Analytical Biochemistry 489 (2015) 17–24

Contents lists available at ScienceDirect

Analytical Biochemistry

journal homepage: www.elsevier.com/locate/yabio

Detection of quercetin based on Al^{3+}-amplified phosphorescence signals of manganese-doped ZnS quantum dots

Zhifeng Zhang, Yanming Miao, Linwang Lian, Guiqin Yan*

Shanxi Normal University, Linfen, Shanxi 041000, China

ARTICLE INFO

Article history:
Received 10 April 2015
Received in revised form
26 July 2015
Accepted 5 August 2015
Available online 13 August 2015

Keywords:
Quantum dots
Signal amplification
Quercetin
Detection

ABSTRACT

A simple phosphorescence method is proposed for quercetin detection based on Al^{3+}-amplified room-temperature phosphorescence (RTP) signals of 3-mercaptopropionic acid (MPA)-capped Mn-doped ZnS quantum dots (QDs). The sensor was established based on some properties as follows. Al^{3+} can interact with carboxyl groups on the surface of MPA-capped Mn-doped ZnS QDs via chelation, which will lead to the aggregation of QDs and amplification of RTP signals, After the addition of quercetin, it can form more stable complex with Al^{3+} in alkaline aqueous solution and dissociate Al^{3+} from the surface of Mn-doped ZnS QDs, which will result in significant recovery of RTP intensity of the MPA-capped Mn-doped ZnS–Al^{3+} system. Under the optimized conditions, the change of RTP intensity was proportional to the concentration of quercetin in the range from 0.1 to 6.0 mg L^{-1}, with a high correlation coefficient of 0.996 and a detection limit of 0.047 mg L^{-1}. The proposed method is potentially suitable for detection of quercetin in real samples without complicated pretreatment.

As a new type of nanomaterial, quantum dots (QDs) have attracted a lot of attention during recent years owing to their unique properties such as high quantum yield, pronounced photostability, and broad absorption spectra coupled with narrow and symmetrical emission spectra [1–3]. QDs are excellent optical materials that have been widely used to detect specific analytes, including ions, toxic molecules, small molecules, and biomacromolecules [4–6]. However, the construction of many analytical methods is based on the fluorescence properties of QDs. Currently, more and more attention has been paid to the phosphorescence properties of long-lived room-temperature phosphorescence (RTP) QDs [7–10]. Phosphorescence originates from the triple state and has a longer average life than fluorescence. Therefore, an appropriate delay time is allowed by phosphorescence, and the interference from scattered light and autofluorescence can be effectively avoided accordingly [11]. Besides, the selectivity is also enhanced because it is less common than fluorescence [12,13]. The RTP QDs are endowed with potential superiority and applicability in complex chemical and biological analyses due to all of these properties.

More interesting, the large surface of QDs is favorable for attaching variable ligands. After the introduction of large-surface QDs, some ions, small molecules, and biomacromolecules will undergo physical or chemical reaction with QDs and further change the structure or charge composition on the surfaces of the QDs, so some more excellent controllable properties will be obtained accordingly [14]. Several studies related to interactions between QDs and metal ions reveal that the surface capping ligands will profoundly affect the luminescence response of QDs to some metal cations [15–19]. Detection methods established under the interaction between metal ions and QDs are widely reported, but the sensing mechanisms of these methods are mostly based on the fact that metal ions can quench the fluorescence or phosphorescence signals of QDs [20,21]. Probes based on the quenching of fluorescence signals often suffer from very large background interference, which results in a high detection limit. In comparison, probes based on emission enhancement encounter only very low background interference. Therefore, the development of probes based on enhancement of QD phosphorescence or fluorescence is very significant for improving the capability of detection.

Abbreviations: QD, quantum dot; RTP, room-temperature phosphorescence; HPLC, high-performance liquid chromatography; MS, mass spectrometry; MPA, 3-mercaptopropionic acid; TEM, transmission electron microscope; FT-IR, Fourier transform infrared; SEM, scanning electron microscope; RLS, resonance light scattering; DLS, dynamic light scattering; UV/Vis, ultraviolet/visible; RSD, relative standard deviation.

* Corresponding author. Fax: +86 (0)357 2051009.
E-mail address: gqyan2013@163.com (G. Yan).

http://dx.doi.org/10.1016/j.ab.2015.08.002
0003-2697/

Quercetin (3,3′,4′,5,7-pentahydroxylflavone) (Fig. 1) is one of the most abundant natural flavonoids and is widely distributed in vegetables and fruits, especially in traditional Chinese herbs, and can reach in the human diet with a level of 16–25 mg/day [22]. Over recent years, quercetin has drawn much attention not only because of its various beneficial influences on human health, including anticancer, anti-inflammatory, antitumor, antiulcer, antiallergy, antiviral, and antioxidant effects [23,24], but also because it enables protecting human DNA from oxidative attack in vitro [25]. In spite of a high dietary intake of quercetin, only very low amounts are excreted in the serum and urine of humans. For instance, after the intake of quercetin in the human body, only 0.4–1% of quercetin can be excreted in urine [26,27]. In addition, the content of quercetin in serum is approximately 0.12–0.35 mg L^{-1} after taking quercetin drug (500 mg) [28]. Thus, a very sensitive method is required for determining quercetin in pharmaceutical drugs and biological samples.

Currently, many highly sensitive and effective methods have been used to determine the content of quercetin such as liquid chromatography [26,29,30], spectrophotometry [31], mass spectrometry [28], Raman spectroscopy [32], ionic liquids-based monolithic cartridge molecular imprinting [33], and electrochemistry [34–36] techniques. However, some of these methods are limited by large time consumption and/or technical complexity. For example, high-performance liquid chromatography (HPLC) and HPLC–MS (mass spectrometry) require complicated pretreatment. Despite high sensitivity and effectiveness, the electrochemical methods often require sophisticated electrode modification. Hence, the development of a simple, economical, and sensitive analytical detection method would have very high application value.

As a Lewis base, quercetin structurally possesses super delocalizability, a complete π bond conjugated system, strong coordination oxygen atoms, and appropriate space configuration. Therefore, quercetin can selectively interact with Lewis acid Al^{3+} to form a stable chelate through acid–base adduct [37,38]. Based on such interaction, quercetin was used to selectively determine and trace Al^{3+} [39–41], which was used as an effective probe to detect quercetin [42,43]. Moreover, it was found that Al^{3+} can efficiently amplify the RTP signals of 3-mercaptopropionic acid (MPA)-capped Mn-doped ZnS QDs. Therefore, the ternary interaction among Al^{3+}, MPA-capped Mn-doped ZnS QDs, and quercetin seems to be adopted as a basis for the development of the RTP method for quercetin detection.

Inspired by these capabilities, we presented a simple quercetin detection system based on the RTP of MPA-capped Mn-doped ZnS QDs. This sensing system was composed of MPA-capped Mn-doped ZnS QDs and Al^{3+} without any sophisticated process of functionalization or conjugation. Here, Al^{3+} not only acted as coordination ions to amplify the RTP signals of MPA-capped Mn-doped ZnS QDs but also served as a probe to recognize quercetin. As illustrated in Fig. 1, Al^{3+} can interact with MPA-capped Mn-doped ZnS QDs via covalent complexation and further lead to the aggregation of QDs and amplification of RTP intensity. On its addition, quercetin can compete with MPA-capped Mn-doped ZnS QDs to bind with Al^{3+} and form a more stable complex and can further detach Al^{3+} from the surface of MPA-capped Mn-doped ZnS QDs. As a result, the RTP intensity of MPA-capped Mn-doped ZnS QDs will be recovered with the increase of quercetin concentration. Based on this strategy, the sensing system will be endowed with high selectivity and more convenience for quercetin detection. What is important is that this detection method provides a basis of optical detection for other flavonoids because quercetin is a major representative of other flavonoids.

Materials and methods

Materials and apparatus

Mercaptopropionic acid is purchased from J&K Scientific Ltd., $Zn(Ac)_2 \cdot 2H_2O$, $Mn(Ac)_2 \cdot 4H_2O$, $Na_2S \cdot 9H_2O$, and $Al(NO_3)_3 \cdot 9H_2O$ were purchased from Tianjing Kermel Chemical Reagent (Tianjing, China). Quercetin was bought from Sigma–Aldrich. All other chemicals were of analytical grade, and the resistivity of water used in this study was higher than 18 M Ω cm.

The morphology and microstructure of QDs were characterized by a JEM-2100F transmission electron microscope (TEM, HRTEM, Japan) and a D8 Advanced X-ray diffractometer (Bruker, Germany, Cu K_α), respectively. Besides, samples for HRTEM were obtained by drying sample droplets from water dispersion onto a 300-mesh Cu grid coated with a lacey carbon film. Fourier transform infrared

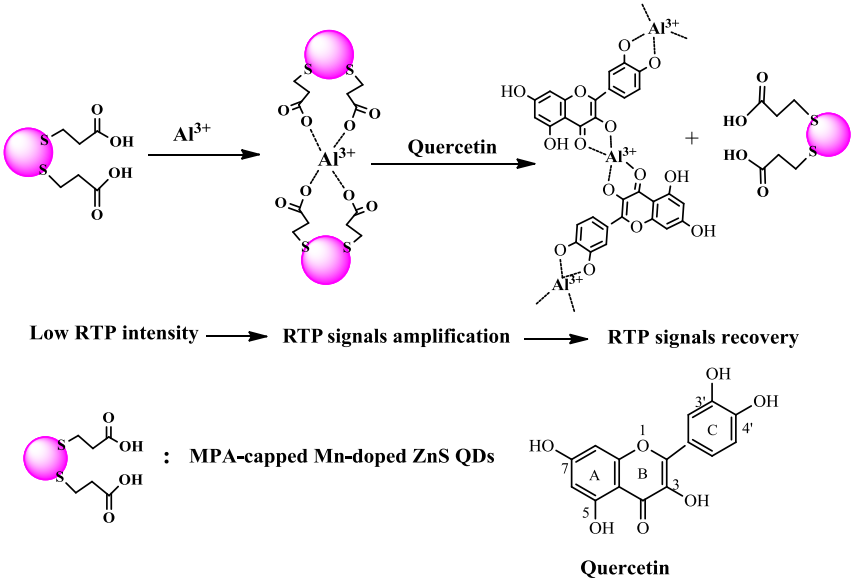

Fig.1. Schematic illustration of fabricating Mn-doped ZnS QDs for quercetin detection.