A Comparative Study of Reductive Capacity of Silver Nanoparticles, Ruthenium Nanoparticles and Ag-Ru Bimetallic Nanoparticles

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In the present study, silver nanoparticles (AgNPs) have been prepared by reduction of silver salts using $NaBH_4$ as reducing agent and polyvinylpyrrolidone (PVP) as stabilizing agent. Formation of AgNPs is characterized by UV-visible spectroscopy and TEM analysis. Ruthenium nanoparticles (RuNPs) have been prepared by reduction of ruthenium salts using microwave assisted glycol reduction method and PVP is used as stabilizing agent. Formation of RuNPs is characterized by TEM analysis and diffused reflectance spectra. The AgNPs and RuNPs thus formed have been used for the preparation of Ag-Ru bimetallic nanoparticles by subsequent stirring and sonication. The catalytic activity of these nanoparticles are tested by the model reaction of reduction of 4-nitrophenol to 4-aminophenol. 4-Nitrophenol is not reduced directly by $NaBH_4$. Metal nanoparticles interact with molecular hydrogen produced from $NaBH_4$ and produce active hydrogen, which reduces 4-nitrophenol. The reaction was monitored by UV-visible spectroscopy. The reduction follows first order kinetics.

Keywords: Reductive capacity, Silver nanoparticles, Ruthenium nanoparticles.

INTRODUCTION

The small sizes and large surface area, active physical and chemical properties of metal nanoparticles always attract their catalytic study [1,2]. They have found great importance in research as high potential catalysts as some of them show unusual catalytic activity [3]. They have found uses in other fields also. Silver nanoparticles are extensively used in textiles, cosmetics, hygenic products, cleaning agents, kitchen supplies, toys and building materials [4].

Silver nanoparticles are used frequently in catalysis since they need no drastic conditions to synthesize and are not environmentally hazardous [5]. It can easily be prepared from reduction of silver salts by reducing agents like aniline, $NaBH_4$ *etc.* [5,6]. Ruthenium nanoparticles have been known to display good catalytic activity [7]. Here, we have reported the synthesis of RuNPs by microwave assisted glycol reduction of $RuCl_3 \cdot 3H_2O$. Recently, bimetallic catalysts are given much importance as they are reported to display higher catalytic activity than the constituents singly. They are reported to show greater catalytic activity owing to additional degrees of freedom. But most of the neat nanoparticles are not stable. Polymers and surfactants are used to prevent their agglomeration in solution [8]. Polyvinylpyrrolidone can be used to stabilize and to prevent agglomerization of metal nanoparticles [9].

4-Aminophenol is an useful chemical which has found applications in manufacturing of analgesic and antipyretic drugs like paracetamol, as photographic developer, as anticorrosion lubricants, corrosion inhibitor *etc*. [10,11]. 4-Nitrophenol acts as a common precursor for the synthesis of 4-aminophenol. 4-Nitrophenol is a byproduct in the production of pesticides, herbicides and a pollutant with high toxicity. Therefore, a suitable and low-cost method for conversion of 4-nitrophenol to 4-aminophenol is always in great demand. Metal nanoparticles like Ag [12-16], Au [16], Ni [17], bimetallic Pt-Ni [18] are reported to show good catalytic activity towards the hydrogenation of 4-nitrophenol to 4-aminophenol. It is reported that bimetallic coinage metal nanoparticles have catalyzed 4-nitrophenol reduction with rates that strongly differ from a simple linear interpolation between the rates of the two pure metals [19].

The reduction of 4-nitrophenol to 4-aminophenol using $NaBH_4$ as reducing agent can be used as a suitable model reaction for determining the catalytic activity and kinetic study of metal nanoparticles [20]. The progress of the reaction can be monitored by UV-visible spectroscopy.

EXPERIMENTAL

The materials used were silver nitrate from E-Merck, sodium borohydrate, polyvinylpyrrolidone, ruthenium chloride, ethylene glycol from Loba Chemie and distilled water is from

Millipore filter. All the chemicals were used as such without further purification.

The solution UV spectra were recorded in HITACHI U-3210 spectrophotometer, the diffused reflectance spectra (DRS) of RuNPs was recorded in HITACHI U-4100 spectrophotometer taking Barium Sulphate as reference. For HRTEM/SAED analysis, the suspensions of metal nanoparticles in water were poured and dried on a carbon coated Cu grid and the images were recorded in a JEOL JEM-2100 electron microscope.

Preparation of silver nanoparticles: 0.2 g of polyvinyl-pyrrolidone was added pinch wise with constant stirring to 60 mL of water in a 100 mL conical flask. To the solution, 0.05 g of $NaBH_4$ in 20 mL of water is added and the resulting solution is cooled for 30 min in an ice-bath. Now, 20 mL of 10^{-3} M $AgNO_3$ solution is added drop wise and stirring was stopped as soon as all the $AgNO_3$ was added. A yellow coloured solution forms, indicating the formation of AgNPs.

Preparation of ruthenium nanoparticles: To a solution of 0.026 g of ruthenium chloride trihydrate ($RuCl_3 \cdot 3H_2O$) in 50 mL of ethylene glycol taken in a 100 mL conical flask, 0.2 g of polyvinylpyrrolidone was added pinch wise with constant stirring to get a brown colour solution. The solution was transferred to a doubled-necked round bottom flask and kept in microwave oven at 280 watt. In 2 min, colour changed from brown to light yellow, then to green. In 4 min the colour of the solution turned dark red indicating the formation of RuNPs.

Preparation of ruthenium-silver bimetallic (1:1) nanoparticles: 66.67 mL of AgNPs solution and 5 mL of RuNPs solution already prepared were taken in a 100 mL beaker, sonicated for 1 h and allowed to stand for overnight to get a grey colour solution.

Catalytic hydrogenation reaction: To study the catalytic activity of the already prepared samples of nanoparticles, 5 mL of 10^{-4} M 4-nitrophenol solution and 5 mL of freshly prepared 3×10^{-3} M $NaBH_4$ are placed in a conical flask. The catalyst was added in the mole ratio, metal:4-nitrophenol:$NaBH_4$ = 1:20:600. The amounts of the catalysts were 166.67 μL for AgNPs, 12.5 μL for RuNPs and 94.6 μL for Ag-RuNPs. The reactions were monitored by UV-visible absorption spectra. The amount of $NaBH_4$ is taken in excess in order to do the kinetic study.

RESULTS AND DISCUSSION

Characterization of catalysts: The UV-visible spectra of AgNPs showed characteristic surface plasmon resonance band at 395 nm and polyvinylpyrrolidone stabilized AgNPs at 400 nm (Fig. 1). The TEM images (Fig. 2) and particle size distribution histogram (Fig. 3), showed that the AgNPs are mostly spherical shape having diameter in the range 10-15 nm. Fig. 2 shows the SAED pattern of AgNP's crystalline nature. The diffused reflectance spectra (DRS) of $RuCl_3 \cdot 3H_2O$ shows two peaks at 580 nm and 456 nm. The reduction of Ru(III) to Ru(0) is evident from absence of the peaks in diffused reflectance spectra (Fig. 4). The TEM images (Fig. 5) confirmed the formation of ruthenium nanocubes of size in the range 2-4 nm (Fig. 6). Planes were assigned to corresponding diffraction rings from the SAED pattern indexing which confirmed the formation of crystallites of ruthenium nanoparticles having
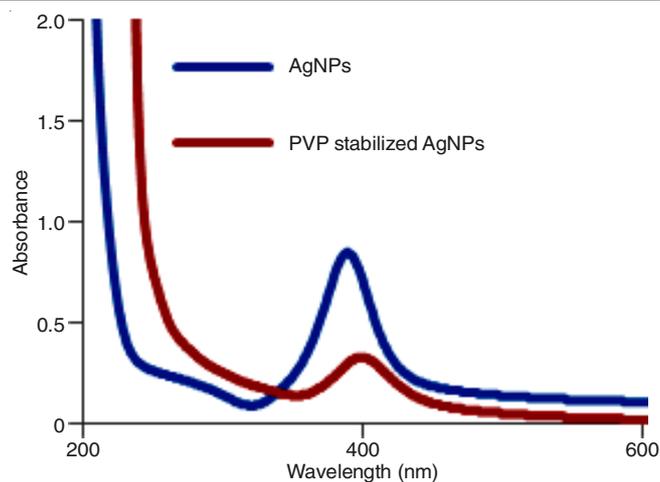

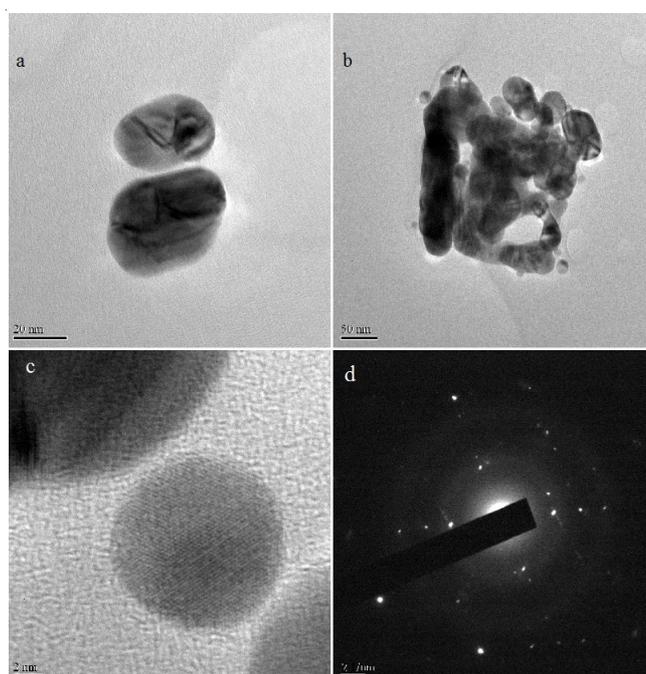
Fig. 1. UV-Visible spectra of AgNPs
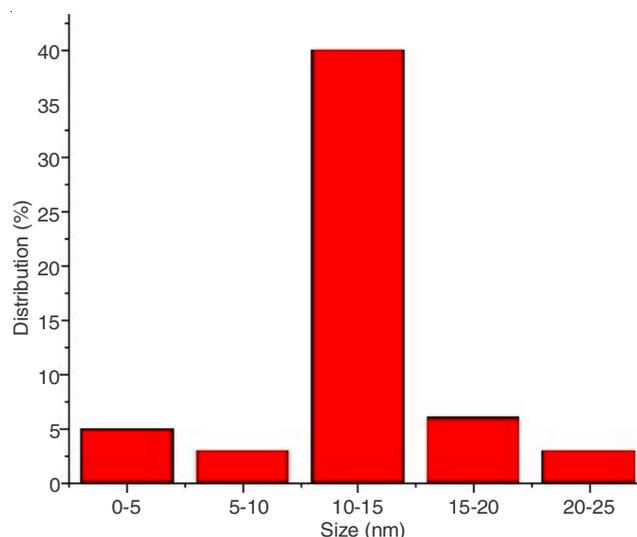

Fig. 2. TEM and HRTEM images of AgNPs

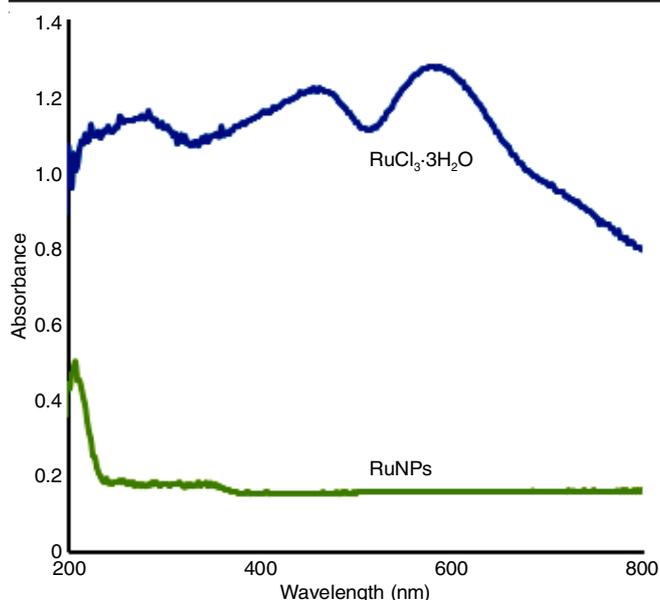Fig. 3. Particle size distribution histogram of AgNPs

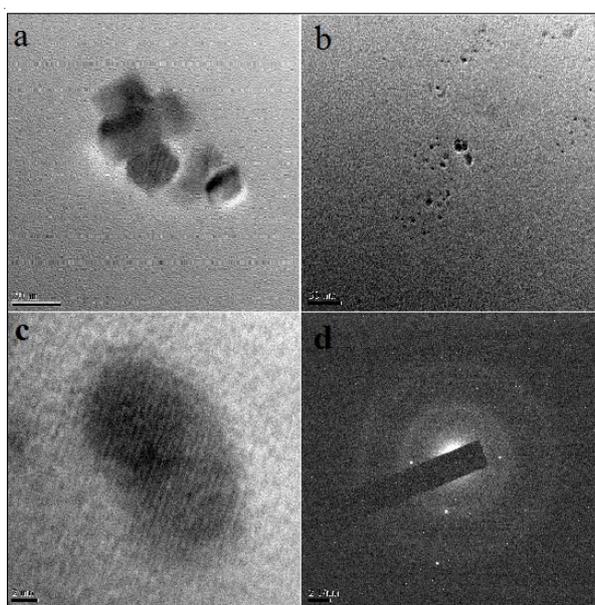Fig. 4. Diffused reflectance spectra of RuNPs

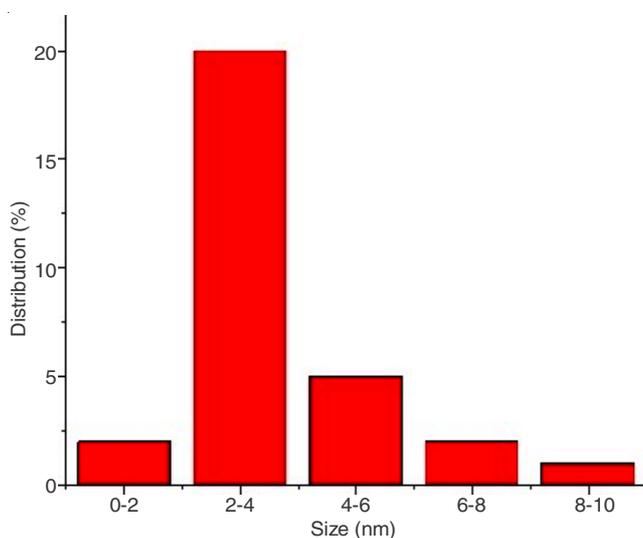Fig. 5. TEM and HRTEM images of RuNPs

Fig. 6. Particle size distribution histogram of RuNPs

fcc lattice structure. The inter-planar spacing of 0.22 nm is found from the lattice fringe of the SAED pattern of RuNPs. Fig. 7 shows the TEM and HRTEM images for bimettalic Ru-AgNPs. The SAED pattern shows lattice fringe having inter-planar spacing of 0.23 nm.
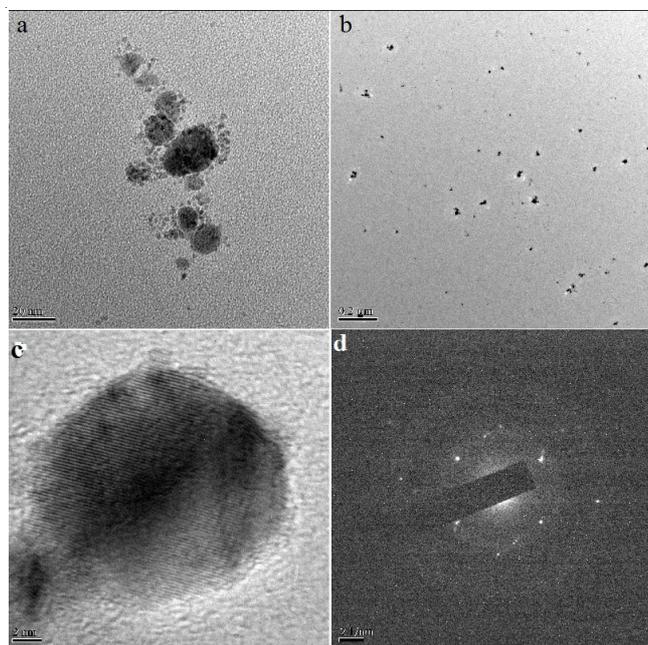

Fig. 7. TEM and HRTEM images of Ag-Ru bimetallic nanoparticles

Hydrogenation of 4-nitrophenol: The hydrogenation of 4-nitrophenol is monitored by UV-visible spectroscopy. 4-Nitrophenol shows a peak at around 315 nm. On addition of $NaBH_4$ the band shifts to higher wavelength due to the formation of phenolate ion. After the addition of catalyst, the reaction proceeds which is evident from the decrease of absorption peak due to phenolate ion and the appearance of a new peak at around 300 nm due to the formation of p-aminophenol (Fig. 8). It takes 60 min for AgNPs, 16 min for RuNPs and 10 min for Ru-Ag bimetallic nanoparticles to reduce 5mL of 10^{-4} M 4-nitrophenol solution. The hydrogenation reactions of 4-nitrophenol using the three catalysts show that the bimetallic Ru-Ag bimetallic nanoparticles act as a better catalyst than Ag and RuNPs (Table-1). Even RuNPs acts as much better catalyst than commonly used AgNPs. The apparent rate constants for the reaction using the three different catalysts are calculated using following equation:

$$k = 1/t \ \ln C_0/C_t$$

Conclusion

Ag, Ru and Ru-Ag bimetallic nanoparticles are prepared without using any drastic conditions and these are used for

TABLE-1 HYDROGENATION OF 4-NITROPHENOL USING Ag, Ru AND Ag-Ru BIMETALLIC NANOPARTICLES			
Catalyst	Amounts	Time (min)	Apparent rate constant (s^{-1})
AgNPs	2.5×10^{-8} mol (125 µL)	60	4.30×10^{-4}
RuNPs	2.5×10^{-8} mol (12.5 µL)	16	7.50×10^{-4}
Ru-Ag bimetallic NPs	2.5×10^{-8} mol (40.6 µL)	10	1.17×10^{-3}

the reduction of *p*-nitrophenol to *p*-aminophenol. The AgNPs thus prepared is stable for some days whereas the RuNPs and Ru-Ag bimetallic NPs are stable for months. Both the RuNPs and Ru-Ag bimetallic nanoparticles are much better catalyst than AgNPs.

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Fig. 8.   UV-visible spectra for reduction of 4-nitrophenol using AgNPs and RuNPs