Construction of a Turn-off-on Fluorescent System Based On Aggregation Induced Emission of Acetaldehyde Using Carbonized Polymer Dots and Tb^{3+}

Rentian Guan

Liaocheng University

Shuai Zhang

Liaocheng University

Xiaoyu Fan

Liaocheng University

Xiaodong Shao

Tubular Goods Research Institute

Yingying Hu

Liaocheng University

Tao Liu

Liaocheng University

Shuhao Wang

Liaocheng University

Qiaoli Yue (✉ yueqiaoli@yahoo.com)

Liaocheng University <https://orcid.org/0000-0002-7882-9818>

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Abstract

It was the first time to report the aggregation induced emission (AIE) of acetaldehyde (AA) on the surface of carbonized polymer dots (CPDs) with the auxiliary of Tb^{3+} . Based on the AIE of AA, a turn-off-on fluorescence method was established for AA detection using the porous CPDs- Tb^{3+} system. The one-pot hydrothermal method was used to obtain CPDs, using milk and polyethyleneimine (PEI) as precursors. In the presence of Tb^{3+} , CPDs aggregated immediately, and the fluorescence intensity decreased obviously for the precipitate. AA can effectively embed on the surface of CPDs- Tb^{3+} due to the porous structure. AA displayed obviously blue fluorescence with excitation wavelength at 370 nm (emission peak at 460 nm), while there was no fluorescence peak when excited at 460 nm. In the CPDs- Tb^{3+} solution, AA exhibits obvious fluorescence enhancement effect (I_{ex} 460 nm, I_{em} 545 nm). And then, AA can be determined by the turn-off-on system based on the linear relationship between fluorescence enhancement and the concentration of AA ranging from 0.04 mM to 42.48 mM. The limit of detection (LOD) was 0.02 mM. The turn-off-on system was successfully applied to determine AA in wine samples. The strategy may be exploited to monitor AA in more drinking or foodstuff samples.

1. Introduction

Acetaldehyde (AA), a colorless liquid aldehyde, is volatile and water-soluble. AA exists widely in fermented foods and beverages as well as many kinds of alcoholic drinks [1]. The moderate content of AA is one of evaluations to distinguish high-grade and low-end liquors [2]. Meanwhile, it can be noticed that AA is carcinogenic for human and excessive intake of AA is harmful for health [3]. Furthermore, owing to the long-term exposure to AA, the risk of mutational damage of DNA can increase and even induce tumors like esophagus cancer [4, 5]. Therefore, it is significant to explore a sensitive, selective and simple approach to detect AA. Traditional methods for AA determination are gas and liquid chromatography techniques, which show excellent selectivity and sensitivity [6, 7, 8]. However, these technologies generally need complicated operations and extra time-consuming sampling steps [8, 9]. By comparison, fluorometry shows some advantageous properties such as quick response, simplicity, and easy to realize real-time detection [10, 11].

Carbonized polymer dots (CPDs) are a kind of brand-new fluorescent carbon-based nanomaterials, which are generally less than 10 nm in size [12]. CPDs deriving from specific polymerization and carbonization systems provide impetus to overcome current challenges of carbon dots (CDs). Owing to their bright luminescence, easy surface modification, good solubility and biocompatibility in water, CPDs have attracted considerable attention [13, 14]. These excellent properties make CPDs show enormous potential in chemical and biological sensing [15, 16]. In the sensing application, photoluminescence of CPDs is one of the most valuable properties and a key factor. Most CPDs show excitation-dependent emission, which can be ascribed to different fluorescence centers and complex energy levels [17, 18, 19]. In this case, extraction of specific emission fraction is reported by separation using column chromatography [20, 21].

To improve the fluorescence of CDs, surface modification is usually used to change the surface state of CDs, which can be carried out by the introduction of functional groups with small or polymer molecules [22, 23]. Rare earth ions especially terbium (Tb) and europium (Eu) ions are also employed to modify CDs surface [24]. Most of these works try to keep origin properties of metal ions and avoid easy aggregation of CDs in the presence of rare earth ions [25, 26]. In fact, the aggregation of CDs caused by metal ions is an unnecessary bad thing. In addition, it is not reported the system of CPDs combined with Tb^{3+} is used as a fluorescent probe in the application of sensing.

In this work, we synthesized CPDs with bright green fluorescence using pure milk and polyethyleneimine (PEI) as precursor materials. The fluorescence system of CPDs- Tb^{3+} was explored for the efficient determination of AA. There was a high specificity for AA detection rather than formaldehyde (FA), propionaldehyde (PA), and butyraldehyde (BA). To obtain CPDs, one pot hydrothermal method was used to heat precursor materials at 180 °C for 5 hours (Scheme 1). There are various functional groups on the surface of CPDs due to the rich elements in milk, which can coordinate with Tb^{3+} leading to CPDs aggregation and the fluorescence quenching. In the presence of AA, CPDs can disaggregate due to the complex of AA and Tb^{3+} . The interaction between AA and Tb^{3+} brings about the fluorescence recovery of CPDs. And then a turn-off-on system was built to detect AA. Moreover, the strategy was successfully applied for the determination of AA in wine samples. Importantly, this design may be able to detect other analytes in food and drinking samples.

2. Experimental Section

2.1. Chemicals

Pure milk was purchased from Liaocheng University campus supermarket. The metal salts were obtained from Aladdin Reagent Co., Ltd. (Shanghai, China). They included $Tb(CH_3COO)_3$, $Nd(CH_3COO)_3$, $Pr(CH_3COO)_3$, $Er(CH_3COO)_3$, NaCl, and NaOH. Polyethyleneimine (PEI, MW=10000, 99%) was ordered from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). Acetaldehyde (AA), dimethylformamide (DMF), acetone, methanol, chloroform, acetonitrile, ether, ethyl acetate (EA), formaldehyde (FA), propionaldehyde (PA), and butyraldehyde (BA) were provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals used in relevant experiments were analytical grade and without further purification. Deionized water supplied by the Milli-Q water Purified system was used in all experiments.

2.2. Apparatus

CPDs were synthesized using a poly (tetrafluoroethylene) Teflon-lined autoclave (25 mL) in a Boxun GZX-9140MBE electrothermal blowing drying oven. Hitachi F-7000 spectrophotometer was used for the measurement of fluorescence spectrum and fluorescence intensity. Absorption spectra were collected with UV-750 ultraviolet spectrophotometer (PerkinElmer, USA). At an accelerated voltage of 200 kV, the sample was loaded on a ultra-thin carbon supporting film, and transmission electron microscope (TEM) data were obtained by Hitachi JEM-2100F electron microscope. Scanning electron microscopy (SEM)

image and energy-dispersive X-ray spectroscopy (EDS) measurements are made by loading a sample on conductive copper and sputter-coated with a thin layer of gold on the sample to increase its conductivity. SEM and EDS were performed from a Thermo Fisher Scientific FIB-SEM GX4 (Thermo Scientific Ltd., USA). Zeta potentials and dynamic light scattering (DLS) of CPDs and CPDs-Tb³⁺ were measured using a Zetasizer Nano-ZS System (Malvern, China). In order to record the crystalline phase information, powder X-ray diffraction (XRD) measurements were carried out at room temperature using D/Max-2500 Diffractometer (Rigaku, Japan). X-ray photoelectron spectroscopy (XPS) measurements were undertaken with a K-Alpha spectrometer (Thermo Scientific Ltd., USA). The chromatographic data were obtained by a GC-2030 gas chromatography spectrometry (GC) (Shimadzu, Japan).

2.3. Preparation of CPDs

CPDs were synthesized by hydrothermal method with reference to the previous literatures and some modifications [27]. Briefly speaking, 4 mL of 25 mg/mL PEI aqueous solution was mixed with 6 mL pure milk, transferred to poly (tetrafluoroethylene) Teflon-lined autoclave (25 mL). The solution was heated at 180 °C for 5 h, and then the autoclave was naturally cooled to room temperature. To remove large particles, the CPDs were centrifuged at 8000 rpm for 10 min. The obtained CPDs were stored in a refrigerator at 4 °C for further characterization and use. As control experiments, we used the same method to obtained M-CDs from milk and P-CDs from PEI.

2.4. Preparation of CPDs-Tb³⁺

The CPDs and Tb(CH₃COO)₃ (200 mM) were mixed at room temperature with a volume ratio of 9:1 for 3 min. The mixture was then centrifuged at 8000 rpm for 5 min. The precipitate was washed with deionized water for three times to remove unreacted CPDs and Tb(CH₃COO)₃. Finally, the obtained precipitates were uniformly dispersed in an equal volume of deionized water and stored at 4 °C for further use.

2.5. Determination of AA

AA was detected in aqueous solution at room temperature. Firstly, AA aqueous solution was diluted into ultrapure water, a concentration range of standard stock solutions was prepared. Different concentrations of AA were added into CPDs-Tb³⁺ system solutions and incubated for 10 min. In the presence and absence of AA, the fluorescence spectra of CPDs-Tb³⁺ were measured with excitation wavelength at 460 nm. The peak intensity was recorded which can be used for the sensitivity and selectivity measurements.

2.6. Pretreatment of real samples

Wine samples were purchased from the campus supermarket of Liaocheng University. The blank sample is aqueous solution of ethanol (ethanol: water = 1:1). The wine and blank samples were diluted 10 times by deionized water. The fluorescence spectra of CPDs-Tb³⁺ were recorded after the wine samples were spiked with a series of AA standard solutions, respectively. Furthermore, in order to verify the accuracy of the method, the same sample was determined by gas chromatography in the presence and absence of AA.

3. Results And Discussion

3.1. Design principles

A sensitive and selective turn-off-on sensing system was constructed for AA detection based on CPDs with green emission as fluorescence probes (Scheme 1). There are many elements and rich of coordination groups on the surface of CPDs to capture Tb^{3+} forming complexes. The green fluorescence of CPDs can be quenched by Tb^{3+} . With the addition of AA, the fluorescence intensity at 545 nm was enhanced significantly (Fig. 1A).

(1) The fluorescence turn-off system of CPDs- Tb^{3+} . There are a large amount of surface functional groups covered on CDs including carboxyl, hydroxyl, and amine. These groups make CDs exhibit excellent water solubility as well as convenience for compositing with other materials such as metal ions [28]. And then Tb^{3+} can easily chelate with the carboxyl and hydroxyl groups of CDs. For example, CDs- Tb^{3+} systems are employed to enhance the fluorescence of Tb^{3+} because Tb^{3+} as one of the rare earth ions usually has low luminescence efficiency [25, 29]. It can be ascribed from the line-type Tb^{3+} emission due to the energy transfer from CDs to Tb^{3+} [30]. However, the fluorescence of CDs is often not an output signal and there are some challenges for the construction of CDs- Tb^{3+} fluorescence system especially for easy aggregation. How about CPDs? CPDs possess both properties of CDs and polymer. Furthermore, CPDs own carbonization, high crosslinking, and close knit polymer frame structures [31, 32]. CPDs can easily aggregate in the presence of Tb^{3+} due to the association of Tb^{3+} with the rich function groups and polymer chains on the surface of CPDs. Why were the CPDs made from milk and PEI? The CDs products from milk or PEI were investigated for the detection of AA with results shown in **Fig. S1** (in Supporting Information). It can be found that the present CPDs represent highest sensitivity with milk and PEI (with the PEI concentration of 25 mg/mL) as precursor materials. Moreover, CDs show lower sensitivity with milk alone as precursor material. When PEI was used as the precursor material, Tb^{3+} cannot induce CDs aggregation. Thus, the CPDs were used in the experiment, which were prepared with milk and PEI.

The fluorescence spectra, photos and absorption spectra were obtained for CPDs, CPDs- Tb^{3+} , CPDs- Tb^{3+} +AA, respectively (Fig. 1A and **B**). The absorption and fluorescence peaks of CPDs were obvious at 272 nm and 570 nm, respectively. For CPDs, the absorption peak disappears and the fluorescence intensity decreases significantly in the presence of Tb^{3+} , respectively. There is a blue shift for the fluorescence peak of CPDs with Tb^{3+} . As expected, there are no obvious peaks of absorption and fluorescence spectra for Tb^{3+} in the range of 250-400 nm and 520-620 nm, respectively. The fluorescence of CPDs can be quenched by Tb^{3+} as observed in Fig. 1A. To study the fluorescence quenching mechanism of Tb^{3+} for CPDs, the Stern-Volmer plots were obtained under different temperatures (Fig. 1C). These plots are all in good linearity under different temperatures with the concentration of Tb^{3+} ranging from 0.05 to 20 mM. According to the Stern-Volmer equation (eq. 1), the quenching constant K_{SV} can be calculated as 26.6 M^{-1} , 21.4 M^{-1} , and 15.9 M^{-1} , at 4 °C, 19 °C, and 34 °C, respectively.

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

In eq. 1, F and F_0 mean the fluorescence intensity of CPDs with and without quencher (Tb^{3+}), respectively. $[Q]$ and K_{SV} represent the concentration of quencher and the quenching constant, respectively. The fluorescence quenching mainly derives from the dynamic and the static modes. The static quenching mode results from the non-fluorescent complexes between ground state fluoresce and quencher. It is obvious that K_{SV} values decrease with temperature increase, which is probably owing to the static quenching mode. There may be a large amount of complexes between CPDs and Tb^{3+} . In order to further prove the static quenching mode of CPDs fluorescence by Tb^{3+} , the fluorescence lifetime tests of CPDs were investigated with and without Tb^{3+} (Fig. 1D). The average fluorescence lifetime values of CPDs and CPDs- Tb^{3+} are 3.57 and 3.49 μs , respectively, which are similar. It can be inferred that the static quenching mode is probably responsible for the quenching effect of Tb^{3+} on the fluorescence of CPDs.

(2) Aggregation induced emission (AIE) of AA. To confirm the enhancement effect of AA for the fluorescence emission of CPDs- Tb^{3+} at 545 nm, a series of fluorescence experiments were carried out (Fig. S2, in Supporting Information). Firstly, the fluorescence spectra of AA alone were measured with increasing concentrations with the excitation at 460 nm (Fig. S2A, in Supporting Information). There are no obvious fluorescence peaks for AA with different concentrations. With the excitation of 370 nm, however, there are significant emission peaks for AA in the concentration range of 88.5-4425 mM (Fig. S2B, in Supporting Information). The result is consistent with the previous works [33, 34]. There is a significant fluorescence enhancement of AA in the system of CPDs- Tb^{3+} , while the fluorescence intensity of AA in the CPDs or Tb^{3+} solutions hardly changed (Fig. S3A, B and C, in Supporting Information). Thus, the unique structure of CPDs- Tb^{3+} is necessary and important for the fluorescence enhancement of AA.

3.2. Characterization of CPDs

The CPDs prepared in this study were characterized by the following methods.

3.2.1 Morphological characterization

Figure 2 shows the TEM images of CPDs, CPDs- Tb^{3+} , and CPDs- Tb^{3+} +AA. The results show that the CPDs with similar particle size, spherical and monodisperse (Figure 2A). By counting the size distribution of more than 100 CPDs, it was observed that the size distribution of CPDs ranged from 2 to 6.5 nm, with an average size of 3.75 nm. About 75% of CPDs were in the range of 2.5 to 4.5 nm (Figure 2B). In the presence of Tb^{3+} , CPDs aggregate severely, while the addition of AA makes the aggregation almost disappear (Figure 2C and D).

Fig. 3 shows the SEM images of CPDs- Tb^{3+} and CPDs- Tb^{3+} +AA. It can be observed that the CPDs- Tb^{3+} show amorphous and porous structures, which enhanced the adsorption capability of AA (Fig. 3A). In the presence of AA, CPDs- Tb^{3+} also exhibit amorphous structure, and the porous structures decrease (Fig.

3B). SEM/EDS method has also helpful for the analysis of CPDs-Tb³⁺ and CPDs-Tb³⁺+AA element composition. **Fig. S4** (in Supporting Information) and **Fig. S5** (in Supporting Information) are the results of element map scanning during the EDS analysis. CPDs-Tb³⁺ and CPDs-Tb³⁺+AA are mainly composed of C, N, O, P and Tb.

Fig. 4A shows the XRD patterns of CPDs and CPDs-Tb³⁺. There is a broad diffraction peak at 20.8°, while it shifts slightly to 23.5° for CPDs-Tb³⁺, which may be ascribed from the bonding of Tb³⁺ on the surface of CPDs [26]. And the XRD patterns also show CPDs display amorphous structures with and without Tb³⁺. The result consists with that of TEM. **Fig. 4B** exhibits DLS results of CPDs, CPDs-Tb³⁺, and CPDs-Tb³⁺+AA, respectively. The hydrodynamic size values of the three CPDs species are greater than those from TEM results. Nevertheless, both TEM and DLS data show that CPDs-Tb³⁺ has the greatest particle size and the CPDs has smallest size. The XPS (**Fig.4C**) is used to explore chemical bonds and surface elements of CPDs. Four peaks at 284.5, 399.5, 531.6, and 1241.7 eV belongs to C 1s, N 1s, O 1s, and Tb 3d, respectively[35]. The zeta potentials (**Fig.4D**) show that the CPDs are slightly positively charged, while the CPDs-Tb³⁺ exhibits considerably positive potential owing to the introduction of Tb³⁺ ion.

3.2.2 Optical properties

The optical properties of CPDs (Fig. 5) were characterized including tuning excitation wavelength, quantum yield (QY) and Stern-Volmer curves. Fig. 5A shows that the fluorescence peak intensity increases in the range of 420-460 nm and decreases with the excitation wavelength from 460 nm to 500 nm. The emission peak wavelength displays a slight red shift from 560 nm to 576 nm. Fig. 5B exhibits the fluorescence intensity increases with the increase of absorbance using Rhodamine B (Rh B) as reference. After calculation, the QY of CPDs is about 0.26. In addition, it can be found that the fluorescence of CPDs can also be quenched by Er³⁺, Nd³⁺, and Pr³⁺ from the Stern-Volmer plots (Fig. 5C). Herein, CPDs-Tb³⁺ system was used as a model in this paper.

3.3. Optimization conditions for AA detection

The CPDs for the determination of AA was synthesized by hydrothermal method (Scheme 1). The effect of experimental conditions on the determination of AA was studied carefully. The conditions for the synthesis of CPDs and the experimental conditions for the detection of AA were studied. These conditions include temperature, time and PEI concentration, pH and ionic strength, and reaction time of CPDs with Tb³⁺.

(1) Effect of synthesis conditions.

Figure S6A (in Supporting Information) shows the fluorescence intensity change of CPDs-Tb³⁺+AA in the reaction temperature range from 160 °C to 200 °C. It can be seen from the figure, when the reaction temperature reaches 180 °C, the fluorescence intensity of AA detection can reach the peak. The fluorescence intensity of CPDs-Tb³⁺+AA at different reaction times was recorded when the reaction temperature was changed from 4 h to 8 h, and the optimal reaction time was obviously 5 h (**Fig. S6B**, in

Supporting Information). Therefore, the reaction time of 5 h at 180 °C was the optimal condition for subsequent experiments.

Secondly, the optimal PEI concentration was also explored, as shown in **Fig. S6C** (in Supporting Information). Obviously, with the increase of PEI concentration from 10 mg/mL to 25 mg/mL, the fluorescence intensity increases gradually for AA detection. When the concentration of PEI continues to increase to 40 mg/mL, the fluorescence intensity gradually decreases. Therefore, when the concentration of PEI is 25 mg/mL, the fluorescence intensity for AA detection reaches a peak.

(2) Effect of sensing conditions

Firstly, the reaction time between CPDs and Tb^{3+} was investigated, as illustrated in **Fig. S7A** (in Supporting Information). After mixing CPDs and Tb^{3+} for different times, the fluorescence intensity was recorded in the presence of AA. The fluorescence intensity of CPDs- Tb^{3+} +AA increases rapidly with the increase of reaction time between CPDs and Tb^{3+} , and exhibits steady after 3 min. It indicates that the complexes of CPDs and Tb^{3+} can form within 3 min.

As shown in **Fig. S7B** (in Supporting Information), the obtained CPDs- Tb^{3+} precipitates were redispersed in deionized water with pH of 2-11, and the fluorescence intensity of AA was detected with different pH values. It can be seen that the fluorescence enhancement of AA (ΔF) remains basically stable in the range of pH 3-10, which means pH is almost no effect on the detection of AA within this range.

Ionic strength is one of the most common challenges for nanosensor systems. Therefore, NaCl solutions with different concentrations were used to study the effect of ionic strength as shown in **Fig. S7C** (in Supporting Information). It shows that CPDs and CPDs- Tb^{3+} systems have no significant fluorescence changes in the concentration range of 0-100 mM, indicating that the CPDs products and CPDs- Tb^{3+} systems display stable in NaCl solutions. For CPDs- Tb^{3+} +AA, the fluorescence intensity changes slightly. Therefore, it can be inferred that this method has excellent salt tolerance and good stability. Considering the environmental friendliness, deionized water is selected as medium for the detection of AA.

The results show that the optimal synthesis time, temperature and PEI concentration were 5 h, 180 °C and 25 mg/mL, respectively. The reaction time of CPDs with Tb^{3+} was 3 min, and the detection medium was deionized water.

3.4. Sensitivity

Under the optimum conditions, such as synthesis time of 5 h, temperature of 180 °C, 25 mg/mL PEI, reaction time of CPDs with Tb^{3+} within 3 min, and deionized water as medium, the sensitivity and selectivity of AA were detected by CPDs- Tb^{3+} system. Fig. 6A depicts that the fluorescence intensity of CPDs- Tb^{3+} changes regularly with the concentration of AA (0-70.80 mM). This indicates that the fluorescence of Tb^{3+} quenched CPDs can be recovered gradually with the increase of AA concentration. Fig. 6C shows a good linear relationship between the fluorescence intensity change (ΔF) and AA

concentration in the range of 0.04 ~ 42.48 mM ($r = 0.9949$). The fluorescence intensity was recorded at 545 nm. Using the formula of $3.29S_B/m$, the limit of detection (LOD) is estimated to be 0.02 mM. The standard deviation of the blank ($n = 5$) and the slope of the calibration plot correspond to S_B and m in the formula, respectively. These results suggest that CPDs-Tb³⁺ as a fluorescent probe can be used as an effective sensing system for the detection of AA.

3.5. Selectivity

Under the optimum conditions, the interference of some common organic molecules was studied. These organic molecules include DMF, acetone, methanol, chloroform, acetonitrile, ether, EA, FA, PA, and BA. Fig. 6D shows that the fluorescence intensity system increases significantly when AA (20 mM) is added. In contrast, the fluorescence intensity changes negligibly with the addition of other organic compounds even with high concentration (100 mM). It can be deduced that the sensing system of CPDs-Tb³⁺ has a special fluorescence response to AA rather than common organic molecules with similar structure.

3.6. Application

The practical application of CPDs-Tb³⁺ fluorescence system was studied for the determination of AA in wine samples. After the pretreatment of wine samples according to the experimental section, AA is detected in samples using the present and gas chromatography (GC) methods, respectively. The results of AA content, RSD and recovery are listed in Table 1. For the two wine samples, the present content of AA were about 0.76 and 0.53 mM, and the AA contents by GC method were about 0.63 and 0.62 mM. The results from the two methods agree well with each other. For the present method, the RSD is less than 5.66% and the recovery ranges from 98.7–101.2%, which means the method has good accuracy and precision. The proposed fluorescence method may be applied to the analysis of AA in other real samples.

Table 1
The detection results of acetaldehyde in wine.

Sample	Added mM	Found mM	Recovery %	RSD %	GC method mM
	0	0.76±0.01	--	1.32	0.63
Wine-1	14.16	15.35±0.36	103	2.88	14.03
	21.24	21.72±0.40	98.7	1.91	21.31
	0	0.53±0.03	--	5.66	0.62
Wine-2	14.16	14.86±0.40	101.2	2.79	14.53
	21.24	21.71±0.10	99.7	0.47	21.58

4. Conclusions

In summary, based on the AIE of AA on the porous CPDs-Tb³⁺ system, a turn-off-on fluorescence method was established for AA detection. CPDs were prepared by a one-pot hydrothermal method with milk and PEI as precursors. CPDs show high QY and photostability. Based on the rich functional groups on the surface, CPDs can effectively combine with Tb³⁺, and they even can easily form precipitation. The results show that Tb³⁺ can significantly quench the fluorescence of CPDs. AA displays negligible fluorescence with the maximum excitation wavelength of CPDs. In the CPDs-Tb³⁺ system, however, AA shows obvious fluorescence. The enhancement of fluorescence intensity increases linearly with the concentration of AA. AA can be determined sensitively rather than FA, PA, and BA. The turn-off-on system is successfully used for the detection of AA in wine samples. It can be inferred that the CPDs-Tb³⁺ system can be exploited for AA determination in more beverage or foodstuff applications.

Declarations

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Author information

Affiliations

School of Chemistry and Chemical Engineering, Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology, Liaocheng University, Liaocheng 252059, China

Rentian Guan, Shuai Zhang, Xiaoyu Fan, Yingying Hu, Tao Liu, Shuhao Wang & Qiaoli Yue

State Key Laboratory for Performance and Structure Safety of Petroleum Tubular Goods and Equipment Materials, Tubular Goods Research Institute, Xian 710077, China

Xiaodong Shao

Contributions

Experimental work done and Manuscript written by Rentian Guan and Qiaoli Yue, Manuscript checked and supervised by Shuai Zhang, Xiaoyu Fan, Xiaodong Shao, Yingying Hu, Tao Liu and Shuhao Wang. All authors read and approved the final manuscript.

Corresponding author

Correspondence to Qiaoli Yue.

Ethics declarations

Ethics Approval

Not applicable.

Consent to Participate

Not applicable.

Consent for Publication

Not applicable.

Conflict of Interest

The authors declared that there is no conflict of interest.

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Supporting information

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Data Availability

All data generated or analyzed during this study are included in this published article and its supplementary materials.

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Figures

Figure 1

Fluorescence (A, inset: photos of different systems under UV irradiation) and absorption (B) spectra of different systems, Stern-Volmer plots of CPDs-Tb³⁺ under different temperatures (C) and fluorescence decay curves of CPDs and CPDs-Tb³⁺ (D).

Figure 2

TEM images of CPDs (A), histogram of particle size distribution of CPDs (B), TEM images of CPDs-Tb3+ (C) and CPDs-Tb3++AA (D).

Figure 3

SEM images of CPDs-Tb3+ (A) and CPDs-Tb3++AA (B)

Figure 4

XRD (A), DLS (B), XPS (C), and zeta potential plots (D) of different species.

Figure 5

Fluorescence spectra of CPDs with different excitation wavelength (A), rhodamin B (Rh B) as reference to measure the QY of CPDs (B), and Stern-Volmer curves of CPDs with Tb³⁺, Er³⁺, Nb³⁺, and Pr³⁺ (C).

Figure 6

Fluorescence spectra of CPDs-Tb in the presence of AA with various concentrations (A), the corresponding scatter plot of A (B) and linear response between fluorescence recovery (ΔF) and AA concentration (C), and the fluorescence intensity of CPDs-Tb3+ with different species (D).

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