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

Gobinda Prasad Sahoo, Dipak Kumar Bhui, Debasish Das, Ajay Misra *

Department of Chemistry and Chemical Technology, Vidyasagar University, Midnapore 721 102, WB, India

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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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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

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.

* Corresponding author. Fax: +91 3222 275329.

E-mail addresses: ajaymsr123@gmail.com, ajay@mail.vidyasagar.ac.in (A. Misra).

Here, we propose a simple, facile, efficient, and economical route for high yield synthesis of anisotropic gold nanoparticles through seed-mediated 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 from Bengal Chem. Pvt. Ltd and was doubly distilled before used 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 Au⁰. 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 Au³⁺ 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 re-disperse gold hydrosol was added to the above mixture with constant stirring. The color of the solution changes gradually from reddish-yellow 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 dual 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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