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Synthesis of silver nanoparticles: Effects of anionic ligands on formation and catalytic activity

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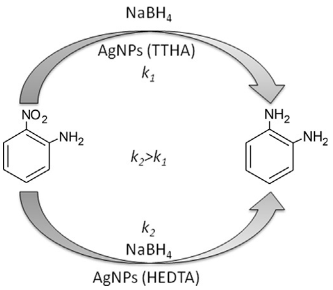
HIGHLIGHTS

- Formation of Ag nanoparticles using anionic ligands as reducing agents and stabilizers.
- Number of –COOH groups in the ligands affect the formation of particles.
- The formed nanoparticles show good catalytic activity.
- Number of –COOH groups in the ligands affect the catalytic activity of the particles.

GRAPHICAL ABSTRACT



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ABSTRACT

We report a facile method to synthesize water soluble Ag nanoparticles (NPs) using various anionic complexing ligands as reducing as well as stabilizing agents. The formation of the particles depends on the initial molar ratio of ligands to silver nitrate. Also, the alkaline condition of preparative solution is found to be necessary for the formation of Ag NPs. It has been important to mention here that the temperature of the reaction mixture plays an important factor on the rate of formation of the particles. The particles were characterized by UV–vis spectroscopy, transmission electron microscopy, dynamic light scattering and X-ray diffraction techniques. The formed particles were found to be stable for more than a month. Zeta potential measurements suggest that the negative potential created by the adsorbed complexing ligands contribute to the stability of the Ag NPs suspensions. The effect of the ligands on the formation, stability and catalytic activity of the Ag NPs was evaluated. The obtained Ag NPs exhibit a good catalytic activity toward reduction of o-nitroaniline. The results reveal that the presence of more coordination sites in the ligands affects the catalytic activity of the particles.

1. Introduction

The application of noble metal nanoparticles (NPs) in various fields of research has increased drastically due to the unique optical, catalytic and magnetic properties which are the consequences of their nanometer dimensions [1–8]. With the advances in the field of nanotechnology, Ag and Au NPs are being extensively exploited in the field of biomedical applications due to their inert, biocompatible nature and novel optical properties [4]. However, Ag NPs in particular are being explored more because of their extraordinary efficiency at absorbing and emitting light. Due to this, surface plasmon resonance which is a collective oscillation of the conduction electrons on exciting by light of specific wavelength is more intense in Ag as compared to Au [1–7].

There are many routes available for the synthesis of metal NPs. The wet chemical method usually involves the reduction of metal ions in solutions in the presence of reducing reagents. These methods include Creighton method, in which reduction of $AgNO_3$ is

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done by sodium citrate, radiolytic reduction and photolytic reduction, to name a few [1–7]. The high surface energy of the nanosized particles makes them extremely unstable and leads to aggregation when their surface is not well protected or passivated. Generally, to keep the metallic particles remain suspended in the solution various stabilizers like surfactants or polymers are used [1–8]. Many of these stabilizers contain organic moieties that show reactivity towards reducing or oxidizing radicals. Recently, attempts have been made to make Ag and Au NPs without using stabilizers and their catalytic property was tested [9–11].

The members of the polyamino carboxylic acid family of ligands viz. ethylenediaminetetraacetic acid (EDTA), *N*-(2-hydroxyethyl) ethylenediaminetriacetic acid (HEDTA), etc. are being used in industrial applications due to their role as chelating agent as under alkaline conditions they have high complexing constants with metal ions [12,13]. There are a number of reports in the literature in which the metal NPs have been synthesized using complexes of Ag^+-EDTA, Ag^+-DTPA, etc. In most of these studies, reduction was carried out either by strong reducing free radicals generated by water radiolysis [14] or by boiling the solution in autoclave at high temperature [15–19]. However, very few studies exist in the literature in which reduction of Ag^+-Ligand complexes was carried out without using any reducing agent [20–23]. Very recently, the well known Turkevich method was re-examined and it has been shown that the sequence of addition of reactants play a role in the formation of nanoparticles [24,25]. Thus, it is important to compare the efficacy of complexing ligands in the formation and stabilization of the particles under identical conditions. However, there is no detailed report exists in literature where, the formation and stability of the particles has been studied in the presence of various complexing ligands as a function of pH and Ag^+:ligand ratio. In the present work, we have studied the effect of various complexing ligands on the formation and stability of the Ag NPs under the identical experimental conditions and shown that the sequence of addition of reactants plays a significant role in the formation of the particles.

As mentioned above, potential applications of metal NPs as redox catalysts has been recognized and detailed mechanisms to describe the catalytic processes on their surfaces have been proposed [1–3]. Catalytic reactions over the surface of metal NPs are in the focus of on-going research because of their dependence on tunability of particle size [26], shape [27] and stabilizers [11,28,29]. However, only a few studies are reported in literature in which the effects of stabilizers on the catalytic processes have been discussed [11,28,29]. The reduction of aromatic nitro compounds to corresponding amino derivatives with an excess amount of $NaBH_4$ in the presence of metal NPs is a standard system to test the catalytic capability of the as prepared NPs [30–35]. The conversion process of nitro to amino derivatives has industrial relevance, i.e., for aniline and paracetamol production. Inspired by these works, the objective of the present study is twofold: first to study the reducing abilities of various anionic complexing ligands for silver ions and secondly, to check the catalytic activity of Ag NPs synthesized in their presence. To achieve the goal, the Ag NPs were prepared in the presence of various anionic complexing ligands using the optimum molar concentration ratio of Ag^+:ligand and their catalytic activity was checked. The results obtained are discussed.

2. Materials and methods

2.1. Materials

Ethylenediaminetetraacetic acid (EDTA), *N*-(2-hydroxyethyl) ethylenediaminetri-acetic acid (HEDTA), nitrilotriacetic acid (NTA), triethylenetetramine-*N*,*N*,*N*′,*N*″,*N*‴-hexaacetic acid (TTHA) and iminodiacetic acid (IDA) of Analytical grade were used as received. Their structures are shown in Scheme 1. Silver nitrate (BDH, India), sodium dodecyl sulfate (Sigma), sodium hydroxide (BDH, India), o-nitroaniline (Sigma) and sodium borohydride (Sigma) were used as received. All solutions were prepared just before the experiments and kept in dark to avoid any photochemical reactions. Water purified through a Millipore system was used. All experiments were done at room temperature and at higher temperature ~80 °C under aerobic condition at pH 10.

2.2. Methods

The synthesis of Ag NPs was carried out in the pyrex volumetric flask. Each synthesis followed the same basic procedure. In a typical synthesis, 1 mL of $AgNO_3$ solution (0.01 M) was added to the volumetric flask containing 1 mL of ligand solution (0.01 M) at pH 10 then the solution was diluted to 10 mL using Millipore purified water. All the ratios of [ligand]/[Ag^+] were prepared accordingly except for TTHA where, [ligand]:[Ag^+] ratio was kept 0.5.

A standard catalytic test reaction was carried out in 4.5 mL quartz cuvette. An aqueous solution containing 2 mL of 0.1 mM o-nitroaniline (o-NA) was mixed with 1 mL of ice cold 0.1 M sodium borohydride solution followed by the addition of various amounts of Ag NPs. The solution was stirred vigorously to avoid diffusion limitation. Immediately after the addition of Ag NPs, time dependent absorption spectra were collected at various intervals for at least 30 min at temperature 25 °C. The color of the solution changed from yellow to colorless.

2.3. Characterization of Ag NPs

UV–vis absorption spectra were collected on Jasco-650 spectrophotometer. Particle sizes were determined by TEM using a Zeiss-Carl (Libra-120) and JEOL-TEM instruments. Specimen for TEM analysis was prepared on Lacey Formvar/carbon-coated 200 mesh copper grid from Ted-Pella. The 20 μL droplet of the sample was put on the grid and kept on filter paper to remove excessive solution. The TEM image was taken by air-drying of the NPs. Zeta potentials were determined by Nanosizer Z (Malvern Instruments). Dynamic light scattering measurements of the solution were performed using a Malvern 4800 Autosizer employing 7132 digital correlator. Spherical symmetry was assumed in the interpretation of the results. Crystallographic information about the samples was obtained from powder X-ray diffraction (XRD) using a Phillips Analytical (PW 1729) diffractometer employing Cu K_α radiation.

3. Results and discussion

3.1. Synthesis of Ag NPs

Addition of $AgNO_3$ to the solution containing HEDTA (1×10^{-3} M) at pH 10 showed no change in the color of the solution. The color of the solution appeared to be colorless and the UV–vis spectra of the reaction mixture showed no evidence of absorption in the spectral window 300–700 nm due to the formation of Ag NPs. When the same solution was heated in a water bath at ~80 °C for ~3 min, the solution turned pale yellow indicating the nucleation of Ag clusters. The color of the solution intensified on further heating for 2–3 min. UV–visible spectroscopy is one of the most widely used techniques for structural characterization of the Ag NPs. The UV–vis spectra of the formed yellow colored Ag NPs showed a weak and broad surface plasmon absorption band with maximum at around 420 nm indicating the presence of spherical or roughly spherical Ag NPs. The optical absorbance of the Ag NPs