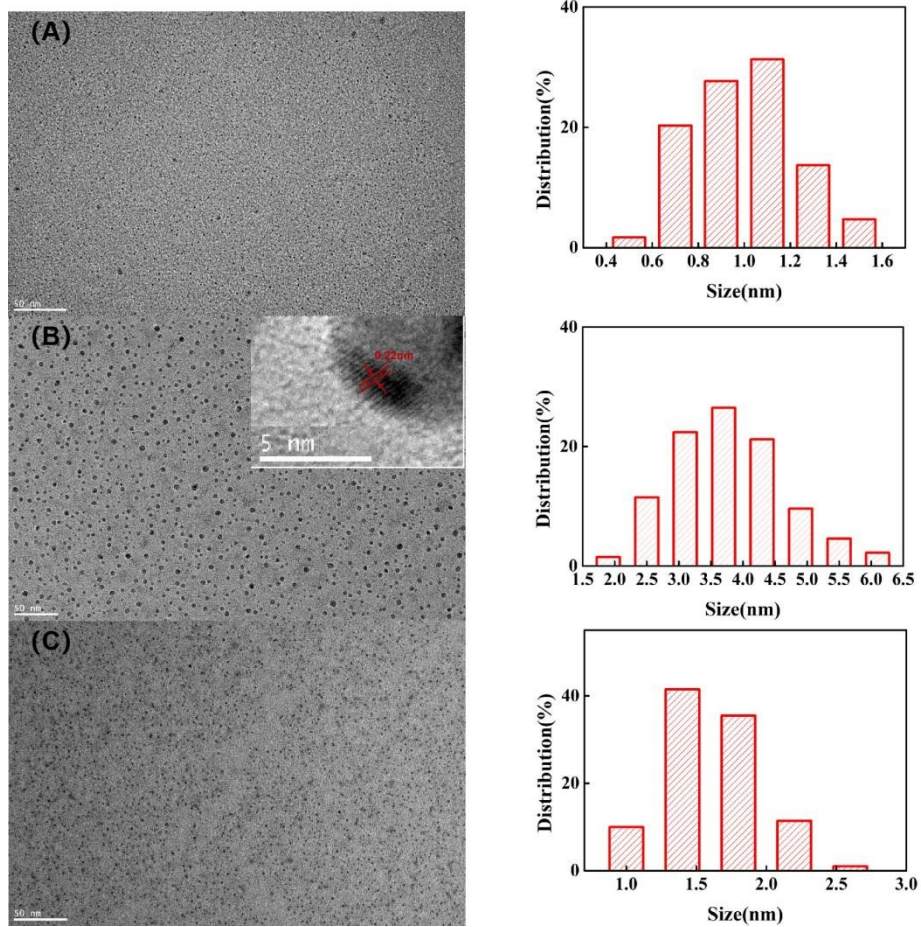


Figure S4. TEM images of CDs (left) and particle size distribution (right): (A) b-CDs; (B) r-CDs-H; (C) r-CDs-S

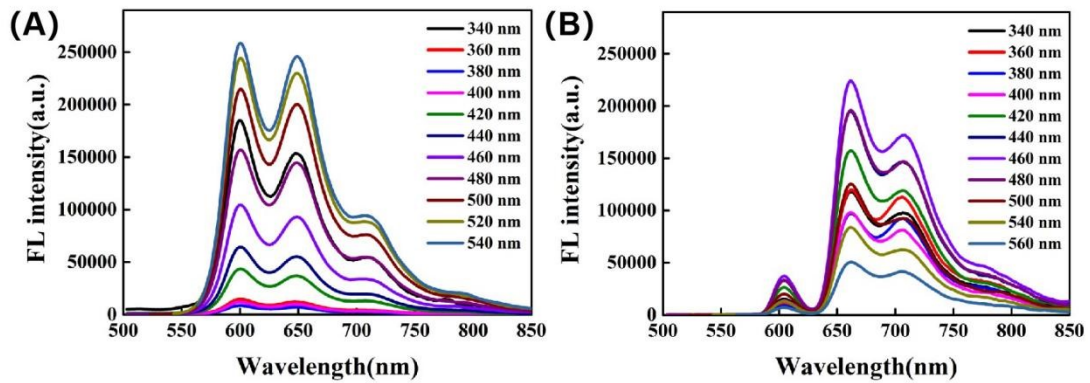


Figure S5. Fluorescence emission spectra of r-CDs prepared at different molar mass ratios of SA and oPD under multiple excitations in ethanol solution: (A) $m_{SA}:m_{oPD} = 1:3$; (B) $m_{SA}:m_{oPD} = 3:1$

Table S1. The constituent elements of CDs and their contents

elements	C	N	O	S
CDs	(at.%)	(at.%)	(at.%)	(at.%)
b-CDs	50.85	8.51	31.14	9.5
r-CDs	79.26	8.25	11.85	0.64
y-CDs	77.77	19.34	2.88	
r-CDs-H	81.13	16.7	2.17	
r-CDs-S	79.49	15.72	4.37	0.41

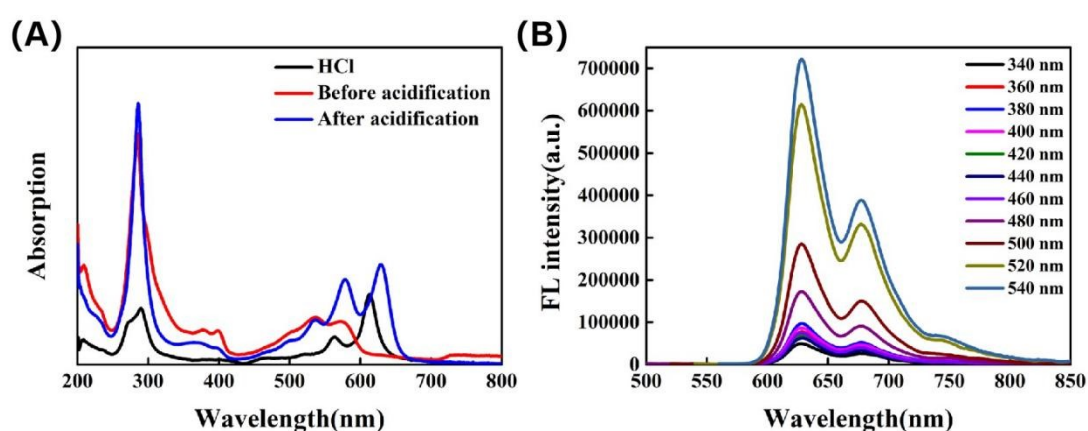
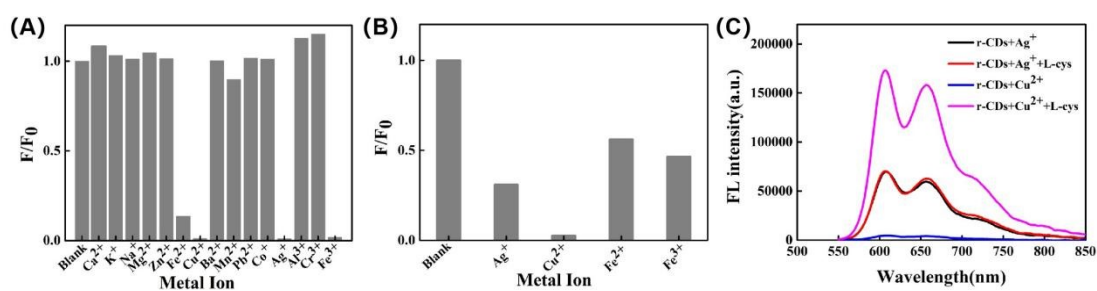
**Figure S6.** (A) UV-visible absorption spectra of r-CDs in ethanol or HCl before and after acidification; (B) Fluorescence emission spectra of r-CDs in HCl solution ($\lambda_{em} = 540$ nm)**Figure S7.** (A) Fluorescence intensity changes of r-CDs mixed with 1 mM metal ions; (B) r-CDs quenching by different metal ions at 0.1 mM concentration; (C) effects of L-cys on fluorescence properties of two mixed systems (r-CDs-Ag⁺, r-CDs-Cu²⁺)

Table S2. Comparison of Sensing Performance of Different Carbon Dots-Based Fluorescence Sensors for Cu^{2+} and Ag^+ Detection

	The fluorescent color of CDs	Detection Range	Detection Limit	Ref
Cu^{2+}	red	0-8 μM	0.165 μM	this paper
	red	0-10 μM	40 nM	[6]
	orange-yellow	2-80 nM	1.8 nM	[7]
	blue	10-1100 nM	6 nM	[8]
	blue	0-10 μM	2.3×10^{-5} mM	[9]
Ag^+	red	0-90 μM	1.53 μM	this paper
	red	30-90 μM	0.12 μM	[10]
	yellow	1-7 μM	0.2 μM	[11]
	blue	1-10 mM	0.31 μM	[12]

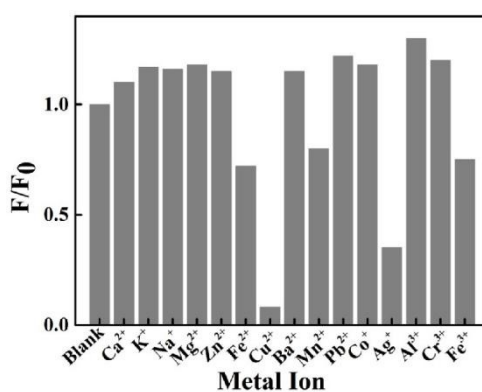


Figure S8. Selective fluorescence response of r-CDs solution after adding different metal ions at a concentration of 0.01 mM (F were the fluorescence intensity in the presence of metal ions, F_0 was the fluorescence intensity in the absence of metal ions)

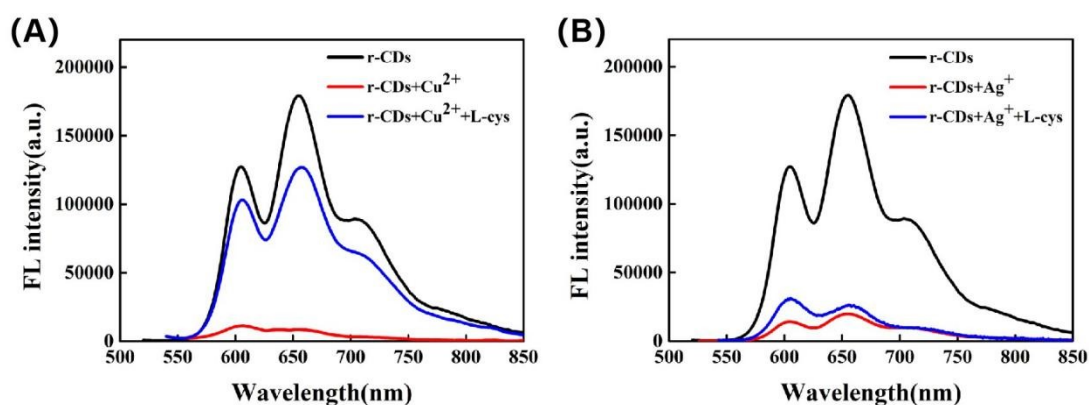


Figure S9. (A) Fluorescence spectra of r-CDs- Cu^{2+} system before and after L-Cys addition; (B) Fluorescence spectra of r-CDs- Ag^+ system before and after L-cys addition

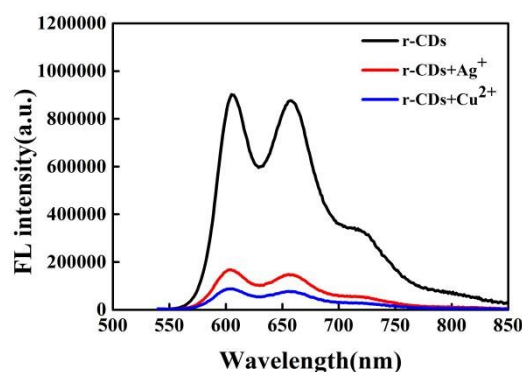


Figure S10. r-CDs detection simulates the fluorescence spectra of metal ions (Cu^{2+} and Ag^+) in real samples

REFERENCES

- (1) Deng Y, Qian J, Zhou Y, et al. Regulatory Preparation of N/S Doped Carbon Quantum Dots and Their Applications as Fe(III) Ion Sensors[J]. *ChemistrySelect*, 2020, 5(17):5306-5311.
- (2) YafengDeng, JunQian, YihuaZhou, et al. Preparation of N/S doped carbon dots and their application in nitrite detection[J]. *RSC Advances*, 11.
- (3) Chao, Daiyong, Lyu, et al. Solvent-dependent carbon dots and their applications in the detection of water in organic solvents[J]. *Journal of Materials Chemistry, C. materials for optical and electronic devices*, 2018, 6(28):7527-7532.
- (4) Tan C, Su X, Zhou C, et al. Acid-assisted hydrothermal synthesis of red fluorescent carbon dots for sensitive detection of Fe (III)[J]. *Rsc Advances*, 2017, 7(65):40952-40956.
- (5) Liu J J, Li D, Zhang K, et al. One - Step Hydrothermal Synthesis of Nitrogen - Doped Conjugated Carbonized Polymer Dots with 31% Efficient Red Emission for In Vivo Imaging[J]. *Small*, 2018, 14(15).
- (6) Chen D, Xu M, Wu W, et al. Multi-color fluorescent carbon dots for wavelength-selective and ultrasensitive Cu^{2+} sensing[J]. *Journal of Alloys and Compounds*, 2017, 701:75-81.
- (7) Vedamalai M, Periasamy A P, Wang C W, et al. Carbon nanodots prepared from o-phenylenediamine for sensing of Cu^{2+} ions in cells[J]. *Nanoscale*, 2014, 6(21): 13119-13125.
- (8) Dong Y, Wang R, Li G, et al. Polyamine-functionalized carbon quantum dots as fluorescent probes for selective and sensitive detection of copper ions[J]. *Analytical chemistry*, 2012, 84(14): 6220-6224.
- (9) Zong J, Yang X, Trinchi A, et al. Carbon dots as fluorescent probes for “off-on” detection of Cu^{2+} and l-cysteine in aqueous solution[J]. *Biosensors and Bioelectronics*, 2014, 51: 330-335.
- (10) Jiao Y, Gao Y, Meng Y, et al. One-step synthesis of label-free ratiometric fluorescence carbon dots for the detection of silver ions and glutathione and cellular imaging applications[J]. *ACS applied materials & interfaces*, 2019, 11(18): 16822-16829.
- (11) Jiang K, Sun S, Zhang L, et al. Bright-yellow-emissive N-doped carbon dots: preparation, cellular imaging, and bifunctional sensing[J]. *ACS applied materials & interfaces*, 2015, 7(41): 23231-23238.
- (12) Song T, Zhu X, Zhou S, et al. DNA derived fluorescent bio-dots for sensitive detection of mercury and silver ions in aqueous solution[J]. *Applied Surface Science*, 2015, 347: 505-513.