



Metal nanoparticles with high catalytic activity in degradation of methyl orange: An electron relay effect

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ABSTRACT

Gold, silver and platinum nanoparticles have been synthesized following a green approach by reducing the corresponding salt using tannic acid as reducing agent at room temperature in aqueous medium. The reaction is instantaneous and the average diameter of the particles formed is around 10 nm in all the three cases as measured by TEM. These nanoparticles have been used as a catalyst for the degradation of methyl orange in the presence of sodium borohydride (NaBH₄). Silver nanoparticles have a drastic catalytic effect as compared to gold or platinum nanoparticles on the degradation of methyl orange in the presence of sodium borohydride. From the kinetic data it is concluded that the rate constant follows the order: $k_{\text{Ag nanoparticles}} \gg k_{\text{Au nanoparticles}} > k_{\text{Pt nanoparticles}} \gg k_{\text{uncatalyzed reaction}}$. The high catalytic effect of silver nanoparticles has been attributed to its low value of work function as compared to Au and Pt. The uncatalyzed reaction does not show any decrease in the absorbance value within the given experimental time due to the large kinetic barrier, i.e. high activation energy. Decrease in absorbance value for uncatalyzed reaction is observed after nearly 48 h that too at a very high concentration of reducing agent, thereby indicating that reaction is extremely slow and reduction of methyl orange is thermodynamically feasible.

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1. Introduction

There has been growing interest for the creation of nanoscale materials with a complex shape and controlled size under ambient conditions in aqueous solutions. For metallic nanoparticles, interesting optical and electronic effects [1–4] are expected in the size range of 10–100 nm since the mean free path of an electron in a metal is 10–100 nm [5,6]. There are various routes of synthesis of metal nanoparticles [7–14] in the size range of 10–100 nm but the subsequent use of these particles for various applications are either hampered by the drastic method of synthesis or removal of hazardous chemicals which are used for synthesis. Recently attention has been given to the green route of synthesis of metal nanoparticles because of its soft nature as well as safety and environmental concerns [15–18]. Some fundamental studies have revealed that biomolecules can selectively recognize inorganic surfaces [19,20]. Tannic acid is typically hydrolyzed to tannin, a mixed gallotannin composed of gallic acid esters of glucose, which has been used for the biomimetic growth of inorganic nanoparticles [21]. Controlling the size and shape of nanocrystalline materials is a key issue in

catalysis. Generally, sphere-shaped inorganic nanoparticles, both semiconducting and metallic, have been of particular interest for such type of catalytic reactions. It was observed that the optical properties of silver and gold nanoparticles are tunable throughout the visible and near-IR regions of the spectrum as a function of the nanoparticle size, shape and local environment. Nanoparticles of gold and silver with nanometer scale dimensions are of particular interests as catalysts in organic and inorganic reactions [22,23].

The electron transfer step plays a vital role in the degradation of dyes. This step depends on the potential difference, as there can be large redox potential difference between the donor and acceptor, which can hinder the passage of electrons between them [24,25]. An effective catalyst, such as silver, gold or platinum nanoparticles with an intermediate redox potential value between the donor and acceptor helps in the electron transfer and thus acts as an electron relay system [26]. Gold, silver and platinum nanoparticles are well-known examples of this type of redox catalyst and it is known that when metal particles become nanoparticles, their electrode potential differs from each other. The turnover frequency (TOF) of metal nanoparticles increases as the size decreases [27]. However, the probability of aggregation also increases as the size decreases [28]. Therefore, the presence of stabilizers and various surfactants is desirable to have a control over this problem. Tannic acid an important component of green tea leaves can be used as reduc-

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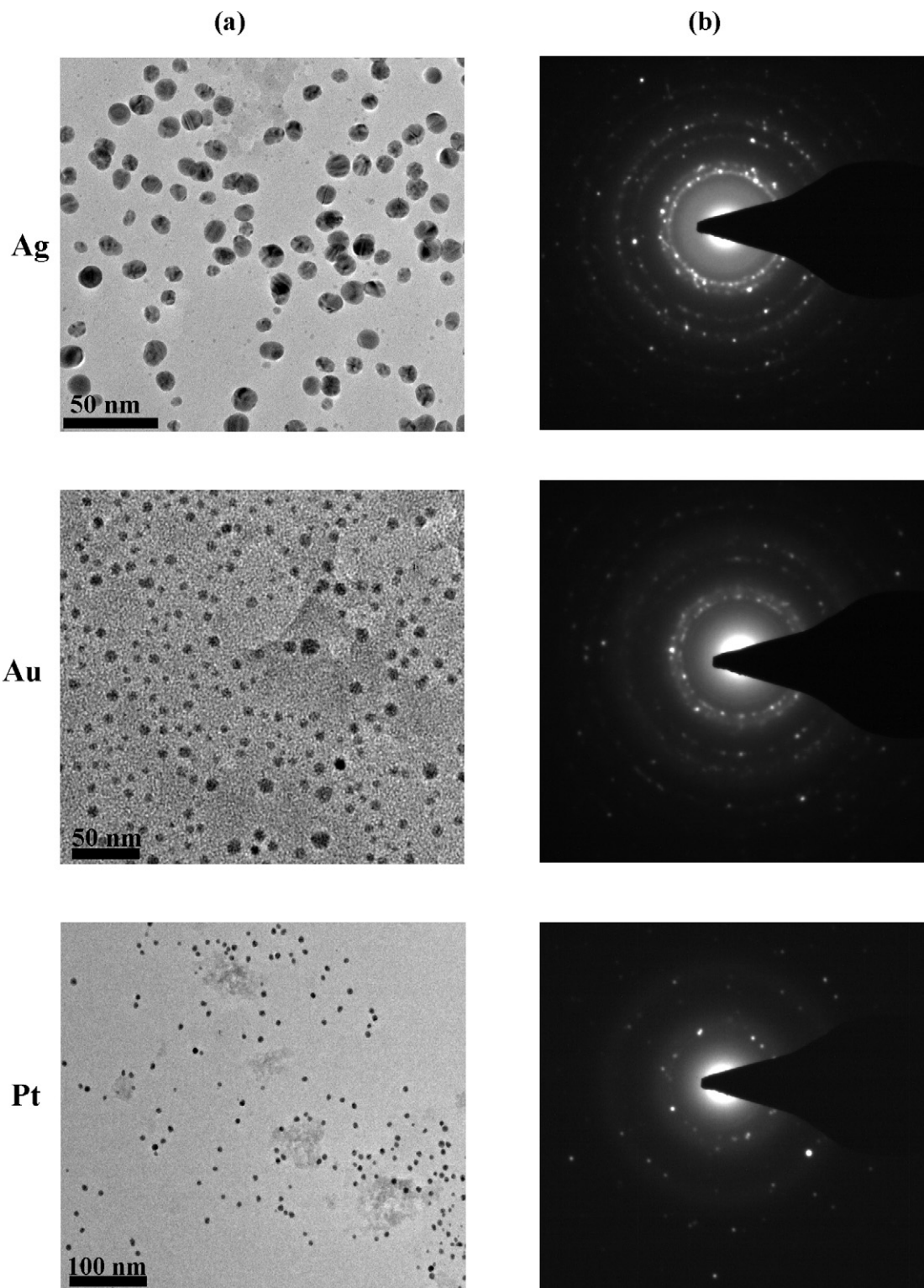


Fig. 1. (a) High resolution transmission electron microscopic pictures of Ag, Au and Pt nanoparticles and (b) SAED pattern of Ag, Au and Pt nanoparticles.

ing agent to reduce noble metal salts into metallic nanoparticles as well as it works as a capping agent to stabilize the particles so that no surfactant is necessary [29,30].

In this study we have synthesized Au, Ag and Pt metal nanoparticles using tannic acid and shown their applications as a catalyst in the degradation of methyl orange. The reduc-

tion of methyl orange by NaBH_4 in absence of catalyst is thermodynamically favourable, but it is kinetically difficult. Metal nanoparticles provide an alternative path for the reaction as they reduce the activation energy, hence reducing kinetic barrier, thereby making it thermodynamically and kinetically favourable.

2. Experimental

2.1. Materials

All the chemicals used were of AR grade. The aqueous solution was prepared in double-distilled water. Chloroauric acid (HAuCl_4), silver nitrate (AgNO_3) and chloroplatinic acid (H_2PtCl_6) were purchased from SRL, Merck and Spectrochem respectively. Tannic acid and sodium borohydride (NaBH_4) was obtained from Merck and spectrochem respectively. Methyl orange was procured from Thomas baker. All chemicals were used as such without any further purification.

2.2. Equipment

All spectra were recorded in UV–Vis Spectrophotometer-1601, Shimadzu and constant temperature water circulator from Haake instruments was used to maintain the temperature throughout the reaction.

2.3. Experimental procedure

2.3.1. Synthesis of gold, silver and platinum nanoparticles using tannic acid

To 5 mL of tannic acid (1.4×10^{-4} M), 100 μL of 3% w/v HAuCl_4 or 1 mL of 0.05% w/v AgNO_3 or 100 μL of 2% w/v H_2PtCl_6 was mixed to synthesize gold, silver or platinum nanoparticles respectively. The mixture was stirred for 2 min at room temperature for gold nanoparticles and for 1 min for silver nanoparticles while it was stirred for a longer time, i.e. for about 5 min at room temperature for platinum nanoparticles. The solution changes to violet, yellowish brown and yellow for gold, silver and platinum nanoparticles respectively. The synthesized metal nanoparticles was as such used as catalyst for the degradation of methyl orange by NaBH_4 and the rate constants (k) were determined.

2.4. Characterization of the metal nanoparticles

2.4.1. High resolution transmission electron microscopy (HRTEM)

TEM pictures were taken with TECNAI G²-30 U TWIN instrument. After preparation the metal nanoparticles were centrifuged and re-dispersed in double distilled water by sonication for 2–3 min. A drop of diluted solution was put on the copper grid and the grid was dried under ambient conditions. After complete drying of the grid, a TEM picture of the particles was taken.

2.4.2. Kinetic study for the degradation of methyl orange

To a mixture containing 50 μL of methyl orange (5×10^{-3} M) and 100 μL of sodium borohydride (0.5% w/v) solution, 50 μL of 0.01% aqueous dispersion of metal nanoparticles was added in a 3.5 mL capacity quartz cuvette. Total volume of the mixture was made up to 3.2 mL by adding the required amount of double distilled water. The reaction was studied in a spectrophotometer cuvette kept at a desired temperature by circulating water from a thermostated water bath. For the uncatalyzed reaction 50 μL of metal nanoparticles was replaced by an equal amount of double distilled water. The reaction was followed by studying the time-dependent absorbance (A) in a UV–visible spectrophotometer at 464 nm for 10 min and the fall in A with time at desired temperature was noted.

3. Results and discussion

We have adopted the greener route for the synthesis of metal nanoparticles in aqueous phase using pure tannic acid instead of strong and harmful reducing agents. In our approach, tannic acid is serving a dual role, i.e. it is acting as a reducing agent as well as

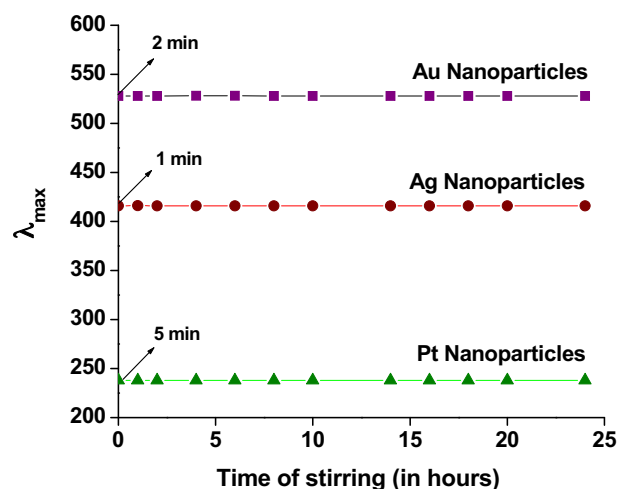


Fig. 2. The plot of λ_{\max} of all the three metal nanoparticles (Au, Ag and Pt) versus the time of stirring.

stabilizer for metal nanoparticles. The λ_{\max} of the prepared metal nanoparticles was observed at 528 nm for Au, 416 nm for Ag and 238 nm for Pt. The average particle size of all the three metals is around 10 nm as measured by transmission electron microscopy [Fig. 1(a)]. The particles obtained are spherical and reasonably monodispersed as seen from TEM images. The electron diffraction pattern (SAED) as shown in Fig. 1(b) clearly concludes that the particles are crystalline in nature. Due to capping effect of tannic acid, no aggregation of these nanoparticles occurs and size remains constant irrespective of the time of stirring of reaction mixture. The prepared nanoparticles are stable as their λ_{\max} value does not change with the time of stirring (Fig. 2) due to the presence of capping agent in tannic acid. We noticed that the dispersion of these nanoparticles in water is clear and quite stable for more than 150 days. The metal nanoparticles thus prepared by the above-mentioned procedure were used as catalyst for the reduction of methyl orange by NaBH_4 . The rate of degradation of colour of MO in the presence of NaBH_4 was monitored in the presence and absence of metal nanoparticles spectrophotometrically at a wavelength of 464 nm in water as a medium as shown in Fig. 3. The figure shows that the reduction of MO with NaBH_4 in absence of catalyst at 20 °C occurs at an extremely slow rate which is not visible from Fig. 3(d), indicating that the reaction is very slow under the given time constraint. But on the addition of metal nanoparticles degradation of the dye MO is greatly enhanced, especially in case of silver nanoparticles as compared to gold and platinum nanoparticles [Fig. 3(a–c)]. The catalytic efficiency of different metal nanoparticles are different as shown in Fig. 3 and from the graph we observed that there is a rapid decay in concentration of MO in the presence of Ag nanoparticles in just 9 min ($\Delta\text{OD}_{9\text{ min}} = 1.63$), as compared to Au ($\Delta\text{OD}_{40\text{ min}} = 0.70$) and Pt ($\Delta\text{OD}_{40\text{ min}} = 0.52$) nanoparticles in 40 min whereas there is no degradation up to 100 min for the uncatalyzed reaction ($\Delta\text{OD}_{100\text{ min}} = 0$). The reduction of MO in the presence of NaBH_4 using tannic acid instead of metal nanoparticles shows exactly the same pattern as in case of absence of metal nanoparticles [similar to Fig. 3(d)] which confirmed that metal nanoparticles are acting as a catalyst and not tannic acid. The rate of reduction of MO has been found to be more in case of silver nanoparticles than platinum or gold nanoparticles, i.e. it follows the order— $\text{Rate}_{\text{Ag nps}} > \text{Rate}_{\text{Au nps}} > \text{Rate}_{\text{Pt nps}}$ as shown in Fig. 4. The difference in the rate of reduction in the presence of three metals can be attributed to difference in their work function values (eV). From Fig. 5, it is clearly indicative that as the value of the work function decreases, total change in the absorbance of MO increases by suffi-

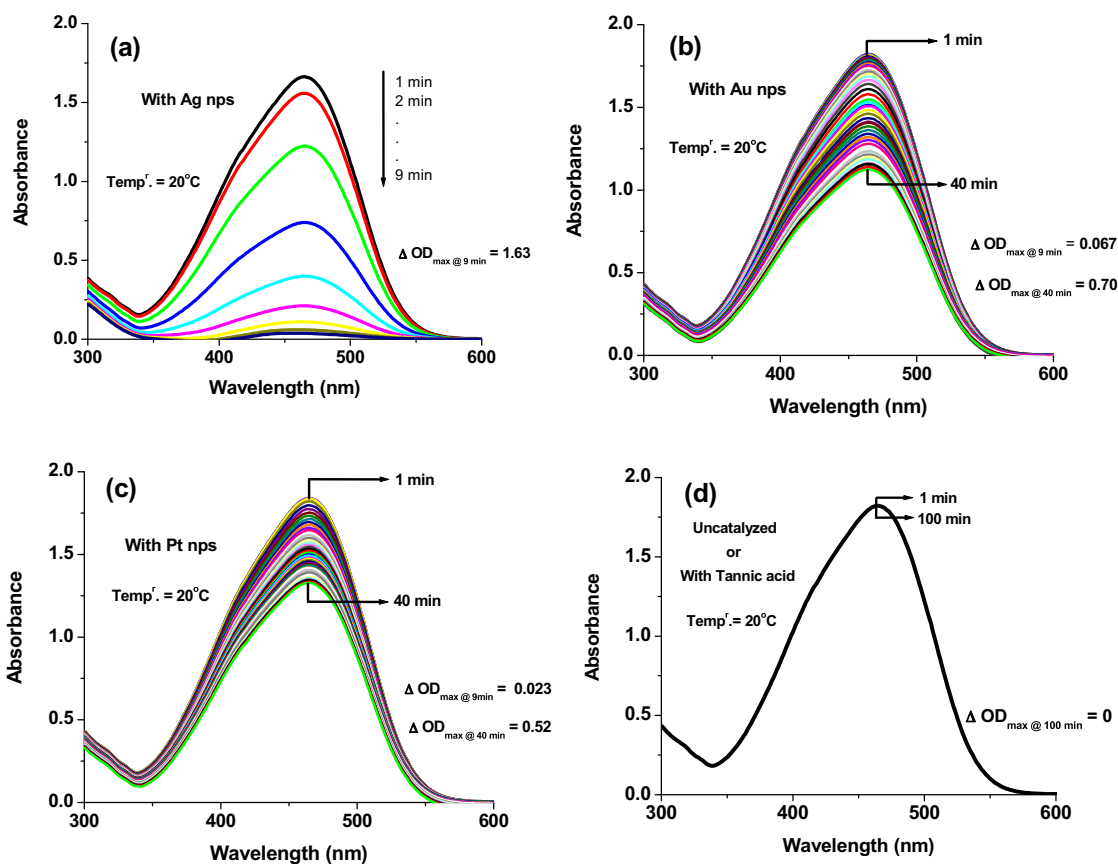


Fig. 3. Comparison of plot of absorbance versus wavelength for the reduction of methyl orange in the presence of NaBH₄ at 20 °C using (a) Ag nps, (b) Au nps, (c) Pt nps and (d) only tannic acid (uncatalyzed).

cient amount, i.e. work function and change in OD are exponentially related to each other.

From the expression,

$$-dl = (8\pi^3/3h^2)|\mu_{lm}|^2(I/c)hv_{lm}(NC/1000)dl \quad \text{and}$$

$$A = \{8\pi^3N/3hc(1000)\}v_{lm}|\mu_{lm}|^2$$

It is concluded that, $-dl = AICdl$

Which on integration gives,

$$I = I_0 e^{-ACl}$$

Here I is the energy associated with the radiation, A is the integral absorption coefficient, C is the molar concentration and L is the path length [31]; we concluded that the energy is exponentially related to absorbance and this is in accordance with our observation of work function (or energy) with OD (or absorbance).

The degradation of methyl orange follows first order kinetics, and from Table 1, it can be seen that the rate constant, k ,

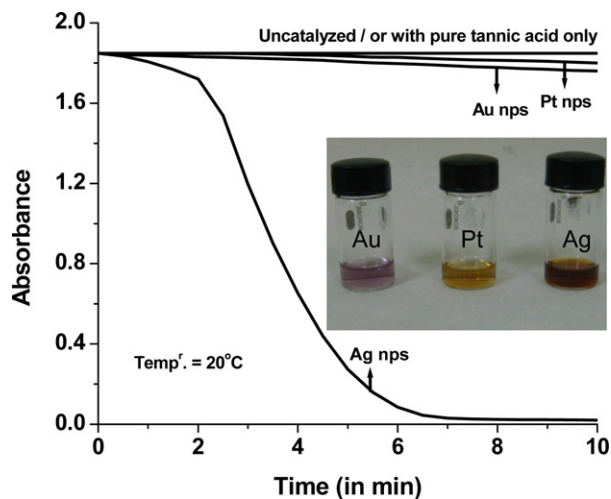


Fig. 4. Comparison of plot of decrease in absorbance versus time for catalyzed and uncatalyzed reaction at 20 °C; inset: digital photograph of the prepared nanoparticles (after 150 days).

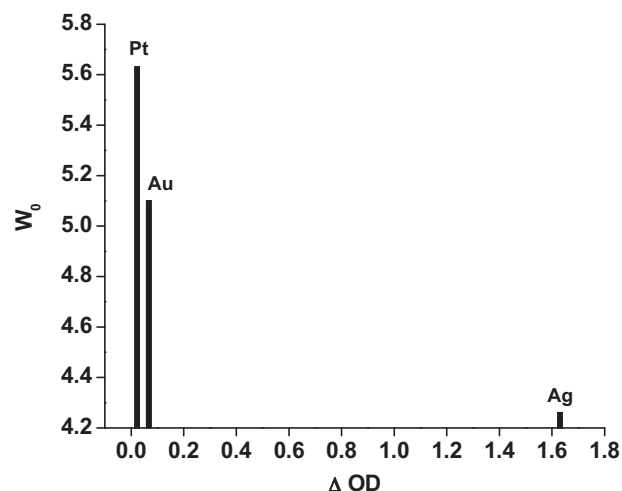


Fig. 5. Plot of work function (W_0) versus ΔOD for reaction catalyzed by different metal nanoparticles after 9 min at 20 °C.

Table 1
Comparison of rate constant (*k*) for the catalyzed reduction using different catalysts (Au, Pt and Ag nanoparticles) with uncatalyzed reduction.

S. no.	Concentration of catalyst	Concentration of MO	Concentration of NaBH ₄	Temperature (°C)	Rate constant (<i>k</i>) (min ⁻¹)
1	100 μL of 0.01% Pt nps solution	50 μL of 5 × 10 ⁻³ M	100 μL of 0.5%	20	0.0029
2	100 μL of 0.01% Au nps solution	50 μL of 5 × 10 ⁻³ M	100 μL of 0.5%	20	0.0049
3	100 μL of 0.01% Ag nps solution	50 μL of 5 × 10 ⁻³ M	100 μL of 0.5%	20	0.5853
4	Without catalyst	50 μL of 5 × 10 ⁻³ M	100 μL of 0.5%	20	Very small of order 10 ⁻¹⁷ (negligible)

calculated for Pt, Au, Ag nanoparticles as catalysts and uncatalyzed reactions are 0.0029 min⁻¹, 0.0049 min⁻¹, 0.5853 min⁻¹ and 10⁻¹⁷ min⁻¹ respectively. Therefore, it is concluded that Ag nanoparticles reduces the coloured methyl orange to its colourless form faster as compared to Au and Pt nanoparticles. These metal nanoparticles can be used in the industries for the degradation of various dyes, as the dyes are harmful when decanted without reducing them to colourless form.

4. Conclusion

We have described the green aqueous synthesis of spherical Au, Ag and Pt metal nanoparticles having an average diameter of 10 nm using tannic acid at room temperature. These metal nanoparticles has been used for the catalytic degradation of methyl orange in the presence of NaBH₄ and comparison has been made to show their different catalytic activity by measuring the rate constant (*k*). These differences are attributed due to their different work function values which are exponentially related to the absorbance. Silver nanoparticles acts as a much better catalyst as compared to gold and platinum nanoparticles due to its least work function value. Sodium borohydride being such a strong reducing agent is not able to reduce methyl orange in absence of catalyst, indicating the catalytic efficacy of metal nanoparticles.

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