Copper Nanoclusters for Heavy Metal Ions Detection

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Heavy metal ions (HMIs) can accumulate in the human body and cause poisoning. They can enter the biological chain from nature in many ways and are difficult to degrade in the body. HMIs can be detected by colorimetric methods, fluorescence methods, and point-of-care testing (POCT). POCT technology based on smartphone has the advantages of on-site diagnosis and portability. However, the technology relies on a wide variety of accessories that can be affected by environmental changes. Colorimetric methods for color evaluation are an important problem, and another problem is the stability of color. The fluorescence method is widely used in HMIs determination because of its advantages of simple operation, low cost, and high sensitivity. In addition, the fluorescence sensor has the characteristics of strong specificity, fast detection speed, and high accuracy. CuNCs are used as sensors to detect HMIs. The low-cost detection method brings convenience to the actual detection.

copper nanoclusters fluorescent sensors heavy metal ions

1. Silver Ion

Silver is used in cosmetics, industry, catalysts, and other fields. The discharge of waste liquid is widely used in industry and will also pollute water and soil [1]. Ag^+ has a great influence on human health. The accumulation of Ag^+ in the human body can cause cytotoxicity, body failure, and mitochondrial dysfunction [2]. Therefore, it is necessary to develop a simple and rapid silver ion detection method. The requirement of silver ion detection can be satisfied by using CuNCs as probes. Shao et al. made MMI-CuNCs as a probe to detect Ag^+ [3]. The protective agent was MMI, and the reducing agent was hydrazine hydrate. The detection limit was 6.7 nM, which could be applied to the detection of Ag^+ in human serum samples. Shao et al. also proposed to make a nanoprobe with dithiothreitol and eggshell membrane (ESM) [4]. Concurrently, they made a sensor to complete the detection of Ag^+. It caused fluorescence quenching in the presence of Ag^+. Zhang et al. synthesized CuNCs by sonochemistry using N-acetyl-L-cysteine (NAC) [5], which can be used for the selective detection of Ag^+. The limit of detection (LOD) was as low as 7.76×10^{-11} M. The detection mechanism was attributed to dynamic quenching. The addition of Ag^+ made the particles aggregate and the fluorescence lifetime of the NAC-CuNCs system decreased. Importantly, the synthesis process only takes 15 min, and the detection time is short in actual water samples. Glucose (Glc) was used as a reducing agent to prepare Glc-CuNPs [6], and the detection was completed by the fluorescence turn-off mechanism caused by the interaction between the probe and Ag^+. The fluorescence of Glc-CuNPs changed significantly with increasing Ag^+ concentration. In addition, CuNCs/ZIF-8(72) was prepared using CuNCs, $Zn(NO_3)_2 \cdot 6H_2O$, 2-methylimidazole (2-MIM,72 mg) as raw materials [7]. Interestingly, CuNCs/ZIF-8(72) can also be used for Ag^+

detection by fluorescence turn-off mechanism. The mechanism is the strong complexation between sulfhydryl in CuNCs/ZIF-8 (72) and Ag^+. The above-mentioned works (**Table 1**) prove the practicability and broad application prospect of CuNCs in Ag^+ detection. In the reports the researchers investigated, the lowest detection limit of Ag^+ detected by CuNCs was 1.2 pM [8]. These works are performed by fluorescent turn-off mechanism to complete Ag^+ detection, which is applied to human serum or actual water samples. Using eggshell membrane as raw material to synthesize NCs has the advantages of green and low cost [9][10][11]. The synthesis of NCs by ultrasonic chemistry is also a useful way.

Table 1. Report on detection of Ag^+ by CuNCs.

Type of CuNCs	$\lambda_{ex}/\lambda_{em}$ (nm)	Read Out	Sensing Mechanism	Reaction Time	Limit of Detection	Published Time	Reference Value	Ref.
MMI-CuNCs	322/476	Turn-off	AIQ, Static quenching	30 min	6.7 nM	2022	1.2 pM 2021 [8]	[3]
CuNC/ESM	360/623	Turn-off	high-affinity metallophilic interactions	—	—	2019		[4]
NAC-CuNCs	340/630	Turn-off	dynamic quenching	2 min	7.76×10^{-11} M	2022		[5]
Glc-CuNPs	472/542	Turn-off	AIQ	30 min	—	2022		[6]
CuNCs/ZIF-8	360/627	Turn-off	the formation of Ag-S bonds	3 min	0.33 μM	2022		[7]

2. Mercury Ion

Major sources of mercury include fossil fuel burning and mineral industry production. Mercury does not degrade naturally and enters the human body through the biological chain causing serious effects [12]. Mercury can accumulate in various forms in living organisms. Long-term exposure to mercury can cause neurological dysfunction and interferes with cell function [13]. Therefore, the detection of mercury levels is essential for environmental and biological health. The reducing agents were $N_2H_4{\cdot}H_2O$, $NH_2OH{\cdot}HCl$, and Vitamin C, and a strip sensor was made to detect Hg^{2+} [14]. The fabrication of sensing bands makes it easier and more convenient to monitor ions in real-time. Vasimalai et al. synthesized TG-CuNCs using 1-thio-β-glucose as a ligand [15]. The detection limit of Hg^{2+} is 1.7 nM. At the same time, a smartphone-assisted paper kit was designed for on-site monitoring of Hg^{2+} in tap water, rivers, and ponds. Furthermore, CuNCs prepared with turmeric root extract as a template can be used as a fluorescence probe to detect Hg^{2+}, and its quenching mechanism was AIQ [16]. At room temperature, the linear range was 0.0005–25 μM, and the detection limit is 0.12 nM. The analysis of tap water, river water, and canal water demonstrated that the method had good accuracy. Importantly, the biomass used to synthesize CuNCs comes from nature and is more environmentally friendly. Yang et al. made carbon dots-CuNCs (CDs-CuNCs) with dual-emission wavelengths [17]. In the presence of Hg^{2+}, the pink fluorescence changes to blue fluorescence. The addition of Hg^{2+} decreased the red fluorescence of CuNCs. A simple and sensitive test paper was developed for rapid detection and visualization. Zhang et al. used $AgNO_3$ and Cu $(NO_3)_2$ to construct silver/copper bimetallic nanoparticles (AgCu-BNPs) [18]. The addition of Hg^{2+} enabled the bimetallic probe to perform selective detection by colorimetric and fluorescence modes. The minimum concentration limits of colorimetric and fluorescence methods were 89 nM and 9 nM, respectively. The blue fluorescence of AgCu-BNPs was quenched by Hg^{2+}, and the system was accompanied by the visible color change. The quenching mechanism was attributed to IFE, static quenching, and dynamic quenching. Dual-mode detection made the detection more simple and more reliable. The above reports are related to the detection of Hg^{2+} by CuNCs (**Table 2**). The probes were designed into strip sensor belts or combined with a smartphone [19], which was more suitable for detection in complex environments. The NCs prepared by turmeric root extract extends the application value of biomass materials. CDs-CuNCs are nanocomposites with dual emission wavelengths assembled by simple electrostatic discharge. The synthesis of double-emission materials by green materials and chemical means is also worth studying. In a survey of the latest work [20][21], gold nanoparticles were combined with a resolution matrix-assisted laser desorption ionization time-of-flight mass spectrometer (MALDI-TOF MS) for measurement [20]. The detection limit of Hg^{2+} was 0.19 pmol/μL.

Table 2. Report on detection of Hg^{2+} by CuNCs.

Type of CuNCs	λex/λem (nm)	Read Out	Sensing Mechanism	Reaction Time	Limit of Detection	Published Time	Reference Value	Ref.
CuNCs@ESM	—	Turn-off	high-affinity metallophilic interactions	1 h (Hg^{2+}: 500 μM)	—	2018	0.19 pmol/μL 2023 [20]	[14]
TG-CuNCs	350/430	Turn-off	static and dynamic quenching	3 min	1.7 nM	2020		[15]
CuNCs	365/440	Turn-off	AIQ	22 min	0.12 nM	2018		[16]
CD-CuNCs	dual-emission	—	strong affinity	—	0.31 nM	2021		[17]
AgCu-BNPs	350/442	Turn-off	IFE, static and dynamic quenching	—	9 nM	2021		[18]

3. Iron Ions

The presence of Fe^{3+} allows many physiological processes to proceed normally. However, too much Fe^{3+} can lead to serious diseases such as cancer, Parkinson's, and Alzheimer's [22]. Among the methods for detecting iron ions (**Table 3**), the fluorescence method is a good choice for sensor manufacturing because of its high sensitivity [23]. Cao et al. recently assembled BSA-CuNCs @ $[Ru(bpy)_3]^{2+}$ from bovine serum albumin (BSA)-CuNCs and $[Ru(bpy)_3]^{2+}$ to detect Fe^{3+} in tap water and spirits [24]. BSA-CuNCs @ $[Ru(bpy)_3]^{2+}$ show two distinct emission peaks. $[Ru(bpy)_3]^{2+}$ did not respond to Fe^{3+}, and fluorescence quenching occurred in BSA-CuNCs. Additionally, a POCT platform based on a smartphone was designed for the actual detection of Fe^{3+}. Moreover, Cysteamine functionalized nanoconjugate materials (CA-CuNCs) can be used to determine Fe^{3+} in human urine [25]. The detection mechanism was based on electron transfer and AIQ. Importantly, the stratified test strips were designed, and the brightness changed greatly before and after adding Fe^{3+}. Ai et al. used duplex oligonucleotide (dsDNA) as a template to prepare copper nanomaterials (dsDNA-CuNCs), which showed its applicability as a Fe^{3+} sensor; fluorescence quenching was caused by the aggregation of nanomaterial particles [26]. The detection limit was 5 μM when Fe^{3+} concentration was 5–100 μM. Hemmateenejad et al. synthesized Penicillamine-capped bimetallic Gold-Copper NCs (PA-AuCu-bi-MNCs). The milky water solution demonstrated orange fluorescence under a UV lamp [22]. It can be used for simple quantitative detection of Fe^{3+}, utilizing the detection mechanism of IFE. It was important that the detection process is free from Fe^{2+} interference. In the literature investigated, the minimum detection limit of Fe^{3+} detected by CuNCs was 10 nM. CuNCs made of bovine serum albumin (BSA) by Debanjan Guin et al. could be applied to the detection of ions in wastewater and human serum samples [27].

Table 3. The recent report on the detection of Fe^{3+} by CuNCs.

Type of CuNCs	λex/λem (nm)	Read Out	Sensing Mechanism	Reaction Time	Limit of Detection	Published Time	Reference Value	Ref.
BSA-CuNCs@ $[Ru(bpy)_3]^{2+}$	Dual - emission	—	AIQ	3 min	0.086 μM	2022	10 nM 2022 [27]	[24]
CA-CuNCs	385/467	Turn-off	electron transfer, AIQ	—	423 nM	2020		[25]
dsDNA-CuNCs	312/400	Turn-off	AIQ	1 h	5 μM	2020		[26]
PA-AuCu-bi-MNCs	275/605	Turn-off	IFE	5 min	0.1 μM	2019		[22]

4. Cobalt Ion

Cobalt is an essential trace element, but ingesting high concentrations or prolonged exposure can still cause illness, including contact dermatitis, pneumonia, allergic asthma, and lung cancer [28]. Shao et al. used dithiothreitol (DTT) to make DTT-CuNCs to detect Co^{2+}, and the detection mechanism was AIQ [29]. The DTT-CuNCs probe was fixed to the filter paper and designed as a visual paper sensor with the help of a mobile phone, which had good applications in water samples and other environments. Ling et al. found that GSH-AuNCs made from glutathione (GSH) can selectively detect Co^{2+} [30]. The detection process was accomplished by adjusting the pH. When the pH was 6, the presence of Co^{2+} can effectively quench the fluorescence of NCs, and the quenching mechanism was static quenching. He et al. used lysozyme (Lys) and hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) as raw materials to make Lys-CuNCs, which showed strong yellow fluorescence under an ultraviolet lamp [31]. It can be used for sensitive and selective detection of Co^{2+} in an aqueous solution with a detection limit of 2.4 nM. Above are related reports on the application of MNCs in Co^{2+} detection (**Table 4**), which needs to be further developed. In recent work, Tong et al. used silicon nanoparticles/gold nanoparticles complex as a fluorescent probe to detect Co^{2+}, and the detection limit was as low as 60 nM [32]. The detection of ions by GSH-AuNCs was completed by adjusting pH, indicating that pH value would have an impact on the detection process and was also an important factor affecting the fluorescence of substances.

Table 4. The list reported HMIs detection via CuNCs.

Metal Ions	Type of CuNCs	$\lambda_{ex}/\lambda_{em}$ (nm)	Read Out	Sensing Mechanism	Reaction Time	Limit of Detection	Published Time	Reference Value	Ref.
Co^{2+}	DTT-CuNCs	382/627	Turn-off	AIQ	30 min	25 nM	2021		[29]
	GSH-AuNCs	412/500	Turn-off	Static quenching	15 min	0.124 μM (Co^{2+}: 2.0–50.0 μM)	2021	60 nM 2022 [32]	[30]
	Lys-CuNCs	334/596	Turn-off	—	—	2.4 nM	2018		[31]
Cr^{6+}	bi-ligand CuNCs	330/411 (Cu NC-2 [a])	Turn-off	IFE	—	0.03 mM	—	—	[33]
Mn^{2+}	CuNCs@T [b]	354/561	Turn-on	AIE	40 min	10 μM	—	—	[34]
Cd^{2+}	GSH@CDs-CuNCs	dual-emission	—	AIE (750 nm)	15 min	0.6 $\mu mol{\cdot}L^{-1}$	—	—	[35]

Cu NC-2 [a]: TA-to-CysA molar ratio of 1:1, T [b]: Rich-thymine.

5. Other Ions

CuNCs have also been synthesized for the detection of other HMIs. For instance, Cr (VI) contamination is highly associated with atopic dermatitis, carcinogenesis, and mutations in animals and humans. Hu et al. synthesized CuNCs using thiosalicylic acid (TA) and cysteamine (CysA) as ligands [33]. Because the IFE effect quenches the fluorescence of CuNCs, a fluorescence sensor was designed to detect Cr (VI). In addition, He et al. synthesized water-soluble CuNCs stabilized by DNA single base thymine and performed selective detection of Mn^{2+} based on AIE [34]. Cadmium is highly toxic, known as a carcinogen, and in large quantities can damage the liver, bones, and kidneys. Furthermore, high levels of cadmium have been linked to diabetes, cancer, and heart disease [36]. Liu et al. used the glutathione@carbon dots (GSH@CDs) as a template for the synthesis of GSH@CDs-CuNCs, which can be used to detect Cd^{2+}. The linear range of Cd^{2+} was 0~20 $\mu mol \cdot L^{-1}$, and the limit of detection was 0.6 $\mu mol \cdot L^{-1}$ [35].

Those listed above are just a few examples of CuNCs detecting HMIs. (**Table 4**) These works further elucidate the possibility of CuNCs for ions detection and provide a new approach for the detection of HMIs.

6. Selectivity Difference of CuNCs in Detecting HMIs

Heavy metal ions have a great influence on organisms and the environment, so fluorescence sensing for HMIs detection is of great significance. There were significant differences in CuNCs detection among different HMIs. For example, different fluorescence responses, and different fluorescence intensities. Huang et al. prepared CuNCs using bovine serum albumin (BSA) and thiosalicylic acid (TSA) as protective ligands [37]. The fluorescence changes produced by TSA/BSA-CuNCs interacting with various metal ions (incubated in sodium phosphate buffer) were observed. Only Cr^{6+} showed significant fluorescence quenching on TSA/BSA-CuNCs due to the IFE. Cr^{6+} provides sufficient oxidative etching of copper ions/atoms. Olga Garcia et al. designed a sensor for the detection of Hg^{2+} by taking advantage of the differences in the detection of metal ions by CuNCs [38]. CuNCs were tested on various metal ions under the same conditions, and the fluorescence attenuation was nearly 50% only in the presence of Hg^{2+}, and the effect was small in the presence of other ions. CuNCs were incubated with a series of Hg^{2+} concentrations, and the hydrodynamic size was gradually increased. No changes in the hydrodynamic size were detected in the presence of Cd^{2+}. This kind of CuNCs can be used as selective probes to detect Hg^{2+} in the presence of other ions. It has also been mentioned that the CDs-CuNCs synthesized by Yang et al. have dual emission wavelengths [17]. The addition of Hg^{2+} reduced the red emission of CuNCs, while the blue emission of CDs remained stable. As a result, the fluorescent color changes from pink to blue.

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