

INFLUENCE OF SOME PARAMETERS ON STABILITY OF COLLOIDAL SILVER NANOPARTICLES

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Abstract

Colloidal silver nanoparticles (AgNPs) were prepared using silver nitrate (AgNO_3) as a precursor, sodium borohydride (NaBH_4) as a reducing agent and Poly Vinyl Alcohol(PVA) a surfactant stabilizing material. By using molar ratios of reducing agents (4mM, 6mM and 8mM) and stabilizing agent in the formation of AgNPs, the influence of parameters such as reducing agent concentration, stirring period on the sample stability and the degree of dispersion of AgNPs were investigated. The quality of the synthesized samples was characterized by UV-Vis and Cyclic Voltammetry measurements.

Keywords: Colloidal silver nanoparticles, reducing agents, stirring period, UV-Vis, Cyclic Voltammetry

Introduction

The application of nanoscale materials and structures is an emerging area of nanoscience and nanotechnology. Silver nanoparticles (AgNPs) are increasingly used in various fields, including medical, food, health care, consumer, and industrial purposes, due to their unique physical and chemical properties. These include optical, electrical, and thermal, high electrical conductivity, and biological properties. Nanotechnology is the design, characterization, production and application of materials, devices and systems by controlling the shape and size of the nanometre scale. Nanoparticles are particles that have a size of 1 to 100 nm in at least one dimension and possess unique physical and chemical properties due to their large surface area to volume ratio and smaller size.

There are two basic approaches used in nanoparticle synthesis: the top-down (communication and dispersion) approach and the bottom-up (nucleation and growth) approach. The decision on which method to adopt depends on the approach that can deliver the specified properties and on cost. The three main methods of nanoparticle synthesis are physical, chemical and biological. Each method has advantages and disadvantages with common problems being costs, stability, particle sizes and size distribution and so on. Physical and photochemical methods to prepare nanoparticles are usually need the very high temperature and vacuum conditions, and expensive equipment. Among the existing methods, the chemical methods have been mostly used for production of AgNPs.

It is well known that chemical method can successfully produce pure, well-defined nanoparticles and is also the most common method because of its convenience and simple equipment. Chemical methods provide an easy way to synthesize AgNPs in solution, because they can be implemented under simple and mild conditions. In chemical approach, the preparation of AgNPs with colloidal dispersions in water or organic solvents is performed by chemical reduction.

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The reduction of silver ions in solvents yields colloidal silver nanoparticles with different particle diameters. An increasingly common application of AgNPs can be found use in electronics industry. For example, inks, pastes and filler utilize AgNPs for their high electrical conductivity; molecular diagnostics and photonic devices take advantage of the novel optical properties of AgNPs. Extracts from bio-organisms may act both as reducing and capping agents in silver nanoparticles synthesis. The reduction of Ag^+ ions by combinations of biomolecules found in these extracts such as enzymes/proteins, amino acids, polysaccharides, and vitamins.

Characterization of AgNPs is important to understand and control nanoparticles synthesis and applications. Various techniques are used for determination of different parameters. The morphology of AgNPs is obtained using transmission and scanning electron microscopy (TEM, SEM). The size distribution of AgNPs can be measured with a Zetasizer Nano Series analyzer. Energy dispersive X-ray spectroscopy(EDS) measurements are used with an emission scanning electron microscope equipped with an EDS instrument. X-ray photoelectron spectroscopy (XPS), X-ray diffractometry(XRD), Fourier transform infrared spectroscopy (FTIR), and UV-Vis spectroscopy are also used to characterize AgNPs. UV-Vis spectroscopy is used to confirm AgNPs formation by showing the Plasmon resonance. Cyclic Voltammetry Characterization is the electrochemical activity of the synthesized nanoparticles.

In this review, we describe the chemical reduction methods based on our studies, which are successful in the synthesis of AgNPs. The parameters are such as concentration of reducing agent, stirring time, stabilization with a stabilizing agent used during AgNPs synthesis. During this research the above-mentioned parameters will be controlled to find a reliable way for manufacturing AgNPs with certain characteristics. We also describe there action mechanism of AgNPs and parameters affecting particle size. The characterization of synthesis of pure colloidal silver nanoparticles was investigated by UV-Vis spectroscopy and Cyclic Voltammetry measurement.

Materials and Methods

Chemical reduction of silver nanoparticles involves the reduction of a silver salt such as silver nitrate AgNO_3 with a reducing agent like sodium borohydride and Poly Vinyl Alcohol (PVA), used as stabilizing agents. The syntheses were performed at room temperature.

Preparation of Silver Nitrate Solution: The analytical grade silver nitrate (99.5% purity) was purchased from market in Yangon. About 0.0085grams of analytical grade AgNO_3 (99.5% Purity) was weighed using an analytical weighing balance and then transferred into a 250 mL volumetric flask that contained 100 mL of distilled water. This was followed by stirring for 15 min to ensure that all the solid AgNO_3 dissolved. The concentration of silver nitrate was determined to be 0.001 M.

Preparation of Sodium borohydride (NaBH_4) Solution: One of the most popular methods to synthesize silver nanoparticles is by the use of ice-cold sodium borohydride NaBH_4 to reduce silver nitrate. The solution sodium borohydride NaBH_4 in different concentration (4mM, 6mM, 8mM) were prepare by dissolving in distilled water 100ml, add a magnetic stir bar and place the flask in an ice bath stirring constantly on a magnetic stirrer plate. Ice bath is used to slow down the reaction and give better control over final particle size/ shape. Stir and cool the liquid for about 20 minutes.

Preparation of stabilizing agent Poly Vinyl Alcohol(PVA) Solution: The stabilizer solution of PVA in concentrations (0.004M) was prepared by dissolving in 100ml distilled water. The stabilizing agent will prevent aggregation of the nanoparticles by lowering the surface tension between the solid particles and the solvent. This is achieved through adsorption of stabilizer-ions onto the nanoparticles in solution. The stabilizing agent ensures formation of metal-surfactant complexes in the reaction solution.

Synthesis of Silver Nanoparticles (AgNPs): Silver nanoparticles (AgNPs) were prepared by reacting silver nitrate solution (0.001 M) with the solution of sodium borohydride NaBH_4 (0.004M, 0.006, 0.008M) as the reducing agent. The 10 ml of each of NaBH_4 solution and 2ml of AgNO_3 solution was added and allowed to dissolve stirring constantly on a magnetic stirrer plate for 15 min. From the first series of experiments, the best result AgNPs mixture solution was controlled by using the PVA solution in different concentrations, which were stirring on a magnetic stirrer plate for 5 min. The effect of reducing agent concentration on the formation of silver colloids was also studied by monitoring the UV-Vis absorption spectrum. The stability of AgNPs were also investigated.

The second series of experiments were carried out of the variation of stirring times (10min, 20min, 30min). For this work, the reducing agent concentration ratio at room temperature that gave the best results (most distinct and most narrow UV-Vis peak) from the first series were performed again.

Results and Discussion

The nanosized silver colloids were prepared by a chemical reduction process in aqueous solution in the presence of PVA as a stabilizing agent. During the experiments, colour changes in the solutions were noticeable. In this study, the UV-Vis spectrophotometer and cyclic voltammetry were used to characterize the AgNPs of various formulations and process parameters of AgNPs in laboratory scale.

Firstly this work investigated the effect of the concentration of sodium borohydride NaBH_4 as a reducing agent in the aqueous solution of silver nitrate on the optical properties of colloidal silver nanoparticles AgNPs. The UV-Vis spectra Fig-1A illustrate strong peak round about 400nm in all samples, which proved AgNPs formation. The UV-Vis Characterization showed that the highest and narrow absorbance peak and shifted somewhat to shorter wavelengths of $\text{NaBH}_4:\text{AgNO}_3$ (4:1) AgNPs colloid. The AgNPs (4:1) SPR became more distinctive and sample colour also change to bright yellow colour. Fig-1B show colloidal AgNPs sample with different concentration (4mM, 6mM, 8mM) of sodium borohydride NaBH_4 . After that the stability of the synthesized AgNPs were investigated for time taken 4-days, 8-days and 16-days. Fig-2 show the stability test for UV-Vis spectra of colloidal AgNPs with different concentration of sodium borohydride NaBH_4 in different times. From the figure, the best result of stability AgNPs was obtained at the (4:1) ratio and the AgNPs sample (6:1 and 8:1) ratios have wider SPR peak after 8- days and 16-days. Also, another SPR peak shows at 550 nm indicating that some of the particles have aggregated for sample (6:1 and 8:1) ratios. It was seen that peak intensity and stability of AgNPs colloidal depend on concentration of NaBH_4 reducing agent.

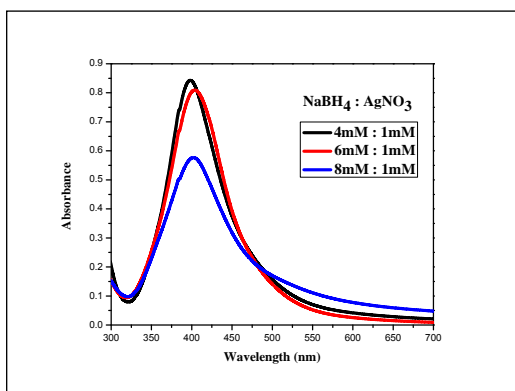


Figure 1A UV-Vis Optical absorption spectra of colloidal AgNPs with different concentration of NaBH_4 .



Figure1B colloidal AgNPs with different NaBH_4 concentration.

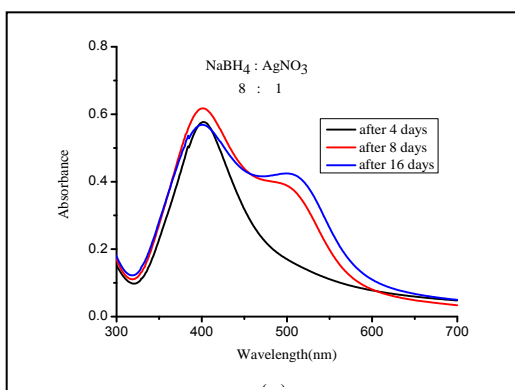
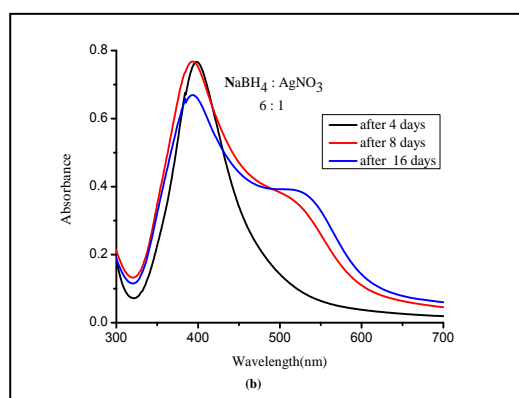
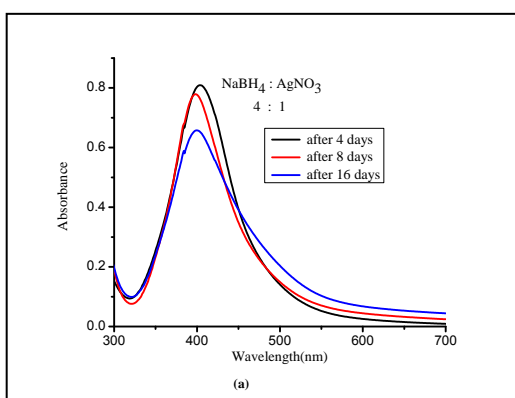


Figure 2 UV-Vis spectrum of Stability test of AgNPs with different concentration ($\text{NaBH}_4:\text{AgNO}_3$) (a) (4:1 ratio) (b) (6:1 ratio), (c) (8:1 ratio)

The best result absorbance and stability of ($\text{NaBH}_4:\text{AgNO}_3$ (0.004M:0.001M)) of AgNPs colloid was used for investigate the effect of stirring time in AgNPs. The reaction time for 10 min, the colour of AgNPs was clear yellow. When the stirring was extended for 20min and 30 minutes, the solution started to turn darker yellow, then dark brown as the nanoparticles aggregate. This is presented in Fig- 3. The reaction trends show that the reaction time for 10 min resulted in a very high NPs nucleation process. However, increase in the reaction time for 20 and 30 min favored the agglomerations and coalescence of the nanoparticles by forming large particle size. UV-Vis graphs in Fig-4show that the SPR peak became started wider and shift towards longer wavelengths when stirring was extended. Therefore prolonged stirring increases the probability of collision between particles, leading to aggregation.

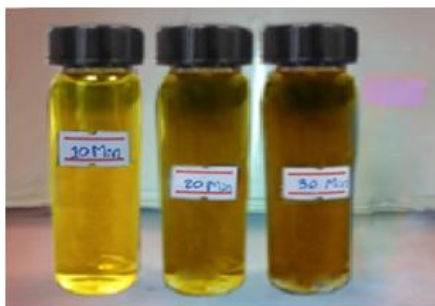


Figure 3 stirring time of Colloidal AgNPs sample (a)for 10- min, (b) for 20-min, (c) 30 min

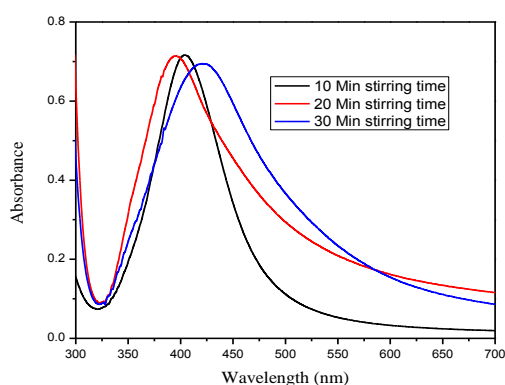


Figure 4 UV-Vis spectrum of effect of stirring time of Colloidal AgNPs (a)for 10 min, (b) for 20-min, (c) 30 min

Electrochemical behavior of Ag^+/Ag^0 was studied by carrying out cyclic voltammetry in the potential range +0.5 V to -0.5V vs Ag/ AgCl in a repetitive scanning mode at a scan rate of 10mVs^{-1} , consuming almost 200s for one cycle of forward cathodic and reverse anodic scan. Fig- 5 shows the record of cyclic voltammograms of 1mM silver salt solution in aqueous 0.1M KNO_3 medium. In AgNPs (4:1) cyclic voltammograms a well defined redox signal with anodic peak at +0.55V (E_{pa}) vs Ag/AgCl electrode correspond to the electrochemical re-oxidation Ag^0 to Ag^+ during first anodic scan. CV scanning was continued for 5 more cycles, as revealed in Fig- 5. The anodic current (I_{pa}) is $0.002\mu\text{A}$ produced by chemical reduction of Ag^+ giving rise to cathodic current along with electrochemical diffusion current (EC mechanism). Further, shift of anodic peak shifted towards more positive potential and marked decrease in peak current observed in subsequent cycles is also an indication of stabilized Ag^0 undergoing oxidation.

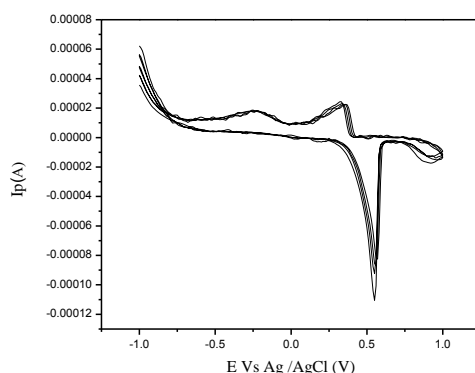


Figure 5 Cyclic voltammograms of AgNPs (4:1) colloids.

Conclusion

Silver nanoparticles were prepared by chemical reduction method. The UV-vis spectra were observed strong peak over 400nm in all samples, which proved AgNPs formation for the effect of concentration of sodium borohydride NaBH_4 as a reducing agent in the aqueous solution of silver nitrate (AgNO_3). The optimum conditions for this process were reactant ratio $\text{NaBH}_4:\text{AgNO}_3$ (4:1) and 10 min stirring time. This process yields stable, spherical silver nanoparticles of AgNPs colloids. The electrochemical characterization performed by using cyclic voltammetry show significant response for change in reduction potential of Ag^+ ion from higher oxidation state to Ag^0 oxidation state. The formation of silver nanoparticles can be observed by using other parameters such as effect of temperature, and of pH value.

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