A Turn-off Fluorescent Sensor for Simple Detection of Vanillin Based on N-doped Carbon Dots

Hongyan Zeng¹, Li Li¹, Yaping Ding¹, Qi Zhuang¹, Chaolin Wang¹, Xiaojing Si²

¹Department of Chemistry, Shanghai University, Shangda Road, Baoshan District, Shanghai 200444, P.R.C

²School of Public Health, Shanghai Aurora College, Shanghai 201908, PR China Corresponding e-mail address: wdingyp@sina.com, lilidu@shu.edu.cn

Abstract:

Vanillin (Van) is an important fragrance, which is widely used as flavoring agents or perfume fixative in food, cosmetics, tobacco industry, medicine, etc. To our knowledge, carbon dots were first applied as fluorescence sensor for the quantitative determination of Van. The as-synthesized N-CDs were characterized by transmission electron microscopy (TEM), the fourier transform infrared spectra (FT-IR), UV spectrophotometer and spectrofluorophotometer, respectively. The fluorescent detection of Van was successfully conducted in aqueous media and incubation time was as short as 5 min. The proposed probe showed a great linear relationship between fluorescence intensity function $\log(F_0/F)$ and concentration of Van in range from 5 μ M to 140 μ M with a detection limit (S/N=3) of 0.4 μ M.

Key words: carbon dots, Vanillin, fluorescent sensor, simple detection, turn-off

Introduction

(4-hydroxy-3-methoxybenzaldehyde, Van) is an important flavouring extracted from vanilla beans, also is one of the largest productive spices in synthetic fragrances over the world. It is widely used as flavoring agents or perfume fixative in food [1], cosmetics, tobacco industry, medicine, etc. However, it can still be harmful to human's health when the concentration of Van is high enough [2]. Therefore, the determination of Van in various products is required. Comparing to other detecting method, fluorescent sensor is an alternative detection method which has some superior advantages of simple operation, high sensitivity and cost-effectiveness for the trace analysis [3]. Carbon dots have been widely used as good fluorescent probes in the detection of various substances [4] due to their great water solubility, photochemical stability and strong fluorescence.

In this work, we use p-Phthalic acid and ethylenediamine as carbon source and nitrogen source, respectively. Then the N-CDs were synthesized by a simple one-pot hydrothermal method. The as-prepared N-CDs were first used as the fluorescent probe for the detection of Van.

Characterization of N-CDs

Fig. 1 is the morphology of the as-synthesized N-CDs investigated by TEM. As shown in Fig. 1, the N-CDs are uniform spherical nanoparticles and the diameter range from 3 to 5 nm.

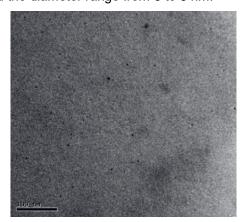


Fig. 1 TEM of N-CDs

As depicted in Fig. 2A, most spectral peaks of N-CDs are similar to that of PTA, except for the strong peaks located at 1544 and 1369 cm⁻¹ which are attributed to bending vibration of N-H and stretching vibration of C-N, respectively. And the new peak of N-CDs located at 3327 cm⁻¹ is attributed to stretching vibration of N-H. The above descriptions indicated that nitrogen is successfully doped in the carbon dots. In

order to explore the optical properties of the N-CDs, UV-Vis absorption and fluorescence spectra are obtained in Fig. 2B, the N-CDs typically display optical absorption in the UV-Vis region with an absorption peak at 240 nm, and a strong emission peak at 430 nm appeared upon excitation at 350 nm. The excitation and emission spectra of carbon dots are symmetrical.

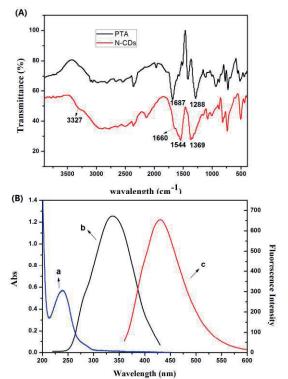


Fig. 2 (A) FT-IR spectra of p-Phthalic acid(PTA) and N-CDs; (B) a) UV-Vis absorption, b) fluorescence excitation and c) fluorescence emission spectra of N-CDs.

Experimental result

In order to explore the optimal detecting environment of fluorescent sensor, optimization experiments of pH and reaction time was carried out in this work. As depicted in Fig. 3A and Fig. 3B, we chose water as the reaction media and 5 minutes as reaction time for our experiment, which made the sensor more simple and time-saving. As Fig.3C shows that the fluorescence intensity of N-CDs decreased obviously with gradually increased concentration of Van from 5 µM to 140 µM. And Fig.3D demonstrates that the fluorescence intensity function log(F₀/F) are linearly increase with Van's concentrations. The corresponding linear regression equation was $log(F_0/F) =$ $0.0116C_{Van} + 0.0149$ (R= 0.999), where F₀ and F are the fluorescence intensities of N-CDs at 350 nm in the absence and presence of Van, respectively. The detection limit was calculated as 0.4 µM, (S/N=3).

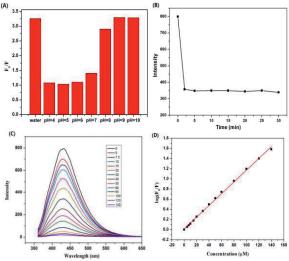


Fig.3 (A) The relative fluorescence intensity (F_0/F) at different pHs and water; (B) Effect of incubation time on the fluorescence intensity of (N-CDs)-Van system; (C) Fluorescence spectra of N-CDs with addition of different concentrations of Van from 0 to 140 μ M; (D) The linear relationship between $log(F_0/F)$ and Van concentration in the range of 0-140 μ M, where F_0 and F are fluorescence intensities in the absence and presence of Van, respectively.

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