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RESEARCH ARTICLE

Water Extract of *Piper Nigrum* Seed Assisted Synthesis of Silver Nanoparticles and Reduction of Various Nitro Compounds by $NaBH_4$ in the Presence of AgNPs as a Catalyst

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Abstract: An attempt has been made for eco-friendly synthesis of silver nanoparticles by water extract of *Piper nigrum* seed. Formation of AgNPs and their morphology was confirmed by using different advanced characterization techniques such as UV-Visible spectroscopy, XRD and FE-SEM images of AgNPs. Further we wish to report for the first time reduction of various nitro compounds to corresponding amines by $NaBH_4$ in the presence of AgNPs as a catalyst. After reaction course, AgNPs can be recycled and reused without any apparent loss of activity which makes this process cost effective and hence eco-friendly. The structures of all the corresponding reduced products were confirmed by comparing their IR, ^{1}H NMR, spectra with the authentic samples.

Keywords: AgNPs, Biosynthesis, *Piper nigrum* seeds, Reduction, FE-SEM

Introduction

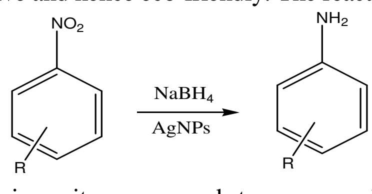
Nanomaterials often show unique and considerable change in physical, chemical and biological properties of materials as compared to their macro-scale counterparts. Due to exotic properties nanoparticles are sometimes considered as fourth state of matter[1]. The surface Plasmon resonance arises from the coherent existence of free electrons in the conduction band. The band shift depends upon particle size, chemical surrounding and adsorbed species on the surface and dielectric constant of the medium. Traditionally metal nanoparticles are prepared and pacified by physical and chemical routes[2]. The chemical approach involves chemical reduction reaction, electrochemical techniques and photochemical reactions. Chemical reduction is the most frequently used method for the synthesis of nanoparticles. The reduction of silver ions in aqueous solution generally yields colloidal silver with particle diameter of several nanometers. Previous studies reveal that a strong reducing agent such as sodium borohydride resulted in small particle size that was somewhat mono-dispersed and the generation of larger particle was difficult to control in this method. On the other hand, weaker reducing agents resulted in decreased rate of reduction and particle size distribution over a broad range[3-5].

Greener synthetic routes are always appreciated compared to their physicochemical production method counterpart. This is not only because of economical aspects, but also because of contamination free nanoparticles with well defined size and morphology rendered by biological routes[6]. Plant extracts are often environmentally and ecologically friendly material and recently have been widely explored in the synthesis of silver nanoparticles. It has been proposed by earlier researchers that the parts of the plant containing anti-oxidant or sugar are responsible for the nanoparticles synthesis process. So they can replace some hazardous chemicals like hydrazine, sodium borohydride *etc.* The plant extract can work in the synthesis of nanoparticles so effectively because of the presence of phytochemicals that acts as reducing and capping agents for pacifying and stabilizing the nanoparticles.

It is believed that proteins from plant extract containing thiol groups (-SH) are capable of reducing the silver ions and act as stabilizing agent during synthesis. Afore said statement is deduced on the observation that after interaction with the metal ions, the secondary structure of proteins was found to be altered. By altering the concentration of $AgNO_3$ (the most common precursor for synthesis of AgNPs) and concentration of plant extracts, the size and shape of nanoparticles can be controlled. Biogenic nanoparticles can be formed by both intra and extra-cellular methods. If nanoparticles are produced extra-cellularly, the extraction would be easier and amount of nanoparticles produced could be massive[7-9].

Plant produces a wide variety of secondary metabolites which have multiple functions throughout the plant's life cycle. Plant's secondary metabolites are responsible for various functions including germination and fertility of pollen grains. A large numbers of secondary metabolites of plants are used in food additives, fragrances, pigments or in medicines. Flavonoids are used as important neutraceuticals and pharmaceuticals[10-12]. This article is concerned with the synthesis of silver nanoparticles by using *Piper nigrum* seeds' water extract.

Generally nitro compounds are reduced to corresponding amines by high pressure hydrogenation[13]. This is a well known fact that alone $NaBH_4$ does not reduce nitro compounds. However, when the same reagent is combined with transition metal halides or their salts such as $NaBH_4/CoCl_2$, $NaBH_4/FeCl_2$, $NaBH_4/CuSO_4$ *etc.*,[14-17] can reduce the nitro compounds in to the corresponding amines. Further we wish to report for the first time reduction of various nitro compounds to corresponding amines by $NaBH_4$ in the presence of AgNPs as a catalyst. After reaction course, AgNPs can be recycled and reused without any apparent loss of activity which makes this process cost effective and hence eco-friendly. The reaction is depicted in Scheme 1.



Scheme 1. Reduction of various nitro compounds to corresponding amines by $NaBH_4$ in the presence of AgNPs as a catalyst (**R=**H,4-CHO,4-NH_2,4-Cl,4-CH_3,4-OCH_3)

Experimental

All reagents were purchased from Sigma Aldrich India and Loba and used without further purification. Melting points were measured in open capillary and are uncorrected. The products were characterized by IR spectra and ^{1}H NMR. IR spectra were recorded on Perkin–Elmer FT-IR-1710 instrument. ^{1}H NMR was recorded on Bruker MSL-300 MHz and Bruker MSL-200 MHz instrument using TMS as an internal standard.

Preparation of water extracts of Piper nigrum seed

Piper nigrum seed were purchased from local market Pune, India. The seeds were carefully washed with water to remove any traces of dirt or foreign impurities. They were then thoroughly rinsed with de-ionized water (Millipore, with conductivity 18 mΩ) before crushing them into smaller pieces. About 25 g of seed powder were weighed and soaked in 75 mL of de-ionized water and then grinded in grinder mixer. The resulting homogenous solution was further diluted to 100 mL and filtered through cotton plug. The filtrate was collected in stopperd glass bottle and stored at 4 ºC temperature. The seed broth was discarded. The filtrate was used for further experimental process.

Synthesis of AgNPs

100 mL (0.1 M) of silver nitrate solution was taken in 500 mL beaker and a magnetic needle was gently inserted. *Piper nigrum* seed extract was gradually added in the beaker with constant stirring using a burette. The addition of each drop of extract resulted in the development of black color in the solution. After addition of 50 mL of *Piper nigrum* seed extract, complete precipitation in the form of AgNPs took place. Then beaker containing reaction mixture was removed from magnetic stirrer. The beaker contains sufficient amount of black colored precipitate which was allowed to settle down. The supernatant solution was decanted and discarded. The precipitate was thoroughly washed by ethanol several time and dried in autoclave and crushed in mortar and used for further characterizations.

Common procedure for reduction of the nitro compounds

In a round-bottomed flask (15 mL) equipped with a magnetic stirrer, a solution of nitro compound (1 mmol) in ethanol (5 mL) was prepared. To the resulting solution, AgNPs (0.001 g, 0.1 mmol) was added and the mixture was then stirred for 5 min. Afterwards, $NaBH_4$ (0.151 g, 4 mmol) as a fine powder was added to the reaction mixture and a fine black precipitate was immediately deposited. The mixture continued to be stirred for 20-30 min and the progress of the reaction was monitored by TLC (eluent; *n*-hexane: ethyl acetate, 8:2). After completion of the reaction solvent was evaporated on rotavapour followed by addition of 5 mL distilled water and 10 mL dichloromethane and AgNPs were removed by filtration using Whatman filter paper no. 41 and dried in autoclave for reuse. Dichloromethane layer was separated and aqueous layer was extracted (2x10 mL) and combined organic layer was dried over anhydrous sodiumsulfate. Evaporation of the solvent and short column chromatography of the resulting crude material over silica gel (eluent; *n*-hexane/ethyl acetate: 8/2) gave the pure amine compound.

Results and Discussion

The formation of AgNPs was primarily indicated by visual inspection of reaction mixture. The change of color of reaction mixture from colorless to dark brown indicates the synthesis of AgNPs in the solution. The intensity of brown color depends upon degree of bio-reduction of silver particles. Formation of AgNPs and their morphology was confirmed by using different advanced characterization techniques described as follows.

UV-Visible spectroscopy

The blackish brown colored sample powder was dissolved in deionized water then sonicated. The solution was analyzed using UV-Visible spectroscopy. Because of the surface Plasmon resonance (SPR) phenomena resonant peak occurs at different wavelength for different nanoparticles and as per the theory of resonance maximum wavelength is absorbed at resonant wavelength. It is reported in the literature that typical AgNPs show the characteristic SPR at the wavelength in the range of 400-480 nm. Figure 1 shows SPR for the sample solution to occur at the wavelength of 440 nm which indicates the formation of silver nanoparticles in the prepared solution. The SPR absorbance is sensitive to the nature, size and shape of particles present in the solution and also it depends upon their inter particle distance and the surrounding media.

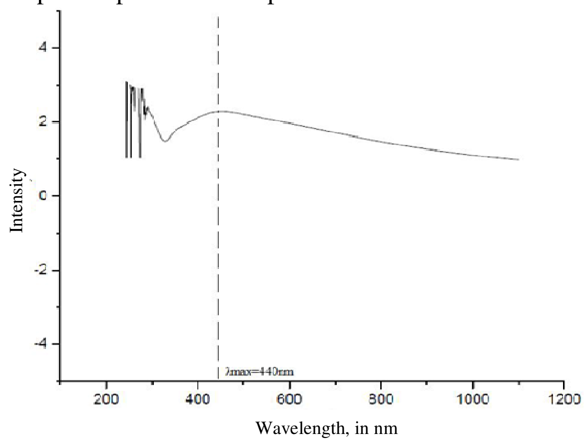


Figure 1. UV-Visible Spectroscopy of AgNPs

XRD pattern showing silver nanoparticles

XRD patterns of synthesized material are shown in Figure 2 where seven major peaks appeared. The peak position explains about the translational symmetry namely size and shape of the unit cell and the peak intensities give details about the electron density inside the unit cell. Thus this pattern confirms the crystalline nature of the synthesized nanoparticles. These peaks are an indication of cubic structure of synthesized silver nano crystals.

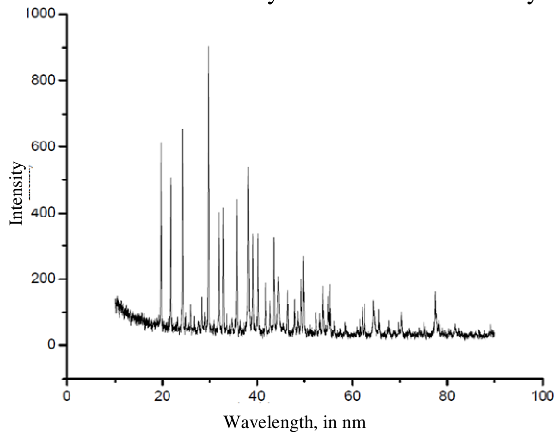


Figure 2. XRD Pattern of synthesized nanomaterial

FE-SEM image of silver nanoparticles

Field emission scanning electron microscopy (FE-SEM) is a powerful tool for imaging of synthesized nanomaterials with special resolution in nano-scale. During such measurements the conductive sample is scanned by focused electron beam to study its surface topography. The FE-SEM image from Figure 3 reveals the formation of irregular cubic and spherical structure of silver nanoparticles with non uniform distribution.

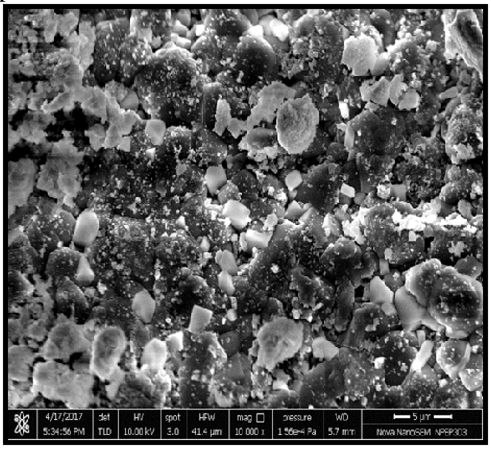


Figure 3. FE-SEM Image

Applications of synthesized AgNPs

Silver nanoparticles due to their unique properties find use in many day to day applications in human life including textile industries, water treatment, sunscreen lotions *etc*. They find wide range of applications in house cleaning chemicals, fabric cleaners and anti reflection coatings. Stable silver nanoparticles are used in a wide range of applications such as drug delivery, spectral selective coatings for solar energy absorption, optical receptors, bio-labeling, intercalation materials for electrical batteries *etc*. They are also used to improve transfer of heat from collectors of solar energy to their fuel tanks to produce high performance delicate electronics, filters, antimicrobial agents, bimolecular recognition, bio-sensing, cancer treatment, molecular imaging and in hundreds of other applications[18,19].

Some chemical reactions take place at room temperature and in short span of time while the other take more time for completion. The rate of reaction can be altered by addition of some foreign material termed as catalyst which remains unchanged at the end of chemical reactions. The term catalyst was coined by Berzelius in 1853. If the reactants and catalyst both exists in the same phase then this phenomenon is called homogeneous catalysis and if they are in different phase then the phenomenon is called heterogeneous catalysis. The catalytic efficiency of material depends upon many factors and one of them is active sites. The active site depends upon the surface area *i.e.* with increase in surface area higher numbers of active sites are available in nanoparticles. Herein, we have studied an organic transformation or synthesis reaction which is described as below[20,21].

Organic transformation

These are simple organic reactions in which one functional group can be converted into another functional group. Such type of conversion usually requires some reagents which can bring about the chemical changes. Here it has been tried to study organic transformation reactions using silver nanoparticles. Sodium borohydride is widely used as a mild reducing agent of selective and also stereo-specific actions. The reaction medium used may be alcohols, amines, ethers such as tetrahydrofuran, dioxan, diglyme or triglyme *etc*. Metal nanoparticles have drawn attention for application as catalyst as they possess high surface to volume ratio. These studies lead to nanocatalysis where catalytic activities and mechanism of noble structures as catalyst are determined using simple reaction. Here simple organic reduction reactions have been studied. Normally sodium borohydride can reduce carbonyl group. But in presence of silver nanoparticles the reduction of nitro group into amino group is taking place. However, in case of *p*-nitro benzaldehyde both the nitro group and aldehyde group are reduced to land up with the product *p*-amino benzyl alcohol. Results are depicted in Table 1.

Table 1. M.P. / B.P. of the Samples with reference to literature values

Entry	R	Product		M.P./B.P.	
		Entry	Name	Observed	Reported
1	H	**1a**	Aniline	184-185	184[22]
2	4-CHO	**2b**	4-Amino benzyl alcohol	58-60	60-63[22]
3	4-NH_2	**3c**	1,4-Diaminobenzene	142-143	143-145[22]
4	4-Cl	**4d**	4-Chloroaniline	70-72	68-72[22]
5	4-CH_3	**5e**	4-Methyl aniline	44-46	41-46[23]
6	4-OCH_3	**6f**	4-Methoxy aniline	58-60	56-58[24]

Conclusion

The use of natural products for green synthesis of nanoparticles is an emerging and exciting area of nanotechnology. The green synthetic method reported here is easy, economical and eco-friendly way to synthesize metallic nanoparticles at room temperature. Moreover, this plant assisted bio-synthesis represents a considerable improvement such as reduced reaction time, no need of capping agent and better control over size and shape. Further, these AgNPs were used as catalyst for reduction of various nitro compounds to corresponding amines by $NaBH_4$.

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