The influence of gold nanoparticles on reduction of $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{NO}_3)_2$ by iron(II)

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Abstract

Variable size (50–220 nm), intrinsically mono-dispersed, single shaped gold (Au) nanomaterials was made showing man-made replica of nature's flower like structures associated with vast kinetic activity. 220 nm Au nanopopcorns and nanoflowers have been synthesized simply by controlling the concentration of the reducing agent and reaction time. Other spherical metal nanoparticles made of platinum (Pt), Au and palladium (Pd) also show catalytic effect on the rate of the reduction of $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{NO}_3)_2$ by iron(II), which was taken as a model reaction. Their activity increases with increased loading. Catalytic activity follows the order: $\text{Pt} > \text{Au} > \text{Pd}$, which has been compared with that of the various Au nano-formations (popcorns and flowers). The larger Au nanopopcorns and nanoflowers induce appreciable reduction in the rate of the reaction compared to the effects of similar concentrations of the spherical nanoparticles.

Graphic abstract Catalytic activity follows the order: $\text{Pt} > \text{Au} > \text{Pd}$, which has been compared with that of the various gold nano-formations (popcorns and flowers). The larger gold nanopopcorns and nanoflowers induce appreciable reduction in the reaction rate compared to the effects of similar concentrations of the spherical nanoparticles.

Keywords Gold nanoparticles · Noble metal nanoparticles · Reducing agent · Reaction time · Catalytic control

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1 Introduction

Synthesis of noble metal nanomaterials of various shapes and sizes is practiced vividly nowadays to promote applications in advanced research areas that include sensing, biomarking, catalysis, optical measurements, energy devices, calculating reaction rates, etc. Ample reports are available for such synthetic methods and subsequent applications. However, tuning the shapes maintaining the parent symmetry and protrusions on the nanomaterials to monitor reaction kinetics quantitatively has scarcely been reported. Colloidal transition metal nanoparticles (NPs) are candidates of recent interest as they are promising substances in the applications towards development of new multiuse devices [1–4]. Their inherent quantum size effect (1–10 nm) infest them with valuable physical properties as well as surface defined characteristics to be used in catalysis and different reactions including hydrogenation [5–7], hydrosilylation [8, 9] and hydration of unsaturated organic molecules [10]. Redox reactions [11] and various electron transfer phenomena such as splitting of water [12, 13] and photocatalytic hydrogenations [14] can be controlled by these nano systems. Since the particle size affects the catalytic activity and selectivity strongly, hence synthesis of colloidal NPs with controlled size becomes important. In particular, the transition-metal NPs are attractive candidates to be used as catalysts due to their high surface-to-volume ratio and high surface energy, which enhance the activity of their surface atoms. Herein, we have reported the catalytic effects of colloidal platinum (Pt), palladium (Pd) and gold (Au) NPs on the reduction of $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{NO}_3)_2$ by Mohr's (Fe^{II}) salt in aqueous solution. The catalyzed reaction is several times faster (under the present experimental conditions) over the non-catalyzed one [15, 16] and the reaction is surface controlled. Moreover, we temporally and chemically controlled the synthesis of the Au NPs to achieve flower like nanostructures. The free energy of formations of the crystal-facets and the rational use of the reducing agent (sodium borohydride,

NaBH_4) explains the mechanism of growth of the nanopopcorns (NPOPs) and nano-flowers (NFIs). The NPOPs and the NFIs induced considerable descend in kinetic activity for the $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{NO}_3)_2$ —Mohr's salt reaction compared to the smaller nanoparticles.

2 Experimental

All the chemicals and reagents were either of GR or AR grade. Mohr's salt, auric chloride ($\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$), chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) and palladium chloride (K_2PdCl_4) of high purity were procured from SRL, India and used as received. The $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{NO}_3)_2$ complex was prepared and purified by a standard method [17]. All the aqueous solutions were prepared in deionized and double distilled water.

An Agilent 8453E UV–visible spectrophotometer was used for the kinetic and spectral measurements. The high resolution transmission electron microscopic (HR-TEM) studies on the particles were conducted at a resolution of 0.24 nm of FEI, Tecnai S-Twin Electron Microscope. The HR-TEM specimens were prepared by drop casting the samples on a carbon film supported by a copper grid.

The metal NPs of Pt, Pd and Au were synthesized from the three respective precursors: H_2PtCl_6 , K_2PdCl_4 and HAuCl_4 . These sols were prepared with a standard procedure in nitrogen atmosphere and stirred on a magnetic stirrer for 5 min. Ice cold NaBH_4 was added to this solution as reducing agent [18]. The products, to be used as catalysts, were stored in brown bottles. The colors of the Pt, Pd and Au sols were brownish red, black and pink, respectively. The size of the metal NPs was in the region of ~ 7 nm. The Au NPOPs and Au NFIs were synthesized using a similar procedure as the Au NPs but the formations appeared by changing the concentration of the reducing agent (NaBH_4) and the reaction time (Table 1 and Fig. 1).

The kinetic studies on the reaction between $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{NO}_3)_2$ and Mohr's salt (Fe^{II} salt) in the absence and presence of the different NPs were studied spectrophotometrically at 298 K. The concentration of Mohr's

Table 1 Structural statistics of Au NPOPs and Au NFIs providing the particle diameter, core diameter, number of petals on each Au NFI and average width and length of petals for different NaBH_4 concentrations

$[\text{NaBH}_4]$ (mmol L^{-1})	Core diameter (nm)	Average diameter (nm)	Average no. of petals	Individual average petal width (nm)	Individual average petal length (nm)	Time allowed for the formation of the Au NPs (min)
0.75	175	175	0	0	0	2
1.25	200	200	0	0	0	2
1.25	60	100	8	8	25	5
1.25	50	120	10	10	12	7
1.25	50	120	10	18	30	10

Fig. 1 HR-TEM images of **a** Au NPoPs, **b** Au NFIs, **c** magnified image of the Au NFI showing the petals

salt was kept in considerable excess to ensure the pseudo first order condition. All the kinetic runs were performed at 298 K by mixing required volumes of the thermostated reactants with proper dilution.

3 Results and discussion

Redox reaction between the Co^{III} complex salt (the oxidizing agent), $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{NO}_3)_2$ and Fe^{II} salt (Mohr's salt) (the reducing agent) follows second order kinetics in aqueous solution [19].

This reaction generally proves that the aquation process occurs to an appreciable extent; but the relative effect of aquation is minimized at high Fe^{II} concentration.

The mechanism of this redox process is well established. It proceeds through a bimolecular bromo-bridged inner sphere complex [20]. An electron can be transferred from Fe^{II} to Co^{III} through the bromo-bridge to the bridged complex with both the metals occupying the octahedral centers. The electron transfer is accomplished by the halide ligand as electron mediator. The heavier halide ions are more effective because of their higher polarizability. The k_{obs} value for the electron transfer reaction between $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$ and $\text{Fe}(\text{ClO}_4)_2$ with ionic strength of 1.7 mol L^{-1} corroborates to that with ionic strength 0.8 mol L^{-1} [21]. Thus, the reaction has first order dependence on the Co^{III} complex as well as the Fe^{II} salt:

$$-\frac{d[\text{Co}^{\text{III}}]}{dt} = k[\text{Co}^{\text{III}}][\text{Fe}^{\text{II}}].$$

The influence of Mohr's salt on the absorption spectrum of the pure Co-complex is shown in Fig. 2. There is a

Fig. 2 Absorption spectra of the reaction mixture at different time intervals: $[\text{Co}^{\text{III}}]_0 = 0.01 \text{ mol L}^{-1}$, $[\text{Fe}^{\text{II}}]_0 = 0.11 \text{ mol L}^{-1}$, ionic strength = 0.8 mol L^{-1} and temperature = 298 K

decrease in absorbance at 550 nm and increase at 425 nm through a well-defined isosbestic point at 507 nm. The time dependent reduction in the absorbance (A_t) of the reaction mixture was recorded at 550 nm. The rate equation, $A_t = A_\infty + a_1 \exp(-k_{\text{obs}}t)$, was used to determine the observed pseudo first order rate constant k_{obs} .

It is evident that the measured use of NaBH_4 along with controlled reaction time holds the key for the formation of the Au NPoPs and Au NFIs. Apparently the Au NPoPs act as nucleation centre which grew inside the Au NFIs in the presence of measured amount of the reducing agent. The corresponding TEM image of the Au NFIs (Fig. 1c) shows predominant petal (15–20 nm) structures. It is implied that under-potential deposition of metallic gold on the crystal facets of the Au NPoPs leads to break the existing symmetry and develop the branched Au NFIs [22]. As the Au NFIs were formed, the spiky nanosphere held its original shape but the size of the spikes or petals gradually increased. Blunting of the petal tips was seen in some of the particles.

The growth of the petals in the flower-like formation is likely due to the interchange between the free energy

of the crystal-facet formation and reducing agent controlled Au^{3+} ion movement to the Au NPoPs and successive absorption as Au^0 ($E_{\text{Au/Au}}^{03+} = 1.35 \text{ V}$, $E_{\text{Au/Au}}^{03+0} = 1.5 \text{ V}$ and $E_{\text{Au/Au}}^{0+0} = 1.83 \text{ V}$). It is clear that though $\text{Au}^{3+} \rightarrow \text{Au}^+$ is an appreciative path as compared to $\text{Au}^{3+} \rightarrow \text{Au}^0$, adverse reduction potential for $\text{Au}^+ \rightarrow \text{Au}^0$ forces Au^{3+} ions to directly reduce to Au^0 to generate the Au nanostructures.

A closer look into the mechanism of formation of the Au NFLs using HR-TEM puts forward four different structures to understand the growth mechanism (Fig. 3). The corresponding HR-TEM and selected area (electron) diffraction (SAED) images confirm the crystallinity of the Au nanosystems. Orientation of the tips of the icosahedral Au NPoPs towards the $\{110\}$ direction

can be observed from Fig. 3a. The free energies of the crystallographic plane of an fcc metal increases as $\gamma(-110) < \gamma(100) < \gamma(011)$. Hence, our findings match accurately with the existing literature and state that the Au NPoPs are the energetically most stable formations. The growth direction existed from $\{-110\}$ to $\{011\}$ (Fig. 3b) indicating orientation of the direction of the crystal growth of the Au NFLs toward configurations with lower surface energy.

The growth direction changes from $\{011\}$ to a $\{100\}$ and $\{-110\}$ equiproportional mixed facets leading to half-grown NFLs. Similar analysis for all the tips of the half-blossomed Au NFLs indicates acquiring of its lower surface energy configurations. Enhanced addition rates of atoms on the facets with high-energy limit their participation in the crystal growth due to large unsaturated coordination between the high-energy facets and the surface atoms. However, this does affect the growth direction for the fully grown Au NFLs (Fig. 3d). The calculated free energy supports the full-grown Au NFLs with the $\{-110\}$ facets. Large concentration of NaBH_4 promotes migration of Au^{3+} to get reduced to Au^0 to the relatively stable $\{100\}$ facets. This synergistic effect results into occurrence of an optimal structure of the fully grown Au NFLs with mixed $\{100\}$ and $\{-110\}$ facets. We observed reduction of the core size of the Au NFLs with increase in the diameter of the nanomaterials, which could be due to accommodating more petals in expense of the core surface. Evidently, NaBH_4 serves a dual role of directing selective deposition of Au on crystal facets and retarding the rate of formation of metallic gold (Au^0). The structural statistics of each of the Au NFLs are provided in Table 1. The HR-TEM images showed that gradual twinning leads to the branching out of petals. This leads to the development of polycrystalline core in the Au NFLs with surface branched single-twinned crystal petals, which are stable at room temperature.

To find out the applications of the synthesized Au NFLs, we checked their kinetic activity where we used $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{NO}_3)_2$ and Mohr's salt as the analytes. We found that the rate of electron transfer reaction increases with the NP concentration. The plot of k_{obs} versus initial Au NP concentration, $[\text{Au}]_0$ (Fig. 4) is nonlinear with a saturation limit, which indicates the surface catalyzed phenomenon of the Au NPs. Several factors are responsible for this kinetic activity including: (a) larger surface area of the Au NFLs compared to the Au NPoPs hold more analytes on the surface, (b) the electron transfer sites are favored by the large number of petals possessing barbed tips and jagged edges, (c) the reactants are trapped inside the vicinal petals and the available space between the core and the petals acting as functional sites (nanopockets). To confirm the morphology of the Au NFLs before and after the addition of the Co^{III} complex, we recorded their HR-TEM images.

Fig. 3 HR-TEM images to obtain, **a** Au NPoPs, **b** non-blossomed Au NFLs, **c** fully blossomed Au NFLs, **d** blunted petal Au NFLs using 0.75 and 1.25 mmol L^{-1} NaBH_4

Fig. 4 Plots of k_{obs} versus $[Au NP]_0$ for the reaction between the Co^{III} complex and the Fe^{II} salt. $[Co^{III}]_0 = 0.01 \text{ mol L}^{-1}$, $[Fe^{II}]_0 = 0.11 \text{ mol L}^{-1}$, ionic strength = 0.8 mol L^{-1} and temperature = 298 K

Fig. 5 TEM images of the Au NFIs, **a** in the absence, **b** in presence of the Co^{III} -complex

The images do not show any aggregation or breakdown of the NPs (Fig. 5).

The nano-formations of the Au NPs (Au NPoPs and Au NFIs) show variation in the rate constants for the Co^{III} complex and the Fe^{II} salt reaction. As mentioned earlier, that on varying the amount of added reducing agent ($NaBH_4$) between 0.75 and 1.25 mM we obtained the Au NPs as nanopopcorns to closed-petal and open nanoflowers. These formations affect the rate of the reaction between Co^{III} complex and the Fe^{II} salt at different stages. Table 2 shows the dependence of the rate constant on the concentration of the Au nano-formations.

Pt, Au and Pd NPs were used in this reaction to note their effects on the reduction rate of $[Co(NH_3)_5Br](NO_3)_2$ with Mohr's salt. We observed enhancement in the rate of the reaction in the presence of all the three metal NPs under unchanged experimental conditions. The amount of the catalyst was varied keeping other parameters constant to determine the effect of the catalyst concentration on the rate of the reaction. The experimentally calculated

Table 2 Rate constants (k_{obs}) for the Co^{III} complex and the Fe^{II} salt reaction at different concentrations of gold nano-formations

$10^5 [Au \text{ nanoformations}]_0 \text{ (mol L}^{-1}\text{)}$	$10^3 k_{obs} \text{ (s}^{-1}\text{)}$	
	Au NPoPs	Au NFIs
0	1.134	1.134
5	1.82	2.82
12	3	4.12
18	4.42	5.79
25	5.87	6.98
30	6.32	8.621

$[Co^{III}]_0 = 0.01 \text{ mol L}^{-1}$, $[Fe^{II}]_0 = 0.11 \text{ mol L}^{-1}$, ionic strength = 0.8 mol L^{-1} and temperature = 298 K

Fig. 6 Plots of k_{obs} versus $[NP]_0$ for the reaction $[Co^{III}]_0 = 0.01 \text{ mol L}^{-1}$, $[Fe^{II}]_0 = 0.11 \text{ mol L}^{-1}$, ionic strength = 0.8 mol L^{-1} and temperature = 298 K

Table 3 Rate constants (k_{obs}) for the Co^{III} complex and the Fe^{II} salt reaction at different concentrations of the noble metal nanoparticles

$10^6 [NP]_0 \text{ (mol L}^{-1}\text{)}$	$10^3 k_{obs} \text{ (s}^{-1}\text{)}$		
	Pd	Au	Pt
0	1.134	1.134	1.134
5	1.3	2.0	2.5
10	1.7	3.2	4.8
15	2	5	10.1
20	2.5	7.4	16.5
25	4.8	10.5	27.5

$[Co^{III}]_0 = 0.01 \text{ mol L}^{-1}$, $[Fe^{II}]_0 = 0.11 \text{ mol L}^{-1}$, ionic strength = 0.8 mol L^{-1} and temperature = 298 K

rates are plotted against varying amounts of the catalysts are shown in Fig. 6 and given in Table 3. As expected, reduction rate of $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{NO}_3)_2$ got enhanced on increasing the amount of catalyst. The catalytic property exhibited by the Pt NPs is highest. Pt and Au are less prone to oxidation due to their nobility. The electron transfer reaction in presence of Au NPs is a diffusion-controlled phenomenon [23], while with the Pt NPs it is a surface controlled one. The sizes of the NPs are about 7 nm. It was observed that the less the size the more pronounced is the catalytic property. Smaller particles are more active due to the larger numbers of surface sites available for catalysis. The data show that on using spherical metal nanoparticles of diameter ~ 7 nm, the reaction can be increased by tenfold compared to those happening on the Au NPs and the Au NFIs with particle size lying between 50 and 220 nm.

The reason for the enhancement in the reaction rate in presence of the metal NPs can simply explained as follows. The catalytic reduction of Co^{III} to Co^{II} is an electron transfer process which is schematically represented in Scheme 1. In the present case, the electron transfer takes place from Mohr's salt to the Co^{III} -complex through adsorption of the reactant molecules on to the catalyst surface [20]. The heterogeneous catalytic reaction may occur in four steps: (1) diffusion of the reactant molecules to the active sites of the surface of the NPs, (2) adsorption of the molecules to the surface and formation of adduct, (3) reaction of the complex to form the products, and finally (4) desorption of the products from the surface. In this case, the rate of the reaction increased due to the available surface area and the amount of the catalysts. This assumption could be attributed to the higher driving force for particle-mediated electron transfer caused by their large Fermi level shift in the presence of electron transferring species such as Co^{III} -complex and Mohr's salt [20].

4 Conclusion

Syntheses of Au NPs and NFIs and a unique nanocrystal growth mechanism by exploiting the crystal-facet free energy and controlled use of NaBH_4 in Au^{3+} migration have been reported. The Au NFIs were 50–220 nm in size with

Scheme 1 Reaction schematic in presence of Pt NPs

20–60 nm petal length. The synthesized Au NFIs show important kinetic activity suitable in catalysis. However, the nano-projections on the Au NPs considerably slow down the reaction rate compared to the smaller (7 nm) spherical metal NPs. The Pt NPs look to be better and efficient catalysts than the Au and Pd to promote electron transfer on the surface of NPs.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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