A novel sensitive colorimetric sensor for Cu²⁺ based on in situ formation of fluorescent quantum dots with photocatalytic activity

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ABSTRACT

This work demonstrates the use of quantum dots (QDs) with photocatalytic activity as a sensitive, inexpensive and rapid colorimetric platform for Cu²⁺ sensing. Based on the simple thiol compound mediated QDs growing method, CdS QDs can be quickly formed in situ, which possess excellent photocatalytic ability for the oxidation of 3,3',5,5'-tetramethylbenzidine (TMB) to produce a colored product under light irradiation. Cu²⁺ can catalyze the oxidation of sulfhydryl groups in glutathione (GSH) which act as a stabilizer for CdS QDs. In the presence of Cu²⁺, GSH is oxidized and loss the stabilization ability for the growth of CdS QDs, thus resulting in the decrease of the absorbance. Under optimum conditions, as low as 5.3 nM Cu²⁺ can be detected. This sensing system is simple, reliable and holds great potential to provide a new general platform for ultrasensitive monitoring of a variety of analytes.

Keywords: Colorimetric sensor, copper ions, quantum dots, photocatalytic activity

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2 **1. Introduction**

3 Copper is an essential trace element which is needed by most animals. It can be
4 found throughout the body tissues. The lack of copper ions (Cu^{2+}) may lead to growth
5 restriction and metabolic disorder (Ma et al., 2011). On the other hand, copper is one
6 of the heavy metals and become toxic at high concentration levels. Thus, excessive
7 intake and accumulation of Cu^{2+} in the body may cause a series of harmful effects
8 (Georgopoulos et al., 2001; Hou and Zagorski, 2006). Considering both the positive
9 and negative effect of Cu^{2+} , its maximum allowable limit in drinking water is 20 μM
10 (U.S. EPA, 2012). So the development of sensitive and selective detection methods
11 for Cu^{2+} in the environment and biological samples is of great importance.

12 The progresses in nanotechnology enable the development of new methods for
13 Cu^{2+} detection based on nanomaterial, including fluorescence (Qing et al., 2016; Su et
14 al., 2016; Yin et al., 2016), electrochemical (Lin et al., 2010; Wang et al., 2016) and
15 colorimetric assay (Guo et al., 2011; Lou et al., 2011; Ma et al., 2011). Among them,
16 colorimetric assay has received much attention due to its simple operation, easy read
17 out by naked eyes and great potential for high throughput analysis. Traditionally,
18 horseradish peroxidase (HRP) or alkaline phosphatase (ALP) was often used as labels
19 in colorimetric sensors (Su et al., 2007; Wang et al., 2009; Yu et al., 2015). However,
20 their application is limited by the use of expensive protease, which is instable and
21 easy to denature. As alternative catalytic probes, some stable and economic
22 nanomaterials with enzyme-like characteristics (nanozymes) were employed in

1 colorimetric assay to catalyze the oxidation of the well-known chromogenic
2 enzymatic substrate TMB or 2, 2'-azinobis (3-ethylbenzthiazoline-6-sulfonic acid)
3 (ABTS) to form a colored product (Dong et al., 2012; Song et al., 2010; Zhang et al.,
4 2014). These nanozymes catalyzed oxidation process usually request for the
5 introduction of an oxidant, hydrogen peroxide (H_2O_2), which is unstable. Furthermore,
6 when mixed with H_2O_2 , substrate can be oxidized slowly even in the absence of
7 nanozymes, raising its background and complicating its application.

8 Recently, it has been reported that peroxidase-mimicking DNAzyme can catalyze
9 the oxidation of thiols to disulfides without exogenously added H_2O_2 (Golub et al.,
10 2013). This specific catalytic ability of DNAzyme has been used to modulate the
11 fluorescence of the assay, through control of the growth of quantum dots (QDs)
12 (Garai-Ibabe et al., 2014). The intrinsic advantages, such as high emission quantum
13 yields, long lifetime and good photochemical stability, make QDs attractive optical
14 probes in biological assays. Traditionally, pre-synthesized QDs were used as labels
15 tethered to recognition elements in biosensors, which may complicate the sensing
16 procedure and increase the background signal by nonspecific adsorption. To make up
17 for these deficiencies, some biocatalytic processes were applied to the synthesis of
18 QDs (Malashikhina et al., 2013; Saa et al., 2012; Saa and Pavlov, 2012).

19 Compared with fluorescence characteristics, the catalytic ability, especially
20 photocatalytic activity of QDs is rarely investigated and applied in the recognition
21 events. Various nanomaterials with photocatalytic activity have been widely employed
22 in the degradation of organic pollutants or hydrogen generation under visible or

1 ultraviolet light (Kumar et al., 2013; Xiang et al., 2012; Zhou et al., 2013). However,
2 the study of this photocatalytic activity in analytical chemistry field is still nearly
3 blank. Until very recently, dsDNA–SYBR Green I complex has been used as a
4 photocatalyst for DNA detection by Zhang et al. (Zhang et al., 2015). Besides, Pavlov
5 et al. developed a light-powered nanosensor for glucose oxidase based on enzymatic
6 generation of photocatalytical nanoparticles (Grinyte et al., 2015).

7 It is reported that Cu^{2+} can catalyze the oxidation of thiols to form disulfides (Pecci
8 et al., 1997). Some sensitive sensing platform has been fabricated based on these
9 unique catalytic properties (Lu et al., 2012; Yin et al., 2015). Inspired by these reports,
10 a simple, rapid and economic colorimetric sensor for the sensitive detection of Cu^{2+}
11 has been developed. CdS QDs, which acted as photo-catalyst, can be synthesized
12 within several minutes under simple operation and mild conditions. Specifically, no
13 extraneous oxidant was required during the catalytic oxidation process of TMB. The
14 absorption signal can be regulated by Cu^{2+} through catalyzing the aerobic oxidation of
15 GSH, which acts as a stabilizer in the formation of CdS QDs. The oxidation of TMB
16 catalyzed by CdS QDs requires irradiation with a portable ultraviolet lamp, and it
17 cannot proceed under ambient light, which promise the reproducibility and stability of
18 the read-out signal during the sensing process.

19 **2. Experimental**

20 **2.1. Materials**

21 GSH and TMB were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China)
22 and Beyotime Institute of Biotechnology (Shanghai, China), respectively. All other

1 reagents, such as citric acid, sodium citrate, cadmium acetate, H_2O_2 (30%), $\text{Cu}(\text{NO}_3)_2$
2 and Na_2S were purchased from Sinopharm Chemical Reagent Co., Ltd. The reagents
3 were of analytical grade and used without further purification. Ultrapure water
4 (Millipore, $\geq 18.2 \text{ M}\Omega \text{ cm}$) was used in all experiments. TMB was first dissolved in
5 DMSO to form a stock solution of 1 mg/mL and then diluted with citrate buffer (10
6 mM, pH 3.5) to a concentration of 2.4 mM for further use. 10 mM $\text{Cu}(\text{NO}_3)_2$ stock
7 solution was prepared with ultrapure water containing 5% HNO_3 .

8 2.2. Instruments

9 The UV–vis absorption spectrum of TMB solution was recorded using UV–2600
10 spectrophotometer (Shimadzu, Japan). Fluorescence measurement was carried out by
11 using a Cary Eclipse fluorescence spectrofluorometer (Agilent, USA). A triple UV
12 analyzer WFH-203B (Shanghai Jingke Industrial Co. Ltd., China) was used
13 for ultraviolet irradiation. High-resolution transmission electron microscopy (HRTEM)
14 image was characterized by a Philips Tecnai G2 F20 microscope (Philips, Netherlands)
15 with an accelerating voltage of 200 kV.

16 2.3. Colorimetric detection of Cu^{2+}

17 GSH (2 μL , 10 mM), 160 μL citrate buffer (10 mM, pH 3.5, containing 10 mM
18 KBr) and certain volume of ultrapure water were added into each tube. Afterwards,
19 different amount of Cu^{2+} was introduced into above tubes. The reaction was
20 performed in the dark for 1 min. Afterwards, sodium sulfide (5 μL , 10 mM) and
21 cadmium acetate (2 μL , 10 mM) was successively added and vigorously stirred for 5
22 min. Then, TMB (200 μL , 2.4 mM) was introduced and the catalytic reaction was

1 performed under 365 nm UV irradiation. The total volume of each tube is 400 μL .
2 After a reaction time of 3 min, the absorption spectra of the solutions were recorded in
3 the wavelength range from 500 to 800 nm. The maximum absorption peak at 660 nm
4 was used as the detection signal. The procedure of selectivity evaluation was the same
5 as Cu^{2+} , except that other metal ions were used instead of Cu^{2+} .

6 **3. Results and discussion**

7 3.1. Detection principle of the colorimetric sensor for Cu^{2+}

8 The schematic diagram for the sensing of Cu^{2+} is shown in Scheme 1. By the use of
9 GSH as stabilizer, S^{2-} can interact with Cd^{2+} quickly to generate fluorescent CdS QDs
10 with photocatalytic activity in situ. Under the irradiation of ultraviolet light, the CdS
11 QDs can be used as a catalyst to accelerate the oxidation of TMB to form colored
12 product without the need of additional H_2O_2 . There are three functional groups in
13 GSH: a mercapto group, an amino group and two carboxyl groups. Through the thiol
14 linkage, GSH molecule can binds to the surface of the growing CdS QDs. The amino
15 and the carboxyl groups of GSH confer hydrophilicity to the QDs in aqueous solution.
16 In the presence of Cu^{2+} , the oxidation process of the thiol in GSH is catalyzed by Cu^{2+}
17 to form disulfide bond. Due to the lack of free thiol group, the formed GSSG
18 (oxidized glutathione) has low binding ability and cannot stabilize the QDs, which
19 results in the decrease of the amounts of formed CdS QDs and the absorption signal
20 of TMB solution. As a result, sensitive detection of Cu^{2+} can be achieved through
21 measuring the characteristic absorption peak of the oxidation product of TMB.

22 Scheme 1

3.2. Characterization of the formed CdS QDs

The UV/Vis absorption spectrum and fluorescence emission spectrum of the GSH-stabilized CdS QDs are shown in Fig.1A (blue and red lines, respectively). From the UV/vis spectrum, it can be observed that the absorption gradually increased below 500 nm and reached a peak at about 350 nm, which is typical for nanoparticles with a diameter around 3 nm (Matsumoto et al., 1996). When exciting the CdS QDs at 260 nm, a fluorescence emission peak at about 520 nm is produced. HRTEM was further used to image the formed CdS QDs. As shown in Fig.1B, spherical shape CdS QDs with a median diameter of ~3 nm is appeared.

Fig.1

3.3. Photocatalytic ability of CdS QDs for the oxidation of TMB

In order to confirm that the absorption signal was caused by the formed CdS QDs with photocatalytic activity, a number of control experiments were carried out under different conditions. The experimental results are shown in Fig.2. The absorption of the TMB solution alone is negligible after UV irradiation (curve a). In the absence of TMB or UV irradiation, the formed CdS QDs also cannot produce detectable absorption signal (curve b and d). When all the essential components, such as GSH, Cd^{2+} , S^{2-} , TMB and UV light were presented, a remarkable absorption peak at 660 nm was produced (curve c). These results demonstrate that the formed CdS QDs can be used as a photocatalyst for the oxidation of TMB without the addition of H_2O_2 . To confirm the effect of Cu^{2+} itself on the photocatalytic reaction, some experiments were further performed. As shown in Fig.S1, no obvious absorption signal is observed

1 only in the presence of Cu^{2+} (curve a) or without addition of GSH (curve b, c). These
2 results indicated that Cu^{2+} cannot initiate the photocatalytic reaction to produce
3 colored product and GSH was essential for the formation of QDs with photocatalytic
4 activity. The absorption signals produced by different amount of the synthesized CdS
5 QDs are shown in Fig.S2. The absorption of oxidized TMB generated by
6 photocatalytic reaction is positively related to the amount of CdS QDs. Thus, through
7 regulating the formation amount of CdS QDs, quantitative determination of Cu^{2+} can
8 be achieved. The effect of Cu^{2+} on the fluorescence signal of CdS QDs was also
9 investigated (Fig.S3). It can be seen that without GSH as stabilizer, the CdS QDs
10 cannot be effectively synthesized after the reaction between S^{2-} and Cd^{2+} to produce
11 detectable fluorescence signal (curve e). The fluorescence intensity of the formed
12 QDs was decreased with the increasing concentration of Cu^{2+} (curve a-d). These
13 results indicated that after Cu^{2+} catalysis, the formed QDs amount was reduced due to
14 the oxidization of GSH to GSSG catalyzed by Cu^{2+} .

15 Fig.2

16 3.4. Catalytic ability of Cu^{2+} for the oxidation of GSH

17 To confirm the GSH stabilization ability for the synthesis of CdS QDs with
18 photocatalytic activity, GSSG was used instead of GSH during the synthesis process.
19 TEM image showed that the aggregation of bulk particles were formed (Fig.S4). In
20 addition, the fluorescence intensity of the product was very weak (Fig.S5, curve b).
21 These results presented that GSSG cannot be used as stabilizer to efficiently
22 synthesize the QDs. As shown in Fig.S6, only very low absorption signal was

1 obtained in the presence of GSSG (curve b). On the contrast, a strong absorption
2 signal was produced by the use of GSH as a stabilizer (curve a). These results
3 indicated that the hydrosulfuryl group of GSH was essential for the synthesis of
4 catalytically active CdS QDs.

5 It has been reported that the oxidization process of GSH to GSSG by O₂ can be
6 accelerated with the help of Cu²⁺ (Kachur et al., 1998). HPLC-MS measurement was
7 performed to verify the catalytic ability of Cu²⁺ for the oxidization of GSH (Fig.S7).
8 We found that the amount of GSH was remarkably decreased in the presence of Cu²⁺,
9 accompanied by the increase of GSSG. Hence, it can be inferred that GSH was
10 oxidized to GSSG via the catalytic effect of Cu²⁺ during the experiment. Absorption
11 spectra were conducted to study the oxidation process of GSH catalyzed by Cu²⁺
12 (Fig.S8). After addition of 10 μM Cu²⁺ to 200 μM GSH, an absorbance with a peak at
13 260 nm and a shoulder at 300 nm was produced (Fig.S8A, curve c). Generation of the
14 complex of GSH with cuprous (GS-Cu^I-SG) is responsible for this absorbance.
15 According to the report by Pecci et al. (Pecci et al., 1997), it can conclude that the
16 GS-Cu^I-SG complex is the catalytic species involved in the oxidation of GSH. After a
17 defined length of time, the absorbance at 260 nm decayed (Fig.S8A, curve b). In the
18 presence of excess GSH, the absorbance at 260 and 300 nm is proportional to the
19 amount of added Cu²⁺ (Fig.S8B). These results are similar with the reported Cu²⁺
20 catalytic oxidization process of cysteine (Pecci et al., 1997).

21 To further investigate the Cu²⁺ sensing mechanism, Cu²⁺ was added after the
22 synthesise of GSH stabilized QDs and added together with Cd²⁺ to form the QDs,

respectively (Fig.S9). We found that the absorption signals were only a little decreased under these conditions (curve b, c). However, the absorption was significantly decreased when Cu^{2+} was added to catalyze the oxidation of GSH first, and then other reagents were introduced to synthesize the QDs (curve d). These results indicated that adsorption of Cu^{2+} on the QDs or co-reaction with CdS after the catalytic GSH oxidation has no obvious effect on the TMB oxidation and the Cu^{2+} sensing principle was mainly based on the catalytic reaction.

3.5. Feasibility of the colorimetric sensor for Cu^{2+} detection

In order to examine the feasibility of the designed colorimetric sensor for the detection of Cu^{2+} , the absorption signals before and after addition of Cu^{2+} were investigated. From Fig.3, it can be observed that in the absence of Cu^{2+} , the absorption signal was strong (curve a), and the resulting solution showed a deep-green color (inset a). After addition of $1.0\ \mu\text{M}$ Cu^{2+} , the absorption signal was significantly decreased due to the lack of sufficient GSH as stabilizer for the growth of CdS QDs (curve b). At the same time, the color of the solution became lighter (inset b). When the Cu^{2+} concentration was increased to $5.0\ \mu\text{M}$, the absorption signal was almost disappeared (curve c), and the solution became colorless (inset c). These results indicated that the photocatalytic activity of the formed CdS QDs is highly sensitive to the concentration of the stabilizing molecule (GSH). Thus, a simple colorimetric assay can be established based on the catalytic ability of Cu^{2+} for the oxidation of thiol group to consume the GSH and modulate the absorption signal.

Fig.3

3.6. Sensitivity of the Cu²⁺ sensing system

Some experimental conditions were optimized to obtain the best sensing performance (Fig.S10). According to the results, 0.125 mM Na₂S, 0.05 mM Cd(Ac)₂, 0.05 mM GSH and 3 min irradiation time was used in subsequent experiments. To evaluate the sensitivity and dynamic range of the proposed colorimetric sensor for Cu²⁺ detection, various concentrations of Cu²⁺ were tested under the optimal conditions. As shown in Fig. 4A, the absorption signal was decreased with increasing concentration of Cu²⁺, accompanied by the color fading of the solution. The more Cu²⁺ was added, the more GSH was depleted, which reduces the formation amount of QDs with photocatalytic activity. A good linear response of the absorption signal against the concentrations of Cu²⁺ in the ranges from 10 nM to 2.0 μM with a correlation coefficient of 0.993 is obtained (Fig. 4B). According to triplicate standard deviation over the blank response (3σ), the detection limit of Cu²⁺ was estimated to be 5.3 nM, which was sensitive enough for Cu²⁺ detection in drinking water.

As shown in Table S1, the sensitivity of the proposed Cu²⁺ sensor was higher than that of some reported colorimetric, fluorescence and electrochemical methods. Such high sensitivity was attributed to the excellent catalytic efficiency of Cu²⁺ for accelerating the oxidation of GSH and the photocatalytic ability of CdS QDs for oxidation of TMB. In addition, the proposed sensor is simple, rapid and economical due to the mild synthesis of QDs in situ within several minutes and without the need of expensive reagents, such as nucleic acid or precious metals.

Fig.4

3.7. Selectivity and recovery performance of the Cu^{2+} sensor

In order to investigate the selectivity of the proposed sensor, interference study towards other metal ions that existed in the environment was performed in the absence or presence of Cu^{2+} . The absorption signal was tested at the same conditions, except that 5.0 μM of other metal ions were used instead of Cu^{2+} . As shown in Fig.5, the absorption signal was greatly reduced only in the presence of Cu^{2+} . The absorption signal was not significantly changed in the coexistence of Cu^{2+} with other metal ions (Fig.S11). Importantly, this selectivity can be visualized by the naked eye. Therefore, the developed colorimetric sensor was specific for Cu^{2+} detection. Compared to the detection methods which use the Cu^{2+} specific DNzyme as recognition elements, the selectivity of the proposed colorimetric sensor may be limited within relatively low concentration region. However, the cost of the colorimetric assay was much lower than the DNzyme based sensing methods.

Fig.5

The practical application of the designed Cu^{2+} sensor was also tested through determination of Cu^{2+} in lake water, river water, waste water and tap water samples (Table S2). The original concentration of Cu^{2+} in these water samples were determined to be 31.0, 59.9 and 426.8 nM by ICP-MS. Different concentrations of other metal ions were also found in these samples (detected by ICP-MS), including Cr^{3+} , Co^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} and Hg^{2+} etc. It can be found that the Cu^{2+} concentration obtained by the proposed method was in good agreement with those obtained by the ICP-MS method. These results indicated that other metal ions in the complex water

1 matrix have no significant effect on Cu^{2+} detection. Spiked samples were prepared
2 with further addition of different concentrations of standard Cu^{2+} to the tap water.
3 Each sample was repetitive measured for three times. The recovery values ranging
4 from 98.5% to 103.5% were obtained, and the relative standard deviation (RSD) was
5 lower than 10%. These results revealed that the developed sensor has acceptable
6 accuracy and reproducibility for the sensing of Cu^{2+} in real samples.

7 **4. Conclusions**

8 In summary, a novel simple and rapid colorimetric sensor, which does not require
9 any expensive reagents and complex modification procedures, has been developed for
10 the sensitive detection of Cu^{2+} based on GSH mediated growing of QDs with
11 photocatalytic activity. The whole sensing process can be completed within ten
12 minutes. Through application of the specific catalytic ability of Cu^{2+} for the oxidation
13 of thiol group to modulate the formation of QDs in situ, highly sensitive and selective
14 detection of Cu^{2+} in real water samples can be achieved. More importantly, the
15 proposed sensing strategy can provide a new general and high-throughput sensing
16 platform for a wide range of analytes based on detection of Cu^{2+} release from the
17 captured copper nanomaterials.

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3 **Appendix A. Supplementary data**

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- 9

1 **Figure Captions**

2 **Fig. 1.** (A) UV/Vis absorption spectrum (blue line) and fluorescence emission
3 spectrum (red line) of the GSH-stabilized CdS QDs. (B) HRTEM image the
4 GSH-stabilized CdS QDs.

5 **Fig. 2.** Absorbance spectra of the solution under different conditions: (a) TMB, (b)
6 GSH+Na₂S+Cd(Ac)₂, and (c) GSH+Na₂S+Cd(Ac)₂+TMB, under UV light; (d)
7 GSH+Na₂S+Cd(Ac)₂+TMB without UV irradiation.

8 **Fig. 3.** Absorption signals of the solution before (a) and after addition of (b) 1.0 μM
9 and (c) 5.0 μM Cu²⁺ (Inset: the different color changes of the solutions under
10 corresponding conditions.).

11 **Fig. 4.** (A) Absorption responses of the colorimetric sensor for Cu²⁺ at various
12 concentrations (Up to down: 0 ~ 5.0 μM). (B) The corresponding calibration plot of
13 absorption signal against the Cu²⁺ concentrations in the range from 10 nM to 2.0 μM.

14 **Fig. 5.** Selectivity investigation of the proposed sensor for Cu²⁺ detection.

15 **Scheme. 1.** Colorimetric sensor for Cu²⁺ based on the formation of quantum dots with
16 photocatalytic activity.

Fig.1

Fig.2

Fig.3

Fig.4

Fig.5