8.1 Overview

This chapter compares the catalytic properties, of different types of nanoparticles/composites prepared as a part of doctoral thesis. This is being done to draw additional inferences. Such comparison enables the delineation of the best catalytic system, among those considered and also with those in the literature (if any), for the three different reactions investigated. Given the incremental nature of modifications made in the nanoparticles/composites studied in each chapter, this could also enable better understanding of some aspects of the mechanism(s) involved. In the following the comparisons are made for each reaction separately, since the mechanism involved will be specific. As mentioned earlier, for the reactions studied in this thesis, mostly of the publications in literature have given the TOF (or the PTOF) values. Therefore, in such cases, these values have been calculated using the information given in the respective publication in literature. Thereafter, at the end, a short discussion on the future scope of this work is presented.

8.2 Catalytic reduction of Nip by $NaBH_4$

Table 1 gives the order and the TOF value of this reaction when it was catalyzed by different nanoparticles/composites. The first thing to note is that for all catalysts used the order of the reaction is always 1. This is in agreement with the existing literature. The best TOF values are obtained for curcumin stabilized AgNPs samples, A1 and A2. It must also be mentioned that these c-AgNPs are the smallest (excepting CuNPs) among all nanoparticles synthesized with some Ag component in it. However, the difference between these values and the TOF values of other systems is quite large. Therefore, it is quite clear that curcumin stabilization affects the catalytic properties. But larger amount of curcumin stabilization decreases the activity in relative terms. On the other hand, anisotropy also influences the catalytic properties.

Table 8.1. Comparison of Turn over frequencies for Nip reduction with $NaBH_4$.

Catalyst		Thermal		Reference
		Order	TOF (min^{-1})	
AgNPs (Polyol) (Chapter 3)	C0	1	~ 160	This work
	C1	1	~ 386	This work
	C2	1	~ 302	This work
	C3	1	~ 258	This work
	C4	1	~ 170	This work
c-AgNPs (Chapter 4)	A1	1	~ 1081	This work
	A2	1	~ 1600	This work
AgNPs		1	~ 40	[Chang *et al*. (2012)]
AgNPs/PANINF		1	~ 202	[Chang *et al*. (2012)]
AgNP-PG-5K		1	~ 320	[Baruah *et al*. (2013)]
CuNPs (Chapter 5)	B1	1	~ 356	This work
	B2	1	~ 673	This work
CuNPs		1	~ 0.012	[Deka et al. (2014)]
Cu Cubes		1	~ 136	[Zhang et al. (2013)]
SiNWAs–cu		1	~ 220	[Yang et al. (2014)]
Ag-Cu BNPs (Polyol) (Chapter 6)	S1	1	~ 180	This work
	S2	1	~ 399	This work
	S3	1	~ 192	This work
	S4	1	~ 179	This work
	S5	1	~ 161	This work
Pd-Ag		1	~ 43	Janairo (2015)
Ag-Cu BNPs (Chapter 6)	S6	1	~ 367	This work
	S7	1	~ 212	This work
Ag@Cu (Chapter 6)	S8	1	~ 112	This work
Cu@Ag (Chapter 6)	S9	1	~ 125	This work
Cu_2O@Ag		1	~ 4	Kandula and Jeevanandam (2016)
Ag-Cu/rGO composite (Chapter 7)	G1	1	~ 184	This work
	G2	1	~ 96	This work
	G3	1	~ 225	This work
	G4	1	~ 74	This work
	G5	1	~ 98	This work
Ag-Au/rGO		1	~ 3	Hareesh et al. (2016)

Thus sample C1, which has the highest fraction of anisotropic nanostructures, also exhibits high TOF value for this reaction. CuNPs are much more economical, but they also give catalytic activity similar to that found for C1. Among BNPs high synergistic

catalytic activity is observed for S2. Considering the larger sizes of these BNPs prepared by polyol techniques, it may be concluded that bimetallic composition and nanostructures always exhibit better activities. Comparable activities are found when Ag shell Cu core BNPs are used for catayzing this reaction. Finally synergistic activity is also observed when BNPs/rGO composites catalyze this reaction. However, absolute values are not as good as those obtained when S2 or S6 BNPs catalyzed reactions.

8.3 Nip reduction by Gly

As discussed earlier, Gly is an environmentally friendly, renewable and cheap substance. Moreover, the oxidation products of Gly are also important intermediates in the chemical industry. Therefore, the advantages of using such a green hydrogen source, instead of $NaBH_4$, far outweigh the relatively lesser TOF values found in this case. Though comparing only the cases where the experiment was carried out in absence of light, CuNPs, core-shell BNPs, and S8, S9 exhibit zero order kinetics but rest of the catalysts lead to second order kinetics with respect to Nip. This indicates the difference in mechanism between the two cases. Among the normally catalyzed cases, C1 and S6 gave the best catalytic activities for this reaction. Moreover, the TOF value obtained when S6 was used as the catalyst exceeds the other catalytic activity values by far. It seems having a core-shell geometry with the higher reduction potential metal as core provokes more active sites on the shell. A comparison with respect to activation energies is not made here since similar activation energies have been found for these reactions with other catalysts as well, but the TOF values are much lower. No reduction was possible when BNPs/rGO composites were the catalysts. Since this type of BNPs does show reasonably good catalytic activity alone, therefore, from this it can be inferred that, possibly, r-GO does not allow the adsorption of glycerol on the composite surface.

The visible light plasmonic enhancement was drastic in case of A1. The

enhancement was not that much when A2 was used. This clearly demonstrated the different roles curcumin plays in the thermal and the photocatalytic cases as discussed in Chapter 4. Plasmonic light re-emission leads to much enhanced sensitising properties of curcumin. An excess of curcumin on the surface results in better photocatalytic activity, in contrast to the experiment done in absence of light. Comparable photocatalytic activity values are obtained when anisotropic AgNPs (C1 and C2) are used as the catalysts. Overall, the photocatalytic activity of core-shell S6 still remains the best, although the plasmonic photocatalytic one is the best.

Table 8.2. Comparison of thermal and photocatalytic Turn over frequencies for Nip reduction with Gly.

Catalyst		Thermal		Photocatalytic	
		Order	TOF (min^{-1})	Order	PTOF (min^{-1})
AgNPs (Polyol) (Chapter 3)	C0	2	~ 3.6	2	~ 8.3
	C1	2	~ 13.5	2	~ 21.9
	C2	2	~ 11.8	2	~ 20.2
	C3	2	~ 9.4	2	~ 19.4
	C4	2	~ 9.7	2	~ 17.6
c-AgNPs (Chapter 4)	A1	2	~ 3.9	0	~ 22.0
	A2	2	~ 5.7	0	~ 12.0
CuNPs (Chapter 5)	B1	0	~ 2.5	0	~ 6.0
	B2	0	~ 3.5	0	~ 4.5
Ag-Cu BNPs (Polyol) (Chapter 6)	S1	2	~ 3.6	2	~ 8.3
	S2	2	~ 5.0	2	~ 4.1
	S3	2	~ 3.5	2	~ 3.2
	S4	2	~ 2.7	2	~ 2.5
	S5	2	~ 1.3	2	~ 2.1
Ag-Cu BNPs (Chapter 6)	S6	0	~ 26.0	2	~ 32.0
	S7	0	~ 9.0	2	~ 14.0
Ag@Cu (Chapter 6)	S8	0	~ 5.7	0	~ 10.5
Cu@Ag (Chapter 6)	S9	0	~ 7.7	0	~ 14.0

8.4 Fenton like MO oxidative degradation

In absence of light, MO oxidative degradation, exhibits second order kinetics with all catalysts, except BNPs/rGO composites. For these composite particles, the MO degradation follows zero order kinetics. Another aspect is that all BNPs/rGO composites exhibit higher activities, with G3 exhibiting the best (synergistic) value. Clearly the mechanism followed by the reaction catalyzed by BNPs/rGO is different from other nanostructures. Other than the BNPs/rGO composites, the best TOF is found for S2 (polyol BNPs). Moreover, here as well BNPs systems do exhibit synergistic catalytic activities.

Table 8. 3. Comparison of thermal and photocatalytic Turn over frequencies for oxidative MO degradation.

Catalyst		Thermal		Photocatalytic	
		Order	TOF (min^{-1})	Order	PTOF (min^{-1})
AgNPs (Polyol) (Chapter 3)	C0	2	~ 1.5	2	~ 3.0
	C1	2	~ 3.0	2	~ 6.0
	C2	2	~ 1.8	2	~ 5.8
	C3	2	~ 1.2	2	~ 2.8
	C4	2	~ 1.0	2	~ 3.2
c-AgNPs (Chapter 4)	A1	2	~ 0.9	0	~ 5.1
	A2	2	~ 1.4	0	~ 2.8
CuNPs (Chapter 5)	B1	2	~ 0.5	0	~ 1.5
	B2	2	~ 1.2	0	~ 1.7
Ag-Cu BNPs (Polyol) (Chapter 6)	S1	2	~ 1.0	2	~ 1.1
	S2	2	~ 5.0	2	~ 7.4
	S3	2	~ 2.9	2	~ 2.6
	S4	2	~ 1.8	2	~ 2.9
	S5	2	~ 1.3	2	~ 2.8
Ag-Cu BNPs (Chapter 6)	S6	2	~ 4.0	0	~ 7.4
	S7	2	~ 2.1	0	~ 5.0
Ag-Cu BNPs (Chapter 6)	S8	2	~ 1.6	2	~ 2.9
Cu@Ag (Chapter 6)	S9	2	~ 2.2	2	~ 3.1
Ag-Cu/rGO composite (Chapter 7)	G1	0	~ 12.0	0	~ 15.0
	G2	0	~ 7.0	0	~ 14.0
	G3	0	~ 15.0	0	~ 18.0
	G4	0	~ 5.0	0	~ 12.0
	G5	0	~ 10	0	~ 8.0

Again, the best photocatalytic enhancement is obtained when A1 was used as the catalyst. However, the value is still not near to the values found when rGO based composite particles are used for this purpose. The enhancement is also quite good when ansiotropic AgNPs samples C1 or C2 are used. The order of the reaction does not change when rGO based composite particles are the catalyst for the reaction carried out under visible light. Therefore, the mechanisms remain the same, with plasmonic excitation of electrons enhancing the photocatalytic activity.

8.5 Future scope of this work

In conclusion, this thesis emphasizes that the anisotropic shapes, composition, size and stabilizers having sensitizing effect significantly influence the catalytic activity of Ag, Cu and their bimatallic nanoparticles. Therefore, the following aspects can be considered for future study:

- Synthesis of isotropic shapes of mono and bimetallic nanoparticles with uniform sizes can be investigated for their catalytic activities.
- Detailed plasmonic activity of Ag, Cu and their BNPs need to be investigated.
- Other photoactive sensitizers can also be studied in place of curcumin.
- Effect of visible light intensity on plasmonic photocatalytic activity of these catalysts can also be studied.
- Effect of other support materials, such as other carbon derivatives in the stability and reusability of catalyst need to be investigated.