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Determination of Hypochlorous Acid in Tap Water Using Highly Fluorescent Graphene Oxide

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Abstract

We report on the effect of hypochlorous acid (HClO) in the fluorescence emission of a fluorescent graphene oxide modified by hexylenediamine (GO-C₆NH₂). The synthesis process and the optical property of GO-C₆NH₂ were also introduced in detail. We found a strong quenching effect by HClO on the fluorescence emission of the fluorescent graphene oxide. The fluorescent quenching efficiency of GO-C₆NH₂ establish as a function of the amount of HClO, which the fluorescence intensity ratio is proportional to the different concentrations of HClO employed for the measurement. The results show that this fluorescent naomaterials are a promising tool for sensing trace HClO in tap water.

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1. Introduction

As we know, hypochlorous acid (HClO) is playing an important role in water treatment and living organisms [1]. Endogenous HClO is essential to life and shows vital antibacterial properties. Normally, Hypochlorite is used in the concentration range of 10⁻⁵–10⁻² M [2], since concentrated HClO is a potential health hazard to human and animals [3]. It has been reported that excessive or misplaced instake of HClO was damaged to host tissues (particularly proteins), observed in and leded to numerous diseases (e.g., atherosclerosis, kidney disease, and some cancers) [4], which may relate to the reaction of hypochlorite with

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DNA, RNA, fatty acids, cholesterol, and proteins *in vivo*. On the other hand, it is not fully understood about the exact interaction mechanism of hypochlorite to destroy invading microorganisms and cause these diseases. Therefore, a rapid and sensitive method for the determination of hypochlorite is desirably needed to investigate the functions of HClO in water.

It is a vital task for detection of trace amount of HClO in water with a broad range of implications from national security to the cleanup of demilitarized installations. So far, there are many methods available for the hypochlorite determination, such as the normalized and well-known iodometric titration, many colorimetric methods based on reaction of hypochlorite with organic reagents [5]. However, these strategies require cumbersome preparative procedures of sensing molecule and/or unwieldy sample preparations. Furthermore, they had to be carried out either in organic medium or organic/water medium, directly limiting their use in real-life situations. Therefore, nanotechnology is ideally suited to serve the Nation needs by providing new materials and methods that can be employed for trace HClO detection. Fluorescent nanomaterials, like nanoscaled graphene oxide, have the potential to be applied in trace HClO detection in a number of drinking water environments. The fluorescent graphene oxide has recently received increasing attraction due to its special surface properties and high stability. The fluorescence quantum yield (QY) of graphene oxide through the functional modification with alkylamines [6-9] has been reported to be greatly enhanced. In our work, we report here the addition of HClO shows great effect on the fluorescence emission of the fluorescent graphene oxide. It is proposed that the fluorescent graphene oxide can react with HClO, leading to the quenching fluorescence.

2. Experimental section

2.1. Materials

Natural graphite flakes, N,N-dimethylformamide (DMF), dichlorosulfoxide, tetrahydrofuran (THF), 1, 6-hexylenediamine, were purchased from Shanghai Chemical Reagent Co. The pH of solution was adjusted by phosphate buffer. The phosphate buffer was prepared by disodium hydrogen phosphate dodecahydrate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$) and sodium dihydrogen phosphate dihydrate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$). Aqueous solutions were all prepared using ultrapure water (18.2 M Ω -cm) from a Millipore water purification system.

2.2. Synthesis of fluorescence graphene oxide

The starting graphene oxide powder was obtained from natural graphite by a modified Hummers method [10]. The fluorescent graphene oxide (GO-C₆NH₂) with the modification of hexylenediamine was prepared by the following procedure. About 20 mg of dried graphene oxide was dispersed in DMF (5 mL), then, refluxed in 20 mL of SOCl₂ at 80 °C for 24 hours. The supernatant was discarded and the remaining solid was washed with anhydrous THF two times to remove excess SOCl₂ and DMF after the centrifugation at 10000 rpm for 10 min. Then, the activated GO acyl chloride (GO-COCl) was stirred at 80 °C for 48 hours following by the addition of hexylenediamine. The reaction solution then dispersed in ethanol (20 mL). A light yellow supernatant was obtained after the mixture was vacuum filtered. The suspension shows bright blue fluorescence under UV illumination and the maximum fluorescence intensity is located at 440 nm with a 365 nm excitation wavelength.

3. Results and discussion

It is shown in figure 1 that highly fluorescent GO nanosheets were successfully synthesized through the

amide reaction and ring-opening reaction at the surface of GO nanosheets functionalized with hexylenediamine, which is covalently attached on the surface of GO. Unmodified GO nanosheets with a weak fluorescence at about 560 nm have a number of carboxyl groups, which could react with SOCl_2 to yield GO-COCl . Hexylenediamine is added to be covalently attached on the surface of GO to form the fluorescent nanomaterial $\text{GO-C}_6\text{NH}_2$. The $\text{GO-C}_6\text{NH}_2$ aqueous suspension exhibits strong blue fluorescence under UV irradiation which can be easily seen with naked eyes and recorded with a digital camera. The PL quantum yield of $\text{GO-C}_6\text{NH}_2$ was measured to be $\sim 11.2\%$, which is about six hundred folds that of the original GO nanosheets (0.02%). So, this highly blue fluorescent $\text{GO-C}_6\text{NH}_2$ could be applied to detect HClO in drinking water.

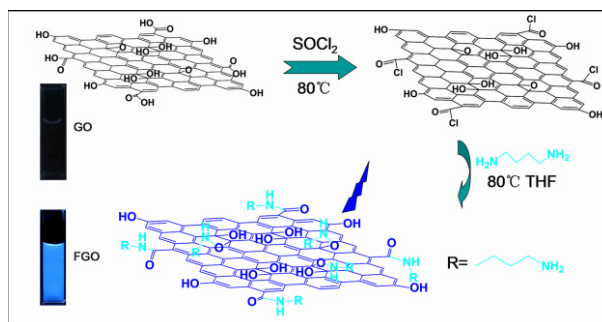


Fig. 1. Schematic illustration of the synthesis process of the fluorescent graphophene oxide functionalized with hexylenediamine.

It can be seen in figure 2 that the graphene oxide shows highly blue fluorescence after hexylenediamine treatment, and absorption bands at 276 nm and 350 nm become more pronounced and resolved, compared with the absorption peak around 230 nm of GO, which is assigned to the $\pi\text{-}\pi^*$ transitions of $\text{C}=\text{C}$. The results suggest the formation and increase of new luminescent centers at the surface of $\text{GO-C}_6\text{NH}_2$ nanosheets. Moreover, the fluorescence stability of the as prepared $\text{GO-C}_6\text{NH}_2$ against time was also evaluated. The fluorescence intensity kept almost unchanged each five minutes for two hours during the ultraviolet light irradiation. The result indicates that the fluorescent probe is enough stable to measure the amount HClO in water.

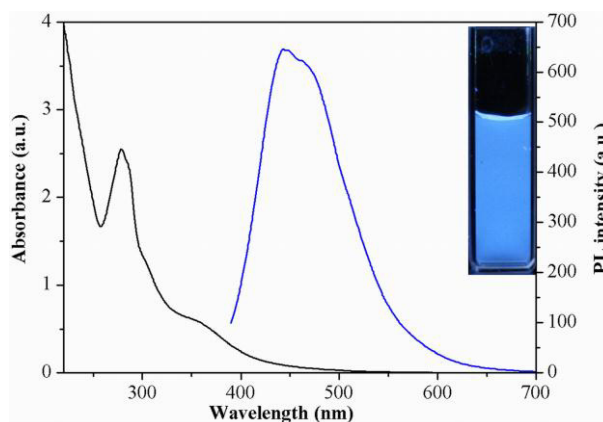


Fig. 2. The fluorescence emission and UV-vis absorption of $\text{GO-C}_6\text{NH}_2$ in water. The emission spectrum was obtained under excitation at 365 nm, the photograph was taken under 365 nm irradiation.

Representative fluorescence spectra of GO-C₆NH₂ in water exposed to various amounts of HClO are displayed in figure 3. The blue fluorescence of GO-C₆NH₂ aqueous solution is centered at 440 nm under excitation wavelength of 365 nm. The fluorescence intensity is independent of the amount of water added, as verified in independent measurements. Figure 3 summarizes the results from quantitative analysis of fluorescence intensities as a function of the amount of HClO added to GO-C₆NH₂ aqueous solution employed for the measurements. The fluorescence relative peak decreases with the addition of HClO to the solution. This decrease in fluorescence intensity is not related to a dilution effect, as verified by independent measurements performed on GO-C₆NH₂ exposed to volumes in absence of HClO. Moreover, it can clearly see that the fluorescence color of GO-C₆NH₂ aqueous solution gradually fades as the concentration of HClO increases, and finally disappears when the concentration is up to 0.1 mM, and the corresponding fluorescence intensity is decreased by 76 %. Such measurements show that the fluorescence intensity ratio is proportional to the concentration of HClO in drinking water. Then, we conclude based on the results presented in figure 3, that the fluorescence of the GO-C₆NH₂ could be clearly quenched by the added HClO.

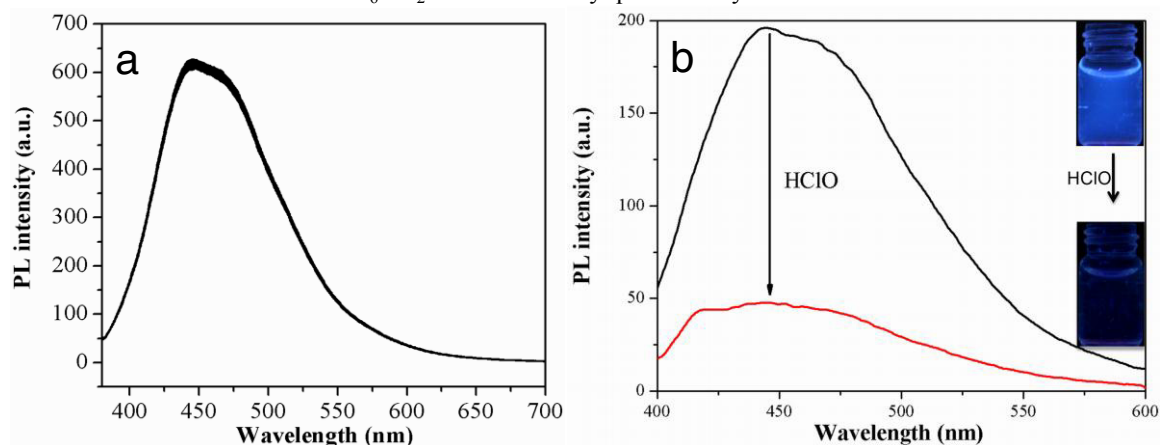


Fig. 3. the fluorescence emission of GO-C₆NH₂ in water with the addition of the same concentrations of water and HClO, the excitation wavelength is 365 nm, the photograph was taken under 365 nm irradiation

4. Conclusion

The results presented here the extensive quenching and a change in the fluorescence emission of GO-C₆NH₂ by HClO. The results prove that the GO-C₆NH₂ may find applications in HClO sensing from observations of the fluorescence decrease, distinctive from the fluorescence emission of the GO-C₆NH₂ in the absence of HClO. The changes in the fluorescence intensity as a function of added HClO are the major finding of the work presented here. Due to the strong nucleophile of graphene oxide which may act as an electron donor, the change may be accounted for by a charge transfer mechanism (IT) or intramolecular charge-transfer (ICT) between grapheme oxide and HClO, which is still an argument. Independent UV-visible absorption measurements (not shown) failed to show a change in the leading edge of the absorption spectra of the GO-C₆NH₂ upon the addition of HClO, indicating that the results presented here cannot be explained by a mechanism that induces the quenching fluorescence. In view of the above arguments, we believe that either a CT and/or ICT mechanism may be responsible for the effect of HClO in the fluorescence of the GO-C₆NH₂. Further work will be needed to clearly establish the mechanism of the quenching fluorescence of the GO-C₆NH₂ in the presence of HClO. And further real application in determination for the amount of HClO in

portal water using the fluorescent graphene oxide as a sensitive and selective sensor will be needed to study.

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