

Gold nanoparticles for sensing Mn^{2+} in water

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Abstract: Gold nanoparticles coated with polymers like chitosan, polyvinyl alcohol (PVA), polyvinyl pyrrolidone (PVP) and poly acrylic acid (PAA) can effectively be used to detect the presence of Mn^{2+} ions in water. A shift in the optical absorbance peak of the Au colloid is observed in the presence of Mn^{2+} ions. The shift in the absorbance peak wavelength is directly proportional to the concentration of Mn^{2+} ions in water. Chitosan capping was found to give the maximum shift and as such was selected for the development of a sensor for detecting Mn^{2+} ions in water. The variation in photo-energy of the photons after passing through the colloidal dispersion of chitosan coated Au nanoparticles varies the conductivity of the detector and this can be related to the concentration of the Mn^{2+} ions in water. Two different detectors were tested, a nanosensor and a light dependent resistor, with the latter demonstrating better response.

Key words: Gold nanoparticles, Chitosan, Polyvinyl Alcohol, Polyvinyl Pyrrolidone, Poly Acrylic Acid, Mn^{2+}

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I. Introduction

Water contamination is a serious problem encountered in almost all parts of the world, due to undue deposition of metal toxins, industrial waste, agricultural and urban waste in water reserves. Presence of heavy metal ions in drinking water is a major concern. Heavy metals can lead to many health hazards like heavy metal poisoning in children and can also disturb the normal functioning of vital organs. People exposed to mercury beyond the normal limit are prone to heart, kidney, nervous system and gastrointestinal disorders. Heavy metals into the marine environment have increased their levels to large extents within past a few decades. These pollutants tend to accumulate in the bottom sediments. As a result, ecosystems such as seaports or other industrialized coastal areas that have chronic inputs of metals have highly contaminated sediments. This characteristic has led to concerns over the ecological effects that may be associated with sediment [1]. So far the Mn^{2+} and iron are concerned the Water containing excessive amounts of iron and manganese can stain clothes, discolor plumbing fixtures, and sometimes add a “rusty” taste and look to the water. Surface water generally does not contain large amounts of iron or

manganese, but iron and manganese are found frequently in water systems that use groundwater. The Safe Drinking Water Act secondary standards (aesthetic, not health related) for iron in drinking water is 0.3 parts per million (ppm) and 0.05 ppm for manganese. If water contains more than 0.05 ppm iron or 0.01 ppm manganese, the operator should implement an effective hydrant-flushing program in order to avoid customer complaints [2].

Metals in water cannot always be detected by vision, smell or taste and can only be detected using laboratory water tests. Heavy metal ions can be toxic even at low concentrations [5]. Some heavy metals like zinc, copper and chromium are essential for our body in small quantities but can also be toxic if consumed in large amounts [4]. More poisonous metal ions include lead, mercury, arsenic and cadmium [6]. Therefore for the constant monitoring and detection of toxic heavy metal level in soil and water resources [3, 4], a fast reliable and highly sensitive sensor is of utmost necessity. Currently the detection of heavy metal ions in many places are carried out by sending technician to the field to collect the samples and test them in the laboratory for analysis.

This procedure is time consuming as well as expensive. With the advancement of time a number of other techniques have been developed for the detection and analysis of heavy metal ions. They include inductively coupled plasma mass spectrometer, Anodic stripping voltametry, X-ray fluorescence spectrometry and Microprobes, etc. However, these techniques are very expensive and needs skilled sample preparation before testing. Therefore for the detection and constant monitoring of toxic heavy metal levels in soil and water resources a simple, inexpensive, selective and sensitive method is needed. Surface Plasmon Resonance (SPR) observed in metallic nanoparticles can be used to guide, enhance emission and modify optical fields. Based on this phenomenon, a novel SPR sensor is hereby proposed that can be used to detect the presence of heavy metal ions like Mn^{2+} , Hg^{2+} , Zn^{2+} , Cd^{2+} , Cu^{2+} , etc. in water.

II. Experimental

Synthesis of Au nanoparticles:

Au nanoparticles were synthesized by reducing a 0.2 mM chloroauric acid ($HAuCl_4$) aqueous solution with a 1.4 mM trisodium citrate ($Na_3C_6H_5O_7$) solution in water (Turkevitch process). Reaction was carried out at boiling point. The mild yellow solution gradually turns reddish with the nucleation and successive Ostwald Ripening process. Reaction was stopped through quenching in an ice bath once the colour of the colloid becomes stagnant. The polymers chitosan (CTS), polyvinyl pyrrolidone (PVP), polyacrylic acid (PAA) and poly vinyl alcohol (PVA) were added to the Au salt solution prior to the addition of the reducing agent.

Detection of metal ion Mn^{2+} :

Spiked samples were prepared in water with manganese acetate as the source of Mn^{2+} ions. 2 ml of polymer capped Au nanoparticle colloid was mixed with 1 ml of spiked metal ion sample of different concentrations in a polymethyl methacrylate (PMMA) cuvette. UV-visible absorption spectroscopy was then carried out and the shift in the SPR peak between bare sample and sample with metal ions noted.

III. Result and Discussion:

Fig 1(a) shows the change in optical absorption of CTS-AuNP's with different concentration of Mn^{2+} . A shift in the absorption peak was observed with increasing Mn^{2+} concentration. The change of SPR peak in the absorption spectra can be seen very distinctly with naked eyes. The detection of Mn^{2+} from 166 ppm to 333 ppm is reported in this work.

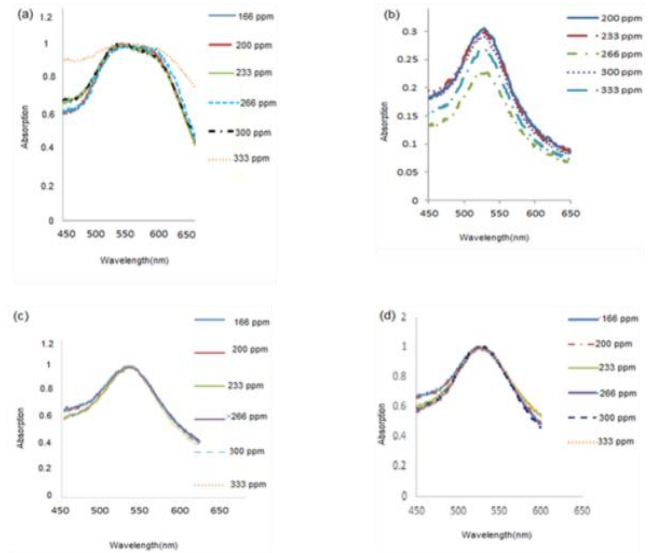


Fig.1: SPR peak of various concentration of Mn^{2+} using (a) CTS coated Au nanoparticles (b) PVP coated Au nanoparticles (c) PAA coated Au nanoparticles and (d) PVA coated Au nanoparticles

Table I: Shift in SPR peak at different concentrations of Mn^{2+}

Conc. of Mn^{2+} (ppm)	CTS		PAA		PVP		PVA	
	λ_{spr} (nm)	λ_{shift} (nm)	λ_{spr} (nm)	λ_{shift} (nm)	λ_{spr} (nm)	λ_{shift} (nm)	λ_{spr} (nm)	λ_{shift} (nm)
166	538	13	526	16	524	2	524	8
200	542	17	523	19	528	6	526	10
233	549	26	526	16	530	8	527	11
266	558	33	521	21	520	2	528	12
300	552	27	524	18	527	6	539	7
333	565	40	520	22	531	9	527	9

Since the purpose of this work is the sensing of heavy metal ion (Mn^{2+}) in water, therefore we are discussing only the characteristics of CTS-AuNP, PVP-AuNP's, PAA-AuNP's and PAA-AuNP's. Upon the addition of metal ion the shift in the SPR was observed. Chitosan capping and PVA capping were most efficient as compared to other capping in detection of Mn^{2+} with concentration ranges from 500 ppm to about 1000 ppm. The shift of plasmonic peak was between 10 to 30 nms

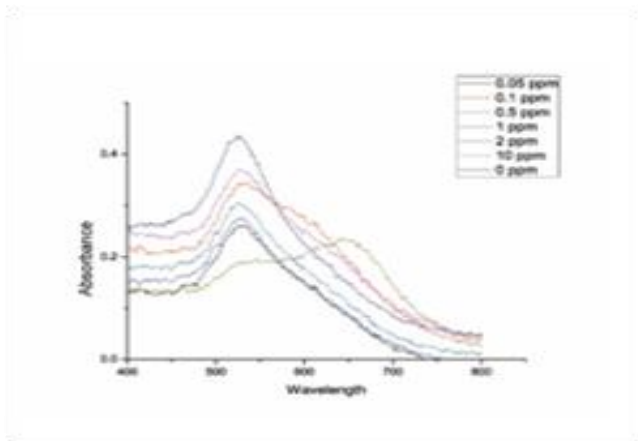


Fig.2. SPR peak of various concentrations of Mn²⁺ using CTS coated Au nanoparticles

As it was observed that chitosan capping is the most efficient one as compared with other capping, similar testing using chitosan capping gold nanoparticles was carried out with an LDR, the characteristics of which are shown in Fig.2 and the peak shifts are shown in Table II.

Table II: Shift in SPR with different concentration of Mn²⁺ using LDR

Sl.No	CTS	
	λ_{spr} (nm)	λ_{shift} (nm)
1	525	0
2	531	6
3	532	7
4	530	5
5	529	4
6	527	2
7	568	10

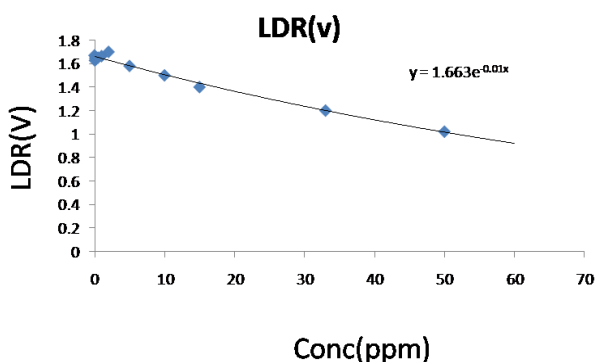


Fig.3: Voltage vs concentration curve of LDR

Fig.3 shows the variation in the LDR output (voltage cross the LDR) as a function of concentration of Mn²⁺ ions. The plotted points are fitted with an exponentially decaying function of the form given in expression (1) and it was used to calibrate the system to estimate unknown concentrations based on the voltage across the LDR.

$$y=1.663 e^{-0.01x} \dots\dots\dots(1)$$

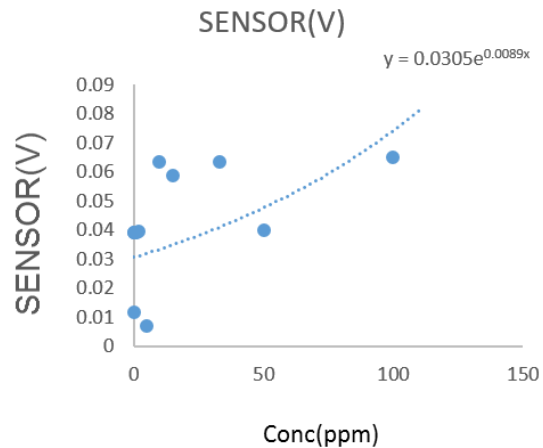


Fig.4: Voltage vs concentration curve of Nano sensor

Similar measurements carried out using the Nanosensor yielded the expression (2) through a 2nd order polynomial fitting.

$$y=0.0305e^{0.0089x} \dots\dots\dots(ii)$$

A comparative chart of the outputs of the LDR and nanosensor are shown in Table III. The outputs of the nanosensor can be made comparable to the LDR through the inclusion of an amplifier circuit.

Table III: Nanosensor voltage and LDR voltage

Concentration (ppm)	LDR (v)	Nanosensor(v)
0.0	1.67	0.115
0.05	1.7	0.03901
0.1	1.66	0.03902
0.5	1.65	0.03911
1	1.64	0.03923
2	1.62	0.0394
5	1.58	0.0686
10	1.5	0.0633
15	1.4	0.0586
33	1.2	0.0633
50	1.01	0.040
100	0.61	0.065

IV. CONCLUSION:

A complete system to estimate the concentration of Mn²⁺ ions present in water is reported in this work. Au nanoparticles capped with different metal chelating polymers was used as the active sensing material. Chelation in the presence of metal ions leads to aggregation of the Au

nanoparticles resulting in a shift in the surface plasmon resonance peak. This shift is noted using a UV-vis spectrophotometer.

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