Carbon Dots-based Hybrid Fluorescent Sensor for Detecting Free Chlorine in Water Media

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Abstract: A novel fluorescence sensor has been prepared for quantitative detection of free chlorinein water media. The sensor contains fluorescence carbon dots (CDs) and Rhodamine B (RhB) nanohybrid, which possesses their respective emission peaks at 445 and 580 nm under excitation wavelength of 380 nm. The fluorescence of CDs could be quenched by free chlorine through combination of chemical bonds and energy transfer while the peak of RhB almost keeps constant, leading to color changes

that can be recognized by naked eyes. The designed sensor could achieve the detection of free chlorine rapidly with detection limit as low as 4 μM.

Key Words: fluorescence sensor, carbon dots, Rhodamine B, free chlorine

1. Introduction

Free chlorine, the main effective composition of disinfection in cities' tap water, has been widely used as a decolorizer in many fields like daily life, medicine, water treatment and so on.[1, 2] Free chlorine can come into the body through inhalation, eat and skin contact absorption. Excess free chlorine can lead to palm sweating and hair loss. [3, 4] As the progress of regional urbanization become faster, and urban water consumption is greatly increased, free chlorine is inevitably poses a safety hazard to human health. The WHO drinking water standard states that the maximum amount of chlorine allowed is 5 mg L^{-1} (140 μM), while 2－3 mg L^{-1} (56~84 μM) chlorine gives satisfactory disinfection and residual concentration.[5] Therefore, the precise determination of free chloride in water is of great importance. Up to now, many methods have been developed to detect free chlorine concentrations, including iodine stoichiometry titration method,[6] colorimetric method,[7, 8] continuous flow method [9] and electrochemical method.[10] However, these methods are either not precise enough or too complicated.[8-13]

Recently, novel nano-materials have attracted a lot of attention in biological analysis and detection.[14] Carbon dots (CDs) is a kind of novel fluorescence nano-material with low cost, low toxicity, good optical properties and good biocompatibility.[15-18] Due to its unique characteristic, CDs have been widely used[19-25] for detecting Cu^{2+},[23] Hg^{2+},[24] Fe^{3+},[25]and so on.

On account of this, we designed a fluorescence sensor based on nanohybrid of CDs and RhB for the detection of free chlorine. To our knowledge, it is the first time to use CDs-RhB hybrid system for quantitative detection of free chlorine. There are two fluorescence peaks in CDs-RhB nanohybrid and the fluorescence of CDs would be quenched with addition of NaClO while the peak of RhB almost keeps constant. In the Scheme 1, an obvious color change (rose red to lilac) is accompanied in the process which is very convenient to distinguish by naked eyes.

2. Experimental section

2.1 Materials and reagents

Ethylenediamine, citric acid, nitric acid and sodium carbonate (Na_2CO_3) were obtained from Sinopharm Chemical Reagents Co., Ltd. Rhodamine B was supplied by Amresco (USA). Phosphate buffer solution (PBS) was prepared using 0.01 M Na_2HPO_4, 0.01 M KH_2PO_4, 0.1 M HCl and 0.1 M NaOH. A standard free chlorine solution was prepared by diluting a sodium hypochlorite aqueous solution (Shantou Lotus Pond Chemical Co., Ltd). All the other chemicals were of analytical grade and were used as received.

Fluorescence spectra were obtained by using an FL-4600 spectrometer (Hitachi, Japan). UV-visible absorption spectra were collected on a Shimadzu UV-2450 spectrophotometer. Transmission electron microscopy (TEM) images were obtained with a T20 FEI TECNAI G2 (America, FEI).

2.2 Preparation of fluorescence carbon dots (CDs)

CDs were synthesized according to a reference method.[26, 27] 670 mL ethylenediamine and 2.1 g citric acid were dissolved in 20 mL deionized water. The solution was then transferred to a Teflonlioed autoclave (30 mL) and heated at 250 □ for 5 h. Subsequently, in order to obtain abundant carboxyl groups on the surface of CDs, the crude suspension of CDs was mixed with concentrated nitric acid and heated at reflux for 12 h. The solution obtained above was first neutralized with a Na_2CO_3 solution after cooling to room temperature. Then obtained nanoparticles were dialyzed against Milli-Q water for 3 days to remove all salts. Finally the suspension appeared homogeneous light yellow was stored at 4 □ in icebox. As estimated from TEM images, the diameter of the carbon dots was around 8 nm.

2.3 Detection of free chlorine

15μL of CDs (0.7 mg/ mL) suspension and 10μL of RhB (0.5 mmol/L) solution were first mixed in PBS (0.1 M, pH 8) at room temperature and shaken for half an hour. Then, a series of 20 μL of NaClO solutions with different concentrations were added and the final mixture solution was diluted to 250 μL with PBS. After 30 minutes shaken to ensure sufficient reaction, the fluorescence intensities of the resulted solution were recorded under an optimal excitation wavelength of 380 nm.

2.4 Analysis of real sample

The real sample of tap water was obtained from canteen of Central South University. The water sample was centrifuged at 7500 rpm for 30 min, and then the subsequent steps were similar to the detection of free chlorine except that the PBS solution was replaced by real tap water.

3. Results and Discussion

3.1 Characterization of CDs-RhB

We first synthesized CDs using citric acid and ethylenediamine as precursors. Figure 1 shows the TEM image of CDs. From the image, it is indicated that the diameter of the nanosized carbon dots is around 8 nm. Moreover, the fluorescence spectra of RhB and CDs with addition of 140 μM of NaClO were investigated, respectively (Figure 2). As shown from Figure 2a, it is obvious that the fluorescence peak of RhB at 580 nm declined a little (576 a.u).However, the fluorescence intensity of CDs at 445 nm decreased largely after the addition of 140μM of NaClO (4915 a.u, Figure 2b).

For the CDs-RhB hybrid system, we used UV-vis absorption and fluorescence spectra to study the interaction between CDs and RhB (Figure 3). Figure 3a is the UV-vis absorption spectra of CDs, RhB and CDs-RhB represented by black, red and blue line, respectively. The spectra display characteristic absorption bands of CDs and RhB. The maximum absorption of CDs and RhB are at about 224 and 556 nm, while the hybrid system of CDs-RhB emerged two absorption peaks at 224 and 556 nm that corresponded to the peaks of CDs and RhB. Figure 3b displayed fluorescence intensity of CDs, RhB and CDs-RhB. Obviously, we can recognize that there exist two fluorescent peaks in CDs-RhB hybrid system, which are due to the fluorescent peaks of CDs and RhB.

3.2 Optimal experimental condition

In order to obtain better results, the effects of pH in nanohybrid system and NaClO detection procedure were investigated (Figure 4). As shown in Figure 4, curve a, the I_{445}/I_{580} ratio of CDs-RhB solution is relatively stable in a wide pH range of 2-9. With addition of 140 μM NaClO, the fluorescence of CDs-RhB quenched largely. The ratio of I_{445}/I_{580} increased gradually with the increase of pH at the range of 2 to 8 and it obtained maximum when pH was 8. When pH >8, the ratio decreased with the increase of pH. The reason may be that the strong alkaline environment may destroy the structure on the surface of CDs, which decreases reaction between the hybrid system and NaClO.

3.3 Determination of free chlorine in PBS and real sample

Under optimal experimental conditions, different concentrations of NaClO in PBS (0.1 M, pH 8) were detected in the CDs-RhB nanohybrid system. As shown in Figure 5, the fluorescence of CDs-RhB solution with different concentrations of NaClO declined regularly. We could obviously find that the peak at 445 nm declines largely while the peak at 580 nm drops slightly. That is to say, the fluorescence intensity of CDs in CDs-RhB hybrid system declines largely while the RhB's drops slightly. We suggest that the oxidation ability of NaClO is so strong when the concentration reached a certain value that it would destroy the surface structure of RhB or CDs.[28-30] Figure 5c shows photos about color change trends after addition of different concentrations of NaClO. Obviously, color from rose red turned to light lilac was found after the addition of NaClO with its concentration from 0 to 140 μM.

Figure 6 shows the relationship between the ratio of I_{445}/I_{580} and concentration of NaClO. As shown from Figure 6, the ratio of I_{445}/I_{580} decreased regularly with the increase of concentration of RhB. From the inset, we can find a good linear relationship between the ratio of I_{445}/I_{580} and concentration of NaClO (I_{445}/I_{580}=5.46-0.01×$\mathbf{C}_{NaClO}$, R^2=0.986.) from 10 μM to 140 μM with the detection limit is 4 μM which is approached to the previous literature. [31] The relative standard deviation (RSD) values of 8 parallel measurements of 5 μM free chlorine concentrations was 2.1%. These results indicated that the CDs-RhB as a new-type sensor for detecting free chlorine is very simple, rapid and convenient which would have great potential for practical application.

After we explored CDs-RhB fluorescence sensor for detection of free chlorine in PBS buffer solution, we tried to test its application by detecting of free chlorine in tap water. The tap water sample was centrifuged at 7500 rpm for 30 min. The characteristic peaks at 445 and 580 nm are clearly observed after mixed with CDs-RhB and tap water. After estimated that the fluorescence ratio of I_{445}/I_{580} of the sample was 4.88 and under regression equation (I_{445}/I_{580}=5.46-0.01×$\mathbf{C}_{NaClO}$, R^2=0.986), we calculated the concentration of free chlorine in tap water sample was 58μM, which is approximate to standard value of 2 mg L^{-1} (56 μM) about free chlorine in drinking water issued by the WHO. Distinctly, this result indicates the CDs-RhB fluorescence sensor could successfully detect free chlorine quantitatively by data analysis in real water sample.

4. Conclusions

In a summary, we have demonstrated that CDs can form a hybrid system with RhB, and this system could act as a fluorescence sensor for free chloride detection in water solution. The detection limit of the sensor was as low as 4 μM. Compared with other methods, our hybrid fluorescence system is very simple and fast. In addition, this is the first time to combine CDs and RhB together to detect free chlorine and showed a great potential.

Acknowledgements

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Captions of figures

Scheme 1. Procedure charts about CDs-RhB and its characteristic changes.

Figure 1. TEM image of CDs.

Figure 2. Fluorescence curve of (a) RhB and (b) CDs in PBS solution (0.1 M, pH 8) with addition of 140 μM NaClO. (λex= 380 nm)

Figure 3. (a) UV-vis absorption and (b) fluorescence intensity curve of CDs (black curve), RhB (red curve), and CDs−RhB (blue curve) solutions.

Figure 4. Influences of pHs on the I_{445}/I_{580} number of CDs-RhB in the presence and absence of 140 μM NaClO.

Figure 5. (a) UV-vis absorption and (b) fluorescence curves of CDs−RhB in PBS (0.1 M, pH 8) with different concentrations of NaClO. (λex = 380 nm) (c) Photos about color change trend after addition of different concentrations of NaClO.

Figure6. Fluorescence intensity ratio (I_{445}/I_{580}) of CDs−RhB with different concentrations of NaClO. (illustration) It shows the linear relationship between concentrations of NaClO and I_{445}/I_{580}.

Scheme 1.

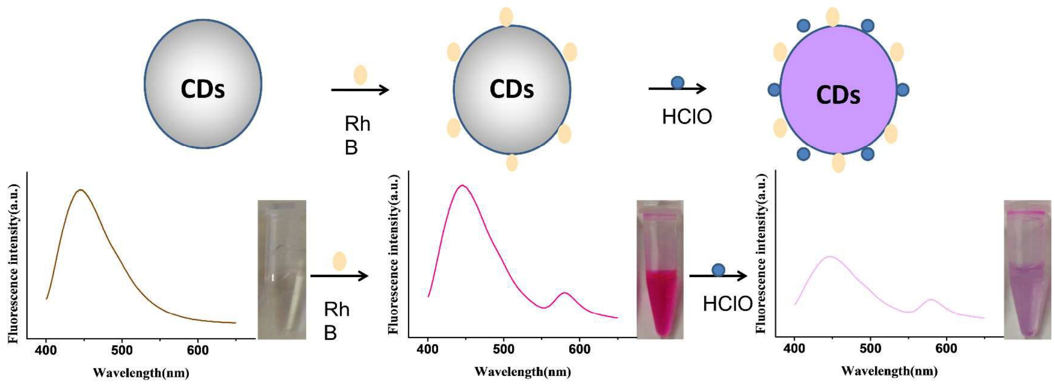

CDs
Rh
B
CDs
HClO
CDs
Fluorescence intensity(a.u.)
400
500
600
Wavelength(nm)
Rh
B
Fluorescence intensity(a.u.)
400
500
600
Wavelength(nm)
HClO
Fluorescence intensity(a.u.)
400
500
600
Wavelength(nm)

Figure 1.

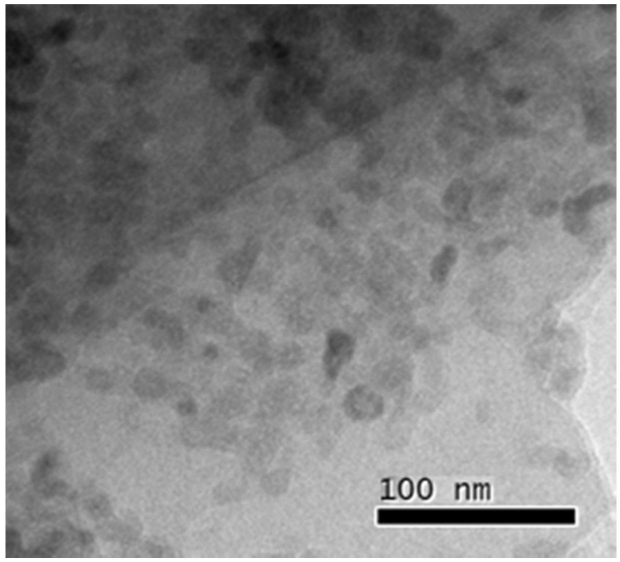


Figure 2.

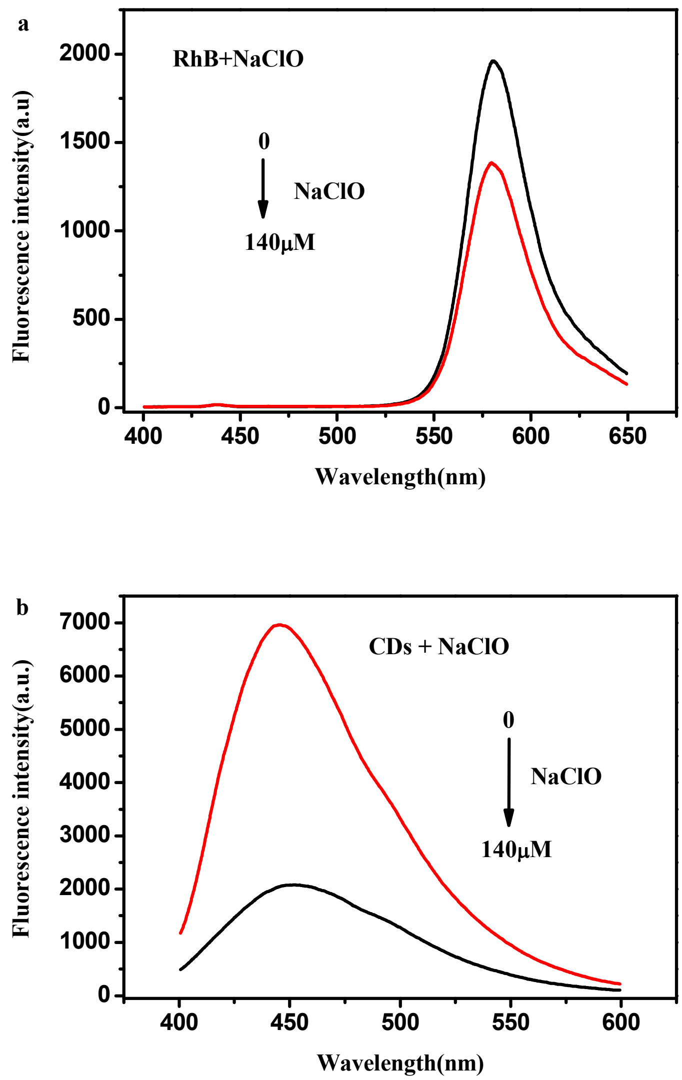

a
RhB+NaClO
0
NaClO
140μM
Fluorescence intensity(a.u)
Wavelength(nm)
b
CDs + NaClO
0
NaClO
140μM
Fluorescence intensity(a.u.)
Wavelength(nm)

Figure 3.

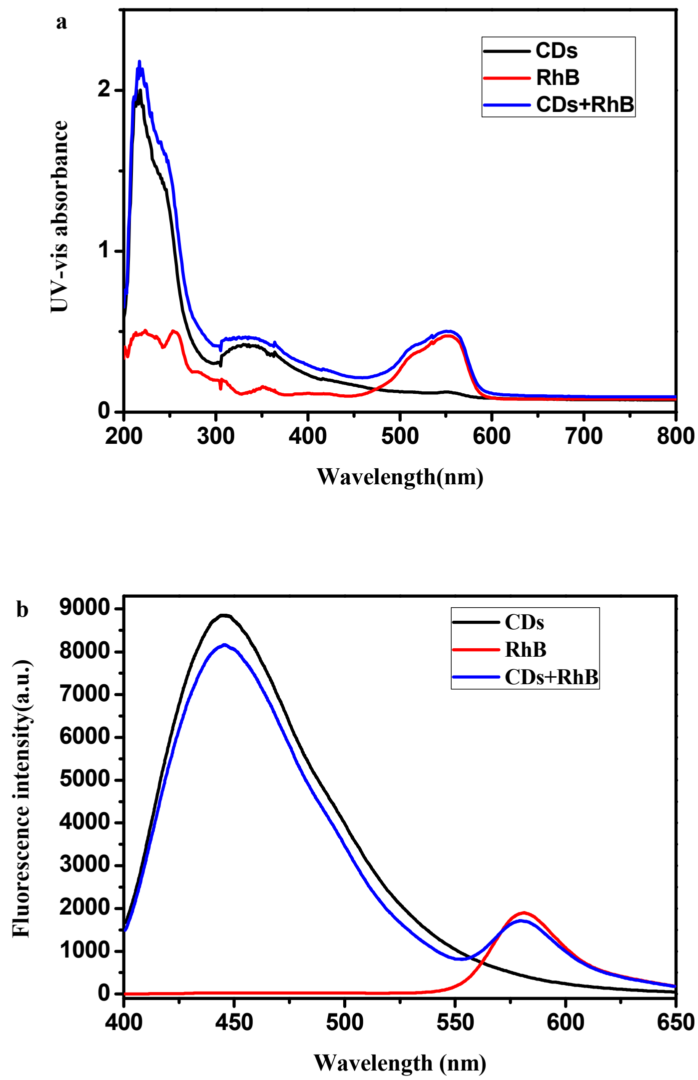

a
UV-vis absorbance
CDs
RhB
CDs+RhB
0
1
2
200
300
400
500
600
700
800
Wavelength(nm)
b
Fluorescence intensity(a.u.)
CDs
RhB
CDs+RhB
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
400
450
500
550
600
650
Wavelength (nm)

Figure 4.

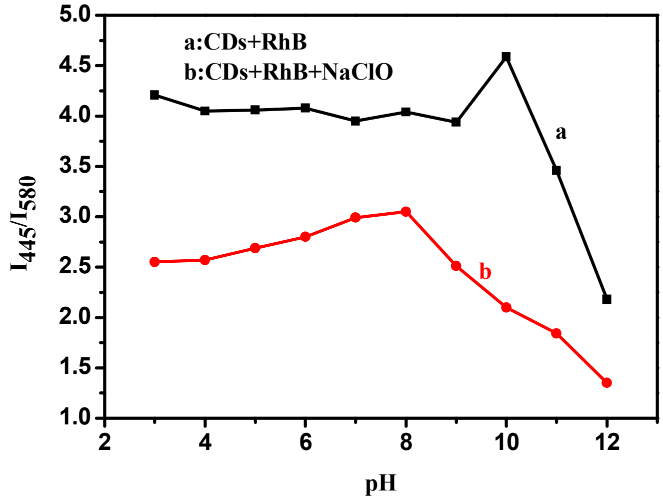

a:CDs+RhB
b:CDs+RhB+NaClO
a
b
I445/I580
pH
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
2
4
6
8
10
12

Figure 5.

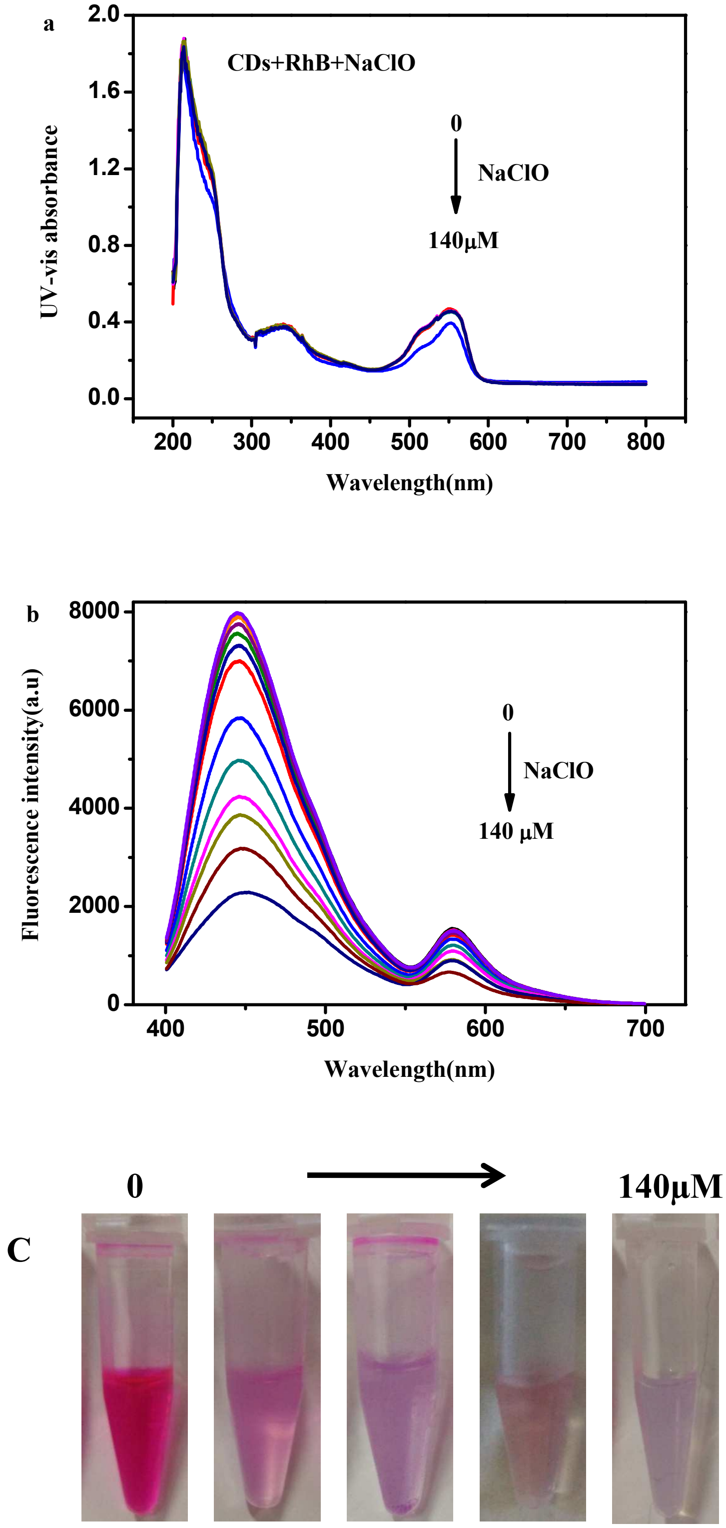
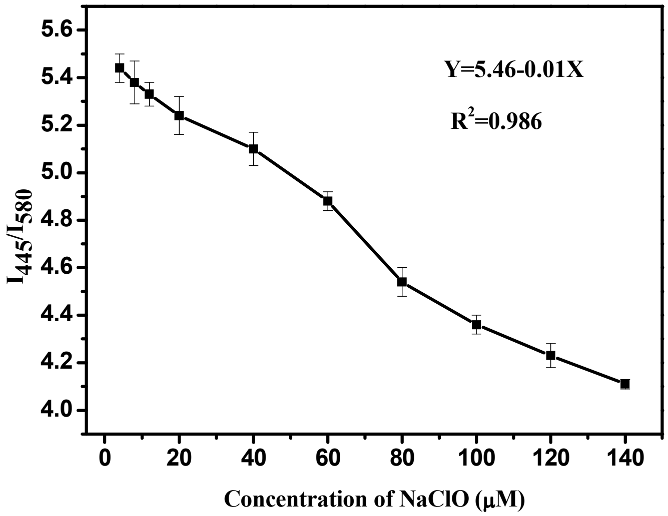
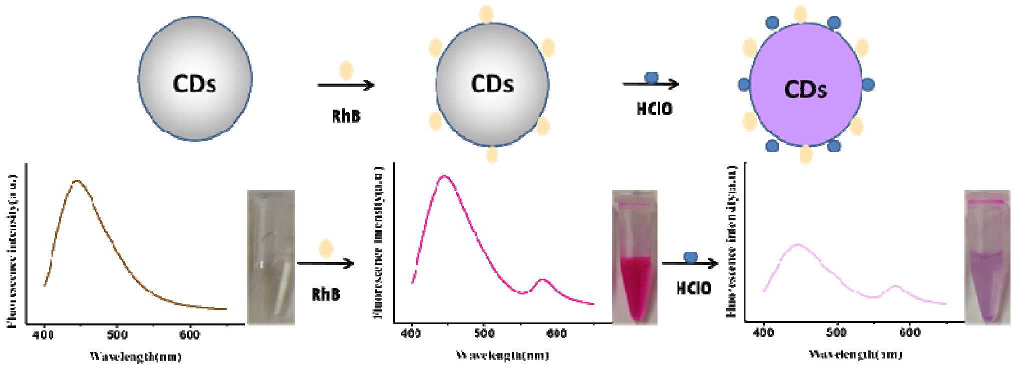

a
CDs+RhB+NaClO
0
NaClO
140μM
UV-vis absorbance
Wavelength(nm)
b
0
NaClO
140 μM
Fluorescence intensity(a.u)
Wavelength(nm)
0
140μM
C

Figure 6.


Y=5.46-0.01X
R2=0.986
I445/I580
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
0
20
40
60
80
100
120
140
Concentration of NaClO (μM)



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