

*Supporting Information for*

**Facile fabrication of N/S/P tri-doped carbon dots for tetracycline  
detection by internal filtering effect of a two-way matching strategy**

Zideng Gao,<sup>a</sup> Mingyang Liu,<sup>a</sup> Ke Xu,<sup>a</sup> Menglei Tang,<sup>a</sup> Xiaowen Lin,<sup>a</sup> Shuwen Hu<sup>\*a</sup> and Xueqin Ren<sup>\*a</sup>

<sup>a</sup> College of Resources and Environmental Sciences, China Agricultural University,  
Beijing 100193, China.

\*Corresponding Authors

Shuwen Hu. Tel.: +86 010 62731255; fax: +86 010 62731016.

Xueqin Ren

\*E-mail: shuwenhu@cau.edu.cn (Shuwen Hu)

renxueqin@cau.edu.cn;

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# 1. Materials and Instruments

## Materials

Thiamine pyrophosphate (TPP), tetracycline (TC), minocycline (MINO), doxycycline (DOXY), oxytetracycline (OTC), chlortetracycline (CTC), methacycline (MTC), kanamycin (KAN), amikacin (AMK), neomycin (NM), streptomycin (STR), sulfachloropyridazine (SCP), sulfapyridine (SP) and gentamicin (GEN) were obtained from Shanghai Aladdin, Ltd. (Shanghai, China). Sodium hydroxide and all metal salts (NaCl, LiCl, BaCl<sub>2</sub>·2H<sub>2</sub>O, HgCl<sub>2</sub>, CdCl<sub>2</sub>·2½H<sub>2</sub>O, ZnSO<sub>4</sub>, MgCl<sub>2</sub>·6H<sub>2</sub>O, CaCl<sub>2</sub>, CuSO<sub>4</sub> and FeCl<sub>3</sub>) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). All the chemicals were analytical grade and used as received without further purification. The milk sample was purchased from a local supermarket (Beijing, China). Tap water samples and deionized water were supplied by China Agricultural University (Beijing, China).

## Instruments

FT-IR spectra were recorded on a Nicolet NEXUS-470 Spectrometer (Madison, USA) from KBr pellets at room temperature, using an accumulation of 32 scans and a resolution of 4 cm<sup>-1</sup>, in the range of 4000~500 cm<sup>-1</sup>. Samples (2 mg) were thoroughly ground with KBr and pelletized using a hydraulic press under a pressure of 600 kg/cm<sup>2</sup>.

Fluorescence spectra were recorded on an F-7000 fluorescence spectrophotometer (Hitachi, Tokyo, Japan). All fluorescence intensity measurements were performed under the same conditions: the excitation and emission slit widths were both 5 nm, and the excitation wavelength was set at 370 nm, with a recording emission range of 390~650 nm. The photomultiplier tube voltage was set at 700 V. All ultraviolet-visible (UV-Vis) spectra were recorded on a WTF UV-2102PC UV-Vis spectrophotometer (UNICO Shanghai Instrument Co., Ltd., China).

X-ray photoelectron spectroscopy (XPS) results were collected by Thermo escalab 250Xi spectrometer (USA), which uses advanced Avantage data acquisition and processing system to ensure that as much information as possible is extracted from the test data. XPS pre-processing process: appropriate amount of samples are pressed into a tablet less than 1cm.

High-resolution scanning/transmission electron microscope (STEM) (FEI Talos F200 series 200kV) was used to study the morphology of QCDs.

## **2. Synthesis of N/P/S-CDs**

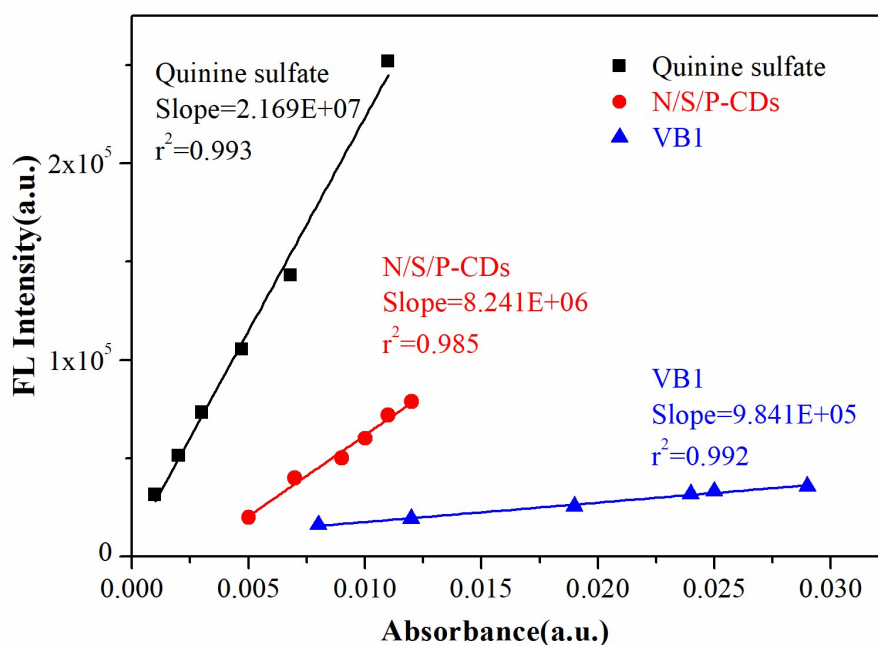
First, 10 mL of 1 M NaOH solution was added to an aqueous solution of thiamine pyrophosphate (TPP) (20 mM, 40 mL). The mixture was subjected to ultrasonic treatment at room temperature; the temperature of the ultrasonic bath was maintained at room temperature by changing the water every hour. The solution was initially yellow after the addition of the NaOH solution, and gradually became colorless gradually over the course of the reaction. The reaction was carried out for a total of 4 h and was terminated by adjusting the pH to neutral (pH = 7.0) with HCl. Subsequently, the above solution was dialyzed by using a dialysis bag of 2000 MW for 48 h to remove the salt and unreacted precursors. The N/S/P-CDs were finally obtained after freeze drying.

### 3. Quantum yield measurement

The quantum yield ( $\Phi$ ) of N/P/S-CDs was determined by comparing the integrated fluorescent intensities (excitation at 370 nm) and absorbance values (at 370 nm) of the N/P/S-CDs with those of quinine sulfate (in 0.1M H<sub>2</sub>SO<sub>4</sub> solution as standard). The quantum yield was calculated using equation (S1), where  $\Phi$  is the quantum yield,  $k$  is slope,  $\eta$  is the refractive index of the solvent,  $S$  is the standard and  $X$  is the sample.

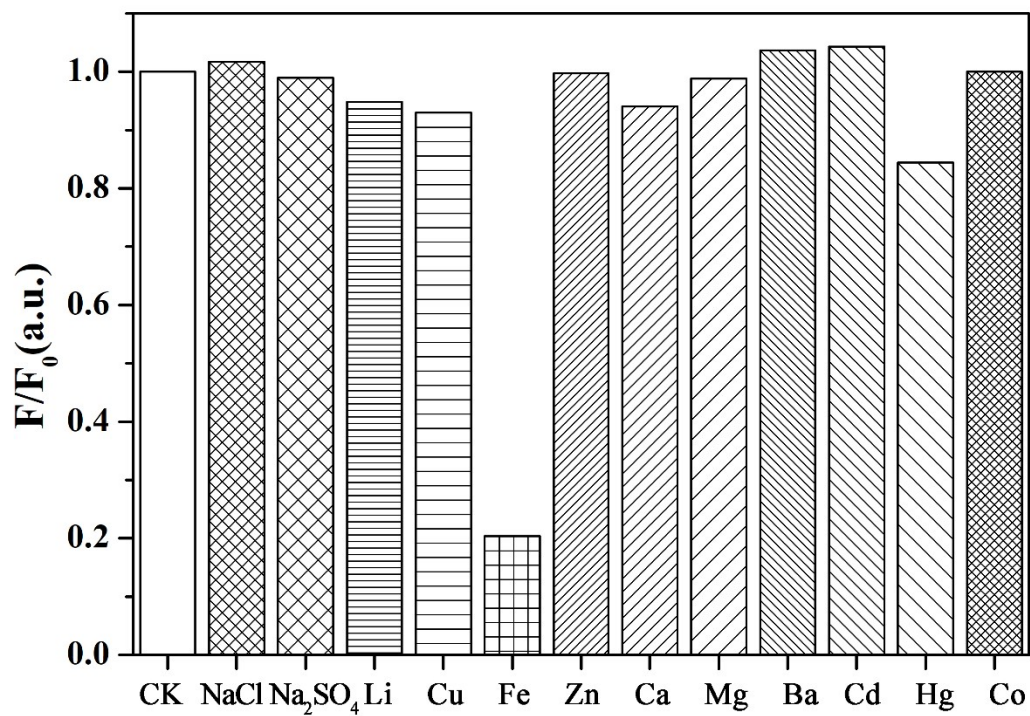
$$\Phi_x = \Phi_s \left( \frac{K_x}{K_s} \right) \left( \frac{\eta_x}{\eta_s} \right) \quad (S1)$$

Fig. S1 Liner plots for quinine sulfate (0.1M H<sub>2</sub>SO<sub>4</sub> solution,  $\phi_f=0.54$ ), N/P/S-CDs and VB1-CDs



#### 4. Study on the salt stability of N/P/S-CDs

Fig. S2 The impact of the salt on the fluorescence emission of the N/P/S-CDs (100 $\mu$ M NaCl, Na<sub>2</sub>SO<sub>4</sub>, LiCl, BaCl<sub>2</sub>·2H<sub>2</sub>O, HgCl<sub>2</sub>, CdCl<sub>2</sub>·2½H<sub>2</sub>O, ZnSO<sub>4</sub>, MgCl<sub>2</sub>·6H<sub>2</sub>O, CaCl<sub>2</sub>, CuSO<sub>4</sub> and FeCl<sub>3</sub>)



## 5. Fluorescence stability of N/P/S-CDs and N/P/S-CDs +TC

Fig. S3 The duration stability of the N/P/S-CDs and N/P/S-CDs +TC measured by fluorescence spectrophotometer every 10 min ( $\lambda_{ex} = 370 \text{ nm}$ ,  $\lambda_{em} = 443 \text{ nm}$ )

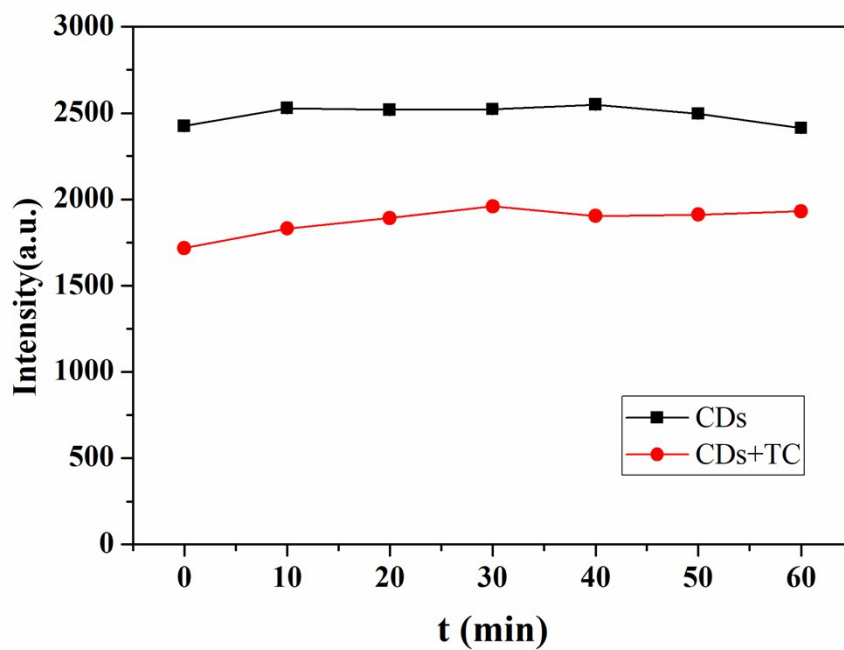


Fig. S4 The pH stability of the N/P/S-CDs and N/P/S-CDs +TC ( $\lambda_{ex} = 370 \text{ nm}$ ,  $\lambda_{em} = 443 \text{ nm}$ )

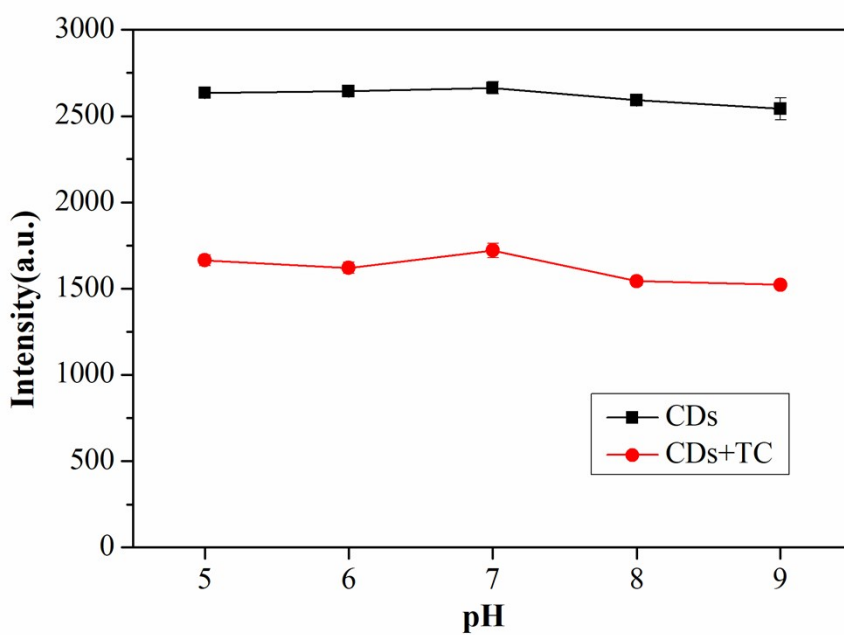
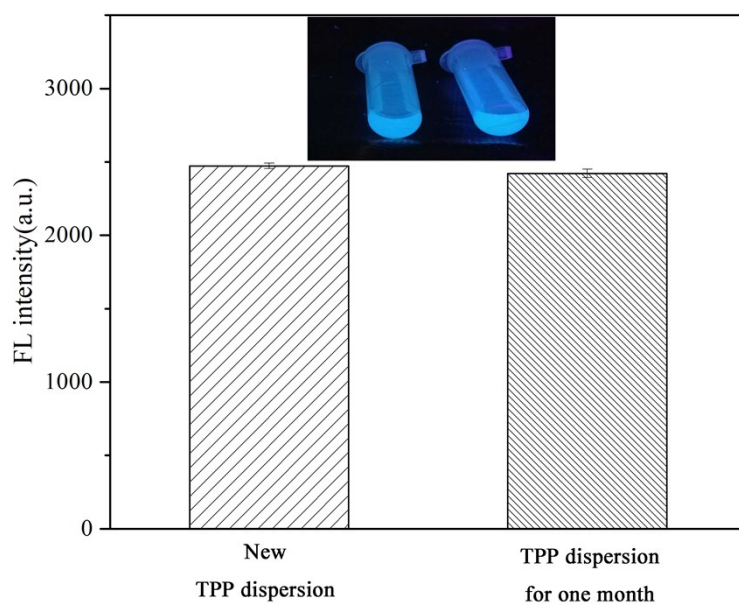


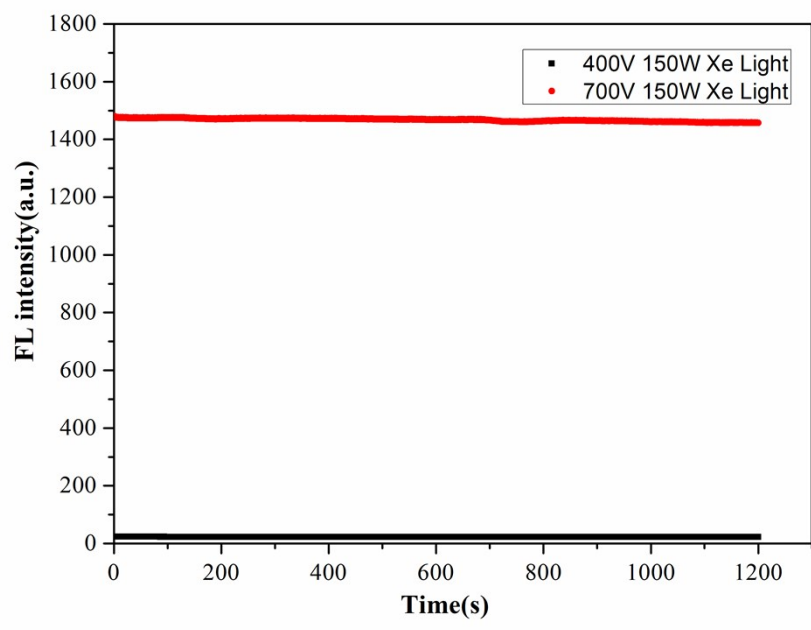
Fig. S5 The characterization of storage stability of N/S/P-CDs ( $\lambda_{ex} = 370 \text{ nm}$ ), insert: digital photographs of the new N/P/S-CDs dispersion(left) and the N/P/S-CDs dispersion prepared



for one month(right) under 365 nm UV light.

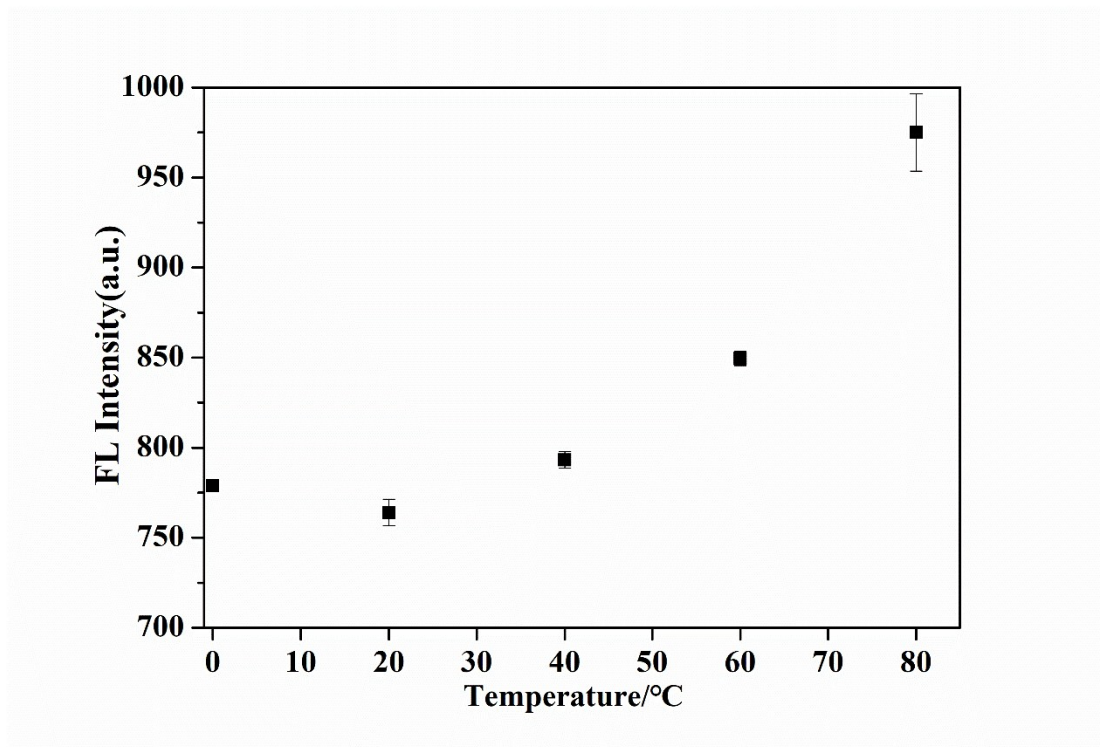
Fig. S6 Real-time fluorescence intensity of N/S/P-CDs under continuous irradiation of xenon lamp (150 W  $\lambda = 370 \text{ nm}$ )





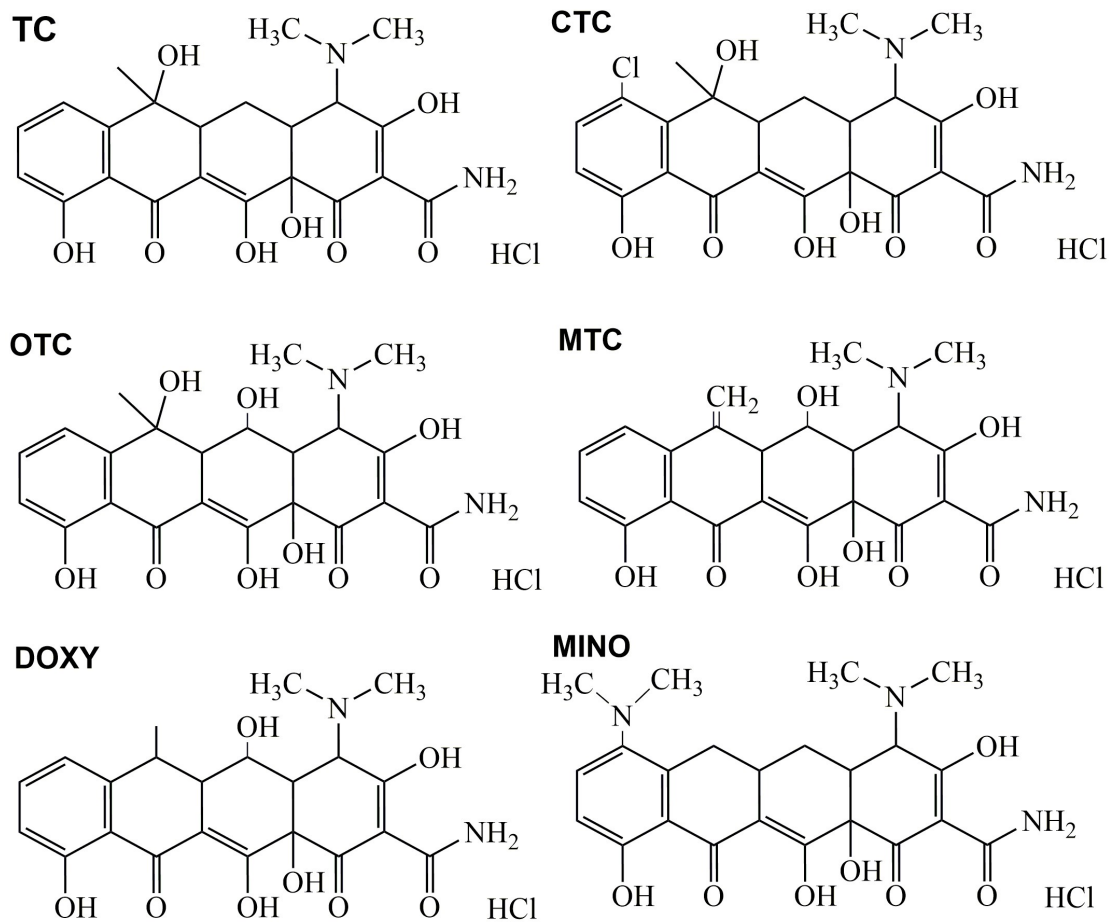
## 6. Temperature sensitivity of N/P/S-CDs

Fig. S7 FL intensity of EM–temperature plots of N/P/S-CDs during heating and cooling processes.



## 7. Molecular formulas of six tetracyclines

Fig. S8 Molecular formulas of six tetracyclines



## 8. UV absorption spectrum of tetracycline with metal ions

Fig. S9 UV absorption spectrum of 10  $\mu\text{M}$  tetracycline with 50  $\mu\text{M}$  metal ions

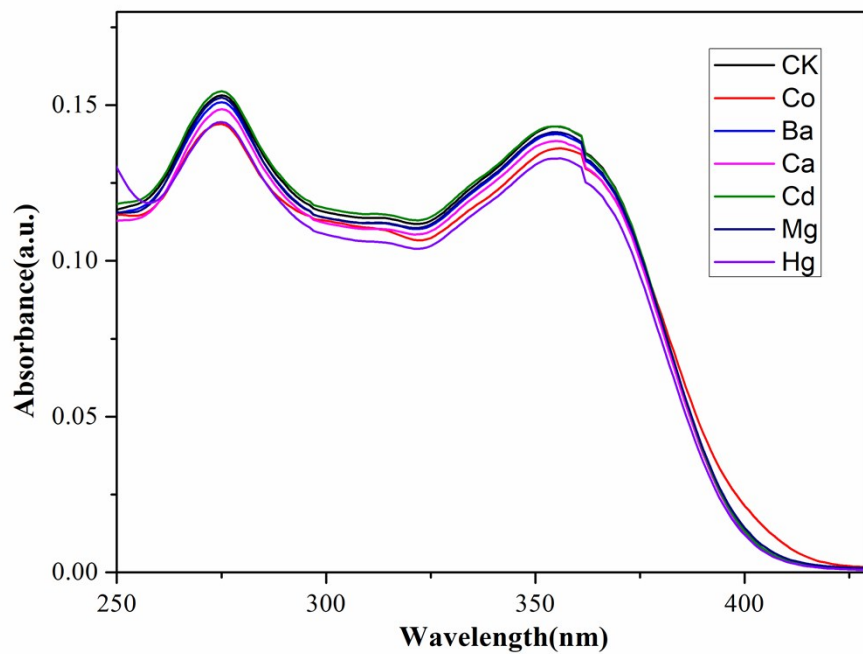
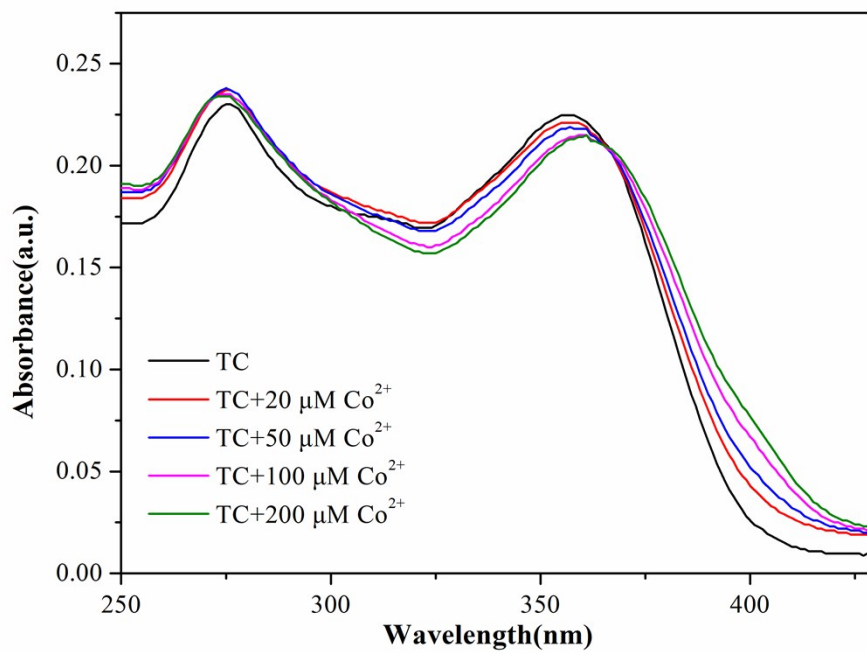


Fig. S10 The optimization experiments of the amount of  $\text{Co}^{2+}$



## 9. Detection of tetracycline residue in the real samples

Sample pretreatment was performed follow the reported method [1]. Trichloroacetic acid was poured into the milk/tap water and ultrasonication applied for 20 min. Then the proteins were separated and removed by centrifugation (12000 rpm, 10 min). Finally, the supernatant was filtered with a 0.22 membrane to remove impurities. The treated milk samples were diluted 50 times with deionized water. Then the four TCs with total concentrations of 25  $\mu\text{M}$  and 50  $\mu\text{M}$  were added to the samples for detection. The specific parameter of HPLC-UV method refer to the work of Shahbazi [2].

Table S1 Detection of tetracycline residue in the real samples (unit:  $\mu\text{mol/L}$ )

<b>Samples</b>	<b>Method reported in this work</b>	<b>HPLC-UV</b>
Milk	Not detected	Not detected
Tap water	Not detected	Not detected

## 10. Comparison of analytical features for TC assays reported

Table S2 Comparison of analytical features for TC assays reported

Methods	LOD/ $\mu\text{M}$	Linear range/ $\mu\text{M}$	RSDs/%	TC specificity	Ref.
HPLC-RRS	1.5	24.7-427.5	3.9	Yes	3
HPLC-UV	0.011	0.003-0.20	7.13	Yes	2
Fluorescence spectroscopy	$8.2 \times 10^{-3}$	0-20	4.17	No	4
Fluorescence spectroscopy	$4.0 \times 10^{-3}$	0.01-5	3.5	Yes	5
Colorimetric	0.071	0.1-5.0	3.05	Yes	6
Fluorescence spectroscopy	0.044	0.1-20	4.9	Yes	This work

## 11. Reference

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