



Recent advances in the analytical applications of copper nanoclusters

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ABSTRACT

Metal nanoclusters (MNCs) are composed of several to tens of atoms and have drawn considerable research interest due to their unique electrical, physical and optical properties. However, in comparison to the extensively investigated Au NCs and Ag NCs, analytical applications of the copper nanoclusters (Cu NCs) are relatively limited and still at an early stage. In this review, we focus on recent advances in the analytical applications of Cu NCs based on their optical, electrochemical, and catalytic properties for the detection of various analytes, including metal ions, anions, biomolecules (proteins, nucleic acids etc.), small molecules and pH. In addition, their applications in biological labeling and bioimaging were summarized.

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1. Introduction

Metal nanoclusters (MNCs) are composed of very few atoms, with a core size in the sub-nanometer regime, providing the missing link between atomic and nanoparticle behavior in metals [1]. Their sizes are comparable to the Fermi wavelength of electrons, which results in molecule-like properties including discrete electronic states and size-dependent fluorescence (FL) [2]. Exploiting these unique properties has resulted in many important findings of MNCs, and MNCs have drawn considerable research interest in recent years due to their unique electrical, physical and optical properties for use in electronic devices, catalysis, biological imaging, and chemical sensors [3–6]. In particular, compared to quantum dots and organic dyes, MNCs exhibit excellent photostability, large Stokes shift, and low environmental hazard [7,8]. Inspired by the existing and potential applications of MNCs, studies on MNCs are growing rapidly in the past few years. To date, great efforts have been paid to noble metal nanoclusters (mainly Au and Ag) due to their chemical stability and facile synthetic procedure [9–11]. However, very promising copper nanoclusters (Cu NCs) have received less attention. In fact, compared to the noble metal Au and Ag, the metal Cu is significantly cheaper and widely used in industries because of its high conductivity, similar properties to Au and Ag. Furthermore, compared with the expensive precursors for the synthesis of Au NCs and Ag NCs, the precursor for the preparation of Cu NCs is relatively abundant, inexpensive and readily available from commercial sources, therefore the Cu NCs are more favorable for various applications than the noble metal NCs.

In this review, we mainly focus on the analytical applications of Cu NCs in the past few years rather than their synthetic methods, which have been reviewed in detail in previous publications [5,10,11]. However, for every analytical application, we will briefly introduce the synthetic strategy for the Cu NCs and then their analytical applications. In the coming text, we highlight recent advances in the analytical applications of the Cu NCs-based optical, electrochemical, and catalytical methods for the detection of various analytes, including metal ions, anions, biomolecular (proteins, nucleic acids etc.), small molecules and pH. Also, their applications in biological labeling and bioimaging were covered. And these recent applications are summarized in Table 1.

2. Photophysical properties of Cu NCs

When metal nanoparticles (NPs) change to metal NCs, the properties of particles disappear and the bands turn into more or less discrete energy levels. Thus, the collective oscillation of electrons is obstructed and metal NCs do not give rise to surface plasmon resonance effect, and exhibit unique optical properties such as molecule-like absorption and strong luminescence [5]. It is well known that the UV-Vis absorption of Cu NPs is dominated by surface plasmon resonance peaks at 560–600 nm [12]. However, significantly different from large Cu NPs, the UV-Vis absorption of Cu NCs exhibit molecular-like optical transitions with absorbance bands between 216 nm and 468 nm (Table 1). These molecular-like optical transitions in UV-vis absorption spectrum are due to the quasi-continuous electronic energy band structure and quantum confinement effects of Cu NCs. Similar to that of Au NCs and Ag NCs, the fluorescence properties of Cu NCs are dependent on their chemical environments, including the cluster size, solvent and surface capping ligands or Cu NCs prepared from different synthetic strategies etc (Table 1).

3. Cu NCs-based fluorescence sensors

The fluorescent Cu NCs always have been applied as optical probes for the detection of various targets such as metal ions, anions, biomolecules, small molecules and solution pH. It is also an at-

tractive choice for the biological labeling and imaging owing to their unique features, like optical activity, biocompatibility, and nontoxicity. In the following section, we highlight recent advances in the analytical applications of Cu NCs based on their fluorescent properties.

3.1. Metal ions sensors

The Cu NCs have been used as new fluorescent probes for the detection of heavy metal ions, including Hg^{2+} , Pb^{2+} , Cu^{2+} , Fe^{3+} , Cr(VI) and Cr^{3+} .

3.1.1. Hg^{2+} sensor

Ghosh et al. [13] found that hydrazine reduction of Cu^{2+} derived Cu NCs stabilized by citric acid and CTAB can be used as a fluorescence probe to detect Hg^{2+} based on its quenching effect of the fluorescent Cu NCs, with a limit of detection (LOD) of 1 nM. Also, Yang et al. [14] synthesized L-cysteine Cu NCs, which were used for assaying Hg^{2+} based on the FL quenching of the Cu NCs due to strong interactions between Hg^{2+} and L-cysteine on the surface of the Cu NCs. The linear detection range for Hg^{2+} is 0.1 – 1000 μM with a LOD of 24 nM.

In contrast to previously reported preparation of fluorescent Cu NCs using ds-DNA as templates, Liu et al. [15] used ss-DNAs as templates to prepare Cu NCs in the presence of Hg^{2+} . It is found that upon addition of Hg^{2+} , a more intense fluorescence response was observed. This is caused by Hg^{2+} mediated T–T base pair to favor the formation of fluorescent Cu NCs, demonstrating the key role of DNA thymine in producing red-emissive fluorescent Cu NCs on ss-DNA templates. Due to highly specific role of Hg^{2+} in mediating a T–T base pair, a highly selective turn-on fluorescence sensor was designed for the detection of Hg^{2+} . Using 34T as templates, the limit detection of 10 nM is obtained, which is comparable to the permitted maximum level (about 10 nM) for Hg^{2+} in drinking water from the United States Environmental Protection Agency (EPA).

Recently, Liao et al. [16] reported a new strategy for the fast synthesis of Cu NCs by using BSA and hydrogen peroxide, in which H_2O_2 plays both a ligand to combine with BSA–Cu complex to form BSA–Cu– H_2O_2 complex and an oxidizing agent to partly destroy disulfide bonds in BSA. The obtained Cu NCs showed strong fluorescence emission at 420 nm. Interestingly, it was found that Hg^{2+} can significantly quench the FL of as-prepared Cu NCs through introduction of Cu NCs aggregation due to formation of Hg–S covalent bond and a part destruction of Cu–S bonds in Cu NCs by Hg^{2+} . The as-prepared Cu NCs provided ultrahigh sensitivity for the detection of Hg^{2+} with a LOD of 4.7 pM.

3.1.2. Pb^{2+} sensor

Early in 2011, Goswami et al. [17] succeeded in BSA templated synthesis of fluorescent Cu NCs from CuSO_4 precursor under alkali media for the first time and subsequently used for selective sensing of Pb^{2+} at the part-per-million level. The detection mechanism is based on the luminescence quenching of the Cu NCs in the presence of Pb^{2+} due to the Cu NCs aggregation induced by the complexation between BSA and Pb^{2+} ions. Based on a similar principle, in another work, Chen et al. [18] introduced the use of dsDNA as template for the preparation of Cu NCs through Cu^{2+} reduction by ascorbate according to the previously reported method [19,20]. The Stern–Volmer plot of the fluorescence quenching by Pb^{2+} displayed a linear range of 5 to 100 nM with a LOD of 5 nM, which is much lower than the maximum permitted level (72 nM) of Pb^{2+} in drinking water by EPA.

Another interesting piece of work introduced the use of the electrochemically synthesized Cu NCs as FL probe for the detection of Pb^{2+} ions [21]. In this work, Vilar-Vidal et al. found that medium copper (Cu_{13}) clusters are very selective for Pb^{2+} ions by FL quenching and exhibited a LOD of 4.9 μM . However, small Cu NCs (Cu_7) show

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