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REVIEW

Applications of Metal Nanoclusters in Environmental Monitoring

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Abstract: Novel optical materials are crucial for environmental monitoring. Metal nanoclusters (metal NCs), typically consisting of several to tens of metal atoms, have attracted more and more attention in recent years. Due to their ultra-small size, strong fluorescence, low toxicity, excellent stability and unique core-shell structure, metal NCs have been considered as the promising optical materials for construction of excellent fluorescent sensors. In this review, we mainly focus on the recent application progress of NCs in environmental monitoring, including the detection of pH, heavy metal ions, inorganic anions and nitroaromatic explosives.

Key Words: Metal nanoclusters; Environmental monitoring; Fluorescence sensing; Review

1 Introduction

With the development of modern society and economy, environmental pollutions become increasingly serious. Large quantities of chemicals used in industry, agriculture and daily life are discharged into the environment. A large part of the pollutants are long-existed in the environmental medium and easily enriched in the food chain, which have threatened heavily to environments and human health. In order to protect the ecological environment security and human health, it is particularly important to develop the determination of the regular pollution index. Currently, various common test methods have been developed, including atomic absorption method, UV-Vis absorption spectroscopy, ion chromatography, inductively coupled plasma mass spectrometry and fluorescence analysis[1]. Due to the attractive features, such as high sensitivity, simplicity, cost efficiency and ease of miniaturization, fluorescence analysis has been considered as an important analytical tool[2]. Optical material or probe is an indispensable part of the fluorescence analysis method, and the choice of the optical probe is the key to decide the performance of the fluorescence analysis. In the past few decades, several types of optical probes have been applied into the construction of fluorescent sensors, including organic dyes[3], polymer dots[4], quantum dots[5,6], upconversion nanoparticles[7,8], carbon dots[9] and metal nanoclusters (NCs)[10,11]. Among these optical probes, due to their ultrasmallsize, bright fluorescence, and good photostability, metal NCs have especially been recognized as the rising stars and attracted considerable attention in recent years in environmental monitoring.

Metal NCs, typically consisting of several to tens of metal atoms, are an important transition between the metal atoms and large metal nanoparticles[12], as shown in Fig.1. The conduction band of large metal nanoparticles (> 2 nm) exhibits quasi-continuous energy level. Under the excitation of light, free electrons in the conduction band proceed the coherent oscillating back and forth and displayed the surface plasma resonance effect. With the decrease of the size of metal nanoparticles, the physical and chemical properties

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would change markedly. When their size decreases to the level of the electron Fermi wavelength, the quasi-continuous energy level renders discrete and generates the molecule-like electronic state, meanwhile the surface plasma resonance disappears. Due to the unique discrete energy level and quantum size effect, metal NCs present a series of outstanding features, such as strong fluorescence, good photostability and excellent biocompatibility. At present, various metal NCs displaying fluorescence property were reported, such as Au NCs Ag NCs, Cu NCs, Pt NCs, as well as alloy NCs consisting of two or more species of metal atoms[13]. Among these metal NCs, Au NCs and AgNCs were extensively studied. Recently, a growing number of studies about the synthesis and application of Cu NCs and other metal NCs have also been presented.

It should be pointed out that several excellent review papers have discussed about the property, synthesis and applications of metal NCs[10,11,13–19]. However, these previous reviews focused on one kind of metal NCs or presented their applications in brief, but lacked of the special research about their applications in environmental monitoring. In this review, we presented the fluorescence property and the synthesis of metal NCs, and their recent advances in the applications of environmental monitoring. In the final part, we gave a brief conclusion and discuss on current challenges in their environmental applications.

2 Fluorescence properties of metal NCs

The fluorescence of bulk metal is extremely weak and their luminescence efficiency is typically 10^{-10}, which is attributed to very fast non-radiative transition and the quasi-continuous energy levels[20]. When the size of metal reduces to the nanometer scale, the luminescence efficiency is enhanced significantly. As their size further reduces to a value close to the Fermi wavelength of an electron, the metal nanoparticles at this point are considered as metal NCs. Metal NCs present bright fluorescence, and their quantum yield is seven to nine orders of magnitude higher than that of bulk metal. The luminescence of metal NCs is usually attributed to inter-band transitions between the ligand/d-band and the sp band or electronic transitions between HOMO-LUMO orbitals[17]. With the in-depth studies on metal NCs, researchers have a further understanding about their luminescence mechanism. The studies suggest that there may be two major luminescence sources for metal NCs: one source is the metal core with its intrinsic quantization effects, and the other source is the particle surface governed by the interaction between metal core and surface ligands[21].

In previous studies, the fluorescence of metal NCs were found to be very sensitive to the chemical environment, including the size and component of core, surface ligands and solvent. Dickson group[22] studied the effect of the core size on their fluorescence though the preparation of a range of poly(amidoamine) dendrimers (PAMAM) protected Au NCs. It was found that they could emit from violet to near-infrared fluorescence through regulating the number of Au atoms in metal core. Xie *et al*[23] reported that Ag^+ could deposit on the core surface of bovine serum albumin (BSA) stabilized Au NCs (BSA-Au NCs) and cause the formation of AuAg alloy NCs, which could emit much stronger fluorescence. Ras *et al*[24] found that polymethylacrylic acid (PMAA) stabilized Ag NCs displayed obvious solvatochromic effects, and their emission peak shifted 80 nm by adjusting the polarity of the solvent. Subsequently, the Ag NCs protected by other ligands were also reported to have similar solvatochromic effects, such as DNA[25], polystyrene-b-methyl methacrylate copolymers[26] and polyethyleneimine (PEI)[27]. In addition to the influences of metal core and solvatochromic effect, the electron donation capability of the ligands played a significant role in determining the quantum yield of metal NCs. Taking Au_{25} NCs protected by different ligands for example, the ligands showed extremely obvious effects on their fluorescence[28]. The quantum yield of $[Au_{25}(SC_6H_{13})_{18}]^-$, $[Au_{25}(SC_{12}H_{25})_{18}]^-$ and $[Au_{25}(SC_2H_4Ph)_{18}]^-$ were found to be 2×10^{-5}, 5×10^{-5} and 1×10^{-4}, respectively. The results revealed that the

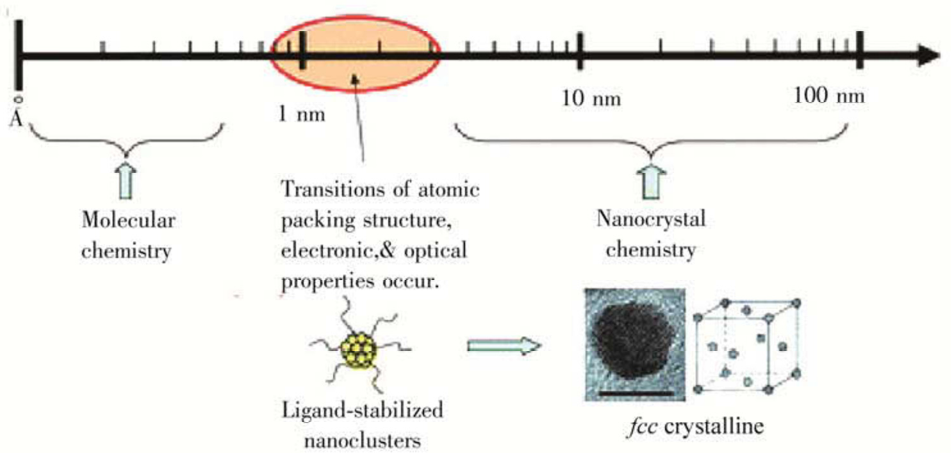

Fig.1 Metal nanoclusters (NCs) bridge metal atoms and nanocrystals[12]