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Study on the interaction of nucleic acids with silver nanoparticles—Al(III) by resonance light scattering technique and its analytical application

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ABSTRACT

It is found that Al(III) can further enhance the intensity of resonance light scattering (RLS) of the silver nanoparticles (AgNPs) and nucleic acids system. Based on this, a novel method of determination of nucleic acids is proposed in this paper. Under optimum conditions, there are linear relationships between the enhancing extent of RLS and the concentration of nucleic acids in the range of 1.0×10^{-9}–1.0×10^{-7} g mL^{-1}, 1.0×10^{-7}–2.0×10^{-6} g mL^{-1} for fish sperm DNA (fsDNA), 1.0×10^{-9}–7.0×10^{-8} g mL^{-1} for calf thymus DNA (ctDNA) and 1.0×10^{-9}–1.0×10^{-7} g mL^{-1} for yeast RNA (yRNA). The detection limits (S/N = 3) of fsDNA, ctDNA and yRNA are 4.1×10^{-10} g mL^{-1}, 4.0×10^{-10} g mL^{-1} and 4.5×10^{-10} g mL^{-1}, respectively. The studies indicate that the RLS enhancement effect should be ascribed to the formation of AgNPs–Al(III)–DNA aggregations through electrostatic attraction and adsorption bridging action of Al(III). And the sensitivity and stability of the AgNPs–fsDNA system could be enhanced by Al(III).

1. Introduction

Metal nanoparticles such as AgNPs have attracted considerable interest because of their particular optical, magnetic, electronic and catalytic properties. AgNPs are widely utilized in material science, physics and chemistry fields [1]. Moreover, they also has important curatorial function in inflammation, antivirus, anti-AIDS and especially in anticancer [2,3]. As we know, DNA is an attractive template because of its large aspect ratio (length/diameter), well-defined sequences of DNA base, a variety of superhelix and a high affinity for metal cations. So with chemical reduction, many metal cations could form metallic nanowires following the contour of the DNA template [4–10], for example, silver [4], copper [7], gold [8] and so on. Recently, it has been demonstrated that silver nanocluster [11] and silver nanoring [12] can be formed through a DNA-templated process. And the determination of nucleic acids using AgNPs has aroused abroad interest and attention [13,14].

In this paper, a new method for nucleic acids determination was developed using the system of AgNPs–Al(III)-nucleic acids. The experiments indicated that the enhanced intensity of RLS was in proportion to the concentration of nucleic acids. The interaction mechanism of the system was also studied by the transmission electronic microscopy (TEM), circular dichroism spectra (CD), zeta potentials and UV spectrometry.

2. Experimental

2.1. Chemicals

Stock solutions of nucleic acids (100 μg mL^{-1}) were prepared by dissolving commercial fsDNA (Sigma), ctDNA and yRNA (Beijing Baitai Co., China) in 0.05 mol L^{-1} sodium chloride solutions. Silver nanoparticles prepared: a stock solution of silver nanoparticles (2.0×10^{-4} g mL^{-1}) was prepared by dissolving 0.0158 g of $AgNO_3$ in 40 mL of 0.22 μm-filtered doubly distilled water, 2 mL sodium citrate (1%) was added slowly in above $AgNO_3$ solution by heating at 86 °C with stirring for 30 min, the solution color changed gradually from colorless to olivine, diluting to 50 mL finally. Above solutions were stored at 0–4 °C. A 0.01 mol L^{-1} potassium hydrogen phthalate (KHP)–NaOH buffer solution was prepared by dissolving 0.5106 g KHP in distilled water and adjusting the pH to 5.6 with 0.2 mol L^{-1} NaOH. A stock solution of aluminium nitrate (2.0×10^{-2} mol L^{-1}) was prepared by dissolving 0.7503 g $Al(NO_3)_3$ in 100 mL volumetric flask with water. All the chemicals used were of analytical reagent grade and double-distilled water was used throughout.

2.2. Apparatus

The RLS spectra and the intensity of RLS were performed on a LS-55 spectrofluorimeter (PE, USA). All CD spectra were collected

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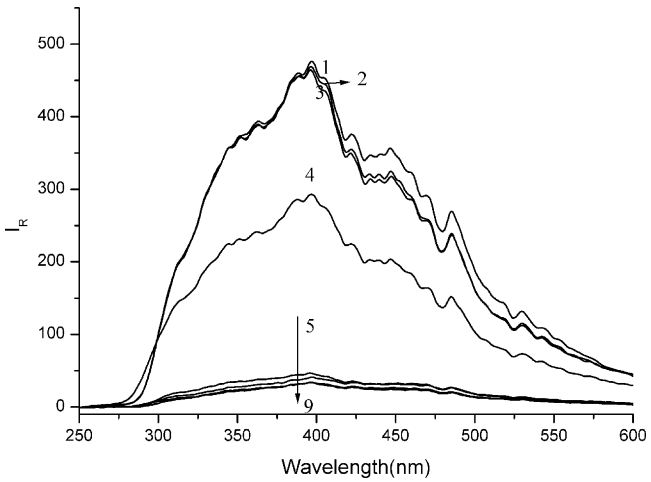

Fig. 1. Resonance light scattering spectra. (1) AgNPs–Al(III)–ctDNA; (2) AgNPs–Al(III)–fsDNA; (3) AgNPs–Al(III)–yRNA; (4) AgNPs–fsDNA; (5) Al(III)–fsDNA; (6) AgNPs; (7) AgNPs–Al(III); (8) Al(III); (9) fsDNA. Conditions: AgNPs: 1.4×10^{-6} g mL^{-1}; Al(III): 2.0×10^{-3} mol L^{-1}; fsDNA: 1.0×10^{-6} g mL^{-1}; ctDNA: 1.0×10^{-6} g mL^{-1}; yRNA: 1.0×10^{-6} g mL^{-1}; KHP: 8.0×10^{-4} mol L^{-1} (pH 5.6).

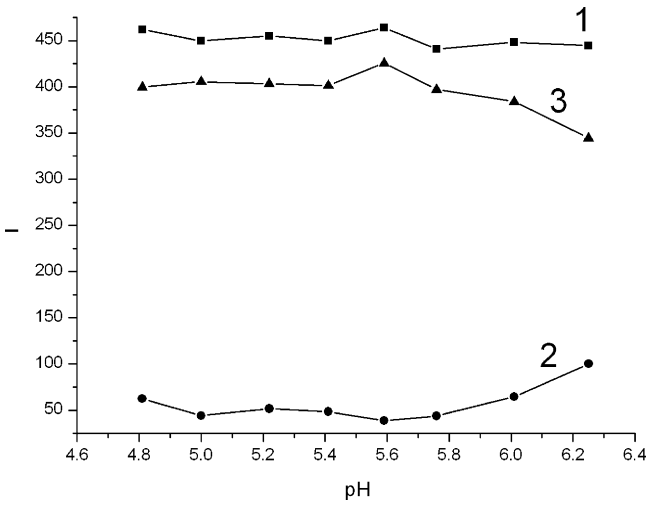

Fig. 2. Effect of pH. (1) I_0; (2) I_R^0; (3) ΔI. Conditions: AgNPs: 1.4×10^{-6} g mL^{-1}; Al(III): 2.0×10^{-3} mol L^{-1}; fsDNA: 1.0×10^{-6} g mL^{-1}; KHP: 8.0×10^{-4} mol L^{-1}.

on a J-810S Circular Dichroism Spectrometer (JASCO, Japan). All absorption spectra were measured on a U-4100 spectrophotometer (Hitachi, Japan). TEM images were measured on JEM-100 CXII Transmission Electron Microscope (JEOL, Japan). Zeta potentials (ζ) were measured with a JS94H micro-television electrophoretic instrument (Powereach, Shanghai). All pH measurements were made with a Delta 320-S acidity meter (Mettler Toledo, Shanghai).

2.3. Procedure

To a 10 mL colorimetric tube, the solutions were added in the following order: buffer, AgNPs, Al(III) and nucleic acids. The mixture was diluted to 5 mL with water and allowed to stand for 10 min. The RLS spectra were obtained by simultaneously scanning the excitation and emission monochromators over the range of 250–600 nm (i.e. $\Delta\lambda = 0$ nm). The intensity of resonance light scattering was measured at the maximum wavelength (398 nm) in a 1 cm quartz cell, with the slit width at 10 nm for the excitation and emission. The enhanced RLS intensity of AgNPs–Al(III)-nucleic acids system was represented as $\Delta I = I_R - I_R^0$, where I_R and I_R^0 were the RLS intensities of the systems with and without nucleic acids.

3. Results and discussion

3.1. Light scattering spectra

Fig. 1 shows the RLS spectra of AgNPs–Al(III)–ctDNA, AgNPs–Al(III)–fsDNA, AgNPs–Al(III)–yRNA, AgNPs–fsDNA, Al(III)–fsDNA, AgNPs, AgNPs–Al(III), Al(III) and fsDNA systems. As can be seen, nucleic acids can increase the RLS intensity of AgNPs and Al(III). Additionally, when AgNPs, Al(III) and nucleic acids are mixed together, the RLS intensity is further enhanced and reaches a maximum at 398 nm, which indicates that there are interactions between AgNPs–Al(III) and nucleic acids. We think that the RLS of the system at 398 nm is ascribed to the absorption of AgNPs in the range of 250–280 nm. In comparison with AgNPs, the system of AgNPs–Al(III) has lower intensity of RLS in the detected wavelength range.

3.2. Effects of pH and buffers

The effect of pH on the RLS intensity of this system is shown in Fig. 2. It can be seen that ΔI value reaches the maximum at the pH 5.61, so pH 5.61 is used for subsequent work. The buffer also have a large effect on the intensity of the system. The ΔI (%) for hexamethylenetetramine (HMTA)–HCl, NaAc–HAc, KHP–HCl, succinic acid–NaOH, BR and critric acid–K_2HPO_4 are 3.7, 94.8, 100, 84.3, 95.4 and 94.6, respectively. Further experiments indicate that 0.4 mL of 0.01 mol L^{-1} KHP–NaOH is the most suitable buffer.

3.3. Effect of AgNPs concentration

From Fig. 3 it can be seen that the ΔI value of this system reaches a maximum when the concentration of AgNPs is 1.8×10^{-6} g mL^{-1}. At the same time, the RLS intensity of the system of AgNPs–Al(III) is high, too. As can be seen that when the concentration of AgNPs is 1.4×10^{-6} g mL^{-1}, I_R/I_R^0 (%) value of this system reaches a maximum and the value of I_R^0 is lower. Considering the effect of the system regent blank, 1.4×10^{-6} g mL^{-1} AgNPs is chosen for further experiment.

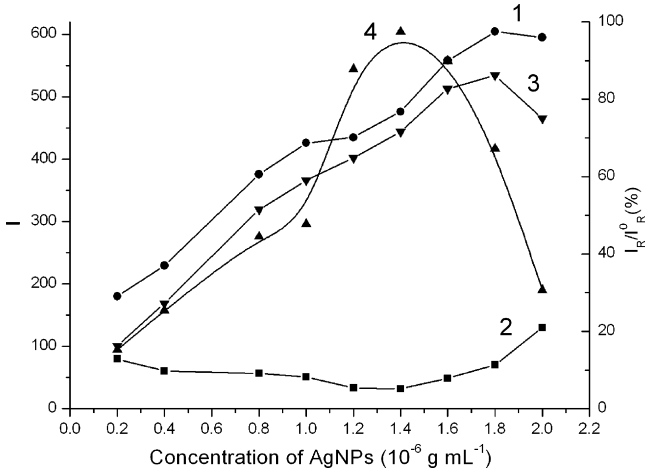

Fig. 3. Effect of the concentration of AgNPs. (1) I_0; (2) I_R^0; (3) ΔI; (4) I_R^0/I_0. Conditions: Al(III): 2.0×10^{-3} mol L^{-1}; fsDNA: 1.0×10^{-6} g mL^{-1}; KHP: 8.0×10^{-4} mol L^{-1} (pH 5.6).