

Poly Acrylic Acid Capped Gold Nanoparticles for Heavy Metal Sensing In Water

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Abstract

Traditional heavy metal analysis methods require trained staff, equipment and it is time consuming, thereby limiting the use of metal ion sensors to specialists. Surface plasmon resonance as an indicator of the heavy metal ion content can be used to disseminate the application of continuous water quality management even in remote sites. When heavy metal ion is added to colloid of gold nanoparticle capped with polymer, functionalized group in polymer attaches with metal ion leading to the shape and size of nanoparticles to be changed, resulting in a change in surface plasmon resonance frequency. A comparison of the optical absorption spectra of the colloidal suspension before and after the exposure to metal ions gives a good indication of the concentration of the heavy metal ions. If gold nanoparticles are capped with anions like poly acrylic acid (PAA), excellent results can be achieved in terms of attachment of metal ions which then leads to the change of the shape and size of nanoparticles and SPR frequency measurements can be followed up. Even lower concentrations of copper and zinc ions are reportedly detected in this process. This simple

metal ion sensor can be implanted in lab-on-chip type of applications for easier implementation.

Keywords: heavy metals, gold nanoparticles, chelation, surface plasmon resonance, capping agent, poly acrylic acid.

Introduction

Day by day increase of water pollution by toxic metals is becoming a serious environmental problem [1]. Different governments have set up environmental laws to determine amount of heavy metal ion in drainage from various sources. The toxic contaminants and pathogens are getting released into air, soil and water from different toxic chemical wastes, manufacturing waste, rapidly growing industries, spills and even underground storage tanks and this is becoming increasingly critical for environmental monitoring for the protection of the public and environment [2-4]. Nanotechnology can be thought of as a solution to minimize or eliminate the use of toxic materials and also to monitor them before it is exposed to environment. Monitoring the toxic metal ions with current methods are costly and

time intensive and several limitations are encountered while in sampling and testing with the analytical techniques [2]. Also, the time and expenses involved in sample acquisition, sample preparation, and laboratory analysis of the pollutants have led to the renewed interest for finding newer solutions so as to analyze the water contamination. Therefore fast and cost-effective field-analytical technologies are concern of the hour which can increase the number of analyses and reduce the time required drastically.

The unique optical properties of metal nanoparticles such as particle size and shape, particle-particle distance, and the dielectric properties of the surrounding solution are caused by the phenomenon namely surface Plasmon resonance (SPR). The various methods for SPR sensing have been used quite some time now besides the traditional methods of heavy metal ion sensing [6-11]. Amongst the various metal nanoparticles, the gold nanoparticles have the chemical inertness and resistance to surface oxidation and this makes synthesis of gold nanoparticles easier in comparison to other metal nanoparticles [7]. When heavy metal ion is added to gold nanoparticle capped with polymer, functionalized group in polymer attaches with metal ion leading to the shape and size of nanoparticles being changed, resulting in a change in surface plasmon resonance frequency [6]. Chitosan is a heavy metal chelating agent and it has been used as a capping agent on gold nanoparticles for some time now [6]. Chitosan acts as a chelating agent because of the presence of free amines in its monomer, which gets protonated in dilute acidic media [8]. These protonated amines form the multiple bonding sites in chelation of heavy metals like Mn^{2+} , Cu^{2+} , Cr^{2+} and Zn^{2+} [6]. Like chitosan poly acrylic acid (PAA) is also a very good chelating agent which can be successfully used as a capping agent with gold

nanoparticles. The carboxyl group serves as a trap for chelation. PAA has been used as a capping agent with different nanoparticles for various uses [14-18]. PAA grafted luminescent silicon nanoparticles are used for biological applications [16]. Also, silver nanoparticles capped with PAA are formed by UV Irradiation for various uses [17]. PAA has got some applications in manganese filter [7]. Poly acrylic acid is polymerization of acrylic acid which is water soluble. PAA has been used in power plants, steel factories, chemical fertilizer plants, refineries and air conditioning systems as scale inhibitor and dispersant in circulating cool water systems.

The optical properties of PAA give adequate response to the change in pH value and temperature. The removal of metal ions from wastewater by adsorption is highly dependent on the pH of the solution and it affects the surface charge of the adsorbent, the degree of ionization, and the speciation of the adsorbent species [13]. The change in its optical properties is fine enough to use it as a colorimetric sensor along with gold nanoparticles. Colorimetric sensors are used in various fields for some time now [7-9]. There is not much work yet reported with PAA capped gold nanoparticles in the field of metal ion chelation whereas lots of works are in literature for chitosan capped gold nanoparticles. In this paper, we are trying to cap gold nanoparticles with PAA which in turn behaves as a heavy metal chelating agent in wastewater.

Experimental

Spherical poly acrylic acid (PAA) capped gold nanoparticles were synthesized by chemical precipitation technique. Briefly, chloroauric acid [$HAuCl_4$] (Sigma-Aldrich) solution of adequate concentration (~50 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, PAA is immediately added to it so and the final concentration of PAA in the solution was maintained to about 0.01%. This resulted in the formation of PAA-AuNPs in solution, which was then cooled to room temperature in order to remove unreacted PAA, the solution was centrifuged at 4000 rpm and the precipitate was washed several times before re-dispersing them in aqueous media. The PAA-AuNPs were then carefully stored for further characterization and experimentation.

Zinc sulphate [$(CH_3COO)_2Zn \cdot 2H_2O$] (Univar) solution was used as the source of Zn^{2+} ions for the sensing experiments. For the sensing, about 1 ml of PAA-AuNPs were taken in polymethyl methacrylate (PMMA) cuvettes. To this Zn^{2+} ions were added such that the final Zn^{2+} ion concentration in the cuvettes become homogeneous and in parts per million (ppm) range. Then the cuvettes (containing PAA-AuNPs and Zn^{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+} ions. Similarly Copper sulphate [$CuSO_4 \cdot 5H_2O$] (Univer) solution was used as the source of Cu^{2+} ions for the sensing experiments.

Result and Discussion

Zn^{2+} ions sensing: The as-prepared PAA-AuNPs were ruby red in color which gradually turns bluish red upon exposure to Zn^{2+} ions of increasing concentrations for samples, as shown in Figure 1. This change of color, which is known to indicate the destabilization of the colloidal PAA-AuNPs, serves as a good colorimetric indicator for the presence of Zn^{2+} ions in the solutions. Though the color change was gradual and each concentration of Zn^{2+} ions did induce minute change in color, no efforts were made to correlate the color to the Zn^{2+} ion concentration as this is straightforward and can be carried out by simple image analysis. A more precise and quantitative measurement of Zn^{2+} ions was attempted by recording the optical absorption spectra of the colloids which is very sensitive technique. Along with the decrease in optical absorption, a shift in the absorption peak towards bluish red could be observed with increasing Zn^{2+} concentration in Figure 3 and 4. The pH value is taken into account for the testing of samples and this value was kept at around 3 to 4. We could detect till 2ppm Zn^{2+} ions in water with this PAA capped AuNPs.

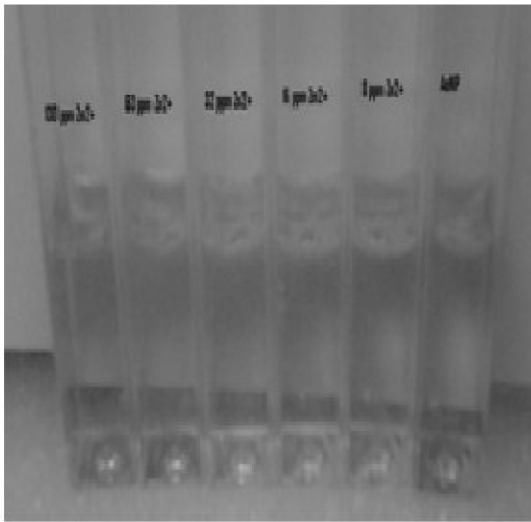


Figure 1: Color change observation of gold colloid with varying concentrations of Zinc (II) ions

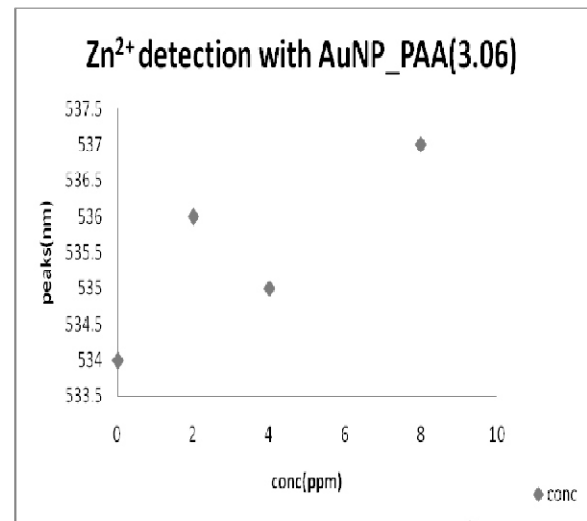


Figure 2: (b) Analysis with increasing Zn²⁺ ion concentrations versus SPR peaks.

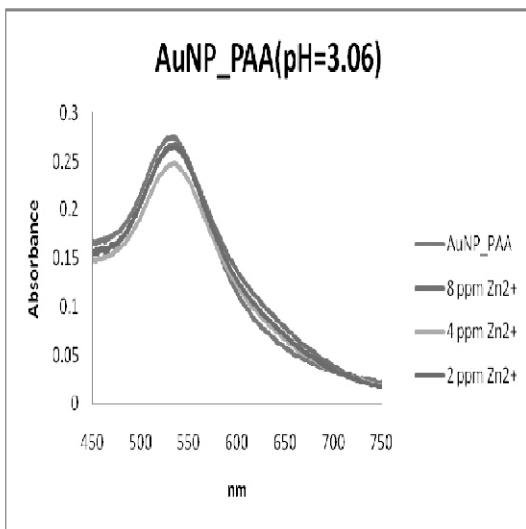


Figure 2: (a) UV-vis absorption spectra of gold nanoparticles

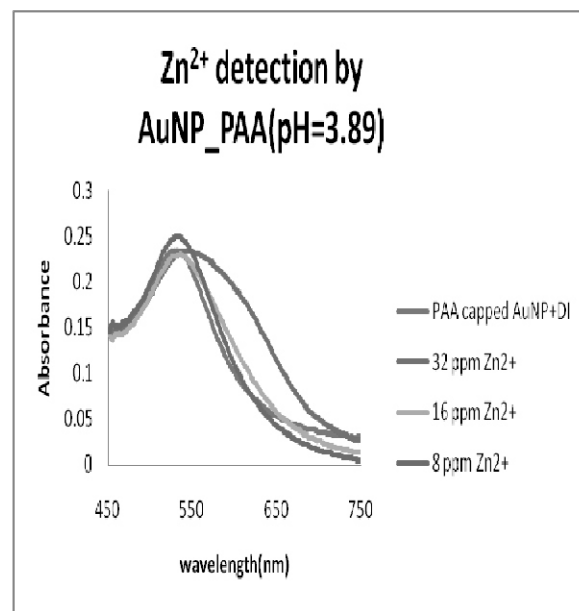


Figure 3: (a) UV-vis absorption spectra of gold nanoparticles

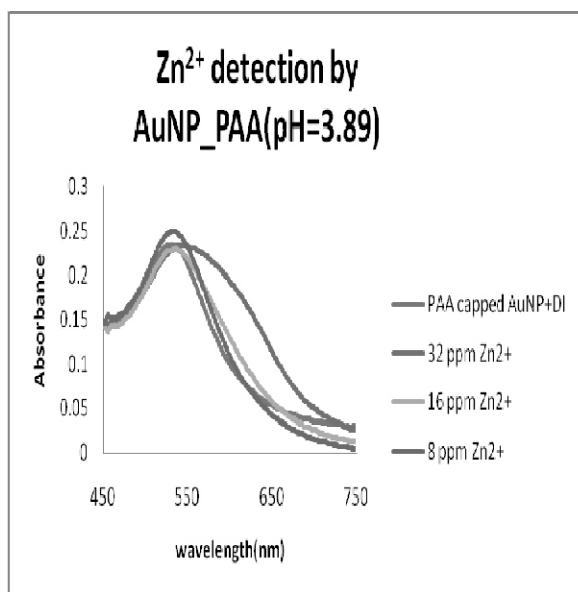


Figure 3: (b) Analysis with increasing Zn^{2+} ion concentrations versus SPR peaks.

Cu^{2+} ion sensing: The maximum acceptable limit for copper(II) ions in water is 2 ppm[4]. Using SPR on gold nanoparticles, copper(II) ions are detected till this limit using PAA capping on gold nanoparticles. The following results are based on the effect of pH values of the gold colloid as the chelating property of PAA capped gold nanoparticle (AuNP) is found to be varying for different values of pH. Modification of the surface of gold nanoparticles is necessarily done to achieve the adequate charge on the colloidal nanoparticles which is carried out by PAA capping for our work. Also, adjustment of the pH value of the colloidal solution is needed as the degree of ionization of the capping polymer or polyelectrolytes vary with the pH value. Most of the detection of metal ions by PAA capped AuNP is found at around pH=3.

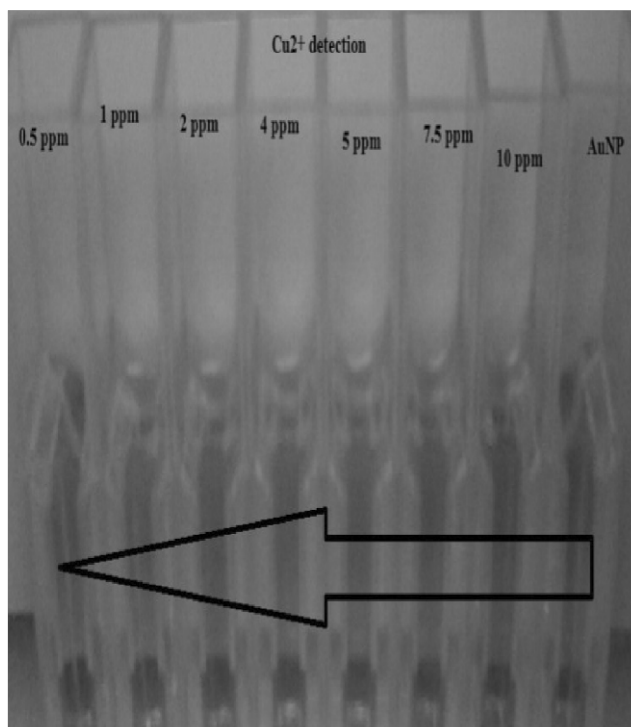


Figure 4: Color change observation of gold colloid with varying concentrations of Copper (II) ions

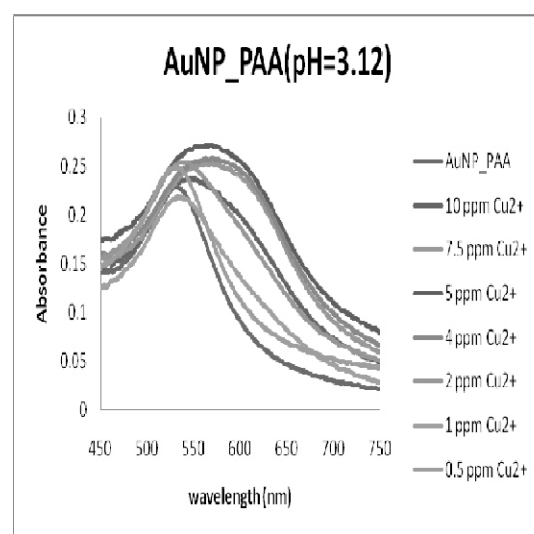


Figure 5: (a) UV-vis absorption spectra of gold nanoparticles

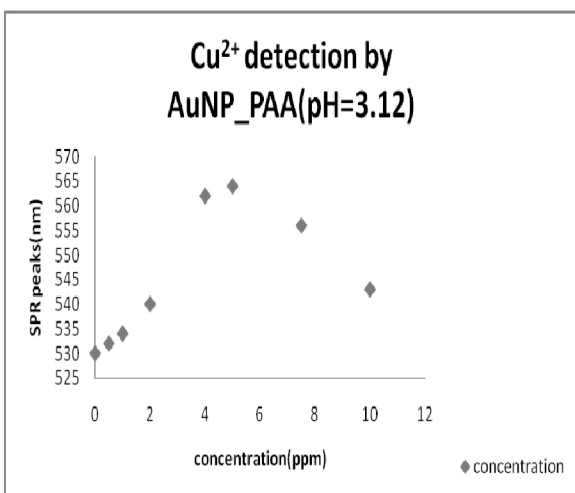


Figure 5: (b) Analysis with increasing Cu^{2+} ion concentrations versus SPR peaks.

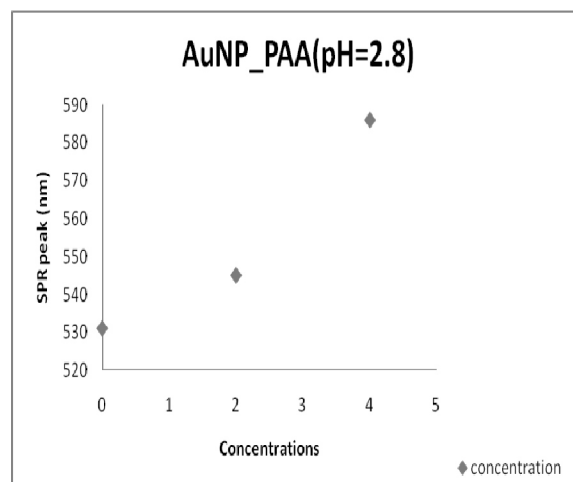


Figure 6: (b) Analysis with increasing Cu^{2+} ion concentrations versus SPR peaks.

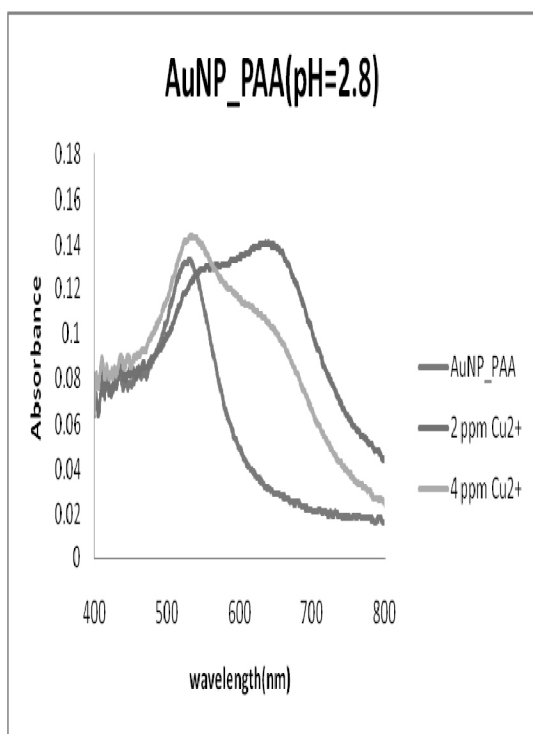


Figure 6: (a) UV-vis absorption spectra of gold nanoparticles

Sensitivity And Portability

In its present state, this detection technique does have its limitations in terms of sensitivity. There are more sophisticated methods that can detect very low levels of Zn^{2+} and Cu^{2+} ions even to ppb levels. However, Zn and Cu being a transition metal and one of the essential minerals, the concentration of Cu^{2+} and Zn^{2+} ion that causes health hazards is quite high compared to other heavy metals like Cd and Hg etc. It is known that in soil ~ 500 ppm or more of Zn may cause health threats, which could be easily detected by the reported method [8]. Same case is with Cu ion. As discussed so far that our system can actually detect Cu^{2+} and Zn^{2+} ions in similar concentration range (till 2ppm) and has the potential to be improved further. The technique also has an added advantage of good portability as it does not require high end instrumentations for the detection. Thus this simple colorimetric technique seems potentially

a simple yet cost effective technique for the detection of Cu^{2+} and Zn^{2+} ions. Further work needs to be done to address the issue of selectivity and to improve the sensitivity of the technique.

Conclusion

We have used the chemical precipitation method to obtain PAA-AuNPs by reducing gold chloride solution with monosodium glutamate (MSG). The PAA-AuNPs based colloidal system thus obtained had a distinct ruby red color and sharp SPR peak which changed when exposed to Cu^{2+} and Zn^{2+} ions. The detection of Cu^{2+} and Zn^{2+} ions were hence carried out by analyzing the UV-visible spectra of the PAA-AuNPs. The technique in our report could detect till 2ppm concentration of both Zn and Cu ions in water which is a satisfactory detection range. 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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