



Polymer Stabilized Bimetallic Alloy Nanoparticles: Synthesis and Catalytic Application



Charu Dwivedi^{a,*}, Abhishek Chaudhary^b, Srija Srinivasan^c, Chayan K. Nandi^{c,*}

^a Department of Chemistry, School of Physical Sciences, Doon University, Dehradun, Uttarakhand, India

^b Department of Biotechnology and Bioinformatics, Jaypee University of Information Technology, Waknaghat, Himachal Pradesh, India

^c School of Basic Sciences, Indian Institute of Technology, Mandi, Himachal Pradesh, India

ARTICLE INFO

Keywords:

Bimetallic nanoparticles
Alloy nanoparticles
4-Nitrophenol
4-Aminophenol

ABSTRACT

A simple, single pot synthesis method has been described for the synthesis of Au–Ag alloy nanoparticles using cationic long chain polymer. Unlike other methods for alloy NP synthesis, our method is unique because of its fast synthesis rate and robust nature. The high stability of the synthesized monometallic and bimetallic nanoparticles is attributed to the combined effect of the steric hindrance and electrostatic repulsion provided by polymeric stabilizer. Efficient reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) in the presence of alloy nanoparticles and NaBH₄ is investigated and is found to depend upon the gold content in the nanoparticles.

1. Introduction

Bimetallic nanoparticles (BNPs) are emerging as a new class of nanomaterial due to their unique electronic, catalytic and optical properties [1]. Such fascinating characteristic properties of BNP are different from the single component metallic nanoparticles. Moreover, these properties of the BNP can be tailored according to the specific application by controlling the size, shape and metallic composition of the particles [2]. BNP containing gold as one of the elements have begun to show opportunities for developing novel catalytic systems. Several research groups have already demonstrated diverse production techniques of bimetallic nanoparticles of this type [3]. A large segment of the studies focus on noble metal Au core-shell nanoparticles. Metallic core and gold shell combination is in particular seems very appealing as gold provides an established platform for surface functionalization, and being a noble metal gold shell provides protection against oxidation and helps to maintain long-term stability of the particles [4]. Despite all these advantages, the core-shell particles have their own challenges. For example, it is difficult to control the uniformity and thickness of the metal shell and additionally the high density of the grain boundaries at the gold surface offers poor diffusion barrier [5]. These shortcomings of the core shell BNP can be minimized by forming alloy nanoparticles. Gold containing alloy nanoparticles are solid solutions where other metal atoms substitute gold sites in the face center cubic lattice [6]. The incorporation of even a little content of the other metal changes the catalytic activity significantly. Haruta and Hutchings, in their groundbreaking work around 1987, introduced Au based catalysts [7]. Since

then, nano-particulate gold catalysts have been intensively investigated, to be used as catalyst in oxidation and reduction reactions. The aerobic oxidation of alcohols the aldol reaction, addition of alcohols in alkynes, hydrogenation of alkenes and reduction of nitrocompounds, etc., are just to name a few examples [8]. Au–Pd, Au–Pt, and Au–Cu have already been investigated as well as Au–Ag as bimetallic gold catalysts [9–11]. In case of Ag–Au, the difference in the work functions of the two metals leads to electron enrichment in the gold near the interface which facilitates the reduction of the reactant on the gold surface as compared to monometallic nanoparticles [12]. There are many reports available on core-shell Ag–Au BNP but literature concerning the synthesis of Ag–Au bimetallic alloy nanoparticles is scarce. Very recently, Zhang et al. have reported synthesis of poly(N-vinyl-2-pyrrolidone) (PVP)-protected Ag/Au BNPs by physical mixtures using colloidal dispersions of Ag and Au NPs [13]. In another work, authors have described a method for the synthesis of Ag–Au alloy BNPs by exposing maltose coated AgNP seeds to Au³⁺ ions in EO100-PO65EO100 (Pluronic F127) aqueous solutions [14]. The subsequent Au³⁺ reduction on the surface of the silver NPs leads to alloy BNP formation. Generally Ag–Au alloy BNP are synthesized by reacting preformed Ag and Au nanoparticles as co-reduction of silver and gold precursors. However, this method does not yield alloy BNP with uniform size and composition. Herein, we have reported a simple, one pot synthesis method for Ag–Au BNP, using a bio-compatible polymer, poly diallyldimethyl ammonium chloride (PDADMAC), as stabilizing agent. The synthesized alloy BNPs have been analyzed thoroughly using various techniques. The catalytic activities of as prepared alloy BNPs with

* Corresponding authors.

E-mail addresses: cdwivedi.ch@doonuniversity.ac.in (C. Dwivedi), chayan@iitmandi.ac.in (C.K. Nandi).

various compositions have also been investigated for reduction of 4-nitrophenol.

2. Material and Methods

2.1. Materials

All glassware were washed with aqua regia (3 HCl: 1 HNO₃), followed by rinsing with double distilled water for several times. All the chemicals gold (III) chloride hydrate (HAuCl₄·3H₂O 99.99%), sodium borohydride (NaBH₄, 99%), silver nitrate (AgNO₃, 99.5%), 4-nitrophenol, poly diallyldimethylammonium chloride (PDADMAC, 20% aq. solution) were purchased from Sigma Aldrich. Double distilled deionized water (18.3 mΩ, Elga Pure Lab Ultra) was used throughout the preparation of solutions.

2.2. Synthesis of Monometallic Gold and Silver Nanoparticles

Monometallic silver and gold nanoparticles were prepared by reduction of AgNO₃ and HAuCl₄ in the presence of PDADMAC by NaBH₄ in aqueous medium. A solution of 100 mM AgNO₃ was prepared by dissolving 169.87 mg of AgNO₃ in 10 mL water. A stock solution containing 0.1 wt% NaBH₄ was prepared by adding 10 mg of NaBH₄ in 10 mL of water. 2% PDADMAC aqueous solution was used as stock solution. To 4.15 mL of double distilled water, 100 μL of 2% PADADMAC solution was added followed by addition of 25 μL of 100 mM AgNO₃. The solution was stirred well and then NaBH₄ solution (250 μL of 0.1 wt%) was added into it with vigorous stirring. The solution turned light yellow instantaneously indicating formation of AgNP. The AgNP colloid solution was left overnight and was used for further studies. The monometallic gold nanoparticles were prepared by similar procedure using HAuCl₄ as gold precursor. An instantaneous color change from light yellow to bright ruby red on addition of NaBH₄ indicated the formation of GNP.

2.3. Synthesis of Bimetallic Gold–Silver Alloy Nanoparticles

Ag–Au alloy nanoparticles were prepared by NaBH₄ induced co-reduction of silver and gold salts in presence of PDADMAC. The concentration of AgNO₃ was kept constant at 0.5 mM and concentration of gold salt was varied from 0.05–2.5 mM. The final concentration of the stabilizing polymer, e.g. PDADMAC was maintained at 0.04% by wt. The concentration of reducing agent was varied from 0.001%–0.01% in different solutions. In all the cases the reaction was instantaneous and accompanied with the visible color change in the solution.

2.4. Characterization of the Synthesized Monometallic and Bimetallic Nanoparticles

Particle size and dispersity of the synthesized nanoparticles were characterized by using a TECNAI 200 kV TEM (FEI, Electron Optics). Fast Fourier transform (FFT) analysis was done from selected area of the HRTEM image of the edge of the synthesized nanoparticles, which has been enclosed by the white box in the image. The lattice images were constructed by the selective masking of the spots obtained from the FFT analysis of the area enclosed in the white box. The UV–vis absorption spectra were recorded on a Shimadzu 2450 UV–vis Spectrophotometer. The zeta potential of the nanoparticles were measured by using Zeta Sizer Nano, equipped with a He–Ne laser illumination at 633 nm in a single photon counting mode using avalanche photodiode for signal detection (Malvern Instrument). XRD diffraction patterns were recorded on Rigaku SmartLab X-Ray diffractometer using Cu Kα radiation as X-ray source ($\lambda = 1.5418 \text{ \AA}$) at room temperature. The voltage and current for the measurement were kept 45 kV and 100 mA respectively.

2.5. Catalytic Studies

The catalytic reduction of 4-nitrophenol is chosen as model reaction to study the catalytic efficiency of both monometallic and bimetallic nanoparticles. This reduction reaction is known to follow pseudo-first order decay kinetics. All reactions were performed in a standard 3 mL quartz cuvette with a 1 cm path length. Stock solutions of the 4-nitrophenol was prepared first and an appropriate amount of the same solution was added into the reaction cell containing predetermined amount of double distilled water. To the 4-NP solution, freshly prepared NaBH₄ solution (final concentration in the reaction mixture 1.6 mM) was added just before the start of measurement followed by addition of monometallic or bimetallic nanoparticles. To study the effect of the concentration of 4-NP on the rate of reaction, the concentration was varied from 33 to 100 μM keeping concentration of nanoparticles and NaBH₄ constant at 100 μL and 1.6 mM, respectively. In another experiments, the effect of the concentrations of the synthesized nanoparticles on the catalytic reduction of 4-NP was investigated by varying the concentrations from 50 to 100 μL at fixed concentration of 4-NP (60 μM) and NaBH₄ (1.6 mM). The concentration of 4-nitrophenolate was determined from the absorbance at 400 nm ($\epsilon = 19,200 \text{ M}^{-1} \text{ cm}^{-1}$).

3. Results and Discussion

Fig. 1 shows the UV–vis spectra for gold, silver monometallic nanoparticles and all of the Au–Ag nanoparticles with varying gold concentration. Au and Ag nanoparticles show their characteristics absorption peaks at 520 and 410 nm, respectively. On simultaneous reduction of gold and silver ions by sodium borohydride in the same solution, gold–silver alloy particles are formed. The alloy formation is concluded from the fact that the optical absorption spectrum shows only one plasmon band and the wavelength at which maximum absorbance occurs in a linear fashion. In general, the core-shell type nanoparticles show two plasmon bands in the absorption region corresponding to the constituent core and shell metal [15]. In another scenario, if the metal of shell layer forms a thin uniform film (3–4 nm) on the core particles, the surface plasmon absorption band depicts only one peak resulting from the metal of shell layer. Such possibility of core-shell formation is ruled out by the TEM and HRTEM images of the synthesized Au–Ag nanoparticles [15]. The average size of the monometallic Ag and AuNP is determined to be 11 nm and 6 nm, respectively (Fig. 2a–b, 2e–f and Fig. S1, Supporting information). Although, the polydispersity in the size of the monometallic particles is observed, still the large fraction of nanoparticles has size < 10 nm. The polydispersity in the shape as well as size of the alloy nanoparticles is comparably less than that of monometallic nanoparticles and their average size is found to be ~4 nm. As it is evident from the Fig. 2k, the alloy nanoparticles does not show any difference in the contrast on the surface and core of the nanoparticles, therefore, it can be concluded that the nanoparticles are nano alloy of Ag and Au. Moreover, the distortion observed in the fringe pattern of the Ag–Au nanoparticles in Fig. 2l also indicates towards the defects created during alloying of Ag with Au.

The co-reduction of the metal salts results in formation of Au⁰ and Ag⁰ in the reaction mixture which coalesce to form nanoparticles. Since, melting point of metal decrease with the decrease in their size, the diffusion coefficient of the metals increases and alloying of Ag and Au takes place in the nanodomain [16]. Moreover, the similarity in the atomic size of Au and Ag also makes the interdiffusion between Au atoms and Ag atoms easy. During the synthesis process the initial nucleation of both Au and Ag nanoparticles may start simultaneously and the growth process completes in several seconds evident by the change in color of the reaction mixture (Fig. 1d). The lattice parameters of silver and gold are almost identical and both crystallize in an fcc lattice and can form solid solutions (alloy) [17]. This is also evident from the HRTEM image of the Ag–Au alloy nanoparticles in which no

Download English Version:

<https://daneshyari.com/en/article/6977050>

Download Persian Version:

<https://daneshyari.com/article/6977050>

[Daneshyari.com](https://daneshyari.com)