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# Fluorescent carbon nanoparticles for the fluorescent detection of metal ions

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ABSTRACT

Fluorescent carbon nanoparticles (F-CNPs) as a new kind of fluorescent nanoparticles, have recently attracted considerable research interest in a wide range of applications due to their low-cost and good biocompatibility. The fluorescent detection of metal ions is one of the most important applications. In this review, we first present the general detection mechanism of F-CNPs for the fluorescent detection of metal ions, including fluorescence turn-off, fluorescence turn-on, fluorescence resonance energy transfer (FRET) and ratiometric response. We then focus on the recent advances of F-CNPs in the fluorescent detection of metal ions, including $Hg^{2+}$, $Cu^{2+}$, $Fe^{3+}$, and other metal ions. Further, we discuss the research trends and future prospects of F-CNPs. We envision that more novel F-CNPs-based nanosensors with more accuracy and robustness will be widely used to assay and remove various metal ions, and there will be more practical applications in coming years.



**Contents**



## 1. Introduction

A variety of functional materials contained metal ions have been widely used all over the world and bring about great convenience to our life. However, metal ions that are released from these materials are detrimental to human health and the environment. Therefore, the detection of these metal ions is urgent for researchers and the government. Researchers have developed a wealth of methods for sensing metal ions, including optical methods (Nolan and Lippard, 2008), capillary electrophoresis (Ali and Aboul-Enein, 2002), electrochemical methods (Aragay and Merkoçi, 2012), atomic absorption spectrometry (Fang et al., 1984), inductively coupled plasma mass spectrometry (Townsend et al., 1998), and so on, which can provide satisfactory results. However, most of these methods show some limitations, such as complicated processing, high-cost instruments and time-consuming operations. Therefore, simple and low-cost methods for the detection of metal ions are highly desirable. As a new kind of carbon nanomaterials, fluorescent carbon nanoparticles (F-CNPs) have recently captivated the attention of scientists due to their unique properties, such as robust chemical inertness, low photobleaching, low toxicity, good biocompatibility, good water solubility, easy preparation, etc. (Qu et al., 2012b). These properties are, however, not found in organic dyes or semiconductor quantum

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**Table 1**
Comparison of the performance of various analytical methods for detecting $Hg^{2+}$ based on the LOD.

| Analytical methods | LOD[a] | Reference |
|---|---|---|
| Optical methods (fluorescence) | 10 μM<br>46.5 nM | Zhang et al., 2014b; Tian et al., 2014 |
| Capillary electrophoresis | ~3.86 nM<br>~7.48 nM | Ge et al., 2014;<br>Yang et al.,2014 |
| Electrochemical methods | 5 nM<br>0.2 nM | Zhang et al., 2013a;<br>Xuan et al., 2013 |
| Atomic absorption spectrometry | ~2.19 nM<br>0.15 nM | Türker et al., 2014;<br>Giakisikli et al., 2013 |
| F-CNPs-based methods | 10 nM<br>0.5 nM | Guo et al., 2013;<br>Qin et al., 2013 |

[a] Limit of detection.

dots (QDs). F-CNPs are thus promising to replace these highly toxic semiconductor QDs. Fluorescent carbon nanomaterials were accidentally found by researchers in the procedure of purification of single-walled carbon nanotubes (SWCNTs) fabricated by arc-discharge methods in 2004. They found that the short SWCNTs oxidized from long SWCNTs showed fluorescence, which is dependent on the size of SWCNTs (Xu et al., 2004). This accidental discovery has drawn great attention and provides new ideas for the fabrication of F-CNPs. Researchers have developed a handful of methods to prepare F-CNPs which exhibit desirable properties (Baker and Baker, 2010).

F-CNPs have recently been widely applied in various fields, including bioimaging, sensors, photocatalysis, optoelectronics, and so on (Esteves da Silva and Gonçalves, 2011; Li et al., 2012; Shen et al., 2012). The fluorescent detection of metal ions is one of the most important applications due to their high quantum yield (QY), good photostability and low toxicity. The F-CNPs with high QY can still exhibit strong fluorescence intensity even at very low concentration. The good photostability of F-CNPs guarantees the stability of the fluorescence signal, ensuring the accuracy of the detection results. And there is no need to worry about their poisoning effect on human health and the environment. Therefore, it is facile to qualitatively determine metal ions without costly instruments or complicated operations, and quantification can also be simply achieved by monitoring the change of the fluorescence intensity. Moreover, F-CNPs are water soluble, thus the recontamination resulted from toxic organic solvent that is commonly required to disperse organic dyes can be avoided. Hence, F-CNPs exhibit great promise in the fluorescent detection of metal ions and many case studies have been explored and investigated. And we compare the performance of various analytical methods for detecting metal ions based on the limit of detection (LOD) taking $Hg^{2+}$ as an example. The performance of capillary electrophoresis, electrochemistry and atomic absorption spectrometry is superior to the optical methods (fluorescence) and F-CNPs-based methods. However, these methods including capillary electrophoresis, electrochemistry and atomic absorption spectrometry require expensive instruments and complicated operations. And the performance of the F-CNPs-based methods is better than the performance of the optical methods (fluorescence) (Table 1). Particularly, the F-CNPs-based methods are relatively inexpensive and very simple when compared to the performance of these instrumental methods and the optical methods (fluorescence). The F-CNPs can be easily synthesized from low-cost carbon sources via simple methods, such as hydrothermal methods and microwave-assisted methods (Guo et al., 2013; Barman and Sadhukhan, 2012). And the quantification of metal ions can be easily achieved based on the change of the fluorescence intensity. The F-CNPs-based methods are thus promising candidates for the fluorescent detection of metal ions in aqueous solution. Review on the recent advances in F-CNPs for the fluorescent detection of metal ions is necessary. In the review, we mainly summarize the recent progress on the development of F-CNPs for the fluorescent detection of metal ions. It should be notified that F-CNPs in the review include all kinds of fluorescent carbon nanomaterials, including carbon dots, carbon nanodots, graphene quantum dots (GQDs), g-$C_3N_4$, and so forth.

## 2. Detection mechanism

F-CNPs have been widely used to detect various metal ions in aqueous solution. There are mainly four types of fluorescence response modes: fluorescence turn-off, fluorescence turn-on, fluorescence resonance energy transfer (FRET) and ratiometric response. Most of F-CNPs-based nanosensors are fluorescence turn-off and the real fluorescence quenching mechanism induced by metal ions has not been fully elucidated. However, lots of researchers have tried to explain the fluorescence quenching mechanism. Most of the fluorescence quenching mechanism is mainly attributed to the electron, charge or energy transfer resulted from the selective interaction between F-CNPs and metal ions. The reason is ascribed to the functional groups on the surface of F-CNPs, such as carboxyl groups, hydroxyl groups, amino groups, etc. These functional groups can selectively interact with the specific metal ions, resulting into the complex of F-CNPs with metal ions. The complex may change the electronic structure of F-CNPs and affect the distribution of excitons, which accelerates the non-radiative recombination of the excitons through effective electron, charge or energy transfer, further results in the fluorescence quenching (Guo et al., 2013; Zhou et al., 2012). Moreover, the inner filter effect is another reason for fluorescence quenching caused by metal ions. The inner filter effect is due to the absorption of the excitation and/or emitted light by absorbers in the detection system when the absorption spectrum of the absorbers overlap with the fluorescence excitation or emission spectra of F-CNPs. The inner filter effect can enhance the sensitivity compared to other mechanisms because the changes in the absorbance of sensors can transform exponentially into fluorescence intensity changes (Badarau and Dennison, 2011; Dong et al., 2012; Zheng et al., 2013). The above mentioned reasons can contribute the fluorescence quenching of F-CNPs in the presence of the specific metal ions. For the F-CNPs-based nanosensors with fluorescence turn-off, the fluorescence signal is easily influenced by the detection medium, thus the obtained results may be not accurate. The nanosensors with fluorescence turn-on, FRET or ratiometric response may improve the accuracy of the detection results. However, there are only a few case studies. In the future, more efforts have to be devoted to the development of F-CNPs-based nanosensors with fluorescence turn-on, FRET or ratiometric response.

## 3. Assays of metal ions

### 3.1. Mercury ions

Mercury, one of the most toxic metal ions, has received considerable attention due to its extremely harmful effects on human health and the environment (Nolan and Lippard, 2003, 2008). Mercury vapor is easily oxidized to water-soluble mercury ions and the subsequent biotransformation will produce more toxic organic mercury, which can accumulate environmentally through the food chain (Benoit et al., 1998; Harris et al., 2003; Ma et al., 2011; Renzoni et al., 1998). Particularly, mercury is a severe neurotoxin and long-term exposure to high levels of mercury can cause damage to the brain, nervous system and