ISSN: 2664-9640

Application Progress of Metal Fluorescent Nanomaterials in Toxic Ion Monitoring

Shi Hailan [1,2,3,4,5], Zhang Zhaorong[1,2,3,4,5]

[1] Shaanxi Provincial Land Engineering Construction Group Co., Ltd. Xi'an 710075, China;

[2] Institute of Land Engineering and Technology, Shaanxi Provincial Land Engineering Construction Group Co., Ltd. Xi'an 710021, China;

[3] Key Laboratory of Degraded and Unused Land Consolidation Engineering, the Ministry of Natrual Resource Xi'an 710021, China;

[4] Shaanxi Provincial Land Consolidation Engineering Technology Research Center， Xi'an 710021, China;

[5] Land Engineering Technology Innovation Center, Ministry of Natural Resources， Xi'an 710021, China;

Abstract

In recent years, with the continuous discovery of pollutants types in the environment, the pollution of toxic pollutants in various environmental media has a negative impact on the environment and human beings. Among them, he excessive toxic ions has become a topic of great concern. Therefore, the requirements for the detection of toxic ion pollutants in the environment are also increasing. The use of metal fluorescent nanomaterials has opened up a new way to create simple, highly selective and sensitive real-time accurate analysis. Because they can meet the needs of quantitative analysis quickly and effectively. more and more scholars pay attention to them. Here, this paper discuss their applications in toxic ions detection. It comes up with some challenges that currently faced and future outlooks for metal fluorescent nanomaterials.

Keywords

Metal nanomaterials; ion detection; fluorescent probe; fluorescence sensing.

1. Introduction

Toxic ions will accumulate in the soil, be absorbed by plants and animals, be transmitted through the food chain, and finally enter the human body, causing harm to people's health. The current conventional detection methods for toxic ionic pollutants mainly include ion chromatography[1], voltammetry[2], atomic absorption spectrometry[3], and inductively coupled plasma-mass spectrometry[4]. These methods usually require highly qualified technicians, expensive instruments, and complicated sample preparation processes, which make on-site and real-time detection difficult. The fluorescence analysis methods based on metal nanoclusters have low cost of ownership, are simple, fast, and easy to operate. , High sensitivity, good selectivity and many other advantages, it has now become an important instrumental analysis method.

Metal fluorescent nanoclusters are a kind of fluorescent nanomaterials composed of metal atoms with a size between atoms and bulk objects. Metal nanoclusters have the advantages of small size, good biocompatibility, low toxicity to the environment, and good light stability. Metal nanoclusters have shown great application prospects in the fields of biology, food and

ISSN: 2664-9640

environmental protection. This article focuses on the application of metal nanoclusters in the detection of toxic ions in recent years, and prospects for future development.

2. Detection of metal ions by metal nanoclusters

In recent years, many types of fluorescent metal nanoclusters have been developed and applied to the detection of toxic ions in the environment[5]. This highly sensitive and selective analysis method has gradually entered the public eye. The content of metal ions in the environment has always been a hot spot for research. Many metal ions necessary for human bodies, such as Fe^{2+}, Cu^{2+}, and Co^{2+}, are also toxic at high doses. In addition, other heavy metal ions, such as Ag^{+}, Hg^{2+}, As^{3+}, Pb^{2+} and Cd^{2+}, are highly toxic to humans and aquatic organisms even at very low concentrations in the environment. Heavy metal ions can produce human health and the environment. Unrecoverable damage[6], the development of a new method for detecting metal ions, is of great significance to environmental monitoring.

2.1. Cu^{2+} detection

Copper is an essential transition metal in the human body, and excessive intake of Cu^{2+} can cause serious damage to the human body, leading to liver and kidney damage, disturbing cell homeostasis, and damage to the central nervous system. Su et al. developed a simple and sensitive fluorescence detection method. The solution is composed of 3-mercaptopropionic acid (MPA) and DNA-Cu/AgNCs in aqueous solution to detect Cu^{2+}. The fluorescence of DNA-Cu/AgNCs is quenched by 3-mercaptopropionic acid, and the fluorescence is recovered in the presence of Cu^{2+}. In the presence of MPA, the fluorescence of DNA-Cu/AgNCs increases with the increase of Cu^{2+} concentration (5~200 nM). The detection limit of the fluorescent probe for copper ions is 2. 7 nM[7]. Yang et al. successfully synthesized fluorescent AuNCs using $HAuCl_4$ and $N_2H_4 \cdot H_2O$ with lysine as a template, and combined them with bovine serum albumin-stabilized AuNCs for the determination of Cu^{2+}, providing a simple method for Cu^{2+} detection. , A fast method with a detection limit of 0. 8x10^{-12} M[8].

2.2. Detection of Pb^{2+}

The accumulation of high concentrations of lead in children can cause irreversible brain damage and hinder mental and physical development. D. Bain et al. reported a synthetic light-stable, water-soluble AuNCs. AuNCs are synthesized in aqueous media through ligand exchange and etching techniques. Depending on the length of the etching time, AuNCs emit light at different wavelengths. AuNCs showed a very bright emission at 510 nm after 96 h of etching time. Continue to extend the etching time without any change in emission wavelength. This confirmed the completion of the reaction under this condition and the detection of Pb^{2+} in water was obtained. The limit is as low as 10 nM[7].

2.3. Hg^{2+} detection

Mercury can accumulate in organisms, interact with sulfhydryl groups in proteins, cause serious damage to the central nervous system, and pose a serious threat to human health and the natural environment. Guo et al. used guanidine hydrochloride and TCEP denatured BSA as stabilizers to synthesize fluorescent AgNCs with high stability and excellent water solubility. Due to the interaction between the exposed thiol groups in dBSA and the metal core, they were made The dBSA can be combined with Ag^{+}. The size of AgNCs is about 1 nm, and it has high stability even when exposed to high salt conditions (up to 1 M NaCl). The dBSA coated AgNCs detect Hg^{2+} through the specific interaction between Hg^{2+} and Ag^{+}[7].

2.4. As^{3+} detection

Arsenic is a highly toxic carcinogen. It is widely distributed and can easily cause health problems, such as skin lesions, circulatory system problems and bladder cancer. Arsenic mainly

ISSN: 2664-9640

exists in the form of inorganic arsenic and arsenate. Drinking water is the main route of exposure to arsenic, which often exceeds the World Health Organization's guideline value of $10x10^{-3}$mg/L. Gong et al. reported a colorimetric method for the determination of As^{3+} in aqueous solutions of citrate-terminated gold nanoparticles (AuNPs). The nanoparticles interacted with citrate in the presence of As3 + and aggregated. The color of the system changes from wine red to blue. The detection limit is as low as 1 in the range of 4x10-3 mg /L~100 × 10^{-3} mg /L. 8x10-3 mg/L, which is lower than the standard value of $10x10^{-3}$ mg/L. This method has been successfully used for the determination of arsenic ions in spiked drinking water[10].

2.5. Co^{2+} detection

Cobalt is beneficial to the human body to a certain extent, because it is a part of vitamin B12. A small amount of Co^{2+} is essential for life, but it is reported that the increase in serum cobalt concentration may be related to certain diseases. Cobalt and some of its compounds are considered to be potential pathogenic toxins and have carcinogenic effects. Zhang et al. used thiosulfate-stabilized gold nanoparticles induced in the presence of ethylenediamine (en) to detect Co^{2+} in aqueous solutions. Co^{2+} first forms the $Co(en)^{2+}{}_3$ complex in the aqueous solution, then oxidizes $Co(en)^{2+}{}_3$ to $Co(en)^{3+}{}_3$ by dissolved oxygen, and then $Co(en)^{3+}{}_3$ Attacking the $S_2O_3{}^{2-}$ ligand adsorbed on the surface of AuNPs, forming positively charged (en) $2CoS_2O^{3+}$ on the surface of AuNPs, which reduces the surface charge of AuNPs and induces AuNPs to aggregate. This process is accompanied by a red shift of the absorption spectrum and a visible color change from wine red to blue, with a linear range of 0. 1 to 0. 7 mM, the detection limit is 2. $36x10^{-3}$ mg/L[11].

2.6. Cd^{2+} detection

Cadmium is a non-essential life element. It is widely used in fertilizers, pesticides, nickel-cadmium batteries, dyes, pigments, and coatings on steel and various alloys, causing widespread pollution in the air, soil and water. Cadmium ion is considered to be a very toxic heavy metal ion. Cadmium exposure can cause anemia, abdominal pain, nerve, hypertension and kidney damage. Huang et al. reported a method to detect Cd^{2+} in real samples using 1-amino-2-naphthol-4-sulfonic acid (ANS)-AgNPs as a probe. ANS-AgNPs,it shows specific recognition of Cd^{2+}, accompanied by a color change from bright yellow to reddish brown. This detection mechanism is the aggregation of ANS-AgNPs induced by Cd^{2+}. The concentration of Cd^{2+} is in 1. Between 0 and 10 μM, the detection limit is as low as 87 nM. This method has been successfully used for the determination of Cd^{2+} in milk powder, serum and lake water[12].

2.7. $Cr^{3+}$and Cr^{6+} detection

Zhang et al. proposed a simple one-step method for the synthesis of fluorescent GSH-AuNCs. Because the fluorescence quenching ability of Cr^{3+} and $^{6+}$ depends on the change of pH value, at pH 6. Under 5 conditions, the relative fluorescence intensity of GSH-AuNCs is related to the concentration of Cr^{3+}, which can realize the direct detection of Cr^{3+}. The detection of Cr^{6+} is based on the pH 3.3, 5. At 0, the difference between the relative fluorescence intensity of GSH-Au-NCs is realized. At pH 6. Cr^{3+} can be directly detected under the condition of 5, but Cr^{6+} has almost no quenching ability on AuNCs fluorescence. Since the fluorescence quenching ability of Cr^{3+} at these two pH values is similar, no interference of Cr^{3+} is observed. This method realizes the detection of Cr^{3+} and Cr^{6+} by changing the pH value of the sample solution[13].

3. Detection of inorganic anions

Certain inorganic anions participate in the composition of organisms and maintain the normal physiological activities of organisms. Some inorganic anions can cause harm to the human body, such as S^{2-} and CN^- which can act on cell mitochondria and inhibit cell activity. The detection of environmentally harmful anions is also a hot spot for everyone.

3.1. CN-detection

CN^- is a highly toxic substance that can inhibit the activity of enzymes in mitochondria and hinder cell respiration. Z. Shojaeifard et al. developed a new type of ratio fluorescence sensor to detect cyanide ions (CN^-) in aqueous media. In the presence of CN^-, the interaction between AuNCs and Cu(PcTs) is disturbed, so the fluorescence of Cu(PcTs) that has been quenched by AuNCs is found to be effectively restored. In the concentration range of 100-220 μM, the detection limit is 75 nM, which is far lower than the highest concentration of cyanide in drinking water allowed by the World Health Organization (WHO) (2 μM)[14].

3.2. S2-Detection

Vasimalai et al. synthesized MTT as a ligand for the synthesis of MTT-AuNDs. The synthesized MTT-AuNDs are used as fluorescent probes for detecting S^{2-}. During the experiment, it was found that the degree of fluorescence quenching of MTT-AuNDs was related to the added S2-dose. This fluorescence quenching is attributed to the formation of Au_2S complexes. This sensor is an environmentally friendly and easy to detect S2-sensing platform in the water[15].

4. Conclusions and prospects

In recent years, with the development of fluorescence analysis technology, nano-fluorescent materials have been widely used in various research fields. Especially in the field of clinical medicine and environmental testing, it has become a hot topic. From many studies, we have found that the application methods of metallic nano-fluorescent materials in environmental monitoring are maturing through continuous improvement, and the types of detection materials and detection objects continue to be enriched. Although fluorescence nano-detection technology has achieved certain results, there are still many aspects that need to be improved.

(1) The development of fluorescence sensing is to improve the sensitivity and the precise selection of target detection objects from the substances that may affect the experiment. Accurate selection of the object to be tested is the basis of the detection method. In order to give full play to its potential and improve the sensitivity and selectivity of nanoprobes, new sensing mechanisms can be developed, the excitation method of nanoprobes can be changed, and nanoprobes with multiple modes of functionalization can be developed.

There is a lack of a universal and effective method. The synthesized fluorescent nanomaterials are limited to the detection of one or a few analytes, which is likely to cause material waste, increased detection costs, and low detection efficiency. Realizing simultaneous multiple detection of different ions is an exciting future development direction. Although a few metal nanomaterials have achieved this through masking agents, the number of ions analyzed in the same detection is still limited.

References

[1] Daraei H,Maleki A,Mahvi A H,et al. Simultaneous determination of inorganic anions in bottled drinking water by the ion chromatography method[J].Journal of Water Chemistry& Technology, 2015,37(5) : 253-257.

[2] Lee S,Bong S,Ha J,et al. Electrochemical deposition of bismuth on activated graphene-nafion composite for anodic stripping voltammetric determination of trace heavy metals[J]. Sens. Actuators,B,2015,B215(aug.) : 62-69.

[3] Apiric,Vuckovic Z,Stafilov I,et al.Air Pollution Study in Croatia Using Moss Biomonitoring and ICP-AES and AAS Analytical Techniques[J].Arch.Environ.Contam.Toxicol, 2013,65(1) : 33-46.

ISSN: 2664-9640

[4] Drennan — Harris L R,Wongwilawan S,Tyson J F J. Trace determination of total mercury in rice by conventional inductively coupled plasma mass spectrometry[J].Anal At Spectrom,2013,28(2) : 259-265.

[5] Chakraborty I,Udayabhaskararao 23T,Pradeep T.J.Luminescent sub — nanometer clusters for metal ion sensing: A new direction in nanosensors[J].Hazard Mater,2012,211-212: 396-403.

[6] Jarup L. Hazards of heavy metal contamination[J].Br Med Bull,2003,68: 167- 182.

[7] Su Yuting ,Lan Guoyu ,Chen Weiyu,et al. Detection of copper ions through recovery of the fluorescence of DNA-templated copper/silver nanoclusters in the presence of mercaptopropionic acid[J].Anal Chem,2010,82 (20) : 8566-8572.

[8] Yang X,Yang L,Dou Y,et al. Synthesis of highly fluorescent lysine-stabilized Au nanoclusters for sensitive and selective detection of Cu2+ ion[J].J Mater Chem C,2013,1(41) : 6748-6751.

[9] Irudayaraj C G A J. Fluorescent Ag clusters via a protein-directed approach as a Hg (II) ion sensor[J].Anal Chem,2011,83(8) : 2883-2889.

[10] Gong L,Du B,Pan L,et al. Colorimetric aggregation assay for arsenic(III) using gold nanoparticles[J]. Microchim.Acta,2017,184(4) : 1185-1190.

[11] Zhang Z,Zhang J,Lou T,et al. Label-free colorimetric sensing of cobalt (ii) based on inducing aggregation of thiosulfate stabilized gold nanoparticles in the presence of ethylenediamine[J]. Analyst,2011,137(2) : 400.

[12] Huang P,Liu B,Jin W,et al. Colorimetric detection of Cd2+ using 1-amino-2-naphthol-4-sulfonic acid functionalized silver nanoparticles[J].J Nanopart Res,2016,18(11) : 327.

[13] Zhang H,Liu Q,Wang T,et al. Facile preparation of glutathione-stabilized gold nanoclusters for selective determination of chromium (III) and chromium (VI) in environmental water samples[J].Anal Chim Acta,2013,770 (7) : 140-146.

[14] Shojaeifard Z,Hemmateenejad B,Shamsipur M. Efficient on-off ratiometric fluorescence probe for cyanide ion based on perturbation of the interaction between gold nanoclusters and a copper(ii)-phthalocyanine complex[J].ACS Appl Mater Interfaces,2016,8(24) : 15177-15186.

[15] Vasimalai N,Fernández-Argüelles M T,Espi a B. Detection of sulfide using mercapto tetrazine-protected fluorescent gold nanodots: preparation of paper-based testing kit for on-site monitoring[J].ACS Appl Mater Interfaces,2018,10(2) : 1634-1645.