



Fluorescence switching sensor for sensitive detection of sinapine using carbon quantum dots

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ABSTRACT

A new fluorescence switching sensor for sensitive detection of sinapine (SP) was developed based on aggregation and disaggregation of carbon quantum dots (CDs) with the assistance of copper ions (Cu^{2+}). In the detection, carboxyl group on the surface of CDs enables the aggregation triggered by Cu^{2+} due to the effective coordination, inducing obvious fluorescence quenching. Upon the addition of SP into the solution, higher affinity between SP and Cu^{2+} is found to form SP-Cu coordination complex, leading to re-dispersion and fluorescence recovery of CDs. The fluorescence switching sensor for SP detection has advantages of simplicity, rapidness, high sensitivity and selectivity. The quantitative range for SP detection is from 0.04 to $5 \mu\text{g mL}^{-1}$ with the detection limit of $0.02 \mu\text{g mL}^{-1}$. In practical samples, the recoveries of the samples ranged from 87.9% to 117.0%.

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1. Introduction

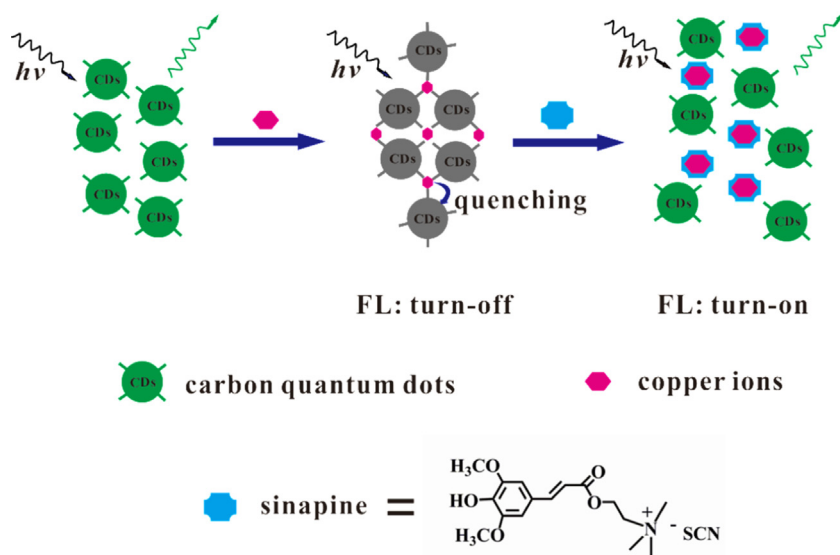
Plant-derived small molecules play vital roles in function of life [1–3]. As one of small molecules widely present in rapeseed and medical plants, sinapine (SP) has been paid much attention because of its unique health property and biological activity that can lower blood pressure, inhibit prostatic hyperplasia induced by testosterone propionate and resist to aging [4,5]. Therefore, the content of SP is often used as a key marker in assessing the qualities of the related plant products. The analysis of SP is of great significance for biomedical research and nutritional science. There is a demand for convenient and sensitive methods for real-time SP monitoring. Up to date, various strategies for detection of plant-derived small molecules have been reported by the use of UV–vis spectroscopy [6–9], chromatography [10,11], mass spectrometry [12], and electrochemical analysis [13–15]. Compared with other analytical methods, fluorescence spectroscopy has significant advantages due to its high sensitivity, simplicity, and nondestructive properties. Therefore, we adopt fluorescence technique for SP detection, which may be a valuable research.

Fluorescent probes have been recognized as the most efficient tools application to biological, medical and chemical fields because of its high sensitivity and high spatiotemporal resolution. In the last few decades, quantum dots (QDs) have become one of the most extensively optical nanomaterials in various sensors owing to high emission quantum yields and size tunable emission profiles [16,17]. However, heavy metals are essential elements in those QDs materials. New concerns have been raised over the potential toxicity and environmental hazards.

Carbon quantum dots (CDs), as newly emerging carbon-based materials, compared with organic dyes and common QDs, possess much superiority including good photostability, excellent biocompatibility, low toxicity, cheap raw materials and outstanding water solubility [18,19]. Thus they are endowed as the best alternative of fluorometric indicator to practical sensors [20–23]. Recently, Feng's group reported that the fluorescence of CDs could be effectively quenched by copper ions, nickel ions and cerium ions owing to aggregation of CDs induced by the coordination of metal ions with the carboxyl group of CDs [24–28]. With the introduction of target, however, the CDs-Cu aggregates are broken with the occurrence of stronger affinity or specific interaction between target and metal ions. These findings form a basis for constructing fluorescence sensors. Inspired by these, a design for the detection of SP could be available by using the advantages of CDs.

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Scheme 1. Schematic illustration of the fluorescence switching strategy for detection of sinapine (SP) based on carbon quantum dots (CDs) and copper ions (Cu^{2+}).

Herein, we propose a novel fluorescence switching sensor allowing highly sensitive and selective detection of SP based on aggregation and disaggregation of CDs with the assistance of copper ions (Cu^{2+}). The principle is illustrated in Scheme 1. To impart the fluorescent switching properties of the sensor, Cu^{2+} are interacted with CDs firstly. The presence of Cu^{2+} triggers aggregation of CDs because of effective coordination between Cu^{2+} and CDs through carboxyl groups, inducing obvious fluorescence quenching of CDs. Based on the unique molecular structure of SP, higher affinity of SP toward Cu^{2+} than CDs is found with the addition of SP to form SP-Cu complex. Consequently, the CDs-Cu aggregates are broken and free CDs are release, leading to fluorescence recovery of CDs. By monitoring the fluorescence change of CDs, the concentration of SP could be quantified. This strategy provides an effective and alternative way for highly sensitive and selective detection of SP.

2. Experimental section

2.1. Chemicals and apparatus

Sinapine thiocyanate (SP) was obtained by National Institutes for Food and Drug Control, China. Caffeic acid (CA), cinnamic acid (CA), sinapic acid (SA), ferulic acid (FA), protocatechuic acid (PA), syringic acid (SyA), *p*-coumaric acid (CoA), gallic acid (GA); tannin (TA) were obtained by Sigma-Aldrich Co. Ltd., USA. Activated carbon and bluestone (CuSO_4) were purchased from Aladdin Co. Ltd, China. The buffer solution used was as follows: 10 mM MOPs (pH 8.0), 150 mM NaCl. Milli-Q purified water was used to prepare the solutions. The chemical reagents were dissolved with methanol as stock solutions.

Fluorescence emission spectroscopy was performed on an F-7000 fluorescence spectrophotometer (Hitachi, Japan). The sample cell was a 300 μL quartz cuvette. The luminescence intensity was monitored by exciting the sample at 470 nm and measuring the emission at 526 nm. The slits for excitation and emission were set at 10 and 10 nm, respectively. The fluorescence emission spectrum of the solution was then measured 10 min later. UV-vis absorption spectra were performed on a UV-2550 Spectrophotometer (Shimadzu, Japan). TEM images were obtained on a Hitachi H7000 electron microscope. Fluorescence intensity decay curves were measured on a FELIX32 system (Photo Technology International). The sensor was put in a ZF-20D black-box type UV analyzer (Shang-

hai electro-optical instrument factory), and the fluorescent photos were taken by a digital camera.

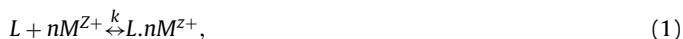
2.2. Preparation of CDs

CDs were prepared as follows according to Ref. [25]: activated carbon was added into a mixture of concentrated sulfuric acid and nitric acid, and heated at 80 °C for 5 h. Then the mixture was cooled, diluted and neutralized by using sodium hydroxide. Finally, the solution was dialyzed in a dialysis bag (1000 Da) for 3 days, and then continually treated with the dialysis bag (50,000 Da) to remove large non-fluorescent materials. The outside solution of the bag was collected, concentrated and kept at room temperature for further experiments.

2.3. Determination of quantum yield of CDs and the deduction of Benesi-Hildebrand equation

The quantum yield of CDs was obtained using Rhodamine 6G as standard reference according to Ref. 25: the quantum yield of the CDs was calculated using the equation: $\Phi = \Phi_s [(I_s n^2)/(I_n A n_s^2)]$, where Φ is the quantum yield, I is the integrated intensity, A is the optical density, n is the refractive index of the solvent, and s refers to the standard reference of known quantum yield.

According to references [29–32], the binding interaction and association constant (K) of compound (L) and metal ions (M^{2+}) could be evaluated and obtained based on Benesi-Hildebrand equation. The deduction of equation is shown as follows: the binding ratio between L and M^{2+} is presumed to 1: n when the reaction reaches equilibrium. The reaction equation could be expressed as:



thus the binding constant K of L and M^{2+} is obtained as:

$$K = \frac{[L \cdot n\text{M}^{2+}]}{[L][\text{M}^{2+}]^n} = \frac{[L \cdot n\text{M}^{2+}]}{([L]_0 - [L \cdot n\text{M}^{2+}])([\text{M}^{2+}]_0 - n[L \cdot n\text{M}^{2+}])^n}, \quad (2)$$

where $[L \cdot n\text{M}^{2+}]$, $[\text{M}^{2+}]$ and $[L]$ denotes the concentrations of complex (ML), M^{2+} and L at the equilibrium state, $[L]_0$ and $[\text{M}^{2+}]_0$ denotes the original concentrations, respectively. With $[\text{M}^{2+}]_0 \gg [L \cdot n\text{M}^{2+}]$, K is shown as:

$$K = \frac{[L \cdot n\text{M}^{2+}]}{([L]_0 - [L \cdot n\text{M}^{2+}])[\text{M}^{2+}]^n} \quad (3)$$

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