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Synthesis and Characterization of Silver Nanoparticles by Green Polyol Method for Supercapacitor Applications

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Abstract - *Supercapacitors, also known as ultra capacitors and electrochemical capacitors, are the next generation energy storage devices. They possess higher energy density and higher power density when compared with conventional capacitors and batteries respectively. Motivation of this work is to develop novel materials for energy materials. For this, pure silver nanoparticles (AgNPs) were synthesized by a simple polyol method with green sources as reducing agents. Nanoparticles of pure Ag were synthesized by reduction of $AgNO_3$ in ethylene glycol using neem, henna (green sources) and $CuCl_2$ as reducing agents and PVP as capping agent. Structural and morphological properties are investigated by X-ray diffraction, FTIR and Scanning electron microscopy. The result obtained by this work of developing Ag nanoparticles can attract the attention of energy applications, especially as materials for supercapacitors.*

Key Words: **Supercapacitor, Silver Nanoparticles, Polyol, Henna, Neem, $AgNO_3$**

1.INTRODUCTION

The development of alternative or non - traditional sources of energy with high energy and power densities is driven by rising global energy demand [1]. Batteries, fuel cells, and supercapacitors are examples of non-traditional energy technologies that use the electrochemical energy conversion principle. They are used in a wide range of applications like mobile phones, emergency doors, hybrid vehicles and televisions [2]. Supercapacitors (SCs) have gotten a lot of interest as an alternative to traditional energy storage devices because of their quick charge-discharge, extended stability, and moderate energy density [3]. The supercapacitor is similar to a conventional capacitor, except that it has a significantly higher capacitance in a much smaller container. In a battery, static charge is used to store energy. Whereas a voltage differential between the positive and negative plates is used to charge the supercapacitor [4]. A conventional capacitor is made up of conductive foils and a dry separator; a supercapacitor, on the other hand, is made up of unique electrodes and an electrolyte.

When a voltage is supplied to the terminals, a double layer forms at the interface between the electrode (activated carbon) and the electrolyte, which is the working principle of a supercapacitor. Although the energy storage in double-layer type capacitors is predominantly electrostatic rather than faradaic as in batteries, it is likely to have a so-called pseudocapacitive component to contribute [5].

As supercapacitors have such distinctive energy storage principle, high rates of charge and discharge, little degradation over thousands of cycles, low-toxicity constituent materials, good reversibility, and high cycling efficiency (more than 95 percent), they gained immense focus as next-generation energy storage devices. The main objective is to increase the energy density (charge storing capacity) of the supercapacitor by using nanomaterials as electrode material. Nanostructured materials play a significant role in electrochemical devices because they have a large specific surface area and can withstand quick redox reactions; the nanostructure of the materials improves capacitive electrochemical performance. A capacitor's energy storing capacity is directly proportional to the capacitance, which in turn is proportional to the area of the plates [6]. As a result, there are three types of electrode materials with microstructures that are suitable for supercapacitors in this scenario. They have a great suction power. They are activated carbons with a large surface area, metal oxides, and conducting polymers. The effective area of the electrodes can be greatly expanded by using such materials as electrodes, hence increasing the supercapacitors' capabilities.

Due to their inherent potential for high specific capacitance, transition metal oxides have become the focus of research. This was demonstrated by the performance of RuO2 as an electrode material, which had a very high specific capacitance of 1580 F/g [7]. However, because Ruthenium is a rare earth element, it is more expensive. Consequently, In commercial applications, supercapacitor electrode uses are less realistic.

Metal nanostructures such as silver, copper, gold and nickel have a wide range of applications in catalysis and optoelectronic devices [8]. Silver stands out among these conductive metals due to its high compatibility, electrochemical, and electrocatalytic properties. Silver metal has a variety of properties that can be enhanced, tweaked, or developed. Controlling particle morphology on the nanoscale scale can improve a variety of properties in silver metal. Silver nanoparticles (AgNPs) exhibit remarkable electrical, optical, thermal, optoelectronic, catalytical, anticancer, and biological properties that are shape and size dependent, making them ideal for a wide range of applications.

Green chemistry approaches emphasise the use of non-toxic pathways and chemicals for environmental protection. These techniques seek to decrease or eliminate the usage of hazardous chemicals and their production during chemical processes. Researchers have used a 'green synthesis' strategy to manufacture Ag nanoparticles, which includes the use of a plant extract as a reducing agent to reduce the amount of chemicals used [9]. This method is simple, environmentally friendly, low-cost, and non-toxic. As a result, the use of a green synthesis methodology to make Ag nanoparticles has attracted researcher's interest as a viable alternative to physical and chemical methods. The diversity of flora life forms has allowed us to investigate numerous plant and fruit extracts, such as guava leaf [10], green tea [11] neem leaf [9], onion[12] and lemon [13].

In this paper, synthesis of silver nanoparticles by a simple polyol process with green sources as reducing agents for obtaining improved energy storing capacity of a supercapacitor, as a consequence of increased surface area of electrode material is presented. AgNPs were synthesized by reducing $AgNO_3$ metal salt by ethylene glycol using $CuCl_2$ (chemical) , neem and henna (green sources) as reducing agents and Polyvinylpyrrolidone (PVP) as capping agent.

This project is organized under 6 chapters. Chapter-1 elucidates the introduction. Chapter-2 presents related work carried out on nanomaterials for supercapacitor applications. Chapter-3 gives details about the experimental synthesis. Chapter-4 deals with results obtained and discussion. Chapter-5 explicates conclusions. At the end, Chapter-7 presents references.

2. RELATED WORK

Rasu Ramachandran et al. [14] have reported that supercapacitors have emerged as a significant alternative energy technology with excellent electrochemical characteristics, high energy density, and strong cycle stability. Carbon materials (CNT, activated carbon and carbon nanofibers) have substantially improved super capacitance performance because of their high surface area, low porosity, and excellent thermal and electrochemical conductivity. Although some of the carbon materials had low capacitance, the authors explained that by incorporating metal oxides into the activated carbon electrode materials, the capacitance might be increased.

Bei Wang [15] had an announcement on an investigation into V_20_5/carbon nanocomposites as supercapacitor electrode materials. These nanocomposite powders were prepared via spray pyrolysis and had an enhanced specific surface area, 18 m^2g^{-1}. The maximum concrete capacitance of 295 F g^{-1} was obtained in 2 M KCl electrolyte at a 5-mV s scan rate, exhibiting excellent electrochemical performance.

Muhammad Naeem Ashiq et al. [16] have reported the enhancement of electrochemical properties by nanoparticles of silver-coated zirconia for supercapacitor. Nanoparticles were prepared by two step methods i.e., simple co-precipitation and the reduction method. Silver-coated ZrO2 nanoparticles showed specific capacitance of 792F/g at scan of 10mV/s, they also showed power density about 274.5W/kg at current density of 5mA/cm2. The results indicated that silver coated ZrO2 is suitable for supercapacitor electrode material.

Girish K.[17] described that green synthesis of NPs using plant extracts has gained much interest in recent years due to non-toxicity and very low cost of synthesis. He proposed that the plant extracts act both as reducing agent as well as capping agent. Neem (Azadirachta indica A. Juss) is a well-known medicinal plant and has been studied for the biosynthesis of NPs in this paper. An indica has various phytochemicals identified that can reduce the metal ions. The bioreduction of NPs from neem extract is eco-friendly and efficient.

Shohreh Hemmati et al.[18] have summarized that synthesis of AgNWs is generally onerous and the final cost of commercial products is high but polyol flow synthesis overcomes these challenges through continuous mixing control in small amounts, which can provide a high yield of AgNWs. A polyol solvent in the presence of a salt precursor and a polymeric capping agent is heated to produce a metal colloid. In the case of AgNWs, ethylene glycol (EG), poly vinyl pyrrolidone (PVP) and silver nitrate (AgNO3) usually acted as the polyol, capping agent and salt precursor, respectively.

3. EXPERIMENTAL DETAILS

3.1 Synthesis of AgNPs using $CuCl_2$ as reducing agent

Silver nanoparticles were synthesized by the reduction polyol method. For this purpose, 1M (1.69g) solution of silver nitrate ($AgNO_3$) was prepared in 25 mL of ethylene glycol. Then, a weighted amount of polyvinylpyrrolidone (PVP) (0.35g) as a capping agent was added separately in 5ml of EG under vigorous magnetic stirring. After 20 min of vigorous stirring, it is added slowly to a solution of 0.05 g of copper(II) chloride ($CuCl_2 . 2H_2O$) which acts as a reducing agent and 5ml of EG. The colour of the solution turned to light green. This solution was further added drop by drop to the initial solution of $AgNO_3$ and EG. The colour of the solution turned to bluish green. This colloidal solution was stirred further at 120°C till the color change was observed which affirmed the formation of silver nanoparticles. The formation of the silver nanoparticles was further confirmed by the characterizations.

3.2 Synthesis of AgNPs using a green source Neem as reducing agent

Silver nanoparticles were synthesized by the reduction polyol method. For this purpose, 1M (1.69g) solution of silver nitrate ($AgNO_3$) was prepared in 25 mL of ethylene glycol. Then, a weighted amount of polyvinylpyrrolidone (PVP) (0.35g) as a capping agent was added separately in 5ml of EG under vigorous magnetic stirring. After 20 min of vigorous stirring, it is added slowly to a solution of 0.05 g of $CuCl_2$, 5ml of green source Neem which acts as reducing agents and 5ml of EG. This solution was further added drop by drop to the initial solution of $AgNO_3$ and EG. The colour of the solution turned to grey. This grey coloured colloidal solution was stirred further at 120°C till the color change was observed which affirmed the formation of silver nanoparticles. The formation of the silver nanoparticles was further confirmed by the characterizations.

3.3 Synthesis of AgNPs using a green source Henna as reducing agent

Silver nanoparticles were synthesized by the reduction polyol method. For this purpose, 1M (1.69g) solution of silver nitrate ($AgNO_3$) was prepared in 25 mL of ethylene glycol. Then, a weighted amount of polyvinylpyrrolidone (PVP) (0.35g) as a capping agent was added separately in 5ml of EG under vigorous magnetic stirring. After 20 min of vigorous stirring, it is added slowly to a solution of 0.05 g of $CuCl_2$, 5ml of green source Henna which acts as reducing agents and 5ml of EG. This solution was further added drop by drop to the initial solution of $AgNO_3$ and EG. The colour of the solution turned to blue. This blue coloured colloidal solution was stirred further at 120°C till the color change was observed which affirmed the formation of silver nanoparticles. The formation of the silver nanoparticles was further confirmed by the characterizations.

Fig -1: Synthesized AgNPs using a) $CuCl_2$ (before drying) b) Neem c) Henna

4. RESULTS AND DISCUSSION

4.1 XRD studies of synthesized Ag nanoparticles by $CuCl_2$, Neem, Henna as reducing agents.

Powder XRD is used to characterize the nanoparticles synthesised by these methods in order to validate that they are silver and to get structural information.. Figure 2 shows the XRD patterns of silver nanoparticles.

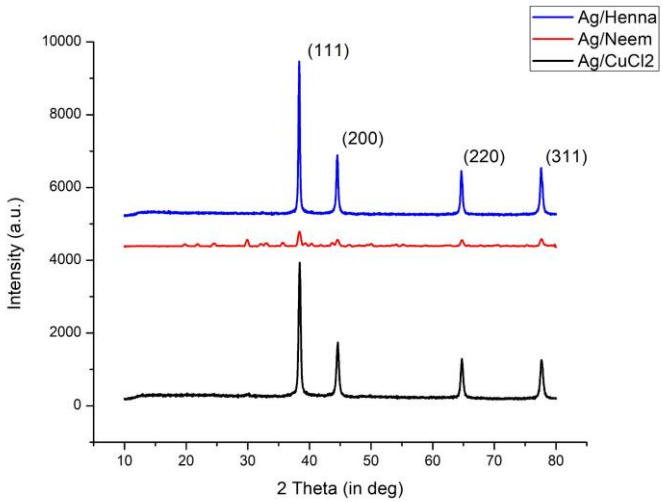

Fig -2: XRD Plot of Ag/$CuCl_2$, Ag/Neem, Ag/Henna

The high peaks in the XRD study indicated the active silver content. The pattern clearly shows the main peaks at (2θ) 38.42, 44.62, 64.74 and 77.62 corresponding to the (111), (200), (220) and (311) planes, respectively. By comparing JCPDS (file no: 89-3722), the typical pattern of synthesized AgNPs is found to possess an FCC structure. A few unassigned peaks observed could be due to the presence of some bioorganic compounds/protein(s) in the neem extract and crystallizes on the surface of the silver. The average crystallite size of the silver nanoparticles was estimated using Debye–Scherrer's equation.

$$D = K\lambda / \beta \cos \theta$$

Where D is crystallite size (in nm), K=0.9 (scherrer's constant), λ= 0.154nm (wavelength of X ray) and β is FWHM (full width at half maximum of the peak in radians). The average crystallite sizes of the synthesized nanoparticles from $CuCl_2$, neem extract and henna extract as reducing agents are found to be 22.86 nm, 20.15 nm and 26.94 nm respectively.

4.2 FTIR Spectra of synthesized Ag nanoparticles by $CuCl_2$, Neem, Henna as reducing agents.

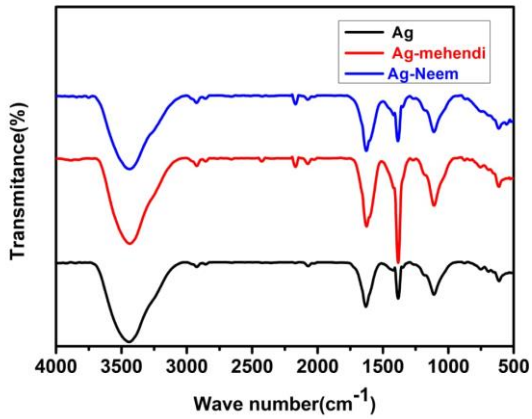

Fig -3: FTIR Spectra of Ag/$CuCl_2$, Ag/Neem, Ag/Henna

Ag/$CuCl_2$: FTIR measurements were carried out to identify the potential functional groups of the molecules in the compound $CuCl_2 . 2H_2O$, which are responsible for reduction of silver ions into silver nanoparticles. The strong peak appearing at 3447.6 cm^{-1} is mainly attributed to the O-H stretching vibration of $CuCl_2 . 2H_2O$. The peak at 1635.06 cm^{-1} is associated with the Cu-Cl stretching vibration and also the O-H bending vibration of water [19].

Ag/Neem: FTIR measurements were carried out to identify the potential functional groups of the biomolecules in the leaf extract of Azadirachta indica (neem), which are responsible for silver ions into silver nanoparticles. From comparison with FTIR of leaf extract of pure neem and green synthesized silver nanoparticles , the observed peaks at 1620.73 cm^{-1} , 1383.51 cm^{-1} , 1.109.67 cm^{-1} are more characteristic of terpenoids and flavanones that are ample in neem plant broth. The peak observed at 1620.73 cm^{-1} indicating C=C groups, 1,383.51 cm^{-1} occurring to the germinal methyls and 1,109.67 cm^{-1} shows ether linkages, suggesting the presence of terpenoids or flavanones adsorbed on the surface of silver nanoparticles [20]. These reducing sugars could be responsible for the reduction of silver ions into silver nanoparticles.

Ag/Henna: FTIR spectra of aqueous extract of fresh Henna leaves and silver nanoparticles is shown here. Due to the interaction of silver nanoparticles with the extract, the vibrations are lesser in Ag – Henna extract FTIR spectrum when compared to only Henna extract FTIR spectrum. It showed the presence of groups/bonds due to free O-H stretching (around 3495cm^{-1}), (polyols) C≡N stretching vibrations, (around 2076cm^{-1}), C=O stretching vibrations (around 1631cm^{-1}), aromatic stretching vibrations (616cm^{-1}) [21]. Their presence is indicative of the terpenoid group of compounds present in the aqueous Henna extract which may be responsible for the reduction of silver nitrate into silver nanoparticles.

4.3 FE-SEM analysis of synthesized AgNPs using $CuCl_2$, Neem and Henna as reducing agents.

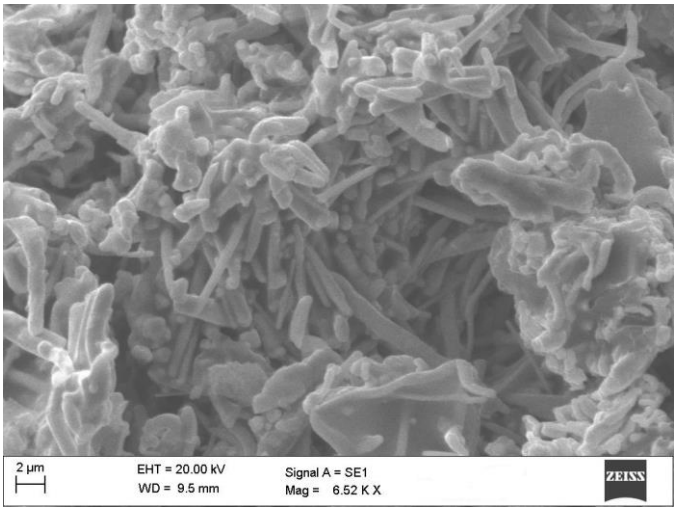

Fig -4: FESEM of $CuCl_2$/Ag nanoparticles

The FESEM images of the silver nanoparticles are shown in Fig. 4. The morphology of AgNPs surface showed an even and cylindrical shape. In the present study, the histogram of the particle size ranges from 12 - 20 nm. Similar result of the size of silver nanoparticles was reported by XRD Analysis. Nanofibres/Nanorods can be observed whose morphology is smooth and continuous. The cross section of the rods was observed to be not hollow (or) solid. Few nanoflakes and little agglomeration were also observed. The porous nature aids the electrochemical storage.

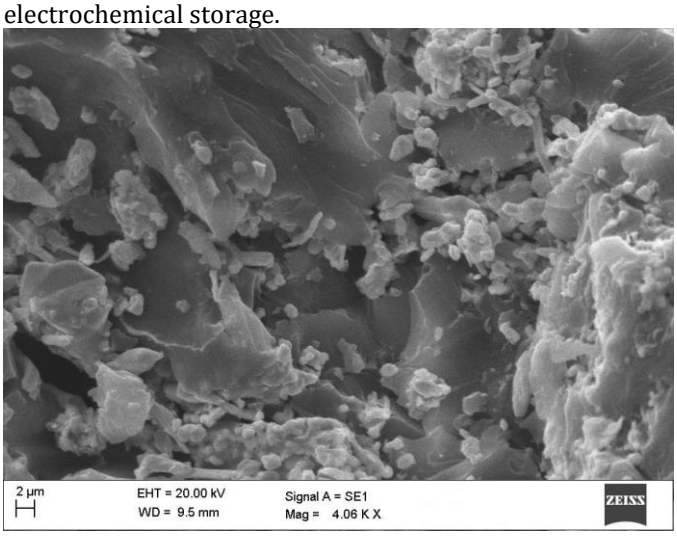

Fig -5: FESEM of Neem/Ag nanoparticles

The shape, size and surface morphology of the silver nanoparticles were analyzed by Scanning Electron Microscope. Figure 5 shows the SEM image of AgNPs synthesized from neem extract. The SEM images show silver nanoparticles which are predominantly like discontinuous/rough flakes and sheets in shape as well as a number of aggregates with no defined morphology. The presence of biomolecules in the neem extract has resulted

in the synthesis of sheet-like silver nanoparticles and the high agglomeration may be due to the presence of secondary metabolites in the leaf extracts. The porous nature can help the charge storage for electrochemical application.

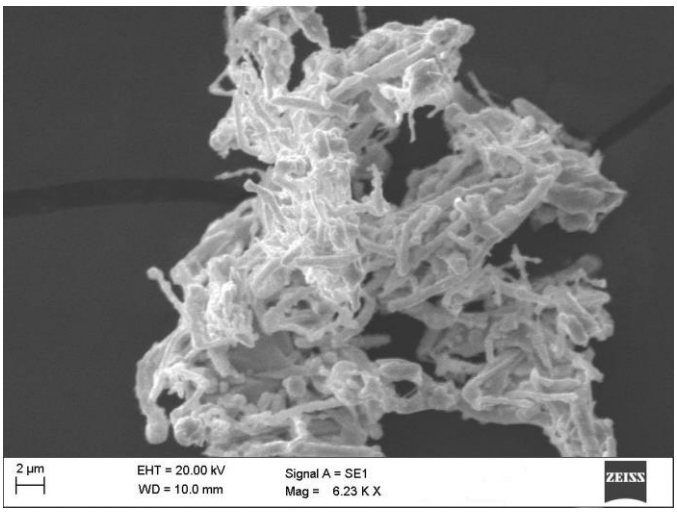

Fig -6: FESEM of Henna/Ag nanoparticles

The size, shape and surface morphology of the silver nanoparticles were analyzed by Scanning Electron Microscope. Figure 6 shows the SEM image of silver nanoparticles synthesized from henna extract. In the present study, the histogram of the particle size ranges from 10 - 20 nm. The SEM images show silver nanoparticles which are predominantly like discontinuous/rough nanofibres/nanowire in shape. The presence of biomolecules in the henna extract has resulted in the synthesis of wire-like silver nanoparticles and the slight agglomeration may be due to the presence of secondary metabolites in the leaf extracts. The nanowires are not hollow in cross section and they are found to be entangled closely with each other. The porous nature can help the charge storage for electrochemical application.

5. CONCLUSIONS

Pure silver nanoparticles (AgNPs) were synthesized by a simple polyol method with green sources as reducing agents. Nanoparticles of Ag were synthesized by reduction of $AgNO_3$ in ethylene glycol using neem, henna (green sources) and $CuCl_2$ as reducing agents and PVP as capping agent. Structural and morphological properties are investigated by X-ray diffraction, FTIR and Scanning electron microscopy where XRD and FTIR confirmed that the material obtained were silver nanoparticles. The average crystallite size was found to be 22.86nm, 20.15nm, 26.94nm for AgNPs synthesized using $CuCl_2$, Neem, Henna as reducing agents respectively. SEM images confirmed the particle structure, agglomeration and porous nature of the obtained material. The result obtained by this work of developing Ag nanoparticles can attract the attention of energy applications, especially as materials for supercapacitors with enhanced energy density (charge storing capacity) by increasing the surface area and porosity.

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