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Investigation on the Effect of Addition of Fe^{3+} Ion into the Colloidal AgNPs in PVA Solution and Understanding Its Reaction Mechanism

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ABSTRACT

Analysis of Fe^{3+} ion present in aqueous solutions is always of interests. Recently, this ion has been analyzed by colorimetric methods using colloid of silver nanoparticles (AgNPs) in capping agents of polymers. The reaction mechanism between AgNPs and Fe^{3+} is still subject to the further investigation. In this work, 1,10-phenanthroline was used to probe the reaction mechanism between AgNPs and Fe^{3+} ion in the solution. The colloids of AgNPs were prepared in the polyvinyl alcohol (PVA) solution and reacted with Fe^{3+}. The colloid surface plasmon absorbance decreases linearly along with the increase in Fe^{3+} concentration. The addition of 1,10-phenanthroline to mixture changes the solution to red, indicating that the reaction produces Fe^{2+}. It suggests that the reduction of the AgNPs absorbance is the result of oxidation of the Ag nanoparticles along with the reduction of Fe^{3+}.

***Keywords**: AgNPs; Fe^{3+} sensor; colorimetry; 1,10-phenanthroline; SPR absorbance*

ABSTRAK

Analisis ion Fe^{3+} yang ada dalam larutan berair selalu diminati para peneliti. Baru-baru ini, ion tersebut telah dianalisis dengan metode kolorimetri menggunakan koloid perak nanopartikel (AgNP) dalam agen penstabil polimer. Namun, mekanisme reaksi antara AgNPs dan Fe^{3+} masih harus diselidiki lebih lanjut. Pada penelitian ini 1,10-fenantrolin digunakan untuk menyelidiki mekanisme reaksi antara ion AgNP dan Fe^{3+} dalam larutan. Koloid AgNP disiapkan dalam larutan polivinil alkohol (PVA) dan direaksikan dengan Fe^{3+}. Fluks koloid menurun secara linear seiring dengan peningkatan konsentrasi Fe^{3+}. Penambahan 1,10-fenantrolin ke campuran mengubah larutan menjadi merah, menunjukkan bahwa reaksinya menghasilkan Fe^{3+}. Hal ini menunjukkan bahwa penurunan absorbansi AgNPs adalah hasil oksidasi nanopartikel Ag bersamaan dengan pengurangan Fe^{3+}.

***Kata Kunci**: nanopartikel Ag; sensor Fe^{3+}; kolorimetri; 1,10-fenantrolin; SPR*

INTRODUCTION

Colorimetric chemical analysis based on localized surface plasmon resonance (LSPR) is of interests for many researchers. The optical LSPR phenomenon is generated when monochromatic light interacts with conductive nanoparticles that have size smaller than the incident wavelength [1]. This oscillation results in unusually strong scattering and absorption properties. The methods based on LSPR assisted by nanoparticles have been studied by many researchers mainly due to good sensitivity and selectivity. They offer sensitive detection of ions, organic compounds and volatile organic compounds. In the past few years, we saw works on the use of nanoparticles in chemical sensing either in solutions or in gaseous phases [2]. There is growing interest in applying the optical properties of AgNPs. AgNPs are capable of both absorbing and scattering the incident light.

In detection Hg^{2+}, the decrease in the LSPR absorbance is believed to be due to the redox reaction between AgNPs and Hg^{2+}. Meanwhile, the addition of calixarene to the Fe^{3+} solution will produce a complex with Fe^{3+} leading to nanoparticle-based fluorometric method of the cation. The N-acetyl-L-cysteine-stabilized silver nanoparticles have also been used for Fe^{3+} [3]. Starch-stabilized AgNPs were used for a colorimetric method for detection of Hg^{2+} [4]. Pyridyl-appended calix-[4]-arene has been used to change AgNPs that show a high selectivity for sensing of Fe^{3+} [5]. Dithizone functionalized CdSe/CdS quantum dots can be used as turn-on fluorescent probe for ultrasensitive detection of Pb^{2+} ion [6]. The detection limit for such methods is lower than that of the other common methods. The sensitivity and selectivity of this sensing method can also be tuned by using the co-stabilizing agent of organic compounds [7].

Although colloidal AgNPs have been used for sensing agent of ions and organic molecules, the

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reaction mechanism that leads to the changes in its UV-Vis absorbance or fluorescence still needs further explanation. Henglein et al. suggest that adsorbed Cd^{2+} on AgNPs can be reduced Cd^{+} in the presence of 1-hydroxyethylmethyl radicals [8]. Fan et al. and Farhadi et al. have suggested that decrease in absorbance of the colloidal AgNPs is due to the reduction-oxidation of AgNPs and Hg^{2+} ions [4,9].

In this contribution, we report on the use to understand the reaction between Fe^{3+} ions and AgNPs in the PVA solution that results in the decrease in the peak of UV-Vis spectra. The ligand reacts with the Fe^{2+}, the product of the reaction, to form red complex solution for lowering the colloidal UV-Vis absorbance in more details.

EXPERIMENTAL SECTION

Materials

Polyvinyl alcohol (PVA), silver nitrate, ascorbic acid, 1,10-phenanthroline, iron(III) nitrate, and other salts (with metal ions of Cd^{2+}, Mn^{2+}, Zn^{2+}, Cr^{3+}, Mg^{2+}, Ni^{2+}, Ca^{2+}, Pb^{2+}, Cu^{2+}, Co^{2+}, and Fe^{3+} used in this work) were supplied by Merck and used as received. Doubly distilled water was used as the main solvent.

Instrumentation

The UV-1700 Shimadzu UV-Vis spectrometer was used for UV-Vis spectra data acquisition. The TEM images of the samples were recorded on a JEOL JEM 1400 using accelerating voltage of 120 kV. The Rigaku Mini Flex-600 XRD was used for crystal structure determination of the AgNPs. All experiments were carried out at room temperature without humidity control.

Procedure

Synthesis and characterization colloid of AgNPs

Synthesis of colloidal AgNPs in PVA media using ascorbic acid as reducing agent can be found elsewhere [10]. Typically in this work, a 200 mg/L $AgNO_3$ solution in doubly distilled water was made. A 1.0% PVA solution was prepared by dissolving the PVA powder in double distilled water. The PVA solution was stirred for 1 h while being heated at 80 °C. The $AgNO_3$ solution in PVA was made by mixing the same volume of the two solutions. The mixture was heated to 80 °C and added 1 h of stirring. The colloid of AgNPs in PVA was prepared by reacting with ascorbic acid solution. The molar ratio of ascorbic acid to silver ion was kept at 2:1. The ascorbic acid solution was added dropwise as the mixture was kept at 90 °C on a hot plate magnetic stirrer. The colloid was formed after 1 h of heating. The formed colloidal AgNPs were characterized using UV-Vis spectrophotometer, XRD and TEM. A series of colloidal AgNPs with starting concentration from 50 to 200 mg/L were prepared. For the UV-Vis measurement, the AgNP concentration was adjusted to 5,000 µg/L (5 mg/L).

UV-Vis spectra of colloid of AgNPs in the presence of another cation

The colloid was diluted to meet the suitable range of the UV-Vis absorbance. First, the UV-Vis spectra of 5,000 µg/L colloids of AgNPs were recorded. Second, a series of colloids of AgNPs were made where certain cation was added with a concentration of 10,000 µg/L each. The spectra of the colloids were recorded and compared with the blank.

UV-Vis spectra colloid of AgNPs in the presence of Fe^{3+}

The UV-Vis spectrum of a colloid of AgNPs before addition of Fe^{3+} was recorded. In a separate experiment, the solution of Fe^{3+} was added to the colloid to give its final concentration starting from 10 µg/L to 5,000 µg/L. The UV-Vis spectra were recorded and compared with the blank.

Effect of addition of 1,10-phenanthroline on the UV-Vis spectra of AgNPs and Fe^{3+} mixture

Colloids of AgNPs having the concentration of 5,000 µg/L were prepared in a series of 50 mL volumetric flasks. A solution of Fe^{3+} was added and shook well to make final colloid of AgNPs concentration of 5,000 µg/L. The solution of 1,10-phenanthroline was added to the mixture at a concentration of 10,000 µg/L. The UV-Vis absorbance for the colloid was recorded before addition of Fe^{3+}, after addition of Fe^{3+}, and after addition of Fe^{3+} and 1,10-phenanthroline.

RESULT AND DISCUSSION

The color of the obtained colloid of AgNPs in aqueous PVA solution is yellow. The colloid has initial UV-Vis peak absorbance at 421 nm. AgNPs have a color that depends on the size and the shape of the particle. The earlier reports indicated that the colloid of AgNPs with the particle size of 35-50 nm had peak absorbance around 420-438 nm. AgNPs with the diameter of 1-10 nm and spherical shape will have UV-Vis peak absorbance at the low wavelengths. Vasileva et al. reported that AgNPs obtained in starch had UV-Vis peak absorbance of 408 nm in which the size was about 14 nm [11]. Recently, smaller AgNPs were obtained when the colloid was stabilised by secondary amines [12]. Shape and size of AgNPs can be controlled by the medium, capping and reducing agents.

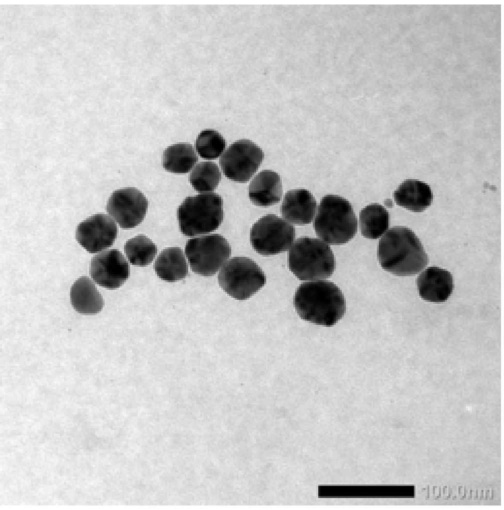

Fig 1. TEM image of AgNPs produced by reduction of $AgNO_3$ with ascorbic acid in PVA solution

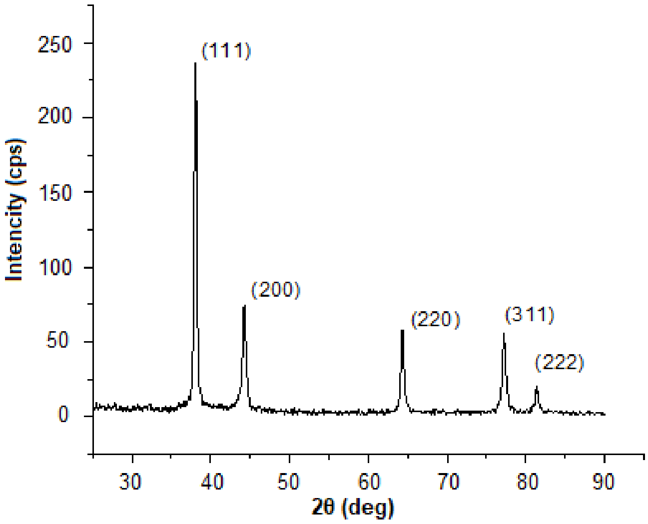

Fig 2. XRD pattern of AgNPs obtained by reduction of $AgNO_3$ with ascorbic acid in the PVA solution

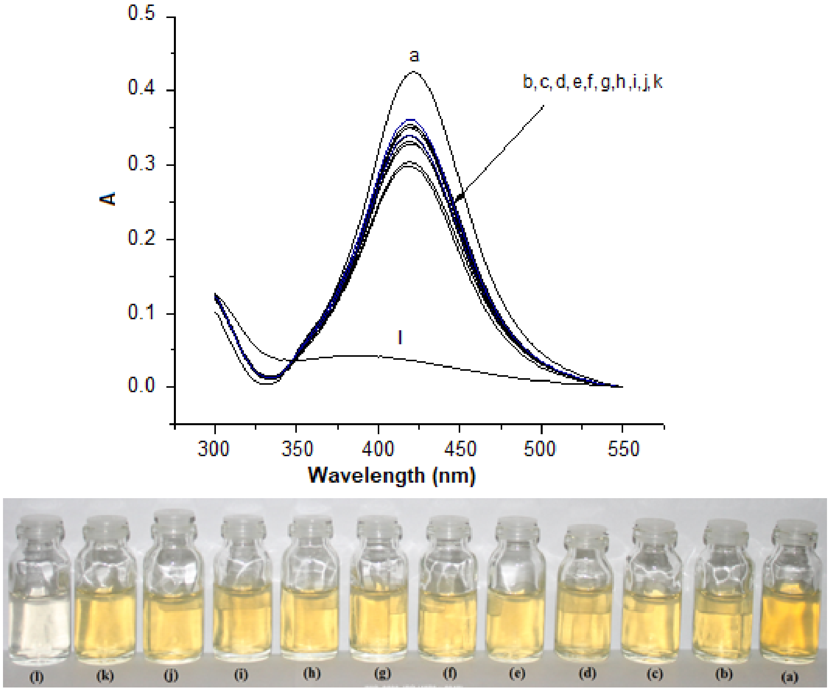

Fig 3. Combined UV-Vis spectra of the colloidal AgNPs after addition of various ions; (a) initial, in the presence of (b) Cd^{2+},(c) Mn^{2+}, (d) Zn^{2+}, (e) Cr^{3+}, (f) Mg^{2+}, (g) Ni^{2+}, (h) Ca^{2+}, (i) Pb^{2+}, (j) Cu^{2+}, (k) Co^{2+}, and (l) Fe^{3+}. The photographs of change in color of the colloids are also shown

Reduction by hydrogen gas in organic media gave the size of AgNPs as low as 14 nm [12].

Fig. 1 shows TEM image of the AgNPs produced in this work. The shape of the nanoparticles is almost spherical. The size, however, is not uniform. The estimated average diameter of the AgNPs is about 26-50 nm. The colloids of AgNPs with particle size around 30 nm have an SPR absorbance peak of about 420 nm. This colloid of AgNPs has very similar UV-Vis spectra to the data reported earlier. It is known that the smaller size nanoparticles will have a spherical shape.

$$d = \frac{180 \cdot K \cdot \lambda}{FWHM \cdot \pi \cdot \cos\theta} \quad (1)$$

Fig. 2 is the powder XRD pattern of AgNPs. The XRD pattern of the product exhibits fcc crystal system with the unit cell of 4.0780 Å. The colloid of AgNPs with

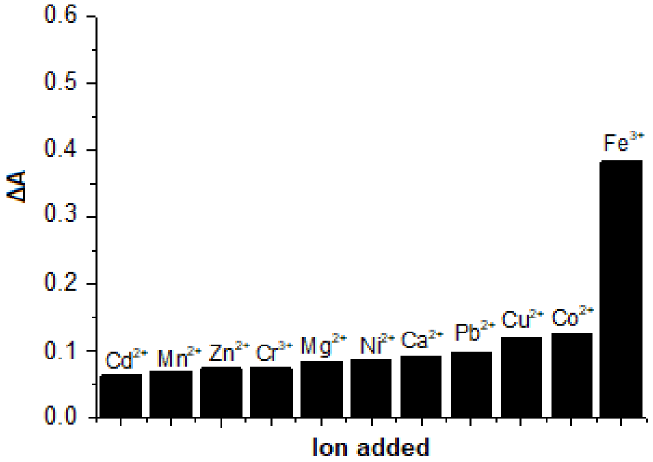

Fig 4. Decrease in the UV-Vis peak absorbance at 421 nm of the colloidal AgNPs after addition of predetermined ions at a concentration of 10,000 µg/L

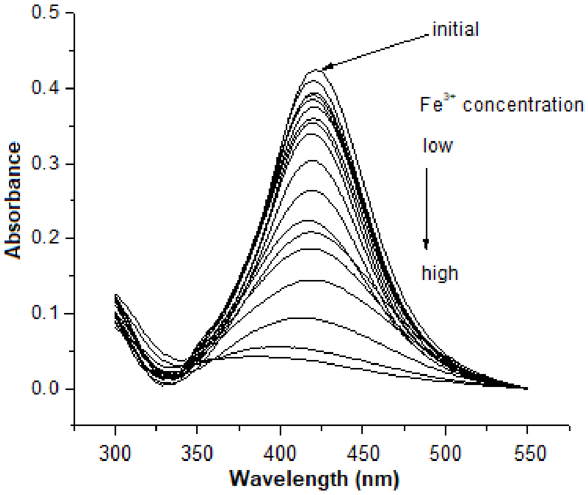

Fig 5. UV-Vis spectra of colloidal AgNPs after addition of Fe^{3+} with concentration from 10-5,000 µg/L

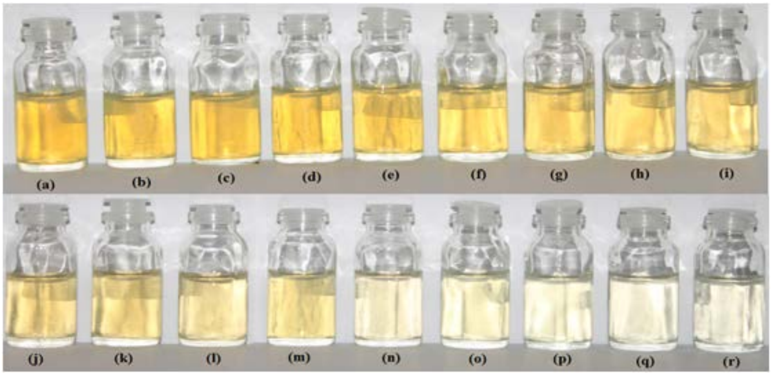

Fig 6. Images of the colloidal AgNPs, (a) initial, and after addition of the Fe^{3+} ion with concentration of (b) 10, (c) 30, (d) 50, (e) 70, (f) 100, (g) 300, (h) 500, (i) 700, (j) 1,000, (k) 1,500, (l) 2,000, (m) 2,500, (n) 3,000, (o) 3,500, (p) 4,000, (q) 4,500, and (r) 5,000 µg/L

fcc crystal system commonly has the unit cell of 4.0860 Å. This is comparable with other reported works [15]. The XRD data were used to estimate the average particle size of the particles. The average particle size calculated using Debye-Scherrer equation (1) was found to be 23.25 nm. In the equation d = average particle size in nanometer, K is constant (0.9), l is the wavelength of X-ray in nanometer, FWHM is full width at half maxima (2θ) and θ is the Bragg angle in degree [14]. The calculated value is usually lower than the actual value obtained by electron microscopic imaging systems of either by SEM or TEM.

The collated LSPR UV-Vis spectra of 5,000 µg/L colloidal AgNPs upon addition of ions i.e. Cd^{2+}, Mn^{2+}, Zn^{2+}, Cr^{3+}, Mg^{2+}, Ni^{2+}, Ca^{2+}, Pb^{2+}, Cu^{2+}, Co^{2+}, and Fe^{3+} are presented in Fig. 3. The addition of cations with similar concentration causes the absorbance to decrease. A large decrease in UV-Vis peak absorbance at 421 nm was observed when Fe^{3+} was added i.e., from 0.425 to 0.035. The drops in absorbance upon addition of other cations were around 0.060 to 0.125, which is relatively small. Overall decreases in UV-Vis absorbance peak (ΔA) at 421 nm of the colloidal AgNPs are presented in Fig. 4. Drop in UV-Vis absorbance of AgNPs was also observed in the Fe^{3+} in the presence of a capping agent of N-acetyl-L-cysteine [3].

The combined UV-Vis spectra of colloidal AgNPs after addition of the Fe^{3+} ions with various concentrations (10-5,000 µg/L) are presented in Fig. 5. The peak absorbance at 421 nm continues to decrease along with the increase in concentrations. The UV-Vis peak absorbance shifted to lower wavelength when a high concentration of ions was added. Other work shows that the linear range for detection of Fe^{3+} N-acetyl-L-cysteine using the capping agent of N-acetyl-L-cysteine is from 0-4,000 µg/L (0-70 µM) [3], which is similar to this report. The photograph of the colloids shows the progress of the color change upon addition of Fe^{3+} (Fig. 6).

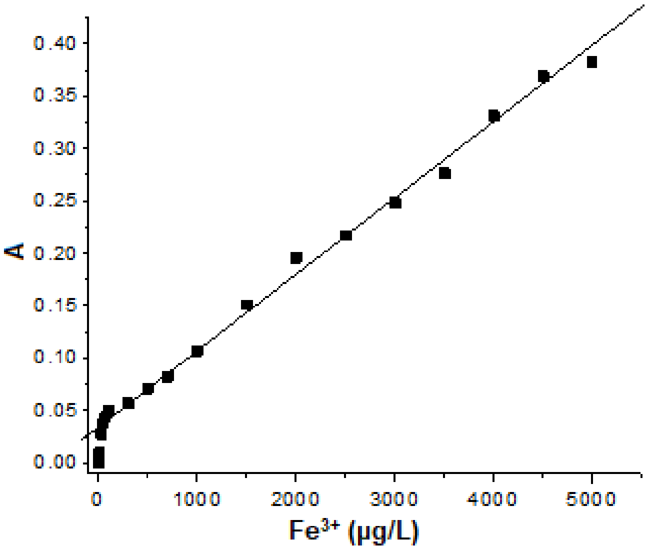

Fig 7. Calibration curve of colorimetric Fe^{3+} analysis in the concentration range of 10-5,000 µg/L

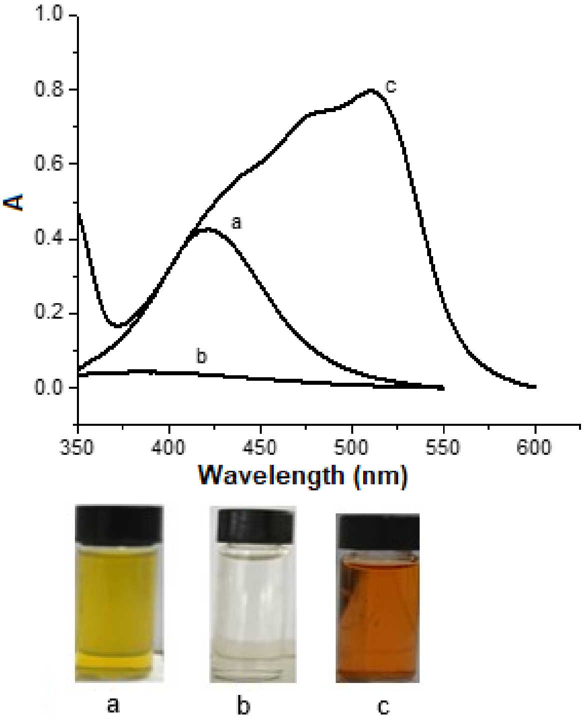

Fig 8. UV-Vis spectra of 5,000 µg/L colloidal AgNPs, (a) in the absence of Fe^{3+}, (b) in the presence of 5 µg/L Fe^{3+}, (c) in the presence of 5 µg/L Fe^{3+} and 10,000 µg/L of 1,10-phenanthroline. The progress of the solution color change is included

The calibration curve for Fe^{3+} detection using AgNPs is presented in Fig. 7. The plot of Fe^{3+} concentration versus absorbance gives a linear line in the concentration range from 50 to 5,000 µg/L. The estimated limit of detection and limit of quantification for Fe^{3+} obtained from the calibration curve are about 20 µg/L and 60 µg/L, respectively. The correlation coefficient for the plot is 0.9905.

Fig. 8 shows the UV-Vis spectra of 5,000 µg/L colloidal AgNPs before and after addition of Fe^{3+}, after addition 5,000 µg/L Fe^{3+} and 0.10 mM 1,10-phenanthroline. The peak at 510 nm corresponds to the tris(1,10-phenanthroline)iron(II) complex [16]. The absorbance of the colloidal Ag nanoparticle decreased when Fe^{3+} was added. Addition much higher concentration of Fe^{3+} to the colloid causes a further decrease in the peak absorbance at 421 nm. When 1,10-phenanthroline was added to the mixture, the peak absorbance of at about 510 nm was observed. The spectrum of tris(1,10-phenanthroline)iron(II) complex is very obvious to support the redox mechanism.

It was reported earlier that the colorimetric sensing of Hg^{2+} using AgNPs prepared by green synthesis was due to the change in the surface plasmon absorbance of the colloidal AgNPs [9]. Similarly, the increase in the concentration of the analytes causes the absorbance of the Ag nanoparticle to decrease. The limit of detection (LOD) is usually further evaluated based on accepted standard methods [16]. The LOD for Hg^{2+} ion was 2.2 × 10^{-6} mol L^{-1}, which was considered good. Moreover, the linear reduction in the surface plasmon absorbance upon addition of Hg^{2+} ion was speculated to be due to the redox reaction between AgNPs and the Hg^{2+} ions. Studies have been performed to have a clear mechanism not only for this sensing method but also other similar methods. The limit of detection (LOD) and limit of quantification (LOQ) are estimated using equation (2) and (3).

$$\mathrm{LOD} = \frac{3 \times \mathrm{SD}}{a} \qquad (2)$$

$$\mathrm{LOQ} = \frac{10 \times \mathrm{SD}}{a} \qquad (3)$$

In this work, we propose to rationale the mechanism of the lowering surface plasmon absorbance of the AgNPs upon addition of the ions. The decrease in the UV-Vis spectra is believed to be due to the redox reaction between AgNPs and Fe^{3+} ion. The AgNPs react with Fe^{3+} ion to produce Ag^+ and Fe^{2+} ions. In this case, the AgNPs are oxidized to Ag^+ and Fe^{3+} ions are reduced to Fe^{2+}. The reaction mechanism is obvious when 1,10-phenanthroline is added. 1,10-phenanthroline reacts with Fe^{2+} to produce tris(1,10-phenanthroline)iron(II) complex, which has red color. The reactions can be proposed by reaction (4) and (5).

$Ag(s) + Fe^{3+}(aq) \rightarrow Ag^+(aq) + Fe^{2+}(aq)$ (4)

$Fe^{2+}(aq) + 3\ phen(aq) \rightarrow (phen)_3Fe(II)(aq)$ (5)

The peak absorbance at 510 nm is confirmed to be (1,10-phenanthroline) iron(II) complex [16]. We also tested that the increase in the Fe^{3+} concentration caused the peak absorbance at 510 nm to rise. In other words, the tris(1,10-phenanthroline) iron(II) UV-Vis peak absorbance is dependent on the concentration of Fe^{3+}. This further indicates that the reaction between AgNPs and Fe^{3+} is stoichiometric. Therefore, it is clear that redox reaction between AgNPs and Fe^{3+} ions takes place. The light extinction by AgNPs is dependent on the Fe^{3+}concentration.

The Fe^{3+} ions are reduced to Fe^{2+}, causing a linear decrease in SPR absorbance, which is dependent on Fe^{3+} concentration [3]. We show in this work that the redox reaction between AgNPs and Fe^{3+} can be detected spectrophotometrically by using 1,10-phenanthroline as a ligand, which forms a complex ion with Fe^{2+}. The color change is obvious from initially red to colorless. Addition of 1,10-phenanthroline to the colloid causes the color to change to red (Fig. 8, bottom).

Gao et al. believe that the colorimetric detection of Fe^{3+} based on the sensitive plasmonic response of n-acetyl-L-cysteine-stabilized silver nanoparticles (NALC–Ag NPs) is due to the redox reaction between AgNPs with the Fe^{3+} ions in the solution [3]. The intensity decrease of the prepared NALC–Ag NPs can be attributed to the reduction of Ag NPs in the solution but not to the particle size change. When Fe^{3+} ions are added into the colloidal NALC–Ag NPs, the Ag NPs can be oxidized by Fe^{3+} ions to produce Ag^{+}.

CONCLUSION

Colloids of AgNPs in the stabilizing agent of PVA can detect Fe^{3+} ions. The limit of detection of Fe^{3+} ion analysis using this colorimetric method is estimated to be 20 µg/L (equivalent to 0.36 µmol/L). The Fe^{3+} ions react with AgNPs to yield Fe^{2+} and Ag^{+} ions. The reaction mechanism was confirmed by addition of 1,10-phenanthroline, which formed a red complex ions of Fe(II)-1,10-phenanthroline. The color change of AgNPs is due to the redox reaction with Fe^{3+} ions. The reaction mechanism of aqueous ions and colloids of nanoparticles may be of importance in the future analysis based on the colorimetric methods.

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