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BIOCOMPATIBLE SYNTHESIS OF SILVER NANOPARTICLE AND ITS APPLICATION

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Abstract- Starch stabilized silver nanoparticles of 20-80 nm in diameter have been prepared from an aqueous Silver nitrate precursor, using a simple wet chemical method. The synthesized nanoparticles can be separated easily from the aqueous sols by a high speed centrifuge. The synthesized silver nanoparticles have been characterized by UV-visible optical absorption spectroscopy, transmission electron microscopy techniques and XPS. And the effect of synthesized silver nanoparticles has been studied on absorption of Histamine and vice-versa.
Keywords- Silver nanoparticles, starch, Reduction

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Introduction

During the past several years, there has been a growing interest in the novel materials called nanomaterials that have a very high surface or interfacial area and exhibit dramatic changes in properties. Among them, metal nanoparticles have been extensively investigated because of their unique physical and chemical properties and wide potential applications, especially silver nanoparticle, which can be used as catalyst, refrigeration dilution agent, immunity sensor and antimicrobial[1,2]. At present, there are lots of techniques available for the synthesis of metal nanoparticles, which includes gas reduction process[3,4], precursor pyrolysis [5,6], microwave plasma synthesis , hydrodynamic cavitations and liquid chemical reduction[7-10] and laser ablation [11]. A key issue among these techniques is the control of particle size and agglomeration, which is very important in applications. While the use of gas reduction process can produce very small particles with size of less than 10 nm and narrow distribution, the expensive raw gas material and equipment results in high cost. Therefore, many researchers pay more attention to the solution chemical reduction method because of its low cost. Presently, small metal nanoparticles can be readily synthesized by chemical reduction in a liquid medium through choosing proper surfactants and protect agents,but invariably form hard agglomerates.

Silver nanoparticles are nanoparticles of silver, i.e. silver particles of between 1 nm and 100 nm in size. While frequently described as being 'silver' some are composed of a large percentage of silver oxide due to their large ratio of surface to bulk silver atoms. There are many different synthetic routes to silver nanoparticles. They can be divided into three broad categories: physical vapor deposition, ion implantation, or wet chemistry. Ionic silver has a long history of use in topical medical applications, and it has been shown that ionic silver, in the right quantities, is suitable in treating wounds.[12],[13]. According to Atiyeh et al. (2007), "The gold standard in topical burn treatment is silver sulfadiazine (Ag-SD), a useful antibacterial agent for burn wound treatment".[13] The US Food and Drug Administration has approved the use of a range of different silver-impregnated wound dressings. Silver nanoparticles are now replacing silver sulfadiazine as an effective agent in the treatment of wounds.[14],[15].

Allergic Reaction: While there is anecdotal evidence suggesting the possibility of a silver allergy, an extensive review of the medical literature does not lend any credence to this possibility. Some silver alloys that include nickel do elicit an allergic reaction.

Argyria and Staining: Ingested silver or silver compounds, including colloidal silver, can cause a condition called argyria, a discoloration of the skin and organs. In 2006, there was a case study of a 17-year-old man, who sustained burns to 30% of his body, and experienced a temporary bluish-grey hue after several days of treatment with Acticoat, a brand of wound dressing containg silver nanoparticles. Argyria is the deposition of silver in deep tissues, a condition that cannot happen on a temporary basis, raising the question of whether the cause of the man's discoloration was argyria or even a result of the silver treatment. Silver dressings are known to cause a "transient discoloration" that dissipates in 2-14 days, but not a permanent discoloration.

Silzone heart valve: St. Jude Medical released a mechanical heart valve with silver coated sewing cuff (coated using ion beam-assisted deposition) in 1997. The valve was designed to reduce the instances of endocarditis. The valve was approved for sale in Canada, Europe, the United States, and most other markets around the world. In a post-commercialization study, researchers showed that the valve prevented tissue ingrowth, created paravalvular leakage, valve loosening, and in the worst cases explantation. After 3 years on the market and 36,000 implants, St. Jude discontinued and voluntarily recalled the valve.

In this study we simply report a wet chemical method for synthesis of starch stabilized silver nanoparticles from silver nitrate using common laboratory conditions. The synthesized silver nanoparticles were characterized by UV-visible absorbance spectrophotometer, transmission electronic microscopy (TEM) and XPS techniques. And the effect of silver nanoparticles on absorption of Histamine was studied.

Experimental details

All the reagents used were of AR grade. Nanopure water was used throughout the experiment to prepare the solutions. Silver nitrate was purchased from Merk. 1%, 2%, 3% and 4% starch stock solution was prepared by addition of 1 gm, 2 gm, 3 gm and 4 gm starch in 100ml nanopure water. 0.4M $AgNO_3$ solution was prepared, Histamine an important biogenic amine was prepared in different concentration (0.1 µg - 5 µg/ml was dissolved in nanopure water), which was then mixed with 100 µl of 3M NaOH, 100 µl of 3 N HCl and 50 µl of 2 % ophthalaldehyde.

The UV-visible spectra of each solution were measured in a SHIMADZU UV-1800 double beam digital spectrophotometer. TEM images were obtained on JEOL 2010 microscopes. The TEM sample was prepared by dropping a sample suspension in acetone on a Cu grid coated with a carbon film.

Briefly, In this we had prepared a graded serious of stock solution of stabilizer (i.e. starch) starting from 1% to 4%. In each system 2ml, 4ml, 6ml, 8ml $AgNO_3$ solution was added respectively (~0.4M) was added then it is followed by the addition of ethyl alcohol (~ 50ml). These solutions were mixed together using electrically operated stirrer ~2-3min. and were refluxed in 100ml round bottom flask at 70^0C for 1 hour. The refluxing carried out still the colouless mixture turns to reddish brown. The U.V. spectra were taken after each 5 minutes during refluxing. Both these solutions are diluted as per required concentrations, for different experiments. The described above and silver nanoparticles were scanned individually using UV-Visible spectrophotometer in the range 200-400 nm so as to observe the absorption behavior of nanoparticle in presence as well as in absence of histamine. Spectra were recorded in two different manners, once by keeping concentration of Silver nanoparticles constant and later by keeping concentration of histamine constant. During laboratory synthesis the pictures were taken Fig.1

Result and Discussion

Optical absorption studies (U.V.)

The reddish brown coloured silver nanoparticle sols of different intensities, obtained at different temperature, as shown in figure 1.

Figure 2 shows the effect of concentration of silver nitrate and starch on the UV-visible optical absorption spectra of the silver nanoparticle sols. The absorption spectrum of silver nanoparticles does not have any clear maximum in the studied wavelength region. Absorption maximum may be present at the wavelength 350-550 nm. The nature of the spectrum matches very well with those reported in literature [18]. Reported results indicate that sols with particles of mean diameter of about 100 nm or more show an absorption peak at about 409 nm or higher wavelength, depending on size while those with smaller particles do not show any regular absorption peak in the UV-visible region. The yellow colour of colloidal sample is indicative of the silver nanoparticles [17], providing another piece of evidence for the formation of silver nanoparticles. It is worthwhile mentioning that $AgNO_3$ can be completely reduced to form silver nanoparticles. The silver nanoparticles thus formed are stable for several weeks without observable aggregation.

The absorbance gradually increases in intensity, which may be assigned to considerable increase in the amount of reduced silver. On the other hand, the absorption band narrows and shifts continuously to longer wavelengths, which may be attributed to the growth of silver particles. Within 15 minutes, the absorption band shift to 409 nm, after which, no further spectral change occurs, indicating completion of the reaction.

TEM studies

Transmission electron microscopy is very important technique, which provides information about particle size, shape, surface topography etc. Therefore morphology and structure of synthesized selenium nanoparticles were also determined by TEM technique.

TEM image provides a further evidence for formation of silver nanoparticles (figure 3). Clearly the silver nanoparticles thus formed are well separated from each other. Resulting silver nanoparticle is 2-6 nm in length.

XPS pattern of silver nanoparticles

To further confirm the formation of metal Ag from $AgNO_3$ XPS was used to identify the change in oxidation states for Ag after the heat -treatment. Figure 3 shows the XPS spectra of pre capitates obtained from centrifuging colloidal silver solution thus formed. Two peaks centered at 367.8 and 373.8 eV are seen, which can be assigned to the metal silver 3 peaks, indicating the formation of metal silver.

Effect of silver nanoparticle on absorption of histamine and vice versa

Histamine solution as described above and silver nanoparticles were scanned individually using UV-Visible spectrophotometer in the range 200-400 nm so as to observe the absorption behavior of nanoparticle in presence as well as in absence of histamine. Spectra were recorded in two different manner, once by keeping concentration of Silver nanoparticles constant and later by keeping concentration of histamine constant. Fig.5

Conclusions

The spontaneous formation of silver nanoparticles can be attributed to the direct redox between starch and Ag^+ in alcoholic medium because there is no other reducing agent in the system. It is also expected that the chain type nature of starch influences the nucleation and growth kinetics of silver nanoparticles. As the redox reaction takes place silver ions are reduced to form silver atoms. With the elapsed time, new Ag atoms are generated in the system and nucleation occurs as the concentration of silver atom reaches a critical supersaturation, resulting in the formation of nuclei. The nuclei further grow into silver nanoparticles by attaching other free silver atoms. It should be noted that the flexible starch chain also serves as quite an effective protective agent to prevent agglomeration of the as-formed silver nanoparticles, leading to well stable, starch protected silver nanoparticles.

Silver nanoparticle showed change in absorption spectra of histamine indication some chemical reaction in between and hence can be useful in many aspects such as pharmaceuticals, medicine. This is not only opening new opportunities for treatment but also for drug interactions well as exploring the ancient us silver in medicines.

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