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Heavy metal cations and anions sensing studies of N-(2-hydroxybenzyl)-isopropylamine surface functionalized AgNPs

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The phenolic and guest interacting functionality of N-(2-hydroxybenzyl)-isopropylamine (1) used for developing silver nanoparticles (1-AgNPs) based colorimetric sensor for metal cations (Ni^{2+}, Co^{2+}, Cd^{2+} and Ca^{2+}) and oxalate and phosphate anions in aqueous solution. Interestingly, 1-AgNPs showed distinguishingly different colour for oxalate (dark grey), dihydrogen phosphate (light grey) and monohydrogen phosphate (orange). Ni^{2+} addition showed clear wine-red colour whereas Co^{2+} showed pinkish colour. Cd^{2+} and Ca^{2+} addition resulted in orange colour formation. Absorption spectra of 1-AgNPs with metal cations and anions also exhibited selective change for metal cations (Ni^{2+}, Co^{2+}, Cd^{2+} and Ca^{2+}) and oxalate and phosphate anions. HR-TEM studies indicate that aggregation of AgNPs due to selective metal coordination or anion interaction with surface functionality caused colour change. Differences in the aggregation lead to different colour for metal cations and anions. 1-AgNPs exhibited 10^{-6} M detection level for both cations and anions as well as high selectivity for Ni^{2+} and oxalate ions. Thus metal coordinating phenolic chelating ligand represent a potential candidates for fabricating AgNPs colorimetric assay for metal cations and anions.

1. Introduction

Noble metal nanoparticles in the size range of 1-100 nm exhibit unique optical, electronic and chemical properties due to high surface to volume ratios and quantum confinement phenomena.[1,2] The recent advances in the field of nanoscience and nanotechnology have widely exploited the unique properties of nanomaterials for developing range of applications, including electronics, opto-electronics, catalysis, biomedical diagnostic and surface enhanced Raman spectroscopy.[3-10] Particularly, the strong optical properties of Ag and AuNPs that arises due to localized surface plasmon resonance (SPR) draws considerable attention for fabricating colorimetric assays for sensing heavy metal ions and biomolecules.[11-13] Selective sensing and screening of heavy metal ions and anions in water is important because of increased environmental and industrial pollution.[14-15] The strong colour of Ag and AuNPs due to excellent SPR properties makes easy for observing the visual colour change without using costly instrumentation.[11-13] Ag and AuNPs exhibit stronger molar absorption coefficient than conventional organic dye molecules.[11] The intense colour coupled with interparticles distance dependent SPR properties of Ag or AuNPs provides practical platform for developing colorimetric sensors for various chemicals including toxic heavy metal cations, anions and bio-molecules in aqueous solution.[16-18] Of these two noble NPs, AgNPs have advantages of low cost and wide range of colour tunability compared to AuNPs. Colorimetric assay based on AgNPs have been developed using two different strategies; colour change due to direct reaction of analytes with NPs (amalgamation or oxidation)[19-20] and supramolecular interaction of analytes with surface functionality that induces NPs aggregation.[21-22] The synthetic versatility of organic functionality makes the latter approach exciting as well as challenging to control the selectivity of analytes. Hence, AgNPs synthesis with new surface functional organic units and exploration of selective analyte interaction received greater attention in recent years.

AgNPs functionalized with glutathione lead to selective sensing of Ni^{2+},[23] whereas pyridyl-appended calix[4]arene and dopamine functionalized AgNPs exhibited Fe^{3+} and Cu^{2+} colorimetric sensing, respectively.[24-25] Gallic acid functionalized AgNPs exhibited selective sensing of Pb^{2+},[26] triazole-ester modification showed Cd^{2+} sensing,[27] dopamine functionalization resulted in Cu^{2+}[28] and tripolypyrophosphate functionalization of AgNPs exhibited Mn^{2+} sensing.[29] The effect of AgNPs shape stabilized with glutathione on the colorimetric sensing of metal cations was investigated by H. K. Sung *et. al.*[30] Green synthesized AgNPs with biofunctional agents exhibited selective colorimetric sensing of Hg^{2+}, Pb^{2+} and Zn^{2+}.[31-34] AgNPs based colorimetric assays have also been reported for selective sensing of biomolecules such as cysteine, melamine and thrombin.[35-37] However, AgNPs based colorimetric sensor for anions have been rarely reported compared to metal cations.[38-39] In our lab, we have been working with phenolic chelating ligands for fabricating AgNPs based colorimetric sensor by taking advantage of silver ions reducing property of phenols and versatile coordination with metal ions. Amino acid based reduced Schiff bases were successfully employed to develop AgNPs based tunable metal ions sensor.[40] The phenolic chelating ligands were chosen because of their strong coordination ability with metal ions that often resulted in intriguing supramolecular structure.[41-42]

In this manuscript, we have used N-(2-hydroxybenzyl)-isopropylamine (1) phenolic ligand as reducing and surface functionalizing agent for AgNPs and colorimetric sensing of metal cations (Ni^{2+}, Co^{2+}, Cd^{2+} and Ca^{2+}) and oxalate and phosphate anions in aqueous solution. 1-AgNPs was characterized by UV-Visible, FT-IR and HR-TEM techniques. 1-AgNPs showed selective colorimetric sensing Ni^{2+} (wine-red), Co^{2+} (pinkish), Cd^{2+} and Ca^{2+} (orange) metal cations. Interestingly 1-AgNPs also exhibited selective colorimetric sensing of oxalate (dark grey) and dihydrogen phosphate (light grey) and orange (monohydrogen phosphate) anions. Importantly distinguished colour was observed for different metal cations and anions. The mechanistic studies suggest that AgNPs aggregation due to metal cations or anions interaction with surface ligand was responsible for different colour. The concentration dependent studies of 1-AgNPs demonstrate linear change of absorption for both cations and anions with the detection limit up to 10^{-6} M. Hence a simple phenolic chelating ligand were used as reducing, stabilizing and surface functionalizing agents for developing AgNPs colorimetric assay for multiple metal cations and anions.

2. Experimental Section

Salicylaldehyde, cyclohexane diamine, $NaBH_4$ and $AgNO_3$ were obtained from Sigma-Aldrich. Isoproylamine, ethanol and NaOH were obtained from Ranbaxy fine chemicals. The metal cations and anions solution (10^{-3} M) used for the experiments were prepared by dissolving in Milli-Q water.

2.1. Synthesis of 1 (N-(2-hydroxybenzyl)-isopropylamine).

Reduced Schiff base phenolic chelating ligand, 1, was synthesized by following the reported procedure.[39] Typically isoproyl amine (0.6 g, 0.01 M) was dissolved in 30 ml water and mixed with ethanol (10 ml) solution of salicylaldehyde (1.24 g, 0.01 M). The solution turned immediately bright yellow colour and the solution was heated at 60 °C for 30 min. The reaction mixture was cooled in ice-bath and sodium borohydride (0.58 g, 0.015 M) was added in portion-wise. The bright yellow colour was slowly disappeared and neutralization of the reaction mixture produced white precipitate of 1. The precipitate was filtered, washed with cold ethanol and dried in vacuum. Yield = 1.34 g (80 %). ^1H NMR ($CDCl_3$) δ 7.25-7.32 (m, 2H), 6.86-6.95 (m, 2H), 4.12 (s, 2H), 3.56 (q, 1H), 1.09 (d, 6H). ^{13}C NMR ($CDCl_3$) δ 158.1, 134.5, 133.1, 128.4, 124.7, 119.8, 49.2, 43.3, 24.3.

2.2. Synthesis of 1-AgNPs

5 ml aqueous solution of silver nitrate (10^{-3} M) was mixed with 5 ml aqueous solution of 1 (10^{-3} M) under stirring at room temperature. It is noted that 1 was dissolved in water using 1:1 molar ratio of NaOH. The immediate appearance of clear yellow colour suggested the reduction of silver ion into AgNPs. The solution was allowed to stir at room temperature for another 30 min. The reaction was repeated at least three times to confirm the reproducibility of AgNPs formation. The characterization of the synthesized AgNPs was carried out after allowing the solution to stand at room temperature for one day.

2.3. Characterization

The UV-visible measurement of the synthesized AgNPs were analyzed in a Perkin Elmer model UV–Vis double beam spectrophotometer from 250 to 800 nm, at the resolution of 1 nm. The powdered sample of 1-AgNPs was subjected to FT-IR spectroscopy measurement. These measurements were carried out on a Perkin–Elmer Spectrum-One instrument in the diffuse reflectance mode at a resolution of 4 cm^{-1} in KBr pellets.

The size and morphology of AgNPs were investigated using high resolution transmission electron microscopy (HR-TEM). Samples for TEM measurements were prepared by placing a drop of NPs solution on the graphite grid and drying it in vacuum. Transmission electron micrographs were taken using JEOL JEM-2100F operated at an accelerated voltage of 200 kV and an ultra high-resolution pole piece..

3. Results and Discussion

3.1. Synthesis and characterization

The phenolic chelating ligands 1 was prepared by simple Schiff base condensation of isopropyl amine precursor with salicylaldehyde followed by $NaBH_4$ reduction in water-ethanol mixture. The easy ionization property of phenolic hydroxyl group of 1 was utilized to convert silver ions to AgNPs that resulted in clear yellow coloured formation.[43] The intense colour of AgNPs is due to the strong surface plasmon resonance (SPR) vibration.[44]

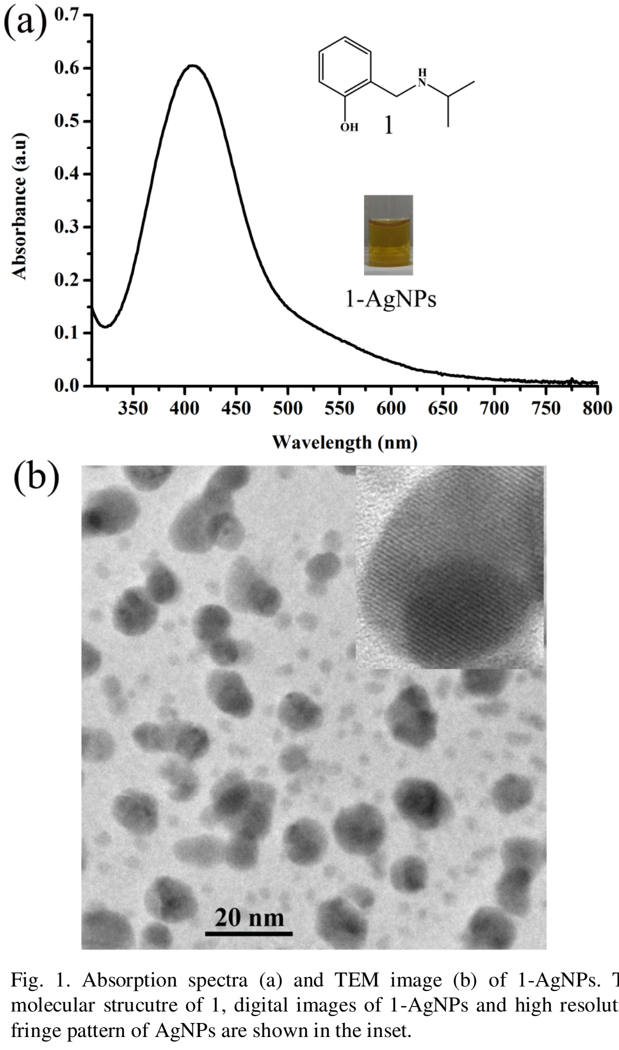


Fig. 1. Absorption spectra (a) and TEM image (b) of 1-AgNPs. The molecular strucutre of 1, digital images of 1-AgNPs and high resolution fringe pattern of AgNPs are shown in the inset.

The phenolic compounds are known to reduce the silver ions and stabilize the AgNPs via electrostatic interactions.[43,45] The formation of clear and transparent yellow colour indicated the good dispersion of AgNPs. The absorption spectrum of 1-AgNPs exhibited a characteristic SPR absorption for AgNPs at 408 nm (Fig. 1a). HR-TEM studies suggest the formation of spherical crystalline polydispersed AgNPs in the size range between 10 – 30 nm (Fig. 1b). The surface functionality of the 1 with AgNPs was characterized using FT-IR spectroscopy. 1 showed peak at 3457 (O-H and N-H-stretch), 2843 (C-H-stretch), 1611 (C-H-stretch) and 1489 (C-H-stretch) cm^{-1} and 1-AgNPs also showed similar peak position and confirms the surface coverage of phenolic chelating ligand (Fig. S1). The incorporation of AgNPs with 1 lead to small shift in the peak position (3453.8 (O-H and N-H-stretch), 2857 (C-H-stretch), 1591 (C-H-stretch)).

3.2. Colorimetric sensor studies of metal cations

Colorimetric sensing of 1-AgNPs was explored by adding different metal cations and monitoring the visual colour and absorption change. Interestingly, 1-AgNPs exhibited selective colorimetric sensing of multiple metal cations with distinguished colour (Fig. 2). Addition of Ni^{2+} to 1-AgNPs resulted in the formation of wine-red colour whereas Co^{2+} addition exhibited pink colour. Ca^{2+} and Cd^{2+} addition into 1-AgNPs produced orange colour formation. Other metal cations addition did not show any significant change in the 1-AgNPs colour. Interestingly, Mg^{2+} that often interferes on the selectivity of Ca^{2+} due to similar chemical properties did not show any colour change.[46,47] The absorption measurement of 1-AgNPs with different metal cations also supported the selective colour change for Ni^{2+}, Co^{2+}, Ca^{2+} and Cd^{2+}. 1-AgNPs exhibited absorption λ_{max} at 408 nm. Ni^{2+} addition into 1-AgNPs lead to the appearance of stronger new absorption at longer wavelength (580 nm) along with 408 nm peak. Co^{2+} addition also showed similar new longer wavelength absorption at 570 nm with weaker intensity compared to Ni^{2+}. Ca^{2+} and Cd^{2+} additions into 1-AgNPs exhibited emergence of weak absorption in the longer wavelength. The appearance of orange colour for Ca^{2+} and Cd^{2+} is due to this weaker absorption. Other metal ions addition did not show any new absorption peak except reducing the 1-AgNPs absorption intensity slightly. Fe^{3+} addition showed strongest reduction in the 1-AgNPs absorption intensity at 408 nm. However, it did not show either a colour change or new absorption peak.

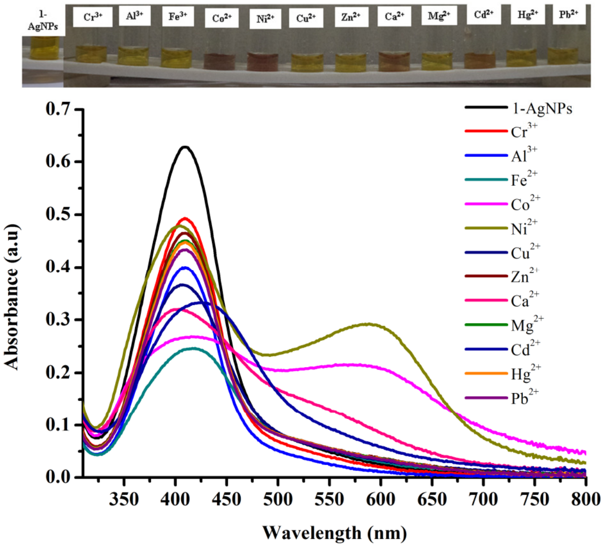


Fig. 2. Absorption spectra and digital images of 1-AgNPs with different metal cations (10^{-3} M).

The concentration dependent studies of 1-AgNPs for Ni^{2+} (10^{-6} M) showed reduction of 408 nm absorption intensity at the initial additions (Fig. 3a). The subsequent addition produced new absorption peak at longer wavelength clearly. The formation of new absorption peak was completed with the addition of 30 µM of Ni^{2+}. Further addition did not show significant change in the absorption. Similarly Co^{2+} (10^{-6} M) additions also exhibited reduction in the absorption intensity initially followed by new peak appearance at longer wavelength (Fig. 4a). The emerging of new absorption peak was completed with the addition of 40 µM of Co^{2+}. The interference studies of 1-AgNPs for Ni^{2+} and Co^{2+} (10^{-6} M) in presence of various metal cations (10^{-3} M) suggest the high selectivity (Fig. 3b and 4b). Ni^{2+} as well as Co^{2+} addition into 1-AgNPs in presence of other metal cations clearly showed the appearance of longer wavelength absorption peak and suggest that other metal did not have significant influence on the Ni^{2+} and Co^{2+} colorimetric sensing. Addition of Ni^{2+} into 1-AgNPs-Co^{2+} showed stronger absorption peak at longer wavelength. But

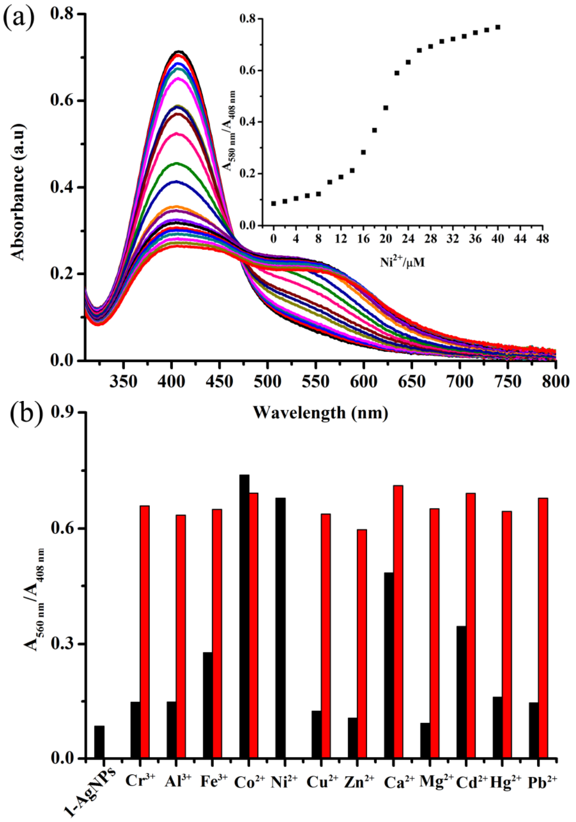


Fig. 3. (a) Absorbance of 1-AgNPs with Ni^{2+} concentration and (b) selectivity studies of 1-AgNPs for Ni^{2+} (10^{-6} M) in presence of different metal ions (10^{-3} M). Black and red bar represent without and with Ni^{2+} ions.

addition of Co^{2+} into 1-AgNPs-Ni^{2+} did not show any characteristic change. The colour intensification was also observed visually when Ni^{2+} was added into 1-AgNPs-Co^{2+}. This result suggests that Ni^{2+} might be having preferential coordination with 1. The concentration dependent studies of Ca^{2+} and Cd^{2+} also showed emerging of new absorption in the longer wavelength with increasing concentration (Fig. S2). Ca^{2+} addition showed slightly stronger intensity compared to Cd^{2+}. However most of the metal cations except Al^{3+}, Hg^{2+} and Zn^{2+} were found to strongly interefere on the selectivity of Ca^{2+} and Cd^{2+} ions. Hence 1-AgNPs could not be used for selective sensing of Ca^{2+} and Cd^{2+} ions in presence of other metal cations.

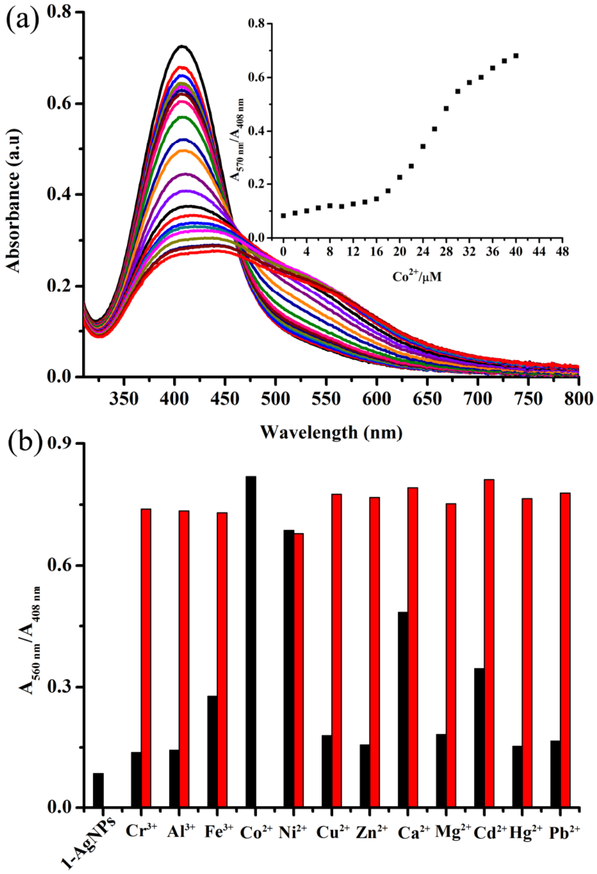


Fig. 4. (a) Absorbance of 1-AgNPs with Co^{2+} concentration and (b) selectivity studies of 1-AgNPs for Co^{2+} (10^{-6} M) in presence of different metal ions (10^{-3} M). Black and red bar represent without and with Co^{2+} ions.

3.3. Colorimetric sensor studies of anions

The colorimetric studies of 1-AgNPs for anions also showed selective sensing of multiple anions with distinguishable colour. 1-AgNPs showed selective colour change for oxalate, di- and mono-hydrogen phosphate (Fig. 5). The phosphate and oxalate anions is part of several biologically active entities, and in many cases plays significant role in the biochemical process.[48,49] Importantly 1-AgNPs showed clearly distinguishable colour for mono- (orange) and dihydrogen phosphates (light grey). 1-AgNPs with oxalates exhibited dark grey colour. Other anions did not show any significant colour change. The absorption studies of 1-AgNPs for anions exhibited selective absorption change for mono- and dihydrogen phosphate and oxalate. Oxalate and phosphate additions into 1-AgNPs showed a new absorption peak in the longer wavelength region. 1-AgNPs with oxalate showed new absorption peak at 610 nm whereas di- and monohydrogen phosphate with 1-AgNPs exhibited new absorption peaks at 590 and 540 nm, respectively. It is noted that oxalate and dihydrogen phosphate addition lead to strong reduction of 1-AgNPs absorption intensity at 408 nm. Other anions addition exhibited slight reduction of absorption intensity at 408 nm without producing any new absorption. Thus 1-AgNPs with all three anions showed different absorption maximum and supports the visual color change.

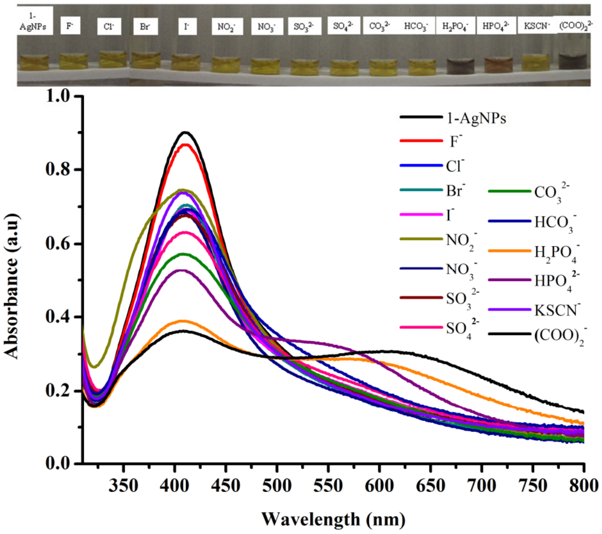


Fig. 5. Absorption spectra and digital images of 1-AgNPs with different anions (10^{-3} M).

The concentration dependent studies of 1-AgNPs for oxalate showed reduction of absorption intensity at 408 nm in the initial additions (Fig. 6a). The subsequent addition showed clearly the appearance of new absorption peak at longer wavelength that was intensified with further addition. The enhancement of intensity was completed with the addition of 30 µM of oxalate. However, dihydrogen phosphate addition showed immediate appearance of absorption at longer wavelength in the first addition itself (Fig. 7a). The intensity enhancement of longer wavelength was completed with the addition of 10 µM of dihydrogen phosphate. Further addition only reduced the absorption intensity at 408 nm. Similarly 1-AgNPs exhibited reduction of peak at 408 nm and appearance of weak absorbance in the longer wavelength for monohydrogen phophate (540 nm, Fig. S3). The interference studies of 1-AgNPs for selective sensing oxalate in presence of other anions indicated high selectivity (Fig. 6b). Addition of oxalate to 1-AgNPs leads to the appearance of clear absorption in the longer wavelength in presence other anions. Similarly dihydrogen phosphate interference studies suggested good selectivity except in presence of oxalate (Fig. 7b). Thus oxalate could be detected in presence other anions whereas dihydrogen phosphate selectivity was interfered by oxalate. Monohydrogen phosphate selectivity was strongly interfered by oxalate and dihydrogen phosphate.

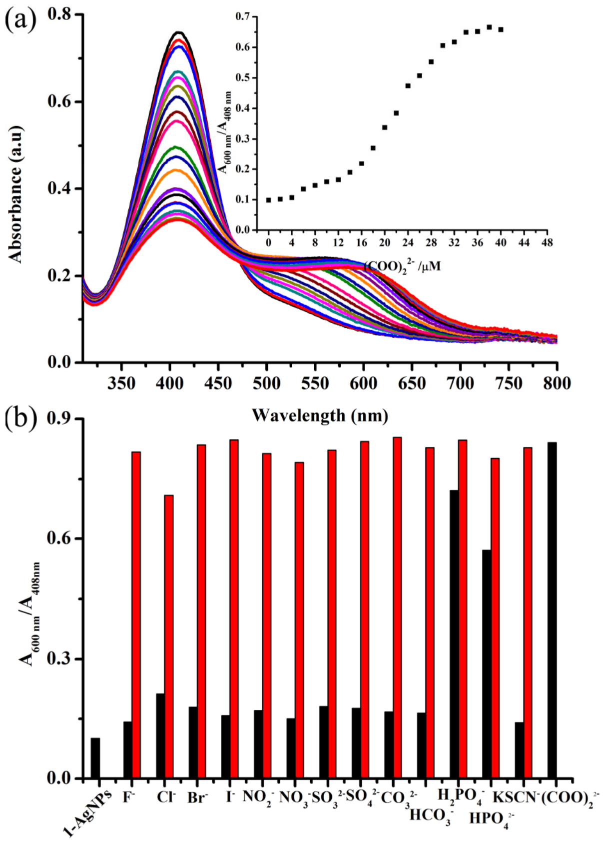


Fig. 6. (a) Absorbance of 1-AgNPs with oxalate concentration and (b) selectivity studies of 1-AgNPs for oxalate (10^{-6} M) in presence of different anions (10^{-3} M). Black and red bar represent without and with oxalate ions.

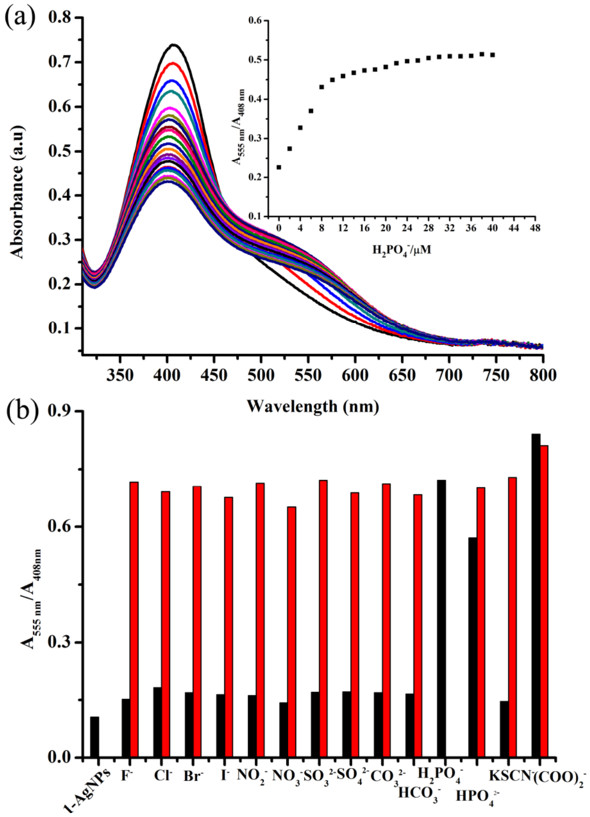
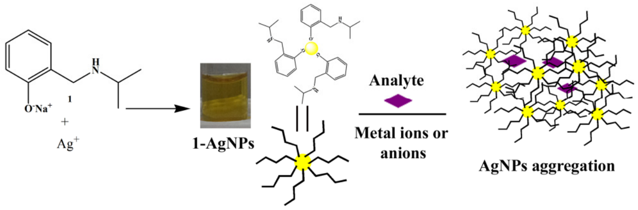


Fig. 7. (a) Absorbance of 1-AgNPs with dihydrogen phosphate concentration and (b) selectivity studies of 1-AgNPs for dihydrogen phosphate (10^{-6} M) in presence of different anions (10^{-3} M). Black and red bar represent without and with dihydrogen phosphate ions.



Scheme 1. Schematic representation of 1-AgNPs aggregation with cations and anions.

3.4. Discussion and recovery studies

Noble metal NPs are known to exhibit distance dependent optical properties due to surface plasmon coupling. Hence the selective colorimetric change of 1-AgNPs for multiple metal cations (Ni^{2+}, Co^{2+}, Ca^{2+} and Cd^{2+}), oxalate and mono-, dihydrogen phosphate anions could be due to the aggregation of AgNPs driven by metal ions coordination and supramolecular (hydrogen bond) interaction of anion with amino group of surface functionality (Scheme 1). Ni^{2+} and Co^{2+} metal cations are known to form strong coordination with amine ligands. Cd^{2+} also had shown strong coordination with amino group and phenolic chelating ligands. But reason for the selective coordination of Ca^{2+} with phenolic chelating ligand is not clear. The colour difference for cations and anions might be due to the differences in the AgNPs aggregation. FE-TEM studies were performed to explore the aggregation of AgNPs. 1-AgNPs with Ni^{2+} and Co^{2+} clearly showed the AgNPs aggregation (Fig. 8). However, it is difficult to find any significant difference in the AgNPs aggregation. In contrast, anions, oxalate, mono- and dihydrogen phosphate, with 1-AgNPs displayed distinctly different aggregation and evidenced the colour change (Fig. 9). Oxalate addition that showed dark-grey colour with 1-AgNPs revealed strong aggregation of AgNPs with smaller size (Fig. 9a). Dihydrogen phosphate with 1-AgNPs lead to aggregation of NPs strongly compared to monohydrogen phosphate anions (Fig. 9b, c). It is noted that phosphate anions added sample showed bigger AgNPs size compared to 1-AgNPs with oxalate. Thus the aggregation difference of 1-AgNPs with oxalate and phosphate anions might have different surface plasmon coupling that lead to the formation of different colour. Addition of metal cations or anions into aqueous solution of 1 did not show any significant change in the absorption or colour except small reduction in the absorption intensity (Fig. S4). This suggests that AgNPs presence facilitate the selective interaction of surface ligand 1 with metal cations (Ni^{2+}, Co^{2+}, Cd^{2+} and Ca^{2+}) and anions (oxalate, di- and monohydrogen phosphate). The applications of 1-AgNPs colorimetric assay for selective sensing of Ni^{2+} and oxalate in presence of different metal cations and anions were also explored. It can be seen from the Table 1, the mean recoveries of such samples were between 92% and 98% and suggest the potential application of 1-AgNPs colorimetric assay for sensing Ni^{2+} cations and oxalate anions in water samples.

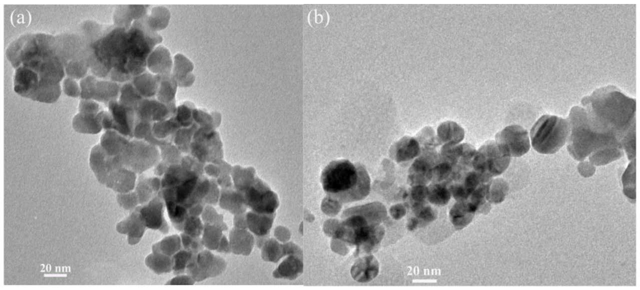


Fig. 8. TEM images of 1-AgNPs with Ni^{2+} (a) and Co^{2+} (b).

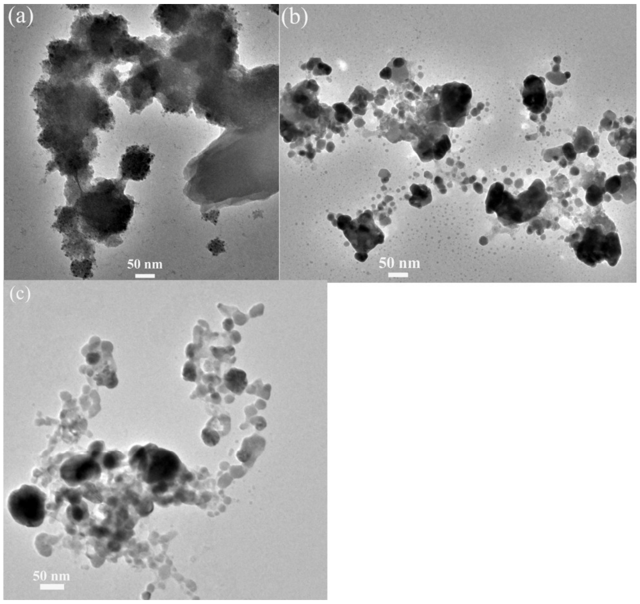


Fig. 9. TEM images of 1-AgNPs with oxalate (a), dihydrogen phosphate (b) and monohydrogen phosphate (c).

4. Conclusion

AgNPs with phenolic chelating ligand surface functionality has been synthesized and used for selective colorimetric sensing of multiple metal cations (Ni^{2+}, Co^{2+}, Ca^{2+} and Cd^{2+}) and anions (oxalate, mono and dihydrogen phosphate). Importantly 1-AgNPs exhibited distinguished colour for different metal cations and anions. 1-AgNPs with Ni^{2+} showed wine-red, Co^{2+} exhibited pinkish and orange colour was observed with Ca^{2+} and Cd^{2+}. Similarly, 1-AgNPs with oxalate showed dark grey colour whereas di- and monohydrogen addition exhibited light-grey and orange colour, respectively. The colour change and differences are due to the aggregation of 1-AgNPs that was caused by the selective interaction of meal cations and anions with surface functionality. Transmission electron microscopy images of 1-AgNPs with metal cations and anions clearly confirmed the aggregation of NPs. The concentration dependent studies indicate that 1-AgNPs can detect up to 10^{-6} M level. Interference studies of 1-AgNPs revealed high selectivity for Ni^{2+} and oxalate ions. Thus phenolic chelating ligand can be used as potential candidate for the fabrication of noble metal NPs colorimetric sensor for metal cations and anions.

Table 1. Determination of Ni^{2+} and oxalate in water samples using the 1-AgNPs colorimetric assay.

Samples	Mean Found (μM)	Mean Recovery[a] (%)	RSD[b] (%)
Ni^{2+} (1.0)[c]+H_2O	0.99	99	0.83
Ni^{2+} (1.0)+Co^{2+}(1.0)+Pb^{2+}(1.0)+Co^{2+}(1.0) +Zn^{2+} (1.0)	0.97	97	0.48
Ni^{2+} (1.0)+Pb^{2+}(1.0)+ Mn^{2+}(1.0)+Cd^{2+}(1.0)+Ca^{2+} (1.0)	0.96	96	0.48
Ni^{2+} (1.0)+Zn^{2+}(1.0)+ Cu^{2+}(1.0)+Mg^{2+}(1.0)+Fe^{3+} (1.0)	0.95	95	1.30
Ni^{2+} (1.0)+ Hg^{2+}(1.0)+ Pb^{2+}(1.0)+Cd^{2+}(1.0)+Zn^{2+} (1.0)	0.92	92	1.01
$(COO)_2^{2-}$(1.0)[c]+H_2O	0.99	99	0.82
$(COO)_2^{2-}$(1.0)+ HPO_4^{2-}(1.0)+ $H_2PO_4^-$ (1.0)+ $KSCN^-$(1.0) +NO_2^- (1.0)	0.98	97	1.30
$(COO)_2^{2-}$(1.0)+ SO_4^{2-}(1.0)+ $KSCN^-$ (1.0)+I^-(1.0)+Cl^- (1.0)	0.96	96	0.85
$(COO)_2^{2-}$(1.0)+CO_3^{2-}(1.0)+ F^- (1.0)+SO_3^{2-}(1.0)+Cl^- (1.0)	0.97	98	0.83
$(COO)_2^{2-}$(1.0)+$KSCN^-$(1.0)+ F^-(1.0)+ CO_3^{2-}(1.0)+NO_3^- (1.0)	0.98	98	0.47

[a] Mean recovery (%) =100 x ($\mathbf{c}_{\text{mean found}}/\mathbf{c}_{\text{mean recovery}}$).

[b] Relative standard deviation of three determination.

[c] Values in parentheses=concentration (μM) of the metal cation and anion added.

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Notes and references

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† Electronic Supplementary Information (ESI) available: IR, concentration dependent, interference spectra for metal ions and anion sensing by 1-3-AgNPs. See DOI: 10.1039/b000000x/

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