PRF # 57010-UR10

Project Title: Green Gold Nanoparticles for Catalytic Reduction of Nitrophenols

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With the increasing applications of nano-gold catalysts for numerous industrial applications, we have designed and synthesized gold nanoparticles (AuNPs) in the size range of 10± 5 nm using a single-step green process. We have utilized the combined reducing/capping ability of naturally available saccharides like fructose (Fru), maltose (Mal), and raffinose (Raf) to synthesize saccharide conjugated nanoparticles (Sac-AuNP). Using these Sac-AuNPs we evaluated and compared the catalytic properties of saccharide conjugated AuNPs (including Fru-AuNPs, Mal-AuNPs and Raf-AuNPs), using a model reaction system based on the reduction of p-nitrophenolate in presence of sodium borohydride ($NaBH_4$). Using the kinetic data obtained from the spectroscopic measurements at three different temperatures (10 °C, 25 °C and 45 °C), we calculated the average rate constant (k), activation energy (Ea), and pre-exponential factor (A) for each type of saccharide conjugated AuNPs. The results indicated Fru-AuNPs to be highly catalytically active in comparison to Mal-AuNPs and Raf-AuNPs, which can be attributed to the availability of greater active surface area for catalysis due to the small size of the ligand. The average rate constant values were found to be in descending order as, Fru-AuNPs, Mal-AuNPs, and Raf-AuNPs. Whereas, the order of activation energy (Ea) was, in ascending order, Fru-AuNPs, Mal-AuNPs, Raf-AuNPs respectively. In conclusion, our studies elucidate the relationship between the size of the conjugated ligand and the catalytic activity of the resultant saccharide conjugated AuNPs (Sac-AuNP) as inversely proportional.

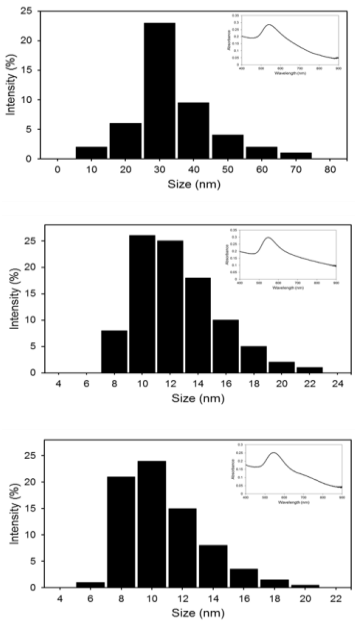

Figure 1. Illustration of the morphological and size characterization of synthesized Sac-AuNPs through UV-Vis, and DLS.

Using the principles of our patented AuNP synthesis methodology, we utilized a single step bio-friendly process for synthesizing catalytically active AuNPs using commonly available saccharides of varying chain length such as fructose, maltose and raffinose. The novelty of the method includes the synthesis of cheap nano-catalysts using a simple process with a wide potential to transform the concept into commercial application. A UV-Vis spectrum of synthesized Sac-AuNPs showed a sharp near-identical peak in the visible region for all the three saccharides, indicating the formation of spherical AuNPs. The peak absorption wavelength (λmax) for Fru-AuNPs, Mal-AuNPs and Raf-AuNPs was 545 ± 3 nm (Figure 1). The average size distribution for Fru-AuNPs, Mal-AuNPs and Raf-AuNPs were found to be 20 ± 10 nm, this slight increase in size can be attributed to the fact that DLS calculations are based on hydrodynamic radius of AuNPs rather than actual diameter as observed by TEM (Figure 1).

UV-Vis spectroscopic measurements for the reduction of 4-nitrophenol in presence of Sac-AuNPs were used in the determination of the catalytic activity. From the reduction assay, it was evident that all Sac-AuNPs were catalytically active since there was a gradual extinction in the intensity of 4-nitrophenol and with complete observable extinction occurring after a reaction time of 2 min, 4 min and 8 min for Fru-AuNPs, Mal-AuNPs and Raf-AuNPs respectively.

It is well known that temperature has a direct effect on the rate at which the reaction proceeds. Correspondingly, the 4-nitrophenol reduction rate was measured at the three different temperatures of 10 °C, 25 °C and 45 °C (Figure 2). Overall, the catalytic activity efficiency was found to be in the descending order of Fru-AuNPs, Mal-AuNPs, and Raf-AuNPs.

A plot of –ln Iext versus time for all the three Sac-AuNPs each of the different temperatures was plotted. The Iext represents the intensity of 4-nitrophenolate ion at 400 nm at the specific reaction time. As seen from the results, the graph showed linear relationships justifying the pseudo-first order reaction. By

applying an analysis of the least squares methodology (LINEST) the average rate constant (k) was calculated individually from the slope for Fru-AuNPs, Mal-AuNPs and Raf-AuNPs at all three temperatures of 10 °C, 25 °C and 45 °C. From the data, shown in (Table 1), the order of rate constant (k) was, in descending order, Fru-AuNPs, Mal-AuNPs, and Raf-AuNPs at all the three different temperatures, which correlates with the previous observations.

By plotting a graph of natural log of rate constant (ln k) at the three different temperatures (T) vs. 1000/T (kelvin) for all Sac-AuNPs, activation energy (Ea) was calculated from the slope (- Ea/R) of straight line. From the results, Ea (kJ mol^{-1}) was found to be lowest for Fru-AuNPs (17.12± 0.77 kJ mol^{-1}) as compared to Mal-AuNPs (31.31 ± 1.39 kJ mol^{-1}) and Raf-AuNPs (40.50 ± 1.28 kJ mol^{-1}) (Table 1). Hence Fru-AuNPs were found to be more catalytically active than the other Sac-AuNPs.

Finally, the pre-exponential factor (A) was determined from the intercept of the plot of ln k vs. 1000/T and was found to be significantly less for Fru-AuNPs (2.34 x 10^2 s^{-1}) in relative to Mal-AuNPs (2.98 x 10^3 s^{-1}) and Raf-AuNPs (7.51 x 10^3 s^{-1}) (Table 1). The plot of ln A vs. E_a for three different Sac-AuNPs showed a linear relationship suggesting the compensation effect, which is usually observed in homogenous and heterogeneous catalyst systems.

Therefore, we observed Fru-AuNPs to possess higher catalytic activity as compared to Mal-AuNPs and Raf-AuNPs from the above catalytic results. This observation was supported by lower values of Ea for Fru-AuNPs in comparison with that of Mal-AuNPs and Raf-AuNPs. The effect can be directly correlated with the ligand size, which is the smallest for Fru-AuNPs. The small size of ligand results in high density of available surface area which is known to be the catalytically active sites for the reduction reaction69. Since all the Sac-AuNPs displayed catalytic ability, the research opens a new path for designing cheap nano-catalyst using widely available, biodegradable and environmentally safe saccharides using a cost-effective synthetic process for many catalytic applications. The synthesized AuNPs can also be used as a supported catalyst on various surfaces for enhancing the catalytic effect.

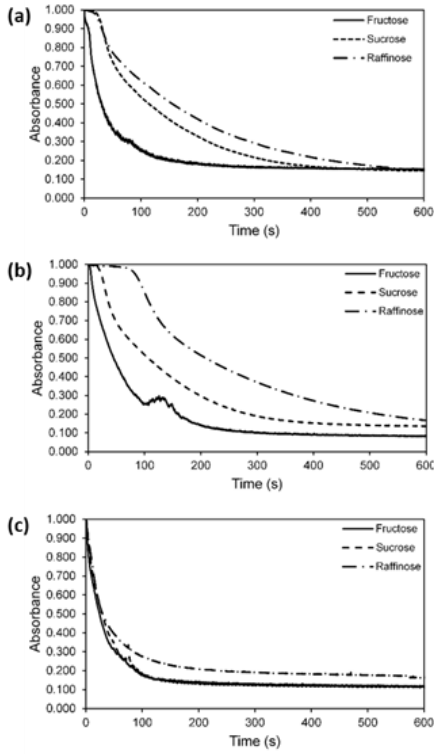

Figure 2. UV-Visible spectroscopic time scan analysis. As the reactions' temperature increase, the t_{abs} decreases and the reaction reaches equilibrium at a greater pace as indicative across the 10 °C (a), 25 °C (b), and 45 °C (c) spectrographs.

Type of Sac-AuNP	Rate Constant (s^{-1})			Activation Energy (kJ mol^{-1})	Pre-Exponential Factor A (s^{-1})
	10 °C	25 °C	45 °C		
Fru-AuNP	4.42 ± 0.063	5.27 ± 0.024	5.95 ± 0.016	17.12 ± 0.77	234.71
Mal-AuNP	4.27 ± 0.035	4.83 ± 0.038	5.24 ± 0.068	31.32 ± 1.39	2982.53
Raf-AuNP	3.63 ± 0.028	3.82 ± 0.029	4.06 ± 0.014	40.50 ± 1.28	7151.28

Table 1. Illustration of the pseudo-first order rate constants (k') of each Sac-AuNPs at 10 °C, 25 °C, and 45 °C. Additionally the interpolated activation energy (Ea) and pre-exponential factor (A), which were calculated from the reaction rate and temperature relationship, are included for all Sac-AuNP samples.

The professional research activity of the PI has tremendously benefited from this grant. During the funding period, more than 20 students involved in various aspects of this project. The students also presented in more than 50 research conferences. We are now drafting a manuscript for a peer-review journal with the data collected so far with student co-authors. These projects also lead to the submission of several other federal grants.