Heavy Metal Ion Sensing By Surface Plasmon Resonance on Gold Nanoparticles

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Abstract: ***Surface Plasmon resonance (SPR) based heavy metal ions sensor is one of the most sensitive sensor for detecting toxic metal ions. It is an inexpensive, portable and also feasible for real time detection. SPR sensor is a type of optical sensor in which toxic metal ions get adsorbed on the functionalized metal (mostly Au) film causes the change in refractive index of the metal (Au)-dielectric (sensing) medium. The change of the refractive index leads to a shift in the angular spectrum of the reflected light and can be accurately monitored by optical methods. In this paper,we are trying to optimize the detection level of heavy metal ions by surface plasmon resonance on gold nanoparticles using UV-VIS spectroscopy. Polymer like chitosan is being used with gold nanoparticles to detect copper and zinc ions and detection till very low concentrations of the toxic metal ions is obtained.***

Keywords: Surface Plasmon Resonance, Optical sensor, metal nanoparticles, reducing agent,chelating agent, polymer capping .

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1. Introduction

Water contamination by heavy metals is a common problem encountered in many countries due to undue deposition of metal-rich mining, agricultural, industrial and urban wastes in water resources. This problem has many health and socio-economic impacts and therefore, there is a dire need for a fast, reliable and highly sensitive sensor networks for continuous detection and monitoring of toxic heavy metal levels in soil and water resources[1,2]. Different governments have set up environmental laws to determine amount of heavy metal ion in drainage, considered to be non-detrimental to the environment. On the other hand, Surface Plasmon Resonance (SPR) spectroscopy is a surface-sensitive technique that has been used to characterize the thickness and refraction index of dielectric medium at noble metal (gold) surface. SPR technique has emerged as a powerful technique for a variety of chemical and biological sensor applications For the last decade, surface plasmon resonance sensors have been extensively studied. [4]. The use of surface plasmon resonance as an indicator of the ion content can be a useful approach to disseminate the application of continuous water quality management. Gold nanostructures characterized by surface plasmon resonances can be used to guide, enhance, emit, and modify optical fields, a phenomena that can be used for novel sensors. Optical sensors based on excitation of surface plasmons, commonly referred to as surface plasmon resonance (SPR) sensors,can be used to detect heavy metal ions (Hg^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+} and Ni^{2+}) in waste water[8].

Different methods for detecting heavy metal ions including Zn, Cu and Mn like direct aspiration absorption and emission spectroscopy using inductive coupled plasma have been reported in the literature [3]. However, these methods require expensive devices and expertise in analysis technique. Besides, the results are not real-time and portability is an issue as well. This motivated us to develop a detection system that is simple and portable.

A broad deviation of optical properties of gold nanoparticles (AuNPs) has been observed due to changes in particle size, inter–particle distance and the dielectric properties of the solvent [4,5]. These variations enabled researchers to develop a simple yet sensitive colorimetric sensors for detecting different chemical analytes by observing the shift in their surface plasmon resonance (SPR) spectra [6,7]. In this work, we have synthesized colloidal AuNPs in aqueous media by chemical precipitation method [8]. The AuNPs were capped with chitosan, a biopolymer, whose metal chelating property has already been well documented [13-16]. The free amines in chitosan get protonated in mildly acidic condition and acts as bonding sites for heavy metal ions. However, when metal ions bind to the chitosan it compromises the stability of the AuNPs which is reflected in their optical spectra. Our present work explores this principle detect Zn^{2+} and Cu^{2+} ions in water using SPR pattern of Cht-AuNPs. The results indicate that very high concentrations of Zn^{2+} and Cu^{2+} ions could be determined by this technique. Therefore, it opens up a simple yet effective way to detect environmentally hazardous materials in real time.

2. Experimental

Spherical chitosan capped gold nanoparticles were synthesized by chemical precipitation technique. Synthesis of gold nanoparticles was based on the well documented Turkevitch process Briefly, chloroauric acid [$HAuCl_4$] (Sigma-Aldrich) solution of adequate concentration (5 mM & 10 mM) was heated to boil. To this boiling solution an adequate amount of monosodium glutamate [$C_5H_8NNaO_4$](Sigma-Aldrich) was added with constant stirring. Monosodium glutamate reduces gold chloride solution that leads a colorless solution to turn wine red, indicating the formation of AuNPs. The size and shape of the AuNPs depends on the molar ratio (MR) of reducing agents to the Au precursor, [MSG/Au] [8]. We choose MSG/Au ratios at 3 and 7 (referred as MR3 and MR7 respectively) as they yielded best stability and morphology[7]. Once AuNPs are formed in the solution, chitosan is immediately added to it so and the final concentration of chitosan in the solution was maintained to about 0.01%. This resulted in the formation of Cht-AuNPs in solution, which was then cooled to room temperature in order to remove unreacted chitosan, the solution was centrifuged at 4000 rpm and the precipitate was washed several times before re-dispersing them in aqueous media. The Cht-AuNPs were then carefully stored for further characterization and experimentation. We have also tested the synthesis of gold nanoparticles by adding only Chitosan (medium molecular weight) directly on the solution of $HAuCl_4.H_2O$ and De-ionised water upon heating and constant steering.In order to demonstrate the detection of heavy metals,zinc acetate [Zn (CH_3COO) 2.2H_2O] (Univar) solution was used as the source of Zn^{2+} ions for the sensing experiments. For Cu^{2+} ion sensing, Copper Sulphate [$CuSO_4$ .5H_2O] was taken as source. For the sensing, about 1 ml of Cht-AuNPs were taken in polymethyl methacrylate (PMMA) cuvettes. To this Zn^{2+} ions (Cu^{2+} ions) were added such that the final Zn^{2+} ion (Cu^{2+} ion) concentration in the cuvettes become homogeneous . Then the cuvettes containing Cht-AuNPs and Zn^{2+} ions (also Cht-AuNPs and Cu^{2+} ions) were promptly characterized with Ultraviolet-visible (UV-Vis) spectroscopy using Ocean optic (Model USB 2000-FLG) to record their SPR spectra. Finally, the SPR spectra from all the samples were analyzed carefully to correlate the changes of SPR spectra with respect to concentration of Zn^{2+} and $Cu^{2+.}$

3. Results And Discussions

Optical absorption spectrum of gold nanoparticles is a good indicator of their size and shape [4]. UV-Vis absorption spectrum of the as-synthesized nanoparticles show a sharp peak centered around 519 nm, corresponding to particles ranging from 10 to 20 nm in diameter [5]. The colloidal suspensions of gold nanoparticles are very sensitive to change in the concentration of ions in the solution due to the stabilization by excess anions (glutamate ions or citrate ions). It is difficult to estimate the concentration of the analyte through optical characterization due to lack of a unique signal for different concentrations as any concentration of the analyte will result in agglomeration [17].

Polycations have shown a strong interaction with the metal precursor, due to the formation of ion-pair with the negatively charged tetrachloroauric acid anions. Moreover the columbic forces are also responsible for the stabilization of negatively charged gold colloids by adding cationic polyelectrolytes . The hydrophobic side-groups in the water-soluble homopolymers copolymers attaches with the metal surface whereas the hydrophilic part combines with the dispersion medium [6]. Chitosan,derived from chitin by partial deacetylation,is a polymer with poly-cationic properties in dilute acidic solutions,enabling electrostatic attraction towards the negatively charged gold nanoparticle surfaces. Addition of aliquots of chitosan into the gold colloid shows a distinguishable change in the transmitted color and its optical absorption spectrum show a slight departure from that of 'as-made' gold colloid [17].

Chitosan is known as an effective chelating agent for heavy metal ions. Chitosan capped nanoparticles are no longer stabilized by physically adsorbed charges,upon exposure to varying concentration of these analytes, a concentration-dependent change in the optical absorption is observed (Figure 1). There was a plasmonic peak shift of up to almost 7 nm when the concentration of copper(II) ions was varied from 0 to 10 ppm as can be seen from the flot shown in Figure 2.

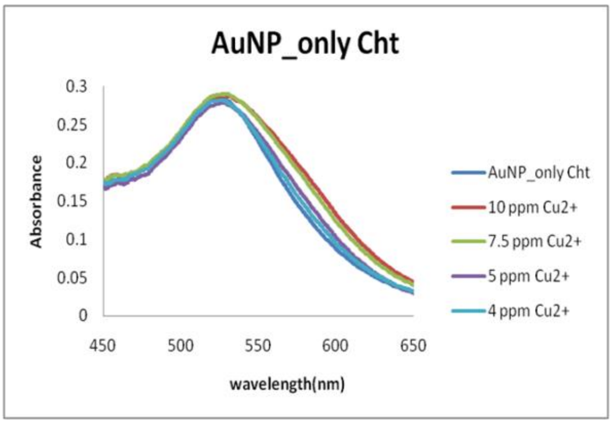

Figure 1. Copper(II) ion detection by chitosan capped AuNP

The change in absorption spectra is very clear in the above figures where the width of the Plasmon resonance peak progressively increases with increase in concentrations of Cu^{2+} and $Zn^{2+.}$ We have also demonstrated Plasmon peaks for gold nanoparticles single capped by chitosan only. In Figure 1, it is seen that the detection of Cu^{2+} ion is till 4 ppm from higher concentrations such as 10 ppm . However, in case of Zn^{2+} ions, we could detect only till 32 ppm [Figures 3, 3, 4 and 5].

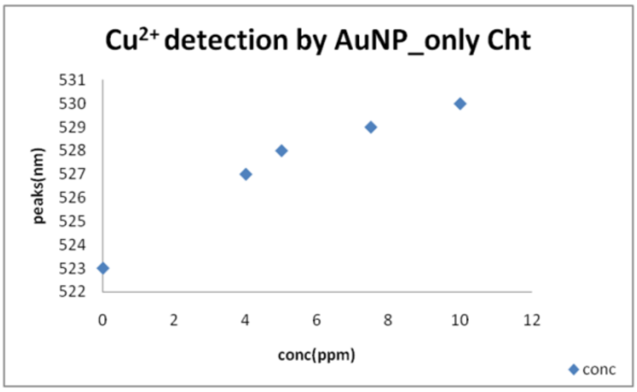

Figure 2. SPR peaks w.r.t. varying concentrations of copper(II) ions

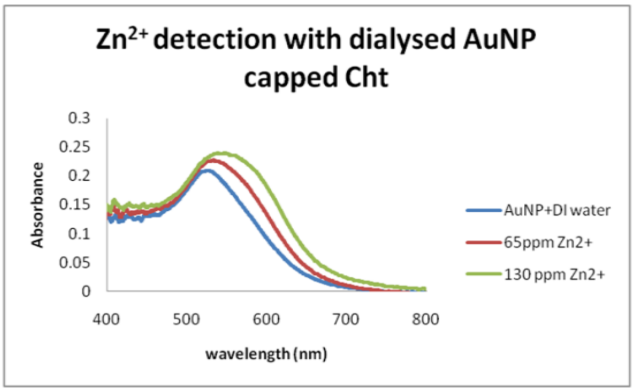

Figure 3. Zinc(II) ion detection by Cht capped AuNP

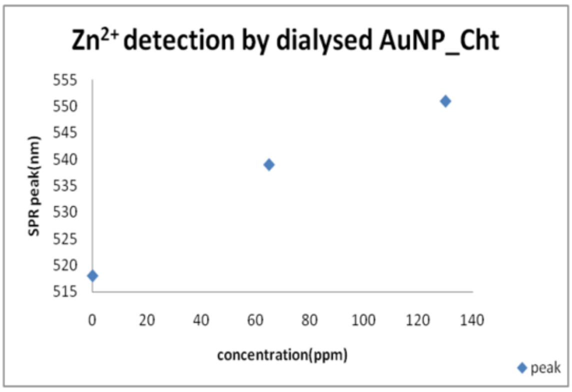

Figure 4. SPR peaks w.r.t.varying concentrations of zinc(II) ions

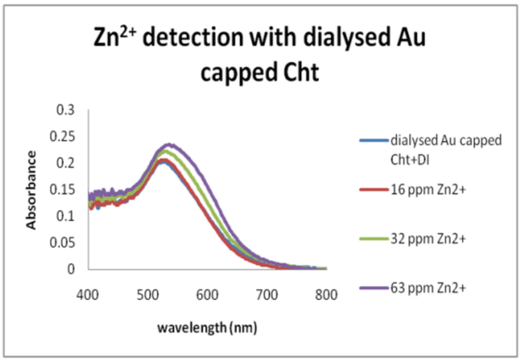

Figure 5. Zinc(II) ion detection by Cht capped AuNP

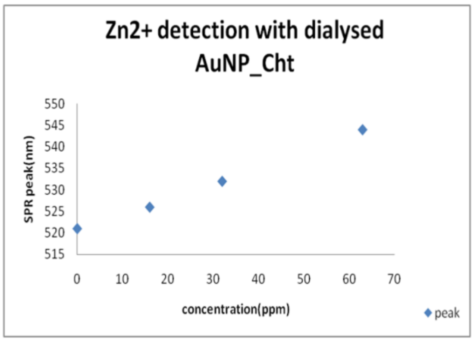

Figure 3b. SPR peaks w.r.t.varying concentrations of zinc(II) ions

Since our aim is the sensing or detection of heavy metal ions,therefore we have checked the morphological and the other detailed characterization of the Chitosan capped AuNPs (Cht-AuNPs). Since, the molar ratios (MSG/Au) 3 and 7 yielded the best results [49],so our sensing experiments were performed using these two nanoparticles only. Gold nanoparticles synthesized at MR3 shows the plasmon resonance at ~ 525 nm and the particles synthesized at MR7 peaks at ~520 nm, which is consistent with the fact that smaller nanoparticles absorb at lower wavelengths [7].

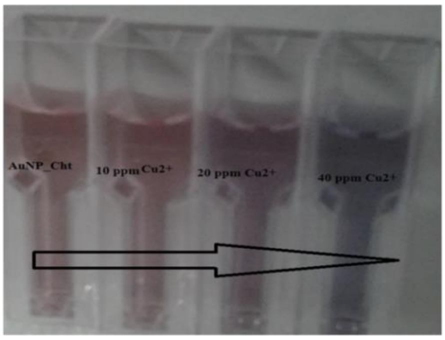

Figure 4a. Colorimetric approach for different concentrations of Cu^{2+}

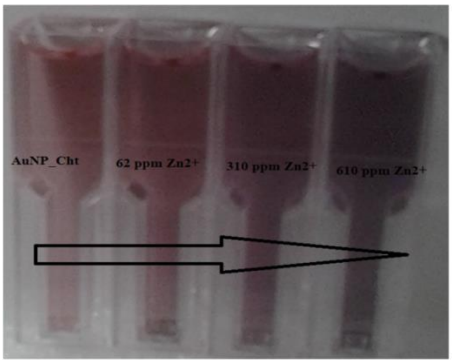

Figure 4b. Colorimetric approach for different concentrations of Zn^{2+}

The phenomenon surface Plasmon resonance enables construction of simple but sensitive colorimetric sensors for various analytes. We have got color change of gold nanoparticles for some higher concentrations of analyte metal ions [Fig:4a and b]. Our research is going on for colorimetric sensing for lower concentrations.

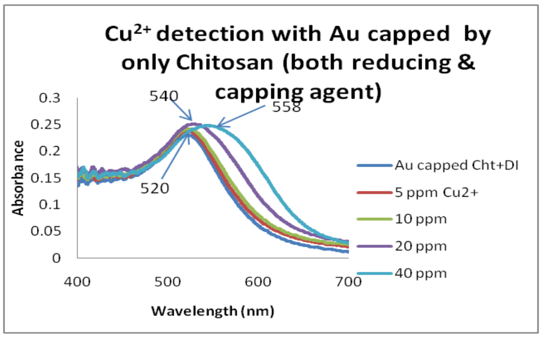

Fig 5. Copper(II) ion detection by only Cht capped AuNP

When tested with chitosan as both reducing and capping agent with gold nanoparticles, we have found few good results for copper as shown in fig 5.

4. Conclusion

We have used the chemical precipitation method to obtain Cht-AuNPs by reducing gold chloride solution with Monosodium Glutamate (MSG). The Cht-AuNPs based colloidal system thus obtained had a distinct ruby red color and sharp SPR peak which is changed when exposed to Zn^{2+} and Cu^{2+} ions. The detection of heavy metal ions were hence carried out by analyzing the UV–visible spectra of the Cht- AuNPs. The technique in our report could detect higher concentrations of Zn^{2+} in water, but is capable of detecting lower concentrations of Cu^{2+} ions which is a satisfactory detection till now in our ongoing research process. Although at this time the detection technique has limitations in terms of high sensitivity and selectivity but its simplicity and portability makes it a potent technology for the future.

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