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Easy and New Chemical Synthesis of Stable Nano Silver using Propylene Glycol and Glycerin as Reducing Agents

Abstract- In this present work we have synthesized stable silver nanoparticles (Ag-NPs) by chemical reduction with aqueous solutions of silver nitrate (i) propylene glycol (ii) glycerin as reducing agents and guar gum as a stabilizer. The reaction were done at room temperature and at pH=8. Systematic characterizations of the Ag-NPs were done using UV-Vis, zeta potential analysis, X-Ray diffraction (XRD), AFM and SEM which reveal stable Ag-NPs. These measurements indicate that the particles are mostly spherical in shape. The UV-Vis spectra of the result solution of Ag-NPs show an absorption peak at 412 nm and 424 nm for using propylene glycol and for using glycerin respectively. These color occurring due to Surface Plasmon Resonance (SPR). The SEM measurements gave a particle size of 40 -70 nm. Nano silver showed stability for long periods of time to more than nine months, and this can be an economical and effective way for wide scale synthesis of Ag-NPs which applicable for various medical therapies.

Keywords- Silver nanoparticles, Surface Plasmon Resonance (SPR), Scanning Electron Microscope (SEM).

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1. Introduction

Nanotechnology stretch across wide range of science, such as touching medicine, physics, chemistry, biology, engineering, and environmental science [1], the nanomaterials have different characteristics and of their behavior at larger scales.

Silver nanoparticles have been scanned due to their optical properties and their application as a catalytic [2], electronics [3], in medicine because it has the antibacterial activity. The small particles size important because their unique properties such as conductivity [4], and nonlinear optical behavior [5]. These characterizations make them suitable for a variety of potential applications on several devices [6,7].

Ag-NPs known as antimicrobial agents because they could be used alternate purifier agents. Ag-NPs that released could show impendence to microorganisms [8]. Ag-NPs can inactivate a broad spectrum of microorganisms. Ag-NPs compared with the other bulk solid it has large surface areas per volume ratio and high reactivity and this gives Ag-NPs antimicrobial properties [9, 10,11], Ag-NPs synthesized using various methods including chemical reduction for silver ion in aqueous solutions with or without stabilizing or capping agent agents [12,18].

The most popular synthesis of Ag-NPs is reducing silver ion solution using sodium borohydride or citrate as reducing agent [19]. Chemical methods have been used widely for the production of Ag-NPs in large quantities of the final product. Nano silver sizes and shapes can be controlled by changing the time, temperature, and the concentration of chemical agents [20].

This paper is focused on Ag-NPs sedentary using new reducing agents and guar gum as stabilizer. These preparations are economical and easy ways of available and cheap materials, and then continue with the stability of the particles over a period of time.

2. Experimental Part

I. Materials

Silver nitrate (AgNO₃) (Sigma-Aldrich, p.a.), glycerin (C₃H₈O₃) (M. Wt. 92.09 g.mol⁻¹, Sigma-Aldrich), sodium hydroxide (NaOH) (Sigma-Aldrich, p.a.), propylene glycol (C₃H₈O₂), (M. Wt. 76.1 g.mol⁻¹, Sigma-Aldrich), and Guar Gum (HIMEDIA), India

II Preparation of Nano silver

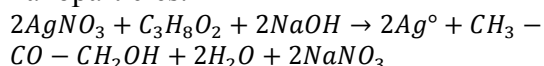
1. Synthesis nanosilver using propylene glycol

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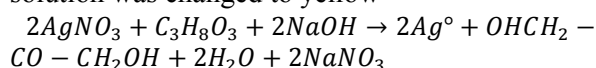
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Guar gum was dissolved in distilled water (0.1 g in 100 mL) at room temperature with stirring in a conical flask 250 mL. To this solution 3 mL of propylene glycol was added drop wise with continuous stirring and then little drops of 2% NaOH were added to set the result solution at pH equal 8. Finally 5 mL of 5.8 mM silver nitrate $AgNO_3$ was added slowly and after 10 minutes the color of the solution was changed to yellow that indicates the production of silver nanoparticles.



2. Synthesis nanosilver using glycerin

Guar gum was dissolved in distilled water (0.1 g in 100 mL) at room temperature with stirring in a conical flask 250 mL. To this solution 2 mL of glycerin was added drop wise with continuous stirring and then little drops of 2% NaOH were added to set the result solution at pH = 8. Finally 5 mL of 5.8 mM silver nitrate $AgNO_3$ was added slowly and after 10 minutes the color of the solution was changed to yellow



3. Result and Discussion

1. Characterization of silver nanoparticles

Ag-NPs were characterized by Ultraviolet-Visible (UV-Vis) spectroscopy Spectrophotometer (UV-VISSP8001, Metertech, Japan) in a range of 200-800 nm, zeta potential analyzes (Malvern zeta seizer 2000, Malvern, UK), x-ray diffraction (6000-Shimadzu), atomic force microscopy (AFM), and scanning electron microscope (SEM) (VEGA3 LM/TESCAN).

a. UV-Vis spectroscopy

UV-Vis spectrophotometer was used to observation the optical properties of nanoparticle solutions. Absorbance band (λ_{max}) of the Ag-NPs occurs in the range of 400- 500 nm according to the effect of surface Plasmon resonance (SPR).

The color of silver nanoparticles solutions was yellow which indicates the formation of the silver nanoparticles as shown in Figure 1.

The (λ_{max}) was at 412 nm for using solution of propylene glycol and 424 nm for glycerin which is typical for Ag-NPs solution. The aggregation state of Ag-NPs has effect on their optical properties. The prepared solutions were measured for different periods of time to more than six months without any change in the absorption

peaks which proved the stability of the prepared Ag-NPs solutions without any aggregation [21].

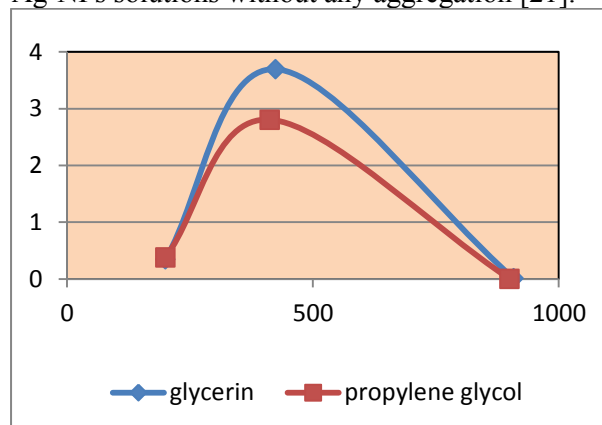


Figure 1: Shows UV-Visible spectra (λ_{max}) of Ag-NPs solutions using propylene glycol and glycerin



Figure 2: Shows color of Ag-NPs solutions using propylene glycol and glycerin

b. Zeta Potential (ζ)

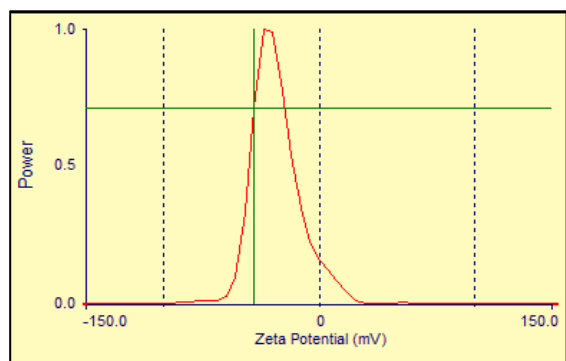
The zeta potential is an instrument that used to measure the surface charge of the nanoparticles. The nanoparticles solution stability was confirmed when values of zeta potential ranged in ± 30 mV [22].

Zeta value of the prepared Ag-NPs in this study was measured and found (-40.24 mV for Ag-NPs prepared using propylene glycol and -41.69 mV for using glycerin) as shown in Figure 2. These values of the zeta potential provide satisfactory evidence that the particle has no tendency towards aggregation through their negative charges. This behavior could attribute to the charges on the particle surfaces that prevent agglomeration the nanoparticles. The capping agent is stabilizing the nanoparticles by make a thick layer around the particles and that will keep all the particles away from each other. The result was obtained suggested that the Ag-NPs solution stable in this work.

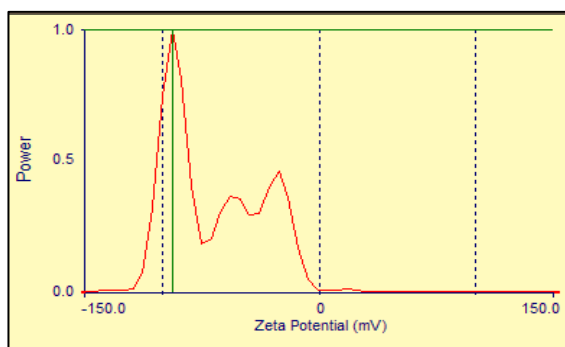
b. XRD-analysis

The structures of prepared Ag-NPs have been verified using X-ray diffraction analysis. Data shows diffraction peak at 2θ equals 36.96° for propylene glycol and 39.66° for glycerin, which

can be indexed to (111) reflection of Face Centered Cubic (FCC) of silver which refer to high intense peak that observed in the sample [23]. No spurious diffractions due to other compound in chart. The reflections refer to produce pure silver metal. The density of peaks indexed to the high degree of Ag-NPs structure as shown in Figure 3.

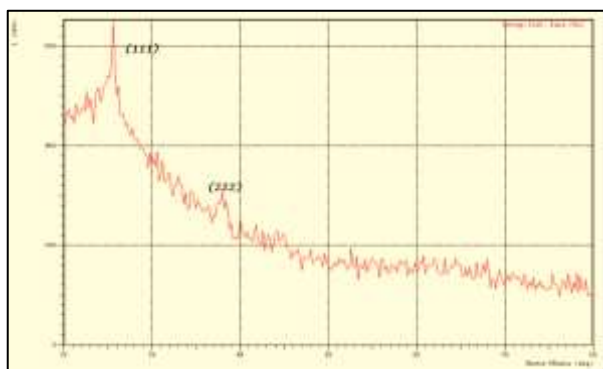


$\zeta = -40.24$ mV using propylene glycol

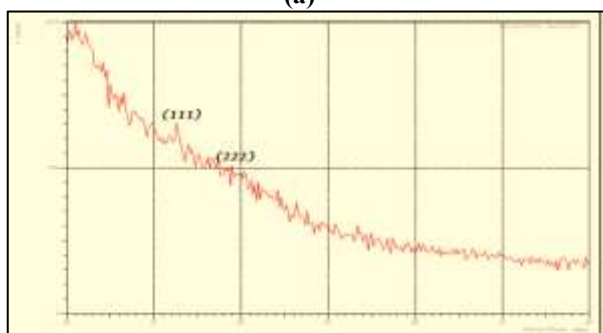


$\zeta = -41.69$ mV using glycerin

Figure 3: Shows Zeta potential of prepared Ag-NPs using propylene glycol and glycerin



(a)



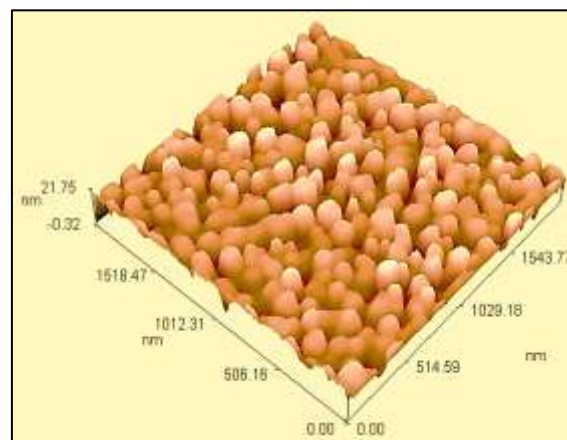
(b)

Figure 4: Shows X-Ray Diffraction pattern of Ag-NPs using (a) propylene glycol and (b) glycerin.

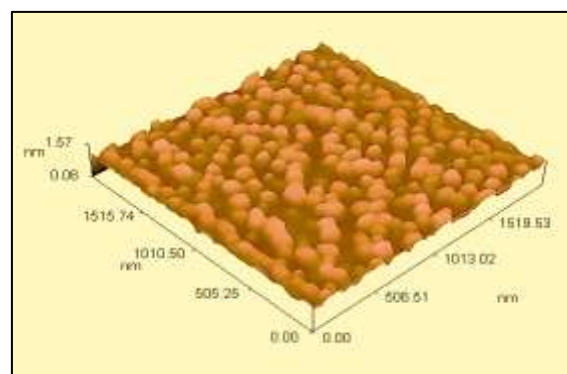
c. Surface morphology by AFM

The presence of deformation in image of AFM is one of the factors that lead to the tip and contamination, and this gave AFM analysis close attention. The important factors were choice the operating mode contact or non-contact ways. Contact mode mean that the needle in contact with the surface of sample which causes damage between capping agent and Ag-NPs due to the pressure force of the tip on the thin film of Ag-NPs and that gave large size in measurements, while in non-contact mode the probe or needle is very close to the surface sample of Ag-NPs as shown in **Figure 4**.

According to the AFM images particle size for propylene glycol solution was 103.72 nm and for glycerin solution was 96.30 nm, these values are larger than the corresponding values obtained by SEM and the reason was the using of the guar gum that protect the silver nanoparticles from growing and agglomeration. The guar gum is a polysaccharide and can coordinate to silver nanoparticles through oxygen atoms which are found in its structure. Due to this coordination a covered layer could generate on the surface of nanoparticles, and this will be reflected in a greater dimension when measured by AFM [24].



using propylene glycol

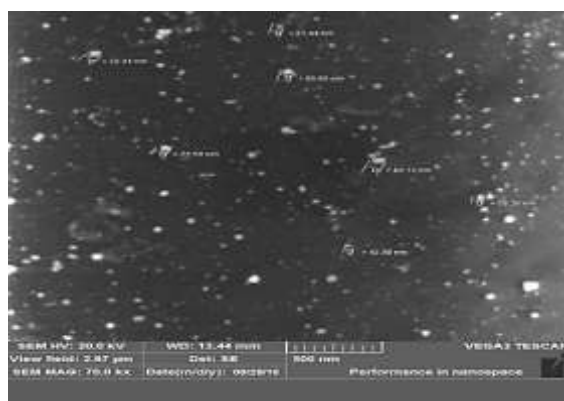


using glycerin

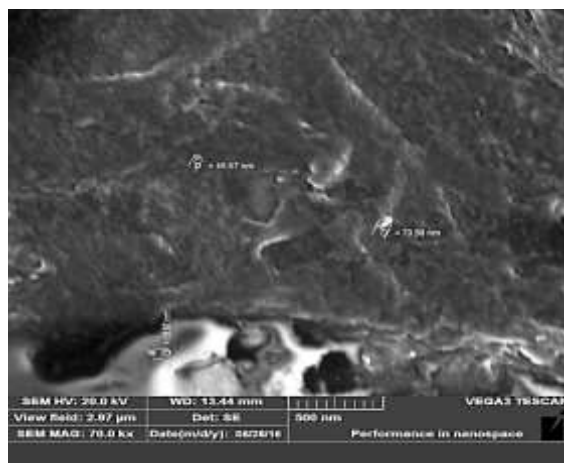
Figure 5: shows the 3D image of the AFM for Ag-NPs film from both solutions

d. Scanning Electron Microscope (SEM)

The SEM analysis confirmed the ability to get a regular distribution of Ag-NPs. SEM images (Figure 5) showed that the Guar gum-stabilized Ag-NPs had a spherical shape with a diameter of 70.38 ± 45.57 nm for propylene glycol and 75.50 ± 42.36 nm for glycerin. The grain sizes of the samples rated from the SEM picture is smaller than the size that obtained from AFM. Most of metals were FCC {111} [25].



using glycerin



using propylene glycol

Figure 6: shows SEM for Ag-NPs from both solutions

4. Conclusion

Silver nanoparticles were synthesized by using silver nitrate as source of silver and propylene glycol, glycerin as reducing agents and guar gum as stabilizer. Systematic characterizations of the Ag-NPs were done using UV-Vis, zeta potential analysis, X-Ray diffraction (XRD), AFM and SEM which reveal stable Ag-NPs. The result of UV-Vis shows that No shift was observed in peak position along a period time for six months which gives a good indication to the stability of Ag-NPs. The stable prepared Ag-NPs in solution are attributed to the presence of guar gum. The

particle size was 40 – 70 nm and it was taken by SEM.

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