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Visual Determination of Copper (II) Using a Biomass Sourced Carbon Quantum Dot (CQD) Ratiometric Fluorescent Probe

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ABSTRACT

Accurate detection of copper ions is crucial since it is an essential trace element. Carbon quantum dots (CQDs) were prepared from apricot leaves using a hydrothermal method. These CQDs, which generated a reference signal, were combined with glutathionebound gold nanoclusters (GSH-AuNCs) synthesized by the reduction of chloroauric acid to form a ratiometric fluorescent probe. The probe exhibited fluorescence emission at 450 nm and 568 nm. The determination of Cu(II) was performed through visual analysis of the color change and the intensity ratio (I_{450}/I_{568}) of the emission peaks. Orange fluorescent GSH-AuNCs responded to Cu(II) with fluorescence, and the blue fluorescent CQDs were chemically inert. The probes changed color from pink to purple to blue in response to different concentrations of Cu(II). The linear range of the fluorescence probe for Cu(II) was 0 to 120 µmol/L, and the limit of detection (LOD) was 0.65 µmol/L. This study has demonstrated that the probe provided good selectivity for detecting Cu(II) in water and has potential practical application.

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KEYWORDS

Carbon quantum dots (CQDs); copper(II); ratiometric fluorescent probe; visual detection

Introduction

Copper is abundant in nature and is used in all aspects of human life. However, excess copper can cause serious environmental pollution (Cui et al. 2023) and has toxic effects (C. H. Wang et al. 2023; Zhang et al. 2024). For these reasons, the copper limits are 15.7–23.6 μ mol/L in human blood and 20 μ mol/L in drinking water according to the U.S. Environmental Protection Agency. In fact, monitoring Cu(II) levels can be an important marker for environmental pollution and biomedical diagnosis.

Thus, many analytical methods, including voltammetry (Shen et al. 2023), inductively coupled plasma-mass spectrometry (ICP-MS) (Van Acker et al. 2023), atomic absorption spectroscopy (AAS) (Drosaki and Anthemidis 2022) and atomic emission spectroscopy (AES) (Ronda et al. 2022), have been reported for Cu(II). However, the use of large instruments for these techniques is not conducive to swift on-site detection and is

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costly (X. F. Wang, Shen, et al. 2021). Fluorescence analysis has garnered significant interest owing to its simplicity, rapid response, and remarkable sensitivity (Chopra et al. 2022; Park et al. 2020).

Recently, extensive research has focused on the preparation of quantum dots (QDs) (Hu et al. 2023; H. Li et al. 2023), including graphene QDs (Roushani et al. 2017), ZnS QDs (Rajabi et al. 2020), CdTe QDs (Roushani, Shamsipur, and Rajabi 2014), ZnTe QDs (Alvand et al. 2019), and carbon quantum dots (CQDs) (Y. Q. Wu et al. 2024), for applications as nanophotocatalysts, fluorescent probes, nanosorbents and antibacterial films. Nevertheless, due to the increasing application of CQDs in fluorescence analysis, the introduction of plant extracts (J. X. Wang et al. 2024) for the synthesis of new fluorescent probes with low toxicity and high sensitivity is of great interest and importance. Tan and Zhou (2024) prepared biomass CQDs from dragon fruit peels. The obtained CQDs displayed exceptional fluorescence quenching toward Fe³⁺, with a remarkable limit of detection of 1.13 μ mol/L and a wide linear range of 0–285 μ mol/L. Han et al. (2019) utilized CQDs that had been hydrothermally synthesized from orange peels to determine dopamine.

However, in conventional fluorescence sensing and imaging, signal acquisition from individual fluorescent nanoprobes relying on absolute intensity is sometimes inaccurate (Lv et al. 2019). This phenomenon can be attributed to various factors, such as fluctuations in instrument parameters (e.g., changes in the excitation wavelength and slit width (Y. H. Li, Dahal, et al. 2021), variations in the microenvironment (Yin et al. 2021), and localized fluctuations in the concentration of the nanoprobes (caused by uneven delivery of the nanoparticles (Post et al. 2019). Importantly, these variations are not the result of differences in chemical bonding or specific signaling pathways (Levine and Margulies 2021).

The aforementioned variables that are unrelated to the detected substance may lead to significant fluctuations in the absolute signal intensity, resulting in inaccurate results (H. Li, Wang, et al. 2021; Fan et al. 2021). Ratiometric fluorescent probes are able to effectively address these challenges, as an additional fluorescence emission wavelength is introduced (Chen et al. 2023; Gong et al. 2022; Han et al. 2019). More importantly, it can also offer a favorable visual detection platform (Park et al. 2020).

To achieve simple and accurate detection, ratiometric fluorescent nanoprobes have been fabricated *via* two design strategies. One approach involves the incorporation of a secondary species whose signal is used as a reference that is unaffected by the target. The other approach involves reversible alteration of the response of both targets to enable ratiometric measurements (X. Huang et al. 2018). The first strategy is important for achieving accurate visualization and quantitative detection of ratiometric fluorescent probes (Bigdeli et al. 2019). W. T. Li et al. (2020) developed an innovative fluorescent probe that exhibits dual-emission properties by combining CuNCs and N-doped CQDs to detect Pb²⁺.

To provide a self-calibrating signal, researchers have detected the target by measuring the change in the ratio of fluorescence intensity between the fluorophores and observing the composite fluorochrome by combining CQDs with blue emission with red-emitting copper nanoclusters. Y. Liu, Su, et al. (2022) constructed a CQD/rhodamine B fluorescence sensor with dual-emission capabilities to quantitatively and visually monitored the