6.1 Introduction

An ever-increasing interest is evinced in recent years on the controlled synthesis of nanometer-sized metal species (Ag, Au, Pt, Pd, etc.) namely metal nanoparticles or colloids, and their application in many fields particularly in catalysis.\(^1\) Synthesis of more efficient, cost-effective noble metal nanocatalysts is of great importance to utilize them in the synthesis of a variety of important compounds. Two key factors determining the catalytic performance of such catalysts are the particle size and the suitable supports used for the dispersion of the noble metals on them.\(^{1b,c}\) The reduced particle size greatly enhances the surface-to-volume ratio, and facilitates improved catalytic performance of the noble metals.\(^2\) Among a wide variety of metal nanoparticles (MNPs) synthesized, gold is of particular interest because of its fascinating properties and potential applications in catalysis,\(^3-7\) biosensing,\(^8\) drug delivery,\(^9\) optics,\(^10\) cancer\(^11\) and electronics.\(^12\)

The metal nanocatalysts can be synthesized by various methods according to the “organic” or “aqueous” nature of the media, the nature of the precursor and, finally, the type of the stabilizers used.\(^{13}\) Various protecting agents, such as polymers, surfactants, ligands, cyclodextrins, calixarenes, dendrimers and ionic liquids, have been used.\(^{14}\) Among these various stabilizers, polymers displaying steric stabilization are strategically considered due to the border with a homogeneous approach. The organic compounds carrying amino group have been widely used for preparing metal nanoparticles because of their simplicity and wide variability. Recently, the use of linear and branched polymer polyethylenimine (PEI) as a reducing and protective agent has been reported.\(^{15-20}\) The alkylated PEI is also used to generate AuNPs.\(^{21,22}\) Though the transition metal nanoparticles have wide ranging applications in catalysis, their tendency to agglomerate during the reactions need to be stabilized for effective utilization.\(^{23}\) PEI is a cationic polymer and the cationic character is derived from the positive charges located on the nitrogen atoms of the polymer backbone (the nitrogen atoms in PEI are present in the form of primary, secondary, and tertiary amines in the molar ratio of 1:2:1).\(^{24}\)

The cationic nature of polymer (PEI) has been widely used in biology, particularly for cell transfection,\(^{25}\) gene vectors,\(^{26}\) and RNA delivery systems.\(^{27}\)
The chemical reduction of nitro group with sodium borohydride (NaBH₄) is extremely slow, and the use of a catalyst is necessary. The final product resulting from this chemical reaction of p-nitro aniline is the p-phenylene diamine which is widely used in industry as an intermediate in the preparation of polymers, azo dyes, dyestuffs and rubber antioxidant. In consequence, efficient catalysts for the chemical reduction of 4-nitroaniline or other nitro compounds have potential industrial applications. Pal and co-workers were the first to identify the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) by sodium borohydride as a model reaction in aqueous medium at room temperature. The progress of the reaction can be easily monitored via UV-vis spectroscopy.

In this context, polymer-stabilized metal nanoparticles are of special interest because polymers can be used to tailor the properties of nanoparticle assemblies. In addition, incorporation of nanoparticles into the polymer matrix can modify the physical properties of the polymer. The combination of the properties of nanoparticles (e.g., optical) and macromolecules (e.g., swelling or shrinking) provides an avenue to prepare composite materials with unique properties compared to the individual nanoparticle and polymer components. In this respect, polymer-nanoparticle composite materials are used in catalysis.

A simple route of AuNPs (diameter <3 nm) synthesis is recently reported using poly(allylamine), PAAm, as both reducing and stabilizing agent to form a PAAm-AuNPs composite. The dual role of the polymer in the synthetic method is an additional advantage in catalysis which results in the formation of stable water-soluble AuNPs. Literature reports show that the attraction between nanoparticles and polymer is essential in order to disperse the particles and control the organization for specific applications. In most cases, the nanoparticle surface is functionalized with polymers containing an amine terminal group, and dispersion of AuNPs in the solution or on the sample matrix is induced due to electrostatic interactions.

In this work, we have investigated the catalytic activity of PEI and PEI-C₁₂ stabilized AuNPs as catalyst in the reduction of 4-nitrophenol (4-NP) with NaBH₄ to produce 4-aminophenol (4-AP) as a model reaction shown in Scheme 6.1. The catalytic performance in terms of the rate constant and the induction period is
discussed through the comparison with the PEI and PEI-C\textsubscript{12} capped AuNPs catalysts reported so far. Our catalysts appear to exhibit the better performance.

Scheme 6.1 Reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) using the AuNPs as catalyst as a model reaction.

The catalytic activity of AuNPs as a selective catalyst for the reduction of 4-NP to the corresponding 4-AP in nearly good yield as a function of their size as a model reaction is investigated.

6.2 Experimental Section

6.2.1 Synthesis of PEI-C\textsubscript{12} capped AuNPs

The acylated polyethylenimine (PEI-C\textsubscript{12}) is prepared by the reported procedure.\textsuperscript{36} The method to synthesize the PEI stabilized AuNPs is similar to that reported earlier.\textsuperscript{15,37,38} In a typical preparation, an aqueous solution of HAuCl\textsubscript{4} (1.4 mM, 25 mL) is added to 1.0 \% (w/w) of PEI or PEI-C\textsubscript{12} (1.0 mL) in round bottom flask. The reaction mixture is stirred vigorously at ambient temperature for about 3-5 h when PEI was used. On the other hand the reaction mixture is heated to 80\textdegree C when PEI-C\textsubscript{12} is used. We notice that the color of the reaction mixture is changed from pale brown to dark red, indicative of the formation of colloidal AuNPs. In fact, the size of the AuNPs is dependent on the amount of polymer added into the reaction mixture. After the completion of the reaction the reaction mixture is ultracentrifuged and filtered, and then the precipitate is washed with copious amounts of deionized water. The polymer capped AuNPs thus obtained are redispersed in water. The surface plasmon resonance (SPR) band of AuNPs appears
at 520 nm in the UV/vis spectrum. This procedure results in the spontaneous formation of AuNPs without the addition of an extra reducing agent. A detailed procedure for the synthesis of the AuNPs stabilized on the PEI-C$_{12}$ matrix is illustrated in Scheme 6.2.

Scheme 6.2 Schematic representation of synthesis of AuNPs by using PEI-C$_{12}$ polymer.

### 6.2.2 Catalytic reduction of 4-nitrophenol

The catalytic reduction reaction is carried out in a standard quartz cell with a 1 cm path length and about 3.0 mL volume. The reaction procedure is as follows: Ice cold NaBH$_4$ (1.0 mL of a 15 mM solution in water) is mixed together with 4-NP (1.5 mL of a 0.20 mM solution in water) in the quartz cell; this results in the change of color from light yellow to yellow-green immediately after addition of AuNPs (0.5 mM). The absorption spectra are recorded with a time interval of 2 sec at room temperature (25°C). The control experiment is also carried out using the mixture of NaBH$_4$ and 4-nitrophenol in the presence of AuNPs and absence of ice cold NaBH$_4$ as given in section 6.3. The absorption spectrum of 4-nitrophenol is unaltered in the
absence of AuNPs. The rate constant of the reduction process is determined by measuring the change in absorbance of the initially observed peak at 400 nm, for the nitrophenolate ion, as a function of time.

6.2.3 Catalytic reduction of 4-nitroaniline

The catalytic reduction reaction is 4-nitroaniline of also carried out following a procedure similar to that used for the reduction of 4-nitrophenol.

6.3 Results and discussion

6.3.1 XRD analysis

After mixing aqueous HAuCl₄ with PEI, the solution is allowed to stir at room temperature for 3-5 h, and colorless homogeneous solution becomes dark red indicating the formation of AuNPs. It is worth noting that in the synthesis, AuNPs are prepared without adding extra reductants. The reduction of gold ions is carried out by amino groups of PEI. XRD pattern obtained is represented in Figure 6.1.

![XRD pattern of AuNPs in PEI-C₁₂ matrix.](image)

Figure 6.1 XRD pattern of AuNPs in PEI-C₁₂ matrix.

X-ray diffraction study is used to confirm the crystalline nature of the particle in solution. The XRD pattern shows intense peaks corresponding to [111], [200],
[220] and [311] Bragg's reflection based on the fcc (face-centred-cubic) structure of AuNPs. The sharp intense Bragg's peaks indicate the formation of gold nanoparticles. The mean size (15.2 nm) of AuNPs is calculated using the Debye-Scherrer's equation by determining the width of the Bragg reflections. It reveals that the product possesses face-centred-cubic structure with a high crystallinity.

6.3.2 TEM analysis

Transmission electron microscopy analysis provides information about the size and shape of the PEI stabilized AuNPs as shown in Figure 6.2.

![Figure 6.2 TEM images of PEI capped AuNPs (a-d); Inset figure of (d) shows respective SEAD pattern.](image)

The TEM image shows that the AuNPs are predominantly spherical in morphology with their size ranging from 10 to 18 nm with an average size of about 15±3 nm. These PEI-capped AuNPs are remained stable for several months without
any obvious colloidal aggregation. The results of TEM analysis confirm the formation of AuNPs with individual particle sizes of ca. 15 nm and their respective SAED are shown in Figure 6.2d.

6.3.3 HRTEM analysis

HRTEM images of the PEI-C\textsubscript{12} capped AuNPs are recorded using the high-resolution mode, showing that the nanoparticles are in a crystalline state as shown in Figure 6.3a-d. HRTEM images of individual and high-magnification of PEI-C\textsubscript{12} capped AuNPs are shown in Figures 6.3c inset figure and 6.3d.

![HRTEM images of PEI-C\textsubscript{12} capped AuNPs (a-d).](image)

Figure 6.3 HRTEM images of PEI-C\textsubscript{12} capped AuNPs (a-d). HRTEM images, indicate (a) 1\(\mu\)m, (b) 50 nm, (c) 10 nm and (d) 5 nm; Inset of figure (d) shows respective SAED pattern.
Spacing as observed for the [111] plane from the electron diffraction pattern these HRTEM images agree well with the powder XRD results. HRTEM image also shows well resolved [111] face-centered-cubic lattice fringes, suggesting that the nanocrystals are highly crystalline in nature as shown in Figures 6.3c and 6.3d. The SAED pattern of the AuNPs shows clear rings ascribed to Au crystals of the face-centered cubic (fcc) structure (Figure 6.3d inset). On the basis of HRTEM and SAED analysis, it can also be confirmed that each Au nanoparticle is a single crystal in spherical shape and its average diameter is about 5-6 nm. The average diameter of AuNPs estimated from the Gaussian fit of the particle size distribution histograms is about 5-6 nm. Concerning PEI polymers supported Au catalysts, the structures and surface functional groups of polymers are expected to play important role to stabilize small AuNPs preventing them from aggregation and to exhibit significant catalytic activity, because of the strong interaction between polymer and AuNPs. The crystalline nature of the nanoparticle is revealed from the corresponding electron diffraction pattern (inset in Figure 6.3d) of single Au nanocrystals. The observed diffraction spots indicate that the product is a single crystal and may have grown preferentially along the [111] direction.

6.3.4 AFM analysis

The AFM images of AuNPs are shown in Figures 6.4a and 6.4b. Figure 6.4a shows the topographic image while Figure 6.4b is in the 3-D mode. Since AuNPs exhibit physical properties different from bulk gold and the properties largely dependent on their size and structure, a good structural characterization becomes necessary.
Figure 6.4 (a) AFM image of PEI-C\textsubscript{12} stabilized AuNPs in (a) 2D and (b) the 3D representation.

A good dispersion of the AuNPs is possible to image them individually using AFM. The AFM results perfectly match with the results obtained from TEM and HRTEM studies. Further, this technique enables measuring the size of the particle, considering the particle height rather than its width because the particle may be distorted by the AFM tip geometry. Sun \textit{et al.}\textsuperscript{41} have reported that an increase in the molar ratio of PEI-C\textsubscript{12} to gold precursor led to increasing particle size. Figure 6.4a shows an average particle size of AuNPs as \textasciitilde10-20 nm and are separated from each other.

6.3.5 UV-visible absorption spectral study

AuNPs exhibit strong surface plasmon resonance (SPR) absorption that is dependent on the size and shape of particles. For spherical AuNPs, the SPR band maximum generally falls at \(\lambda_{\text{max}} = 520\) nm.\textsuperscript{48} As shown in Figure 6.5 for PEI stabilized AuNPs, the absorption band of the AuNPs appeared at \(\lambda_{\text{max}} = 520\) nm is due to the SPR band of the AuNPs,\textsuperscript{43-45} which confirmed the formation of AuNPs under the assistance of polymers.
Figure 6.5 UV-vis spectra of AuNPs prepared by stirring 1.0 mL of 1.4 mM aqueous HAuCl$_4$ with (a) 0.5, (b) 1.0, (c) 1.5 and (d) 2.0 wt % of (3 ml) aqueous PEI solution 3-5 h.

Here PEI acts simultaneously as both protective and reducing agent, thereby significantly simplifying the process for preparing the AuNPs in aqueous medium. In this effort, the concentration of PEI (1-2 %) is varied and the particle size of the resulting products is analyzed as shown in Figure 6.5. Initially, as shown in Figure 6.6a, the aqueous AuCl$_4^-$ solution shows one distinct band at $\lambda_{\text{max}} = 310$ nm caused by the ligand ($\pi$)-to-metal ($\sigma^*$) charge-transfer transition.$^{52}$

Figure 6.6 UV-vis spectra of (a) HAuCl$_4$ solution, (b) mixture of HAuCl$_4$ and PEI solution (c) SPR band of AuNPs. The inset figure shows the absorbance at 520 nm.
The band at $\lambda_{\text{max}} = 310$ nm disappears immediately when PEI is added to the solution (Figure 6.6a). After 3 h, a new band develops at $\lambda_{\text{max}} = 520$ nm (Figure 6.6c) that can be attributed to the surface plasmon resonance (SPR) band of AuNPs. Polymer capped AuNPs are synthesized using water as solvent and the reaction time is 3-5 h respectively. The color change of the reaction process is shown in Figure 6.7.

![Figure 6.7 Color changes of the reaction solution during the course of the AuNPs formation.](image)

The color changes indicate the formation of colloidal AuNPs in PEI polymer matrix. The addition of PEI to HAuCl$_4$ results in the change of color from light yellow to an orange color solution. Gentle swirling with constant stirring for 3-5 h for the time interval for 30 mins, facilitates the formation of a wine red (d-j) colored AuNPs solution. After the formation of AuNPs the stirring is continued for 5-10 min to ensure the completion of reaction. The redox reaction between the amine groups of PEI and Au$^+$ is responsible for the formation of AuNPs. However, Li et al. have confirmed the stabilization of Au colloids with polyelectrolytes which are capable of combining both steric and electrostatic stabilization resulting in electrosteric stabilization.

### 6.3.6 Fluorescence spectroscopy

In the case of gold nanoparticles, $5d$ valence and $6sp$-conduction electrons are responsible for fluorescence spectra. Liao et al. and Varnavski et al. have reported that 15 nm AuNPs are fluorescent. The luminescence spectra of PEI and PEI-C$_{12}$ capped AuNPs, (excitation wavelength at $\lambda_{\text{max}} = 450$ nm) show the emission...
maxima at $\lambda_{\text{max}} = 630$ nm and $\lambda_{\text{max}} = 610$ nm as shown in Figure 6.8. The reason for the photoluminescence is attributed to the interband transition from $sp$-conduction band above the Fermi level to the $d$ band below the Fermi level. The radiative recombination of electron-hole pairs between this $d$-band and $sp$-conduction band produces emission,\textsuperscript{49-55} which occurs at $\lambda_{\text{max}} = 610$ nm for linoleic acid protected AuNPs (8-15 nm), when excited with $\lambda_{\text{max}} = 450$ nm. Moreover, the adsorbed linoleic acid on AuNPs surface further enhances the intensity of emission.\textsuperscript{51-54}

Figure 6.8 Fluorescence spectra of (a) PEI and (b) PEI-$C_{12}$ capped AuNPs.

6.3.7 FT-IR spectroscopy

The functional group vibration peaks for pure PEI, Au-PEI and Au-PEI-$C_{12}$ are recorded and the FT-IR spectra are shown in Figure 6.9 and the data are collected in Table 6.1.
Figure 6.9 FT-IR spectra of (a) neat PEI (b) PEI capped AuNPs and (c) PEI-C$_{12}$ capped AuNPs.

Table 6.1 FT-IR spectral data of PEI, Au-PEI and Au-PEI-C$_{12}$ coated AuNPs.

<table>
<thead>
<tr>
<th>Band assignment$^{[a]}$</th>
<th>PEI (cm$^{-1}$)</th>
<th>Au-PEI (cm$^{-1}$)</th>
<th>Au-PEI-C$_{12}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_{as}$ NH$_2$</td>
<td>3346</td>
<td>3340</td>
<td>-</td>
</tr>
<tr>
<td>$v_1$ NH$_2$</td>
<td>3286</td>
<td>3279</td>
<td>3299</td>
</tr>
<tr>
<td>$\delta$ NH (O)</td>
<td>1598</td>
<td>1591</td>
<td>1554</td>
</tr>
<tr>
<td>$v_2$ C-N</td>
<td>1120</td>
<td>1110</td>
<td>1122</td>
</tr>
<tr>
<td>$v_1$ NH$_2$</td>
<td>1664</td>
<td>1666</td>
<td>-</td>
</tr>
<tr>
<td>$v_{as}$ CH$_2$</td>
<td>2939</td>
<td>2942</td>
<td>2921</td>
</tr>
<tr>
<td>$v_1$ CH$_2$</td>
<td>2886</td>
<td>2892</td>
<td>2852</td>
</tr>
<tr>
<td>$v_2$ C-N</td>
<td>2819</td>
<td>2822</td>
<td>2822</td>
</tr>
<tr>
<td>$\delta$ CH$_2$</td>
<td>1460</td>
<td>1455</td>
<td>1461</td>
</tr>
<tr>
<td>CH$_2$ (w)</td>
<td>1355</td>
<td>1355</td>
<td>1373</td>
</tr>
<tr>
<td>CH$_2$ (tw)</td>
<td>1294</td>
<td>1298</td>
<td>1299</td>
</tr>
<tr>
<td>C=O</td>
<td>-</td>
<td>-</td>
<td>1643</td>
</tr>
</tbody>
</table>

$^{[a]}$Assignments: $v$ (stretch), $\delta$ (bend), w (wagging), tw (twisting) o (overtone).
Subscripts $as$ and $s$ denote asymmetric and symmetric vibrations respectively.
As shown in Figure 6.9, the FT-IR peaks related to the amine functional groups of PEI-C$_{12}$ showed a clear change in terms of both peak frequency and relative peak intensity compared with the FT-IR peaks of pure PEI. For example, asymmetric and symmetric stretching peaks of NH$_2$ group of PEI are observed at 3346 and 3286 cm$^{-1}$, but only one broad peak is observed at 3279 cm$^{-1}$ in the FTIR spectrum of Au/PEI. The stretching frequency peak of functional group amide (C=O) at 1643 cm$^{-1}$ is observed in PEI-C$_{12}$ capped AuNPs.$^{57,58}$ Therefore, the amine groups are strongly bound on the surface of AuNPs through the Au-N bond.

### 6.3.8 Catalytic activity

In order to test the catalytic activity of the above polymer capped AuNPs, the well-established catalytic reduction of 4-NP with NaBH$_4$ is used and the progress of the reaction is followed spectrophotometrically using the standard UV-vis absorption spectrometer.$^{59,60}$ It is seen that an absorption peak of 4-NP at $\lambda_{\text{max}} = 317$ nm undergoes a red shift to $\lambda_{\text{max}} = 400$ nm (due to the generation of 4-nitrophenolate ion) immediately upon the addition of aqueous solution of NaBH$_4$ as shown in Figure 6.10.

![Figure 6.10 UV-vis absorption spectra of the 4-nitrophenol before (a) and after (b) the addition of NaBH$_4$.](image)
This spectral changes are quantitatively monitored by UV-vis spectral technique with time and a successive decrease of the peak height at $\lambda_{\text{max}} = 400$ nm is noted, which is due to the reduction of 4-NP to 4-AP. Figures 6.11a and 6.11b confirm this conclusion, as the absorption band of 4-nitrophenolate ion at $\lambda_{\text{max}} = 400$ nm in the presence of PEI and 401 in the presence of PEI-C$_{12}$ decreases and disappears within 50 seconds after the addition of AuNPs, with the concomitant appearance of new peaks at $\lambda_{\text{max}} = 300$ and 303 nm, respectively (attributed to the generation of 4-aminophenol).

Kong et al.\textsuperscript{61} proposed that the reduction of 4-NA (4-nitroaniline) to $p$-PDA ($p$-phenylene diamine) using NaBH$_4$ as the reducing agent is quite slow if it is performed without using the catalyst. To verify the catalytic activity of the as-
synthesized gold nanowire networks, similar studies are also performed using the reduction of 4-NA as a model reaction. As can be seen in Figures 6.11c and 11d, a broad characteristic band at $\lambda_{\text{max}} = 380$ nm is the absorption of the 4-NA and NaBH$_4$ mixture. When PEI capped AuNPs are employed for the reduction reaction, two new bands drastically develop at $\lambda_{\text{max}} = 241$ and $\lambda_{\text{max}} = 310$ nm. While the PEI-C$_{12}$ capped AuNPs were employed for the reduction reaction of 4-NA, two new bands develop at $\lambda_{\text{max}} = 238$ and $\lambda_{\text{max}} = 315$ nm representing the formation of $p$-PDA. Meantime, it accompanies the flattening the characteristic band at $\lambda_{\text{max}} = 380$ nm, indicating the reduction of 4-NA. When a totally flattened peak at $\lambda_{\text{max}} = 380$ nm is developed it can be a sign of the completion of the reduction reaction as shown in Figures 6.11c and 6.11d. The formation of the reduced product $p$-PDA is also confirmed from the $^1$H NMR spectra (in CDCl$_3$) of the product shown in section 6.5. The $^1$H NMR spectrum consists of two signals at $\delta$ 6.557, and 3.321 ppm, respectively. These chemical shifts are $\delta$ 6.557 and $\delta$ 3.321 are due to the presence of aromatic and amino protons, respectively.

Thus, a proper combination of AuNPs and NaBH$_4$ is essential to carry out the reaction. In the absence of catalysts, the mixtures of 4-NP and NaBH$_4$ show an adsorption band at $\lambda_{\text{max}} = 400$ nm, and for 4-NA show an adsorption band at $\lambda_{\text{max}} = 380$ nm respectively. We have monitored this chemical reaction by UV-vis spectroscopy and the results are shown in Figure 6.12.

![Figure 6.12 Successive UV-vis spectra of the reduction of (a) 4-NP and (b) 4-NA by NaBH$_4$ in the absence of AuNPs.](image)
Thus, there is a very slow decrease of absorbance at 400 nm for 4-NP (Figure 6.12 a) and 380 nm for 4-NA (Figure 6.12b) during the chemical reaction in the absence of catalyst. In addition to the characteristic surface plasmon band of AuNPs persist in 525 nm in the absence of NaBH$_4$ as indicated in Figure 6.13.

Figure 6.13 Successive UV-vis spectra of the reduction of 4-NP by AuNPs as catalyst in the absence of NaBH$_4$.

The advantage of the catalytic reduction of 4-NP is the easy monitoring of the progress of the reaction through UV-visible spectrophotometer. The 4-nitrophenolate anion formation from 4-NP ($p$Ka =7.15) in the initial step upon addition of borohydride is indicated when the peak at $\lambda_{\text{max}}$ = 317 nm (due to 4-NP) is shifted to $\lambda_{\text{max}}$ = 400 nm. This peak remains unaltered with time, indicating that the reduction did not take place in the absence of a catalyst.$^{73,74}$

However, the addition of a small amount of PEI and PEI-C$_{12}$ capped AuNPs to the above reaction mixture causes fading and ultimate bleaching of the yellow color of the reaction mixture. Since excess NaBH$_4$ is present in the reaction solution and the reduction of 4-NP by NaBH$_4$ is negligible in the absence of AuNPs, the reaction could be considered as pseudo-first-order with respect to the concentration of 4NP. The variation of the reaction rate or the catalytic efficiency depends mostly
on the available surface area. Here, initially the 4-NP molecules are adsorbed on the surface of the AuNPs, which play an important role in the electron transfer process. Six electrons and six protons are utilized for the reduction process. The total reduction reaction is summarized in Scheme 6.3.

![Scheme 6.3 Schematic reduction of 4-NP to 4-AP.](image)

The reduction process involves (i) chemisorption of 4-nitrophenolate anions on the catalytic AuNPs surface, (ii) interfacial electron transfer (electron released by sodium borohydride ion) to reduce 4-nitrophenolate ion and (iii) desorption of 4-aminophenol away from the surface. The electron transfer occurs from the negatively charged BH$_4^-$ to the 4-NP via the AuNPs as detailed in Scheme 6.3. This electron transfer process depends upon the number of particles present in the solution as well as the available surface area of the catalyst particles. The reaction rate increases with an increase in the number of particles as well as an increase in surface area of the catalyst particles.

These results indicate that the AuNPs can successfully catalyze the chemical reduction of 4-NA (yellow color) to the colorless $p$-PDA. The logarithm of absorbance of 4-NA at $\lambda_{\text{max}} = 380$ nm (ln $A$) will decrease linearly with reaction time. From the linear regression of the ln $A$ versus time plot, it is estimated the apparent rate constant ($k$) of the reaction. In the case of reduction of 4-NA to $p$-PDA, the ln $A$ versus time plots are given in Figure 6.14.
Figure 6.14 (a) and (b) are the plots of $\ln A$ against time for Au-PEI capped AuNPs catalyzed reduction of 4-NP (25 cycles; time interval 2s); PEI-C$_{12}$ (c) and (d) are the plots for the PEI-C$_{12}$ capped AuNPs catalyzed reduction.

These results indicate that the AuNPs can successfully catalyze the chemical reduction of 4-nitroaniline (yellow color) to the colorless $p$-phenylenediamine (4-PDA). In this reduction process, the concentration of NaBH$_4$ exceeds the concentration of 4-nitroaniline (see the Experimental Section) which means that the reaction rate follows first order kinetics. The logarithm of absorbance of 4-nitroaniline at 378 nm ($\ln A$) will decrease linearly with reaction time.

From the linear regression of the slope of $\ln A$ versus time, it was estimated the apparent rate constant (k) of the reaction. Figures 6.14a and 6.14b shows the plot of $\ln A$ versus time for PEI capped AuNPs used as catalyst (corresponds to Figures 6.11a and 6.11b), whereas Figure 6.14c and 6.14d shows the $\ln A$ plot versus time for PEI-C$_{12}$ capped AuNPs used as catalyst in the reduction process (corresponds to Figures 6.11c and 6.11d).
AuNPs with very small size (5-6 nm) are more effective catalysts than the larger NPs (15.3 nm) because the decrease in the particle size results in an increase in the d-electron density of the Au atoms, which leads to an increased reactivity to hydrogen atoms.62h Panigrahi et al.62c have demonstrated that the rate of the reaction decreases with an increase in particle size in homogeneous and heterogeneous catalytic systems.

6.3.9 The vital role of polymer

Polyethylenimine (PEI) is an organic polymer that has a high density of amino groups, especially attractive in this study because its amino groups allow formation of complexes with a wide variety of transition metal cations.70,71 It is used as a stabilizer in the synthesis of Ag, Au, and Pd metal nanoparticles which are used extensively as catalysts.72-77 There are several features of these modified PEI samples which suggest that they may be able to stabilize the formation of AuNPs and perform efficient catalysis: (i) the PEI framework bearing amine groups will attract and coordinate with the gold ions, an important key feature for the manipulation of gold redox potential (Au^{3+}→Au(0), 1.02V); (ii) acylated PEI (PEI-C_{12}) avoids aggregation of AuNPs by promoting electrostatic stabilization; (iii) the basic characteristics of PEI bearing amide moieties promote the action of the metal nanoparticles by interaction with the metal nanoparticle surface, which appears suitable for catalysis; (iv) The high cationic charge density and the “steric” effect of PEI kept each nanoparticle apart which results in the formation of nanoparticles stable up to three months without any agglomeration, and this is evident from the spectra collected in Figure 6.15.
Figure 6.15 UV-vis absorption spectra of AuNPs (a) as prepared, (b) after 3 months in an aqueous solution at 25 °C. The AuNPs show absorption at 520 nm.

In the present study the stable AuNPs are spontaneously formed by heating a solution containing PEI-C$_{12}$ and HAuCl$_4$. As a result, an additional step of introducing a reducing agent is no longer needed. More importantly, the size, the nucleation and growth kinetics of the as formed AuNPs can be tuned by changing the initial molar ratio of PEI to gold.

6.3.10 Mechanism of reaction

The proposed mechanism of the reduction of 4-NP by borohydride in the presence of AuNPs is given in Schemes 6.4a and 6.4b. The catalytic reduction proceeds on the surface of the metal nanoparticles. In scheme 6.4, two different routes are proposed. In step I of 6.4(a), the AuNPs react with the borohydride ions, to form the metal hydride on the surface of AuNPs. Concomitantly, the adsorption of 4-NP on the AuNPs surface and removal of water molecule to form nitroso compound are schematically shown in step II. After combining with another molecule of hydrogen in step III the nitroso compound is converted into hydroxyl amine (steps IV and V).

In the more direct route, the aromatic nitro compound is reduced to the nitroso compound and then further to the corresponding hydroxylamine in two fast consecutive steps. Finally, the hydroxylamine (step VI) is reduced to the amine.
derivative in the slow reaction step and water as the byproduct schematically represented in **step VI. (direct route in Scheme 4a)**. Corma *et al.* report that AuNPs function dominantly through the direct root, *i.e.*, $\text{R-NO}_2 \rightarrow \text{R-NHOH} \rightarrow \text{RNH}_2$. Assuming that this consecutive reaction mechanism via the hydroxylamine intermediate is also applicable in our system, we propose the mechanism for reduction of nitro compounds with AuNPs in **Scheme 6.4**.

**Scheme 6.4 The proposed mechanism of the reduction of nitro compounds by borohydride (a) direct route and (b) condensation route in the presence of metallic AuNPs.**
The proposed second route 6.4 (b) involves the condensation of one molecule of nitroso compound with a molecule of the hydroxylamine to give the azoxy compound (step I), which is reduced in a series of consecutive steps to the azo (step III), hydrazo (step IV), and amine (step VI) groups (condensation route, in Scheme 6.4b). The performed controlled experiment by Kundu et al.\textsuperscript{62} reveals that the reduction reaction of nitro group is most likely followed by the nitroso and hydroxylamine pathway rather than the azo and hydrazo pathway. In this experiment, electron transfer takes place from BH\textsubscript{4}\textsuperscript{-} to 4-NP only after the adsorption of both onto the catalyst surface. The rate of electron transfer at the catalyst surface can be influenced by two-steps:

(i) adsorption of 4-nitrophenolate ion onto the catalyst surface;
(ii) interfacial electron transfer and desorption of 4-aminophenolate ion away from the surface.

The adsorption of substrates is driven by chemical interaction (chemisorption) between the particle surface and the substrates. The adsorption of 4-nitrophenolate ions onto the particle surface thus helped to overcome the kinetic barrier of the reaction. Again, the rate for electron transfer is faster than the rate for desorption of product from the particle surfaces \textit{i.e.}, $k_e$ (electron transfer rate constant) $>$ $k_d$ (rate constant for desorption).\textsuperscript{79a}

Nanoscale materials exhibit size and shape dependent physical, chemical, electronic and magnetic properties, which are different from the bulk and their isolated atoms/molecules.\textsuperscript{79b} The rate-determining step is the reduction of the adsorbed 4-NP to 4-AP, which desorbs afterward.\textsuperscript{80} The energy levels of the metal particles are therefore most certainly dependent on their size. In particular, for the catalytic reduction of 4-NP by NaBH\textsubscript{4}, it is proposed that the transfer of electrons from BH\textsubscript{4} to 4-NP is relayed by the metal particle surface.\textsuperscript{81} The electron transfer and thus the reaction rate should be directly influenced by the possibly modified energy levels as a result of the quantum size effect. This consequence could boost the catalytic performance of the AuNPs close to that of other noble metals (Ag, Pd, Pt, Cu, etc.) that are conventionally more energetically favourable (\textit{i.e.}, with smaller energy barriers for electron transfer).\textsuperscript{82} The resulting physical properties are neither
those of bulk metal nor those of molecular compounds, but they strongly depend on the particle size, interparticle distance, nature of the protecting organic shell, and shape of the nanoparticles.\textsuperscript{82b} In nanoparticles, there is a gap between the valence band and the conduction band, unlike in bulk metals.\textsuperscript{13b}

The size induced metal-insulator transition, described in 1988, is observed if the metal particle is small enough (about 20 nm) that size-dependent quantization effects occur. Then, standing electron waves with discrete energy levels are formed. \textit{Single-electron transitions} occur between a tip and a nanoparticle, causing the observation of so-called Coulomb blockades if the electrostatic energy, \(E_{\text{el}} = \frac{e^2}{2C}\), is larger than the thermal energy, \(E_T = kT\). The capacitance \(C\) becomes smaller with smaller particles. This means that single-electron transitions can be observed at a given temperature only if \(C\) is very small, \textit{i.e.}, for nanoparticles since they are small enough \((C<10^{18} \text{ F})\). Large variations of electrical and optical properties are observed when the energy level spacing exceeds the temperature, and this flexibility is of great practical interest for applications (transistors, switches, electrometers, oscillators, biosensors, catalysis).\textsuperscript{83,84}

Classical laws of physics fail to explain the origin of the novel properties of materials in this size regime.\textsuperscript{84c} Electrons experience a confinement of motion in space, when one or more dimensions of a crystal are in the nanoscale. This situation can be described in terms of particles in a box and under this condition, quantum mechanics is more suitable to explain the size and shape dependent properties (\textit{vide infra}).

\textbf{6.4 Conclusions}

In summary, in the present study it is established that both highly branched cationic polymers PEI and PEI-C\textsubscript{12} capped AuNPs exhibit excellent catalytic activity for the reduction of 4-NP and 4-NA by NaBH\textsubscript{4} in the aqueous phase. The polymer PEI serves both as a reductant and stabilizer in the process of preparation of nanoparticles, so that no additional reducing agents or treatments are needed. Conversion of aromatic nitro compounds to the corresponding amino compounds confirms that the catalyst is very active for the reduction reaction. Smaller particles
are found to be more active for the reduction reaction suggesting that coordinatively unsaturated surface atoms prevalent in small crystallites are more reactive for the reduction. This preparation strategy of AuNPs appears very simple, stable, green and cost-effective, and exhibits great potential for practical applications. Following this methodology, conversion of nitro to amino compounds in large scale is also possible. Hence, it might have applications in industries.
6.5 Spectral analysis

6.5.1 NMR spectra

Figure 6.5.1 $^1$H-NMR spectrum of the product p-PDA

Figure 6.5.2 $^{13}$C-NMR spectrum of the product p-PDA.
6.5.2 FT-IR spectra

Figure 6.5.3 FT-IR spectra of 4-NA (a) and (b) p-PDA.
6.6 References


77. S. Mori, T. Ohkubo, T. Ikawa1, A. Kume, T. Maegawa, Y. Monguchi, H. Sajiki, 
79. (a) S. Jana, S. K. Ghosh, S. Nath, S. Pande, S. Praharaj, S. Panigrahi, S. Basu, T.
   8814.
82. (a) Y. Lu, Y. Mei, M. Schrinner, M. Ballauff, M. W. Moller, J. Phys. Chem. C 
83. (a) R. P. Andres, T. Bein, M. Dorogi, S. Feng, J. I. Jenderson, C. P. Kubiak, W.
   Mahoney, R. G. Osifchin, R. Reifenverger, Science 1996, 272, 1323. (b) N.
   Toshima, T. Yonezawa, New J. Chem. 1998, 1179. (d) J. H. Fendler, 
84. (a) A. Henglein, J. Phys. Chem. 1993, 97, 5457. (b) J. BeFlloni, Curr. Opin.
   Colloid Interface Sci. 1996, 1, 184. (c) M. Kerker J. Colloid Interface Sci. 1985,
   105, 29. (d) P. M. Paulus, A. Goossens, R. C. Thiel, A. M. van der Kraan, G.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>MNPs</td>
<td>Metal nanoparticles</td>
</tr>
<tr>
<td>CMNs</td>
<td>Colloidal metal nanoparticles</td>
</tr>
<tr>
<td>RuNPs</td>
<td>Ruthenium nanoparticles</td>
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<td>Copper nanoparticles</td>
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<td>PdNPs</td>
<td>Palladium nanoparticles</td>
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<td>Gold nanoparticles</td>
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<td>AgNPs</td>
<td>Silver nanoparticles</td>
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<td>NiNPs</td>
<td>Nickel nanoparticles</td>
</tr>
<tr>
<td>SiNPs</td>
<td>Silica nanoparticles</td>
</tr>
<tr>
<td>TEOS</td>
<td>Tetraethyl orthosilicate</td>
</tr>
<tr>
<td>APTES</td>
<td>3-Aminopropyl triethoxysilane</td>
</tr>
<tr>
<td>PVP</td>
<td>Polyvinylpyrrolidone</td>
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<tr>
<td>PEI</td>
<td>Polyethyleneimine</td>
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<tr>
<td>PEI-C₁₂</td>
<td>Acylated polyethyleneimine</td>
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<td>XRD</td>
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<td>Scanning electron microscopy</td>
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<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
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<tr>
<td>TGA</td>
<td>Thermal gravimetric analysis</td>
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<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrett-Joyner-Halenda</td>
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<tr>
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