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ARTICLE

Highly selective detection of 2,4,6-trinitrophenol by using newly developed terbium-doped blue carbon dots †

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The detection of nitroaromatic explosive is of great importance owing to their strong explosive power and harmful to environments in terms of the homeland security and public safety. Herein, rare earth-doped carbon dots with multifunctional features were at first prepared by only keeping the mixture of terbium (III) nitrate pentahydrate and citric acid at 190 °C for 30 min. The as-prepared terbium doped carbon dots (Tb-CDs) through the rapid and simple direct carbonization route have the size of about 3 nm, and exhibit excitation wavelength dependent emissions of blue fluorescence, which are stable, and can be applied for the selective and colorimetric detection of 2,4,6-trinitrophenol (TNP) in the range of 500 nM-100 μM with a limit of detection of 200 nM based on the inner filtering effect (IFE) of excitation and emission bands of Tb-CDs by TNP and the electron transfer (ET) from Tb-CDs to TNP, giving a precise and high reproducible result for detecting complex water samples.

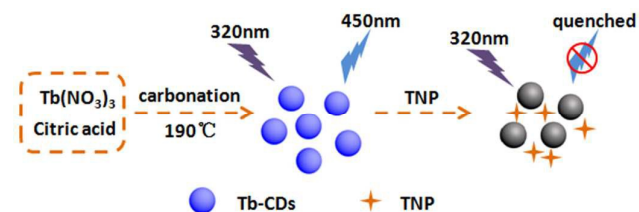
Introduction

2,4,6-trinitrophenol (TNP), a nitroaromatic explosive owning stronger explosive power and higher thermal-expansion than other nitroaromatic compounds such as 2,4,6-trinitromethylbenzene (TNT)^{1,2}, has been widely used in the preparation of matches and fireworks,^{3,4} but seriously threatens the homeland security and public safety.⁴⁻⁶ Once getting into natural waters, TNP would strongly damage human health by irritating eyes or skin and damaging respiratory systems of human beings.⁷⁻⁹ Therefore, developing a rapid, simple, highly selective and sensitive detection assay of TNP is expected. Owing to the similarity of TNP to other nitroaromatic explosives and the complexity of water samples, developing highly selective detection methods of TNP still face big challenge.

Currently, methods involved in X-ray imaging¹⁰, surface-enhanced Raman spectroscopy¹¹ and mass spectrometry⁷, etc have been successfully developed, but complicated, or time-consuming, and generally require a complicate labelling procedure. Meanwhile, electrochemical method is also developed recently due to their high sensitivity.¹²⁻¹⁴ But it is difficult to distinguish nitroaromatic compounds due to their similarity, which limited the further practical application.

Spectrofluorometric methods, owing to their simplicity and low-cost,¹⁵⁻¹⁷ can be effectively applied by developing new fluorescent chromophores such as graphitic carbon nitride (g-C₃N₄) and graphene quantum dots for sensitive detection of TNP in samples of water.^{17,18} In addition, organic crystalline solid probe is also used to detect TNP.¹⁹ These spectrofluorometric methods are sensitive, but still suffer from low selectivity. Therefore, developing a simple, highly selective and sensitive detect method is very necessary.

Carbon dots (CDs), as a new type of fluorescent chromophores with stable photoluminescence, low toxicity and easy preparation,²⁰⁻²⁷ have received high attention as applied for analytical purposes. The developed carbon dots, however, are limited in practical applications owing to be easily oxidized.^{28,29} Herein, we for the first time prepared rare earth-doped carbon dots by only keeping the mixture of terbium (III) nitrate pentahydrate and citric acid at 190 °C for 30 min considering the stable fluorescence emissions of earth elements ions. The as-prepared Tb-CDs through the rapid and simple direct carbonization route (Scheme 1) own excellent emission of blue fluorescence, good salt stability and oxidation



Scheme 1 Illustration of the synthesis process of Tb-CDs from citric acid and Tb(NO₃)₃ by direct carbonization route and the highly selective and sensitive detection of TNP.

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resistance. Most importantly, the common ions have no influence on the fluorescence emission of Tb-CDs, which is greatly different from previously reported CDs whose fluorescence emissions are easily quenched by metal ions such as copper and mercuric ions.³⁰⁻³³ These characteristics make Tb-CDs own high selectivity and satisfied recovery for TNP detection in the complex water samples (such as, lake or river water) based on the inner filtering effect (IFE) of excitation and emission bands of Tb-CDs by TNP and the electron transfer (ET) from Tb-CDs to TNP. Therefore, as a highly selective and sensitive method of detecting TNP, Tb-CDs will have potential applications.

Experimental

Materials

Terbium (III) nitrate pentahydrate ($\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) and citric acid (CA) were commercially available from Aladdin Reagent Co., Ltd. (Shanghai, China) and Kelong Chemical Group Co., Ltd. (Chengdu, China), respectively. Nitroaromatic chemicals, including phenol (PHE), 2,4,6-trinitrophenol (TNP), methylbenzene (MB), 2,4,6-trinitromethylbenzene (TNT), 2-nitrotoluene (*o*-NT), 4-nitrotoluene (*p*-NT), 2,6-dinitrotoluene (DNT), nitrobenzene (NB), 1,3-dinitrobenzene (DNB) were all purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Sodium chloride (NaCl) and a Britton–Robinson (BR) buffer were adopted to adjust the ionic strength and control the acidity, respectively.

Apparatus

The UV absorption spectra of Tb-CDs and citric acid prepared CDs (CA-CDs) were obtained from a Hitachi U-3010 spectrophotometer (Tokyo, Japan). The elemental composition of Tb-CDs was measured with an ESCALAB 250 X-ray photoelectron spectroscopy and an energy dispersive X-ray spectroscopy. The IR spectrum of Tb-CDs was collected on a Hitachi FTIR-8400S Fourier Transform Infrared spectrometer (Tokyo, Japan). The HRTEM data of Tb-CDs were performed on a Tecnai G2 F20 field emission transmission electron microscope (FEI, USA). The fluorescence spectra of Tb- and CA-CDs were recorded with a Hitachi F-2500 fluorescence spectrophotometer (Tokyo, Japan). Zeta potentials of Tb-CDs were measured using a ZEN3600 dynamic laser light scattering (Malvern, English). The Raman spectrum of Tb-CDs on the AgNPs solution was scanned through a LabRAM HR800 Laser confocal Raman spectrometer. The fluorescence lifetime of Tb-CDs was measured with a FL-TCSPC fluorescence spectrophotometer (Horiba Jobin Yvon, France).

Preparation of Tb-CDs and CA-CDs

Tb-CDs were prepared through a simple direct carbonization method. Firstly, 0.84g CA and 0.435g $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ were added into a clear drying round-bottom flask. After shaking up, round-bottom flask filled with the mixture was placed in a thermostated oil bath at 190 °C for 30 min. With the cooling

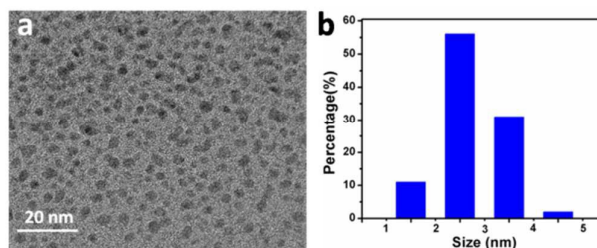


Fig. 1 Morphology and distribution of the as-prepared Tb-CDs (a) HRTEM image; (b) particle size distribution.

down to room temperature, 5 ml of double distilled water was added to dissolve the carbonization products, which then transferred to filter through a 0.22 μm membrane, and a yellow solution of Tb-CDs was available at last. For comparison, CA-CDs were synthesized through the above same direct carbonization process. 0.84g CA was added into a clear drying round-bottom flask, which then was placed in a thermostated oil bath at 190 °C for 30 min. Then the round-bottom flask was cooled down naturally and 5 ml water was added to dissolve the carbonization products. The CA-CDs solution was obtained after filter through a 0.22 μm membrane.

Results and discussion

Synthesis and characterizations of the Tb-CDs

Tb-CDs could be easily prepared through the rapid and simple direct carbonization route by only keeping the mixture of terbium (III) nitrate pentahydrate and citric acid at 190 °C for 30 min. Compared with common hydrothermal route reported before,³⁴⁻³⁶ the direct carbonization is more rapid and simple. Most importantly, we have identified that water-soluble Tb-CDs can only be obtained by the carbonization method, and solid fluorescence powder are available if hydrothermal route applied. Moreover, the Tb-CDs were well synthesized through using different terbium resource, such as TbCl_3 and $\text{Tb}_2(\text{SO}_4)_3$ (Fig. S1, ESI[†]). The fluorescence properties were different with $\text{Tb}(\text{NO}_3)_3$ prepared Tb-CDs, indicating that the introduction of heteroatom (such as S, Cl atoms) had an obvious effect on emission spectra of Tb-CDs.

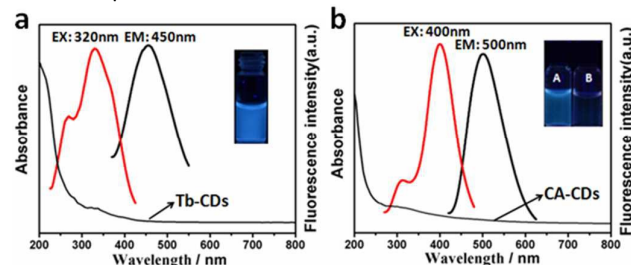


Fig. 2 The fluorescence and absorption spectra of Tb-CDs and CA-CDs. (a) Tb-CDs; (Inset: Tb-CDs solution under the 365 nm UV lights lamp) (b) CA-CDs. (Inset: A, CA-CDs; B, $\text{Tb}(\text{NO}_3)_3$ solution under the 365 nm UV lights lamp).

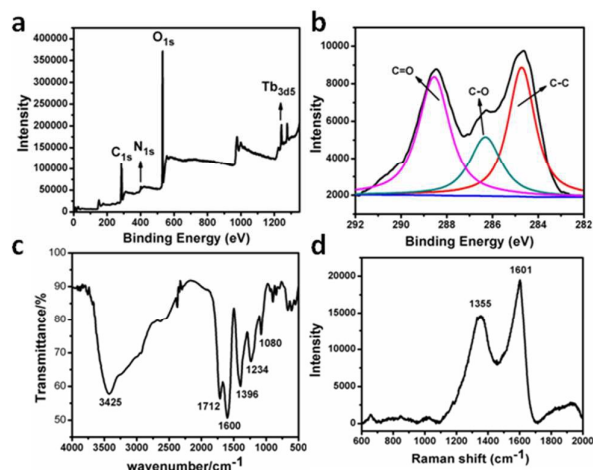


Fig. 3 The elemental and structure analysis of Tb-CDs. (a) XPS; (b) C_{1s} ; (c) FT-IR and (d) Raman spectrum of Tb-CDs.

The HRTEM image of Tb-CDs (Fig. 1a) clearly shows that the resulting carbon dots are well mono-dispersed. Their size distribution ranges from 1 nm to 5 nm (Fig. 1b) with maximum population at about 3 nm \pm 2 nm (100 nanoparticles are accounted). Owing to the π - π^* transition of the nanocarbon,³⁷ the as-prepared Tb-CDs exhibit a very broad UV-vis absorption band (Fig. 2a), and under the excitation of 300 to 380 nm light beam, the as-prepared Tb-CDs show excitation wavelength dependent fluorescence emissions (Fig. S2, ESI[†]), giving emissions with wavelength variations, and the maximum emission could be available at 450 nm with the maximum excitation at 320 nm and a shoulder peak at 265 nm (Fig. 2a). As a comparison, CA-CDs also have a very board UV-vis absorption (Fig. 2b), and the maximum excitation and emission wavelengths of CA-CDs are 400 nm and 500 nm, respectively, giving a visual blue to green fluorescence emission under the 365 nm UV lights lamp (inset in Fig. 2b). It was noticeable that $Tb(NO_3)_3$ after undertaken same procedures does not any fluorescence emission under the excitation of 365 nm UV lights lamp (inset in Fig. 2b).

The as-prepared Tb-CDs mainly consists of carbon, nitrogen and oxygen with a proportion of terbium reaching 5.62% (Fig. S3, ESI[†]), demonstrating that Tb has successfully been doped

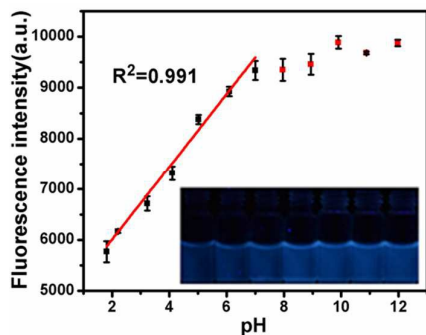


Fig. 4 Dependence of the fluorescence emission of Tb-CDs on pH. EX: 320nm; EM: 450nm. C_{Tb-CDs} , 1 mg/ml.

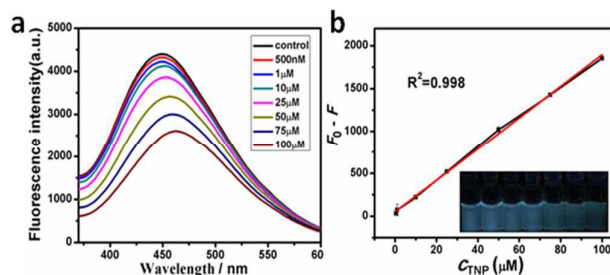


Fig. 5 The fluorescence quenching of Tb-CDs by TNP. (a) The change of the fluorescence spectrum of the Tb-CDs in the presence of TNP (b) The sensitivity of TNP detection. pH, 7.00; C_{Tb-CDs} , 0.4 mg/ml.

into the carbon dots. The XPS spectrum analysis showed that C_{1s} , N_{1s} , O_{1s} and Tb_{3d5} peaks are located about at 284.4, 532.8 eV and 1241.1 eV (Fig. 3a), respectively. Since no other carbon sources, carbon elements in Tb-CDs have to be from the CA, while nitrogen and terbium are from the introduction of $Tb(NO_3)_3$. The C_{1s} spectrum shows three peaks at 284.7, 286.3 and 288.5 eV (Fig. 3b), which have to be ascribed to C-C, C-O and C=O bonds, respectively.³⁸ Additionally, the IR spectrum exhibits characteristic absorption bands of O-H stretching vibrations at 3425 cm^{-1} , C=O stretching vibrations at 1600 cm^{-1} and C-O-C stretching vibrations at 1080 cm^{-1} , respectively (Fig. 3c), which are identical to the reports of literature.³⁹ Raman spectrum shows that the D-band at 1355 cm^{-1} is owing to sp^3 carbons, while the G-band at 1601 cm^{-1} is due to sp^2 carbons (Fig. 3d).

All the above results show that the Tb-CDs are successfully synthesized with functional groups on the surface including C=O.

The stability of the as-prepared Tb-CDs

The as-synthesized Tb-CDs are very stable in a salty medium and at high concentration of H_2O_2 solution. The FL intensity of Tb-CDs slightly changed even if in the medium of NaCl concentration as high as 4 M (Fig. S4a, ESI[†]), indicating that the Tb-CDs could be very stable in a medium of high ionic strength. Considering that most CDs reported are easily oxidized^{28, 29}, we particularly investigated the antioxidant capacity of Tb-CDs (Fig. S4b, ESI[†]), and it was found that the

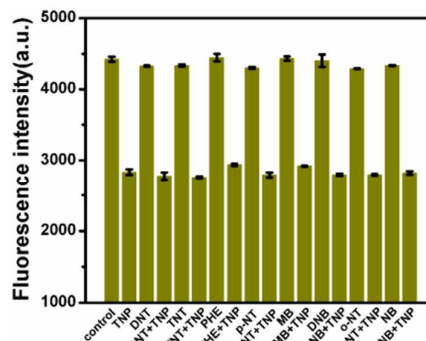


Fig. 6 Fluorescence responses of the Tb-CDs in the presence of 75 μ M of TNP and 100 μ M of other nitroaromatic explosives.

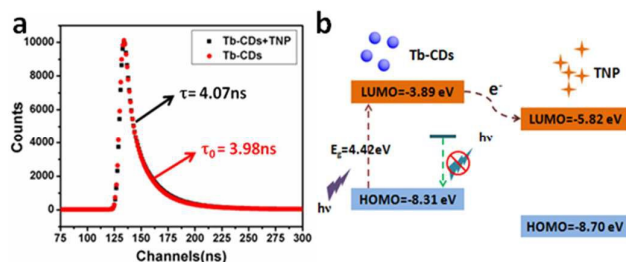


Fig. 7 Sensing principle of the Tb-CDs based probe for TNP. (a) Time-resolved decay of the Tb-CDs with the presence and absence of TNP in BR buffer (pH 7.0); (b) the E_{LUMO} and E_{HOMO} of Tb-CDs and TNP. EX: 320nm, EM: 450nm.

as-prepared Tb-CDs have very smart oxidation resistance even if in a medium of H_2O_2 higher than 0.3 M. Therefore, the Tb-CDs are very stable, which is beneficial for TNP detection in complex samples.

However, it was found that the fluorescence emission of the Tb-CDs is lineally dependent on pH of the medium in the range from 1.81 to 7.00 (Fig. 4), during which the zeta potentials changed from 23.5 mV to -27.0 mV (Table S1, ESI[†]), indicating that the protonation and deprotonation equilibrium has been established in this pH region.

Specific binding of the as-prepared Tb-CDs with TNP

The fluorescence emission of the as-prepared Tb-CDs were found to be quenched by TNP with the characteristic emission red-shift (Fig. 5a), and the FL intensity of the Tb-CDs at 450 nm is proportional to the concentration of TNP in the range of 500 nM-100 μM (Fig. 5b). Accompanied with the increase of TNP concentration, the blue fluorescence of the Tb-CDs is gradually weakened, which supplied a colorimetric assay for TNP detection.

In general, fluorescence quenching can be caused by static quenching effect (SQE), dynamic quenching effect (DQE) or by both simultaneously.⁴⁰ Both DQE and SQE through ground-state complex formation model could be theoretically described by Stern–Volmer equation:⁴⁰

$$F_0/F = 1 + K_{\text{SV}}[Q] \quad (1)$$

wherein, [Q] is the concentration of quencher; F_0 and F are the steady-state fluorescence intensities in the absence and presence of the quencher, respectively. In this work, the corrected fluorescence intensity ratio (i.e., $F_{\text{cor},0} / F_{\text{cor}}$) of Tb-CDs in the absence and presence of TNP is linear with the concentration of TNP ($F_{\text{cor},0} / F_{\text{cor}} = 0.00529 c_{\text{TNP}}/\mu\text{M} + 1$, $R^2 = 0.998$), suggesting that the Stern–Volmer equation should be applied in this case and the Stern–Volmer quenching constant $K_{\text{SV}} = 0.00529 \mu\text{M}^{-1}$.

Due to the different affinity between fluorophore and quencher in SQE and DQE, the Stern–Volmer quenching constant (K_{SV}) is further analyzed to determine which type of quenching was being observed in this study. In SQE, K_{SV} is interpreted as ground-state association constant for Tb-CDs binding to TNP. However, for DQE, the K_{SV} is in the following equation:⁴⁰

$$K_{\text{SV}} = k_{\text{q}} \times \tau_0 \quad (2)$$

wherein k_{q} is the molecular quenching rate constant, and τ_0 is the fluorescence lifetime in the absence of TNP. For Tb-CDs, $K_{\text{SV}} = 0.00529 \mu\text{M}^{-1}$ and $\tau_0 = 3.98 \text{ ns}$. k_{q} was then calculated to be $1.33 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$. This value was unusual high because the largest possible value for a molecule in a diffusion-controlled process in aqueous solution is around $1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.⁴⁰ Therefore, the DQE is not be possibly responsible in the TNP-induced fluorescence quenching process. Fig. 7a shows the fluorescence decay curves for Tb-CDs in the absence and presence of TNP. It can be seen that there are almost no changes of the lifetimes for Tb-CDs before and after adding TNP. Meanwhile, no new absorbance peak occurred (Fig. S5, ESI[†]) for the mixtures of Tb-CDs and TNP solution. These results above confirmed that the TNP-induced fluorescence quenching could be mainly due to SQE, rather than DQE.⁴⁰

The TNP-induced fluorescent quenching of Tb-CDs is highly specific. As Fig. 6 shows, 75 μM TNP and another eight 100 μM nitroaromatic explosives (DNT, TNT, PHE, p-NT, MB, DNB, o-NT and NB) are selected to study the fluorescence performance of the Tb-CDs. Compared with the control group, fluorescence intensity of Tb-CDs have no change when adding to other nitroaromatic explosives separately, indicated that the influence of other nitroaromatics is negligible. Similarly, nitroaromatic explosives have no influence on fluorescence intensity of Tb-CDs in the present of 75 μM TNP as well.

Moreover, the metal ions are also used to investigate the selectivity of TNP detection. All the other metal ions, except for Fe^{3+} , have no influence on fluorescence intensity of Tb-CDs in the presence and absence of TNP (Fig. S6, ESI[†]). Through the Fe^{3+} has a weak interfere with the TNP detection, it can be masked when adding into sodium pyrophosphate (1mM, Fig. S7, ESI[†]).

To verify the binding mechanism of specific binding of the as-prepared Tb-CDs with TNP, the respective UV absorption spectra of all above nitroaromatic chemicals are determined. It is clear that only TNP in the nitroaromatic explosives has one strong absorption band at 354 nm (Fig. S8, ESI[†]). Meanwhile, the excitation and emission spectra of Tb-CDs are scanned, and a large spectral overlap with TNP' absorption band is found, which indicates that there are three possible mechanisms causing fluorescence quenching of Tb-CDs, including electron transfer (ET), fluorescence resonance energy transfer (FRET) and inner filter effect (IFE). No change of the lifetimes for Tb-CDs before and after adding with 75 μM TNP suggested no FRET process occurring between TNP and Tb-CDs. The energy levels of the lowest unoccupied molecular orbital (E_{LUMO}) and the highest occupied molecular orbital (E_{HOMO}) of Tb-CDs are estimated as -3.89 eV and -8.31 eV (Fig. S9, ESI[†]), respectively, according to the empirical formula.⁴¹ Meanwhile, the E_{LUMO} and E_{HOMO} of TNP could be calculated as -5.82 eV and -8.70 eV, respectively, by the B3LYP method in Dmol3 mode. As shown in Fig. 7b, photo-excited electrons in Tb-CDs allowed to undergo electron transfer from the LUMO of the Tb-CDs to the LUMO of the TNP, indicating that ET between Tb-CDs and TNP is possible. Furthermore, It is clear that only TNP in the nitroaromatic explosives has absorption intensity superior to other explosives (DNT, TNT, PHE, p-NT,

MB, DNB, o-NT and NB) at the excitation wavelength of Tb-CDs (Fig. S7, ESI[†]), resulting in a comparable or better IFE effect.

Therefore, the mechanism of both IFE and ET presumably dominates the whole suppression process of Tb-CDs caused by TNP.

Determination of TNP in water samples

The proposed method is applied in the detection of TNP in natural water samples. The reliability and accuracy of the detection method we developed are evaluated through the recovery study, which is carried out on the samples spiked with standard TNP solutions (10, 25, 50 μM). The obtained recoveries of three samples varied from 93.4% to 106.3%, indicating that the potential applications in the detection of TNP in the natural water. Compared with other fluorescence analysis methods¹⁷, the recovery results of this approach are better, which is profited from the good stability and anti-interference ability of Tb-CDs.

The relative standard deviation (RSD) of each sample below 2.1%, revealing the high reproducibility and precision of this approach. Other traditional methods are used to compare with our method (Table S2, ESI[†]), although the LOD of the proposed one is not the lowest, the high reproducibility, sensitivity and selectivity and the similarity make it be a novel and important approach in the detection of TNP.

Table 1. Determination of TNP in three water samples

Added TNP (μM)	found (μM)	Recovery (%)	RSD(%)
Water sample 1 (running water)			
10	10.16	101.6	0.88
25	24.59	98.4	0.83
50	51.59	103.2	0.57
Water sample 2 (lake water)			
10	9.92	99.2	1.14
25	26.58	106.3	2.1
50	51.57	103.1	1.43
Water sample 3 (river water)			
10	9.34	93.4	2.0
25	25.12	100.5	1.6
50	52.64	105.3	1.3

Recovery (%) = $100 \times (\text{concentration found}/\text{concentration added})$

Conclusions

In summary, a facile and rapid preparing method of Tb-CDs is developed in this work. The novel approach firstly synthesizes the rare earth doped carbon dots with multifunctional features. Most importantly, the Tb-CDs have high reproducibility and selectively for detecting TNP in the complex water samples.

Acknowledgements

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Notes and references

- 1.M. Dong, Y. W. Wang, A. J. Zhang and Y. Peng, *Chem. Asian J.*, 2013, **8**, 1321-1330.
- 2.D. K. Singha, S. Bhattacharya, P. Majee, S. K. Mondal, M. Kumar and P. Mahata, *J. Mater. Chem. A*, 2014, **2**, 20908-20915.
- 3.S. R. Zhang, D. Y. Du, J. S. Qin, S. J. Bao, S. L. Li, W. W. He, Y. Q. Lan, P. Shen and Z. M. Su, *Chem. Eur. J.*, 2014, **20**, 3589-3594.
- 4.S. J. Toal and W. C. Trogler, *J. Mater. Chem.*, 2006, **16**, 2871-2883.
- 5.D. T. McQuade, A. E. Pullen and T. M. Swager, *Chem. Rev.*, 2000, **100**, 2537-2574.
- 6.A. Rose, Z. Zhu, C. F. Madigan, T. M. Swager and V. Bulovic, *Nature*, 2005, **434**, 876-879.
- 7.S. Babaee and A. Beiraghi, *Anal. Chim. Acta*, 2010, **662**, 9-13.
- 8.G. He, H. Peng, T. Liu, M. Yang, Y. Zhang and Y. Fang, *J. Mater. Chem.*, 2009, **19**, 7347-7353.
- 9.B. Roy, A. K. Bar, B. Gole and P. S. Mukherjee, *J. Org. Chem.*, 2013, **78**, 1306-1310.
- 10.K. Wells and D. A. Bradley, *Appl. Radiat. Isot.*, 2012, **70**, 1729-1746.
- 11.S. R. Dasary, A. K. Singh, D. Senapati, H. Yu and P. C. Ray, *J. Am. Chem. Soc.*, 2009, **131**, 13806-13812.
- 12.F. Yan, Y. Y. He, L. H. Ding and B. Su, *Anal. Chem.*, 2015, **87**, 4436-4441.
- 13.Y. Liu, H. L. Liu, J. Ma and X. Wang, *Appl. Catal. B*, 2009, **91**, 284-299.
- 14.H. X. Zhang, A. M. Cao, J. S. Hu, L. J. Wan and S. T. Lee, *Anal. Chem.*, 2006, **78**, 1967-1971.
- 15.X. Deng and D. Wu, *RSC Adv.*, 2014, **4**, 42066-42070.
- 16.D. K. Singha and P. Mahata, *RSC Adv.*, 2015, **5**, 28092-28097.
- 17.M. Rong, L. Lin, X. Song, T. Zhao, Y. Zhong, J. Yan, Y. Wang and X. Chen, *Anal. Chem.*, 2015, **87**, 1288-1296.
- 18.L. Lin, M. Rong, S. Lu, X. Song, Y. Zhong, J. Yan, Y. Wang and X. Chen, *Nanoscale*, 2015, **7**, 1872-1878.
- 19.S. Mukherjee, A. V. Desai, A. I. Inamdar, B. Manna and S. K. Ghosh, *Cryst. Growth Des.*, 2015, **15**, 3493-3497.
- 20.S. Zhu, Q. Meng, L. Wang, J. Zhang, Y. Song, H. Jin, K. Zhang, H. Sun, H. Wang and B. Yang, *Angew. Chem.*, 2013, **125**, 4045-4049.
- 21.Y. Dong, J. Shao, C. Chen, H. Li, R. Wang, Y. Chi, X. Lin and G. Chen, *Carbon*, 2012, **50**, 4738-4743.
22. L. Bao, C. Liu, Z. L. Zhang and D. W. Pang, *Adv. Mater.*, 2015, **27**, 1663-1667.
- 23.M. Zheng, Z. Xie, D. Qu, D. Li, P. Du, X. Jing and Z. Sun, *ACS Appl. Mater. Interfaces*, 2013, **5**, 13242-13247.
- 24.S. Mandani, B. Sharma, D. Dey and T. K. Sarma, *Nanoscale*, 2015, **7**, 1802-1808.
- 25.L. Zhao, F. Di, D. Wang, L. H. Guo, Y. Yang, B. Wan and H. Zhang, *Nanoscale*, 2013, **5**, 2655-2658.
- 26.S. Mohapatra, S. Sahu, N. Sinha and S. K. Bhutia, *Analyst*, 2015, **140**, 1221-1228.
- 27.S. Nandi, M. Ritenberg and R. Jelinek, *Analyst*, 2015, **140**, 4232-4237.
- 28.M. Amjadi, J. L. Manzoori and T. Hallaj, *J. Lumin.*, 2015, **158**, 160-164.
- 29.M. Zhang, Q. Yao, W. Guan, C. Lu and J. M. Lin, *J. Phys. Chem. C*, 2014, **118**, 10441-10447.

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- 30.Y. H. Yuan, R. S. Li, Q. Wang, Z. L. Wu, J. Wang, H. Liu and C. Z. Huang, *Nanoscale*, 2015, **7**, 16841-16847.
31. H. X. Zhao, L. Q. Liu, Z. D. Liu, Y. Wang, X. J. Zhao and C. Z. Huang, *Chem. Commun.*, 2011, **47**, 2604-2606.
- 32.Y. B. Lou, Y. X. Zhao, J. X. Chen and J. J. Zhu, *J. Mater. Chem. C*, 2014, **2**, 595-613.
- 33.H. D. Huang, L. Liao, X. Xu, M. J. Zou, F. Liu and N. Li, *Talanta*, 2013, **117**, 152-157.
- 34.Z. L. Wu, M. X. Gao, T. T. Wang, X. Y. Wan, L. L. Zheng and C. Z. Huang, *Nanoscale*, 2014, **6**, 3868-3874.
- 35.M. X. Gao, C. F. Liu, Z. L. Wu, Q. L. Zeng, X. X. Yang, W. B. Wu, Y. F. Li and C. Z. Huang, *Chem. Commun.*, 2013, **49**, 8015-8017.
- 36.D. M. Wang, M. X. Gao, P. F. Gao, H. Yang and C. Z. Huang, *J. Phys. Chem. C*, 2013, **117**, 19219-19225.
- 37.H. Zhu, X. Wang, Y. Li, Z. Wang, F. Yang and X. Yang, *Chem. Commun.*, 2009, **4**, 5118-5120.
- 38.S. Liu, J. Tian, L. Wang, Y. Luo, W. Lu and X. Sun, *Biosens. Bioelectron.*, 2011, **26**, 4491-4496.
- 39.B. B. Chen, H. Liu, C. Z. Huang, J. Ling and J. Wang, *New J. Chem.*, 2015, **39**, 1295-1300.
- 40.J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, 2nd ed.; Kluwer Academic/Plenum Publishers: New York, 1999.
- 41.H. J. Zhang, Y. L. Chen, M. J. Liang, L. F. Xu, S. D. Qi, H. L. Chen and X. G. Chen, *Anal. Chem.*, 2014, **86**, 9846-9852.