



Short communication

Highly luminescent organosilane-functionalized carbon dots as a nanosensor for sensitive and selective detection of quercetin in aqueous solution



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ABSTRACT

The organosilane-functionalized carbon dots (SiCDs) were synthesized using citric acid with *N*-(*b*-aminoethyl)-*g*-aminopropyl methyltrimethoxy silane (AEAPMS). The as-synthesized SiCDs were characterized by IR, TEM, XPS, NMR and fluorescence. The SiCDs showed a strong emission at 455 nm with excitation at 365 nm. The SiCDs exhibited analytical potential as sensing probes for quercetin (QCT) determination. pH effect, temperature effect, interferences, and analytical performance of the method were investigated. It suggested that SiCDs exhibited high sensitivity and selectivity toward QCT: the linear ranges of SiCDs were estimated to be 0–40 μ M while the limit of detection (LOD) was calculated to be 79 nM.

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Flavonoids (or bioflavonoids) are a class of plant secondary metabolites, which found in fruits, vegetables and some beverages [1]. Commonly all the three cycles are substituted by hydroxyl groups or methoxy groups and discrete derivatives differ in the stage of substitution and oxidation [2]. Quercetin (3,3',4',5,7-pentahydroxyflavone, QCT) is one of the most common flavonols present in nature that has attracted the attention from many researchers [3–5]. It is known to exhibit anticancer, antiallergy, antiviral, antimutagenic, cardiovascular protection, cataract prevention, and lipid peroxidation inhibitory effects. The biological actions have been attributed to their antioxidant properties, because of their ability to scavenge free radicals and the influence on the intracellular redox status [6,7]. Therefore, the determination of quercetin is significant in biochemistry, clinical medicine and natural pharmaceutical chemistry. Hitherto, numerous analytical methods have been employed for the quantification of QCT include electrophoresis with a diode array detector, electroanalytical methods, high-performance liquid chromatography, electrochemical methods, fluorescence detection and so on [8–15]. The fluorescence detection attracted the most attention because of its high sensitivity and local observation by fluorescence imaging spectroscopy [16,17]. However, the traditional QCT fluorescence probes have several shortages, for example, the sensitivity to QCT is not enough; the detection of QCT

is susceptible to interference from other flavonoids; last but most important, commonly used fluorescent molecules and quantum dots have cytotoxicity, which limit their applications in biology. Therefore, it is quite demanding to develop low/non-toxic optical sensing materials with a simple preparation process for selective and sensitive detection of QCT.

Carbon dots (CDs), a new member of the quantum-sized carbon analogues, have shown great potential in biological, medical and environmental applications due to their fascinating photoluminescent properties and the ability to serve as nontoxic substitutes for traditional heavy-metal-based quantum dots [18–23]. Due to the spatial confinement in the CDs nanostructures, their radiative recombination rates get enhanced and nonradiative recombination rates are suppressed, making their fluorescence efficiency greatly improved [24,25]. Moreover, CDs have also been widely used in analytical chemistry for the determination of metal ions as well as other inorganic ions, such as Cu^{2+} , Hg^{2+} , Fe^{3+} , NO_2^- and F^- [26–32]. However, research on the application of CDs in organic compounds remains limited. To our knowledge, the determination of flavonoid molecule using CDs as probes has not been previously reported [33].

In this communication, we investigated for the first time the fluorescence interactions between the methyltrimethoxy silane functionalized CDs (SiCDs) and QCT in detail and have found QCT can selectively and sensitively detect QCT in aqueous solution. On this basis, a rapid, selective, and sensitive sensing method based on the SiCDs fluorescence probe has been developed for the

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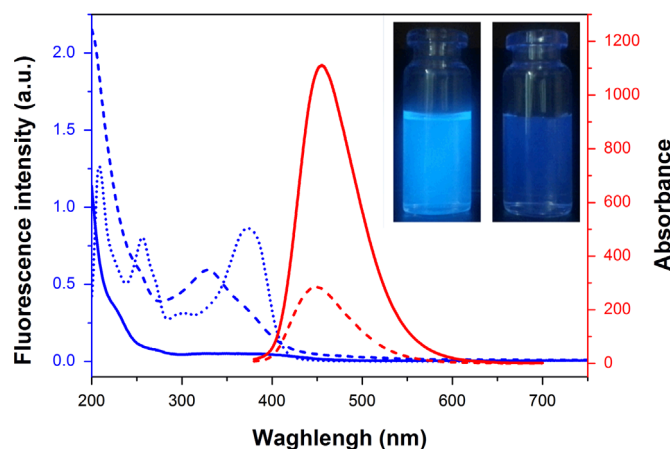


Fig. 1. UV absorption spectra (blue lines) and fluorescence spectra (red lines) of $50 \mu\text{g mL}^{-1}$ SiCDs solution in the absence (solid lines) and presence (dashed lines) of $40 \mu\text{M}$ QCT, and the UV absorption spectrum of $40 \mu\text{M}$ QCT (blue dot line). The inset shows the photos of $50 \mu\text{g mL}^{-1}$ SiCDs solutions in the absence (left) and presence (right) of $40 \mu\text{M}$ QCT illuminated by UV light of 365 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

detection of trace QCT in water. A linear range of F_{455} versus QCT concentration was obtained within $0\text{--}40 \mu\text{M}$, while the limit of detection of 79 nM was obtained.

SiCDs synthesized by the previously reported method [34,35]. The basic procedures include the decomposition and pyrolysis of anhydrous citric acid, accompanied by the formation of gas and condensable vapors together with the surface passivation reaction of the amine groups of *N*-(β -aminoethyl)- γ -aminopropyl methyl-dimethoxy silane (AEAPMS) with the carboxyl groups driven from the pyrolyzed species [36]. SiCDs were characterized by spectroscopic and microscopic methods (see Figs. S1 and S2 in ESI†). The quantum yield of the resultant ultrasmall ($\sim 1.7 \text{ nm}$) SiCDs is as high as 55% (see Figs. S1a and S3 in ESI†). SiCDs dispersed in water emit blue light under 365 nm UV light illumination (Fig. 1 inset).

This strong emission can be attributable to the surface passivation of methyl-dimethoxy silane group, because it introduces a new kind of surface state and makes electrons be able to facilitate a high yield of radiative recombination [37–39]. The UV–vis absorption spectra show that SiCDs feature two peaks at around 250 nm and 345 nm (Fig. 1). The peak centered about 345 nm due to the trapping of excited state energy by the surface states leads to strong emission [40,41].

It was generally considered that fluorescence from carbon dots can be quenched efficiently by either electron acceptor or electron donor molecules in solution [42]. However, SiCDs are insensitive to most heavy metal-ions, anions and organic molecules but show high sensitivity and selectivity to QCT. The selectivity of SiCDs fluorescence sensing system was estimated. As shown in Fig. 2, upon the addition of these flavonoids to the SiCDs in aqueous solution, only QCT caused the remarkable fluorescence quenching, while electron-rich phenolic compounds, quinol, resorcinol and catechol, quenched the emission intensity only to a small extent. Besides flavonoids and phenolic compounds, the effects of 20 other kinds of cations, anions and small molecules, including Al^{3+} , Cd^{2+} , Ce^{3+} , Fe^{3+} , Co^{2+} , Cu^{2+} , Hg^{2+} , K^{+} , Na^{+} , La^{3+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , Ag^{+} , Au^{+} , Au^{3+} , NO_2^- , SO_3^- , methyl sulfonate and phthalate, on the fluorescence response of SiCDs were investigated (Fig. S4 in ESI†). Fluorescence intensity of SiCDs was quenched 25% as soon as Hg^{2+} ($40 \mu\text{M}$) was added, due to the stronger affinity constants between Hg^{2+} and carboxylic groups on the surface of SiCDs. However, it obviously has little significance for the detection of QCT. All these observations indicate that the present fluorescent

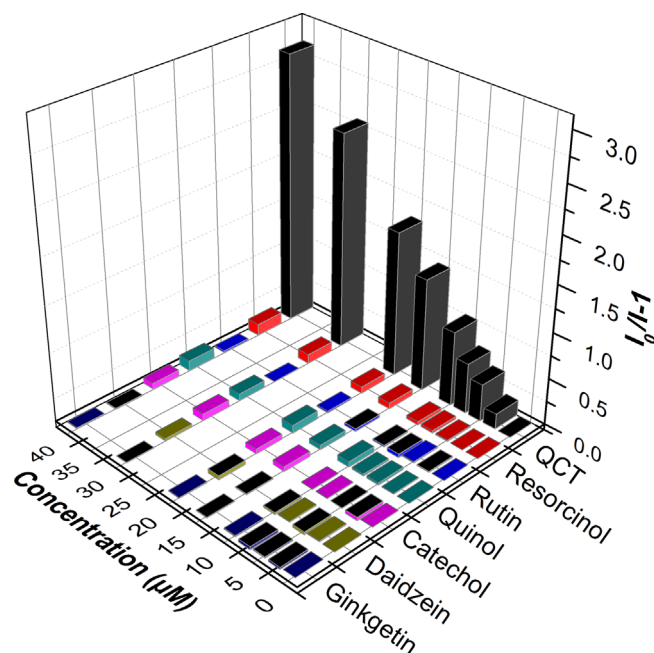


Fig. 2. Quenching efficiencies of QCT and common interferents to the emission of the SiCDs in aqueous solution at different concentrations.

sensing probe exhibits high selectivity toward the QCT detection. The interference of various ions was also investigated. Fig. S5 (ESI†) shows the fluorescence response of the SiCDs toward QCT in the presence of competitive ions. Clearly, these potentially interfering ions do not interfere with QCT bindings with SiCDs as well as the subsequent fluorescence quenching.

For sensitivity study, different concentrations of QCT were investigated in the deionized water. The fluorescence shows continuous quenching with the addition of QCT, but has no effect on the fluorescence wavelength. Besides, the addition of QCT into the SiCDs solution gives rise to a new UV absorption band centered at 328 nm, but the typical absorption peak of QCT at 371 nm was not observed. Upon addition of increasing concentrations of QCT ($0\text{--}40 \mu\text{M}$) to the solution of SiCDs ($5 \times 10^{-5} \text{ g mL}^{-1}$), a new absorption band centered at 328 nm appeared with increasing intensity (Fig. 3b). The absorbance of the mixed solution was found to increase linear relationship with the concentration of QCT in range of $0\text{--}40 \mu\text{M}$ (Eq. (1)). The fluorescence sensing behavior of SiCDs for QCT was also explored. Fig. 3a shows a gradual decrease in fluorescent intensity at emission peaks with increasing QCT concentration, suggesting that this system is sensitive to QCT concentration. In the range of $0\text{--}40 \mu\text{M}$ QCT, the relative fluorescent intensity (I_0/I) of SiCDs could be described by the Stern–Volmer plot with a perfect linear behavior (Eq. (2)).

$$A = 0.01355C + 0.052 \quad (R^2 = 0.99921) \quad (1)$$

$$\frac{I_0}{I} = 0.0744C + 1 \quad (R^2 = 0.99581) \quad (2)$$

where I_0 and I are the fluorescence intensity of SiCDs in the absence and presence of QCT and C represents the concentration of QCT. Herein, we calculated the detection limit of 79 nM , respectively, which suggest that this kind of CDs with strong fluorescence activity have very promising application in the detection of QCT. Table 1 summarized the detection limit, linear range and recovery with different methods for the determination of quercetin. Our method was comparable with chemiluminescence sensor [43], resonance Rayleigh scattering [44] electrochemical detection [45] and other fluorescence detection [46].

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