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Synthesis of fluorescent BSA templated silver nanomaterials and its application of detection of Zn$^{2+}$ and Co$^{2+}$

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Abstract

In this paper, BSA (bovine serum albumin) was used as stabilizer and protectant to synthesize high fluorescent silver nanoparticles (BSA-AgNPs) in ice bath. A method for the detection of metal ions was developed by using silver nanoparticles as fluorescent probes. The experimental results show that the BSA-AgNPs has unique selectivity for cobalt ions and zinc ions. When the cobalt ion exists in the system, the BSA-AgNPs is destroyed and the fluorescence quenching is caused, and the correlation coefficient is $R = 0.97035$ when the concentration of cobalt ion is $100 \, \mu\text{mol} / \text{L} - 600 \, \mu\text{mol} / \text{L}$, and the correlation coefficient is $R = 0.97035$. When the zinc ion exists in the system, the interaction of Zn$^{2+}$ and BSA leads to the rise of the BSA-AgNPs fluorescence, and the Zn$^{2+}$ concentration is in the $100 \, \mu\text{mol} / \text{L} - 600 \, \mu\text{mol} / \text{L}$. BSA-AgNPs shows a good linear relationship. The correlation coefficient is 0.98590. EDTA can be used as a metal ion chelating agent. The rapid complexation of Co$^{2+}$ with EDTA blocked the interaction between Co$^{2+}$ and BSA, and the fluorescence of BSA-AgNPs could be restored. Based on this, the label free detection of zinc ions and cobalt ions was completed. Therefore, the prepared high fluorescence BSA-AgNPs sensor has a good application prospect in ion detection.

As we all know, with the development of industry, zinc mining, processing and the discharge of industrial sewage and polluted gas lead to environmental pollution by zinc and cobalt. Cobalt exceeding the standard in the environment will lead to paralysis, bone growth retardation, carcinogenesis, etc. Although zinc is an indispensable element in the human body, if the zinc in the body exceeds the standard, it will also lead to poisoning. Therefore, the development of high sensitivity, high selectivity, simple and convenient Zn$^{2+}$, Co$^{2+}$ concentration detection method is of great significance for environmental protection.

Although the traditional method of heavy metal ion detection is high sensitivity but the instrument is more expensive, the condition of the sample is higher and the preprocessing is more complicated, it can not meet the demand of modern detection. Fluorescence analysis as a new detection method has attracted wide attention from all walks of life, [1]. As a novel fluorescent probe, metal nanomaterials are widely used in the fields of metal ion [2], nonmetal ion [3], biological small molecule [4], cell imaging and labeling [5], medicine and so on. Guo et al [6] uses lysozyme (dLys) as a stabilizer and protective agent to synthesize dLys-AgNCs, and uses electron transfer mechanism to cause fluorescence quenching. The unmarked detection of $\text{S}^{2-}$ has been realized. Lu et al [7] synthesized BSA NC self assembled silver nanomaterials by using bovine serum albumin as scaffold. The material can be used to visualize Hg ions, with a minimum detection limit of 0.0487 mol L$^{-1}$. Silver Nanomaterials Synthesized by [8] et al By Peng et al Were labeled with $\text{H}_2\text{O}_2$. As the concentration of $\text{H}_2\text{O}_2$ increases, the fluorescence is enhanced. Ramar et al [9] uses glutathione (GSH) as a protective agent to synthesize silver nanomaterials (GSH-AgNCs). The interaction between the carboxyl group in GSH and the hydrogen bond in the amino group of dopamine (DA) results in fluorescence enhancement. Based on this, the label free detection of DA is completed. At present, the phenomenon of metal nanomaterials as probes is mainly...
fluorescence quenching and fluorescence enhancement, the mechanism of which is charge transfer, induced aggregation luminescence, and ligand exchange.

In this paper, we have used Goswami's method to modify the silver nanoparticles protected by bovine serum albumin (figure 1). Zn$^{2+}$ and Co$^{2+}$ were detected by fluorescence quenching and fluorescence enhancement. The method is simple, rapid and sensitive. The fluorescence of BSA-AgNPs can be quenched by Co$^{2+}$, and the fluorescence will be restored after adding EDTA. A fluorescent reversible sensor has been formed.

1. Experimental part

1.1. Instruments and drugs
F-4600 fluorescence spectrophotometer (Hitachi hi-tech company), set up the width of the slit is 10 nm, the width of the slit is 10 nm; JEM2100F transmission electron microscope (Japan Electronic Company): pHS-3C pH meter (Shanghai instrument electric scientific instruments stock company).

Bovine serum albumin (BSA, Shanghai Bioengineering Technology Co., Ltd); Cu(NO$_3$)$_2$·3H$_2$O; Pb(NO$_3$)$_2$; ZnSO$_4$·7H$_2$O (analytically pure, Tianjin wind ship chemical reagent Technology Co., Ltd); Bi(NO$_3$)$_3$·3H$_2$O; ethylene diamine tetra acetic acid (EDTA); Tianjin City North Union Fine Chemicals Development Co., Ltd; AgNO$_3$ (analysis pure, Beijing Puchen chemical reagents Co., Ltd); FeCl$_2$·4H$_2$O (analysis pure, Beijing shle chemical plant); MnSO$_4$.H$_2$O (analysis pure, Beijing Chaoyang District chemical four plant); Bi(NO$_3$)$_3$·3H$_2$O; sodium citrate (analysis pure, Tianjin public and private joint chemical reagent first plant); Cd(NO$_3$)$_2$ (analysis pure, Beijing chemical Co., Ltd); CoCl$_2$·6H$_2$O (analysis pure, Shanghai public and private joint venture factory); test water is the ultra pure water of resistance about 18.25 M Omega.

1.2. Synthesis of BSA-AgNPs
The method of preparing the copper nanoclusters prepared by the Goswami's method with BSA as a stabilizer is modified slightly. The following is as follows: AgNO$_3$ (0.02 mol L$^{-1}$, 1 ml) solution is added to the (5 ml, 15 mg ml$^{-1}$) BSA solution, and the mixture is mixed and stirred for 5 min at room temperature, and then the 1 mol L$^{-1}$ NaOH solution is used to adjust pH to 12, then turn. Move to the ice bath and stir for 8 h. After 4 °C storage the supernatant was preserved by centrifugation.

1.3. Zn$^{2+}$, Co$^{2+}$ detection
The diluted 450 μl BSA-AgNPs was placed in the centrifuge tube of 1.5 ml, and the Co$^{2+}$ (Zn$^{2+}$) solution with different concentrations of 50 μl was added respectively. The fluorescence intensity was measured at room temperature, and the excitation wavelength was at 502 nm.

2. Results and discussion

2.1. detection principle
In this experiment, the principle of detecting Zn$^{2+}$ and Co$^{2+}$ by fluorescent silver nanoparticles is shown in the above image. When Co$^{2+}$ is added into BSA-AgNPs system, the fluorescence decreases obviously. Because of the complexation of Co$^{2+}$ and BSA, aggregation of BSA-AgNPs results in fluorescence quenching [2]. EDTA was used as metal ion chelating agent. After EDTA was added to the system, Co$^{2+}$ was rapidly chelated, blocking the interaction between Co$^{2+}$ and BSA, so that BSA-AgNPs could resume fluorescence. When BSA-AgNPs was
added to Zn\(^{2+}\), the fluorescence increased significantly. Because Zn\(^{2+}\) will weaken the interaction between BSA and Ag\(^{+}\), it will eventually lead to a certain degree of aggregation of BSA-AgNPs. This is consistent with the mechanism of S\(^{2-}\) induced aggregation of FSN nanoparticles (AuNPs) protected by perfluorinated surfactant [11]. The mechanism is consistent with the aggregation of nanoclusters caused by undesirable solvents such as ethanol [12].

2.2. Spectral characteristics of BSA-AgNPs
As shown in figure 2(A), the excitation 389 nm of BSA-AgNPs is emitted at 502 nm. Therefore, the strong light intensity at the emission wavelength was chosen to determine the influence of cobalt ion (zinc ion) concentration and BSA-AgNPs fluorescence intensity. Figure 2(B) is the transmission electron microscope (TEM) diagram of BSA-AgNPs. It can be seen from the graph that the particle size of BSA-AgNPs is smaller than 5 nm. It shows that BSA-AgNPs has been successfully synthesized.

2.3. Ion selective analysis of BSA-AgNPs pairs
In order to illustrate the selectivity of BSA-AgNPs for the detection of cobalt ions and zinc ions, the effects of 18 kinds of common metal ions (Cu\(^{2+}\), Fe\(^{3+}\), Co\(^{2+}\), Zn\(^{2+}\), Hg\(^{2+}\), Pb\(^{2+}\), Cr\(^{3+}\), K\(^{+}\), Na\(^{+}\), Ca\(^{2+}\), etc) were investigated. It can be seen from figure 3 that cobalt ions and zinc ions have great influence on BSA-AgNPs. Therefore, we can confirm that BSA-AgNPs has good selectivity for zinc ions and cobalt ions.

2.4. Sensing performance analysis
As shown in figure 4(A), the fluorescence spectra of BSA-AgNPs with different concentrations of cobalt ions in 502 nm are shown. Figure 4(B) shows the fluorescence linear relationship between BSA-AgNPs and cobalt ions with different concentrations. The experimental results show that with the increase of cobalt ion concentration, the fluorescence intensity of BSA-AgNPs decreases gradually, and the cobalt ion concentration has a good linear relationship in the range of 100 \(\mu\)mol/L–600 \(\mu\)mol/L. The linear correlation equation is \(Y = -1.327C_{Co^{2+}} + 1401\), and the correlation coefficient is 0.970 35. Figure 5(A) shows the fluorescence spectra of BSA-AgNPs with different concentrations of Zn\(^{2+}\) in 502 nm. Figure 5(B) shows the fluorescence linear relationship between BSA-AgNPs and zinc ions with different concentrations. The experimental results show that with the increase of zinc ion concentration, the fluorescence intensity of BSA-AgNPs increases gradually, and the zinc ions concentration has a good linear relationship in the range of 100 \(\mu\)mol/L–600 \(\mu\)mol/L. The linear correlation equation is \(Y = 1.705C_{Zn^{2+}} + 1354\), and the correlation coefficient is 0.985 90.

2.5. BSA-AgNPs fluorescence reversibility analysis
It is mentioned above that Co\(^{2+}\) can make the fluorescence of BSA-AgNPs quenched. The addition of EDTA in Co\(^{2+}\)-BSA-AgNPs solution will restore the fluorescence of quenched BSA-AgNPs. As shown in figure 6(A), when the concentration of EDTA is 2 times the concentration of Co\(^{2+}\), the fluorescence recovery rate of BSA-AgNPs can reach about 98%. The fluorescence intensity is relatively stable. Form a cycle. The fluorescence quenching and recovery cycle can be repeated about 3 times. It is indicated that BSA-AgNPs can be used...
Figure 3. Selectivity of the proposed method towards BSA-AgNPs detection (the concentration of each ion is 100 μmol/L).

Figure 4. (A): Fluorescence emission spectra of BSA-AgNPs in the presence of different concentrations of Co$^{2+}$ (concentration of Co$^{2+}$: 100, 200, 300, 400, 500, 600, μmol/L), and B: linear relationship between fluorescence intensity of as-synthesized BSA-AgNPs and concentration of Co$^{2+}$.

Figure 5. (A): Fluorescence emission spectra of BSA-AgNPs in the presence of different concentrations of Zn$^{2+}$ (concentration of Zn$^{2+}$: 100, 200, 300, 400, 500, 600, μmol/L), and B: linear relationship between fluorescence intensity of as-synthesized BSA-AgNPs and concentration of Zn$^{2+}$. 
repeatedly for the detection of cobalt ions. Similarly, figure 6(B) shows the rate of change in fluorescence enhancement of silver nanomaterials in the absence of EDTA, Zn$^{2+}$ (100 μmol/L) and equimolar EDTA and EDTA. The results show that the effect of Zn$^{2+}$ on the fluorescence enhancement of silver nanomaterials is extremely significant, reaching 42.1%, and the fluorescence enhancement recovery rate reaches 46.2%, while EDTA alone does not change the fluorescence intensity of silver nanomaterials. When the silver nanoclusters with polymethylformamide as the template were detected Cu$^{2+}$, 6 μmol/L Cu$^{2+}$ could cause about 40% fluorescence quenching, while the silver nanocluster fluorescence completely restored when the EDTA of 12 μmol/L was added [13]. Therefore, it is necessary to add absolute excess EDTA to chelate Zn$^{2+}$ to recover the fluorescence properties of Zn$^{2+}$ to silver nanomaterials (the concentration of EDTA is about twice that of Zn$^{2+}$).

3. Conclusion

In this paper, the synthesis of BSA-AgNPs and the detection of two metal ions were studied. The addition of cobalt ions will cause the fluorescence quenching of BSA-AgNPs, while the addition of Zn$^{2+}$ will cause the fluorescence enhancement of BSA-AgNPs. Therefore, a new fluorescent probe sensor was developed to detect zinc ions and cobalt ions. This method is fast and simple. At the same time, EDTA can act as chelating agent, chelate cobalt ions, restore the quenching fluorescence, and form the 3 cycle of quenching and recovery. Make BSA-AgNPs recycle.

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