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## An *in situ* applicable colorimetric Cu<sup>2+</sup> sensor using quantum dot quenching

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In this study, a rapid, convenient and *in situ* applicable Cu<sup>2+</sup> sensor was constructed based on a luminescent layer immobilizing Ru(bpy)<sub>3</sub>Cl<sub>2</sub> with a maximum wavelength of 600 nm, which was taken as the reference background light. The luminescence intensity of the layer was kept constant and isolated from the oxygen change in the solution due to the hybrid polyacrylonitrile–dimethylsulfoxide used in the immobilization of the Ru(bpy)<sub>3</sub>Cl<sub>2</sub>. The CdTe quantum dot (QD) luminescence, with a maximum wavelength of 520 nm, was quenched to different degrees depending on the Cu<sup>2+</sup> concentration in the solution. Using a commercial camera, different colors could be captured in different Cu<sup>2+</sup> concentrations. This color change was caused by the composite light with stable luminescence from the Ru(bpy)<sub>3</sub>Cl<sub>2</sub> layer and the changeable fluorescence of the CdTe QDs. Sensor characteristics, including the co-existing ions, oxygen content, temperature effect, and sensor stability, were investigated.

In recent years, there has been a growing need or demand for the determination of trace metal ions such as Cu<sup>2+</sup>, due to its important role in many biological processes, including blood formation and the functioning of various enzymes.<sup>1</sup> Several methods for Cu<sup>2+</sup> determination at the trace quantity level have been proposed, including atomic absorption spectroscopy,<sup>2</sup> inductively coupled plasma atomic emission,<sup>3</sup> mass spectroscopy,<sup>4</sup> fluorescence spectroscopy<sup>5</sup> and electroanalytical approaches.<sup>6</sup> These methods require relatively high cost apparatus and are not easily adaptable for online monitoring. Therefore, a growing interest has evolved in various laboratories for the development of Cu<sup>2+</sup> monitoring chemical sensors and, in recent years, there have been a number of publications dealing with optical copper sensing.<sup>7,8</sup> Due to their special advantages, such as simplicity, rapidity and feasible readable characteristics, colorimetric sensing approaches<sup>9,10</sup> have attracted much attention. Generally, in the colorimetric sensing system, double light beams with different wavelengths generated from the sensor are employed. Different colors can be obtained when one of the light intensities changes while the other intensity is kept constant. Several successful applications are

reported in the colorimetric sensing determination of oxygen,<sup>9</sup> glucose<sup>11</sup> and pH.<sup>12</sup> Here, we report a colorimetric Cu<sup>2+</sup> sensor based on the luminescence of Ru(bpy)<sub>3</sub>Cl<sub>2</sub> and the quenching of CdTe QDs. The characteristics of the constructed sensor have been investigated.

Tellurium powder, cadmium chloride and CuCl<sub>2</sub>·2H<sub>2</sub>O were purchased from the National Pharmaceutical Group Chemical Reagent Co. Ltd, China; glutathione and Ru(bpy)<sub>3</sub>Cl<sub>2</sub> were obtained from Sigma-Aldrich (USA); dimethyldimethoxysilane (DiMe-DMOS) and tetramethoxysilane (TMOS) were purchased from Fluka (Switzerland); and polyacrylonitrile (PAN) was provided by Xiamen University. All the chemicals were of analytical reagent grade and used without further purification. The pure water for solution preparation was from a Millipore autopure WR600A system (USA), and this was used throughout our study.

In general, the fluorescence of Ru(bpy)<sub>3</sub>Cl<sub>2</sub> is obviously quenched by dissolved oxygen in water. However, the common preparation approaches and materials such as TMOS and DiMe-DMOS for Ru(bpy)<sub>3</sub>Cl<sub>2</sub> immobilization are unsuitable. In the preparation of the Ru(bpy)<sub>3</sub>Cl<sub>2</sub> layer, PAN was selected to increase the film compactability of the hybrid. Typically, 0.05 g PAN was dissolved in 1.0 mL DMSO, and 2 mg Ru(bpy)<sub>3</sub>Cl<sub>2</sub> was then added. The mixture was magnetically stirred for approximately 1 min to ensure homogenization. A film was prepared by pipetting 40 μL of the mixture onto a glass slide (5.3 cm × 1.5 cm × 0.1 cm), which had been soaked in concentrated nitric acid for 12 h and washed with distilled water and ethanol. The area of the layer was approximately 1.5 cm × 2 cm. The prepared Ru(bpy)<sub>3</sub>Cl<sub>2</sub> layer was thermally cured in an oven for 24 hours at 80 °C, and then cooled to room temperature ready for use. The luminescence intensity change for each prepared Ru(bpy)<sub>3</sub>Cl<sub>2</sub> layer was less than 3.5%.

The luminescence spectra of the layer immobilizing Ru(bpy)<sub>3</sub>Cl<sub>2</sub> were measured using an F-4500 spectrofluorimeter (Hitachi, Japan), and an LWMC-205 microwave chemical reactor (Shenzhen, China) and a TG16-WS high-speed desktop centrifuge (Shanghai, China) were used for CdTe QD synthesis. A 1 cm cuvette holder with a 450 nm filter (Ocean Optics Inc., USA) was used in the sensing system. The sensing colors were captured using a Nikon D300 CCD camera (Japan), setting the ISO at 3200, the white balance at 5880 K and the shutter time at 1/1.3 s or 3 s. The experimental temperature was controlled using a Julabo F12-ED (Julabo Inc., Germany) refrigerated/heating circulator.

In the experiment, CdTe was synthesized as reported.<sup>9</sup> 250 μL 10<sup>-5</sup> mol L<sup>-1</sup> CdTe QDs were added into a quartz cuvette containing

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different concentrations of  $\text{Cu}^{2+}$  solution, and then pure water was added to keep the final volume at 2.5 mL. Under the different  $\text{Cu}^{2+}$  concentrations, different fluorescence quenching of CdTe QDs occurred. A glass slide immobilized  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  layer was inserted in the cuvette as shown in Fig. 1 and an LED with a maximum emission wavelength of 396 nm was used as the emission source. After mixing the solution for 3 min, the resulting colors were recorded using the Nikon camera.

Generally, inorganic QDs are of narrow and symmetric photoluminescence, tunable color, wide excitation wavelength and low cost to synthesize. Water-soluble CdTe QDs are ideal fluophors due to their unique optical properties, low cost and ease of scale-up, and have been widely used for multicolor visualized sensing and encoding. In our experiment, the UV-visible absorption and fluorescence characterizations of the synthesized CdTe QDs were observed. As shown in Fig. 2, in the UV-visible spectrum, a clear absorption peak with a peak half-width of 25 nm at 482 nm could be obtained, indicating homogeneity of the synthesized CdTe QDs and narrow size distribution. The maximum fluorescence emission wavelength was found at 520 nm. The green color emission was very suitable and could be used in the colorimetric sensing approach. In addition, the wavelength at 396 nm could be selected for the fluorescence of excitation CdTe QDs, which closely met the maximum emission wavelength of  $\text{Ru}(\text{bpy})_3\text{Cl}_2$ . This characteristic made a simple LED available.

Taken as a background color, the fluorescence intensity should be constant, which requires that dissolved oxygen does not affect the fluorescence intensity of the  $\text{Ru}(\text{bpy})_3\text{Cl}_2$ . It is well-known that oxygen quenches obviously the fluorescence of Ru complexes immobilized in appropriate materials such as organically modified silicates,<sup>9,13</sup> which are of high hydrophobicity and have suitable distribution and diameter apertures in the material. However, using PAN and DiMe-DMOS as precursors, the sensing layer presented lower or even no response of  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  to the change in oxygen concentration because of its lower permeability and higher hydrophilic nature. In our experiment,  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  was immobilized in PAN-DiMe-DMOS and deposited into a cuvette containing  $\text{Cu}^{2+}$  solution. Then, pure  $\text{N}_2$  was bubbled into the solution for 40 min to remove the original dissolved oxygen. Different ratios of  $\text{N}_2$  and  $\text{O}_2$

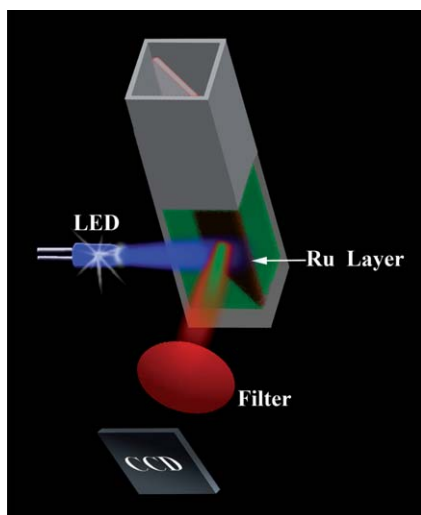


Fig. 1 Colorimetric  $\text{Cu}^{2+}$  sensing assembly.

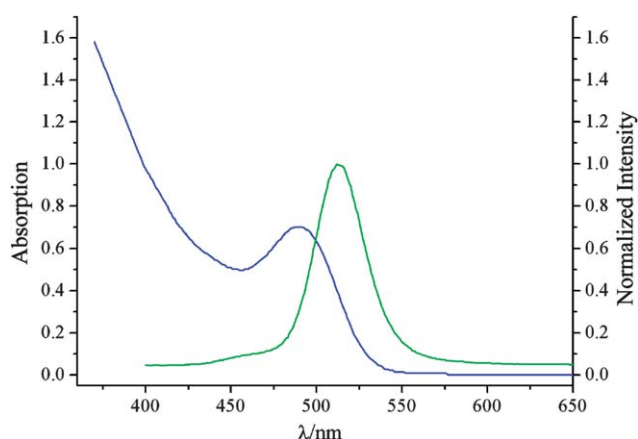


Fig. 2 Absorption and fluorescence spectra of QDs.

gases were mixed and used to investigate the sensing response of the  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  layer to changes in oxygen concentration. As shown in Fig. 3, no obvious change in fluorescence intensity could be found at 600 nm in the different oxygen concentrations, indicating the fluorescence stability of  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  immobilized PAN-DiMe-DMOS. This characteristic ensured that the luminescence from  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  immobilized PAN-DiMe-DMOS could be taken as a stable reference color for the colorimetric sensing of  $\text{Cu}^{2+}$  in aqueous solution.

Because the results of colorimetric determination were directly resolved by the light intensity of two fluophors, in order to know more concerning the applicability of the colorimetric sensor and to obtain a more visible determination range, we needed to determine their fluorescence spectra. By this approach, matching the emission wavelengths for the selected fluophors is a key parameter to obtain higher resolving ability and sensitivity. In our prior results,<sup>9</sup> the 520 nm emission of CdTe QDs (green color) matched well with the Ru complex fluophor with approximately 600 nm emission wavelength (red color). As shown in Fig. 4a, two fluorescence peaks (at 520 nm and 600 nm) could be observed, which corresponded to the emissions of CdTe QDs in solution and the  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  layer, respectively. With the addition of  $\text{Cu}^{2+}$ , the fluorescence intensity at 520 nm of CdTe QDs decreased, but the intensity at 600 nm remained constant.

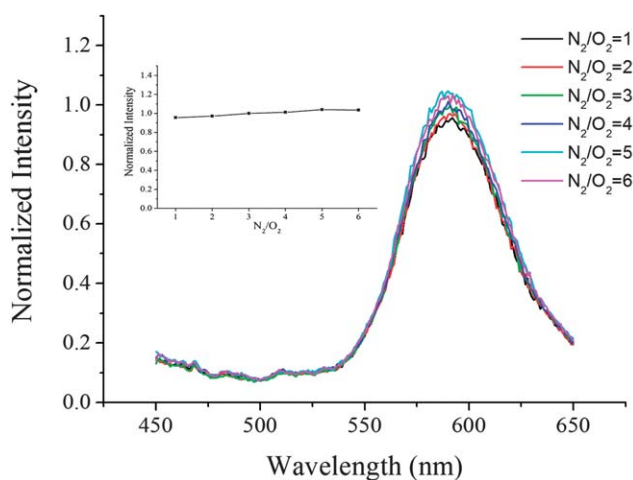
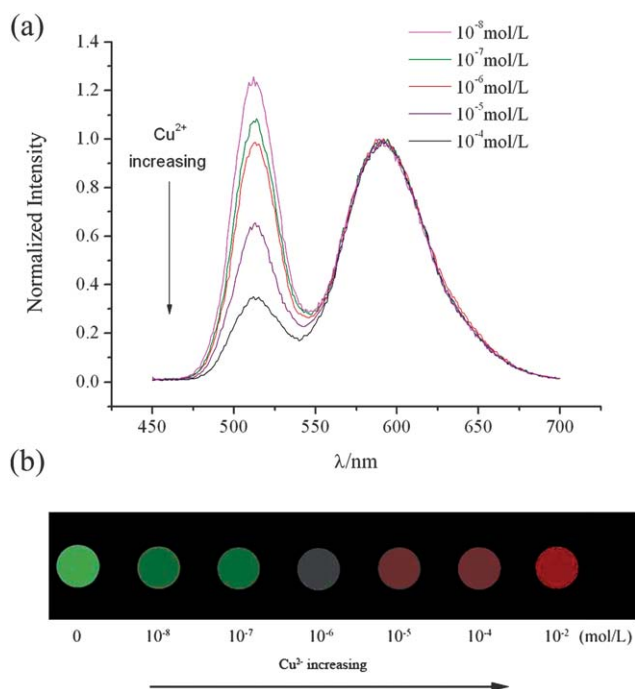


Fig. 3 Response of  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  immobilized in PAN-DiMe-DMOS to different oxygen concentrations.

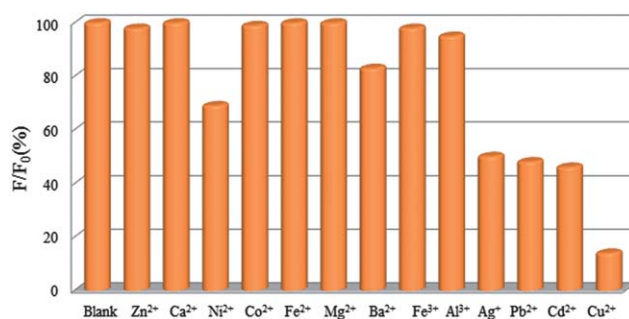


**Fig. 4** Fluorescence spectra (a) and CCD images (b) with different concentrations of  $\text{Cu}^{2+}$ .

These results indicated that CdTe QDs are sensitive towards changes in  $\text{Cu}^{2+}$  concentration due to the  $\text{Cu}^{2+}$  quenching effect, whereas the  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  immobilized in the PAN–DiMe–DMOS layer is inert to such change.

Based on the above results, in the configuration of our colorimetric optical  $\text{Cu}^{2+}$  sensor, the stable red background color from the  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  layer supplied the background light to mix with the CdTe QD fluorescence, so that the intensity signal could be transformed into color. In order to obtain a distinct apparent color, a suitable concentration of  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  in the PAN–DiMe–DMOS layer (which decided the intensity of the background light color) was taken into consideration. The results indicated that  $2.0 \text{ mg L}^{-1}$   $\text{Ru}(\text{bpy})_3\text{Cl}_2$  in DMOS and  $40 \mu\text{L}$  for the layer preparation were suitable to provide a stable and optimal background light. In different  $\text{Cu}^{2+}$  solutions, the responses of the  $\text{Cu}^{2+}$  sensor in terms of its fluorescence spectra are also shown in Fig. 4a. Favorable corresponding color images were captured by the Nikon camera and the results are presented in Fig. 4b. The results indicated that the sensor presented obvious color changes in different concentrations of  $\text{Cu}^{2+}$  solution. Under the selected conditions, the colorimetric optical  $\text{Cu}^{2+}$  sensor gave distinguishable color change at a concentration of  $10^{-8} \text{ mol L}^{-1}$ , and its linearity between the apparent color and  $\text{Cu}^{2+}$  concentration ranged from  $10^{-8}$  to  $10^{-3} \text{ mol L}^{-1}$ . Sensor stability studies revealed that the  $\text{Cu}^{2+}$  sensor presented good stability with a relative standard deviation smaller than 5% in 12 continuous measurements in  $10^{-5} \text{ mol L}^{-1} \text{ Cu}^{2+}$ .

In this  $\text{Cu}^{2+}$  sensing approach, the luminescence from  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  was kept constant, but the fluorescence intensity of the CdTe QDs might be affected by co-existing metal ions, temperature or pH, resulting in color changes of the sensor. In the following experiments, the original fluorescence intensity of CdTe QDs was taken as  $F_0$ , and  $F$  was the corresponding intensity after the addition of the metal ion. Among the tested metal ions were  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{2+}$ ,



**Fig. 5** Quenching ability of metal ions towards CdTe QD fluorescence (metal ion concentrations were all  $10^{-4} \text{ mol L}^{-1}$ ).

$\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  (all  $10^{-4} \text{ mol L}^{-1}$ ) and, as shown in Fig. 5,  $\text{Cu}^{2+}$  gave the most obvious fluorescence quenching of CdTe QDs, and its  $F/F_0$  was found to be about 14%. Furthermore,  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$  or  $\text{Cd}^{2+}$  presented definite quenching ability, and their  $F/F_0$  values were 50%, 45.5% and 45.5%, respectively, which indicated that their effects should be considered for use in  $\text{Cu}^{2+}$  sensing applications. The experimental results further indicated that the addition of  $0.01 \text{ mol L}^{-1} \text{ NH}_4\text{Cl}$  was very helpful to reduce these effects, and the  $F/F_0$  values were reduced to 100%, 83.3% and 83.3% in pH 6.0 buffer solution.

The fluorescence intensity of the CdTe QDs also presented a slight dependence on temperature. The temperature quenching of the CdTe QD fluorescence above  $15^\circ\text{C}$  is reversed to temperature anti-quenching below  $15^\circ\text{C}$ ,<sup>14</sup> and this is accompanied by a slight red shift in the spectrum with increase in temperature. This phenomenon might be caused by inter-QD dipole–dipole interactions.<sup>15</sup> The variation in fluorescence intensity decay of the  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  layer with increase in temperature resulted in this quenching effect becoming tenuous. Comparing a combination of these two effects on the apparent color of our prepared  $\text{Cu}^{2+}$  sensor, temperature had an inconspicuous influence at the present resolution, but at much higher resolution, temperature effects should be taken into consideration. In our study, there was a relationship between the temperature behavior of the QDs and the  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  layer, and so the temperature effect could also be calibrated for more precise quantitative  $\text{Cu}^{2+}$  determination.

In the colorimetric  $\text{Cu}^{2+}$  sensing approach, the  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  layer could be used in different concentrations of  $\text{Cu}^{2+}$  solutions for up to 3 months. The layer could be washed or stored using phosphate buffer solution, and 96% of the fluorescence intensity could be recovered even after 100 times of testing. After being stored in the refrigerator at  $4^\circ\text{C}$  for 6 months, 94% of the fluorescence intensity could be retrieved, and no obvious color variation in the  $10^{-4} \text{ mol L}^{-1} \text{ Cu}^{2+}$  occurred. In aqueous media, the fluorescence intensity of CdTe QDs increased from 30 min to 48 h. After 48 h storage in a dark environment, the intensity remained constant and the prepared CdTe QDs could be used for more than one week.

## Conclusions

We made a direct readout colorimetric optical  $\text{Cu}^{2+}$  sensor. The sensor achieved a detection range from  $10^{-8}$  to  $10^{-3} \text{ mol L}^{-1}$  for  $\text{Cu}^{2+}$  determination. The  $\text{Cu}^{2+}$  concentration could easily be recorded or read using a commercial CCD camera, which made the  $\text{Cu}^{2+}$  determination rapid, convenient and easy. In addition, only a few co-existing metal ions such as  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  affected the sensing

applications, but adding a small amount of NH<sub>4</sub>Cl decreased their interference. This model will provide new routes for colorimetric sensing approaches. For example, after the modification of functional groups or molecularly imprinted polymers onto the surfaces of the CdTe QDs, the sensing selectivity will be obviously improved, which will extend the applications of this sensor.

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