



Stabilization of gold nanoparticles using natural plant gel: A greener step towards biological applications



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ABSTRACT

An innovative method for stabilization of gold nanoparticles (GNPs) in the aqueous solution using natural plant extract from *Aloe vera* is presented in this work. A detailed spectroscopic analysis of the GNPs after the interaction of *Aloe vera* gel in different molar ratios (1:50 and 1:150) and pH values (5.3 and 7.4) reveals the excellent capping property and stabilizing nature of gel. Morphological feature as well as surface protection of GNP surfaces was confirmed by Field Emission Scanning Electron Microscopic (FE-SEM) analysis and Fourier Transform Infra-Red (FTIR) Spectroscopy respectively. It was found that higher ratios of GNPs and Gel lead to more stabilization of nanoparticles. Flocculation parameter was found to be less with increasing ratios at both the pH values indicating the stability of nanoparticles.

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1. Introduction

Gold Nano Particles (GNPs) have taken a giant leap towards numerous applications such as diagnostics and catalysis [1–3] due to their extraordinary attributes at nano-scale. However, chemical protocols dedicated to synthesize GNPs exhibit two cardinal issues for GNPs to be used in drug delivery and other bio-analytical applications:

1. Lack of considerable stability under physiological conditions
2. Inherent toxicity towards biological cells

Most of the surface protecting agents which are used to stabilize GNPs in aqueous solutions contain amine ($-NH_2$) and/or thiol ($-SH$) groups which have very high affinity towards surface of GNPs. Previous efforts attempted to stabilize nanoparticles using thiolated ligands such as poly (ethylene glycol) [4,5], silica encapsulation of metal clusters [6], polymeric capping agents such as amino- or mercapto, dextran [7] and bovine serum albumin [8] have got tremendous success with a common problem of repeatability and stringent parameters involved in surface functionalization. Moreover, most of the protocols are tuned for monolayer protected nanoparticles present in non-polar solvents and water

soluble GNPs have not been worked out to that intensity [9–11]. Also, the inimical effects of synthetic linkers are of major concerns for the *In-vivo* biological applications. With the tremendous flood in exploiting biological molecules such as small peptides or protein as novel protecting agents, stabilization of the GNPs have become considerably easy for the applications like drug delivery, gene transfer and nanoscale monitoring in biological systems [12–15]. However, for protein capped nanoparticles to be extremely stable, an ideal topography and thermodynamics of the capping protein is an important pre-requisite. Keeping these constraints in mind, we have made an attempt to explore naturally occurring protein rich exudates from *Aloe vera* colloquially gel. Gel can play pivotal role in hyper-stabilization due to high content of protein and short peptides [16]. According to Mukherjee and Srivastava [17], along with proteins and proteolytic enzymes, *Aloe vera* gel also contain poly saccharides such as L-Arabinose, L-Fructose, D-Galactose-glucuronic acid and D-Xylose. These functional moieties can fabricate GNP by acting as a reducing agent making gel as dual prong protocol for synthesis as well as stabilization of the nanoparticles in polar solvents like water.

Inherent ability of the gel to protect the surface of GNPs is studied using a general term “Flocculation Parameter”. This is the measure of GNPs stability in the solution based on their spectroscopic measurement with respect to time and concentration of protecting agents. The stability of the GNPs at different values of pH (5.3 and 7.4) and ionic strength was evaluated by change in the color as well as shift in the

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optical spectra. Flocculation parameters were calculated by measuring the integrated absorbance [18] between the longer wavelengths (500–600 nm in the case of GNPs). Following equation was used to compute the integrated absorbance:

$$P = \int_{600}^{800} I_{Abs}(\lambda) d\lambda. \quad (1)$$

2. Materials and methods

Gel was procured from a local *Aloe vera* plant. Chloroauric acid was purchased from Alfa Aesar, USA. All the experiments were performed using ultrapure water. The glassware was rinsed with diluted aqua regia to remove metal contaminants.

2.1. Synthesis of GNPs and spectroscopic analysis of the GNPs-gel at different ratios

GNPs were synthesized using conventional Citrate reduction method [19]. pH of the GNPs was adjusted to 5.3 and 7.4 using 1 M NaOH and acetic acid (HCl was not used to avoid chloride induced flocculation which can bring errors in interpretations of the results). Aqueous solution of Gel of 3000 ppm was prepared by dissolving 0.03 g of gel in 10 mL of cold distilled water. 300 μ L of GNPs were added to 500 μ L of gel solution and total volume was made 3 mL using distilled water to maintain ratio of GNPs to gel as 1:50. Similarly, same amount of GNPs were mixed with 1500 μ L of gel for ratio 1:150. Quantification of the aggregation property with respect to time of different ratios was calculated using Eq. (1).

2.2. Characterization

FE-SEM was performed on a Carl Zeiss Micro imaging, GmbH, Germany. 2–3 drops of the colloidal gold solution were dispensed onto a silicon wafer and dried under ambient condition before studying the morphology of GNPs. FTIR was performed on KBr pellet using JASCO instruments, Japan. The Energy-dispersive X-ray spectrometer (EDAX) (JOEL 6700F, Japan) was used for the surface elemental detection of Au nanoparticles.

3. Results and discussion

3.1. Synthesis of GNPs

Uncapped GNPs made using conventional Sodium Citrate reduction method [19] displayed a characteristic peak at 522 nm by virtue of a quantum mechanical phenomenon called Surface Plasmon Resonance (SPR) arising due to quantum confinement of electrons when the size of the metals decrease to nano- scale. Citrate stabilized GNPs synthesized using this method was extremely unstable in physiological saline at both the pH (5.3 and 7.4). pH of the uncapped GNPs was adjusted using 1 M NaOH and 1 M acetic acid to avoid aggregation at low pH values due to excessive protons. Inherent pH of the Citrate stabilized GNPs were found to be 3.2. Selection of pH values to check the aggregation of gel coated GNPs was due to the following reason:

1. To deliver payloads to cancerous tumors where the pH is acidic (5–6.5)
2. To withstand the neutral pH of the blood before reaching to the target (7–7.2)

In order to comprehend the impact of different ratios of GNPs and Gel on stability, morphology and optical properties of citrate stabilized GNPs synthesized using above method, systematic studies using UV–Vis Spectroscopy is discussed. Citrate stabilized GNPs are just referred as GNPs for further discussions.

3.2. Gel and GNPs interaction at pH 5.3

Interaction of GNPs with gel was studied at pH 5.3 in ratios of 1:50 and 1:150 by assessing the change in peak wavelength due to SPR using UV–Vis spectroscopy. This interaction was studied with respect to time (0 to 90 min) after adding required amount of GNP and gel. Initially, there was a sharp peak at 522 nm without addition of gel. Promptly, after addition of the gel maintaining the molar ratio of GNP and gel as 1:50, there was an increase in intensity followed by minor broadening of the peak which indicates the interaction of GNPs with gel and the size and shape of nanoparticles were also slightly increased. 90 min after addition of the gel, there was a minor red shift of 4 nm as clearly shown in Fig. 1a. The intricate relation between red shift and flocculation was given by Quinten and Kreibitz [20]. As per their studies, when the distance between flocculating spheres is smaller than the radius of the spheres, the resonance shifts to longer wavelengths. These resonances are concentrated above 600 nm in visible spectrum. In our case, no peak can be observed at longer wavelength thus ruling out the probability of flocculation. With increase in ratio to 1:150, there was a light blue shift of 2 nm (522 to 520 nm) which can be clearly seen in Fig. 1b. There was drastic change in the color of nanoparticles after stirring for more than 30 min. GNPs solution changed from violet to wine red color indicating shape modification of GNPs towards lower size. As shown in Fig. 1b, there is enhanced intensity of the peak after 90 min. These outcomes can be summarized as follows:

1. There can be reduction in the size of GNPs due to the surface interaction of Gel and GNPs.
2. Multiple coatings of Gel on the surface of GNPs can also lead to such blue shifts.
3. There can be combined impact of both the above phenomenon.

In order to confirm our findings, we compared SEM image of uncapped GNPs with those protected with gel (Fig. 2). There was more shape control as the ratio was increased with respect to citrate stabilized GNPs. Initial sizes of GNPs were gauged to be $40\text{--}50 \pm 5$ nm. After surface protection with gel (ratio 1:50), size of the GNPs got radically reduced to $5\text{--}45 \pm 5$ nm (Fig. 2b) and finally at ratio 1:150, got exceptionally mono-disperse displaying uniform sized GNPs of 8–10 nm. This strongly proves gel as highly efficient stabilizers. Additionally, we have confirmed about the content of nanoparticles. Elements gold was revealed in Fig. 3(a–c). All these results showed that the nanoparticles have controlled morphological shapes, with confirmed elements. Such surface protected GNPs can be used as molecular vehicles to ferry anti-cancer drugs to solid tumors due to their stability at lower pH. Solid tumors possess pH 5.3–6.5 due to leaky membranes and hyperactive proton pumps. Moreover, gel can be used as natural linkers to attach drugs without involving toxic surface protecting chemical agents.

3.3. Gel and GNP interaction at physiological pH 7.4

In contrast to pH 5.3, physiological pH was found to be more favorable milieu for stability of gel protected GNPs. Spectroscopic analysis with respect to time shows comparatively sharper peaks and less area under the peak as shown in Fig. 1c & d. There was a negligible red shift of 2 nm after 90 min which indicates exceptional stability of GNPs and gel in the ratio of 1:50 (Fig. 1c). Similar trend was seen when ratio was increased to 1:150. But, there was a blue-shift of 2 nm after 90 min and the intensities of the peaks were found to be more significant (Fig. 1d), unlike the previous case. Blue shift is an indication of stabilization of the nanoparticles followed by a decrease in size as shown in SEM image (lower panel of Fig. 2). Sizes of uncapped GNPs at pH 7.4 (Fig. 2d) were found to be 50–70 nm which reduced to 20–30 nm at the ratio of 1:50 and finally to exceptionally small sized GNPs of 5–15 nm after maintaining the ratio of gel-GNPs at 1:150.

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