

**GREEN APPROACH FOR THE SYNTHESIS OF SILVER-NANOPARTICLES AND
EFFICIENT USE IN OXIDATIVE CYCLIZATION**

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ABSTRACT- Highly concentrated and stable suspension of Ag-nanoparticles were synthesized by the chemical reduction of AgNO_3 in a reductant using a macrocyclic Schiff base ligand benzildiethylenetriamine and low molecular weight organic compound, thiosalicylic acid (TSA) used as a protective agent. The average size of the silver nanoparticles prepared from this method was less than 20 nm, which allowed low-temperature sintering of the metal. Ag-nanoparticles provide an efficient catalysis for the synthesis of heterocyclic compounds by coupling salicylaldehyde with aliphatic amines through the oxidative cyclization of Schiff base using 10 mol. % of Ag-nanoparticles in the presence of Na_2CO_3 in MeOH. This method avoids the usage of metal oxides or organic oxidizing agents.

Keywords: Macrocyclic ligand, Ag-nanoparticles, oxidative cyclization

INTRODUCTION

A large number of nanoparticles have been prepared most frequently by dispersion of performed polymers (Kompella, et. al., 2001), solvent evaporation method (Kwon et. al., 2001) and ionic gelation method (Calvo, et. al.1997). In order to produce small particle size, often a high speed homogenization or ultrasonication may be employed. Conventional methods such as solvent extraction-evaporation, solvent diffusion and organic phase separation methods are hazardous to the environment as well as physiological systems. A variety of reducing systems are available to carry out reduction that includes NaBH_4 (Ohkuma, et. al.1995), Cu, Ni, Co complexes (Chandra, et. al. 2009), and macrocyclic ligands (Chandra et. al.2008). We report here the chemical reduction of AgNO_3 in a reductant by using a macrocyclic Schiff base ligand i.e. benzildiethylenetriamine and low molecular weight organic compound, thiosalicylic acid (TSA) used as a protective agent (Zambaux.et. al., 1998). This method avoids the use of hazardous polymers and solvents which are required in excess amounts. In recent years the surface area to volume ratio of solid-supported metal (Rong Tarng et. al., 2008) nanoparticles (1-100) nm in size is mainly responsible for their catalytic properties (Verma, et. al., 1997). There is growing interest on the catalytic properties (Nakagawa et. al., 1997) of transition metal nanoparticles (Stephens, et. al., 1949). These nanoparticles have been found useful in the synthesis of heterocyclic compounds and their derivatives. These were widely used in the treatment of hypertension (Roucoux, et. al., 2002), allergies (Sato, et. al., 1987), and many other popular diseases (Reddy, et. al., 1981).The most popular strategies involve coupling of carboxylic acid or its derivative with 2-aminophenols followed by dehydration catalysed by strong acids or radical (Myeong, et. al., 2002)and oxidative (Yun-kui, et. al., 2009)cyclization of Schiff base derived from the condensation of 2-aminophenols and aldehydes. The most popular Cu (I) by (Shin-ichi, et. al., 2007), and Cu (0) (Mitamura, et. al., 2009) nanoparticles emerged as useful and unique green catalysts whose efficiency is attributed to their characteristics high surface to volume ratio that translate into more number of active sites per unit area compared to dominate the properties of matter as size is reduced to nano scale. As a part of continuing efforts of our laboratory towards the synthesis and use of nanoparticles in new synthetic methodology will be performed (Pileni, et. al., 1993).

EXPERIMENTAL

Materials

Silver nitrate was obtained from Merck specialties Pvt Ltd, salicyldehyde was obtained from Acros organics. Benzil and Diethylenetriamine were purchased from Loba chemie and Tedia Company. Solvents were used of AR grades.

General

Melting point was determined using Thomas Hoover melting point instrument. I.R spectra were recorded on Perkin-Elmer FTIR-1710 spectrophotometer using KBr, ¹HNMR spectra were recorded on FT NMR Hitachi R-600(60MHz). Thin Layer Chromatography (TLC) was performed on precoated Merck silica gel 60 F 254 Plates using 20% Ethyl acetate in n-hexane as eluent. Elemental data was obtained by using a Perkin-Elmer 240C CHN elemental analyzer. Elico model LI-610 pH meter were used for pH in present study. The size of nanoparticles were confirmed as (5-20nm) through quasi elastic light scattering data (QELS) and transmission electron microscopy (TEM). The transmission electron microscopy (TEM) images of nanoparticles were obtained with a JEOL JEM-1200EX transmission electron microscope operating at 120 kV with an energy dispersive spectrometer (EDS). The catalytic yields were determined using ACME6000 series Gas chromatography instrument equipped with a flame ionization detector(F.D) using a DP -5 column of 30m length, 0.53 mm diameter and 5.0 μm film thickness. The mass spectra were recorded on JEOL NMS DX 303 at 70 eV or on a KC455 Waters TOF MS spectrometer.

Methods

Preparation of ligand

To an ethanolic solution (20 cm³) of Diethylenetriamine (0.002 mol), an ethanolic solution of Benzil (0.002 mol) was added. The solution was cooled to ca. 5°C and then conc. HCl was added. The mixture was stirred and refluxed for 6 hours at a temperature (40-60°C). The resulting solid was washed with ethanol and dried (scheme-1). (C₁₈H₁₉N₃; HRMS: M⁺ 271.1 Found: C 77.8; H 6.9; N 15.18; Calculated: C 77.97 H 6.8; N 15.3; Yield=70%, m.p.140-145°C.

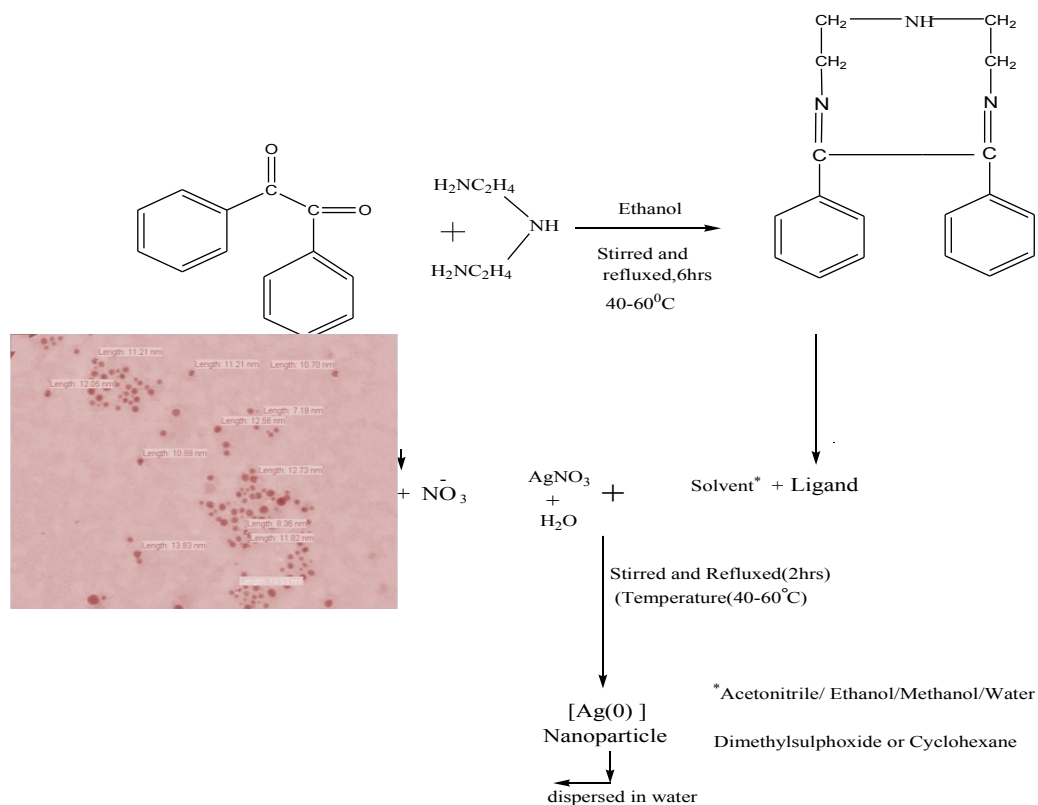
Preparation of Ag-nanoparticles

0.17 g (0.02mol) of AgNO₃ was dissolved in 10 cm³ ionized water. To this solution, a hot ethanolic solution 10 cm³ of ligand benzildiethylenetriamine (0.004 mol.) was added. The (0.2 mol.) thiosalicylic acid (TSA) was used as the protecting agent. After being stirred and refluxed for (1.5-2.0 hours) at moderate temperature, the colour of the solution became pale yellow to black. On keeping the solution overnight, the silver nanoparticles were formed and separated out from the solution by centrifugation (6000 rpm, 10 min.) to remove ligand. The particles were cleaned with acetone and dried at room temperature for 24 hours (scheme-1).

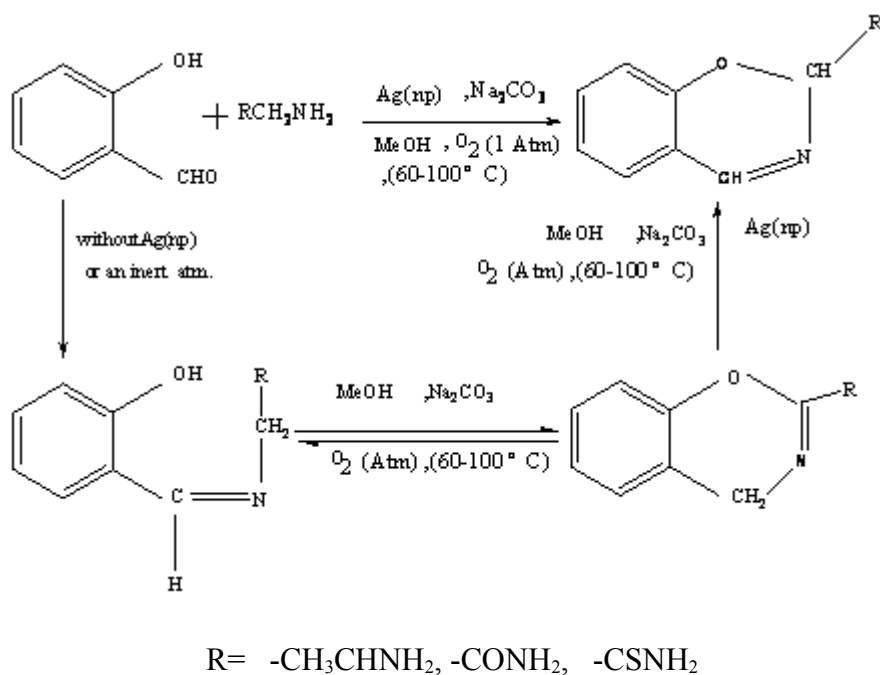
Catalytic activity of Ag-nanoparticles

To an methanolic solution of salicyldehyde(0.001 mol.), R*NH₂(0.001 mol.) was added in 50 cm³ round bottom flask and Ag nanoparticles (18 ± 2nm, 10 mol.%) using 2 equiv. of Na₂CO₃ as the base in methanol was dispersed at room temperature. The solution was stirred and refluxed under an O₂ atmosphere at 60-100°C. The extent of reaction was monitored by TLC. After completion of the reaction the mixture was diluted with distilled water and product extracted with ethyl acetate. The organic layer was dried over anhydrous Na₂SO₄ and the solvent was removed in vacuo. The crude product was subjected to purification by silica gel chromatography using 20% ethyl acetate in petroleum ether as an eluent to yield the product (1-3).

Scheme-1



Scheme-2

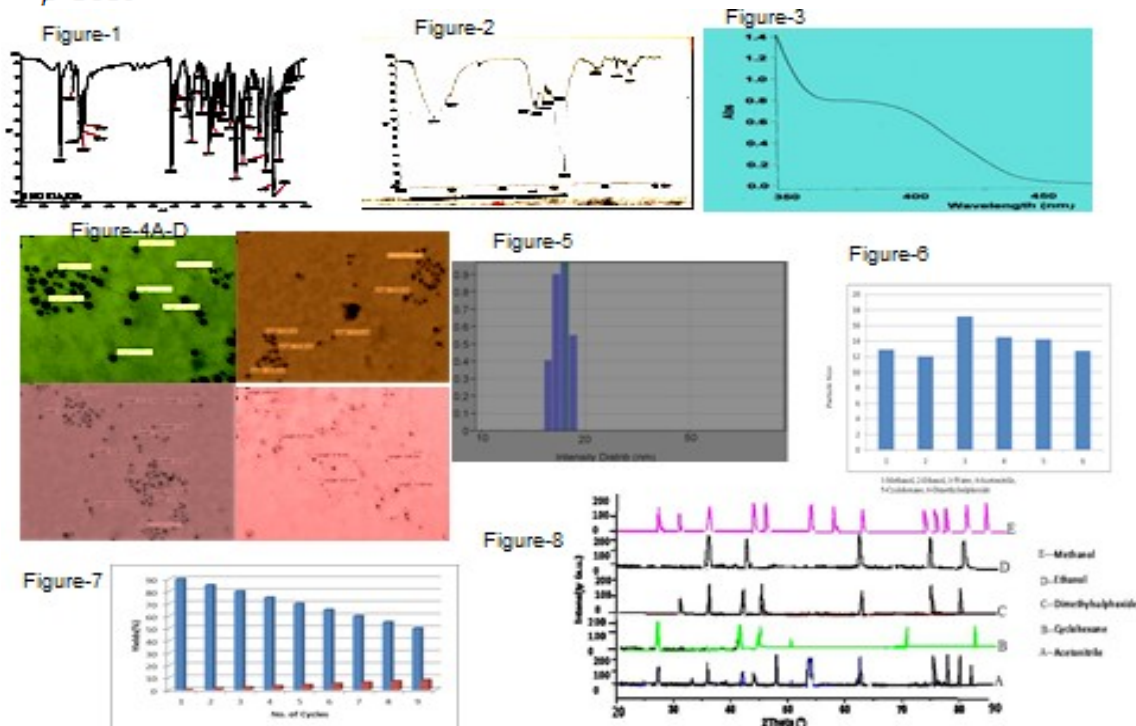


RESULTS AND DISCUSSION

The synthesized ligand was characterized by IR spectra recorded on KBr pellet (Figure-1) shows bands cm^{-1} at 3291, 3064, 2903, 1628, 1446, 1285, 1040, 973, 760, 697. The new C=N bond absorption band at 1628cm^{-1} . The absence of an absorption band at $\text{ca.}3400\text{cm}^{-1}$ in IR spectrum of ligand shows that free amino group are absent. IR Spectra of Ag nanoparticles are shown in Figure-2. $^1\text{H NMR}$ at δ (7.1-7.7) of aromatic hydrogen and δ (3.9-4.1) of amino hydrogen, δ (3.1-3.29) of =C-C-CH₂- and δ 6.02 of NH is present that shows amine changes into amide group. As literature says a low molecular weight organic compound, thiosalicylic acid, was used as the protecting agent (Zambaux.et. al., 1998) to prepare the Ag nanoparticles in order to reduce the sintering temperature. Our macrocyclic ligand works as reducing agent. The reduction of Ag⁺ ions to Ag (0) was a reduction system which employed to prepare the Ag nanoparticles (Scheme-1). Ag nanoparticles prepared was round shape and light grey in colour (colloidal state). The synthesized Ag nanoparticles were dispersed in methanol, UV recorded in the range 350-450nm. The metallic nature of the Ag (0)-nanoparticles was confirmed by a characteristic UV absorption at λ 380-430nm (Figure-3). Size of Ag-nanoparticles was characterized by Transmission Electron Microscopy (TEM) (Figure-4). TEM images conformed that metal particles (West.et. al., 1984) are in nano range and they are approximately spherical in shape. The average size of nanoparticles was 14 ± 2 nm. The sample was prepared by placing a drop of the silver suspension on a carbon-coated Formvar film on copper grids and allowing the solvent to evaporate. The size of Ag nanoparticles were confirmed as (5-20 nm) through quasi elastic light scattering (QELS) technique (Figure-5). The particle size distribution of Ag nanoparticles in methanol, ethanol, water, acetonitrile, cyclohexane and dimethylsulphoxide are shown in Fig 6. Recyclability of Ag nanoparticles are shown in Figure-7. The powder XRD synthesized in different solvents are shown in Figure-8 along with intensity count and 2θ . The powder XRD shows that crystalline nature (Jayesh, et. al., 2008) with peaks corresponding to Ag nanoparticles. Characteristic peak of Ag nanoparticles were on 38.1, 44.3, 63.7, 76.7, and 80.9.

Crystalline size 'D' was obtained by measurement of the broadening of diffraction lines and applying the Debye-Scherrer formula

$$D = \frac{0.94\lambda}{\beta \cos\theta}$$



Where λ the wavelength of XRD radiation, β the full width at half maximum of the peak corresponding to the plane, θ angle obtained from 2θ value corresponding to XRD pattern (Rani, et. al., 2008). Characteristic peak of Ag nanoparticles were on 38.1, 44.3, 63.7, 76.7, and 80.9. Subsequent image analysis revealed that the silver nanoparticles are relatively smaller (5- 20nm). The recyclability of nanoparticles is shown in fig 4. The mechanism of the catalytic action of nanoparticles is dependent on the nanoparticles size. The maximum resultant observed for an average particle diameter of about 20 nm. With a decrease a particle size, a trend of decreasing reaction was found for less than a diameter of about 20nm, while those above this diameter showed a steady decline of reaction rate with increasing size. It has been postulated that in the case of particles of average size less than 20nm, a downward shift of Fermi-level takes place, consequently, with an increase of band gap energy. As a result the particle requires more energy to pump electron to adsorbed ions for electron transfer reaction. This leads to a reduction in reaction rate when catalysed by smaller particles on the other hand, for nanoparticle >20nm in diameter, the change of Fermi-level is not appreciable. Catalytic activity evaluation results to the increase in the 1-50mol. % of Ag-nanoparticles increase the yield of the product (Table1). As these particles exhibit less surface area for adsorption with increase particle size, a decrease in catalytic efficiency results (Table-2). As literature said that nanoparticles worked as a catalyst for the synthesis of very biologically active compounds. Salicylaldehyde was chosen as a representative aromatic aldehyde to optimize the reaction parameters. Thus 1mmol of 1,2-Diaminopropane was treated with varying amount of salicylaldehyde using 2 equiv. of Na_2CO_3 as the base in the presence of 10 mol. % of Ag- nanoparticles in methanol. The best result for obtained on treated 1mmol salicylaldehyde with 1mmol of 1,2-Diaminopropane for 4hours. To our delight, we observed the formation of product in 75-85% yield after 4hours. The synthesized heterocyclic compounds were unambiguously established on the basis of their spectral analysis (Kalsi, 1999) (IR, ^1H NMR and mass spectral data) (Table-3).

Table-1 Catalytic activity evaluation for the synthesis of heterocyclic compounds

Entry	Ag nanoparticles (x mol %)	Time (h)	Yield* (%)
1	0	8.5	00
2	10	4.5	77
3	20	3.5	80
4	30	2.7	82
5	50	2.0	85

a. Reaction conditions: 1.0 equivalent of salicylaldehyde, 1.0 equivalent of 1,2-Diaminopropane, 2.0 equiv. of Na_2CO_3 , xmol%Ag nanoparticles(5-20nm); solvent-methanol; temperature-(60-100 °C) , O_2 (1 atmosphere) . * Isolated and unoptimised yields, yield were checked by GC (Gas chromatography)

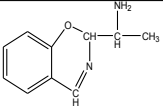
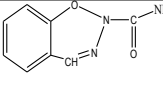
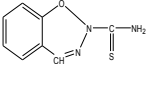
Table-2 Effect of the size on the catalytic activity of Ag-nanoparticles^a

Entry	Ag nanoparticles (x mol %)	Time (h)	Yield* (%)
1	5	5.5	76
2	10	4.5	79
3	15	3.5	82
4	20	2.7	85

^aReaction conditions: 1.0 equivalent of salicylaldehyde, 1.0 equivalent of 1,2-Diaminopropane, 2.0 equiv. of Na₂CO₃, x mol% Ag nanoparticles (5-20 nm); solvent-methanol; temperature-(60-100 °C), O₂ (1 atmosphere).

* Isolated and unoptimized yields, yield were checked by GC (Gas chromatography)

Table 3: Ag nanoparticle promoted synthesis of a library of heterocyclic compounds^a

Entry	Aliphatic Amine	Product	HR-MS M ⁺	IR (KBr), cm ⁻¹	¹ HNMR CDCl ₃ (60MHz)	Time (hrs.)	Yield ^b
1	1,2-Diamino Propane		165.1	3390, 3082, 1666, 1248, 1028	2.12 δ (s, 4H, CH-CH ₃), 1-2 δ (s, 1H, Cyl), 6.5 δ (s, 4H, Ar-H), 3.92 δ (s, NH ₂)	4.0	80
2	Semicarbazide		118.5	3386, 3053, 1648, 1620, 1269, 1009	4.35 δ (s, NH ₂), 7.5-8.5 δ (m, 4 H, Ar-H)	3.5	85
3	Thiosemicarbazide		133.9	3400, 3053, 1633, 1269, 1029	4.2 δ (s, NH ₂), 7.5-8.5 δ (m, 4 H, Ar-H)	4.2	75

^a Reaction condition: 1.0 equivalent of salicylaldehyde, 1.0 equivalent of aliphatic amine, 2.0 equivalent of Na₂CO₃, 10 mol% Ag-np (10±2 nm); solvent: methanol; 60-100 °C; O₂ (1 atmosphere).

^b Isolated and unoptimized yields

Conclusions

Our macrocyclic ligand works as reducing agent for the synthesis of Ag nanoparticles, which is a reduction system. The surface area to volume ratio of solid-supported metal nanoparticles (1-100) nm in size is mainly responsible for their catalytic properties. There is growing interest on the catalytic properties of transition metal nanoparticles. This method avoids the usage of toxic solvent and polymers. This method is efficient and greener route for the synthesis of Ag-nanoparticles and their catalytic properties used for the synthesis of heterocyclic compounds. These nanoparticles have been found in the synthesis of heterocyclic compounds and their derivatives have widely used in the treatment of hypertension, allergies, and many other popular diseases.

Acknowledgement

The authors are thankful to University of Delhi for their junior research fellowship and characterization of samples. The authors are also thankful to Director, Department of Geology, University of Delhi, for recording the XRD analysis and AIIMS, New Delhi for TEM images.

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