Electronic Supplementary Information (ESI)

for

An inner filter effect based sensor of tetracycline hydrochloride as developed by loading photoluminescent carbon nanodots in electrospun nanofibers

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Contents in ESI

Fig.S8 Optimization of conditions for Tc detection

Fig.S9 Cyclic voltammograms of the CDs.

Fig.S10 FTIR spectra of the CDs and the CDs-Tc system.

Fig.S11 TEM images of CDs/PVA nanofibers after crosslinking.

Fig.S12 Photographs of the PVA/CD nanofibrous membrane (NFM) immersing in water before (A) and after cross-linking (B);

Fig.S13 Photographs of the PVA/CD nanofibrous membrane (NFM) under visible light (A) and UV light (D) before (left) and after (right) cross-linking.

2.2 Tables

Table S1 Different reaction conditions for fluorescent carbon nanodots under microwave synthesis route.

Table S2 Relevant data of FL intensities of quinine sulfate (a) and CDs (b).

Table S3 Molar extinction coefficient of Tc and different antibiotics.

3. Notes and references

1. Experimental Section

1.1 Quantum yield Measurements

According to a reported procedure,[1] quinine sulfate in 0.1M H_2SO_4 (literature quantum yield 0.54 at 360 nm) was chosen as a standard and the formula used for QY measurements is as follows:

$$\varphi_x = \varphi_{st}(I_x / I_{st})(\eta_x^2 / \eta_{st}^2)(A_{st} / A_x) = \varphi_{st}(k_x / k_{st})(\eta_x^2 / \eta_{st}^2) \quad (1)$$

Where Φ is the quantum yield, η is the refractive index of the water (1.33) . I is the measured integrated emission intensity and and A is the absorbance at the excitation wavelength. K_x and k_{st} is the slopes of CDs and quinine sulfate. To minimize reabsorption effects, absorbencies were kept under 0.1 at the excitation wavelength (360 nm). The QY of CDs was calculated to be 47 %.

1.2 Cytotoxicity investigation

1×10^5 cells per ml of Human epidermoid cancer cells (Hep-2) in Roswell Park Memorial Institute 1640 medium (RPMI 1640) supplemented with 10% fetal bovine

serum (FBS) were added to each well of a 96-well plate (100μl per well), the cells were cultured first for 24 h in an incubator (37 ℃, 5% CO2). Then we replaced the culture medium with 2% FBS 1640 mediumcontaining the obtained CDs with different concentration (0, 20, 50,100, 200, 400, 500 μg mL-1 for another 24 h. We added 10 μL of Cell Counting Kit-8 (CCK-8) solution and 90μl RPMI 1640 to every cell well for 30 min. The optical density (OD) of the mixture was measured at 450 nm with a Microplate Reader Model. The cell viability was estimated according to the following equation:

$$\text{Cell viability (\%)} = ((OD_{treated} - OD_{PBS}) / (OD_{control} - OD_{PBS}) \quad (2)$$

$OD_{control}$ was obtained in the absence of CDs, OD_{PBS} was the absorption value of PBS around in 96 plate-well, and $OD_{treated}$ was obtained in the presence of CDs.

1.3 Cellular imaging

Hep-2 cells in RPMI 1640 supplemented with 2% fetal bovine serum were added to imaging dishes (1 ml per well) . Then cells were cultured for 24 h in an incubator (37℃, 5% CO_2). After 24 h incubated, the culture medium was replaced with 1 ml PRMI 1640 containing 0.1 mg mL^{-1} CDs and incubated at the incubator for 2h. Then the cells were washed with PBS buffer for 3 times and fixed with 4% paraformaldehyde for 30 min. Finally, the bioimaging photographs were captured with a DSU live-cell confocal microscope (Olympus, Japan) system at laser excitations of DAPI (360-370 nm).

1.4 Calculation the energy levels of CDs

To estimate the HOMO and LUMO energy levels of CDs. Cyclic voltammetry (CV) was carried out by using a standard three electrode system, which consists of platnum sheet as the working electrode, a Pt-wire counter electrode and an Ag/AgCl reference electrode. By using cyclic voltammetry with the potential sweeping between -1.0 and 1.0 V at a scan rate of 0.5Vs^{-1}. ECL signals of the CDs (0.1 mg mL^{-1}) in the the electrolyte containing phosphate buffer solution (PBS) (0.1M, pH 7.4).

The HOMO and LUMO energy levels in eV of CDs were calculated according to the following equations:[2, 3]

$$E_{HOMO}=-e(E_{ox}+4.4)\ (eV)$$
$$E_{LUMO}=-e\ (E_{red}+4.4)\ (eV) \quad (2)$$

Where E_{ox} and E_{red} are onset of oxidation and reduction potential for CDs respectively. The E_{red} was determined to be - 0.49 eV. The corresponding LUMO level was - 3.91 eV. However, the HOMO energy could not be obtained due to the irreversible of the oxidation behavior (data not shown). The HOMO level could be obtained according to the following equation (E_g resulting from the absorption edge in the absorption spectrum):

$$E_{HOMO}=E_{LUMO}-E_g$$

E_g was estimated to be 3.10 eV. So, the E_{HOMO} was calculated to be -7.01 eV.

2.Results

2.1 Figures

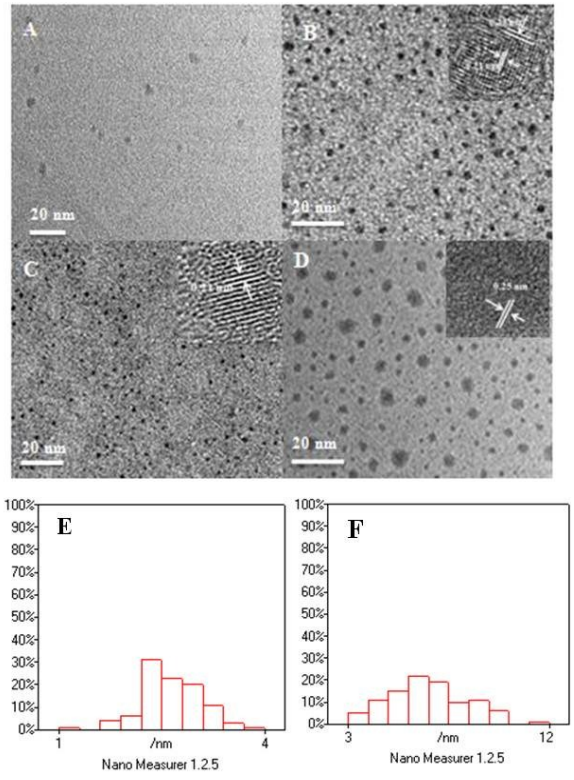


Fig. S1. HRTEM images of CDs under different reaction times (A) 3 min; (B) 5 min; (C) 9 min

and (D) 20 min; (E) size distribution histograms of CDs when reaction time increasing to 9 min and (F) 20 min.

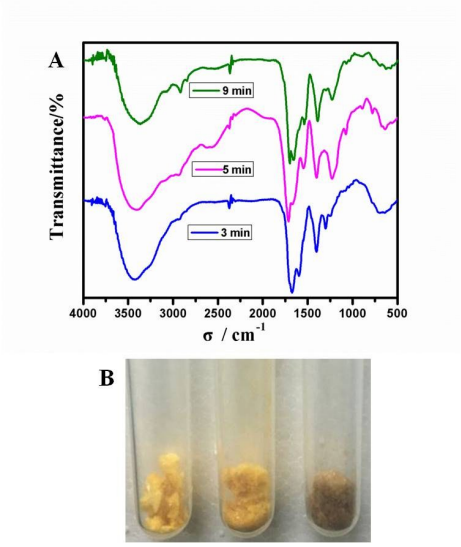


Fig.S2 FTIR spectra and Photographs of the CDs under different reaction times (from left to right: 3, 5 , 9 min).

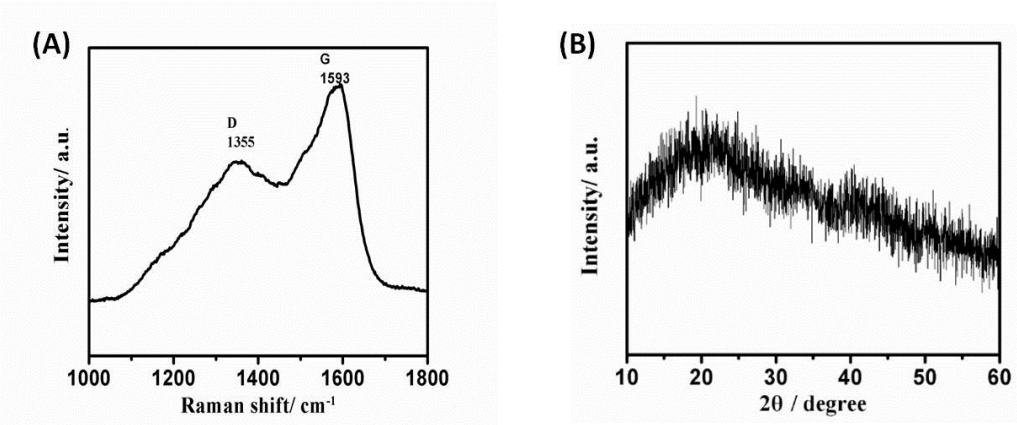


Fig. S3 Raman spectra and XRD pattern of CDs. (A) The Raman spectrum showed the G-band at 1593 cm^{-1} and the D-band at 1355 cm^{-1} which attribute to sp^2 and sp^3 carbons respectively. The relative intensity (I_D/I_G) of the Raman peaks for the TA-CDs is around 0.75, indicating that they have a similar structure to graphite; (B) The XRD pattern with a broad peak centered at 23° is attributed to the graphite lattice spacing and highly disordered carbon atoms.

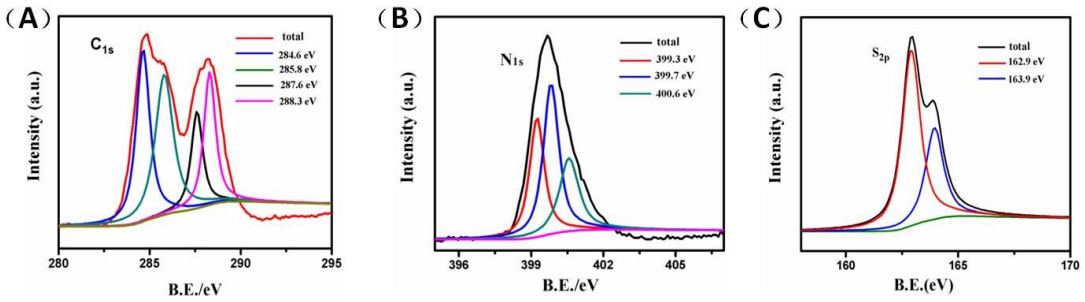


Fig. S4 High resolution XPS spectra of (A) C 1s, (B) N 1s and (C) S2p of the as-prepared CDs.

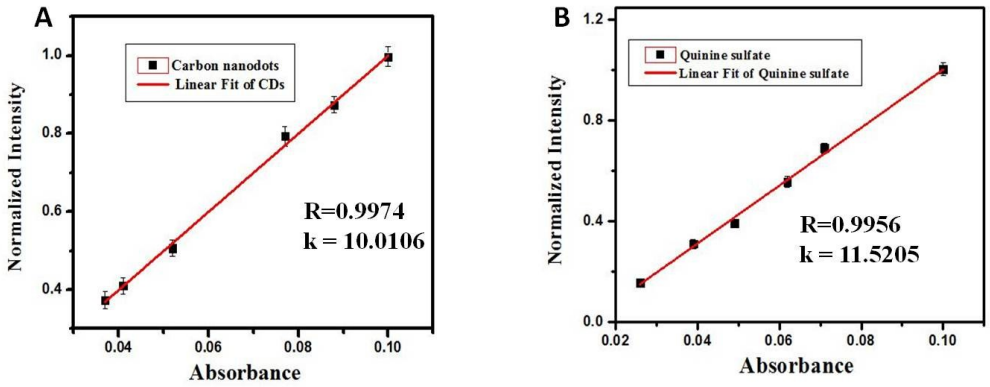


Fig. S5 Linear fitting for quantum yield calculation of CDs and Quinine sulfate. CDs was dissolved in deionized water while quinine sulfate was dissolved in 0.1 M H_2SO_4. All the CDs and quinine sulfate solutions had absorbance less than 0.1 at the excitation wavelength of 350 nm.

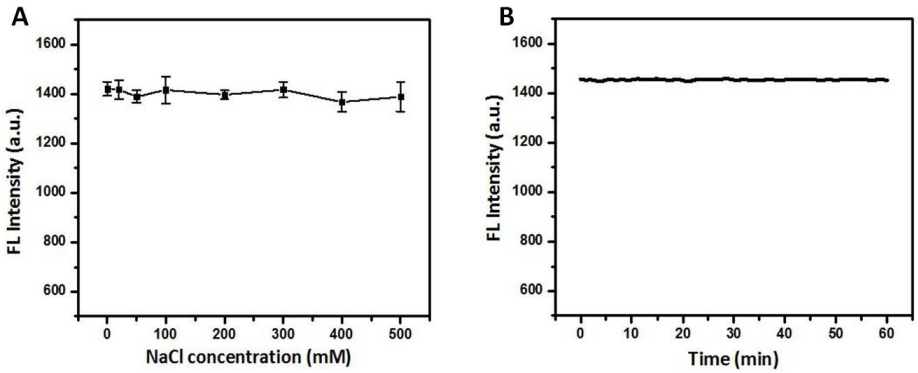


Fig. S6 Effect of (A) ionic strength and (B) continuous excitations on the FL Intensities of CDs.

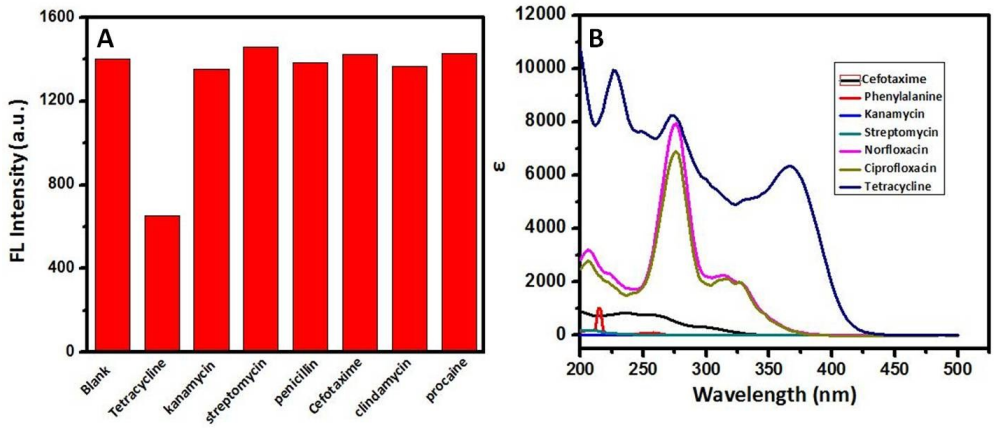


Fig. S7 (A) Fluorescence intensity of CDs in the prescence of Tetracycline, Kanamycin, Streptomycin,Penicllin,Cefotaxine,Clindamycin,Procaine (100 μM),respectively; (B) UV-Vis spectra of Cefotaxime, Phenylalanine, Kanamycin, Streptomycin, Nofloxiacin, Ciprofloxacin,Tetracycline (100 μM),respectively.

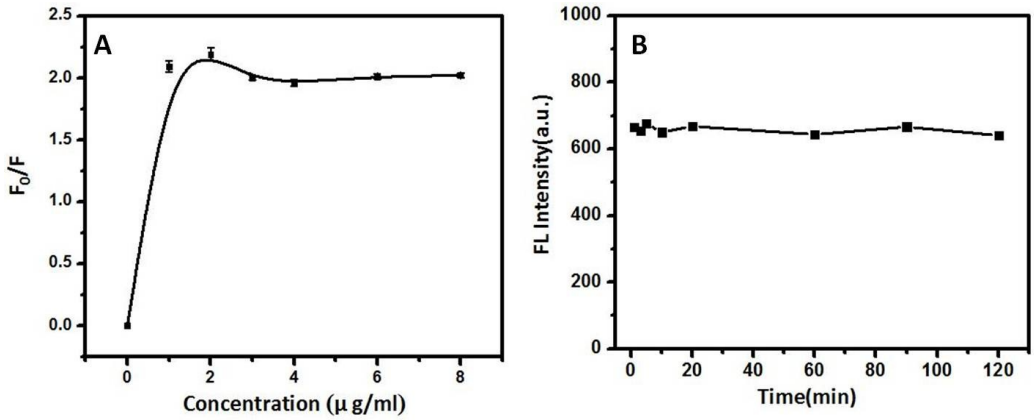


Fig. S8 (A) Effect of CDs concentrations and (B) the incubtation time on the FL intensities of CDs-Tc system. (CDs: 2 μg mL^{-1}; Tc: 100 μM; PBS buffer:7.4)

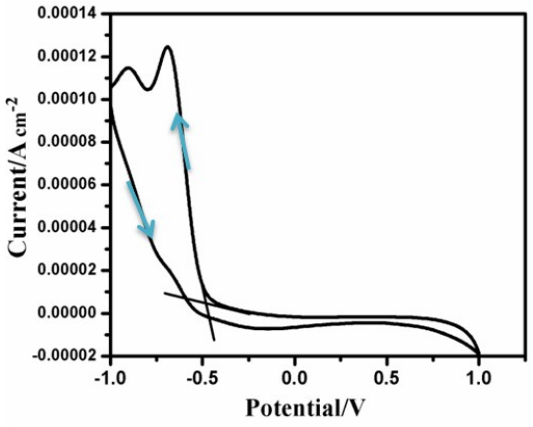


Fig. S9 Cyclic voltammograms of the CDs in the solution state.

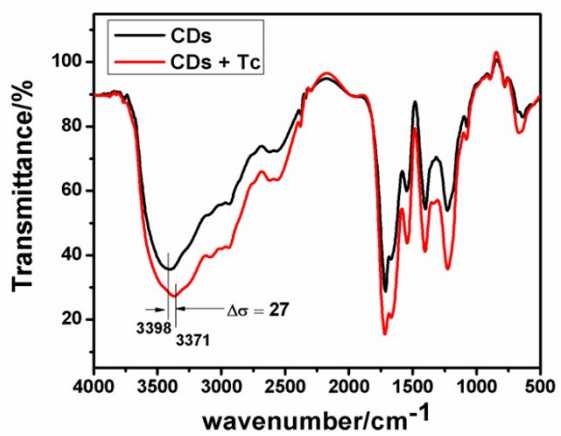


Fig. S10 FTIR spectra of the CDs (black line) and CDs-Tc system (red line).

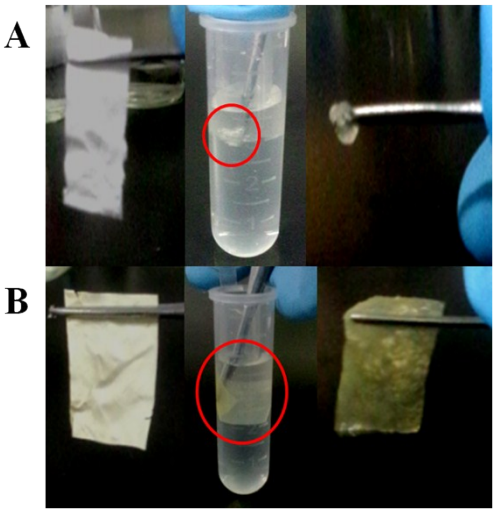


Fig. S11 Photographs of the PVA/CD nanofibrous membrane (NFM) immersing in water before (A) and (B)after cross-linking;

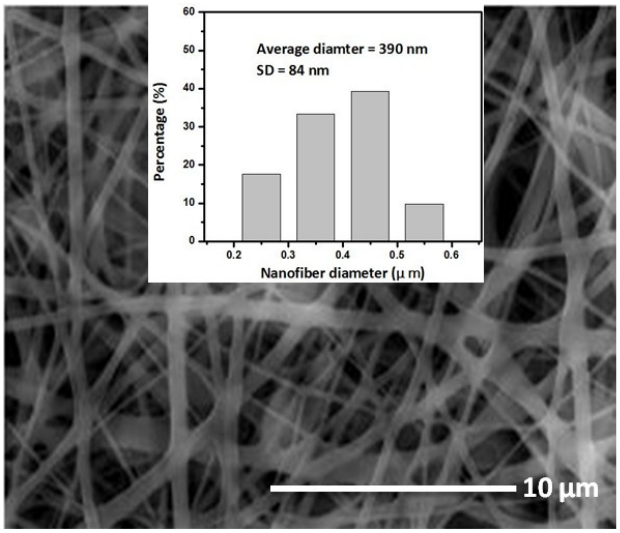


Fig.S12 SEM images and morphology of CDs/PVA nanofibers.The insets are the corresponding size distribution histogram of the above nanofibers.

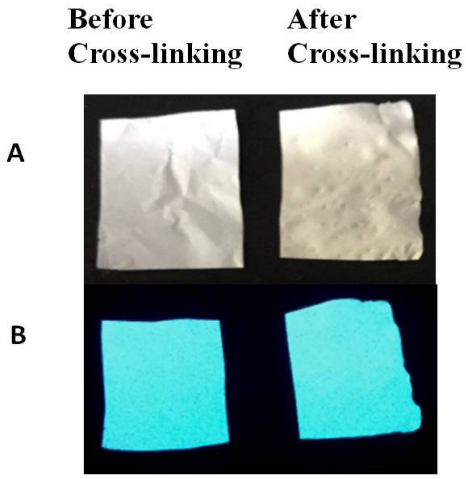


Fig. S13 Photographs of the PVA/CD nanofibrous membrane (NFM) under visible light (A) and UV light (D) before (left) and after (right) cross-linking.

2.2 Tables

Table S1 Different reaction conditions for fluorescent carbon nanodots under microwave synthesis route.

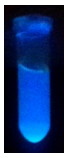
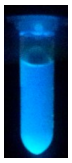
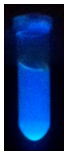
Serial	CDs under different reaction conditions	Photos of CDs aqueous		Absolute QY	Peak position (365 nm excition)
		Visible Light	UV light		
1	Citric acid (only), 5min, 750 W			5.9%	502 nm
2	Citric acid and Glutathione, 3 min, 750W			37.6%	448 nm
3	Citric acid and Glutathione, 5 min, 750W			42.5%	445 nm
4	Citric acid and Glutathione, 9 min, 750W			33.8%	452 nm
5	Glutathione (only), 5 min, 750W			12.3%	462 nm

Table S2 Relevant data of FL intensities of quinine sulfate (a) and CDs (b).

a

Quinine Sulfate						
Abs	0.026	0.039	0.049	0.062	0.071	0.100
FL	196	389	487	694	851	1235
Slope	11.5205					
QY	54%					

b

	CDs					
Abs	0.037	0.041	0.052	0.077	0.088	0.100
FL	225	245	302	477	521	596
Slope	10.0106					
QY	47%					

Table S3 Molar extinction coefficient of Tc and different analytes at 350 nm.

Analytes	ε（350 nm）
Cefotaxime	9
Phenylalanine	≈0
Kanamycin	≈0
Streptomycin	5
Nofloxiacin	670
Ciprofloxacin	600
Procaine	30
Tetracycline	5520

3. Notes and references

1. A. Jaiswal, S. S. Ghosh and A. Chattopadhyay, *Chem. Commun*, 2012, **48**, 407-409.
2. S. Zhu, Q. Meng, L. Wang, J. Zhang, Y. Song, H. Jin, K. Zhang, H. Sun, H. Wang and B. Yang, *Angew. Chem. Int. Ed*, 2013, **125**, 4045-4049.
3. H. Zhang, Y. Chen, M. Liang, L. Xu, S. Qi, H. Chen and X. Chen, *Anal.Chem*, 2014, **86**, 9846-9852.