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Synthesis of aza-crown ether-modified silver nanoparticles as colorimetric sensors for Ba^{2+}

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In this paper, we have demonstrated a facile strategy of preparing aza-crown ether (ACE)-modified silver nanoparticles (Ag NPs) by an efficient nano-conjugate technology named dithiocarbamate. This is the first report of using ACE to modify Ag NPs. ACE-modified Ag NPs have a good recognition of Ba^{2+}, with the detection limit of 10^{-8} mol/l. It is reasonable to believe that Ba^{2+} induced the self-assembly of Ag NPs by the formation of the sandwich structure with ACE.

Keywords: silver nanoparticles; aza-crown ether; colorimetric sensor

Introduction

Colorimetric sensors have attracted much attention due to their wide application in many fields, such as environmental monitoring (*1*, *2*), biological systems (*3*, *4*), etc. What is more, colorimetric sensors merely need minimal instrumentation, achieve high sensitivity and thus can make on-site detection even easier. Recently, much effort has been devoted to the design and development of new types of colorimetric methods with high selectivity and sensitivity, especially of functionalised metal nanoparticles. Because of their unique optical property, these nanoparticles can be used as colorimetric sensors. For example, dispersed nanoparticles, such as gold or silver, are red or yellow but the colour changes upon aggregation (*5*). The phenomenon is termed surface plasmon absorption, and the colour change upon aggregation is due to the coupling of the plasmon absorbance as a result of their proximity to each other (*6–8*). Based on this mechanism, colorimetric sensors can be used to recognise various metal ions and organic molecules. For example, Au nanoparticles (Au NPs) modified by DNAzyme achieved colorimetric sensors for metal ions (*6*, *9–11*). Ag nonoparticles (Ag NPs) have some advantages compared to Au NPs because they possess higher extinction coefficients relative to Au NPs with the same size (*11*). Little attention has been paid to Ag NP-based colorimetric assays due to the susceptibility of the silver surface to oxidation (*5*). So, the surface functionalisation plays a crucial role in improving the stability and analytical applicability of Ag NPs. Xiong and co-workers have reported water-soluble *para*-sulphonatocalix[4]arene-modified Ag NPs and their application as a novel colorimetric sensor for His (*12*). Han and co-workers have synthesised 4-4-bipyridyl β-cyclodextrin-capped Ag NPs for the recognition of the ytterbium ion (*13*). Some or all of the oxygen atoms in crown ethers can be replaced by nitrogen atoms to form aza-crown ether (ACE), which has an effective complexation for alkali metal and alkaline earth metal cations (*14–16*). It is interesting to fabricate ACE-modified Ag NPs as colorimetric sensors for metal ions. The point is how to attach ACE into the surface of nanoparticles. Here, we adopt a simple and efficient nano-conjugate technology named dithiocarbamate (DTC) for the functionalisation of nanoparticles (*11*, *17*, *18*).

Ba^{2+} can cause some health effects at elevated concentrations, such as high blood pressure, decreased serum potassium and cardiac rhythm disorders (*19*). To the best of our knowledge, a direct colorimetric sensor for barium ion using Ag NPs has not been previously reported. To avoid the toxic effect of Ba^{2+}, we have designed and synthesised a newly colorimetric sensor for Ba^{2+} recognition with the spectral detection limit (DL) of about 10^{-8} mol/l.

Experimental section

Materials

All chemicals and solvents, unless otherwise specified, were of analytical grade, and triply distilled water was used throughout. Silver nitrate ($AgNO_3$) and sodium borohydride ($NaBH_4$) were purchased from Shanghai Chemical Factory, Shanghai, China. LiCl, NaCl, KCl, CsCl, $MgCl_2$, $CaCl_2$, $BaCl_2$ and $SrCl_2$ were obtained from Beijing Chemical Co., Beijing, China. All metal ion solutions were dissolved in triply distilled water and stored at room temperature.

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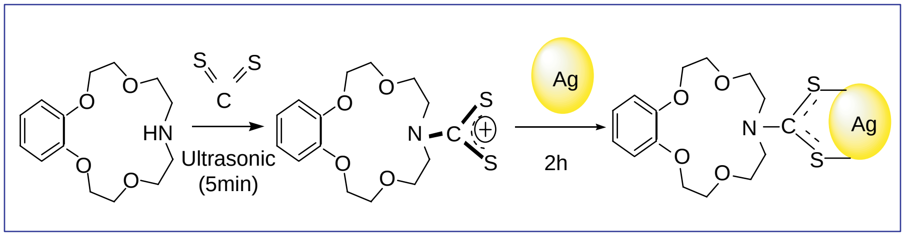


Scheme 1. Schematic illustration, synthesis of ACE-modified Ag NPs.

Characterisation

UV–vis absorption spectra were acquired on a TU-1901 UV–vis spectrometer (Beijing Purkinje General Instrument Co. Ltd, Beijing, China). Transmission electron micrograph (TEM) was recorded using a JEOL-JEM 2010 electron microscope, operating at 200 kV.

Synthesis of ACE-modified Ag NPs

An ethanol solution of CS_2 (1 ml, 1 mM) was added dropwise to a distilled water of ACE (1 ml, 1 mM) and sonicated for 5 min. One hundred millilitres of 10^{-4} M concentrated aqueous solution of $AgNO_3$ were reduced by 0.012 g of $NaBH_4$, stirring for 5 min at room temperature, to yield colloidal silver particles. Then, the above-mentioned CS_2–ACE reaction mixture was added rapidly and continuously stirred for 2 h at room temperature (Scheme 1). The synthesised ACE-modified Ag NPs (ACE-Ag NPs) were purified by repeated centrifugation and redispersion in water (the methods are provided in the Supporting Information, available online). The finally dispersed ACE-Ag NPs can be used as a colorimetric sensor.

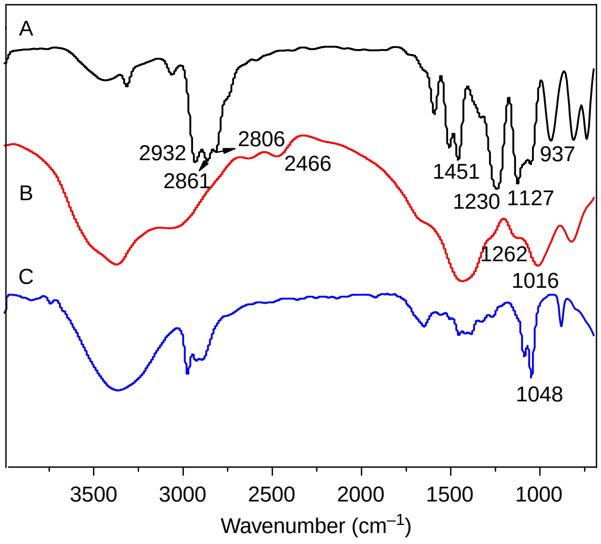


Figure 1. FT-IR spectra of ACE (A) DTC–ACE (B) and ACE-modified Ag NPs (C).

Results and discussion

Spectral characterisations

Ag NPs were prepared by the described process and displayed an absorption band at 400 nm (see Figure S1 in the Supporting Information, available online). The TEM image showed that ACE-Ag NPs were highly dispersed and uniform in aqueous solution, with an average diameter of 8 nm (Figure 1(A) and see Figure S2(a) in the Supporting Information, available online). ACE-Ag NPs remained stable for several weeks. (see Figure S3 in the Supporting Information, available online). We also evaluated the stability of the ACE-Ag NP assembly at

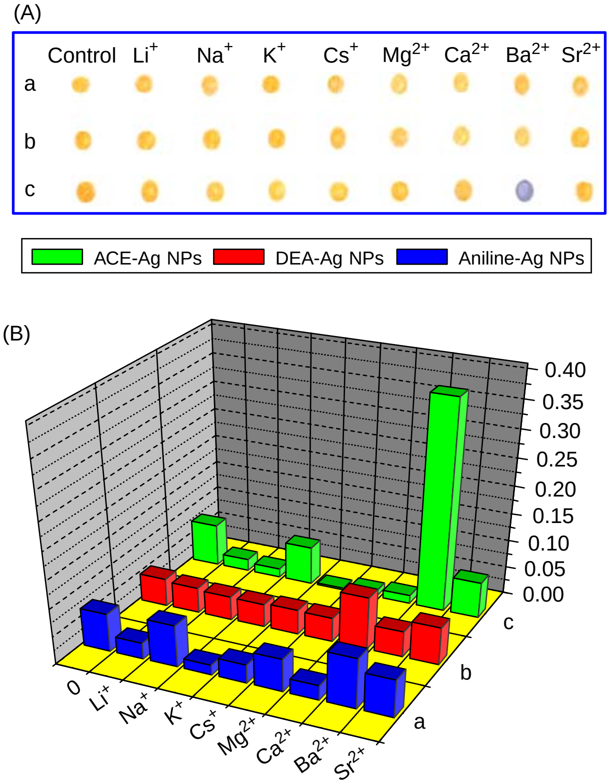
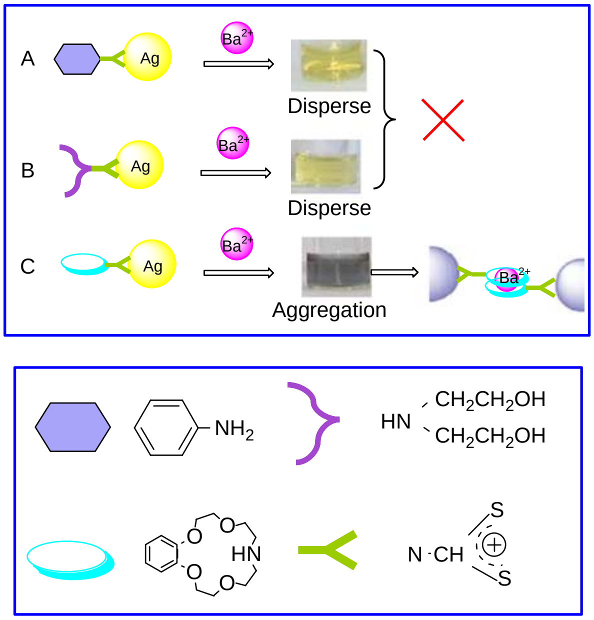


Figure 2. The colour of the sensor developed on an alumina TLC plate with different metal cations (A). Aniline-modified Ag NPs (a). DEA-modified Ag NPs (b). ACE-modified Ag NPs (c). (B) $R(A_{550}/A_{400})$ of every Ag NP solution containing different metal cations after 5 min.



Scheme 2. Schematic illustration of the aggregation of the ACE-Ag NPs in the presence of metal ions [Ba^{2+}].

different pH conditions (see Figure S4 in the Supporting Information, available online), and ACE-Ag NPs were considerably stable in the interval of 2.0–12.0.

Figure 1(A)–(C) depicts typical transmission IR spectra of ACE, DTC–ACE and ACE-modified Ag NPs, respectively. The IR spectrum of Figure 1(A) exhibits the characteristic feature of the crown moiety at 937, 1127, 1230 cm^{-1}, 2932 cm^{-1} (CH_2), 1450 cm^{-1} (benzene ring) and 2861 cm^{-1} (N—CH_3), as shown in Figure 1(B) and (C) with little variation. When compared with the IR spectrum of ACE (Figure 1(A)), new bands were observed for ACE-modified Ag NPs: (C—S) 1016 cm^{-1} and (CS—NH) 1262 cm^{-1}, which unambiguously supports that ACE was successfully modified on the surface of Ag NPs via the carbodithioate (—CS_2) linkage.

Colorimetric sensing of alkali metal and alkaline earth metal cations

To test the selectivity of the system, the metal ion-dependent colour change was monitored. As shown in Figure 2(A), different metal ions, such as Li^+, Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Ba^{2+} and Sr^{2+}, were added to the Ag NP solution, but only the addition of the Ba^{2+} ion solution resulted in a rapid colour change within 5 min. The absorption spectra were broadened and red-shifted after the addition of Ba^{2+} ions to the ACE-Ag NP solution (see Figure S3 in the Supporting Information, available online). The broadening and shifting of the plasmon peak is due to the aggregation of the nanoparticles induced by the Ba^{2+} ions. With the addition of Ba^{2+} cations, the surface plasmon resonance peak of Ag NPs will appear as a new peak at approximately 600 nm. This response can be attributed to the Ag NP aggregation induced by Ba^{2+}, which is supported by a TEM image (see Figure S4(b) in the Supporting Information, available online).

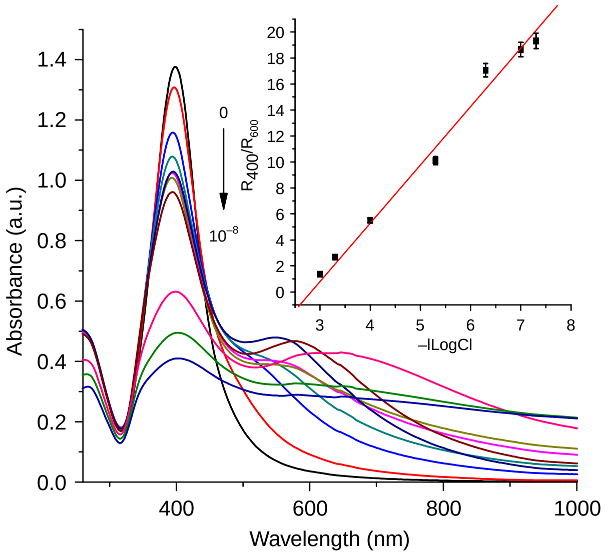


Figure 3. Adsorption spectral changes in Ag NPs after the addition of different concentrations of Ba^{2+} ions in 20 min. A linear correlation exists between R value (A_{400}/A_{600}) and the logarithm of the ion concentration C over the range of 10^{-8}–10^{-3} M. The linear equation is as follows: $Y = -12.196 + 4.447 \times \log[C]$.

In order to study the recognition mechanism of ACE-Ag NPs with Ba^{2+}, diethanolamine (DEA) and aniline-modified Ag NPs were used for control experiments. In contrast with ACE-Ag NPs, aniline-modified Ag NPs were designed to explore whether the benzene ring affects the selectivity; while DEA-Ag NPs were designed with the similarity structure without the ether ring in order to further explore the ability of ACE. The results of the response of the two control experiments to Ba^{2+} ions are shown in Figure 2(Aa) and (Ab), which indicates that Ag NPs do not exhibit selective response towards Ba^{2+}.

On the basis of the known ability of crown ether to interact with Ba^{2+} according to a sandwich-like mode (*7*), ACE that comes from the surface of Ag NPs can form a sandwich structure with barium cations as shown in Scheme 2(C). Aniline and DEA do not have a similar cyclic structure for the unique response to Ba^{2+} (see Scheme 2(A),(B)). According to hard and soft acid and base (HSAB) theory, nitrogen that comes from ACE provides a good coordination site for the barium ion (*20*). It is reasonable to believe that ACE-Ag NPs can have a good recognition of Ba^{2+} through the sandwich structure. The ACE-Ag NPs can also have a good recognition of Ba^{2+} without interference with other metal ions above (see Figure S5 in the Supporting Information, available online).

Figure 3 shows the UV–visible spectra obtained for the ACE-Ag NP solution after the addition of different concentrations of Ba^{2+} over 5 min. A linear correlation exists between R and the logarithm of the Ba^{2+} concentration C over the range of 10^{-3}–10^{-8} M. The DL is 10^{-8} M for Ba^{2+}, which achieves the same level with current fluorescent sensors (*14*, *16*, *21–23*). In comparison with those complicated methods designed for the recognition of Ba^{2+} by synthesising fluorophore ligands, this method is simple, low cost and can be directly observable, yet with high sensitivity without the need of sample preconcentration or pretreatment.

Conclusions

In summary, we have demonstrated a new colorimetric method to identify Ba^{2+} ions in solution by ACE-Ag NPs. In the presence of Ba^{2+} ions, the specific binding of Ag NPs provides an accurate real-time measurement and quantification in the UV spectrophotometer. This method is simple, low cost and can be directly observable, yet with high sensitivity without the need of sample preconcentration or pretreatment.

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