GREEN APPROACH TO SYNTHESIZE SILVER NANOPARTICLES FROM STEM EXTRACT OF GARDEN RHUBARB: EVALUATION OF THEIR STABILITY AND DIELECTRIC PERFORMANCES

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Abstract

Recent advances in Nano-biotechnology, offer potential longer duration storage options for silver nanoparticles (SNPs) with preferable capping agents where a plentiful efforts have been given to minimize the toxicity effects SNPs. To overcome the toxicity scenario of SNPs, a novel green methodology was put forward in the present investigation. Biogenic SNPs were synthesized using water extract of Garden Rhubarb (GR) stems under ambient conditions. The method demonstrates an eco-friendly, instant and easy route for stable SNPs synthesis. The formation of instant SNPs was analyzed by visual observation and monitored by UV-visible (UV-vis) spectrophotometer. The characteristic surface plasmon resonance (SPR) band at 445 nm, revealed the formation of SNPs. The X-ray diffraction (XRD) pattern of green SNPs showed their crystalline structure. SEM and TEM studies revealed that the shape of SNPs was spherical and has approximate diameter within 100 nm range. The zeta potential measurements on 180th day after SNPs synthesis, revealed the stability and size distribution of SNPs. The values are 29.6mV, 28.1mV and 24.1mV for three varied compositions of $AgNO_3$ (1mM) and GR extract. The high dielectric constant (ε') has been observed for GR mediated SNPs, the ε' values were found to reach the minimum value of 40000 at frequency 1MHz. Suitable tuning of the dielectric performances can conclusively prove their applications in multifunctional sensors, optical, and charge storage devices.

Keywords: Green synthesis, silver nanoparticles, zeta potential, dielectric properties

1. INTRODUCTION

The classical physical and chemical routes for the synthesis of nanoparticles has overwhelmed by green protocol. Plant mediated route has gained considerable interest because of the advantages over the conventional synthesis. Silver nanoparticles (SNPs) should be free from toxic contaminants for their effective applications in biomedical field; this can be addressed by green route, wherein, harmless, non hazardous reducing agents were involved [1, 2]. Among the other metal nanoparticles, SNPs exhibits high electrical and thermal conductivity, chemical stability, catalytic activity which promoted thier applications in conductive coatings, flexible electronics, sensors and actuators. With suitable composite materials the technical applications can be reframed in electrochemical sensors [3], biomedicine, and microelectronics [4]. Garden Rhubarb (GR) is phytochemically distinct from Chinese Rhubarb [5] and used for the preparation of edible stuffs such as pizza and cakes in european regions and in some parts of the united kingdom. In the present article, an ecofriendly, economically viable and stable SNPs synthesis is focused following an instant green route where, an aqueous extract of GR stems at ambient temperature was used without the utilization of capping agents. We hypothesize that quinone and emodin type natural phytochemicals [6] are responsible for the reduction of silver salt ($AgNO_3$,) to SNPs. To the best of our knowledge, there has been no report on the synthesis of SNPs using the aqueous extract of GR stems. First time, we reported about the activity of GR stem extract as a bioreductant for silver nitrate solution and capping agent for the stabilized SNPs [7].

2. EXPERIMENTAL SECTION

2.1. Synthesis of GR stem extract and GR-SNPs

10g of fresh GR stems are washed under running water prior to chopping in to pieces of nearly 2 cm dimensions. The chopped stems were added to 50mL of Double Distilled Water (DDW) and heated to 60°C for 1h. The pink turbid solution was filtered through porous (≈11µm) sterilized cellulose membranes. The collected light-pink extract was used as bioreductant for SNP synthesis and stored at <10°C for further use (See **Figure 1**).

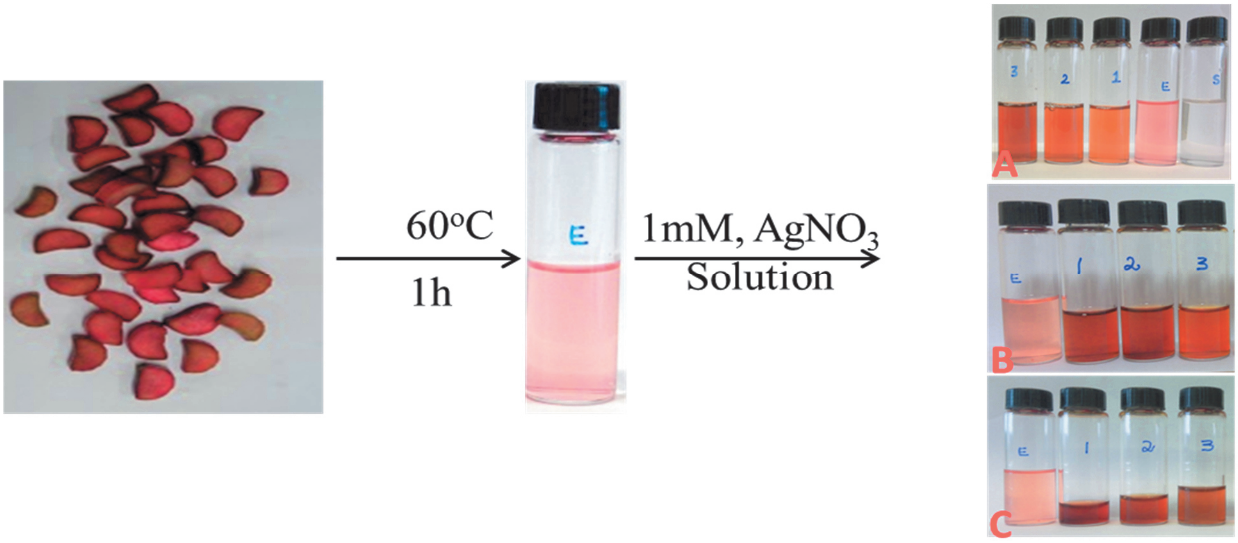

Figure 1 Scheme of GR-SNPs synthesis in different reaction mixture: (A) GR Extract + $AgNO_3$ solution variation, (B) both GR extract and $AgNO_3$ solution variation and (C) GR extract variation+ $AgNO_3$ solution

The protocol for the synthesis of GR-SNPs involves the aqueous silver ions (1 mM solution of silver nitrate) and GR extract (bioreductant) .Typically, 1 mM $AgNO_3$ solution was mixed with GR extract in the volume ratio of 1:2 respectively and stirred occasionally at 150-200 rpm over a period of 10-20 min at room temperature (≈ 18-20º C). The noticeable color change was observed from pink to brown, confirms the formation of colloidal SNPs. It was further confirmed by UV-Vis spectroscopy (VARIAN-EL08043361). The colloidal SNP suspensions were analyzed instantly after 30 min by broadband impedance analyzer (Novocontrol Concept 50) at ambient temperature. Further spectroscopic characterization, GR-SNPs were isolated by centrifugation at 10000 rpm, thereafter, 24h followed by repeated washing of GR-SNPs by DDW and collected as brown solid after drying in an oven at 60 º C for 10h.

2.2. AC electrical measurements of GR-SNPs

The frequency dependence of AC conductivity (σac), dielectric constant (ε') and dielectric loss (tan δ) of the aqueous colloidal suspension of AgNPs comprising GR extract was made in contact with gold plated glass electrodes and performed the measurement by broadband impedance analyzer (Novocontrol Concept 50) at ambient temperature. The amplitude of applied AC voltage was 1V for the analysis. The electrical contacts were checked to verify the ohmic connection and analysis was carried out in the frequency range from 1 Hz to 1 MHz

3. RESULTS AND DISCUSSION

Bioreduction of the $AgNO_3$ to SNPs by GR extract was monitored at ambient temperature and depicted in **Figure 2** The intense absorption band in the range of 420 - 460 nm was observed due to surface plasmon excitation of SNPs, which confirms the formation of GR-SNPs. DLS measurements showed the particles are distributed in the range of 50-120nm and majority of the particles are below 100 nm. The polydispersity index (PI) value for the colloidal suspension was found to be 0.196 with nanoscopic size distribution of GR-SNPs. The formation of GR-SNPs is further evidenced by SEM analysis (**Figure 3**).

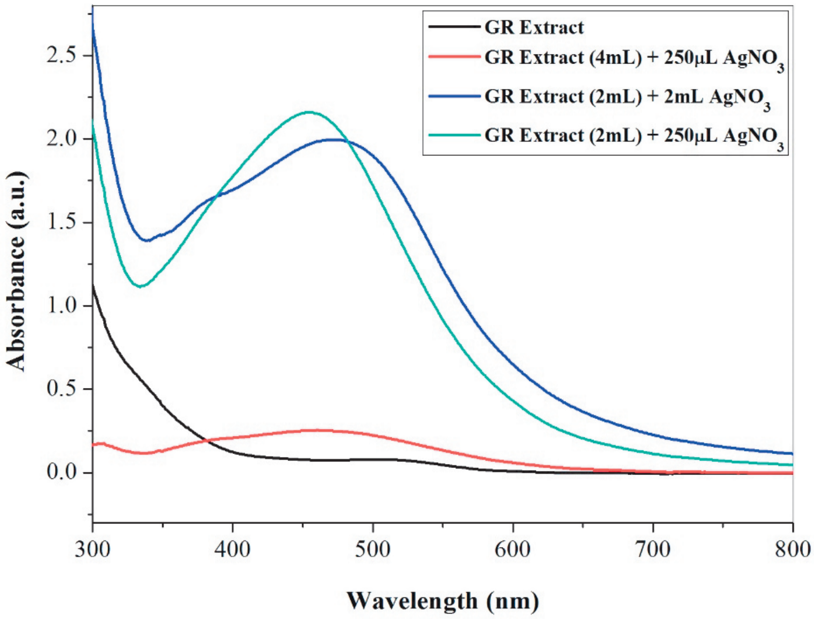

Figure 2 UV-vis spectra of Garden Rhubarb (GR) extract derived SNPs between 420 - 460 nm

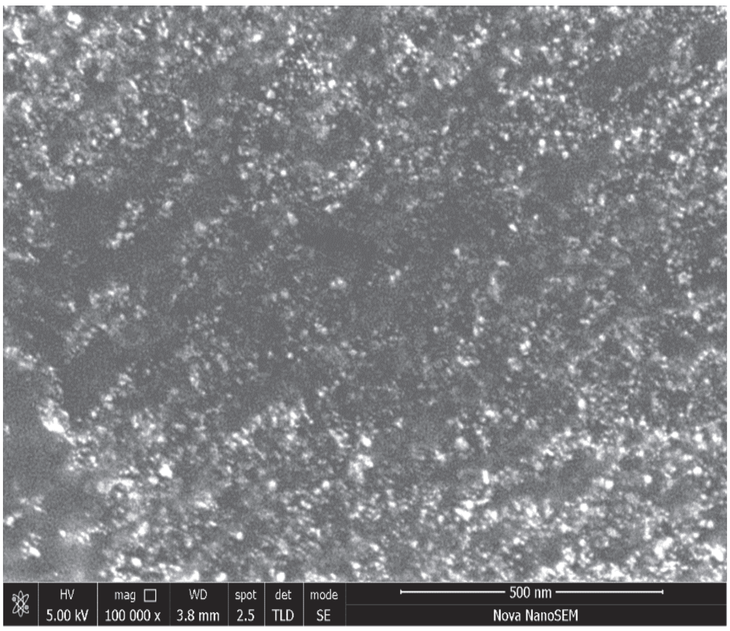

Figure 3 SEM micrograph of GR-SNPs: size and surface morphology

The zeta potential values for GR-SNPs suspensions are 34.8 ±1.5mV on 90th day. It indicates that SNPs capped by GR extract are stable and prevent agglomeration for long duration (**Figure 4a**). The XRD pattern clearly depicts that the GR-SNPs are crystalline and major diffraction peaks are observed at 38.23, 45.64, 64.28, and 76.83^{o} could be attributed to the (111), (200), (220) and (311) crystallographic planes thereby confirming the presence of SNPs (**Figure 4b**).

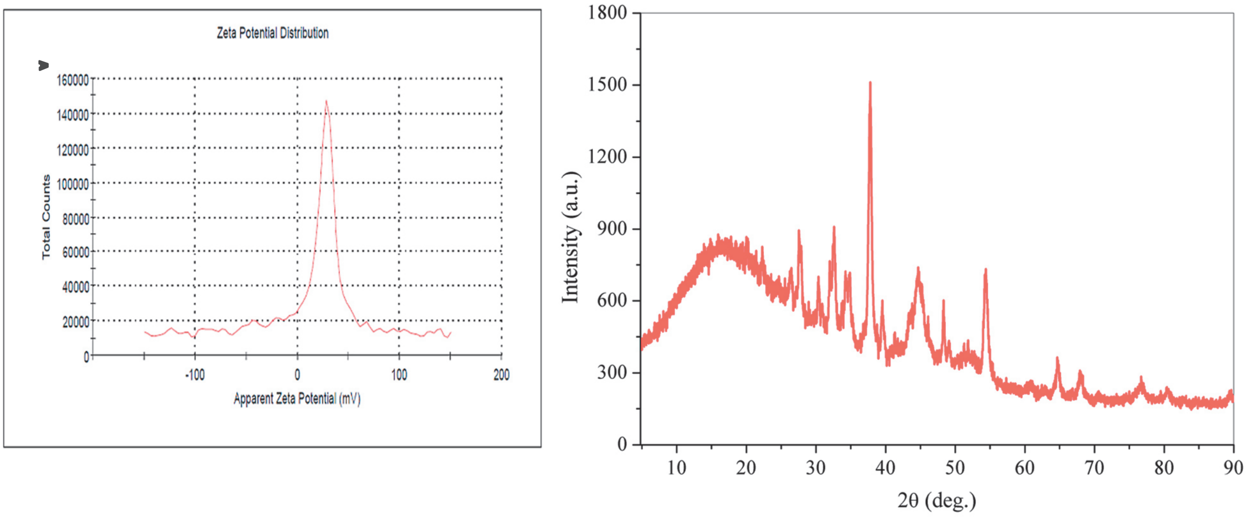

Figure 4 (a) Zeta potential distribution and (b) XRD plot of GR-SNPs

Frequency dependence variation of dielectric constant (at room temperature) was presented in **Figure 5**. The variation of AC conductivity as a function of frequency at ambient temperature is depends on its dielectric nature, at low frequencies; σ_{ac} varies linearly and increases steeply above the frequency 1200 Hz. Frequency independent ac conductivity is observed in low frequency region (<1200 Hz) and is illustrated in **Figure 5a**. It is also observed form the plot of **Figure 5b** that, in general, it follows inverse, as followed by almost all the dielectric and ferroelectric materials. Dispersion with relatively very high dielectric constant can be observed in ε'- frequency plot, the dielectric constant values (measured at 10^6 Hz at room temperature) were found to reach the minimum value of $4x10^4$ at 10^6 Hz. Dielectric loss (tan δ) as a function of frequency increases with increase of frequency and attains a value of 32 at $5x10^5$ Hz (See **Figure 5c**). The dielectric losses of all the SNPs are below 2 at $6.5x10^3$ Hz.

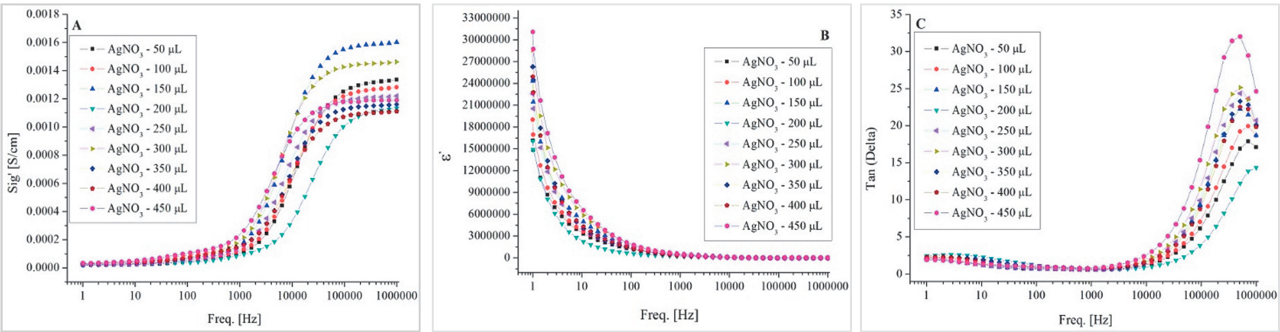

Figure 5 Frequency dependence variation of (a) AC conductivity of GR-SNPs (b) dielectric constant of GR-SNPs (c) dielectric loss of GR-SNPs, for constant volume of GR (4ml) and varied amount of $AgNO_3$ solution

This increase in the dielectric loss with the increasing frequency is usually associated with fast Ag^+ ion drifting in connotation with formed SNPs of various sizes and allowance in dipole polarisation or interfacial polarisation due to interactions of the Ag^+ ions and SNPs [8, 9]. The model is based on the classical hopping of electrons over the barrier. The mechanisms of dipole polarization were more complex, since Ag^+ ions are in random movement with SNPs, which is a conducting material [10]. The AC conductivity reaches constant value of $1.1x10^{-3}$ S/cm to $1.6x10^{-3}$ S/cm at 10^6 Hz. The difference in the ac conductivities was found to be almost negligible. An additional factor affecting the molecular mobility is the in situ reduction of high mobile Ag^+ ions by the aqueous extract of GR.

4. CONCLUSION

The current research mainly focused on biosynthesis of SNPs from GR stem extract and termed as "GR-SNPs". This study reports about an instant, eco-friendly and reproducible method for the synthesis of SNPs. It has been noticed that, the intended use of SNPs in electronic industry is possible by incorporation of SNPs in various polymeric materials which can finally build a hybrid composites.By controlling the arrangements of SNP clusters within the composites, the strength and hardness of the hybrid composites will exhibit an enhanced electrical properties. It has been postulated that, electronic capacitors with high energy storage densities and low operating voltage, materials with high ε' and low conductivity is the necessary criteria [11]. In such applications, it is necessary to develop structurally well defined core/shell particles with GR-SNPs cores surrounded by insulating material. Therefore, suitable tuning of the dielectric performances of polymeric and/or ceramic composite can conclusively prove their applications in multifunctional sensor and high frequency operating devices.

ACKNOWLEDGEMENTS

The work was supported by NPUI (LO1504) Ministry of Education, Youth and Sports of the Czech Republic.

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