CONTENTS

PREFACE

Nanoparticles (NPs) have extensively been used for catalytic purposes owing to their high surface area and thereby surface active sites. The nature of active sites and their density are dependent on the size, shape and composition of catalyst. Frequently, stabilizers are utilized to stimulate the activity, selectivity and stability of NPs. Several commercially important catalysts consist of active NPs dispersed on different support materials such as metal oxides, zeolites, carbon based materials. The support material may be relatively inert or may lead to the modification of chemical and adsorption properties of the catalyst in order to promote their performance for a specific catalytic reaction. Among various possibilities for support materials, graphene is a cost effective material with excellent electrical and thermal conductivity, great mechanical stability, charge transfer mobility, elasticity and very high specific surface area.

Noble metals (Gold (Au), silver (Ag) & copper (Cu)) NPs are widely used in catalysis of many important chemical transformations. Au and Ag possess excellent optical, electrical properties and higher reduction potential, therefore controlled synthesis of Au and Ag NPs have particularly attracted more attention than others. Copper also possesses comparable optical, thermal and electrical properties. Au is more expensive than Ag and Cu. From this perspective the synthesis and catalytic properties of Ag and Cu NPs need to be more intensively investigated. Nanoparticle catalysts composed of two (or more) different metal elements have an altered electronic or surface structure. This may result in improved catalyst/surface properties and hence are of great interest from both technological and scientific views. Therefore, the dependence of catalytic properties of bimetallic nanoparticles (BNPs) on their composition and nanostructure are an important area of interest.

In this thesis Ag, Cu and Ag-Cu BNPs were synthesized by different liquid phase reduction methods for investigating their catalytic properties. Various synthesis protocols were employed for tuning the size, shape and composition of Ag, Cu and Ag-Cu BNPs. The objective was to investigate the effect of their size, shape and composition on their catalytic properties. Ag and Cu precursor salts were reduced by different agents to achieve different sizes and shape of Ag, Cu and their BNPs. These metal nanoparticle syntheses were carried out in presence of different stabilizers and solvents. Catalytic activity has been demonstrated using p-nitrophenol (Nip) reduction with sodium borohydride ($NaBH_4$) as the model reaction. Commercially, $NaBH_4$ is widely used as reductant, but it is toxic and expensive, therefore there is a need of replacing it with more ecofriendly or green hydrogen sources. One such green hydrogen source is glycerol, which is a major byproduct of the biodiesel industries and is also obtained from other industrial processes involving biomass such as during the conversion of cellulose and lignocellulose. The oxidation products of glycerol also have important industrial applications such as in cosmetics. Thus, the catalytic properties of the nanoparticles prepared were investigated for the reduction of Nip by $NaBH_4$ and the green reductant glycerol. After studying catalytic properties of Ag, Cu and Ag-Cu BNPs for Nip reduction, these were also utilized for catalytic oxidative degradation of methyl orange (MO). Moreover, Ag and Cu both show localized surface plasmon resonance (LSPR) absorbance in the visible region and therefore can act as plasmonic photocatalysts under visible light irradiation. Photocatalytic activity may also be enhanced owing to stabilizers that can act as sensitizers in visible light range. For better comparison of catalytic activities obtained in the present thesis with studies in literature, turnover frequencies (TOF) are reported in this thesis.

Chapter 1 introduces the basics of catalysis. The focus is on heterogeneous and nanocatalytic mechanisms involved in the catalytic reactions. Special attention has been given to noble metal nanoparticles as nanocatalyst in different reactions. This chapter also contains detailed literature survey regarding catalytic and photocatalytic reactions involving noble metal nanocatalysts. The in-depth knowledge gained from this literature survey enabled, the framing of the scope and objectives of the present investigation which have been highlighted at the end of this chapter.

Chapter 2 defines the experimental specifications including materials used, catalytic and photocatalytic methodologies and the instrumentation which have been used to characterize the nanocatalysts prepared and studying the reaction kinetics followed by the characterization of catalytic reaction product.

Chapter 3 deals with the synthesis and catalytic properties of anisotropic silver nanoparticles (AgNPs) prepared by polyol method with Cu^{2+} acting as an etchant and poly-vinylpyrrolidone (PVP) as the stabilizer. The percentage of AgNPs formed with anisotropic shapes decreases with the amount of etchant and the average particle size of AgNPs increases. There is a linear relationship between percentage of nanoparticles with anisotropic shapes and the TOF of Nip reduction. This relation is obtained with both the reductants (Nip and glycerol). In Nip reduction with glycerol and MO oxidation two-fold photocatalytic enhancement was observed due to plasmonic property of AgNPs.

Chapter 4 describes the synthesis of curcumin stabilized silver nanoparticles (c-AgNPs). In this synthesis, silver salt solution was reduced by curcumin under probe sonication. Here curcumin acts both as the reductant and the stabilizer. The average particle size increased from ~12 to ~17 nm as the amount of curcumin was increased in the synthesis. With increase in the amount of stabilizer (curcumin) used for catalyst synthesis the rate of Nip reduction decreased, apparently because more stabilizer hinders the adsorption of substrate on catalyst surface resulting in lesser TOF. Same was the trend when glycerol was used as the reductant. However, the trend was reversed for visible light photocatalytic experiments with the c-AgNPs. That is, the photocatalytic activity increases with the amount of curcumin used in the synthesis. There is about five-fold enhancement in photocatalytic TOF of both Nip reduction by glycerol and MO oxidation. Since the HOMO-LUMO gap of curcumin lies in the visible light range, therefore, it seems that the combined effect of plasmonic AgNPs and curcumin results in the drastic enhancement in photocatalytic activity of both Nip reduction and MO oxidation.

Chapter 5 includes the synthesis, characterization and catalytic activity of copper nanoparticles (CuNPs). Two stable aqueous sols of CuNPs of different average size ~ 9 and ~ 11 nm having LSPR values of ~ 593 and ~ 500 nm respectively, were prepared by reducing copper salt solution with strong reducing agent, alkaline hydrazine hydrate (AHH) in presence of PVP as a stabilizer. The catalytic activities of the PVP stabilized CuNPs catalysts were measured for Nip reduction with $NaBH_4$ and glycerol. MO oxidation is also studied with these catalysts. Significantly higher TOF values were obtained compared to CuNPs reported in literature for Nip reduction. The TOF obtained for smaller CuNPs was better than the other. This is also supported by lower activation energy for Ni**p** reduction by $NaBH_4$. Visible light photocatalytic experiments with CuNPs also demonstrated threefold enhancement as compared to the results obtained for normal catalysis.

Chapter 6 describes the investigations into the catalytic properties of Ag-Cu BNPs. These are also compared with pure AgNPs and CuNPs. Ag-Cu BNPs were synthesized by chemical reduction and polyol route of synthesis. By varying the synthesis protocol three types of Ag-Cu BNPs were obtained. Thus, using polyol method the reduction was carried out at ~ 175 ^{0}C in presence of PVP stabilizer. Three silver to copper precursor salt ratios (1:1), (2:1) and (4:1) were taken to obtain Ag-Cu BNPs with different compositions. The average particle sizes also change with the bimetallic composition. Synergistic effect was observed for Ag-Cu BNPs with the ratio (1:1) when Nip reduction was carried with both the reductants. No photocatalytic enhancement could be observed when glycerol was used as reductant. However, visible light photocatalytic enhancement was observed for MO oxidation only when (1:1) Ag-Cu NPs were used as the photocatalysts.

Core shell BNPs were prepared by step wise reduction of core metal salt precursor followed by shell metal precursor salt in ethylene glycol. Utilizing this method, two variations of core shell BNPs were obtained Ag@Cu and Cu@Ag with an average particle size of ~ 220 nm. Both BNPs shows better TOF values and photocatalytic enhancement. Among all the investigated Ag-Cu BNPs, Ag@Cu core shell NPs shows excellent catalytic properties in Nip reduction with glycerol and MO oxidation both thermally and photo catalytically. Ag-Cu BNPs (1:1) and Ag@Cu demonstrate comparable TOF for Nip reduction with $NaBH_4$ and photocatalytic MO oxidation.

In last protocol for Ag-Cu bimetallic nanoparticle preparation, aqueous copper precursor salt solution was added to the $Ag(NH_3)_2^+$ complex with simultaneous addition of strong reducing agent AHH at 60^0C. Two silver to copper precursor salt ratios were considered. This synthesis protocol gave rise to Ag-Cu BNPs of average particle sizes 45 and 60 nm respectively for 1:2 and 1:4 Ag:Cu precursor salt ratios. Due to the smaller sizes of these BNPs the TOF of Nip reduction with glycerol was comparatively better than the BNPs obtained with polyol method.

Chapter 7 considers the effect of reduced graphene oxide support material on catalytic properties of Ag, Cu and Ag-Cu BNPs. To obtain the composites of Ag, Cu and Ag-Cu BNPs with rGO, firstly adsorption of metal salts on to the surface of graphene oxide is carried out followed by reduction with a strong reducing agent AHH at 60 ^{0}C. Here also Ag-Cu (1:1) BNPs supported on reduced graphene oxide showed synergistic effect for Nip reduction and MO oxidation. Remarkable enhancement in photocatalytic TOF for MO was observed. It appears that absorption of visible light results in plasmonic excitation of electron. The electron may be transferred directly to the adsorbate or could be taken up by graphene preventing electron-hole recombination.

Chapter 8 summarizes the catalytic activity, of different types of nanoparticles/composites prepared as a part of this thesis. The comparison enables the delineation of the best catalytic system, among those considered in this work and also with those in the literature (if any), for the three different reactions investigated. Separate comparisons are made for each reaction, since the mechanism involved is specific. Then, at the end, a short discussion on the future scope of this work is presented.