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Lysozyme-stabilized gold nanoclusters as a novel fluorescence probe for cyanide recognition

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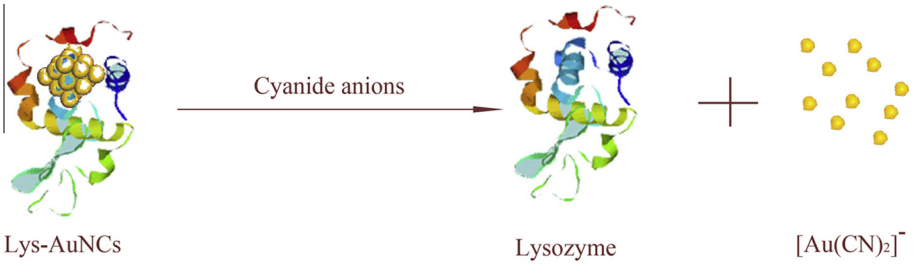
HIGHLIGHTS

- A novel Lys-AuNCs fluorescence probe for cyanide anion detection was developed.
- Lys-AuNCs could be served as a "naked-eye" optical probe for cyanide anion.
- The probe was environmentally-friendly and synthesized conveniently.

GRAPHICAL ABSTRACT



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ABSTRACT

Lysozyme-stabilized gold nanoclusters (Lys-AuNCs) have been synthesized and utilized as a fluorescent probe for selective detection of cyanide (CN^-). Lys-AuNCs had an average size of 4 nm and showed a red emission at 650 nm (λ_{ex} = 370 nm). The fluorescence of Lys-AuNCs could be quenched by CN^-. An excellent sensitivity and selectivity toward the detection of CN^- in aqueous solution was observed. The fluorescence intensity was linear with the CN^- concentration in the range of 5.00×10^{-6} M–1.20×10^{-4} M with a detection limit as low as 1.9×10^{-7} M. Also, the addition of CN^- to Lys-AuNCs could induce an obvious color change from light yellow to colorless. Correspondingly, a bright red fluorescence disappeared and a blue fluorescence appeared. The results indicated that Lys-AuNCs could be applied in detection of cyanide on environmental aspects.

Introduction

Anion recognition has been a challenging area in nanotechnology due to its extensive research activities including environmental, clinical, chemical, and biological application in recent decades [1]. Among the various anions, cyanide was an extremely toxic contaminant that could bind heme cofactors to inhibit the terminal respiratory chain enzyme cytochrome c oxidase and lead to the death of human or other organisms [2]. The hazardous toxic pollutant cyanide was widely released from the industrial settings (1.5 million tons per year) and made it significant research efforts directed toward the detection of cyanide by relevant biological technology and means. Several strategies for detecting cyanide have been developed based on spectrophotometry [3], potentiometry with cyanide-selective electrodes [4] and flow injection amperometry [5], etc. Fluorescence spectroscopy for the detection of cyanide might be favoriate choice in ultratrace quantity [6] by virtue of high sensitivity and easy operation. Additionally, most current fluorescent probes involved were operationally complex, complicated synthetic procedure and utilized in organic solvents for detecting cyanide [7,8]. Consequently developing fluorescent probes with high sensitivity, low cost and green synthesis to directly measure cyanide in aqueous media was competitive.

Recently, gold nanoclusters (AuNCs) possessed distinct physical and chemical attributes that made them excellent optical probes for the fabrication of novel chemical and biological sensing [9]. These features broadened the application of AuNCs toward fluores-

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cence sensing. Dong's group [10] monitored cyanide from dissolution of Rhodamine B-adsorbed Au nanoparticles (RB-AuNPs). Fluorescence of RB-AuNPs was enhanced in the presence of cyanide based on the fact that Au NPs were etched by cyanide. Liu et al [11] developed a novel BSA-stabilized AuNCs for detecting cyanide by etching-induced fluorescence quenching. Up to now, AuNCs could be stablized with amine [12], DNA [13], peptide [14], protein [15], polymers [16], dendrimers [17], and thiolate ligands [18] as scaffolds. Inspired by natural strategy to fabricate biominerals, using biomolecules as scaffold for developing green synthesis protocols to prepare AuNCs have attracted a great deal of interest. Proteins played an important role in the synthesis of AuNCs because the amino, carboxyl and thiol groups in proteins could be served as effective stabilizing agents [19,20].

In this work, water-soluble lysozyme stabilized AuNCs (Lys-AuNCs) could be facilely synthesized and characterized. Interestingly, the synthetic Lys-AuNCs could be utilized as a fluorescence probe for detection of CN^-. Furthermore, the fluorescence of Lys-AuNCs was quenched linearly by CN^-. Thus, a cost-effective and sensitive fluorescence probe for the monitoring of CN^- was constructed.

Experimental

Chemicals and reagents

Aurichlorohydric acid ($HAuCl_4{\cdot}3H_2O$) was purchased from Aldrich (>99.9%, US). Lysozyme was ordered from Shanghai Sangon Biotechnology Co. Ltd (Shanghai, China). Water (>18.2 MΩ cm) used for the experiments was purified by a Milli-Q system.

Apparatus

Absorption spectra were obtained with a TU-1901 spectrophotometer (Persee, Peking, China). An Edinburgh F900 spectrophotometer (UK) was used for fluorescence emission spectra recording. Transmission electron microscopy (TEM) was performed with a JEOL 2100 at 200 kV (Japan). The sample was freeze-dried and provided by infrared spectroscopy between 4000 and 500 cm^{-1} on a Shimadzu FTIR-8400S spectrometer (Japan). A PB-10 pH meter (Sartorius, German) was used to adjust pH values.

Synthesis of Lys-AuNCs

Lys-AuNCs were synthesized according to reference [15]. Briefly, 2 mL of 4 mM $HAuCl_4{\cdot}3H_2O$ solution was added to 2 mL lysozyme solution (16 mg/mL) with vigorous stirring. About 0.2 mL NaOH (1 M) was introduced to adjust the acidity of solution at pH 12. The reaction should proceed at 37 °C for 8 h. Simultaneously, the solution color turned from light yellow to deep brown, indicating the formation of Ag NCs. The solution of Lys-AuNCs emitted the intense red luminescence under UV light (365 nm).

Fluorescence measurements

A typical CN^- detection process was conducted as follows. The as-prepared Lys-AuNCs solutions were 1.25 mg/mL for CN^- detection. NaOH–$NaHCO_3$ buffer solutions were used to adjust the acidity of solution at pH 11.0 for detection. The fluorescence spectra of Lys-AuNCs upon titration with CN^- were recorded by Edinburgh F900 spectrophotometer. To evaluate the selectivity of CN^- fluorescence detection by Lys-AuNCs, other anions such as F^-, Cl^-, Br^-, I^-, CO_3^{2-}, CH_3COO^-, NO_3^-, NO_2^-, ClO_4^-, SCN^-, $EDTA^{2-}$, and $C_6H_5O_7^{3-}$ were also tested and the response recorded and analyzed at pH 11.0.

Results and discussion

Characterization of Lys-AuNCs

Highly fluorescent Lys-AuNCs were obtained via one-pot, "green" synthetic route. As shown in Fig. 1A, Lys-AuNCs were approximately spherical in shape and about 4 nm in diameter. Infrared spectroscopy (FTIR) was a valuable method to analyze the protein secondary structures [21,22]. Secondary structure analysis of proteins was nearly exclusively done using the amide I band (~1650 cm^{-1}), but the amide II (~1550 cm^{-1}) and amide III bands (1400–1200 cm^{-1}) have also been shown useful [21]. Fig. 1B showed the amide I band was no shifted but decreased in the intensity of the peak after assembled to AuNCs. This trend indicated that unordered structures increased and fewer helical structures were present. The appearance of a band at ~1500 cm^{-1} in Lys-AuNCs indicated a deprotonation of Tyr–OH [21].

From the absorption and fluorescence spectra of Lys-AuNCs (Fig. 2), it could be concluded that no apparent surface plasmon resonance absorption peak in 520 nm was observed. When excited at 370 nm, the solution of Lys-AuNCs showed an emission peak centered at 650 nm. The fluorescence quantum yield (QY) of the Lys-AuNCs was calculated to be 5.2% by comparison with rhodamine 6G in ethanol solution (with a standard QY of 95%). The photoluminescence was stable in the pH range of 1–13.

Fluorescence quenching of Lys-AuNCs by CN^-

The fluorescence responses of Lys-AuNCs to CN^- were investigated in Fig. 3A. Upon the addition of 3.05×10^{-4} M CN^-, the emission intensity of Lys-AuNCs at 650 nm decreased. The pH of buffer solution was investigated in order to improve the sensitive detection of CN^- by Lys-AuNCs. CN^- was inclined to capture the available protons in the solution under lower pH conditions

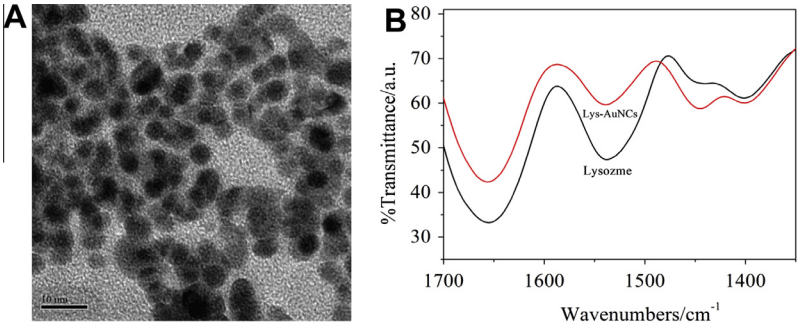

Fig. 1. (A) TEM images of Lys-AuNCs. (B) The FTIR spectra of lysozyme and Lys-AuNCs.