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Label-free silicon quantum dots as fluorescent probe for selective and sensitive detection of copper ions

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ABSTRACT

In this work, label-free silicon quantum dots (SiQDs) were used as a novel fluorescence probe for the sensitive and selective detection of Cu^{2+}. The fluorescence of the SiQDs was effectively quenched by H_2O_2 from the reaction of ascorbic acid with O_2, and hydroxyl radicals from Fenton reaction between H_2O_2 and Cu^{+}. The fluorescence intensity of SiQDs was quenched about 25% in 15 min after the addition of H_2O_2 (1 mM). While the SiQDs was incubated with AA (1 mM) and Cu^{2+} (1 μM) under the same conditions, the fluorescence intensity of SiQDs decreased about 55%. Obviously, the recycling of Cu^{2+} in the test system may lead to a dramatical decrease in the fluorescence of SiQDs. Under the optimized experimental conditions, the rate of fluorescence quenching of SiQDs was linearly dependent on the Cu^{2+} concentration ranging from 25 to 600 nM with the limit of detection as low as 8 nM, which was much lower than that of existing methods. Moreover, the probe was successfully applied to the determination of Cu^{2+} in different environmental water samples and human hair.

1. Introduction

The determination of heavy metal ions in an aquatic environment and biological systems is of great importance owing to their deleterious effects on human health [1]. As one of the heavy metals, Cu^{2+} is one of the vital trace elements for human life. Low-level copper is essential for biological activities such as enzyme regulation, metabolism and immune function [2,3]. However, an overdose of Cu^{2+} can bring about serious threats associated with gastrointestinal disturbance, liver or kidney damage [3–5]. The intracellular Cu^{2+} level is directly associated with the functions of proteins and various neurodegenerative diseases such as Alzheimer's, Wilson's diseases and Parkinson's [6]. Meanwhile, due to its widespread use, Cu^{2+} may lead to serious environmental issues. For example, it has been found that copper is highly toxic to some organisms, including many bacteria and viruses [7]. According to the guidelines for drinking-water quality of the World Health Organization (WHO), copper is identified as a "chemical of health significance in drinking-water". Therefore, the residual level of copper is restricted within 2 mg L^{-1} (32 mM) by WHO in drinking water [3].

In recent years, many analytical methods have been developed to determine copper including electrochemical methods [8,9], inductively coupled plasma mass spectroscopy (ICPMS) [10], atomic absorption spectroscopy [11–13] etc. Unfortunately, these methods require complex modification and expensive instruments and are time-consuming. Fluorescence, in contrast, has been proven to be a more powerful technique for ion detections due to its distinct advantages of high sensitivity, wide linear dynamic range and easy operation [14–16]. Especially, the fluorescent probes (organic dye) for Cu^{2+} analysis are preferable due to their high sensitivity and intrinsic operational simplicity [17–20]. Nevertheless, in terms of practical applications, these probes have some internal defects such as complicated synthesis procedure and photobleaching. Therefore, it is highly desirable to develop a facile, environment-friendly fluorescence probe for the determination of copper ions with high sensitivity and selectivity to meet the requirements in the fields of environmental monitoring, waste management and biology toxicology.

Recently, quantum dots (QDs) have been widely studied due to their outstanding fluorescence properties. Wei and colleagues reported sensing of Cu^{2+} by the manganese modified CdTe/CdS QDs [5]; Liu designed a sensor for the detection of Cu^{2+} by using CdSeTe@ZnS–SiO_2 QDs [21]; however, these heavy metal ions-containing QDs suffer from intrinsic limitations such as potential toxicity, chemical instability and intrinsic blinking [22]. Therefore, it is important to develop novel nanomaterial for fabricating low toxicity, highly sensitive and selective fluorescence probe.

Compared with those heavy-metal-based QDs, SiQDs exhibit many advantages with low toxicity, good stability, easy preparation, and environmental friendliness. What is more, SiQDs has

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been paid more and more attention due to their unique optical and electronic properties, especially the favorable biocompatibility [23].

Herein, we synthesized the SiQDs and firstly used it for fluorescence detecting Cu^{2+}. Under aerobic conditions, AA not only is involved in the reduction of Cu^{2+}, but also reacts with O_2 to produce H_2O_2. Then, the Fenton reaction between Cu^{+} and H_2O_2 resulted in hydroxyl radicals which can effectively quench the fluorescence of the SiQDs. The recycling of Cu^{2+} may dramatically amplify signal transduction. This new method is simple and easy to distinguish other metal ions and can be applied to the determination of Cu^{2+} in bio-sample.

2. Experimental

2.1. Materials and chemicals

All chemicals used in this work were of analytical reagent grade and used directly without further purification. Silicon wafer (phosphorus-doped (p-type), 8 Ω resistivity) and phosphomolybdic acid (POM) were purchased from Sigma-Aldrich. Ascorbic acid was purchased from Shanghai Chemical Reagent Co., Ltd. (China). Anhydrous ethanol (analytical grade), hydrofluoric acid (HF) and hydrogen peroxide (H_2O_2, 30%) were purchased from Shanghai Chemical Reagent. Except the specific statements, the detection buffer was phosphate buffer (PBS, pH 7.0, 10 mM sodium phosphate). Milli-Q ultrapure water (Millipore, $\geq$ 18 MΩ cm) was used throughout.

2.2. Synthesis of SiQDs

SiQDs were prepared according to the literature [23]. Briefly, Si sheet was first cleaned in 20% hydrofluoric acid (HF) for 5 min to remove surface oxides and impurities. The electrolyte was prepared by mixing anhydrous ethanol (35 mL)/HF (10 mL) with a suitable amount of H_2O_2 (30%, 35 mL) and POM (0.015 g) as the catalyst. Silicon wafer worked as the anode and carbon rod served as the cathode with the current density of 4–10 mA cm^{-2}. After etching about 1 h, large amounts of SiQDs formed on the surface of silicon wafer. SiQDs were obtained by ultrasonic treatment with well dispersion in 100 mL ethanol solution.

2.3. Fluorescence determination of Cu^{2+}

Cu^{2+} and AA aqueous solutions were freshly prepared before use. For each experiment, 200 μL of buffer and 50 μL of SiQDs solution were firstly mixed. Afterwards, 20 μL of AA solution (the final concentration was 1.0 mM) and 30 μL of Cu^{2+} stock solutions were sequentially added into the reaction buffer. The mixed solution was incubated for 15 min and then the fluorescence spectra were recorded.

2.4. Analysis of Cu^{2+} in real sample

The sample hair was treated as following: collected human hair was washed with acetone, ether, detergent and pure water, and then dried at 60 °C. 0.4 g treated dry hair was further treated with nitric acid by refluxing it at 100 °C in a conical flask. After evaporating the acid and adjusting the pH and volumne with sodium hydroxide solution and/or water, 100 mL pH 7.0 sample solution was obtained.

The concentration of Cu^{2+} in real sample was detected using the standard addition method. In brief, 30 μL of the above samples were then added to the detection systems (the total volume was 300 μL) subsequently, fluorescence emission spectra were recorded with excitation wavelength at 360 nm.

2.5. Apparatus

SiQDs was synthesized on a CHI 660A electrochemical workstation (CHI Instrument Inc., USA) with the three-electrode system. The silicon wafer with 5.0 cm length (area$\sim$5 cm^{-2}) was served as working electrode, a carbon rod (diameter of 5 mm, from Shanghai Moyang electronic and carbon Co. Ltd.) as the auxiliary electrode and a saturated calomel electrode as the reference electrode. Transmission electron microscopy (TEM) images were collected on a JEOL-1230 transmission electronic microscope (JEOL, Japan). Fourier transforms infrared (FTIR) spectra were collected on a Nicolet Nexus 670 FTIR instrument (Nicolet Instrument Co., USA). An F-4500 fluorescence spectrophotometer (Hitachi Co., Japan) was used to collect the fluorescent emission spectra of the SiQDs. The absorption spectra of the SiQDs were recorded on a UV-2450 spectrophotometer (Shimadzu Co., Japan) and atomic absorption spectrophotometer (AAS) was used to detect the concentration of Cu^{2+}.

3. Results and discussion

3.1. Characterization of SiQDs

The morphology and optical properties of the prepared SiQDs were characterized. As shown in Fig. 1, the transmission electron microscopy (TEM) (Fig. 1A) images show that the SiQDs with sizes of around 8 nm were well dispersed. The lattice fringes (Fig. 1B) and electron diffraction (ED) (Fig. 1C) are observed by HRTEM. HRTEM and ED patterns of SiQDs show that these Si nanoparticles exhibit single crystalline structures. Fig. 1D shows that the emission peaks of SiQDs did not shift with excitations ranging from 350 to 390 nm. The maximum fluorescence emission intensity can be obtained at 360 nm excitation. It has been assumed that the size of the SiQDs is uniform, which agrees with the TEM analysis. The absorption, excitation and emission spectra of SiQDs in an aqueous solution are presented in Fig.1E. The absorbance below 290 nm is due to SiQDs [24]. The emission spectrum of the SiQDs solution has a narrow range from 400 to 500 nm, which further illustrates that the size of the SiQDs is uniform [23]. The surfaces of freshly prepared SiQDs are usually covered with Si–H bonds. As shown in Fig. S1, the IR spectra clearly shows strong absorption at around 900 cm^{-1} and 2100 cm^{-1}, which can be attributed to Si–H and H–Si–Si–H stretching vibration, respectively [25]. Following the Williams method (the detailed process is described in Supporting information), the FL quantum yield of the SiQDs was obtained up to $\sim$9.1%, which was very high than the quantum yields of SiQDs obtained from the reported method [29]. By further investigation, we found that the fluorescence intensity of SiQDs was not affected by the temperature (Fig. S2A) and exhibited the maximum in solution at pH 7.0 (Fig. S3B). Moreover, the SiQDs diluted with PBS (pH 7.0) possessed excellent photostability over 10 h in air under ambient conditions without any protection (Fig. S2C).

3.2. Principle of the Cu^{2+} sensing system

The principle of the SiQDs-based fluorescent probe for Cu^{2+} is depicted in Scheme 1. In the presence of aerobic, AA not only can reduce Cu^{2+} to Cu^{+} rapidly, but also react with O_2 to produce H_2O_2 [26,27]. H_2O_2 and hydroxyl radicals yielded in Fenton reaction [6] can effectively quench the fluorescence of SiQDs by transferring electrons from the conduction band of the SiQDs to the single occupied molecular orbit of the hydroxyl radicals

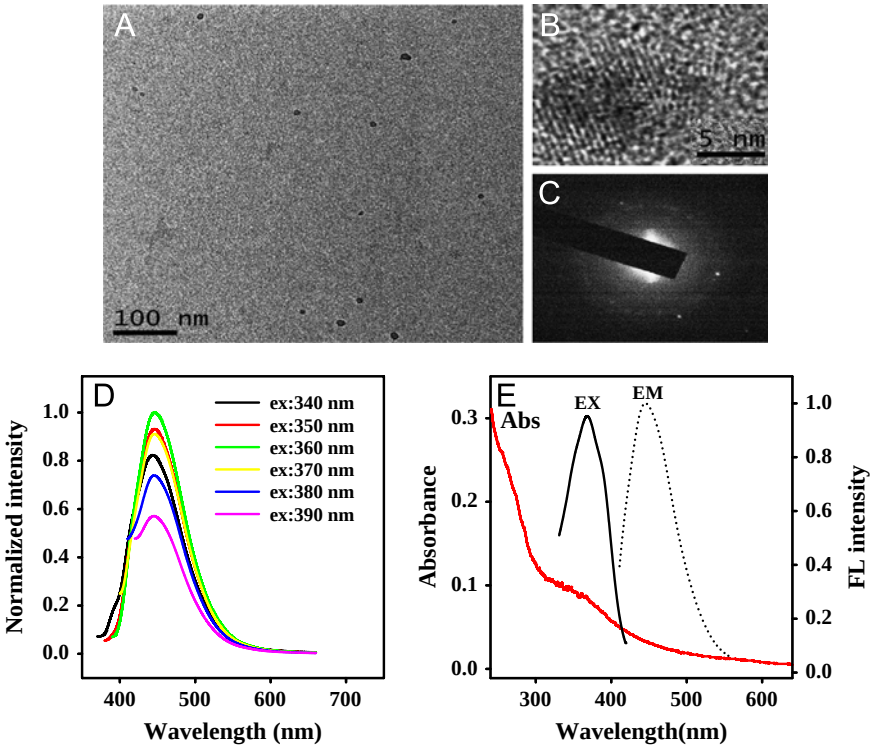
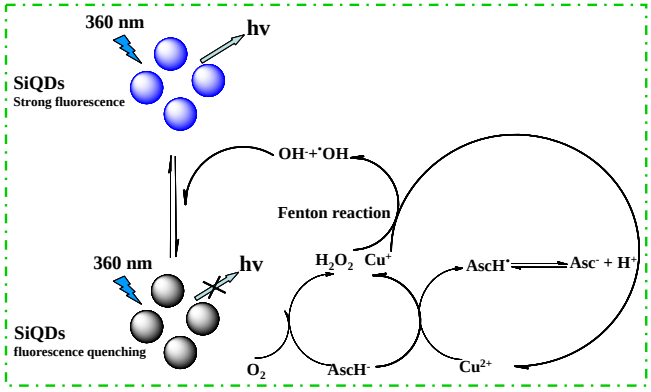


Fig. 1. Typical TEM (A), HRTEM (B) and ED images of SiQDs (C), the normalized FL spectra of SiQDs with different excitation wavelengths (D), and UV–vis absorption (red line) and excitation spectra (solid line) and emission spectra (dot line) of SiQDs (E). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Scheme 1. Illustration of the strategy for the detection of Cu^{2+} based on label free SiQDs and Fenton reaction.

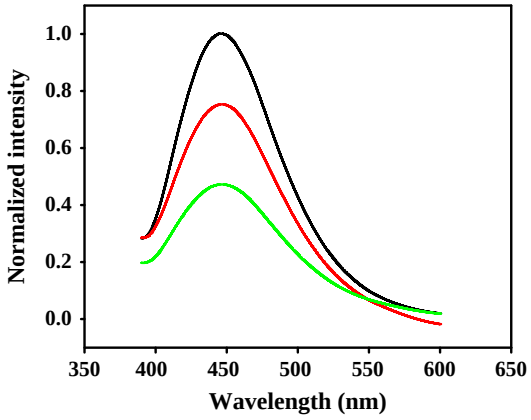


Fig. 2. The normalized FL spectra of SiQDs in pH 7.0 PBS (10 mM) (black line), SiQDs solution incubated with H_2O_2 (1 mM) (red line), SiQDs solution incubated with 1 mM AA in the presence of 1 μM Cu^{2+} for 15 min (green line). λ_{ex}=360 nm. For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

[23,28]. Therefore, the fluorescence intensity of SiQDs should decrease obviously. However, the recycling of Cu^{2+} may dramatically amplify signal transduction. Based on this mechanism, it is possible to detect Cu^{2+} by fluorescent method with SiQDs as the probe.

Some proof-of-concept experiments were performed to verify the feasibility of devolved detection method. As shown in Fig. 2, the free SiQDs showed strong fluorescence (black line). The fluorescence intensity of the SiQDs decreased by about 55% after 15 min of incubation in SiQDs solution containing AA (1 mM) and Cu^{2+} (1 μM) (green line). While the SiQDs were incubated only with H_2O_2 (1 mM) under the same conditions, the fluorescence intensity of SiQDs decreased about 25% (red line). As shown in Fig. S3A, there was only a little decrement in fluorescence when SiQDs was incubated with 0.4 μM Cu^{2+} or Cu^{+} (curves c and d). It is worth noting that the fluorescence intensity of SiQDs was slightly decreased when SiQDs was incubated with AA (curve b in Fig. S3A). It may be that the slight decrease was responsible to H_2O_2 yielded from the reaction of AA with O_2 dissolved in buffer. Curve f in Fig. S3A is the fluorescence emission spectrum of SiQDs incubated with the mixture of AA and Cu^{2+}, which showed a significant decrease in the intensity as comparing with curves a, b, c and d. While Cu^{2+} was replaced with Cu^{+}, as shown by curve e, approximately equal response was observed. This fact implies that Cu^{+} and Cu^{2+} had approximately equal effect on the fluorescence intensity of SiQDs in the test system. As AA is involved in the test system, it should be reasonable to deduct that AA reacts with both O_2 and Cu^{2+} to produce H_2O_2 and Cu^{+} and then Fenton reaction between Cu^{+} and H_2O_2 occurs and results in hydroxyl radicals. The resultant H_2O_2 and hydroxyl radicals can effectively quench the fluorescence of the SiQDs. However, the recycling of Cu^{2+} may dramatically amplify the SiQDs fluorescence signal response in the

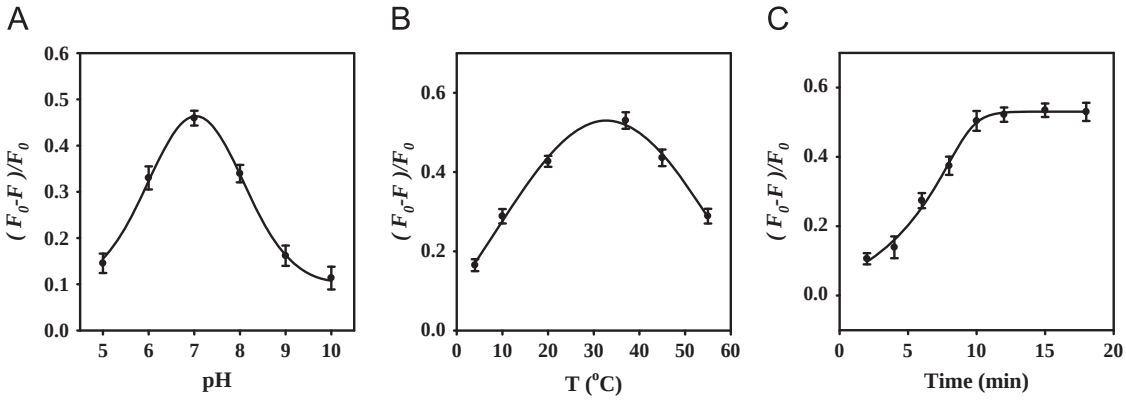


Fig. 3. Effects of pH (A), temperature (B) and incubation time (C) on the fluorescence responses of the sensor for Cu^{2+} detection. [Cu^{2+}]=0.6 μM, [AA]=1 mM. $\lambda_{ex}/\lambda_{em}$= 360/450 nm.

test system. UV–vis absorption spectroscopy of AA was recorded in the presence and absence of Cu^{2+}. As shown in Fig. S3B, the characteristic absorption peak of AA at 264 nm markedly decreased when Cu^{2+} was added into AA solution. This fact implies that AA can react with Cu^{2+} very easily. So far, all the observations support the proposed quenching mechanism.

3.3. Optimization of the sensor

In order to obtain a high-sensitive response for the detection of Cu^{2+}, the optimization of the conditions such as pH, incubation temperature and time is essential. Among the test conditions, the pH value of the solution is one of the most important factors that significantly affect the performance of the sensor. The effect of pH value on the fluorescence intensity of SiQDs was investigated at first. As shown in Fig. 3A, the $(F_0-F)/F_0$ values is termed as the quenching ratio, where F_0 refers to the fluorescence intensity of the original SiQDs and F refers to the fluorescence intensity of SiQDs incubated with the test solution. The florescence response increased gradually with the pH ranging from 5.0 to 7.0 and then decreased when pH is beyond 7.0. Thus, pH 7.0 was used throughout the experiments.

The influence of incubation temperature on the fluorescence intensity of SiQDs was investigated as well and the results are shown in Fig. 3B, which indicate that a maximum $(F_0-F)/F_0$ value was achieved when incubation temperature of 37 °C was used. Therefore, 37 °C was chosen as the optimum incubation temperature. Fig. 3C shows the dependence of fluorescence of the probe on the incubation time. As shown in Fig. 3C, the quenching ratio reached a stable value while SiQDs was incubated with the test solution for 12 min. To ensure the completeness of the reaction, SiQDs was incubated for 15 min throughout the following experiments.

3.4. The analytical performance of the sensor

The analytical performances of the sensor for the detection of Cu^{2+} were investigated under the optimum experimental conditions. As shown in Fig. 4A, the fluorescence intensity of SiQDs decreased with increasing concentration of Cu^{2+} from 0 to 1000 nM. It can be seen that the fluorescence intensity of SiQDs no longer decreased when the concentration of Cu^{2+} was higher than 800 nM. Fig. 4B presents the relationship between the fluorescence intensity of SiQDs and the concentration of Cu^{2+}. A good linear relationship and a detection limit of 8 nM with a signal-to-noise ratio of 3 were obtained in the Cu^{2+} concentration ranging from 25 nM to 600 nM. And the linear regression equation was $(F_0-F)/F_0=0.0193+0.0008C$ ($R^2=0.99$), where F_0 and F refer to fluorescence intensity of the sensor before and after adding Cu^{2+}, respectively. C refers to the concentration of Cu^{2+} in the test solution. These experimental results demonstrate that the proposed method for Cu^{2+} detection is comparable with other reported methods (Table S1, Supporting information).

3.5. Selectivity toward Cu^{2+} detection

To evaluate the specificity of the proposed sensor, the quenching ratios of SiQDs upon addition of various biologically and environmentally relevant ions such as Fe^{3+}, Ag^{+}, Sr^{2+}, Cr^{3+}, Mn^{2+},ClO^{-}, Ba^{2+}, Ca^{2+}, Ni^{2+}, Cd^{2+}, Al^{3+}, Na^{+}, Zn^{2+}, Br^{-}, Fe^{2+}, Cl^{-}, Cr^{6+}, Se^{4+}, Co^{2+}, Hg^{2+}, K^{+}, Mg^{2+}, Mo^{6+}, and V^{5+} were investigated. The results show that the competitive ions exhibited little influence on Cu^{2+} detection even at concentrations 50 times higher than that of Cu^{2+} (Fig. 5). It is worth to note that Fe^{3+} and Fe^{2+} only show weak influence on the fluorescence quenching rate of SiQDs under the tested conditions. This observation could be explained by the fact that the Fe^{3+} and Fe^{2+} involved Fenton reaction strongly depends on the pH value of the system, the reaction only markedly occurs under strong acid condition. Under strong acid conditions, Fe^{2+} was oxidized to Fe^{3+} in the presence of oxygen dissolved in the solution, while at relative high pH, Fe^{3+} was hydrolyzed to $Fe(OH)_3$ and precipitated [30–32]. Therefore, these results demonstrate that the proposed fluorescent sensor is of very high selectivity for Cu^{2+} detection.

3.6. Application of the sensor

The excellent selectivity and high sensitivity of the sensor suggest that the developed method might be directly applied for detecting Cu^{2+} in real samples. The feasibility of this new method label-free SiQDs for the detection of Cu^{2+} in different environmental water samples and human hair was verified by the standard addition method. The different environmental water samples were collected throughout the university campus. The detection of Cu^{2+} in human hair sample and in different environmental water samples was carried out according to the experimental procedure after being pretreated. The results are summarized in Table 1, which shows good agreement between the expected and found values. These results demonstrate that the proposed assay strategy is successful in the detection of Cu^{2+} in real sample. In order to further demonstrate the accuracy of this method, the concentration of Cu^{2+} in tap water was determined by the proposed assay and atomic absorption spectrometry (AAS). The concentrations of Cu^{2+} in tap water which were detected by the proposed assay and AAS are shown in Fig. 6. The results obtained by this assay are consistent with those obtained from

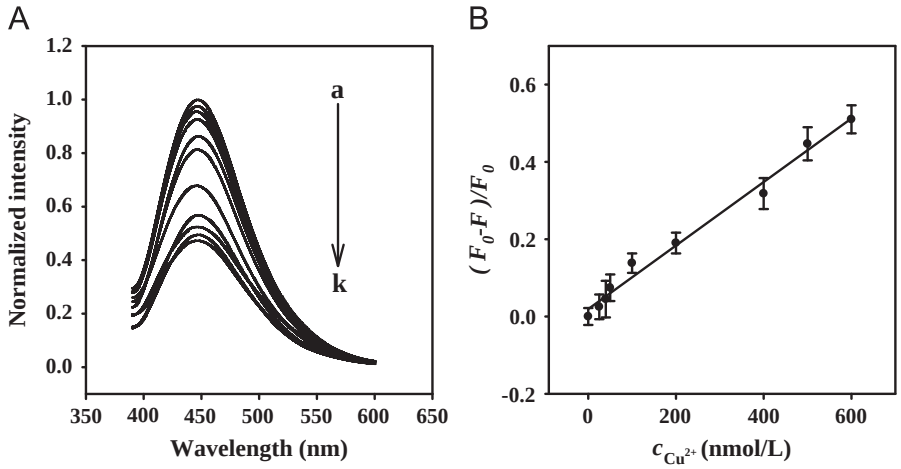


Fig. 4. (A) The normalized FL intensity of SiQDs in the presence of different concentrations of Cu^{2+}: 0, 25, 40, 50, 100, 200, 400, 500, 600, 800 and 1000 nM; [AA]=1 mM. (B) The quenching ratio vs. concentrations of Cu^{2+}.

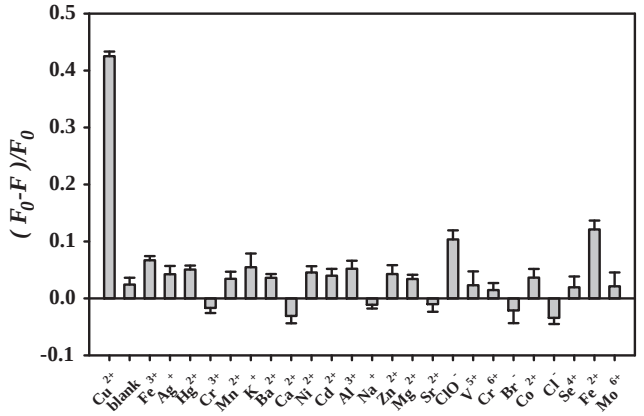


Fig. 5. The quenching ratio of SiQDs in the presence of various metal ions in PBS (pH=7): [Cu^{2+}]=0.5 μM and other ions concentration is 25 μM, [AA]=1 mM.

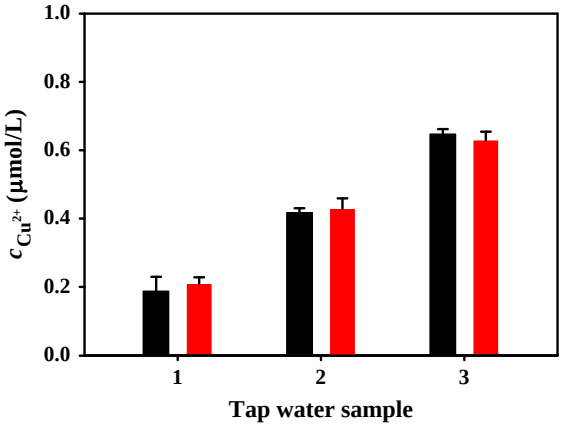


Fig. 6. Analytical results of Cu^{2+} in tap water obtained using the present method (black) and by AAS (red). For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Detection of Cu^{2+} in real sample. [AA]=1 mM. All measurements were performed in PBS, pH=7, thermostated at 37 °C for 15 min.

Sample	Added (μM)	Detected (μM)	Recovery (%)	RSD (%)
Tap wat er	0.20	0.19	95.00	1.32
	0.40	0.42	105.00	0.76
	0.60	0.65	108.33	1.12
Lake water	0.20	0.21	105.00	2.65
	0.40	0.39	97.50	1.06
	0.60	0.61	101.67	1.48
River water	0.20	0.22	110.00	3.23
	0.40	0.41	102.50	1.06
	0.60	0.64	106.67	1.67
Hair sample	0.20	0.19	95.00	2.23
	0.40	0.41	102.5	1.71
	0.60	0.62	103.33	3.54

AAS, indicating that the proposed method can be used to analyze Cu^{2+} accurately.

4. Conclusions

In conclusion, we have developed a novel fluorescent detection system for quantitative analysis of Cu^{2+} based on label-free SiQDs and Fenton reaction. The fluorescence intensity of SiQDs can be steadily quenched by incubating SiQDs with Cu^{2+} containing AA solution at pH 7 under 37 °C. The resultant hydroxyl radicals from Fenton reaction between Cu^{+} and H_2O_2 are responsible to the decrease of the fluorescence intensity of SiQDs. Experimental observations indicate that the fluorescence intensity of the incubated SiQDs is linearly dependent on the Cu^{2+} concentration in the range of 25–600 nM. The label free SiQDs have excellent photostability. Compared with other strategies for Cu^{2+} detection, the proposed sensor not only has a low detection limit, but also has the following advantages: (1) the SiQDs need not to be labeled or modified. (2) Complicated procedures for sample pretreatment is eliminated. Furthermore, our study demonstrated that this method can be used for Cu^{2+} analysis in the different environmental water samples and hair sample. In one word, this novel SiQDs-based Cu^{2+} sensor demonstrated high sensitivity, excellent selectivity and the potential to be applied in practical environmental screening.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.03.031.

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