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Analyte Induced shift in Localized Surface Plasmon Resonance of Silver Nanoparticles in Ammonia and Indole-3- Acetic Acid (IAA) Solution

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Abstract:
A simple strategy for the detection of a simple molecule like ammonia and a phytohormone indole-3-acetic acid(IAA) in solution was proposed based on the localized surface plasmon resonance light scattering (LSPR-LS) of the silver nanoparticles (AgNPs). Citrate capped silver nanoparticles were prepared by chemical reduction, which are found to be30-40 nm in size. The AgNPs were shown to be spherical in shape and fairly monodispersed by scanning electron microscope (SEM) and transmission electron microscopy (TEM). The crystalline nature of silver nanoparticles was characterized using powder X-ray diffraction technique. UV-Visible spectrophotometer was used to study the Sensing of ammonia and IAA in solution. The detection limit of aqueous ammonia and indole-3- acetic acid was in the range of 10^{-4}M and 10^{-3}M respectively at room temperature. The silver nanoparticles were found to act as aggregation sensor for the above analytes. Thus, this method provides means for sensing the presence of the growth hormone IAA in resinous plant material, plant extracts and bacterial excretions and low ammonia level in biological fluids, such as plasma, sweat, saliva, cerebrospinal liquid or biological samples in general for various biomedical applications.

Keywords: *citrate capped silver nanoparticles, LSPR, ammonia, IAA, TEM*

1. Introduction

Optical sensors based on the unique surface Plasmon resonance properties of metallic nanoparticles have shown to be very useful in the analysis of biomolecules, inorganic moieties metal ions and many organic molecules. Noble metal nanoparticles (NPs) such as gold and silver exhibit specific optical characteristics in the visible region (380–750 nm)[vi-i] where the absorbance shows an exponential decay with decreasing photon energy (the so-called Mie scattering) onto which an LSPR band, specific for the material, is superimposed. The surface plasmon energy and intensity have been found to be sensitive to a number of factors, including particle size, morphology, dielectric of the medium, etc.[vii-ii]The colour change that follows from aggregation of gold and silver nanoparticles has found innumerable applications. Thus, metal nanoassemblies offer scope for manipulating light at the nanoscale via morphology-controlled resonances associated with surface plasmon modes. Few literatures are available for the detection of ammonia in solution [i-iii- iii-v]. Similarly, detection of IAA was mostly based on immunoassays [iv-vi] and HPLC fluorescence detection [v-vii].. Therefore spectrophotometric methods have been used to investigate the change in the LSPR band due to the adsorption of species onto the surfaces of silver nanoparticles, aggregation of particles and the interaction between them. As the name suggests, the LSPR response is dominated by events happening within a highly localized (~5–10 nm) region at the nanoparticle surface. Binding of nanoscale analytes, such as proteins, induces large shifts in the LSPR absorbance while refractive index changes in the bulk media do not. However, most of these studies were centered on the adsorption of nucleophilic anions and organic molecules [viii]. The augmentation of electric fields on the nanoparticle surface, owing to plasmon resonance, decays over a distance depending on the size of the particles. This means that when nanoparticles are in contact their fields interact leading to interparticle plasmon coupling and consequently to coupling-induced LSPR shift [ix]. This effect has been exploited in the design of aggregation sensors that form the basis of simple, highly sensitive and low cost colorimetric assays, which have been applied to the detection of small molecules, DNA, proteins, toxic metal ions and pollutants. In some cases, the proper analyte of interest is able to promote nanoparticle aggregation. An interesting example of this type of analyte-induced detection system has been recently described by Huang and co-workers[x]. In yet another strategy, the molecular recognition is performed away from the nanoparticle enabling the use of naked nanoparticles without loss of selectivity has also been recently reported[xi,xii]. Sensors based on Localized Surface Plasmon Resonance(LSPR) were widely studied for detecting toxic and pollutant gases like ammonia[xiii-xiv]. The detection of ammonia levels in exhaled air have great medical significance in the diagnosis of certain diseases [xvi].

Recent reports have shown that AgNPs are superior to AuNPs especially for sensing based on the scattered light, and they find many applications in the fields of medicine, microbiology, and analytical chemistry [xvii- xviii]. Silver nanoparticles have been widely used for sensing organic gases, hydrogenperoxide, and hydrogen sulfide [xix-xxi]

In view of the potential of silver nanoparticles in sensing, we focused our efforts on the synthesis, characterization of spherical silver nanoparticles of size < 50 nm and in sensing ammonia and IAA in solution. The change in absorbance and change in LSPR band was monitored by absorbance spectra. Sensitivity, stability and reproducibility studies were done at room temperature.

2. Experimental

2.1. Materials

Trisodium citrate, ascorbic acid and silver nitrate were purchased from Qualigen chemicals and used without further purification. All aqueous solutions were made using deionized water.

2.2. Preparation of Silver Nanoparticles

An aqueous solution of silver nitrate (50ml, 0.006M) was taken in a 100ml beaker to which 30ml of trisodium citrate solution (0.001M) was added and placed on a magnetic stirrer. To this solution, 5mL of sodium borohydride (0.01M) solution was added drop wise with continuous stirring. On reduction of Ag^+ ions the colour of the solution changes rapidly to reddish brown. This solution was heated in a thermostat. During the whole process the beakers were covered with brown paper to prevent photo-oxidation of silver. The solution, after cooling was centrifuged at 12000rpm (REMI cooling centrifuge) to give a very fine black precipitate which was then dried and dispersed in water to give a yellow sol.

2.3. Characterization Studies

Powder X-ray diffraction (PXRD) analysis was performed using RICHSEIFER powder diffractometer, using nickel filtered copper K-alpha radiations (λ=1.5461 Å) with a scanning rate of 0.02°. UV–Visible spectra of the silver sols were recorded using a Cary 5E UV-VIS- NIR Spectrophotometer.TEM and HRTEM images of the silver nanoparticles were recorded using a JEOL JEM 3010 instrument with a UHR pole piece electron microscope operating at 200 kV. The morphology and size of the nanoparticles were examined using a high resolution scanning electron microscope (FEI quanta FEG 200 - HRSEM)

2.4. Sensing Studies of Ammonia and Indole Acetic Acid (IAA) by Nano Silver

Silver nanoparticles in aqueous medium (silver sol) were used to detect the presence of two analytes namely ammonia and indole-3-acetic acid (IAA) in solution. Different molar concentrations of aqueous ammonia were prepared and stored in brown bottles with airtight lids. The concentration of the ammonia solutions varied from 0.0002M to 0.001M. Similarly alcoholic solutions of IAA were prepared with concentration ranging from 0.0002M to 0.001M.

UV-Visible spectra were recorded for aqueous solution of ammonia, silver sol and the solutions containing silver sol and ammonia similarly for silver sol and alcoholic solution of IAA. The volume of silver sol was kept constant and fixed volumes of the different molar concentrations of analyte were added to it.

3. Result and Discussions

3.1. Optical Studies

The UV–Visible absorption spectrum of the silver sol is shown in Figure 1a. The SPR absorbance of the silver nanoparticles was observed at 413 nm, and the plasmon band is sharp and symmetric, which shows that the solution does not contain many aggregated particles, a conclusion that agrees with the transmission electron micrographs.

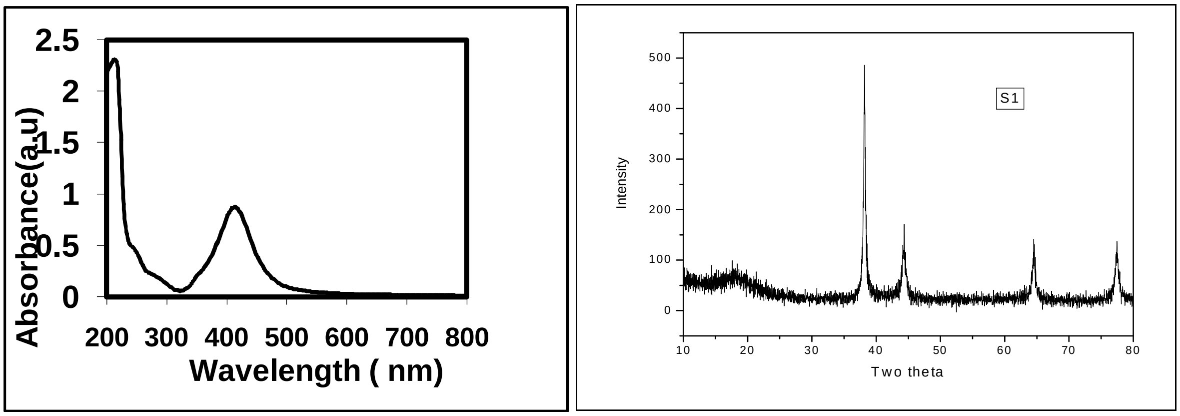

Figure 1: (a) UV-Visible absorption spectrum of nano silver (b) XRD pattern of the silver nanoparticles

3.2. X-Ray Diffraction (XRD) Studies

A comparison of the XRD spectrum with the standard confirmed that the silver nanoparticles formed were crystalline in nature. As evidenced by the prominent peaks at respective 2θ values known for zero-valent FCC silver representing the (100), (111), (200) planes respectively (JCPDS ref. no. 87-0720). The XRD patterns of the as prepared samples are shown in the Figure 1b.

3.3. Size and Morphology of the Nano Silver

The SEM micrograph of the sample is shown in Figure 2a which shows spherical morphology and it also divulges that the particles are moderately monodispersed. The elemental analysis of the silver nanoparticles was performed using the EDS on the SEM. The result indicates that the synthesized product is composed of high purity silver nanoparticles. EDS pattern of the sample is shown in Figure 2b.

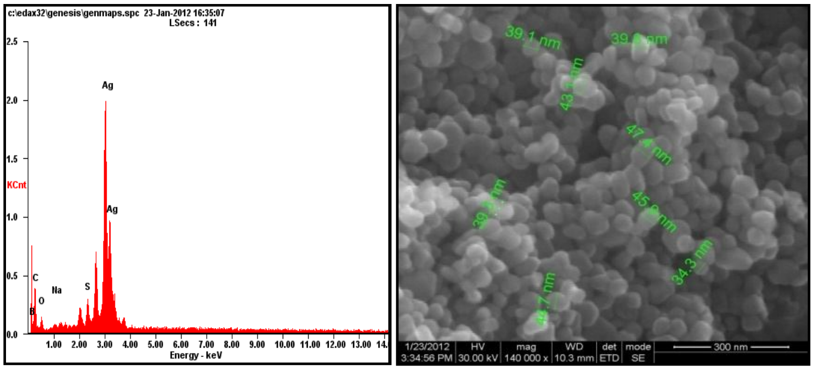

Figure 2: (a) SEM micrograph of silver nanoparticles in 300 nm resolution (b) The EDS pattern of the sample

The transmission electron microscope (TEM) image shown in Figure 3a reveals that the particles are monodispersed with an average diameter of 20 nm. HRTEM images show the lattice fringes of the FCC silver (Figure 3b)

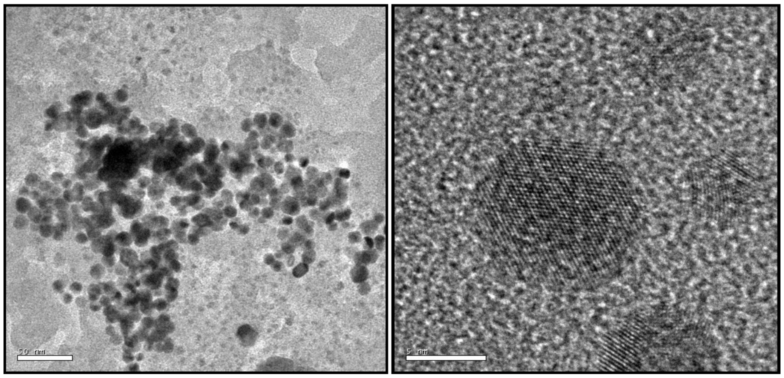

Figure 3: (a) TEM image of spherical silver nanoparticles (b) HRTEM image of a spherical silver nanoparticle

3.4. Sensing of Ammonia by Silver Nanoparticles

Optical study done on the analyte (ammonia) is given in Fig 4. UV-Visible spectra of the analyte solution do not show any characteristic absorbance in the visible region. In order to prevent uncontrolled aggregation, NPs surfaces have been modified with capping molecules that form an electrostatically induced steric barrier between NPs [xxii]. Here citrate is acting as a capping agent for stabilization of NPs. The LSPR peak corresponding to nanosilver appears around 410 nm. The absorbance recorded for solutions containing a specified quantity of the silver sol and various concentrations of the analyte (0.0002M-0.001M) shows LSPR band shifted to longer wavelength(red shift). Appreciable shift in LSPR band begins at 0.0005M and it increases with concentration of ammonia. A shift in wavelength up to 30nm was observed for a concentration of 0.001M. It shows that the analyte is able to promote aggregation of silver nanoparticles due to which the LSPR band shows a red shift. Shipway *et al.* [xxiii] reported a red shift and broadening of the longitudinal plasman resonance in the optical spectrum behavior with gold nanoparticles. Nanoparticle of particular size is the major determining factor in promoting aggregation thus allowing the fast color change while sensing of metal ions at room-temperature. [xxiv].The plasmon band is broadened and red-shifted as a function of the aggregation degree; therefore the change in absorbance may be used to calculate the target concentration.

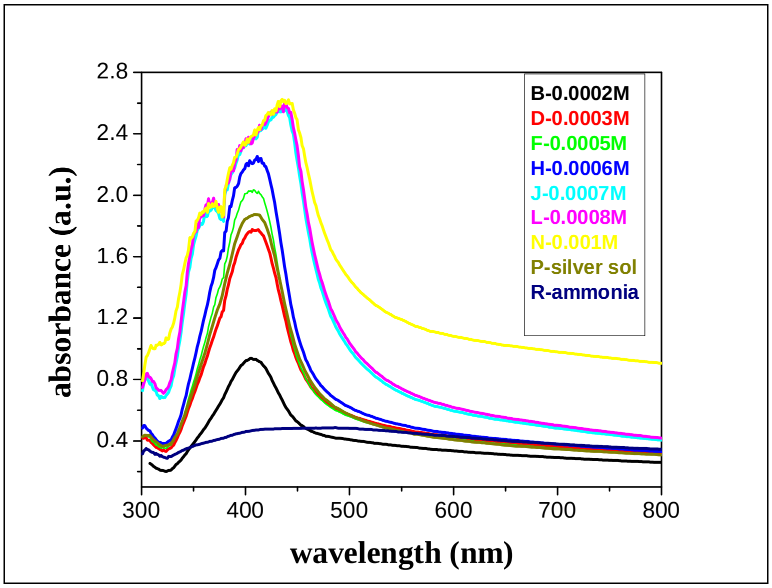

Figure 4: UV-Visible absorption spectra of solution of silver sol With different molar concentrations of ammonia (0.0002M to 0.001M)

3.5. Sensing of IAA by Silver Nanoparticles

UV-Visible spectra of mixture of silver sol with alcoholic solution of IAA of various concentrations are given in Fig 5. There is a prominent shift in the characteristic LSPR peak of silver nanoparticles towards longer wavelength for all the concentrations of IAA.. An increase in the amount of analyte around the assembly is expected to enhance the local refractive index, resulting in a significant red shift of the collective plasmon peak.[xxv]. It is significant to note that the LSPR shift for silver sol is almost the same for concentrations ranging from 0.0002M to 0.001M of IAA showing the potential of silver NPs as a versatile optical sensor. It also implies that the silver nanoparticles may sense further lower concentrations of IAA. How ever the intensity of absorbance is low. The shift to higher wavelength in the SPR peak may be attributed to adsorption of IAA on the surface of silver nanoparticles in addition to aggregation.

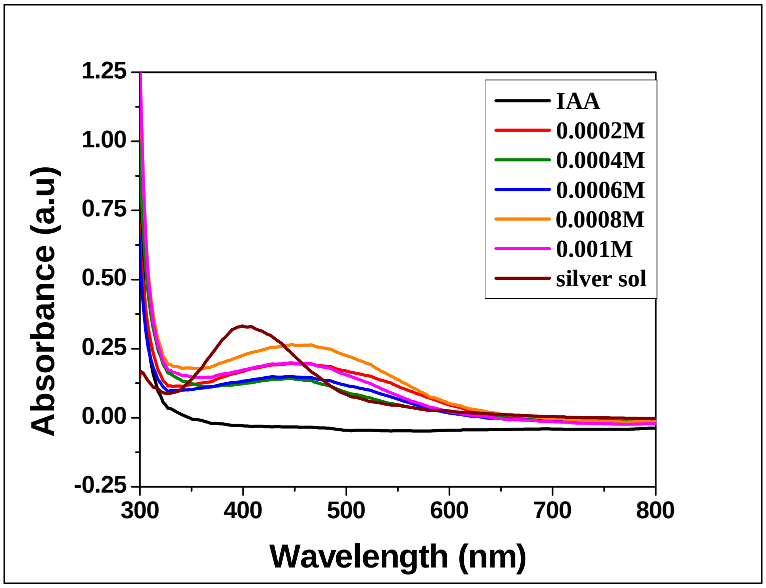

Figure 5: UV-Visible absorption spectra of solution of silver sol With different molar concentrations of IAA (0.0002M to 0.001M)

4. Conclusions

The present study reports the employability of nanosilver in sensing the presence of a small molecule like ammonia and a phytohormone indole-3- acetic acid (IAA) in solution by LSPR shift the absorption of visible light. The method of synthesis of silver is very simple and produces nanoparticles of size < 50 nm that are characterized by UV-Vis spectra, XRD, HRSEM and TEM. Sensing studies were done using a UV-Vis spectrophotometer. In the case of aqueous ammonia shift in LSPR band occurs at a minimum concentration of 5×10^{-4} M and increases further with concentration. On the other hand for alcoholic solution of IAA appreciable shift occurs at concentration as low as 2×10^{-4} M and remains almost the same up to a concentration of 10^{-3} M. The probable reason for LSPR band shift may be due to adsorption of IAA on the surface of silver nanoparticles in addition to aggregation of silver nanoparticles.

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