



Investigation on the catalytic activity of aminosilane stabilized gold nanocatalysts towards the reduction of nitroaromatics



P. Viswanathan, T.S. Bhuvaneshwari, R. Ramaraj*

School of Chemistry, Centre for Photoelectrochemistry, Madurai Kamaraj University, Madurai, 625 021, India

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ABSTRACT

In situ preparation of gold nanoparticles (AuNPs) in the presence of silicate matrix, N1-(3-trimethoxysilylpropyl) diethylenetriamine (TPDT) and cetyltrimethylammonium bromide (CTAB), using strong reducing agents sodium borohydride (NaBH₄) and hydrazine (N₂H₄) was established and their catalytic abilities were examined by choosing industrially important model reactions, in order to find the best reducing agent for the preparation of catalytically more active AuNPs. The prepared AuNPs were characterized using UV–vis absorption spectroscopy, XRD, HRTEM, EDX and SAED analyses. The AuNPs produced by NaBH₄ showed relatively good mono-dispersion and small size than the AuNPs formed by N₂H₄. The catalytic activity of AuNPs produced by NaBH₄ was found to be better than the AuNPs produced by N₂H₄ towards the reduction of various nitroaromatics. The turn over frequency (TOF) values obtained for the catalytic reduction of nitrobenzene (NB), 4-nitrophenol (4-NP) and 4-nitroaniline (4-NA) using the TPDT-Au-CTAB-NaBH₄ catalyst are 0.312, 0.714 and 1.00 s⁻¹, respectively. Moreover, the rate constant (*k*) value obtained for the reduction of 4-NP is very high when compared to the reported results.

1. Introduction

In recent years, extensive investigations on the metal nanoparticles (MNPs) have been carried out by researchers to understand their physical, chemical and catalytic properties, not only to gain scientific knowledge but also to find technological applications [1–4]. When the size of the metal approaches to nanometre regime, i.e. MNPs show significant changes in their electrical, optical, and catalytic properties. While comparing the MNPs to their respective bulk materials, a noticeable change in the reduction potential is observed for MNPs of different sizes as the Fermi potential of nanoparticles (NPs) becomes more negative and this interesting property makes them good candidates as catalysts for various electron transfer processes [5,6]. However, the stability of MNPs is the major problem associated with nanocatalysts due to their high unfavourable surface energies. Hence, for the effective use of MNPs as catalyst, they must be stable and protected from agglomeration. For the stabilization of MNPs, a variety of stabilizing agents are available such as amines, phosphines, thiols, micelles, dendrimers, polymers, and biomolecules [7–10]. In this sense, silicate matrix encapsulated MNPs seems to be advantageous because of their stability, reusability, safer operations, easy scale up, and good catalytic properties [11]. In recent years, our group has reported the catalytic behaviour of various mono- and bi-metallic NPs stabilized by

amine functionalized silicates [12–16].

Nitroaromatics are the class of organic compounds, which are widely known as toxic materials released from chemical industry, diesel and gasoline engines and are widely distributed in the environment and threatening the human population [17]. However, the reduced forms of nitroaromatics i.e. aromatic amines are important starting materials for the preparation of dyes, pharmaceuticals, agricultural products, surfactants and polymers [18]. Moreover, aromatic amines are less toxic when compared to nitroaromatics. Therefore, it is important to develop a simple and efficient method for the catalytic conversion of nitroaromatics into aromatic amines. Conventional method of preparation of aromatic amines is the reduction of nitro compounds using catalytic hydrogenation and a variety of other reduction conditions [19,20]. Among the several reducing agents, metals in the presence of acid are widely employed for the reduction of nitroaromatics. But, this method is environmentally hazardous and untidiness [21]. Hence, in the recent years, NaBH₄ in water has been used as hydride source and reducing agent. But, the reduction of nitro compounds only with NaBH₄, in the absence of catalyst is an extremely slow process. Hence, catalyst is necessary to accomplish the reduction of nitroaromatic compounds in the presence of NaBH₄.

A variety of MNPs such as Ag [11,18], Au [22], AuAg [23], PdAg [24], Pt/C [25], and NiPt [26] have been used as catalyst to drive the

* Corresponding author.

E-mail address: ramaraj@yahoo.com (R. Ramaraj).

reduction of nitrocompounds. Among these MNPs, gold is the widely studied catalyst due to its intriguing catalytic properties [27,28]. Moreover, the properties of MNPs, which are prepared in the solution phase can be tuned by varying its composition and preparation method, especially the reducing agent employed for the reduction of metal salts [29]. Hence, in the present work, we report a facile preparation of AuNPs in the presence of amine functionalized silicate matrix and a surfactant using two different reducing agents, NaBH_4 and N_2H_4 . So prepared AuNPs were successfully applied for the catalytic conversion of various nitroaromatics and their catalytic activities were compared.

2. Experimental section

2.1. Materials and methods

Chloroauric acid (HAuCl_4), cetyltrimethylammonium bromide (CTAB) and N1-(3-trimethoxysilylpropyl)diethylenetriamine (TPDT) were received from Sigma-Aldrich. All other chemicals are analytical grade and were received from Merck. All glassware was thoroughly cleaned with aqua regia (1:3 HNO_3/HCl v/v) (caution: Aqua regia is a powerful oxidizing agent and it should be handled with extreme care) and rinsed extensively with distilled water before use. UV–vis absorption spectra were recorded using Agilent Technologies 8453 spectrophotometer. High resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) analyses were conducted on a TECNAI-T20 operated at 200 kV. The specimen for the HRTEM analysis was prepared by dropping the colloidal solution onto a carbon coated copper grid and dried at room temperature. X-ray diffraction (XRD) pattern was recorded using PAN X'pert Pro instrument.

2.2. Preparation of AuNPs

In a typical experiment, 5 mL of 5 mM CTAB aqueous solution was mixed with 25 μL of 1 M TPDT solution and stirred for 15 min. To this solution, 50 μL of 0.1 M HAuCl_4 solution was added and stirred for 5 min. A 0.3 mL of 0.05 M ice-cold NaBH_4 was slowly added to the above solution and stirring was continued for another 3 h. Colour of the solution changed from light yellow to wine red immediately after the addition of NaBH_4 . This confirms the formation of AuNPs and the NPs represented as TPDT-Au-CTAB- NaBH_4 . The prepared AuNPs were stable for more than a month. CTAB-Au- NaBH_4 , TPDT-Au- NaBH_4 , were prepared either in the presence of only CTAB or TPDT by following the same procedure. Hydrazine reduced AuNPs (TPDT-Au-CTAB- N_2H_4 , CTAB-Au- N_2H_4 , TPDT-Au- N_2H_4) were prepared using 0.3 mL of 0.05 M N_2H_4 by following the same procedure as mentioned above.

2.3. Catalytic reduction of nitroaromatics

Catalytic reduction of nitroaromatics was carried out as follows: 0.1 mL of 2 mM of nitroaromatic compound solution was mixed with 1.150 mL of water followed by 0.75 mL of 0.056 M NaBH_4 . To this mixture 10 μL of AuNPs was added and the reaction progress was monitored using UV–vis absorption spectroscopy.

3. Results and discussion

3.1. Absorption spectral studies

Preparation of AuNPs can be achieved through variety of methods, among them, chemical reduction of metal salts is a more common method, due to its efficiency, low cost and ease of synthesis. Though many reducing agents are available for the preparation of MNPs, NaBH_4 and N_2H_4 are the widely used reducing agents. Moreover, the properties

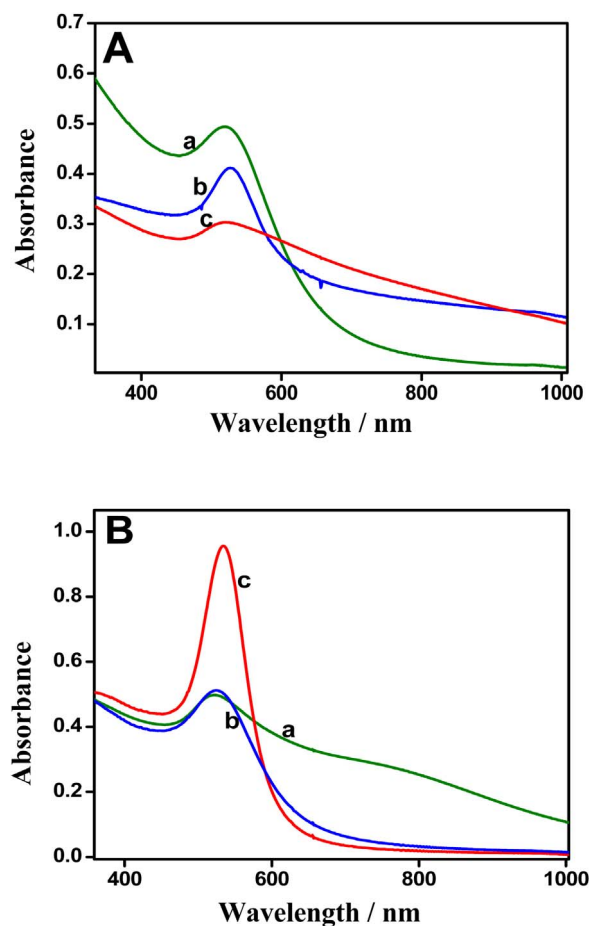


Fig. 1. UV–vis absorption spectra obtained for TPDT-Au-CTAB (a), CTAB-Au (b), TPDT-Au (c), A) NaBH_4 reduced and B) N_2H_4 reduced AuNPs.

of MNPs are highly dependent on the reducing agents used to reduce the metal salts. Hence, it is meaningful to compare the catalytic activities of AuNPs produced by these two reducing agents. The absorption spectroscopy is a fundamental tool to characterize the AuNPs and which can be effectively used to corroborate the particle size and shape and oxidation state of AuNPs derived from TEM and XPS studies [30]. The surface plasmon resonance (SPR) bands of MNPs are strongly dependent on their size, shape, composition and their local environment [10,31]. Fig. 1 shows the SPR band observed for NaBH_4 and N_2H_4 reduced AuNPs. AuNPs prepared in this work by using NaBH_4 and N_2H_4 showed a strong absorption band around 520 nm, which confirms the formation of gold nanostructures in the presence of TPDT and CTAB. TPDT-Au-CTAB- NaBH_4 , CTAB-Au- NaBH_4 and TPDT-Au- NaBH_4 showed the absorption bands (λ_{max}) at 518, 527 and 523 nm, respectively. Similarly, TPDT-Au-CTAB- N_2H_4 , CTAB-Au- N_2H_4 and TPDT-Au- N_2H_4 showed the absorption bands at 521, 523 and 534 nm, respectively. These sharp SPR bands of AuNPs may be due to the formation of mono-dispersed AuNPs. However, when the absorption spectrum of TPDT-Au-CTAB- N_2H_4 was compared with other AuNPs prepared here, TPDT-Au-CTAB- N_2H_4 showed a broad absorption band around 750 nm along with the main SPR band of Au at 521 nm. This longitudinal band is attributed to the formation anisotropic gold nanostructures with rod-like nature. The rod-like nature of TPDT-Au-CTAB- N_2H_4 gold nanostructure was further confirmed through HRTEM studies (Fig. 2D & E). From HRTEM studies of TPDT-Au-CTAB- N_2H_4 , it is observed that some bend rod-like structures were formed in the presence of CTAB and TPDT in addition to the spherical AuNPs. Hence, the absorption studies clearly reveal the formation of AuNPs in the presence of TPDT and CTAB.

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