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Detection of heptavalent manganese ions using polymethacrylic acid assisted silver nanoclusters as fluorescent probes

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Polymethacrylic acid (PMAA) stabilized silver nanoclusters (AgNCs@PMAA) were prepared in one step using UV light irradiation. Based on the fluorescence quenching caused by the interaction of heptavalent manganese ions with AgNCs@PMAA, a highly sensitive method for detecting the heptavalent manganese ions was developed. The results show that when the reaction conditions are optimized, the prepared AgNCs@PMAA nanoclusters have a uniform small nanometer size and strong near-infrared luminescence. AgNCs@PMAA can be used as a highly sensitive fluorescent probe to detect heptavalent manganese ions. The probe shows excellent performance, the change in the fluorescence intensity of AgNCs@PMAA has a good linear dependence on the concentration of heptavalent manganese ions, and its linear range is 0.5 μg/ml–90 μg/l; the minimum detection limit is 0.28 μg/ml. The fluorescent probe has good practical value and application prospects, and also provides a new approach and theoretical support for metal cation detection.

Keywords: silver nanoclusters, heptavalent manganese ion, fluorescence quenching.

Виявлення семивалентних іонів марганцю із застосуванням стабілізованих поліметакриловою кислотою нанокластерів срібла у якості флуоресцентних зондів. *Сюэлин Цао, Фасянь Лю, Цзяньфэн Хоу, Данфэн Хе*

За допомогою обробки ультрафіолетовим світлом на одній стадії були приготовлені стабілізовані поліметакриловою кислотою (ПМАК) нанокластери срібла (AgNCs@PMAA). На основі гасіння флуоресценції, викликаного взаємодією семівалентних іонів марганцю з AgNCs@PMAA, був створений високочутливий метод виявлення семівалентних іонів марганцю. Результати показують, що при оптимізації умов реакції приготовлені AgNCs@PMAA мають однорідний малий нанометровий розмір і сильну люмінесценцію в ближній інфрачервоній області. AgNCs@PMAA можна використовувати як високочутливий флуоресцентний зонд для виявлення семівалентних іонів марганцю. Зонд демонструє відмінні характеристики: зміна інтенсивності флуоресценції AgNCs@PMAA має хорошу лінійну залежність від концентрації семівалентних іонів марганцю, а його лінійний діапазон становить 0,5 мкг/мл–90 мкг/л; мінімальна межа виявлення 0,28 мкг/мл. Флуоресцентний зонд має гарне практичне значення і перспективи застосування, а також забезпечує новий підхід і теоретичну підтримку для виявлення катіонів металів.

1. Introduction

In recent years, the unique properties of precious metal nanoclusters have received extensive attention in the field of analytical chemistry; there are also reports [1–3] that use metal nanoclusters as fluorescent probes to detect heptavalent manganese ions. Compared with other luminescent nanoparticles such as quantum dots [4–6], silver nanoclusters have a small size, low cost, good

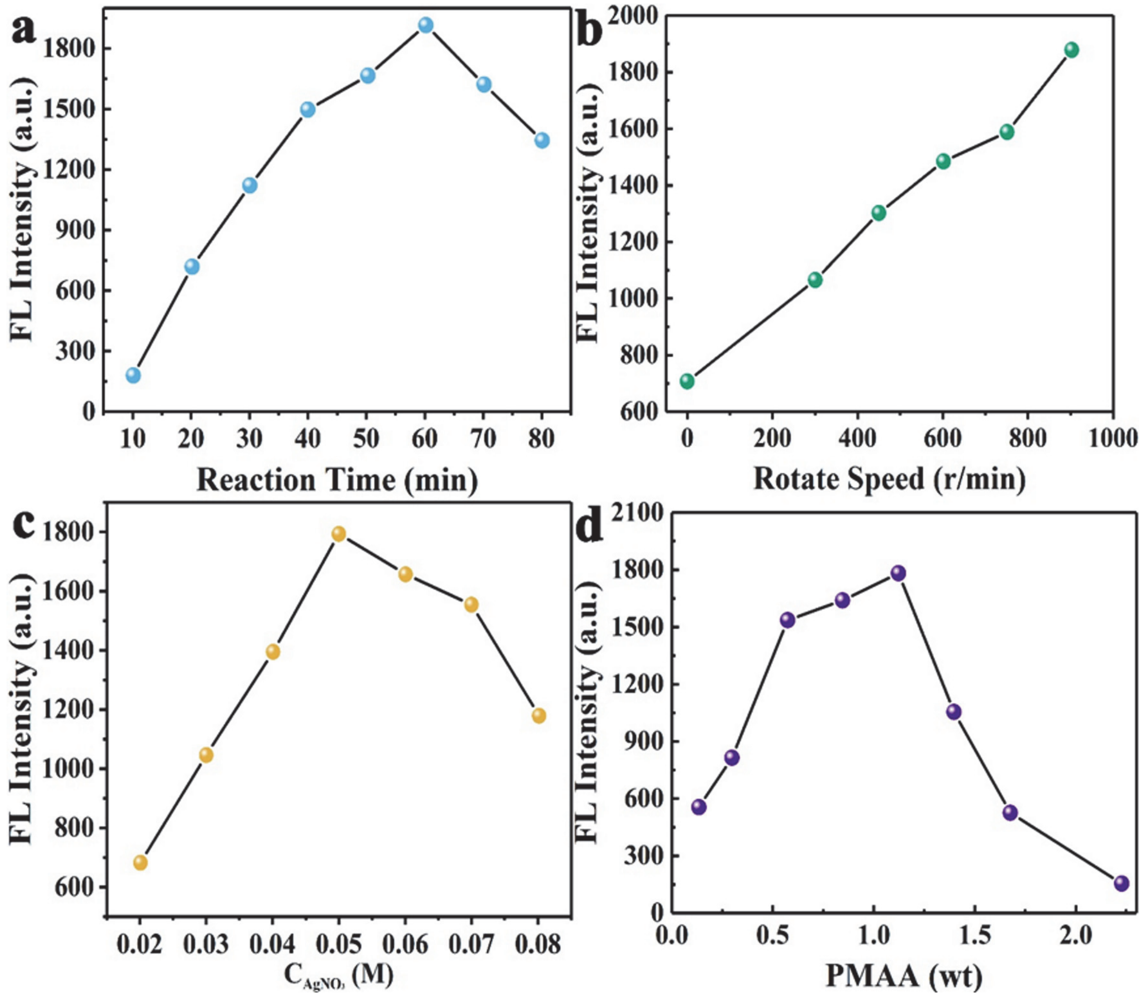

Fig. 1. Effect of reaction time (a), magnetic stirring speed (b), amount of silver nitrate (c) and amount of 1% polymethacrylic acid (d) on fluorescence intensity of AgNCs@PMAA.

biocompatibility, and low environmental risk, and are very promising elements for preparing nanoclusters. Therefore, the research and application of AgNCs has gradually attracted the attention of researchers in recent years [7, 8]. Polymethacrylic acid (PMAA) has been commercialized and is a polymer rich in carboxyl groups, which is simpler and more economical than previously used polymer microgels or dendrimers as matrices; it is an ideal synthetic template and protective agent for silver nanoclusters [9–11].

In this paper, PMAA was used as a template, and the method of ultraviolet irradiation was used to prepare water-soluble fluorescent silver nanoclusters. Based on the fact that heptavalent manganese ions can induce the fluorescence change of AgNCs@PMAA, a detection method for heptavalent manganese ions is examined on real samples.

2. Experimental

Reagents and instruments

Transmission electron microscope (Japan Electronics Co., Ltd.); Fluorescence spectrophotometer (Agilent Technologies Co., Ltd.).

Silver nitrate (Sinopharm Group Chemical Reagent Co., Ltd.); polymethacrylic acid (Tianjin Dingshengxin Chemical); heptavalent manganese ion (Tianjin Damao Chemical Reagent Factory) and other reagents are analytically pure.

Synthesis of AgNCs@PMAA

10 mL of 0.05 M silver nitrate and 10 mL of 1 % polymethacrylic acid were accurately added in a 50 mL small beaker. The reaction solution was stirred at room temperature for 60 mins under UV light irradiation. The color of the reaction solution changed to yellow, AgNCs@PMAA was obtained, and was ready for use.

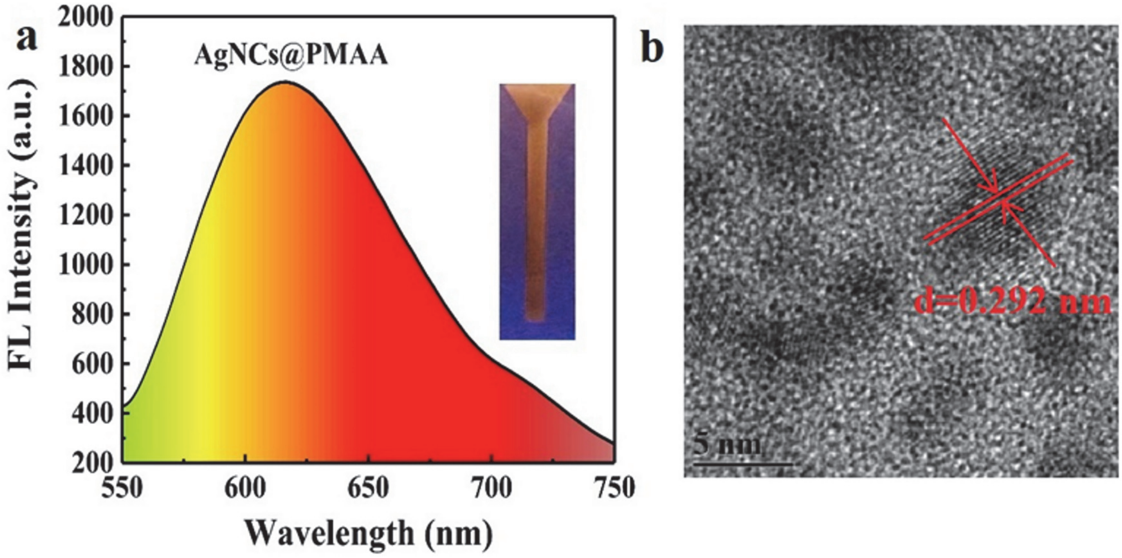

Fig. 2. a — UV-visible spectrum of AgNCs@PMAA; b — HRTEM image of AgNCs@PMAA.

Interference experiment

Metal ions (Zn^{2+}, Pb^{2+}, Na^{+}, Fe^{2+}, Mn^{2+}, Cu^{2+}, Mn^{6+}) 1 mg/mL 100 μL were added in AgNCs@PMAA to measure the change of the fluorescence emission intensity of AgNCs@PMAA.

3. Results and discussion

Optimization of preparation conditions of AgNCs@PMAA

Polymethacrylic acid is the ligand and silver nitrate is the raw material. Under ultraviolet irradiation, AgNCs@PMAA is synthesized in one step. First, the effects of reaction time, stirring rate and reactant concentration on the synthesis of AgNCs@PMAA were investigated, and the reaction conditions were optimized. As shown in Fig. 1a, as the reaction time increases, the intensity of the fluorescence emission peak of AgNCs@PMAA becomes stronger and tends to stabilize after 1 h; therefore, the reaction time was selected to be 60 min. When the rotation speed (Fig. 1b) increases, the fluorescence intensity of AgNCs@PMAA also increases. When the rotation speed reaches the maximum value of the instrument 900 r/min, the fluorescence emission peak intensity is the strongest, so the reaction speed was selected to be 900 r/min. It can be seen from Fig. 1c and 1d that the optimal addition amounts of silver nitrate and polymethacrylic acid are 0.05 M and 1 %, respectively. Through the optimization of the reaction conditions, the best reaction conditions were obtained: the reaction time is 60 min, the rotation speed is 900 r/min, the amounts of silver nitrate and polymethacrylic acid are 0.05 M and 1 %, respectively.

Characterization and properties of AgNCs@PMAA

Fig. 2a shows an ultraviolet-visible spectrum of silver nanoclusters. From the figure, the maximum absorption wavelength of the prepared AgNCs@PMAA is 430 nm. Under the 365 nm ultraviolet lamp, it emits orange-red light. Fig. 2b shows an HRTEM image of AgNCs@PMAA. The selected area electron diffraction of AgNCs@PMAA shows obvious symmetrical diffraction spots, and its lattice fringes can be clearly observed. The calculated lattice spacing is 0.292 nm. This spacing is very close to the (101) crystal plane spacing of silver nanoclusters 0.2915; thus, it was attributed to the silver nanoclusters (101) crystal planes [12]. It can be seen from Fig. 2b that the particles of AgNCs@PMAA are spherical and have good dispersion. From the TEM image, a particle size of about 2.9 nm can be calculated, and the particle size distribution is relatively uniform.

Establishment of detection method for heptavalent manganese ion by AgNCs@PMAA

As shown in Fig. 3a, the maximum fluorescence excitation wavelength of AgNCs@PMAA is 510 nm, the maximum emission wavelength is 610 nm, the emission wavelength is in the near infrared region, and has strong fluorescence intensity. With an increase in the heptavalent manganese ion concentration, the emission intensity of AgNCs@PMAA decreases gradually.

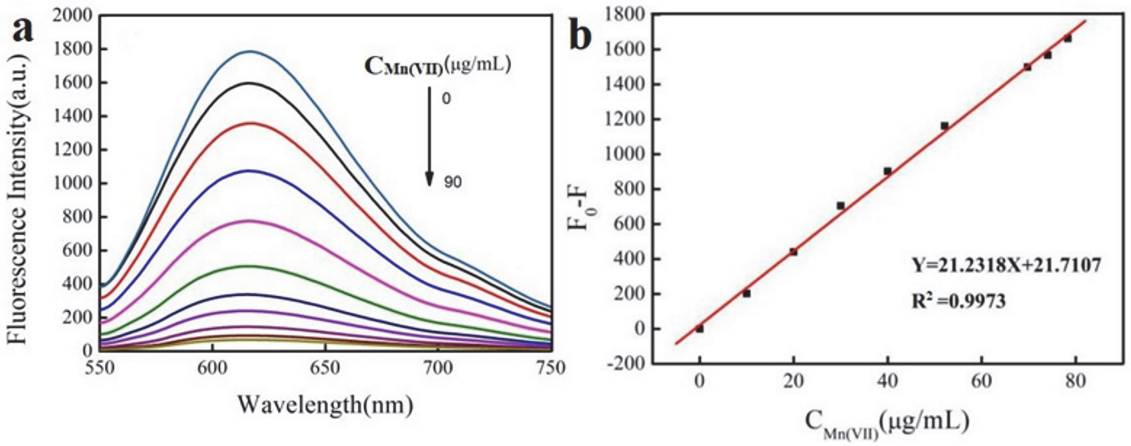

Fig. 3. a — Change in the fluorescence intensity of AgNCs@PMAA depending on the concentration of the heptavalent manganese ions; b— The linear diagram of the relationship between $F_0 - F$ of AgNCs@PMAA and the concentration of heptavalent manganese ions.

When the concentration of heptavalent manganese ions increases to 90 μg/mL, the AgNCs@PMAA emission peak is almost completely quenched and shifted to blue, which indicates a strong interaction between heptavalent manganese ions and AgNCs@PMAA. As shown in Fig. 3b, there is a good linear relationship between the concentration of heptavalent manganese ions in the range of 0.5–90 μg/mL and the change of fluorescence emission peak intensity of AgNCs@PMAA. The linear equation was $F - F_0 = 21.2318C + 21.7107$, the correlation coefficient $R^2 = 0.9973$, and the minimum detection limit was 0.28 μg/mL.

Selective experiment

To apply the developed fluorescence detection method to actual samples, the possible interfering substances Zn^{2+}, Pb^{2+}, Na^{+}, Fe^{2+}, Mn^{2+}, Cu^{2+}, Mn^{6+} were additionally investigated for the AgNCs@PMAA fluorescence emission intensity (Fig. 4). The experimental results show that at the same concentration of interfering ions, only heptavalent manganese ions have a clear quenching in the fluorescence emission spectrum of AgNCs@PMAA, indicating that AgNCs@PMAA has a high selectivity for heptavalent manganese ions and will be more beneficial for use in testing actual samples.

Analysis of heptavalent manganese ion in actual samples

Using AgNCs@PMAA as a fluorescent probe, a detection method for heptavalent manganese ions was developed, which was further applied to the detection of heptavalent manganese ions in real water samples. The actual water samples have not undergone any other pretreatment except for proper dilution. The results are shown in Table 1. The average reduction rate of heptavalent manganese ions in real samples detected by this method is between 97.47 % and 99.45 %, and the relative standard deviation values are less than 1.43 %, which proves that this method has good reproducibility and accuracy. This method can be used for the analysis of heptavalent manganese ion content in actual samples.

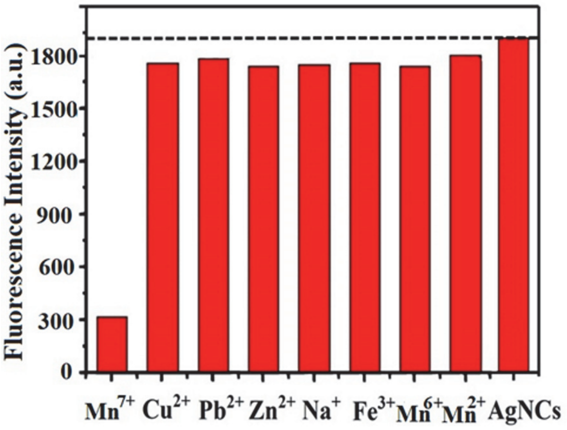

Fig. 4. Effect of interfering ions on AgNCs@PMAA.

4. Conclusions

Using PMAA as a ligand, AgNCs@PMAA with good luminescence was synthesized, and a method for detecting heptavalent manganese ions using AgNCs@PMAA as a fluorescent probe was developed. The detection range of this method is 0.5–90 μg/mL, the minimum detection limit is 0.28 μg/mL; the method was applied to determine heptavalent manganese ions in real water sam-

Table 1. Determination results of heptavalent manganese ions in real samples ($n = 3$)

Sample	Spike, μg/mL	Found, μg/mL	RSD, %	Recovery, %
1	20.00	19.89	1.24 %	99.45
2	30.00	29.24	1.43 %	97.47
3	40.00	39.49	0.97 %	98.73

ples. The results prove that the method of AgNCs@PMAA synthesis has simple steps and mild preparation conditions, and the developed detection method using AgNCs@PMAA has low detection limit and high sensitivity, which provides a theoretical basis for the application of this probe in other related fields.

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