Green Synthesis and Evaluation of Catalytic Activity of Sugar Capped Gold Nanoparticles

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GREEN SYNTHESIS AND EVALUATION OF CATALYTIC ACTIVITY OF SUGAR CAPPED GOLD NANOPARTICLES

A Thesis
Presented To
The Faculty of the Department of Chemistry
Western Kentucky University
Bowling Green, Kentucky

In Partial Fulfillment
Of the Requirement for the Degree
Master of Science

By
Yogesh A. Kherde

August 2014
GREEN SYNTHESIS AND EVALUATION OF CATALYTIC ACTIVITY OF SUGAR CAPPED GOLD NANOPARTICLES

Date Recommended 6/4/2014

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Dr. Bangbo Yan

Dean, Graduate Studies and Research Date 6-10-14
I would like to thank everyone who has helped me complete my master’s degree. First and foremost, I would like to thank God who has guided me through this whole journey. I would like to express my sincerest gratitude to my research advisor Dr. Rajalingam Dakshinamurthy for his guidance, knowledge, motivation and detailed and constructive comments in assisting for the completion of my research. I attribute the level of my master’s degree to his encouragement and effort, and without him this thesis, too, would not have been completed or written.

I would also like thank Dr. Cathleen Web, Department Head and my committee members Dr. Kevin Williams and Dr. Bangbo Yan. They have been constantly helpful and I sincerely appreciate it. To Dr. John Andersland who always helped me with microscopy techniques.

I would also like to thank my fellow lab members, Rammohan Paripelly, Dillon Pender, Vivek Badwaik, Monic Shah, Hitesh Waghwani, Tulsi Modi, The faculty and staff of the Department of Chemistry for their support during my master’s at Western Kentucky University.

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<tr>
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GREEN SYNTHESIS AND EVALUATION OF CATALYTIC ACTIVITY OF SUGAR CAPPED GOLD NANOPARTICLES

Yogesh Kherde
August 2014

Pages 52

Directed By: Rajalingam Dakshinamurthy, Kevin Williams, Bangbo Yan

Department of Chemistry Western Kentucky University

Owing to the importance of gold nanoparticles in catalysis, designing of them has become a major focus of the researchers. Most of the current methods available for the synthesis of gold nanoparticles (GNPs) suffer from the challenges of polydispersity, stability and use of toxic and harmful chemicals. To overcome these limitations of conventional methods, in our present study, we made an attempt to design a method for the green synthesis of monodispersed and stable gold nanoparticles by sugars which act as reducing and stabilizing agent. Characterization of synthesized nanoparticles was done by using various analytical techniques such as transmission electron microscope (TEM), dynamic light scattering spectroscopy (DLS), UV-Vis spectroscopy, scanning electron microscopy and electron dispersion spectroscopy. The synthesized sugar GNPs (S-GNPs) were spherical in shape and in the size range of 10 ± 5 nm. p-Nitrophenol reduction assay was used as a model system to determine the catalytic reduction activity of various sugar capped GNPs, monosaccharides (fructose), disaccharide (sucrose) and trisaccharide (raffinose) GNPs. The effect of temperature and the size of ligand on catalytic activity was also evaluated at different temperature using UV-Vis spectrometer. Using the spectroscopic data, rate constant (k) for three sugar capped GNPs was determined followed by its activation energy ($E_a$) and exponential (A) factor.
Introduction

Background

Over the last two decades, nanotechnology has been one of the most widely researched areas in the field of science due to its potential applications in commercial, medical and environmental sectors. Nanotechnology deals with fine tuning of materials in the size range of 1-100 nm for a wide range of applications.\textsuperscript{1,2} Nanomaterials display remarkably different properties compared to their bulk form, owing to their increased relative surface area and quantum size effect. At the nanoscale, the proportion of atoms on the surface is more than those inside, which confers nanoparticles a much larger surface area per unit mass, which affect their mechanical, thermal and catalytic properties. In addition, due to the quantum size effect, a change in the electronic and optical properties is observed.\textsuperscript{3–5} These unique physico-chemical properties of nanoparticles open up new avenues for extensive research in the fabrication of nanodevices to improve the quality and performance of various consumer products for human benefits. Currently, nanoparticles find numerous applications in food industries: for food packaging,\textsuperscript{6} in biomedical industries: for targeted drug delivery and bio-imaging,\textsuperscript{7} in textiles industries: for the manufacturing of antibacterial and stain-proof textiles.\textsuperscript{8} Along with these applications, one of the oldest and most important applications of nanoparticles can be found in catalysis. As catalytic reactions take place at the surfaces, due to high surface area and high reactivity nanoparticles are used as a catalyst in various chemical reactions.\textsuperscript{9}

Catalysis is of vital importance in our society and chemical industries. About 90% of the industrial products synthesized today involve the use of catalyst in their
production. Catalysis has a long history.\textsuperscript{10} Since its discovery in 1830 by Jacob Berzelius, catalysis has been practiced for nearly a century in petrochemical industries, in pharmaceutical industries for the production of novel drugs quickly and efficiently as well as in environmental protection for removing toxic chemicals using as the catalytic converters.\textsuperscript{9,10} Catalysis has immense potential to solve emerging challenges related to the alternative source of energy, detoxification of industrial byproducts, global warming and manufacturing of safe pharmaceuticals.\textsuperscript{11} This calls for a need to design novel catalyst for enhanced applications.

Chemically, catalysts are the substances that enhance the rate of a chemical reaction resulting in desired product. The catalytic power of a catalyst lies in its ability to accelerate the chemical reaction by decreasing the energy barrier i.e. activation energy ($E_a$) for the conversion of reactants to product (\textbf{Figure 1}). Catalyzed reactions often require low consumption of energy and occur at low temperature when compared to the reaction that lacks a catalyst.\textsuperscript{12}
Figure 1. Potential energy diagrams for a single-step reaction in the presence and absence of a catalyst. The only effect of the catalyst is to lower the activation energy of the reaction. The catalyst does not affect the energy of the reactants or products (and thus does not affect $\Delta E$).\textsuperscript{13}
Nanocatalysis

With a growing population leads to large demand for the products which necessitates for the finding methods to speed up the production in less time with the lesser impact on environment. Nanocatalysts are proving to be a new solution for this need. Nanocatalysts have been used for various commercial and environmental applications and there has been rapid increase in the number of nanocatalysis-related patents granted in a given year (Figure 2A & 2B).14
Figure 2. (A) Application fields related to nanocatalysis and (B) Number of patents granted in the field of nanocatalysis since 2003 (based on a research on the US Patent and Trademark Office Patent Database (http://patft.uspto.gov)).\(^{14}\)
Nanocatalysis research is aimed at the production of catalysts with a high catalytic activity which can be attributed to the available active surface area and the spatial organization of the active sites in a catalyst.\textsuperscript{15} Nanoparticles, due to their small size exhibit high surface to volume ratio and provide larger surface area which can increase speed of chemical reaction efficiently. Achieving 100\% selectivity in order to minimize the formation of byproducts is also crucial challenge in catalysis. With the help of nanocatalyst, having unique morphological and electronic properties, a better control over the selectivity of a reaction can be obtained.\textsuperscript{16}

Different materials such as carbon (carbon black, graphite, graphene), various oxides (Al\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2}, SiO\textsubscript{2}) and metals (iron, cobalt, copper) have been used in the manufacturing of nanoparticles.\textsuperscript{17–21} But nanoparticles produced from these materials severally involve various disadvantages such as catalytic fouling, catalytic poisoning, thermal instability, vapor formation and sludge production.\textsuperscript{22} So there is a need to select suitable material for the formation of highly active and stable nanoparticles.

**Gold Nanoparticles in Catalysis**

Gold has played an important role in the formation of nanoparticles. Many research publications have reflected the use of gold nanoparticles for biomedical applications such as targeted drug delivery,\textsuperscript{23} diagnosis, detection, etc.\textsuperscript{24} In the recent years, gold nanocatalysis has become the central focus of the catalysis research and development.\textsuperscript{25}

Gold in bulk form is considered to be chemically inert and catalytically inactive. However, when gold is transformed into small particles in the nanometer size range, it turns to be a highly active catalyst due to high surface to volume ratio and quantum size
effect. Gold nanoparticles exhibit improved electrical conductivity and significant reduction potential,\(^{26}\) which forms the basis of their application in various catalytic reactions such as,

- CO oxidation\(^{27}\)
- Acetylene hydrochlorination\(^{28}\)
- Water gas shift reactions and CO removal from H\(_2\)\(^{27}\)
- Liquid phase hydrolysis and oxidation\(^{29}\)
- NO reduction with hydrocarbons\(^{30}\)
- Alcohol oxidation to acids and aldehydes\(^{30}\)

There are several reasons for the selection of gold nanoparticles over the other noble metal nanoparticles for catalytic applications. One of the important reasons is their biocompatibility, which reduces the risk of nanotoxicity, generally caused on exposure to other metal nanoparticles.\(^{31}\) Furthermore, low temperature requirement and selectivity towards the particular reaction make gold nanoparticles as important constituents for catalytic reactions.\(^{32}\) In addition, gold nanoparticles are distinguished by their stability as it shows high resistance to sintering, low volatility, high resistance to variation in temperature and long term durability in stationary and transient applications.\(^{32}\) From an economic point of view, gold is considered as the most economical metals of all the noble metals such as palladium, platinum and rhodium.\(^{9}\)
Synthesis of Gold Nanoparticles

Catalytic properties are strongly influenced by catalysts size, shape and composition, which need to be considered when designing of nanocatalysts. Literature cite various methods for the synthesis of gold nanocatalysts using different agents and techniques. Some of the techniques are discussed as follows.

Conventional Methods

Commonly used conventional methods for the synthesis of heterogeneous GNPs are wet impregnation method, co-precipitation methods and sol gel methods. All these conventional methods involve the synthesis of supported gold nanocatalyst, where active gold nanoparticles are dispersed on various oxides such as Al₂O₃, SiO₂, MgO, Fe₂O₃, TiO₂, CeO₂, etc. The polymeric structures and strong crosslinking of oxides impart stability to active gold nanoparticles and increases their reusability. However, conventional methods have poor control over particle size and size distribution. Moreover, particles which are less than 1 nm are hard to detect by microscopic techniques and thereby precludes studies of particle size dependence on the catalytic activity.

Wet Chemical Methods

To obtain well defined gold nanoparticles with an excellent control over the size, shape and morphology, various wet chemical synthetic techniques have been applied. These methods involve the reduction of metal salts in solution followed by subsequent capping of ligand molecules to prevent their agglomeration and to preserve inherent properties. Gold ions in the gold precursors are in the Au³⁺ oxidation state. Precipitation
of GNPs from the dissolved gold salt like HAuCl$_4$ is carried out by reduction of Au$^{3+}$ to Au$^0$ by reducing agents.

Kinetics of the reaction:

\[ \text{AuCl}_4^- \rightarrow \text{Au}^0 + 4\text{Cl}^- \]

\[ n\text{Au}^0 \rightarrow \text{Au}_n^0 \quad \text{(Rapid Step)} \]

\[ \text{AuCl}_4^- + n\text{Au}^0 \rightarrow \text{Au}_n^0 + \text{Cl}_4^- \]

One of the most common techniques for synthesis of gold nanoparticles is the citrate reduction method, which was first discovered by J. Turkevitch in 1951.\textsuperscript{38} It involves the reduction of gold salt (HAuCl$_4$) in a boiling aqueous solution of sodium citrate. Gold nanoparticles with average particles of 10 nm can be obtained with limited polydispersity. Here, sodium citrate acts as both reducing as well as stabilizing agent.

The Brust method was discovered by Brust and Schiffrin in early 1990s.\textsuperscript{39} It is a two phase method and has been widely used for the preparation of thiol stabilized gold nanoparticles. Here, reduction of gold salt is carried out by NaBH$_4$ in organic solvents in the presence of thioalkanes or aminoalkanes. Place exchange reactions are used for further functionalization of gold nanoparticles. By this method, gold nanoparticles in the size range of 10-30 nm can be obtained.

However, synthesis of gold nanoparticles by above mentioned wet chemical methods involve the use of harmful and toxic chemicals, which raises environmental and biological concerns. Moreover, due to high cost and requirement of both reducing as well as capping agent, these procedures are time consuming and economically unfavorable.
Also, obtaining particles of the size more than 50 nm with limited polydispersity by these methods is always challenging.

**Biological Methods**

Owing to the toxicity of the reducing and capping agents used in the wet chemical processes for making gold nanoparticles, search for an alternative routes involving non toxic chemicals, environmental benign solvent and renewable materials is in place. For this purpose, biological components of plants and microorganisms have gained more attention because of their biodegradability, easy accessibility and non toxic nature.\textsuperscript{40–45} Mubarakali et. al. have reported the synthesis of gold nanoparticles by using menthol plant extract.\textsuperscript{46} A recent study showed a successful synthesis of gold nanoparticles from plant extract derived from Breynia rhanmoides.\textsuperscript{47} The synthesis of gold nanoparticles by fungus epicoccum nigrum is another example of biological synthesis method.\textsuperscript{48} However, biological synthesis of gold nanoparticles may require high temperature, other reducing and capping agents, and takes longer time for completion. In addition, impurities like dust and other particles from biological systems, affects the synthesis process and resultant quality of gold nanoparticles.
**Current Research Project**

Current research project deals with the green synthesis of gold nanoparticles by sugars for catalytic applications. The research also studied the effect of sugar chain length, monosaccharide (fructose), disaccharide (sucrose) and trisaccharide (raffinose), on the catalytic activity of gold nanoparticles.

**Synthesis of Sugar Gold Nanoparticles**

Sugars are soluble carbohydrates composed of carbon, hydrogen and oxygen (Figure 3). They are obtained from different sources and classified into monosaccharides, disaccharides and trisaccharides. Due to presence of structural units similar to the other chemicals which have been used in the reduction of gold salt, aqueous solubility, wide availability and low cost, sugars offer an environmental friendly and economical route for the synthesis of gold nanoparticles. Studies have reported the utilization of sugars either as a reducing or a capping agent.38, 47-49 But, the studies on the direct synthesis of gold nanoparticles have not been reported yet.

We reported a direct and environmental friendly synthesis of gold nanoparticles by using different sugars for catalytic applications. Synthesis was done in an aqueous medium, under mild reaction conditions and in a lesser time period. Sugars itself acts as both reducing as well as capping agent, which ruled out the need for the toxic chemicals and further functionalization of gold nanoparticles. Resultant gold nanoparticles were of nearly spherical in shape with an average diameter of 10 ± 5 nm with high stability.
Figure 3. Chemical structures of (A) Fructose (monosaccharide), (B) Sucrose (disaccharide) and (C) Raffinose (trisaccharide)
Catalytic Activity of Sugar Gold Nanoparticles

Catalytic activity of sugar GNPs was determined by the reduction of p-nitrophenol to p-aminophenol in the presence of sodium borohydride. We also studied the effect of sugar chain length on the catalytic activity of gold nanoparticles. For this purpose, three different types of sugar gold nanoparticles, fructose (monosaccharide), sucrose (disaccharide) and raffinose (trisaccharide) GNPs were employed in the reduction of p-nitrophenol in presence of sodium borohydride. To test the efficiency of sugar GNPs at different temperatures, catalytic reduction of p-nitrophenol was studied at 10 ºC, 25 ºC and 45 ºC.

p-Nitrophenol is used in leather and cork insulation industries as a fungicide. It is also used in the synthesis of p-aminophenol, which is common ingredient in the synthesis of paracetamol and other anti-inflammatory drugs. On exposure, p-nitrophenol causes acute toxicity. It shows high stability in water and its degradation is very slow in absence of a catalyst. So finding out the way for the removal of hazardous p-nitrophenol is of an immense importance.

Different approaches have been made for the removal of p-nitrophenols including adsorption, photocatalytic degradation, and microwave assisted degradation. But all these methods involve the use of high energy consumption and organic solvents. Use of iron-acid as a catalyst in the reduction process has many drawbacks: 1) Production of sludge is large, as it involves large amount of iron. 2) Separation of p-aminophenol from Fe-FeO sludge is a very tedious job. 3) Consistency varies batch to batch. 4) Fe particles causes erosion problem of the reactor. 5) Low yield of p-aminophenol. Therefore, there is a need for an alternative method which will effectively reduce toxic p-nitrophenol to p-
aminophenol. Due to high activity, selectivity and stability, sugar GNPs may thus offer clean and economically favorable way for the reduction of p-nitrophenol. Moreover, sugar GNPs have practical advantages over other catalysts because ease of preparation and separation from the reactants and the products, making them reusable.
Materials and Methods

Reagents and Materials:

All the chemicals including sugars, fructose, sucrose, raffinose, and potassium aurochlorate (KAuCl₄) were of analytical grade. Fructose and raffinose were purchased from Spectrum, New Brunswick, NJ; sucrose was purchased from EMD, Gibbstown, NJ, and KAuCl₄ from Sigma-Aldrich, St. Louis, MO.

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>CAS Number</th>
<th>Company</th>
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<tr>
<td>Potassium Aurochlorate (KAuCl₄)</td>
<td>136-82-61-6</td>
<td>Sigma Aldrich</td>
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<tr>
<td>Fructose</td>
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<tr>
<td>p-Nitrophenol</td>
<td>100-02-7</td>
<td>J.T. Baker</td>
</tr>
<tr>
<td>Sodium Borohydride (NaBH₄)</td>
<td>16940-66-2</td>
<td>EMD Chemicals</td>
</tr>
</tbody>
</table>

Table 1. Chemicals used for the synthesis of Sugar GNPs

Synthesis of Sugar GNPs (S-GNPs)
The primary step involved in the synthesis of gold nanoparticles is the reduction of Au$^{3+}$ to Au$^{0}$ (Figure 4). Sugar gold nanoparticles were synthesized by reduction of gold salt (KAuCl$_4$) in the presence of sugars in an aqueous medium. In a typical synthesis, appropriate concentration of both aqueous gold solution and aqueous sugar solution were mixed to avoid any aggregates. Reaction mixtures were then incubated and washed to obtain water dispersible sugar gold nanoparticles.
Figure 4. Schematics showing steps involved in synthesis of sugar capped GNPs.
**Synthesis of Fructose GNPs**

Fructose GNPs were synthesized by adding 0.264 mM of KAuCl₄ solution to 3.33 M fructose solution. The solution was then incubated at 37 °C in an orbital shaker at stirring speed of 150 rpm for 6 hrs. After incubation, the aqueous dispersions containing fructose gold nanoparticles were centrifuged for 10 min at 10,000 rpm. The precipitated particles were washed with twice the volume of gold nanoparticles dispersion by autoclaved nanopure water to remove excess amount of undissolved fructose. The resultant GNPs were concentrated to the desired volume and used for further study.

**Synthesis of Sucrose GNPs**

1.75 M sucrose solution was prepared in autoclaved nanopure water, and was heated at 50 °C with repeated vortexing to dissolve all the sucrose. Once the temperature reduced to 37 °C, 0.132 mM of KAuCl₄ was added. The solution was then incubated at 37 °C in an orbital shaker maintaining stirring speed of 150 rpm for 4 hrs. After incubation, the aqueous dispersions containing gold nanoparticles were centrifuged for 10 min at 10,000 rpm. The precipitated particles were washed with twice the volume of gold nanoparticle dispersion by nanopure water to remove unreacted sucrose. The resultant GNPs were concentrated to the desired volume and used for further study.

**Synthesis of Raffinose GNPs**

0.084 M raffinose solution was prepared in autoclaved nanopure water, and was heated at 50 °C with repeated vortexing to dissolve all the raffinose. Once the temperature reduced to 37 °C, 0.132 mM of KAuCl₄ was added. The solution was then incubated at 37 °C in an orbital shaker at stirring speed of 150 rpm for 12 hrs. Same parameters were
applied for washing raffinose GNPs as that were used for fructose and sucrose GNPs. The resultant GNPs were concentrated to the desired volume and used for further study.

**Characterization of GNPs**

As the properties of nanomaterials are getting affected by morphology, it is important to understand the nature of nanoparticles for specific applications. Various analytical techniques such as transmission electron microscopy (TEM), UV-Vis spectroscopy, scanning electron microscopy (SEM) and electron dispersion spectroscopy (EDS) have been used in investigation of nanomaterials.

**Transmission Electron Microscopy (TEM)**

Transmission electron microscopy (TEM) is a high resolution microscopic technique, which gives precise information about shape, average particle size and particle size distribution. For TEM analysis, 400 mesh size copper grids were first washed with hydrochloric acid followed by water then acetone, and finally air dried. These washed grids were coated with formvar solution. Using a water bath sonicator, 100 µl of GNPs sample was sonicated and from that 5 µl of sample was deposited onto formvar coated Cu grid. The samples were then air dried and observed under JEOL-TEM. The TEM films were developed and scanned. Particle diameter was determined using Ultra-iridium software. The scale marker (size of the grid magnification = size on negative film) of 100 nm for fructose GNPs and 200 nm for sucrose and raffinose GNPs (obtained from the ruler, scanned under same number of pixels as that of negative film scan) was placed on the scanned TEM image file. Images were imported into Ultra-iridium software and then the particle analysis option was chosen to get the particle diameter distribution on the basis of size.
Nanoparticle Number Calculation (Number of particles/mL)

After determining the size of particles, number of particles/mL for fructose GNPs was calculated as follows,

a) Molarity of gold stock solution i.e. 50 mg/mL is 0.132 M

b) 10 µl is added from 0.132 M gold stock to 5 mL of fructose stock solution

\[ 0.132 \times 10 \, \mu l = y \times 5 \, mL \times (5000 \, \mu l) \]
\[ y = 2.64 \times 10^{-4} \, M \]

c) Total number of gold atoms in 1 mL sample (z)

\[ 2.64 \times 10^{-4} \times 6.023 \times 10^{23} \, \text{atoms/mol} \]
\[ Z = 15.9 \times 10^{19} / \text{Lit} = 15.9 \times 10^{16} \, \text{atoms/mL} \]

d) Number of gold atoms in one NP (N_{Au}) = \frac{(V_{NP} \times \text{APF})}{V_{Au}}

Volume of nanoparticles (V_{NP}) = \frac{4\pi r_{NP}^3}{3}

Volume of Au (V_{Au}) = \frac{4\pi r_{Au}^3}{3}

Atomic Packing Factor (APF) - \frac{N_{\text{atoms}} \times V_{\text{atoms}}}{V_{\text{unitcell}}}

(The unit cell of gold is face centered cubic), Therefore,

\[ \text{APF} = \frac{\pi}{3\sqrt{2}} = 0.74048 \]

Number of gold atoms in one NP (N_{Au}) = \frac{(V_{NP} \times 0.74048)}{V_{Au}}

\[ N_{Au} = (\text{Avg. particle size/nm})^3 \times 31 \]
\[ N_{Au} = (10)^3 \times 31 = 3.1 \times 10^4 \]

e) Total number of NPs in 1 mL sample

\[ N_{Au} \text{ in 1 mL sample/} N_{Au} \text{ in one GNP} \]
\[ 15.9 \times 10^{16} / 3.1 \times 10^4 = 5.12 \times 10^{12} / \text{mL} \]
Similarly number of particles/mL for sucrose and raffinose GNPs were calculated by above described method. Table 2 summarizes number of particles/mL for fructose, sucrose and raffinose GNPs.
<table>
<thead>
<tr>
<th>Sugar GNPs</th>
<th>Number of particles/mL</th>
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<tbody>
<tr>
<td>Fructose GNPs</td>
<td>5.12 X 10^{12}</td>
</tr>
<tr>
<td>Sucrose GNPs</td>
<td>2.56 X 10^{12}</td>
</tr>
<tr>
<td>Raffinose GNPs</td>
<td>2.56 X 10^{12}</td>
</tr>
</tbody>
</table>

Table 2. Number of particles/mL for fructose, sucrose and raffinose GNPs
**Dynamic Light Scattering Spectroscopy (DLS)**

Dynamic light scattering (DLS) is an analytical technique used for determination of average size and size distribution of nanoparticles. Gold nanoparticles when subjected to laser, scatter light in all directions based on their sizes. The intensity of scattered light fluctuates over time due to Brownian motion of the particles in the solution. Based on the intensity of light, size of GNPs can be estimated.

Zetasizer Nano S particle size analyzer was used in this work. All the samples were diluted up to 1 mL in autoclaved nanopure water and probe sonicated before analysis. Analysis was done at 25 °C with a scattering angle of 90°. Each sample shows the average of 3 datasets run in autorun mode. Each dataset involved at least 13 runs.

**UV-Visible Spectroscopy (UV-Vis)**

Gold nanoparticles have unique surface plasmon resonance property (SPR). This unique property is because of the quantum size effect at the nanoscale. When the oscillation frequency of electrons in the conduction band matches with the frequency of incoming light radiation, spherical GNPs exhibit characteristic absorbance peak. SPR intensity and peak is influenced by particles size, shape, structure, composition and dielectric constant of the surrounding medium. SPR serves as an important tool for the evaluation of morphological characteristics of synthesized GNPs. Hitachi U-3900 UV-Visible spectrophotometer was used for the analysis. First GNP dispersions were sonicated by probe sonication for 5 min with 10 sec run time and 2 sec pause at 50% amplitude. The gold nanoparticle dispersions were then diluted to desired concentration and analyzed using a UV-Vis spectrophotometer. Two quartz cuvettes of 1 cm path length were used, one as reference (water) and one for GNPs.
SEM-EDS Spectroscopy

In order to determine the composition of sugar GNPs, scanning electron microscopy combined with energy dispersion spectroscopy were used. For EDS study, samples were washed extensively and were spotted on aluminum stub and air dried. These samples were then loaded and elemental analysis was done by using a JEOL JSM-5400 LV with IXRF system.

Evaluation of Catalytic Activity Sugar GNPs

To evaluate the catalytic activity of sugar capped gold nanoparticles, p-nitrophenol reduction by NaBH₄ assay was used as a model system. p-Nitrophenol is a chemical which is used in leather and cork insulation industries as a fungicide. p-Nitrophenol is also used in the synthesis of p-aminophenol, mainly used in pharmaceutical companies for manufacturing paracetamol and other anti-inflammatory drugs. p-Nitrophenol shows high stability in water and its degradation is very slow process in absence of any catalyst. Upon exposure, p-nitrophenol causes acute toxicity. So finding out the way for the removal of hazardous p-nitrophenol is of an immense importance. Gold nanoparticles have played an important role in the reduction of p-nitrophenol to nontoxic p-aminophenol. This reduction process involves color change, based on the concentration of reacting species, providing a simple way of monitoring reaction kinetics using various spectroscopic methods. This catalytic reduction of p-nitrophenol was studied using UV-Vis spectrophotometer. The reaction was carried out in an aqueous solution at three different temperatures (9 ºC, 25 ºC and 45 ºC). 105 µl of 0.105 mM p-nitrophenol was added to freshly prepared 210 µl of 42 mM NaBH₄ solution. The reaction volume was made up to 1 mL by adding nanopure water. For all the
experiments, the concentration of p-nitrophenol and NaBH₄ were same. To the reaction mixture, 25 µl of fructose GNPs, 50 µl of sucrose GNPs and 50 µl of raffinose GNPs were added individually. The concentration of sugar GNPS were 1.28 x 10¹¹/mL for fructose, sucrose and raffinose GNPs. UV-Vis spectra were recorded at different time interval in the wavelength range from 200 to 600 nm and the reaction kinetic was monitored by recording the absorbance at 400 nm. Different kinetic parameters such as rate constant, activation energy and pre-exponential factor were calculated.
Results

Synthesis of Sugar-GNPs (S-GNPs)

In order to evaluate and compare the catalytic activity of S-GNPs, it was necessary to obtain gold nanoparticles of uniform morphology. In this effort, different concentrations of nucleating agent (gold salt) and reducing agent (sugars) were mixed and incubated to different reaction conditions. Samples were observed under TEM to obtain information about the morphology of synthesized GNPs. Finally, after studying various concentrations and effect of different reaction conditions, appropriate concentrations of nucleating agent and reducing agent were selected and incubated at 37 °C at 150 rpm for the specific time period (Table 3).

After specific reaction conditions, color change was observed of the solutions, representing the reduction of Au$^{3+}$ to Au$^{0}$ and subsequent capping on the GNPs surface by sugars. In the case of fructose and sucrose GNPs, the color changed from colorless to pink, whereas for raffinose GNPs, the color changed from colorless to purple.
<table>
<thead>
<tr>
<th>Concentration of reducing and capping agent (M)</th>
<th>Concentration of nucleating agent (mM)</th>
<th>Reaction condition (hrs)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.33 Fructose</td>
<td>0.264</td>
<td>6</td>
<td>37</td>
</tr>
<tr>
<td>1.75 Sucrose</td>
<td>0.132</td>
<td>4</td>
<td>37</td>
</tr>
<tr>
<td>0.084 Raffinose</td>
<td>0.132</td>
<td>12</td>
<td>37</td>
</tr>
</tbody>
</table>

Table 3. Reaction conditions for the synthesis of fructose, sucrose and raffinose GNPs
Characterization of Sugar-GNPs

Transmission Electron Microscopy (TEM)

To obtain information regarding the size, particle size distribution and shape, different samples of synthesized S-GNPs were viewed under TEM. From TEM analysis, it was observed that the resultant particles were of nearly spherical, monodisperesed and less aggregated. TEM study also revealed that the particles were in the size range of 10 ± 5 nm.

Dynamic Light Scattering Spectroscopy (DLS)

DLS was used to confirm the particle size and size distribution of the particles. Results showed that the fructose GNP were in the size range 30 ± 5 nm (did not match with the results from TEM). Whereas sucrose and raffinose GNPs were in the size range of 10 ± 5 nm, which was further validated using TEM analysis (Figure 5).

UV-Visible Spectroscopy (UV-Vis)

The S-GNPs were also studied using UV-Vis spectroscopy. A distinct plasmon resonance peak was observed for fructose, sucrose and raffinose GNPs at 541 nm, 548 nm and 547 nm respectively (Figure 6). UV-Vis spectroscopy results confirmed the formation of nearly spherical shape S-GNPs.
Figure 5. Shows the TEM images and corresponding size distribution graph by DLS of (A) fructose, (B) sucrose and (C) raffinose GNPs. TEM analysis showed all the three S-GNPs were within the similar size range of $10 \pm 5$ nm. From DLS analysis, size of fructose GNPs was found to be $30 \pm 5$ nm. Whereas, results of DLS analysis of sucrose and raffinose GNPs matched with the TEM results.
Figure 6. UV-vis Absorption spectra of fructose, sucrose and raffinose GNPs showing absorbance peak at 541 nm, 548 nm and 547 nm respectively.
Scanning Electron and Electron Dispersion Spectroscopy (SEM-EDS)

To determine the elemental composition of various sugar GNPs, scanning electron microscope combined with electron dispersive spectroscopy was used. Thoroughly washed and air dried S-GNPs samples deposited on aluminum stub were studied under SEM. The SEM-EDS images of S-GNPs, showed strong peaks at 2.138 keV (Figure 7). Results showed the anticipated percent value of gold (Au) (49 %, 43 %, 46 %) and Carbon (C) (34 %, 24 %, 34 %) for fructose, sucrose and raffinose GNPs respectively.
Figure 7. Represents SEM images and EDS spectrum showing elemental composition of S-GNPs. (A) SEM-EDS of fructose GNPs shows 49 w% of gold and 34 w% of carbon. (B) SEM-EDS of sucrose GNPs shows 24 w% of gold and 43 w% of carbon and (C) SEM-EDS of raffinose GNPs shows 46 w% of gold and 34 w% of carbon. This confirms the capping of sugars onto the gold nanoparticles surface and formation of stable S-GNPs.
Catalytic Activity of S-GNPs

p-Nitrophenol reduction assay was used as a model system to evaluate the effect of sugar chain length on the catalytic activity. An aqueous solution of p-nitrophenol exhibits a characteristic absorbance peak at 317 nm. Addition of NaBH₄ to p-nitrophenol shows red shift to 400 nm due to formation of p-nitrophenolate ion. Conversion of p-nitrophenolate ions to p-aminophenol is very slow process and takes more than 8 hrs (Figure 8).

But upon introduction of a catalyst i.e. S-GNPs (dispersion of fructose, sucrose and raffinose GNPs) in the reaction mixture, decrease in the concentration of p-nitrophenolate ion was observed with a gradual drop in the peak intensity at 400 nm. At the same time, a new absorbance peak was observed at 315 nm, indicating the formation of p-aminophenol (Figure 9). Complete disappearance of the peak at 400 nm was observed within 2, 4 and 8 mins for fructose, sucrose and raffinose GNPs respectively. Thus indicating the completion of reduction demonstrating the catalytic activity of synthesized S-GNPs.
Figure 8. UV-visible spectrum of the (A) p-nitrophenol and (B) p-nitrophenolate ions in absence of catalyst at different time intervals. P-nitrophenol shows absorption peak at 317 nm. Addition of NaBH₄ to p-nitrophenol shows red shift to 400 nm, which indicates the formation of p-nitrophenolate ions. In absence of S-GNPs catalyst, there was no reduction in the intensity of peak at 400 nm after 8 hrs, which represents inability of a reaction to proceed without S-GNPs catalyst.
Figure 9. UV-visible absorption spectra for the catalytic reduction of 4-nitrophenol at 25 °C in presence of (A) fructose GNPs, (B) sucrose GNPs, and (C) raffinose GNPs. These spectra represent time dependent decrease in the intensity of absorption peak at 400 nm along with the generation of a new peak at 315 nm, which signifies the generation of p-aminophenol. Complete disappearance of peak at 400 nm was seen after 2 mins, 4 mins and 8 mins for fructose, sucrose and raffinose GNPs respectively.
**Rate Constant (k) Calculation**

In order to compare the catalytic activity, catalytic rate constant (k) was calculated for fructose, sucrose and raffinose GNPs at 10 °C, 25 °C and 45 °C. The reduction in the intensity at 400 nm as a function of time in the presence of fructose, sucrose and raffinose GNPs was monitored by UV-Vis spectroscopy (Figure 10). From the figure it can be seen that certain time was required for the reactants to adsorb onto GNPs surface before reaction could be initiated. This period of time can be defined as the adsorption time (t_{ads}) or induction time. Pseudo first order kinetics was applied to the reaction system. In certain chemical reactions, second order reaction might appear to be first order, when one of the reactants in the rate equation is present in great excess over the other in the reactant.

\[
2A + B \rightarrow P + \text{etc} \quad (P = \text{product})
\]

\[
[A]_o > > [B]_o
\]

So [A] is approximately constant throughout the entire reaction. In present study, concentration of BH\text{4}\text{−} greatly exceeds the p-nitrophenol concentration, so the pseudo first order kinetics was applied with respect to p-nitrophenol to the reaction system (Figure 11). After the induction time, the graph showed a linear correlation, which confirmed the pseudo first order kinetics of reaction. Catalytic activity for each kind of S-GNPs was studied at three different temperatures and the average reaction rate constant was calculated from the slope of linear sections of the plots. Among all the S-GNPs, fructose showed highest reaction rate and shortest adsorption time, whereas lowest reaction rate and highest adsorption time was observed for raffinose GNPs. Table 4 summarizes the rate constant data of S-GNPs at three different temperatures.
Figure 10. Represents the reduction (normalized against the initial point) in the peak intensity at 400 nm for nitrophenolate ions as a function of time in the presence of fructose, sucrose and raffinose GNPs. The experiments were carried out at three different temperatures (A) 10 °C (B) 25 °C and (C) 45 °C. Concentration of the reactants i.e. p-nitrophenol and NaBH₄ were 42 mM and 0.105 mM respectively. The concentration of S-GNPs catalyst was $1.28 \times 10^{11}$ particles/mL in all three cases. Time required for the complete reduction of p-nitrophenol was lowest for fructose GNPs, while it was highest for raffinose GNPs at all the three temperatures.
Figure 11. Represents plots of natural log of absorbance versus time at 400 nm for fructose, sucrose and raffinose GNPs at three different temperatures (A) 10 °C (B) 25 °C and (C) 45 °C. The rate constant (k) was calculated from the slope of the linear fitting of the curve.
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Fructose GNPs</th>
<th>Sucrose GNPs</th>
<th>Raffinose GNPs</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>$1.47 \pm 0.029/\text{min}$</td>
<td>$0.52 \pm 0.014/\text{min}$</td>
<td>$0.27 \pm 0.023/\text{min}$</td>
</tr>
<tr>
<td>25</td>
<td>$2.14 \pm 0.15/\text{min}$</td>
<td>$1.19 \pm 0.078/\text{min}$</td>
<td>$0.60 \pm 0.015/\text{min}$</td>
</tr>
<tr>
<td>45</td>
<td>$5.32 \pm 0.17/\text{min}$</td>
<td>$2.70 \pm 0.056/\text{min}$</td>
<td>$1.91 \pm 0.099/\text{min}$</td>
</tr>
</tbody>
</table>

Table 4. Rate constant (k) of fructose, sucrose and raffinose GNPs at 10, 25 and 45 °C respectively.
**Activation Energy (Ea) and Pre-Exponential Factor (A) Calculation**

Activation energy is an important factor for all the chemical reactions, depicting the relationship between the temperature and reaction rate. Activation energy was calculated using the Arrhenius equation,

\[
\ln k = \ln A - \frac{Ea}{RT}
\]

Where, A is a pre-exponential factor, k is the rate constant of the reaction at temperature T (Kelvin) and R is universal gas constant. The activation energy was calculated from the slope of linear fitting of the graph of natural log (ln) of rate constant (k) at three different temperature versus 1000/T (**Figure 12**). In addition, pre-exponential factor was calculated from the y-intercept of the linear fitting of the curve. The values of activation energy and pre-exponential factor for the catalytic reduction of p-nitrophenol by S-GNPs are summarized in **Table 5** and were found to be in the order of fructose GNPs < sucrose GNPs < raffinose GNPs.
Figure 12. Represents the Arrhenius graph showing the effect of temperature on the reaction rate. The graph was obtained by plotting natural log values of rate constant (k) of fructose, sucrose and raffinose gold nanoparticles versus 1000/T (Kelvin⁻¹). The activation energy (Eₐ) and Pre-exponential factor (A) was calculated from the slope and y-intercept of the graph.
Table 5. Activation energy and Pre-exponential factor of fructose, sucrose and raffinose GNPs

<table>
<thead>
<tr>
<th>GNPs</th>
<th>Activation Energy (E&lt;sub&gt;a&lt;/sub&gt;) (KJ/mole)</th>
<th>Pre-exponential Factor (A) (min&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fructose</td>
<td>27.78 ± 0.62</td>
<td>1.83 x 10&lt;sup&gt;5&lt;/sup&gt;</td>
</tr>
<tr>
<td>Sucrose</td>
<td>34.78 ± 0.19</td>
<td>1.43 x 10&lt;sup&gt;6&lt;/sup&gt;</td>
</tr>
<tr>
<td>Raffinose</td>
<td>42.01 ± 0.03</td>
<td>4.92 x 10&lt;sup&gt;7&lt;/sup&gt;</td>
</tr>
</tbody>
</table>
Discussion

Synthesis of Sugar-GNPs

Many studies have demonstrated the use of sugars in the formation of gold nanoparticles. Sugars contain electron rich hydroxyl functional groups in their structures, which are responsible for the effective reduction of the Au$^{3+}$, having a high reduction potential to Au$^0$. The Au$^0$ thus formed may colloid with neighboring Au$^0$ to form gold nanoparticles. In addition, due to its unique H-bonding ability, hydroxyl groups when dissolved in aqueous medium, forms a supramolecular structure which imparts hydrophilicity and stability to the resultant GNPs.

In our study, we have demonstrated the direct synthesis of monodispersed, nearly spherical gold nanoparticles within the size range of 10 ± 5 nm in an aqueous medium using various sugars for catalytic applications. The synthesis process was eco-friendly and cost-effective as it avoided the use of toxic and expensive chemicals or solvents. Different concentrations of KAuCl$_4$ were dissolved in an aqueous medium containing various concentrations of sugars in order to determine the appropriate concentration of both gold and sugars required to obtain homogeneous particles. Reactions were carried out under mild conditions at 37 ºC. Sugars acted as both reducing and capping agent, which made the synthesis process single step and single phase method.

Formation of gold nanoparticles was indicated by the change in color from colorless to pink/purple. To get more detailed idea about the morphology, synthesized GNPS were subjected to TEM, DLS, UV-Vis spectroscopy and SEM-EDS analysis. TEM and DLS analysis gave an idea about particle size and size distribution. The particle size was observed to be in the range of 10 ± 5 nm. UV-visible spectroscopy showed
absorbance peaks at 541, 548 and 547 nm for fructose, sucrose and raffinose GNPs respectively. These results confirmed the particles were of the same size with good uniformity. SEM-EDS analysis provided more insight towards the capping of sugars onto GNPs surface. Elemental composition study through SEM-EDS showed peaks for gold and carbon, which confirmed the presence of organic moiety i.e. sugars on the gold nanoparticles surface.

**Catalytic Activity of Sugar GNPs**

When subjected to the catalytic reduction of p-nitrophenol to p-aminophenol, S-GNPs demonstrated potent catalytic activity. Conversion of p-nitrophenol to p-aminophenol by NaBH₄ is thermodynamically favored, but in the absence of a catalyst, reaction does not go to completion due to large potential difference between the reactant molecules. However, upon introduction of S-GNPs to the reaction mixture containing p-nitrophenol and NaBH₄, a rapid decrease in the p-nitrophenol concentration along with the generation of p-aminophenol was observed. This catalytic efficacy of S-GNPs is due to their high surface area and high reduction potential, facilitating the transfer of electrons from donor borohydride (BH₄⁻) to the acceptor p-nitrophenol to overcome the kinetic barrier. A possible reaction mechanism involved in the p-nitrophenol reduction assay is the Langmuir-Hinshelwood mechanism. According to this mechanism, reaction proceed via four steps: (1) adsorption of the reactant molecules to the surface, (2) diffusion of the molecules to the active site and formation of the surface complex, (3) reaction of the complex to form the adsorbed product, and (4) finally desorption of the product. GNPs provide sites for the adsorption of reactants, BH₄⁻ as well as p-nitrophenol. Adsorption of BH₄⁻ to the GNPs surface generates surface-hydrogen species, which is then accepted by
p-nitrophenol, thus leading to the formation of p-aminophenol. Here, diffusion of BH$_4^-$ and p-nitrophenol onto the GNP surface and desorption of p-aminophenol are the rate limiting steps, which determines the rate of the reaction.

Among all the S-GNPs, fructose (monosaccharide) GNP displayed highest catalytic activity, while raffinose (trisaccharide) GNP had lowest catalytic activity. This shows the effect of sugar chain length on the catalytic efficacy of GNP. Such diminishing catalytic activity with an increase in the sugar chain length can be attributed to the large surface coverage.

As in case of fructose GNP, gold nanoparticles surface is covered by single unit of saccharide, allowing the diffusion of reactant molecules onto the GNP. On the other hand, for sucrose and raffinose GNP, an increase in the sugar units leads to the larger surface coverage leaving behind very few sites for the diffusion of reactant molecules onto the GNP surface. This decreases the surface to volume ratio of GNP and does not facilitate the reduction reaction.

The effect of temperature on the reaction rate was studied by catalyzing reactions at different temperatures. It was observed that the increase in the temperature causes an increase in the reaction rate which occurs due to an increase in the frequency of collision between reactant molecules. Activation energy and pre-exponential factor was calculated from the slope and y-intercept of the plot of ln of rate constant (k) at temperatures 10°C, 25°C and 45°C and 1000/T (Kelvin) using Arrhenius equation. Fructose GNP showed lowest activation energy and pre-exponential factor values, while it was highest for raffinose GNP. Thus, the length of sugars is the predominant factor in determining the catalytic activity of GNP.
Conclusion

In conclusion, stable monodispersed and catalytically active gold nanoparticles capped with sugar molecules were successfully synthesized via environmental friendly, single step and single phase method. Synthesized GNPs were characterized by various analytical techniques, which suggested the sugars were responsible for effective reduction of gold salt and capping onto GNPs surface. The synthesized GNPs were observed to be well dispersed and nearly spherical in shape within the size range of 10 ± 5 nm.

We demonstrated the use of S-GNPs catalyst for reduction of p-nitrophenol, a toxic pollutant to p-aminophenol. We have also studied the relationship between sugar chain length and catalytic activity. S-GNPs showed potent catalytic activity and it was observed in the descending order of fructose GNPs > sucrose GNPs > raffinose GNPs. Decrease in the catalytic activity with an increase in the sugar chain length is attributed to the available surface area. Given to the high activity and stability, S-GNPs might be useful as a catalyst for wide range of industrial and environmental applications.
References


