Application of Carbon Quantum dot Fluorescent Materials in Metal Ions Detection

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Abstract. The research situation of the application of carbon quantum dot fluorescent materials to the detection of metal ions, including the current research status and preface of recent years, and development trends are summarized. The application of carbon quantum dot fluorescent materials to the detection of metal ions is highlighted, including iron ions, copper ions, mercury ions, lead ions, and silver ions. Finally, the problems and development prospects of carbon quantum dot fluorescent materials for detecting metal ions are discussed.

1 Introduction

Metals are widely distributed, have various forms, are difficult to decompose, and have high toxicity. They can enter soil, air and water through various forms[1]. With the improvement of people's awareness of health and environmental protection, the research on metal detection technology is receiving more and more attention[2]. At present, there are a variety of detection methods to detect metal ions. For example, atomic emission spectrometry, atomic absorption spectrometry, ultraviolet spectrophotometry and fluorescent probe methods, but the detection process is complicated. As a new kind of fluorescent nanomaterial, carbon quantum dots have excellent biocompatibility, typical optical properties, non-toxic carbon source precursors, high water solubility and easy surface functionalization, which can be applied to cell imaging metal ion detection, analysis and photocatalysis[3-4]. The fluorescence of carbon quantum dots in aqueous solution can be quenched by electron acceptor or electron donor, and the photoinduced electron transfer properties of carbon quantum dots can be used for the detection of metal ions by nanometer probes. Therefore, rapid qualitative and quantitative detection of heavy metal ions in

aqueous solution is of great research value[5]. In this paper, the research progress of carbon quantum dot fluorescent materials for metal ion detection in recent years was reviewed.

2 Application of carbon quantum dot fluorescent materials in metal ions detection

2.1 Carbon quantum dot fluorescent materials were applied to the detection of Fe³⁺ ions

In 2018, Guo et al. prepared high fluorescent nitrogen and phosphorus co-doped carbon quantum dots (NP-CQDs) by heat treatment of the mixture of citric acid and o-phosphoethanolamine[6-7], which have good stability and photostability, and the quantum yield was about 8.45%. NP-CQDS can be used for sensitive selective fluorescence detection of Fe³⁺ ions. In 2018 Zhang et al. reported a method for preparing nitrogen-doped lignin carbon quantum dots (N-L-CQDs) using alkaline lignin carbon source and deep eutectic solvent (DES) as solution and nitrogen source to detect Fe³⁺ ions[8]. The results showed that the fluorescence probe had good sensitivity and selectivity for Fe³⁺ ions, and the detection limit is 0.44 μm (figure 1).

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Figure 1. Schematic diagram of N-L-CQDs synthesis and detection mechanism

2.2 Carbon quantum dot fluorescent materials were applied to the detection of Cu^{2+} ions

In 2019, Y Ang et al. synthesized carbon quantum dots using sodium citrate hydrothermal method[9]. The content of P in the synthesized P-CQDs was 8.52 wt.%. P-CQDs had a narrow size

distribution of 2.5-4.5 nm and emitted a strong blue light at 429 nm. The detection mechanism is that the P/O functional groups on the surface of P-CQDs have higher binding affinity and faster chelating force, which promotes the aggregation of PCQDs- Cu^{2+} chelates. Therefore, P-CQDs could be used to detect Cu^{2+} in actual water samples with high sensitivity and accuracy (figure 2).

Figure 2. Schematic diagram of the mechanism of P-CQDs

In 2020, Liu. reported that a highly fluorescent GQD using lignite-derived humic acid as the cost-effective precursor[10]. The

excitation and emission rates are 360/370nm, respectively. The probe has good selectivity and high sensitivity (figure 3).

Figure 3. the formation of GQDs and its application for Cu^{2+} Detection

2.3 Carbon quantum dot fluorescent materials were applied to the detection of Hg^{2+} ions

In 2016, Dan reported CGCS-CDs to detect Hg^{2+} ions by selecting Chinese grass carp scales (CGCs) as carbon source[11-12]. On one hand, the preservation of S atoms in CGCS-CDs can effectively regulate the electron cloud density of

CGCS-CDs to promote the coordination between oxygen atoms of CGCS-CDs and Hg^{2+} ions. On the other hand, due to the strong affinity and unique selectivity between Hg^{2+} and CGCS-CDs surface, it is easy to form S- Hg^{2+} -S hairpin structure with Hg^{2+} ions, which is helpful to realize the specific detection error of Hg^{2+} by using CGCS-CDs[13]. Therefore, CGCS-CDs has high sensitivity and good selectivity to detect Hg^{2+} ions (figure 4).

Figure 4. Schematic diagram of Hg^{2+} detection mechanism of CGCS-CDs

2.4 Carbon quantum dot fluorescent materials were applied to detect Pb^{2+} ions

In 2012, Dong synthesised a new CDs by Sodium citrate and polyacrylamide to detect Pb^{2+} ions [14]. Because Pb^{2+} ions chelates with carboxylic acid

and organic nitrogen groups on the surface of CDs, CDs/ Pb^{2+} complex is formed, CDs / Pb^{2+} fluorescence quenching is achieved through internal filtering effect (figure 5), which is called "turn-off" effect. With the addition of Pb^{2+} ions, the fluorescence intensity of CDs was quenched significantly.

Figure 5. Preparation of CDs and its detection mechanism for Pb^{2+} ions

2.5 Carbon quantum dot fluorescent materials were applied to the detection of Ag^+ ions

Zhang prepared S/N-CDs through simple hydrothermal synthesis using guanidine thiocyanate (GITC) as raw material and N and S elements as dopants[15]. The detection mechanism of Ag^+ by S/N-CDs is that Ag^+ ions

interacts with the carboxyl group or hydroxyl group on the surface of CDs, which accelerated the non-radiative recombination of excited state electrons through effective electron transfer process, thus reducing the fluorescence intensity of CDs. In the presence of Ag^+ , S/N-CDs had the strongest fluorescence intensity, while in the presence of other metal ions, S/N-CDs had a low fluorescence intensity, indicating that CDs had a good selectivity in the detection of Ag^+ (figure 6).

Figure 6. The changes of emission wavelengths with the excitation wavelengths

3 Summary

To sum up, the fluorescent materials of carbon quantum dots have the advantages of wide linear range, high sensitivity and good selectivity in detecting metal ions. Therefore, fluorescent carbon quantum dots have been widely used in the field of metal ions detection, but there are still the following problems. We believe that carbon quantum dot fluorescent probes with excellent performance and simultaneous detection of various metal ions will continue to be developed.

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