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ORIGINAL ARTICLE

A Novel Application of Fluorine Doped Carbon Dots Combining Vortex-Assisted Liquid-Liquid Microextraction for Determination of 4-Nitrophenol with Spectrofluorimetric Method

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Abstract

A simple and fast vortex-assisted liquid–liquid microextraction (VA-LLME) combining with fluorescent carbon dots have been developed for the determination 4-nitrophenol (4-NP). The high fluorescent quantum yield (58.9%) fluorine doped carbon dots (F-CDs) were synthesized using tetrafluoroterephthalic acid as a fluorine source and using citric acid as a fluorine source and using ethylenediamine as a nitrogen source via a one-step hydrothermal method. F-CDs fluorescence was effectively quenched by 4-NP due to inner filter effect (IFE) and the strong interactions between functional groups (-COOH,-OH, -NH_2 and -F groups) of the F-CDs and 4-NP. In VALLME method, n-octanol was employed as extraction solvent, and vortex-mix was exploited as a gentle mix method to reduce emulsification time and improve the extraction efficiency. The detection limits, the quantification limit and relative standard deviation for the 4-NP were found as 15 nM, 50 nM and 3.5%, respectively. Moreover, the obtained F-CDs can be employed as fluorescent probe to detect 4-NP in real environmental water samples.

Keywords Fluorescent carbon dots · 4-nitrophenol · VA-LLME · Detection

Introduction

4-Nitrophenol ($C_6H_5NO_3$, 4-NP) is widely utilized as a precursor and intermediates in the manufacture of pharmaceuticals, pesticides and dyes industries [1–3]. The US Environmental Protection Agency has marked 4-NP as a major pollutant with an allowed limit of 60 μg/L (0.43 μM) in drinking water [4]. A precise reliable techniques for the determination of 4-NP is highly important to monitor the pollutants caused destroy on the ecosystem. Several analytical means have been used for the determination of 4-NP in environmental samples including chromatography [5, 6], spectrophotometry [7], electrochemical method [8], enzyme-linked immunosorbent assay (ELISA) [9] and spectrofluorimetry [10]. Due to the low concentration of 4-NP in environmental samples, different sample pretreatment techniques such as liquid-liquid extraction(LLE) [11], dispersive liquid-liquid microextraction (DLLME) [12], solid-phase extraction (SPE), solid-phase microextraction (SPME) [13], hollow fiber liquid phase extraction (HFLPME) [14] have been applied for the analysis of NPs in environmental samples. Vortex-assisted liquid–liquid microextraction (VA-LLME) is obtained by a dispersion of low-density extraction solvent into water using vortex-mix, a gentle mix method [15].

Carbon quantum dots (CQDs) have attracted tremendous attention due to excellent properties, including high chemical stability [16, 17], excellent water solubility [18–20], facile synthesis route [21–23], bright fluorescence [24], high resistance to photo bleaching, and low toxicity [25–29]. Especially, some fluorescent methods have been developed for the detection of 4-NP, because the fluorescent CQDs usually have high quantum yield (QY) and can be quenched by 4-NP [30–37].

In this work, a novel vortex-assisted liquid–liquid microrextraction (VA-LLME) combining with spectrofluorimetric method for detecting 4-nitrophenol (4-NP) was developed in environmental water samples. The high quantum yield fluorescent fluorine doped carbon dots (F-CDs) were synthesized via a one-step hydrothermal method. The F-CDs were characterized by transmission electron microscopy

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(TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), ultraviolet-visible (UV–vis) spectroscopy and fluorescence spectroscopy. We proposed an effective IFE-based fluorescence sensor for the detection of 4-NP with high selectivity. VA-LLME was also utilized as separation and enrichment for 4-NP in environmental water samples. The practical feasibility of this approach for detection of 4-NP in real samples was demonstrated.

Experimental

Materials

Tetrafluoroterephthalic acid (TFTA, 98%), citric acid (CA, 98%), ethylenediamine (EDA, 98%), N-Ethyl-N-(3-(dimethylaminopropyl) carbodiimide) (EDC, 98%) and N-hydroxysuccinimide (NHS, 98%) were purchased from Alading (Shanghai, China). 2,4-dinitrophenol (DNP, 98%), 4-nitrophenol (4-NP, 98%), and phenol (PHE, 98%) were supplied by Alfa Aesar Ltd. (Tianjin, China). All the reagents used were of analytic grade and used as received without further purification. The stock standard solutions of the NPs (10 mg L^{-1}) were prepared by dissolving methanol and renewed monthly. Deionized (DI) water was used throughout this study.

Synthesis of F-CDs

Briefly, 6 g of CA, 5 mL EDA were added into 100 mL of distilled water, followed by ultrasonic processing for 10 min, and was transferred into Teflon-lined autoclave, which was heated for 6 h at 180 °C. The resulting product was cooled to room temperature, and 0.1 g TFTA, 0.4 g EDC and 0.3 g NHS were added and stirred in the dark at room temperature for 24 h. The product was centrifuged at 10,000 rpm for 10 min and the resultant supernatant was filtered through the 0.22 μm membrane. The result and filtrate containing F-CDs was further dialyzed with a dialysis membrane (1000 Da) for purification and stored at 4 °C in refrigerator before used in further experiments.

Characterization of F-CDs

The morphology and microstructure of the F-CDs were examined by TEM on a TecnaiG2 TF30 instrument with an accelerating voltage of 200 kV. The samples for TEM were prepared by dropping an aqueous solution onto carbon-coated copper grid then dried at room temperature for 12 h. The fluorescence spectra and the UV–vis absorption spectra were recorded by G9800A Cary Eclipse (Agilent Technologies, USA) fluorescence spectrophotometer and UV-2550 (Shimadzu, Japan) spectrophotometer, respectively. FT-IR spectrum was performed on a TENSOR27 FT-IR spectrometer (Bruker, Germany). X-ray powder diffraction (XRD) data were recorded on D/Max 2200 with Cu Kα radiation ($\gamma = 1.5405$ A) ranging from $2\theta = 5°$ to 90° (Rigaku, America). Analysis of X-ray photoelectron spectroscopy (XPS) measurements of F-CDs were recorded on a ESCALAB250Xi spectrometer (ThermoFisher Scientific). X-ray powder diffraction (XRD) data were recorded on D/Max 2200 with Cu Kα radiation ($\gamma = 1.5405$ A) ranging from $2\theta = 5°$ to 90° (Rigaku, America).

Detection of 4-NP

In a typical the detection of 4-NP, 2.0 mL of F-CDs were placed in 0.4 mL of F-CDs (100 μM) solution. The mixture was vortexed for 30s and then incubation for 10 min, and the fluorescence emission spectra were measured at an excitation wavelength of 346 nm (Fig. 1).

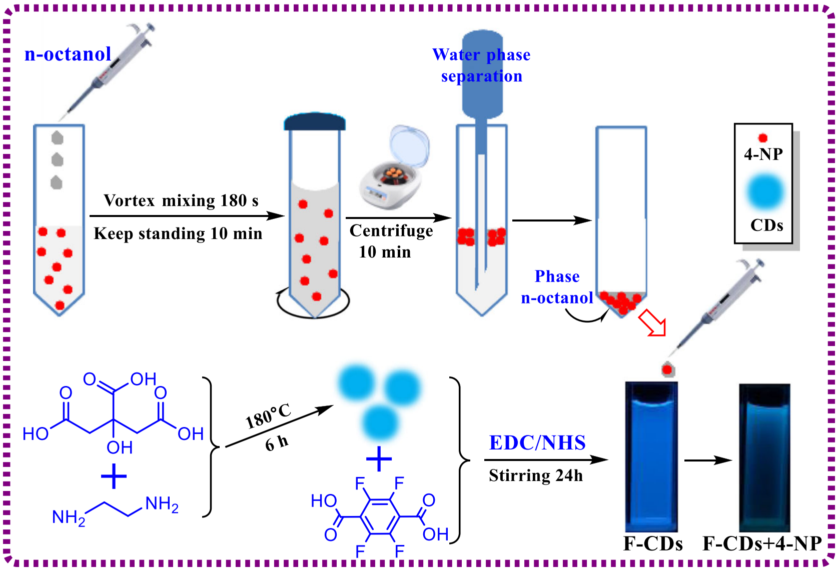
Results and Discussion

Characterization of the F-CDs

Figure 2a shows the UV–vis absorption spectra and fluorescence emission and excitation spectra of F-CDs. The F-CDs show the UV–vis absorption peak at 233 nm and 344 nm, which confirms the presence of the n–π* transition and the contribution of surface moieties. The F-CDs show the maximum emission intensity (QY = 58.9%, quinine sulphate as a reference) at 446 nm with an excitation wavelength of 346 nm. When the excitation wavelength is changed from 306 to 396 nm, the emission peak of F-CDs was red-shifted with decreasing emission peak intensity from 366 nm to 396 nm, and the fluorescence intensity decreases remarkably (Fig. 2b). The result indicates that the fluorescence intensity of F-CDs is strongly dependent on the corresponding excitation wavelength. Meanwhile, the natural kelp itself is non emissive in the studied region, confirming the bright fluorescence is stemming from the synthesized fluorine doped carbon dots.

Figure 2c TEM shows the morphology and microstructure of the F-CDs, revealing that these F-CDs are regular spherical morphology and a relatively narrow size distribution between 2 and 5 nm. The XRD patterns of F-CDs shows a resolvable broad peak centered at 25.98°, which is close to the diffraction peak of the graphite (002) crystal plane at 26.1°.Therefore, all of the above results demonstrate the existence of CQDs. The XPS spectrum was shown in Fig. 3, the as-prepared F-CDs are composed of carbon, oxygen, and nitrogen, and an obvious C1s peak at 283.6 eV, an obvious N1 s peak at 398.0 eV, an O1s peak at 530.8 eV and an F1 s peak at 686.8 eV. The XPS C1s spectrum consists of four deconvoluted Gaussian distributions at 283.10 eV, 284.12 eV, 284.80 eV and 285.42 eV, which can be assigned to C-C/C=C, C-N, C-O, and C=O, respectively. And, the XPS N1 s two deconvoluted Gaussian

Fig. 1 Graphical representation of the VALLME combining F-CDs method



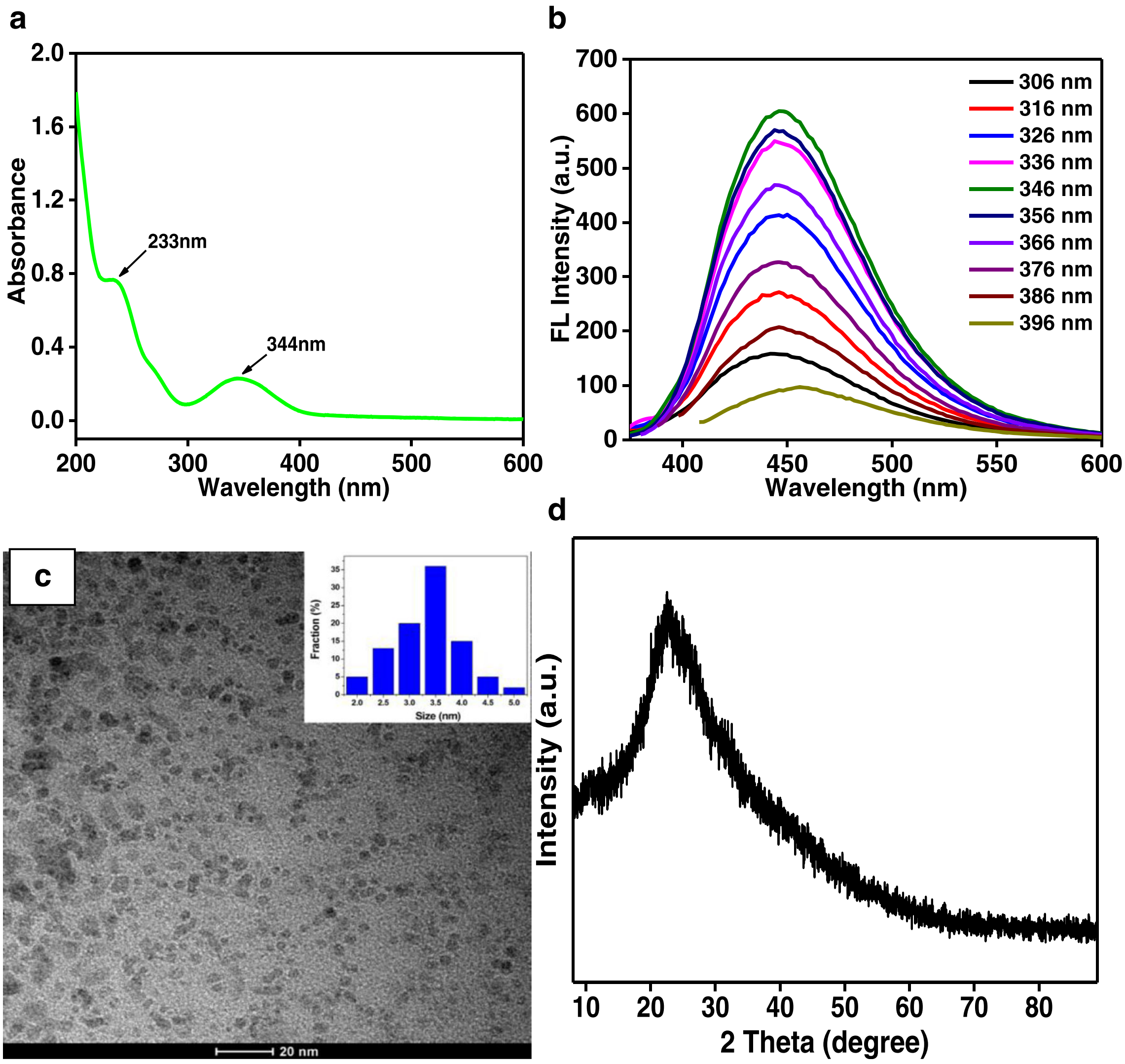


Fig. 2 **a** UV–vis absorption spectra, **b** Fluorescence, **c** TEM images and **d** XRD patterns of the F-CDs

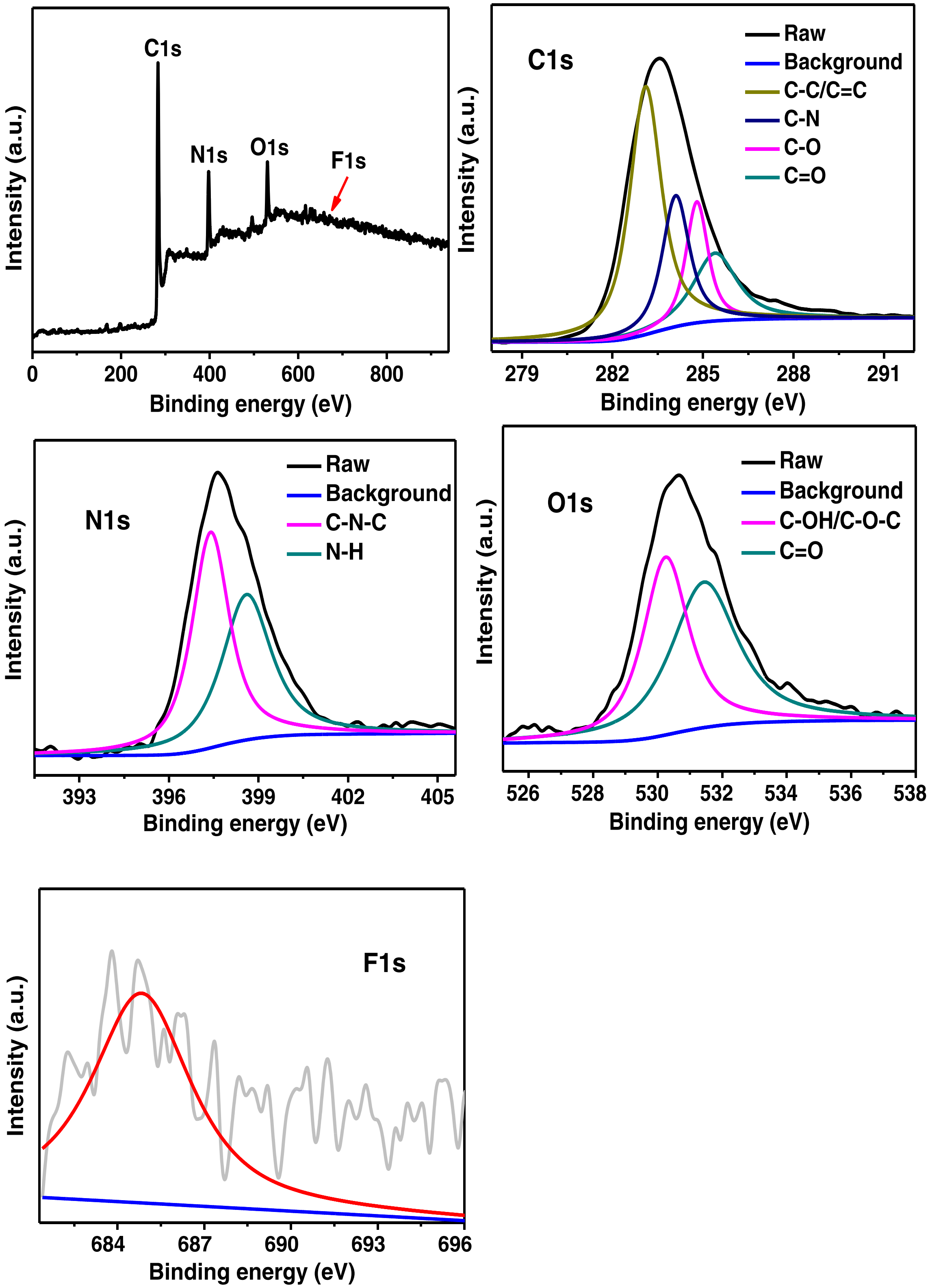


Fig. 3 XPS C1s, N1 s, O1s, and F1 s spectra of the F-CDs

distributions at 397.40 eV and 398.60 eV, which can be assigned to C-N-C and N-H and O1s spectrum consists of two deconvoluted Gaussian distributions at 530.25 eV and 531.43 eV, which can assigned to C-OH/C-O-C and C=O. Moreover, the XPS F1 s spectrum supports the presence of fluorine in CDs

Behavior of F-CDs under Different Conditions

Major factors affecting the applicability of F-CDs include the pH, the ionic strength and the presence of extractant (n-octanol). Therefore, a stability study was carried to evaluate their effect on the fluorescence intensity of F-CDs. The results indicated that the fluorescence intensity of enriched F-CDs in n-octanol of neutral pH was almost invariable and decreased in strong acidic and alkali medium. This appearance may be attribute to the protonation or deprotonation of the functional groups (-COOH,-OH and -NH_2) on the surface of F-CDs in acidic and alkali medium. The results also indicated that the ionic strength and extractant solvent have no effect on the fluorescence intensity of F-CDs.

Optimization of the VALLME Conditions

Effect of the Nature and Volume of Extractant

The extractants should have some properties including high extraction capability on 4-NP and no effect on the fluorescent intensity of F-CDs. Therefore, n-octanol, iso-octyl alcohol, butyl alcohol and isobutyl alcohol were investigated in this work and shown in Fig. 4a. The results indicated that no emulsification was observed using butyl alcohol and isobutyl alcohol as extractants, and n-octanol was the best extractant for the extraction of 4-NP.

Adequately volume of n-octanol is necessary to finish good recoveries, so diverse volumes of n-octanol were fulfilled with the VA-LLME method. The recoveries in Fig. 4b show an increase with the volume from 100 to 700 μL and almost unchanged at >700 μL. Therefore, 700 μL of n-octanol was selected in the following experiments.

Effect of Vortex Mixing Time

The function of vortex-mix is to disperse the water-immiscible extractant in aqueous phase, and the vortex-mix was used as an emulsifier, which increases the surface of impact and shortens the diffusion length between the analytes and extractant and reduce the emulsification time. The recoveries in Fig.

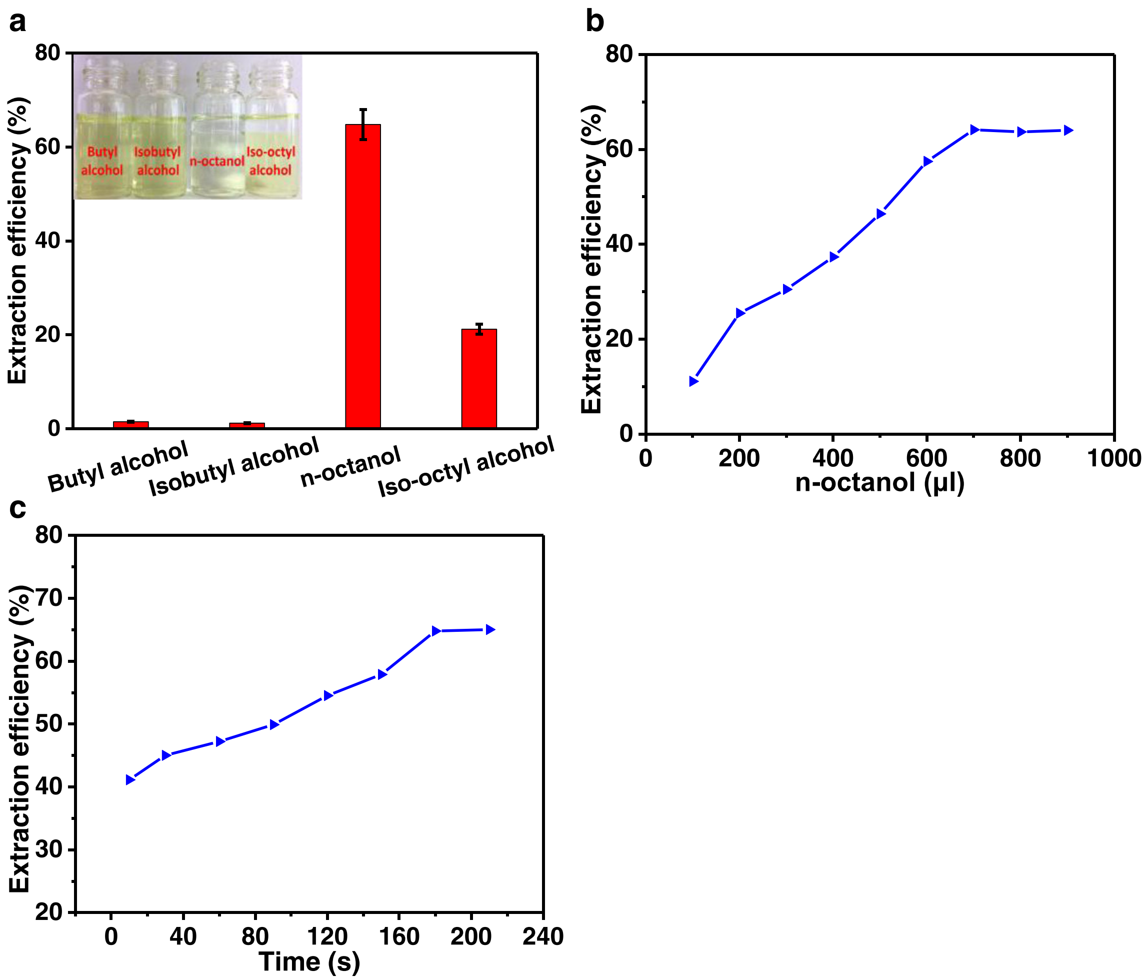


Fig. 4 The effect of (**a**) different extractants, extractant (**b**) volume and (**c**) vortex mixing time

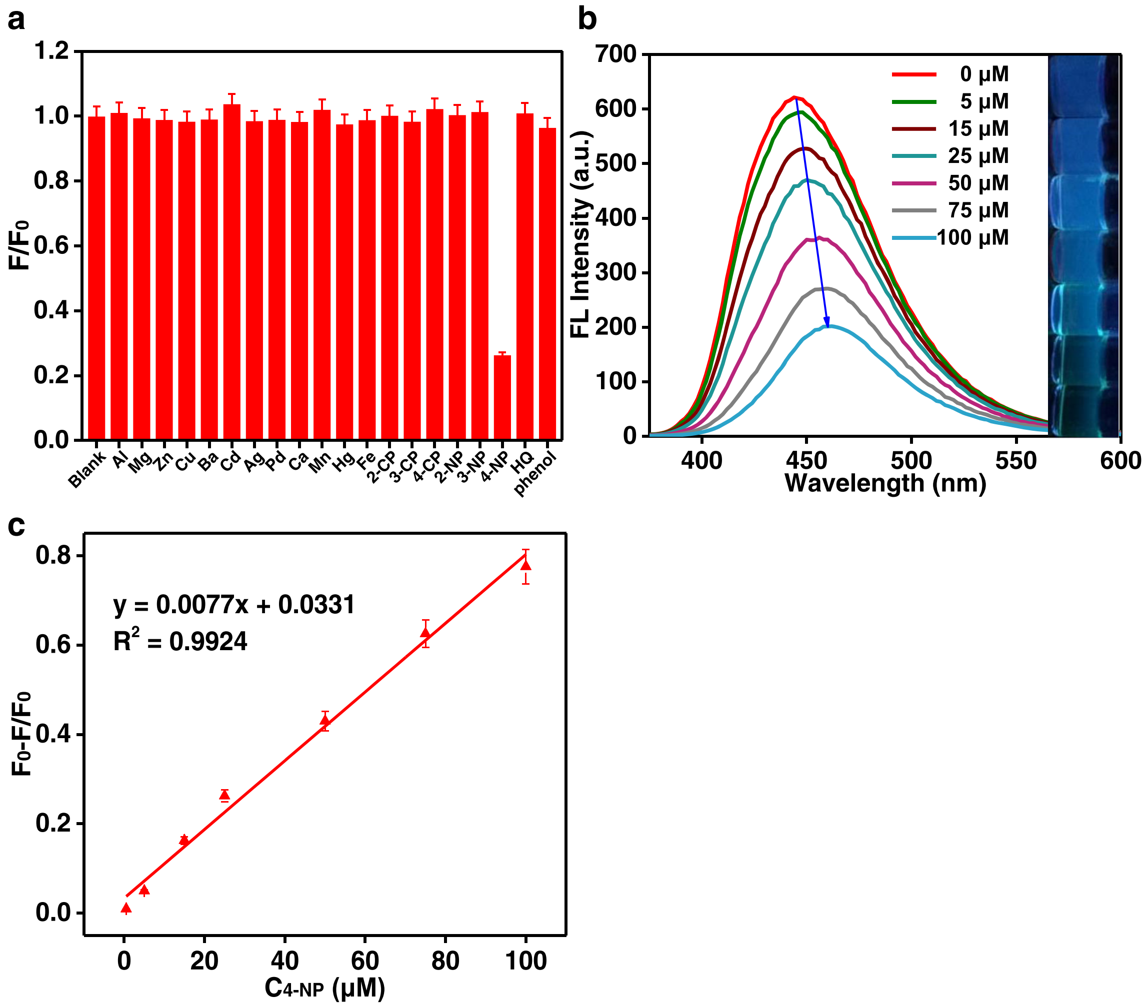


Fig. 5 **a** F/F$_0$ variation of F-CDs in the presence of all matter studied. **b** FL spectra of F-CDs after adding different concentrations of 4-NP (0–100 μM). **c** Linear relationship between F$_0$-F/F$_0$ and the concentration of 4-NP

4c show an increase with the increase of the vortex mixing time from 10 to 180 s and almost unchanged at >180 s.

Effect of Extraction Time

To improve extraction efficiency, multiple times extraction is an effective method. The results indicated that the extraction efficiency of 4-NP arrived 64.79%, 82.77% and 92.65%, respectively, after one, two and three times extraction.

Selectivity and Sensitivity of the Probe

In order to evaluate the selective of the probe towards 4-NP, the metal ions and other phenols (50 μM) including 4-chlorophenol (4-CP), 3-chlorophenol (3-CP), 2-chlorophenol (2-CP), phenol, hydroquinone(HQ), 2-NP, 3-NP, metal ions (Al^{3+}, Mg^{2+}, Zn^{2+}, Cu^{2+}, Ba^{2+}, Cd^{2+}, Ag^{+}, Pb^{2+}, Ca^{2+}, Mn^{2+}, Hg^{2+} and Fe^{3+}, 100 μM) were examined under the identical conditions of 4-NP (10 μM) at 346 nm excitation. The Fig. 5a showed that only 4-NP had more tendencies to

Table 1 Comparison of the proposed method with some of the previously reported methods for determination of 4-NP

Method	LRa (μM)	LOD(nM)	RSD (%)	References
Amine-CQDs@UiO-66	0.01–20.0	3.5	–	[39]
Polymer carbon dots	0.5–60	260	1.85–4.07	[38]
Carbon nanodots	0.05–50	13	–	[37]
Fluorine doped carbon dots -VALLME	0.01–100	15	3.5	This work

Mean ± standard deviation

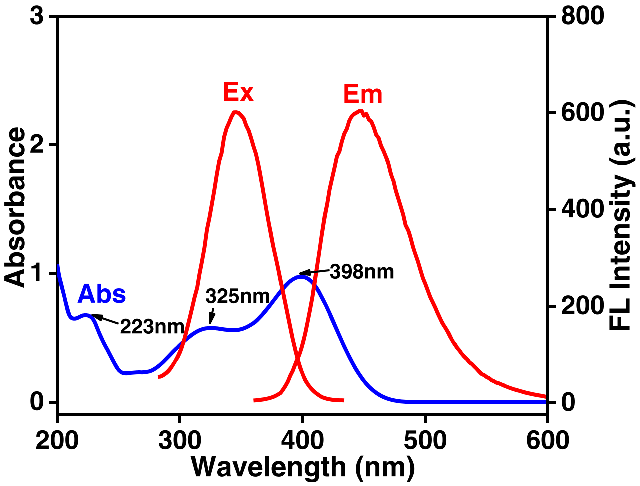


Fig. 6 UV–vis absorption spectrum of 4-NP and excitation and emission spectrum of F-CDs

quench the fluorescence of the F-CDs compared to all other matter studied, which makes the F-CDs as highly selective fluorescent probes for 4-NP.

Analytical Characteristics

Figure 5b showed the fluorescence spectra of the F-CDs after adding different concentrations of 4-NP. The fluorescence intensity of the F-CDs was quenched gradually while increasing the concentrations of 4-NP from 0.01 to 100 μM with a calibration function of F_0-F/ $F_0 = 0.0077$ [4-NP] (μg) + 0.0331($R^2 = 0.9924$)(F_0 and F represent the fluorescence emission intensities of the F-CDs in the absence and presence of 4-NP, respectively) (Fig. 5c). The detection limit of F-CDs for 4-NP was as low as 15 nM. Compared to the reported methods, the proposed VA-LLME coupled with spectrofluorimetric method provided a wide linear range and a low detection limit (Table 1).

Mechanism for Detecting 4-NP by F-CDs

The fluorescence quenching mechanism of F-CDs toward 4-NP was further investigated by UV–vis absorbance spectrum of 4-NP and excitation and emission spectra of F-CDs and the results are displayed in Fig. 6, 4-NP exhibited absorption peaks at 325 and 398 nm, which precisely overlapped with the excitation wavelength at 346 nm of F-CDs. Thus, the excitation wavelength for F-CDs can be absorbed by 4-NP, which resulted in the fluorescence of F-CDs being effectively quenched by the absorber 4-NP and it is the so-called the inner filter effect (IFE). With the increase of 4-NP concentration, the F-CDs-4-NP with red fluorescence intensity under excitation at 346 nm and a remarkable color change from blue to green can be observed by the naked eye. The bathochromic shift of absorption peak of 4-NP may be the -OH of 4-NP with -F, -OH and -COOH of F-CDs to form hydrogen bond.

Detection of 4-NP in Environmental Samples

The method was also applied for the determination of 4-NP in several water samples. For this objective, different concentrations of 4-NP solutions were spiked in water samples, and subsequently analyzed by VA-LLME and spectrofluorimetric method. As shown in Table 2, when different concentrations of 4-NP solutions were spiked in water samples, the recoveries of the method for 4-NP in water samples were from 95 to 103% with the relative standard deviation (RSD%) lower than 1.3, and the method was compared to HPLC. These results indicate that the established method based on F-CDs as

Table 2 Determination results of 4-NP in water samples (*n* = 3)

Sample	Added (μM)	Detected (μM)	HPLC (μM)	Recovery (%)
Lake water	0	nd	nd	–
	5.00	5.1 ± 0.3	5.3	102
	10.00	9.5 ± 0.2	9.8	95
	20.00	19.2 ± 0.1	20.5	96
Groundwater	0	nd	nd	–
	5.00	4.7 ± 0.2	5.3	94
	10.00	10.3 ± 0.3	9.6	103
	20.00	19.4 ± 0.1	19.8	97
Surface water	0	nd	nd	–
	5.00	5.1 ± 0.1	4.9	102
	10.00	10.3 ± 0.2	9.8	103
	20.0	19.5 ± 0.3	19.6	97

Mean ± standard deviation (n = 3)

nd, non detected

fluorescence probes is suitable for the quantitative determination of 4-NP in the environmental water samples.

Conclusion

This research results illustrate that the application of liquid-liquid microextraction coupled with F-CDs procedure for the determination of analyte is feasible. In this method, the high fluorescent quantum yield fluorine doped carbon dots (F-CDs) were synthesized via a one-step hydrothermal method, and n-octanol was used the extractant and vortex mixing was utilized as a mild emulsification procedure to reduce emulsification time and improve extraction efficiency in VALLME. The outstanding advantages of the proposed method are the F-CDs used as fluorescent probe and VA-LLME used as a green pretreatment method for quantitative analysis of 4-NP in environmental samples. The proposed method provide a liquid-liquid microextraction coupled with fluorescent CDs for detection of analyte new way.

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Compliance with Ethical Standards

Conflicts of Interest There are no conflicts to declare.

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