Analytica Chimica Acta 1021 (2018) 140–146

Contents lists available at ScienceDirect

Analytica Chimica Acta

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

A new colorimetric sensor for visible detection of Cu(II) based on photoreductive ability of quantum dots

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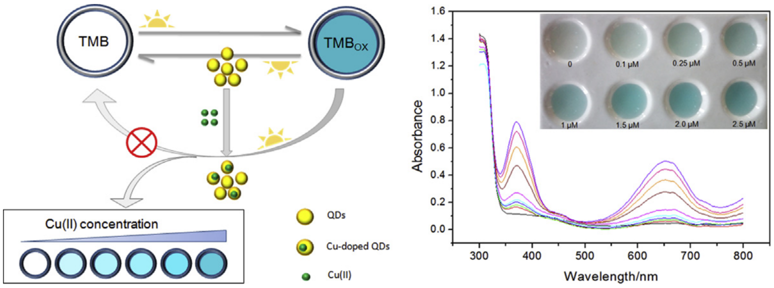
HIGHLIGHTS

- A signal-on colorimetric sensing system based on photoreductive ability of QDs was established.
- Sensitive and selective detection of Cu(II) was achieved with developed system.
- Detection limit is 10 nM via spectrophotometer and 0.1 μM by visible color change.
- Designed sensor was successfully applied for the analysis of real water samples.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 3 January 2018
Received in revised form
7 March 2018
Accepted 9 March 2018
Available online 19 March 2018

Keywords:
Photoreductive ability
Quantum dots
Colorimetric sensor
Copper ion

ABSTRACT

Quantum dots (QDs) have been widely used to develop analytical methods due to their unique fluorescent and photoelectrochemical characteristics. However, analytical strategies based on their catalytic property are rarely reported. Here, we demonstrate that the photoreductive ability of QDs can be utilized to develop a sensitive and selective colorimetric sensor for Cu(II). By using UV irradiation, 3,3′,5,5′-tetramethylbenzidine (TMB) is oxidized to its oxidation product, which can be reduced back to TMB by QDs. The presence of Cu(II) decreases the reductive activity of QDs and results in a color change in a signal-on format. The proposed sensor can be activated using a portable UV lamp or direct sunlight. Under optimized conditions, the detection limit (S/N = 3) is 10 nM via spectrophotometry and 0.1 μM by visible color change. This sensing system was applied to quantify Cu(II) in real samples, such as river water and tap water. Results were in agreement with those obtained using inductively coupled plasma spectrometry (ICP). This study may provide new ideas for the development of QD-based sensors.

1. Introduction

Given that the lack or excessive accumulation of Cu(II) in the human body may cause negative effects [1,2], the copper content has gained considerable concern in a variety of matrices. For instance, the maximum allowable concentration of copper for drinking water is 1.3 mg/L [3] and the migration limit of copper for toys is 156 mg/kg [4]. To ensure conformance to these regulations, the determination of Cu(II) is thus of great importance. A number of analytical approaches have been developed for Cu(II), including atomic absorption spectrometer [5], inductively coupled plasma spectrometry (ICP) [6], electrochemical methods [7–9], fluorescence methods [10,11] and colorimetric methods [12,13]. Among these methods, colorimetric methods are advantageous because they enable visible inspection, which replaces complicated readout

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https://doi.org/10.1016/j.aca.2018.03.011

devices.

The most widely used colorimetric method for Cu(II) is based on chemosensors, which utilize specific chemical probes to create color change [14–18]. Nanoparticles have also gained considerable attention in developing colorimetric sensors due to their unique properties. Au nanoparticles [19], Ag nanoparticles [20] and zinc oxide nanoparticles [12] have been used to develop Cu(II) colorimetric sensors. Quantum dots (QDs), which are fluorescent nanoparticles with unique optical and electronic properties, attracted profound attention in spectroscopic detection [21–23] during the past 15 years. Fluorescence sensors [10,24], photoelectrochemical sensors [25–27], and electrochemiluminescent sensors [28] that utilize the fluorescent or photoelectrochemical characteristics of varieties of QDs have been reported for Cu(II) analysis. However, analytical strategies based on the catalytic property of QDs, including QDs-based colorimetric methods, are rarely reported. Recently, Zhang et al. [29] developed a signal-off colorimetric sensor based on in-situ synthesized CdS QDs. The CdS QDs were used as a catalyst to accelerate the oxidation of 3,3′,5,5′-tetramethylbenzidine (TMB) under UV irradiation and the presence of Cu(II) inhibited the in situ formation of CdS QDs, resulting in a signal decrease. TMB is a well-known chromogenic enzymatic substrate that has been widely used for colorimetric assays [30–32].

In this work, we observed that some types of QDs exhibit photoreductive ability to TMB oxidation products under UV irradiation. On the basis of this observation, a new sensitive and selective colorimetric sensor for Cu(II) was designed, characterized, and optimized. The proposed sensor works in a signal-on manner, with color change from colorless to blue, which is convenient for observation. Its sensing process is uncomplicated because it uses pre-synthesized QDs to avoid the in-situ formation of QDs.

2. Experimental

2.1. Materials

TMB and $CuCl_2$ were purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). Dimethyl sulfoxide was purchased from Amresco LLC (Solon, USA). Mercaptosuccinic acid, trisodium citrate dehydrate, citric acid monohydrate and acetic acid were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All reagents were of analytical grade and were used without further purification. CdTe/CdS QDs (emission wavelength was 560 ± 5 nm, 5 μM) were purchased from Beidajubang Science Technology Co. Ltd. (Beijing, China). ZnSe/ZnS-MPA QDs (emission wavelength was 430 nm, 20 μM) were purchased from Xingshuo Nanotech Co. Ltd. (Suzhou, China). InP/ZnS QDs (emission wavelength was 580 ± 10 nm, 67 μM) were purchased from Xingzi New Material Technology Development Co. Ltd. (Shanghai, China). These QDs were diluted to a certain concentration with ultrapure water for further use. Ultrapure water (Millipore, ≧18.2 MΩ) was used in all experiments. TMB was first dissolved in dimethyl sulfoxide (DMSO) to form a stock solution of 1500 mg/L 10 mM $CuCl_2$ stock solution was prepared and diluted to a certain concentration with ultrapure water for further use.

2.2. Apparatus

The UV–vis absorption spectra were obtained using an UV-3600 spectrophotometer (Shimadzu, Japan). The fluorescence spectra were obtained using a Fluorolog-3 fluorescence spectrophotometer (Horiba, Japan). High-resolution transmission electron microscopy (HRTEM) characterization was performed using a JEM-2100 microscope (JEOL, Japan). ICP measurements were performed using an Optima 8300 inductively coupled plasma spectrometer (PerkinElmer, USA). A 10 W CEL-LUV254 low-pressure mercury lamp (Ceaulight, China, λ = 254 nm) and a xenon lamp (Ceaulight, China) with different wavelength filters were used to provide UV irradiation. The intensity of the UV lamp was measured using a ST512 UVC digital light meter (Sentry, China) with the spectral region ranging from 220-275 nm.

2.3. Colorimetric detection of Cu(II)

Firstly, 20 μL of CdTe/CdS QDs (1 μM), 20 μL of TMB (1500 mg/L), and 200 μL of Cu(II) standard solution of various concentrations were mixed with 160 μL citrate buffer (0.1 M, pH 4.5). The reaction was performed under 254 nm UV irradiation. After the reaction, optical images of the solutions were taken immediately using a digital camera. The absorption spectra of the solutions were recorded from 300 to 800 nm. The absorption peak at 650 nm was used as the detection signal. The spectrum analysis should be performed within 10 min after the sensing procedure.

2.4. Pretreatment of the real samples

River water and tap water were collected using PET bottles from Tonghui River in Beijing and our laboratory, respectively. The analysis was performed no later than 12 h after the collection. Prior to the analysis, the water was filtered through a 0.45 μm cellulose acetate membrane to remove tiny insoluble substances and then purified using an ENVI-carb solid phase extraction (SPE) column to reduce the content of organic compounds. The sample solution was analyzed in accordance with the above-mentioned procedures by replacing the Cu(II) standard solution.

3. Results and discussion

3.1. Design of the proposed sensor

Fig. 1 outlines the brief design of the proposed sensor. Under UV irradiation, the colorless TMB is oxidized to the blue TMB oxidation product (TMB_{ox}). Meanwhile, TMB_{ox} is reduced to TMB by the photo-induced electrons generated from the QDs. By adjusting concentration of the QDs and irradiation time, the solution can remain colorless, which is considered as the initial state of the TMB-QDs sensing system. The presence of Cu(II) triggers a composition change of the QDs, which decreases their reductive activity and changes the solution color. The solution

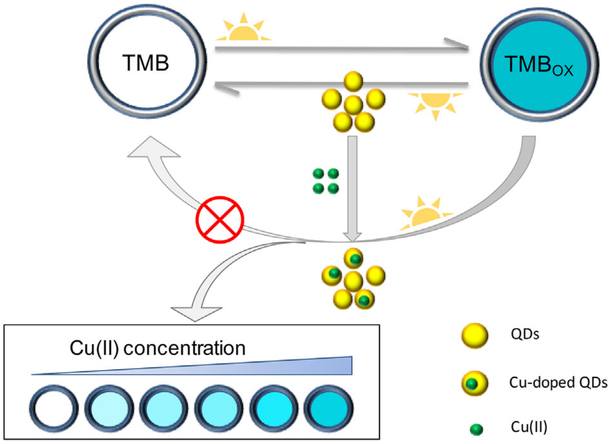

Fig. 1. Schematic illustration of the proposed colorimetric sensor for Cu(II).