



Silicon quantum dots with tunable emission synthesized via one-step hydrothermal method and their application in alkaline phosphatase detection



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ABSTRACT

Alkaline phosphatase (ALP) plays an important role in normal growth. Many diseases will occur if the content of ALP is abnormal. Hence, the development of convenient and sensitive assay for monitoring ALP is extremely important. In this work, hydrophilic silicon quantum dots (SiQDs) with tunable emission were synthesized via hydrothermal method. The fluorescent emission of SiQDs was changed easily by adjusting the pH value of reaction system. The detection of ALP activity has been developed by measuring the fluorescence quenching of SiQDs. Quantitative limited evaluation of ALP activity was 1 U/L and the linear relationship was 1 U/L to 7500 U/L. Meanwhile, the fluorescent of as-prepared SiQDs were stable in physiological environment and embodied an excellent anti-interference of ions. High sensitivity and wider detection range, the proposed assay is capable of proved that they could serve as a new species of fluorescence probes for biosensors.

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1. Introduction

Silicon quantum dots (SiQDs) have biological compatibility, low toxicity and surface paint-ability [1,2]. Basing on those characteristics that mentioned above, the SiQDs have a promising future in biological and biomedical applications [3]. Some synthetic methods have been reported, mainly divided into two strategies. One is so-called “top-down” strategy. Typically, hydrophobic SiQDs had been prepared by using large-size silicon nanomaterials as the silicon source firstly, then the hydrophobic SiQDs modified with hydrophilic ligands to render them water dispersible [4]. This method can synthesize different fluorescent emission SiQDs, but the chemicals in the reaction are highly corrosive (e.g. HF, HNO₃) which may be suffer from intrinsic limitations such as potential toxicity, intrinsic blinking and chemical instability. Furthermore, the modification step invariably degrades the optical and surface properties of SiQDs [5]. The other is “bottom-up” strategy. SiQDs have been prepared via a series of reaction by using silicohydride as the silicon source. The synthesized SiQDs generally emit blue

fluorescence [6]. Therefore, the SiQDs with different fluorescent emission prepared by facile one-pot method are still much in demand.

Alkaline phosphatase (ALP) plays an important role in normal growth. Many diseases, such as nephritis, rickets, and anaemia will occur if the content of ALP is abnormal [7,8]. There are many ways to detect ALP. The frequently-used detection methods for ALP are major in electrochemical [9], chemiluminescent [10], colorimetric [11], chromatographic [12] and spectrophotometric [13]. These methods either require complex instruments or need tedious testing steps. In recent years, fluorescence detection method [14,15] is gradually becoming the main stream that use CdS and CdTe [16–18], but these materials have some toxicity. The carbon quantum dots that more convenient and less toxic gradually replaced QDs [19,20]. However, using SiQDs as detection probes has rarely been reported.

This paper reports that SiQDs have been synthesized with good fluorescence properties to detect the activity of ALP. Compared with other methods, we just use 3-Aminopropyltrimethoxysilane (APS), acrylic acid as reagents via one-step hydrothermal method to synthesized hydrophilic productions and control the fluorescent emission easily by adjusting the pH value of reaction system. The SiQDs exhibit high stability in salt and different pH values conditions. In addition, the detection of ALP activity is based on the

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fluorescence quenching of SiQDs. There are obvious linear relationships between the concentration of ALP and the fluorescence intensity of SiQDs in alkaline buffer solution. Detection range of ALP is from 2 U/L to 7500 U/L with the detection limit of 1 U/L in sensing system. Meanwhile, when the excitation wavelength is 350 nm, the fluorescence emission of the reaction system gradual changes with the further increasing enzyme amount, so that the activity of ALP can be qualitatively detected by the naked eye. From the above, a series of experiments prove the designed SiQDs have great potential applications in biological detection.

2. Experimental section

2.1. Preparation of the fluorescent SiQDs

The SiQDs are synthesized by hydrothermal method. 1 g sodium citrate is dissolved in 30 mL ultrapure water and run through with Ar for 30 mins. Then 420 μ L APS is added and adjusted the solution pH value with acrylic acid. Finally, the mixture is transferred into a 50 mL Teflon-lined stainless-steel autoclave and heated at a constant temperature of 200 °C for 4 h.

The fluorescent of as-prepared SiQDs are tested under a certain concentration and the maximum intensity of the SiQDs quenched with increasing concentrations of ALP.

2.2. Instrumentation

UV–vis spectra are recorded with a Jasco V-570 spectrophotometer at room temperature. Transmission electron microscopy (TEM) is performed with a JEOL JEM 2010F electron microscope operating at 200 kV. Infrared spectra are recorded with Excalibur 3100. Fluorescence measurements are carried out with a Cary Eclipse fluorescence spectrophotometer. The emission spectra of SiQDs are recorded upon excitation at 350 nm and 390 nm.

3. Result and discussion

3.1. Characterizations of the SiQDs

The SiQDs had been synthesized in a Teflon-lined stainless-steel autoclave at different temperatures and pH solution. The schematic illustration of the preparation process was shown in Fig. 1A which was similar to chemical reactions under hydrothermal treatment. Through the process of preparing as described above, the SiQDs with blue emission were synthesized (B-SiQDs). The fluorescence emission was changed to green when adding more acrylic acid (G-SiQDs). The fluorescence emission spectra and UV–vis absorption band were investigated to confirm the property of SiQDs. As show in Fig. 1B and C, a characteristic absorption peak of the SiQDs was observed. Fluorescence spectra of SiQDs at different excitation wavelengths were also measured. The SiQDs were able to fluorescence over a wide range of excitation wavelengths from 310 nm to 450 nm. Compared with the B-SiQDs, G-SiQDs fluorescence scope was wider and red shift more obvious with the excitation wavelengths increasing, so they emitted green fluorescence under ultraviolet light.

The size distribution and morphology of SiQDs were measured by transmission electron microscopy (TEM) image (Fig. 1D). The size distribution of SiQDs was small and the majority fell within the range from 6.5 nm to 8 nm. The resolved (111) and (220) crystalline structure with lattice planes of \sim 0.31 nm and \sim 0.19 nm spacing in the TEM image (Fig. 1D inset) demonstrate excellent crystallinity of the as well-reported SiQDs [21,22]. The Fourier Transform Infrared (FT-IR) spectroscopy also used to identify the bonding composition of SiQDs and the prominent functional groups. As shown in Fig. 1E,

several distinct absorption peaks in the range of 1000–3500 cm^{-1} . The sharp absorbances at 1400 cm^{-1} and 3450 cm^{-1} assigned to the N–H bending vibrations and the N–H stretching vibration. Most importantly, the strong absorbance at 1100 cm^{-1} ascribed to the Si–O bending vibrations that proved successfully prepare SiQDs and the absorption peaks at 1600 cm^{-1} indicated that productions had a lot of –COOH derived from acrylic acid. The results of tests showed that the SiQDs had been successfully prepared.

3.2. Effects of reaction conditions

The influence of fluorescence intensity on temperature, hydrothermal treatment time, the pH of the reaction system and the species of acid investigated. At the beginning of the reaction, the system pH values controlled at 8 to investigate the effect of reaction temperature (Figs. S1 and S2) and reaction time (Figs. S3 and S4). The reaction temperature effected the performance of SiQDs and with the reaction temperature increasing, the maximum fluorescence intensity raised significantly. This phenomenon was due to that the higher reaction temperature, so 200 °C chosen as reaction temperature. These results were consistent with the rule when the pH value was 4. The reaction time also affected the performance of SiQDs. Prolonging reaction time, the peak position of the emission spectra happened red shift (pH = 4) or blue shift (pH = 8). Comprehensive consideration of fluorescence intensity and energy conservation, 4 h was chosen as reaction time. Next, the excitation wavelength was fixed at 390 nm and other response conditions were consistent except pH value. As shown in Fig. 2A, the location of the fluorescence peak was stable at around 440 nm which reflected the blue color. Continue to add acrylic acid, making the reaction system in acidic. The maximum intensity of emission peaks obvious red shift to 480 nm which reflected the green color. In order to distinguish the influence of acrylic acid and pH value, HCl was used instead of acrylic acid to regulate pH value. The image (Fig. 2B) was shown difference between acrylic acid and HCl. The location of the fluorescence peak stable at 440 nm when pH value was 4 adjusted with HCl. All of these studies indicated, SiQDs with different fluorescence emission attributed to the blocking function and oxidation of –COOH derived from acrylic acid. Previous studies have shown that all of those visible light emission observed of SiQDs was result of recombination of electron-hole pairs generated [23]. The SiQDs emitting at 480 nm, recombination happened across the indirect band gap within the quantum dots, or via surface states whose energies coupled to the indirect band-gap energy. The blue emission would be attributable to radiative centers originating in the incomplete surface oxide. This recombination happened at the surface of the incompletely oxidized quantum dots, via centers that were not present prior to oxidation. So different fluorescence SiQDs were prepared through adding different amount of acrylic acid.

3.3. Stability test of SiQDs

To study the chemical stability of the as-prepared SiQDs, the effected of representative metallic ions and pH values on the fluorescence intensity were tested. There was a little change with 200 μ M of different metal ions adding in the solution (Fig. 3A and B). As shown in Fig. 3C and D, no matter G-SiQDs or B-SiQDs, the fluorescence intensity of the SiQDs was relatively stable over a wide range of pH values from 3.5 to 11.0. The fluorescence of B-SiQDs clearly quenched when the materials in the strong acid or alkaline solution. On the contrary, the fluorescence of G-SiQDs enhanced when pH values exceed 10. This observation was unique because previous reported documents had shown pH-quenching properties. The reason for this phenomenon maybe due to the surface

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