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Synthesis of anisotropic gold nanoparticles and their catalytic activities of breaking azo bond in sudan-1

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1. Introduction

Morphology controlled synthesis of nanoparticles is of great significance due to its optical [1], electronic [2] and magnetic [3] properties which depend strongly on the size and shape of the nanomaterials. Noble metal nanoparticles exhibit localized surface plasmon resonances resulting in strong optical extinction at visible wavelengths. With increasing anisotropy of AuNPs, it demonstrates two plasmon resonance absorption bands: one is around 510 nm, resulting from transverse plasmon resonance and the other absorption band in the visible or NIR range is due to the longitudinal plasmon resonance. Shape controlled gold nanoparticles have outstanding applications in a variety of fields, such as photonics [4–6], surface enhance Raman scattering (SERS) [7,8] and catalysis [9,10] in material chemistry research.

Over the last decade, many efficient synthetic approaches were developed that allow precise control over gold nanostructures. Although there were several reports focused on gold nano particles, shape controlled wet chemical synthesis of gold nano particle like rods [11,12], cubes [13], star [14], plates [15,16], wires [17], triangles [18], and nanoribbons [19] is limited. Solution phase approach provides convenient and reproducible routes for the fabrication of nanoparticles with controlled size and shape. The resulting nanoparticles are not only precisely tuned but also to easily dispersed in organic or aqueous media for numerous potential applications in biological systems. The seed-mediated growth technique is one of the most promising methods for

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ABSTRACT

Here, we report the high yield synthesis of different shaped gold nano particles (AuNPs) through seed mediated growth process in aqueous medium. Shape dependent surface plasmon resonance (SPR) and the gradual shift of longitudinal SPR band are observed with increasing anisotropy of AuNPs. Structural changes during the growth processes are observed by transmission electronic microscopy (TEM). Here, spherical nano seeds are transformed into rice and dendrimer shaped nanoparticles in the subsequent four stage growth processes. Gold nanoparticles have been demonstrated to be very efficient catalysts for the cleavage of N=N of sudan-1 and it is investigated by monitoring the reduction of sudan-1 in the presence of excess NaBH₄. It has been observed that the reaction is first order with respect to the concentration of sudan-1 and the catalytic efficiency of dendrimer shaped AuNPs is higher than the other as synthesized AuNPs.

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producing size tunable nanomaterials in the solution phase. Morphology controlled synthesis of metal nanoparticles requires the successful utilization of a template such as CTAB [20], SDS [21], polyvinyl pyrrolidone (PVP) [22], and poly ethylene glycol (PEG) [23] in the growth solution.

Azo dyes are the largest and most versatile class of dyes, which are currently used in dyeing various materials such as textiles, leather, plastics, and cosmetics. During these dyeing processes some amount of dye are released into sewage treatment systems or to the environment. In particular, soluble reactive dyes are being released into the environment. The recalcitrance of the azo dyes to biological degradative processes results in severe contamination of the rivers and ground water in those areas having high growth of dye industries. The current state of the art for the treatment of waste waters containing dyes are physicochemical techniques, such as adsorption, precipitation, chemical oxidation, photo degradation, or membrane filtration. One of the important applications of noble metal nanoparticles is their use as promising heterogeneous catalysts for a variety of chemical reactions like oxidation, reduction, hydrogenation and dye removal [24,25]. Heterogeneous catalysis that benefits from easy removal of catalyst materials and possible use of high temperatures suffered for a long time from lack of selectivity and understanding of the mechanistic aspects is indispensable for parameter improvements. Despite the above mentioned promising attributes, broad applications of nanoparticles as catalysts like molecule synthesis or degradation and removal of toxic hazardous materials from water and environment have yet to find much attention. Keeping the above problem in mind, we have decided to take the catalytic property of gold nanoparticles for the cleavage of azo bond in sudan-1.

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Here, we propose a simple, facile, efficient, and economical route for high yield synthesis of anisotropic gold nanoparticles through seedmediated growth approach. A small volume of gold seed solution was added to a first growth solution. Successive transfer of the nano hydrosol to the next growth solution results in formation of a dendrimer shaped structure of AuNPs after four successive steps. In this work, we also investigated AuNP catalyzed degradation of sudan-1 in the presence of NaBH₄. The as synthesized AuNPs show good catalytic properties and can be easily separated by centrifuging from the solution for recycling. The kinetic data indicate that dendrimer shaped AuNPs are catalytically more active than the other gold nanoparticles.

2. Experimental procedures

2.1. Materials

Chloroauric acid tetra hydrate (HAuCl₄.4H₂O), sodium dodecyl sulphate (SDS), cetyltrimethyl ammonium bromide(CTAB), and L-ascorbic acid were obtained from Merck India Ltd. Silver nitrate (AgNO₃) was purchased from Sigma-Aldrich Chemical Corp. Sodium borohydride (NaBH₄), sudan-1, acetone and cyclohexane were purchased from S. D. Fine Chemicals. All the chemicals were of analytical grade and used without further purification. Ethanol was purchased for experiment. Doubly distilled water was used throughout the experiment. All the glassware were cleaned by freshly prepared aquaregia and rinsed with double distilled water prior to the experiments.

2.2. Synthesis of gold nanostructures

2.2.1. Preparation of SDS capped gold seed

10 mL aqueous solution containing 0.1 mM HAuCl₄.4H₂O and 1 mM SDS was prepared in a round bottom flask. The initial yellowish solution slowly turned into reddish-violet with addition of freshly prepared 0.2 mL 0.1(M) NaBH₄ under ice cooled condition. The above gold nanoparticle solution was used as seeds (sample A) after 2 h for the subsequent growth processes.

2.2.2. Growth process

20 mL of growth solution containing 0.25 mM HAuCl₄.4H₂O, 0.1 M cetyltrimethyl ammonium bromide (CTAB), 0.2 mL acetone and 0.32 mL cyclohexane was prepared in a 50 mL conical flask. 0.02 mL, 0.1 mM silver nitrate (AgNO₃) and 0.1 mL of 0.1 M freshly prepared ascorbic acid were added to the above growth solution with constant stirring. The orange color of gold salt in the growth solution disappeared after the addition of ascorbic acid and this change of color was due to the reduction of Au³⁺ to Au⁺. Now, the growth solution was divided into four parts in four different 25 mL stopper conical flask containing 5 mL growth solution each. They were labeled as B, C, D and E. 1.0 mL of the seed solution (sample-A) was added to the growth solution labeled B (step 1). Rapid development of red color in sample-B indicates the reduction of Au⁺ to Au⁰. After 30 s, 1.0 mL of sample-B was added to the growth solution C (step 2). Solution labeled sample-C turns violet in color indicating the formation of anisotropic gold nanoparticles. Again, after 30 s, 1.0 mL of sample-C was added to sample-D (step 3). In the last step (step 4), 1.0 mL of sample-D was added to sample-E. Sample-E became blue in color and it was due to the formation of highly anisotropic gold nanoparticles. Each solution of gold hydrosol was centrifuged for 10 min at a speed of 8000 rpm to precipitate out the particles from the solution and then re-dispersed in 5 mL doubly distilled water by sonication. The re-dispersed solution was used for further experiment. A schematic presentation of different steps of the above synthesis procedures is shown in Scheme 1.

2.3. Studies of catalytic activity

Reduction of sudan-1 by NaBH₄ in the presence of gold nano hydrosol was carried out to examine the catalytic activity of the AuNPs. Catalytic activity of different shaped AuNPs was carried out using the following procedure. Nanoparticles were precipitated out by centrifugation and then re-dispersed in water, prior to using it as catalyst. 0.1 mL, 10 mM sudan-1 in ethanol was added to a solution containing 10 mL 1:1 ethanol water mixture and 0.1 mL 1.0 M NaBH₄. Then, 0.5 mL redisperse gold hydrosol was added to the above mixture with constant stirring. The color of the solution changes gradually from reddishyellow to transparent as the reaction proceeded. The reaction mixture was extracted with ethyl acetate at room temperature, and the organic layers were combined and dried with anhydrous Na2SO4. After completion of the reaction, products were monitored by TLC (thin-layer chromatography). Purification by column chromatography (silica gel/petroleum ether and ethyl acetate) gave the desired products which were confirmed by FT-IR and ¹H NMR spectroscopy. Main reaction products were identified as 1-amino-2-naphthol and aniline.

UV–Vis absorption study was done to record the change in absorbance at a time interval of 3 min. A controlled experiment without AuNPs was also carried out using mixtures of NaBH₄ and sudan-1 and no change in the UV–Vis spectra of sudan-1 with time was observed.

2.4. Characterizations

UV–Vis absorption spectra were measured using a Shimadzu UV-1601 spectrophotometer. The morphology and size of Gold nanoparticles were investigated using JEOL-JEM-2100 transmission electron microscopy (TEM). Samples for TEM study were prepared by placing a drop of gold hydrosol onto a carbon film supported on a copper grid followed by solvent evaporation under vacuum. FT-IR measurements were done using a Perkin Elmer (Spectrum RX1) spectrophotometer with the KBr disk technique. ¹H NMR (300 MHz) spectra were recorded on a BRUKER-AC 300 MHz spectrometer. Chemical shifts are reported in ppm from tetra methyl silane as the internal standard, with the solvent resonance (deutero chloroform: 7.26 ppm).

3. Results and discussion

3.1. UV-Vis study

Formation and the stability of gold nanoparticles in aqueous colloidal solution are confirmed by UV-Vis spectral analysis which is one of the most important tools for characterizing the metal nanoparticles. The absorption behavior arises from localized surface plasmon resonance (LSPR), which originates from coherent oscillations of electrons in the conduction band induced by the electromagnetic field. Fig. 1(A) illustrates that the pink colored gold seed solution has LSPR maxima at 508 nm. Fig. 1(B-E) shows the UV-Vis extinction spectra of gold hydrosol obtained using four step seed growth protocols (sample B–E). The classical electrostatic model predictions of absorption cross sections for nanospheroids of gold have been demonstrated to split the dipolar resonance into two bands; the band centered about 508 nm is due to surface plasmon resonance along the transverse direction and the bands centered at 680-873 nm are referred to as the longitudinal plasmon absorption [26]. The UV-Vis spectrum of sample-B (Fig. 1B) is broad with a peak at 508 nm and a small hump at the long wavelength (606 nm) region. This duel peaks indicate that AuNPs of sample-B are anisotropic in nature. Both sample-C & sample-D have a transverse resonance band at 508 nm but a longitudinal SPR band is shifted more to the red for sample-D (803 nm) than sample-C (680 nm). These large shifts of longitudinal SPR band indicate that the aspect ratio of particles of sample-D is higher than that of sample-C. On the other hand both the transverse (610 nm) and longitudinal

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Scheme 1. Schematic illustration of the steps used to synthesize anisotropic gold nanoparticles; representative colors are observed for different nanoparticle solution. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

(873 nm) band shifted more to the red (Fig. 1E) compared to other samples and this is due to larger size and greater anisotropy of dendrimer shaped AuNPs of sample-E.



Fig. 1. UV–Vis absorption spectra of (A) gold seed sol and (B–E) the gold sol synthesized in four different steps through seed mediated growth approach. Inset picture shows the color of the solutions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.2. TEM study

TEM images of gold nanoparticles obtained from seed and different growth solution are shown in Figs. 2 & 3 respectively. These pictures illustrate an interesting morphological evaluation as the growth proceeds. Fig. 2A shows TEM images of seed prepared in aqueous SDS using sodium borohydride as reducing agent at 0 °C. Particles are mostly spherical in shape with an average diameter of ~10 nm. SAED image (Fig. 2) suggests that the seed particles are crystalline in nature. Fig. 3-(i) & (ii) shows the TEM images of sample-B & C with uneven spherical and rice like structures. Sample-D and E appear highly anisotropic and dendrimer in shape as shown in Fig. 3-(iii) & (iv). SAED images (inset of Fig. 3-iv) of the dendrimer shaped particles show the diffraction pattern from the different crystal plane of face centered cubic (fcc) gold nanoparticles and the sharp intensity of the circle arising from different crystal plane suggests that particles are mostly crystalline in nature.

3.3. EDX study

Energy dispersive X-ray (EDX) spectroscopy analysis suggests that the signals are coming from pure gold, as shown in Fig. 4. Apart from gold a strong signal at the position of Cu is also observed and this strong signal of Cu is coming from copper grid. The same study is performed on focusing other positions of the grid and the similar signals of Au along

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Fig. 2. TEM image (A) of gold seed synthesized in aqueous SDS. SAED image of gold seed particle.

with Cu are observed. It confirms that our synthesized particles are pure gold particle.

3.4. Effect of foreign ions (Ag^+ ion), SDS and CTAB

Ag⁺ ions are used as catalyst in the growth solution for the anisotropic growth of nanoparticles. Ag⁺ ions in the growth solution are reduced to Ag⁰ slowly in the presence of mild reducing agent ascorbic acid. Since AgBr is produced due to the presence of high concentration of bromide ions in the growth solution, a significant amount of Ag⁰ and/or AgBr are deposited on the surface of the gold seeds. Because of potential deposition or chemisorptions of Ag⁰ and/or AgBr, defects and/or islands are produced on the surface of the seeds that provide active sites for subsequent growth. Gold atoms which are formed due to the reduction of Au⁺ by mild reducing ascorbic acid on the seed surface begin to grow on these active sites of seed particles, yielding anisotropic shaped particles. The morphology of sample-C, D & E becomes highly anisotropic due to the use of irregularly faceted particles i.e. sample-B, C & D respectively as seed. The already nucleating small gold cluster developed on an otherwise smooth facet, and some



Fig. 3. TEM images of (i) sample-B, (ii) sample-C, (iii) sample-D and (iv) sample-E.

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Fig. 4. Energy-dispersive X-ray spectrum (EDAX) of sample-E.

small tips and islands are formed on the surfaces of irregular shaped particles (sample-D). When these irregular shaped particles are added to the growth solution, these small tips acted as nucleation sites for the subsequent growth of gold and this results in dendrimer-shaped (sample-E) particle as shown in Fig. 3-(iv).

The small size AuNP seed can be synthesized in the presence of SDS. In the absence of SDS larger size AuNPs are formed and those particles cannot be used for synthesizing highly anisotropic gold nanoparticles. During growth process, CTAB also plays an important role of template for the formation of anisotropic gold nanoparticles. CTAB not only acts as templates but also helps to stabilize the negatively charged Au(III) and Au(I) species by quantitative binding. In the absence of CTAB, addition of excess ascorbic acid to the aqueous solution of AuCl₄⁻ instantaneously generates small gold nanoparticles at room temperature. Acetone is used to loosen the micellar frame work and cyclohexane is necessary for the increased formation of elongated CTAB micelle [27] which acts as template for anisotropic growth of nanoparticles.

3.5. Effect of ascorbic acid

In CTAB solution, $[Au^{III}Cl_4]^-$ presents as $[Au^{III}Br_4]^-$ with the bromide ions originating from the partially dissociated CTAB. $[Au^{III}Br_4]^-$ is reduced to $[Au^{IB}r_2]^-$ through a two electron process in the presence of ascorbic acid and ascorbic acid is oxidized to dehydro ascorbic acid (a two-electron process). Importantly however, at this stage we find that Au^I ions in the growth solution are not reduced to Au⁰ at any appreciable rate even when an excess of up to five molar equivalents of ascorbic acid is present. But, Au^I ions in the growth solution are reduced to Au⁰ only upon the addition of previously synthesized Au nanoparticles as seed. A key feature of the disproportionation of Au¹ via $3Au^1 \rightarrow 2Au^0 + Au^{III}$ that helps to establish its role during the formation of nanocrystals is that the disproportionate reaction is catalyzed by metallic gold [28] and is therefore autocatalytic [29].

$$\begin{bmatrix} Au^{III}C1_4 \end{bmatrix}^{-} [aq.]CTB \begin{bmatrix} Au^{III}Br_4 \end{bmatrix}^{-} micelle \\ \begin{bmatrix} Au^{III}Br_4 \end{bmatrix}^{-} [micelle]2e^{-} from ascorbic acid \begin{bmatrix} Au^{I}Br_2 \end{bmatrix}^{-} \\ \hline Au^{I}Br_2 \end{bmatrix}^{-} Au^{0} from gold nano seed Au^{III} + Au^{0}(nano crstals)$$

3.6. Catalytic activity of AuNPs

Reduction of azo dye to their corresponding amino derivatives is industrially important. Normally sudan-1 is not reduced by sodium borohydride in aqueous or alcoholic solution. Sudan-1 exhibits a strong absorption peak at 487 nm. Upon addition of NaBH₄ and gold nanoparticles as catalyst (i.e., an aqueous dispersion of the different shaped gold nanoparticles), the absorption peak at 487 nm gradually decreases in intensity as the reduction proceeds (Fig. 5-i) and a new band centered at ~355 nm is appeared and it corresponds to the formation of 1-amino-2-naphthol and aniline. Decreasing intensity of the 487 nm band with time suggests the decreasing concentration of sudan-1 as the reaction proceeds. However, there is no proportional increase in the 1-amino-2-naphthol and aniline peak intensity; probably due to the difference in the molar extinction co-efficient of 1-amino-2naphthol and aniline with respect to sudan-1. Since the peak at 487 nm was much stronger than that at 355 nm, kinetics of the reaction

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T%



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Fig. 5. (i) Typical UV–Vis spectra for the successive reduction of sudan-1 by NaBH₄ in the presence of AuNP hydrosol of sample-C. (ii) Plots of In A_t versus time, t in the presence of different shaped AuNPs as catalyst (sample A–E) at 25 $^{\circ}$ C.

were measured by recording the absorbance of 487 nm band with time. The initial volume of gold hydrosol and the concentrations of sudan-1 and NaBH₄ were kept identical for each set for comparison of the kinetics. UV-Vis spectra exhibit two isobestic point at ~313 nm and ~392 nm respectively (Fig. 5-i), indicating the presence of two or more species, in the solution. AuNP catalyzed products of the above reaction mixture were extracted and identified using TLC, FTIR and NMR spectroscopic analysis. In this case the main reaction product is 1-amino-2-naphthol and aniline. After cooling to room temperature, the reaction mixture was extracted with ethyl acetate, and the organic layers were combined and dried with anhydrous Na₂SO₄. Purification by column chromatography (silica gel/petroleum ether and ethyl acetate) gave the desired products which were confirmed by FT-IR and ¹H NMR. FT-IR spectra (Fig. 6-ii) show strong band at 817 cm⁻¹, 1160 cm⁻¹, 1640 cm⁻¹ and 3200 to 3600 cm⁻¹. The broad band at 3200 to 3600 cm^{-1} is due to -N-H and -OH stretching vibration. The -N-H vibrations (both symmetric and asymmetric) in aromatic compounds often overlap with the aromatic - OH absorption, which also appear in the 3100–3500 cm^{-1} regions to give broad spectra. An out-of-plane N-H bending vibration that appears as a broad band at 817 cm⁻¹ and band at 1640 cm⁻¹ that appears for N-H bending vibrations are present in the product. The band at 1160 cm^{-1} is due to





Fig. 6. (i) ¹H NMR (300 MHz) spectra of 1-amino-2-naphthol. Chemical shifts are reported in ppm using tetra methyl silane as the internal standard, with the solvent resonance (deuterochloroform: 7.26 ppm). (ii) Solid state FT-IR spectra of 1-amino-2-naphthol.

C – N stretching vibration. The product with a melting point of 219–220 °C showed the NMR peak at δ 5.6 (broad s, aromatic amine, 2H), 10.2 (broad s, phenolic 1H) and 7.1 to 7.9 (m, naphthalene 6H) in the NMR spectrum in CDCl₃ (Fig. 6-i).

The proposed mechanism of the AuNPs catalyzed surface reaction is shown in Scheme 2. The catalytic reduction proceeds on the surface of the metal nanoparticles. The AuNPs react with borohydride ions to form the metal hydride. Concomitantly, sudan-1 that adsorbs onto the AuNP surface is reduced by hydride ions on the nano surface. The adsorption/desorption of both reagents on the AuNP surface are fast and can be modeled in terms of a Langmuir isotherm. To check the feasibility of reaction, two blank experiments, one with sudan-1 under identical experimental conditions but no AuNPs and the second one without NaBH₄ were carried out and no significant change in the optical density of sudan-1 was observed. Thus, AuNPs act as catalyst for the reduction of sudan-1 by NaBH₄. Here the rate determining step is the cleavage of the adsorbed sudan-1 to 1-amino-2-naphthol and aniline,

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Scheme 2. Proposed mechanism of N=N bond cleavage of sudan-1 by sodium borohydride in the presence of gold nanoparticles.

which desorbs afterward. Therefore, the rate constants can be evaluated by first-order kinetics when excess NaBH₄ is used. So, the apparent rate constant ' K_{app} ' is proportional to the total surface area 'S' of the nanoparticles [30–32].

$$-\frac{dc_t}{dt} = K_{app}C_t = K_1 S C_t \tag{1}$$

Since $C_0 \propto A_0$ and $C_t \propto A_t$

The above rate equation can be rewritten,

$$\ln A_t = \ln A_0 - K_{app} \cdot t$$

where C_t is the concentration of sudan-1 at time t and K_1 is the rate constant normalized to S, the surface area of nanoparticles. Upon addition of Au-based catalyst, regardless of the morphology a certain period of time is required for sudan-1 to adsorb onto the catalyst's surface before the reaction could be initiated. This is called induction time t_0 in which no reduction takes place. Then the reaction becomes stationary and follows a first order rate law. This induction time is responsible for the non-linear nature of lnA_t vs. t plot. While analyzing, we have fitted the data points beyond the induction time with linear plot. The reaction rate constant using different shaped AuNPs as catalyst is evaluated by plotting the log A_t versus time, where A_t stands for absorbance at time 't' (Fig. 5-ii). Our calculated reaction rate constants (k_{app}) at 25 °C are 7.57 × 10⁻³ s⁻¹, 1.491 × 10⁻² s⁻¹, 2.402 × 10⁻² s⁻¹, 7.871 × 10⁻² s⁻¹ and 1.292 × 10⁻¹ s⁻¹ for the sample (A to E), which indicate a higher catalytic activity for the dendrimer shaped

gold nanoparticles. The higher catalytic activity of dendrimer shaped AuNPs is due to the presence of irregular facets which are presumed to be the reactive site to catalyze the reduction of sudan-1 on the nanoparticles surface in the presence of NaBH₄.

4. Conclusions

The morphological, structural, and spectral changes involved in the seed-mediated growth of gold nanostructures in the presence of CTAB were systematically investigated. A four step protocol for the synthesis of AuNPs that allows the morphology of the products to be changed markedly by varying the number of steps in the seed mediated growth process. This is a facile and effective method for rapid and large-scale synthesis of anisotropic AuNPs. It has been observed that anisotropic AuNPs with attractive optical properties could have promising applications to surface-enhanced Raman spectroscopy, chemical or biological sensing, and the fabrication of nano devices. The present method of synthesis is interesting due to the simplicity of operation, costeffectiveness, high throughput, and lack of elaborate equipments. Here in, we presented the catalytic activities of different shaped gold nanoparticles for the cleavage of azo bond of sudan-1 to 1-amino-2naphthol and aniline. And, it is expected that the gold nano dendrimer with high catalytic activity will greatly promote their practical application to eliminate the organic pollutants from wastewater.

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