

Green synthesis of silver nanoparticles using aqueous plant extracts and its application as optical sensor

Abstract

The syntheses of metal nanoparticles have taken a new route from the emergence of green chemistry. We propose the synthesis of silver nanoparticles through simple bio synthetic method. Metal nanoparticles prepared are characterized by TEM, UV-Vis and FTIR spectroscopy. TEM image show the nanoparticles are nearly spherical in shape with size about 40-50nm. UV-vis spectra show distinct peak of silver at around 427nm corresponding to the surface plasmon peak of silver nanoparticles. The reduction in the surface plasmon peak of silver nanoparticles (Ag NPs) in addition to hydrogen peroxide at increasing concentrations supports our stand that it can be used as an optical sensor. Colorimetric detection of hydrogen peroxide is done with cellulose substrates.

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Introduction

Metal nanoparticles have received a lot of attention in the recent decades due to their unique ability to alter optical, electrical, biological properties.¹⁻⁵ Nanoparticles are also interesting because of their huge increase in surface area and a surge in conductivity compared to their metal counterparts. Moreover, metal nanoparticles also show surface plasmon resonance. These properties make them useful to many applications such as bio-sensing, imaging, drug delivery, HIV treatment, Cancer treatment, optical spectroscopy and Surface Enhanced Raman scattering (SERS).²⁻⁴

Amongst different type of metal nanoparticles Ag NPs (Silver nanoparticles) are of great interest due to their potent antimicrobial activity against different type of pathogens.⁶⁻¹⁰ This extends their application into medicine, wound healing, dental materials, coating of stainless steel material, water treatment, sunscreen lotions, elimination of microorganisms on textile fabrics, cosmetics, optical transparent composites, polymer composites etc.¹¹⁻¹³ The smaller the particle, the greater the antimicrobial activity. However, these particles are very reactive and consequently form aggregates losing their fundamental properties. This leads to the phenomenon called agglomeration. To deal with this challenge passivating agents such as polyvinylpyrrolidone(PVP), poly vinyl alcohol(PVA), hyper branched polyurethane(HP) and polyacrylonitrile(PAN) with reducing agents such as sodium borohydride, hydrazine, glycerol, etc have been used successfully in the synthesis and stabilization of silver nanoparticles.¹⁴⁻¹⁶ The use of these passivating and reducing agents introduced the challenge of high cost and toxicity, thus threatening environmental sustainability and limiting the biological application of these noble materials. Physical methods require highly sophisticated instruments and is of high cost. This crisis can be solved by using eco friendly, environmental benign methods for the synthesis of AgNPs. This eventually led to the entry of green methods for synthesizing AgNPs. Thus, AgNPs are synthesized using varying types of plant extracts, green algae, leaf broths etc. We report the use of aqueous leaf extracts of mangifera indica. They are natural mango leaves abundant in Indian subcontinent.¹⁷⁻²¹ They are largely available and free of cost. The chemical structure of mangifera indica do have OH

groups which can get easily attached to Ag NPs thus forming Ag NPs. The leaf extract acts as both reducing and stabilizing agent. In other words it acts as a surfactant preventing agglomeration.

One of the potential application of Ag NPs is the determination of hydrogen peroxide. Hydrogen peroxide has great relevance pertaining to environmental, pharmaceutical and clinical research.²²⁻²⁴ Hydrogen peroxide is a very good oxidizing agent. In addition, hydrogen peroxide is a byproduct of number of enzymatic reaction involving glucose, cholesterol and lactate. However, higher concentration and amount of hydrogen peroxide can induce potentially serious disease in human body and can cause diseases such as cancer etc. The high concentration rates of hydrogen peroxide can lead to these problems. Thus a stable method for the sensing of different concentrations of hydrogen peroxide has to be developed. Many methods for the sensitive determination of hydrogen peroxide has been developed such as chemiluminescence, optical detection and electrochemical method. Of these, optical detection is found to be the best method as it is convenient and low cost. In the present manuscript, we synthesized silver nanoparticle by green route. The silver nanoparticle synthesized were characterized and coated on a cellulose substrate for optical detection of hydrogen peroxide.

Experimental

Materials required

Leaves of mangifera indica plucked from nearby trees, AgNO₃ (Silver Nitrate) (Sigma Aldrich), Cellulose fibres (1%) (University of Maine, U.S.A)

Synthesis techniques for Ag NPs: Leaves of mangifera indica were taken from a nearby tree. 10gm of mangifera indica leaves were taken. They were rinsed with deionized, double distilled water and cut into small pieces. They were boiled in 75mL of deionized water for 10 minutes. The leaf broth was allowed to cool. Now, it was filtered out and secured. Whatman filter paper (Grade 1) was used for the filtration. The leaf extract (2, 3, 4, 5, 10, 15, 20ml) was added to a vigorously stirred 30ml solution of 1*10⁻⁴ M AgNO₃. Stirring continued for 30 min to get the colloids labelled c1 to c6. 100ml AgNO₃ was prepared using H₂O as the solvent.

Effect of temperature: To different concentrations of AgNO_3 broth solution, the temperature was increased gradually from 30°C to 60°C . The temperature was readily increased 30, 40, 45, 50, 60°C to the broth to AgNO_3 solution having a concentration of about 0.012N. The effect of temperature on the synthesized Ag NPs was studied.

Effect of pH: The pH of the solution was changed and monitored. NaOH (Sodium Hydroxide) solid aqueous pellets were added to the 30ml H_2O . This was added to 10ml nanoparticle in the solution having the broth concentration 0.012N. Thus the pH of the solution was changed from 8 pH to 12 pH. The pH was steadily changed (8, 9, 10, 11, 12 pH). Thus, the syntheses of nanoparticles were optimized by three methods namely

- By changing the concentration of the broth
- By changing the temperature
- By changing the pH range of the colloidal solution.

Application of silver nanoparticles for hydrogen peroxide detection: The synthesis of silver nanoparticles are just the same as explained above using green, leaf extract of mangifera indica. Hydrogen peroxide present in laboratory was taken. Different concentrations of hydrogen peroxide was made from 1M to $1\mu\text{M}$. The concentrations includes 1M, 100mM, 10mM, 1mM, $100\mu\text{M}$, $75\mu\text{M}$, $50\mu\text{M}$, $25\mu\text{M}$, $10\mu\text{M}$ and $1\mu\text{M}$. Hydrogen peroxide of different concentrations was added to the synthesized Ag NPs.

Cellulose coated silver nanoparticle: Cellulose fiber is coated with silver nanoparticle by drop casting method.

Results and discussion

Figure 1 shows UV-Vis spectra of silver nitrate, broth and silver nanoparticle prepared at different broth concentration. The spectra of silver nitrate and broth didn't show any distinct peak. However the distinct peaks are observed for broth reduced silver nitrate at around 427nm corresponding to the surface plasmon peak of silver nanoparticles. As the broth concentration is reduced, two peaks are observed at 380nm and 427nm. As the broth concentration increased, peak at 380 nm disappeared and merge with 427nm peak corresponding to the plasmon peak of silver.¹

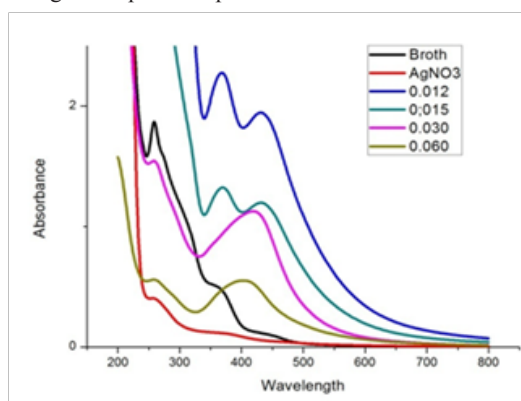


Figure 1 UV-Vis spectra of AgNO_3 , broth and silver nanoparticles prepared at different broth to AgNO_3 concentration ratio's.a

Figure 2 shows the formation of silver nanoparticles at different temperature namely 30, 40, 45 and 50°C . Distinct peak at 427nm is observed at temperature 30 and 40°C . As the temperature is increased further, the sharpness of the peak decreased indicating the agglomeration of nanoparticles. The effect of pH on the nanoparticle

formation is studied and showed in Figure 3. From Figure 3 obtained, it is found that the nanoparticles formed at pH 8 were distinct and seems to be less agglomerated due to the sharpness of the peak. Nanoparticles were found to be get agglomerated above pH 8.³ The FTIR peaks (Figure 4) at 3339.69cm^{-1} shows the presence of OH groups and 1634.87cm^{-1} , C=O groups.⁴ Thus, the presence of C=O groups and OH groups indicates that it can be attached to cellulose matrix having high concentration of hydroxyl group.

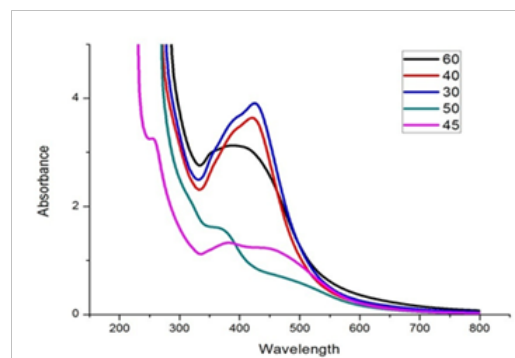


Figure 2 UV-Vis spectra of silver nanoparticles prepared at different temperatures.

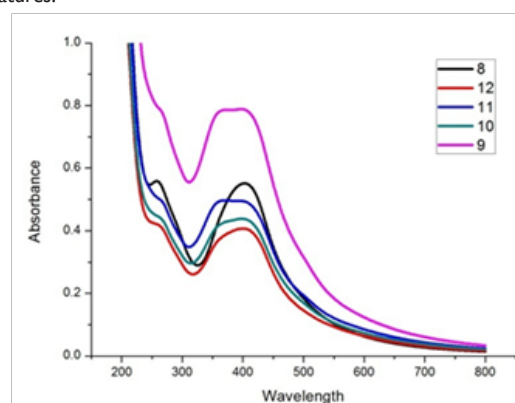


Figure 3 UV-Vis spectra of silver nanoparticles prepared at different pH values.

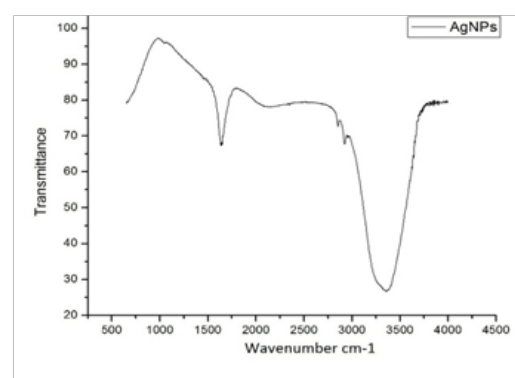


Figure 4 FTIR Spectra of the colloidal solution containing Ag NPs.

The formation of Ag NPs is quiet evident from the TEM image (Figure 5) obtained. Silver nanoparticles in the range having size 40-50nm are observed in the image. The UV-vis data Figure 6 shows the detection of hydrogen peroxide using bio-synthesized silver nanoparticles. The UV-vis data shows constant sharp decline on increasing the concentration of hydrogen peroxide. The peak of Ag NPs steadily decreases upon having higher concentrations of

H₂O₂.²² This aptly defines the fact that the Ag NPs act as an optical sensor. Figure 7 shows the silver nanoparticle solution drop casted on cellulose substrates. Figure 7 shows that the cellulose substrate appears yellowish due to the low concentration of hydrogen peroxide. As the concentration is increased, the cellulose appeared to be white in color. So we can use cellulose for the detection of hydrogen peroxide. It can also be used to stabilize Ag NPs due to the presence of OH groups.

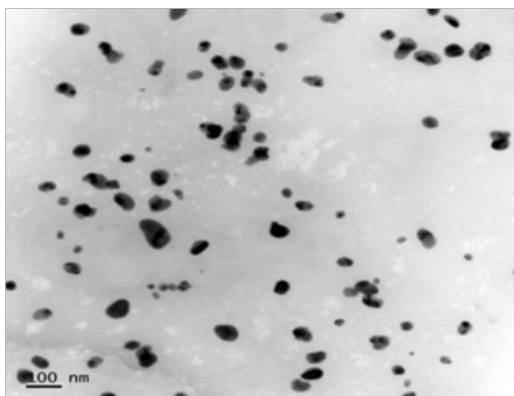


Figure 5 TEM image of Ag NPs.

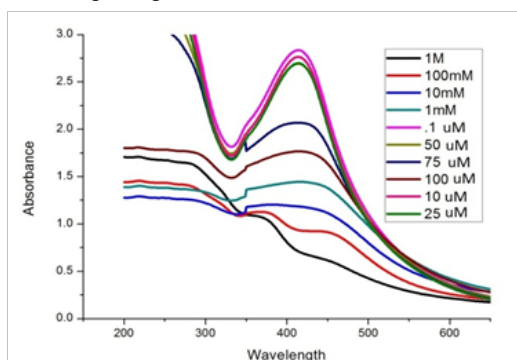
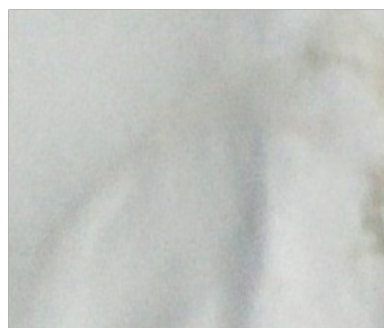


Figure 6 UV-vis spectra of Ag NPs towards different concentrations of H₂O₂.



(A)



(B)

Figure 7 Cellulose coated with silver nanoparticles to different concentration of hydrogen peroxide.

A) $2 \times 10^{-6} \text{M}$; B) $2 \times 0.01 \text{M}$.

Conclusion

A simple colorimetric detection method for hydrogen peroxide is demonstrated. TEM image show the nanoparticles are nearly spherical in shape with size about 40-50nm. UV-vis spectra show distinct peak of silver at around 427nm corresponding to the surface plasmon peak of silver nanoparticles. The reduction in the surface plasmon peak of Ag NPs on addition of hydrogen peroxide at increasing concentrations supports our stand that it can be used as an optical sensor. Colorimetric detection of hydrogen peroxide is done with cellulose substrates. Thus, Ag NPs can be synthesized easily using aqueous plant extracts which can act as surfactants. The shape of nanoparticles can also be controlled by changing the parameters like pH, concentration of reducing agents etc. Paper based technique is developed for the detection of hydrogen peroxide.

Acknowledgements

None.

Conflict of interest

The author declares no conflict of interest.

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