Synthesis, Characterization, and Application of Monodisperse Gelatin-Stabilized Silver Nanospheres in Reduction of Aromatic Nitro Compounds

R. Vadakkekara, M. Chakraborty*, and P. A. Parikh**

Department of Chemical Engineering, Sardar Vallabhbhai National Institute of Technology, Surat—395007, Gujarat, India
e-mail: mch@ched.svnit.ac.in*, pap@ched.svnit.ac.in**

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Abstract—Monodisperse colloidal silver nanospheres were synthesized by the reaction of silver nitrate, hydroxylammonium hydrosulphate \((\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4\) and sodium hydroxide in the presence of gelatin as stabilizer. Colloidal nanospheres were characterized by UV-vis absorption spectroscopy, transmission electron microscopy, X-ray diffraction and dynamic light scattering. X-ray diffraction data confirmed that the silver nanospheres were crystalline with face-centered-cubic structure. Transmission electron microscopy analysis revealed the formation of homogeneously distributed silver nanoparticles of spherical morphology and size of the nanoparticles was in the range of 0.7–5.2 nm. Silver nanospheres were stable for more than two months when stored at ambient temperature. Size and size distribution were studied by varying pH, reaction temperature, silver ion concentration in feed solution, concentration of reducing agent and concentration of the stabilizing agent. Catalytic activity of silver nanospheres was tested for the reduction reaction of nitro compounds in sodium borohydride solution. Monodisperse silver nanospheres showed excellent catalytic activity towards the reduction of aromatic nitro compounds. The reduction rate of aromatic nitro compounds had been observed to follow the sequence 4-nitrophenol > 2-nitrophenol > 3-nitrophenol.

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1. INTRODUCTION

Metallic colloidal micro- and nanospheres are of great interest, since their intrinsic properties can be improved by changing parameters such as diameter of the nanoparticles, chemical composition, bulk structure, and crystallinity. Colloidal silver particles are comparatively well-studied systems [1, 2]. Many researchers reported the synthesis of stable colloidal solutions of silver nanoparticles in polar and non polar solvents. Among the various techniques for the synthesis of silver colloids, the precipitation from homogeneous solution is widely used because it can yield particles of different characteristics by varying concentration of reactants, temperature, pH and stabilizing agent, etc. [3–5].

Various polymers such as polyvinylpyrrolidone, polyvinyl alcohol, polyethylene glycol, poly(methyl methacrylate), polyaniline, polyacrylonitrile and natural polymers like natural rubber, polysaccharides, cellulose, chitosan and starch had been widely used for the well-dispersed silver nanoparticles [6–8]. Gelatin is a natural biopolymer and it has been commonly used as a stabilizer because it prevents agglomeration and growth of synthesized nanoparticles; carriers coating or separating agent, cosmetic manufacturing, photography, gelling agent in food and pharmaceuti-cal. Gelatin forms homogeneous, optically transparent and thermo-reversible physical gel in aqueous solven [5, 9–11]. Darroudi et al. [5] prepared gelatin mediated silver nanoparticles by laser ablation and obtained silver nanoparticles of diameters ranging from approximately 9 nm to 15 nm. Liu et al. [10] prepared gold, silver, and silver-gold bimetallic nanoparticles in gelatin solution at 80°C. They observed that the morphology of the prepared nanoparticles could change with the degradation of gelatin. Vegera and Zimon [12] obtained gelatin stabilized silver nanoparticles by reduction of silver nitrate with sodium borohydride. They found that the aggregation and sedimentation-stable nanodispersion can be obtained at appropriate gelatin concentrations. Yang et al. [13] used gelatin as stabilizer for the preparation of Au nanospheres. The rate of the reaction was found to be increased with temperature of the mixture and nanospheres of Au were formed at 20°C. Yang et al. [14] used gelatin as stabilizer for the synthesis of AgBr spherical nanoparticles with porous structure and diameter of 150–200 nm. They found that at lower temperature gelatin inhibited the direct reaction of Br⁻ ions with AgCl surface and agglomeration of the growing AgBr. Gelatin and glucose–gelatin mixture as a reducing as well as protecting agent was used for the synthesis of silver nanoparticles (Ag-NPs) by Darroudi et al. [15, 16].
et al. [17] also described the synthesis of nanocomposites of gold using gelatin as stabilizing agent. Aromatic amines were commonly used in industry for the synthesis of dyes and pharmaceuticals and in agriculture because of their biological activity [18–21]. From literature, it was found that metallic nanoparticles were widely used for the reduction of nitro compounds with NaBH₄. Kundu et al. [18] studied the catalytic activity of silver nanoclusters on silica for the reduction of nitro compounds in aqueous, organic and micellar media. Jana et al. [19] had exploited polystyrene beads supported silver nanocomposites as a catalyst for the reduction of 4-nitrophenol (4-NP) using of NaBH₄ as hydrogen source. The nanocomposites were acted as potent catalysts for the reduction of 4-NP. Hwang et al. [21] used Pd colloids for the reduction of aromatic nitro compounds in aqueous solution at room temperature. They found that the rate of reduction of 4-NP was significantly higher than other nitro compounds. The reduction of 4-NP by NaBH₄ was also studied to investigate the catalytic activity of polymer supported silver, gold, silver–gold bimetallic nanoparticles. It has been found that Au NPs exhibited excellent catalytic activity [22].

In light of the aforementioned data, we made an attempt to synthesize uniformly distributed stable monodisperse colloidal silver nanospheres. In this study, gelatin was used as stabilizing agent because it is cheap, easily available and has no harmful effect on the environment compared to other stabilizing agents. Different parameters, which affect particle size and size distribution, were studied systematically. The reduction of 4-NP, 3-nitrophenol (3-NP) and 2-nitrophenol (2-NP) was carried out to compare the catalytic activity of colloidal nanospheres.

2. EXPERIMENTAL

2.1. Materials and Methods

Silver nitrate (AgNO₃), gelatin, sodium hydroxide (NaOH), hydroxylammonium hydrosulphate ((NH₂OH)₂ ⋅ H₂SO₄), sodium borohydride (NaBH₄), 4-nitrophenol, 3-nitrophenol and 2-nitrophenol were received from Finar Chemicals, India. All aqueous solutions were prepared using Millipore distilled water (Millipore, Elix, India).

2.2. Synthesis of Colloidal Silver Nanospheres

Silver nanospheres were synthesized by the reduction of silver nitrate with (NH₂OH)₂ ⋅ H₂SO₄. Reducing power of (NH₂OH)₂ ⋅ H₂SO₄ was maintained by NaOH and gelatin was used as protecting agent. 2 mol % of gelatin was mixed separately in 100 mL of 3 × 10⁻³ mol L⁻¹ AgNO₃ solution and 1 × 10⁻² mol L⁻¹ (NH₂OH)₂ ⋅ H₂SO₄ solution, respectively. The pH of the silver nitrate solution was adjusted to 9. Then, two solutions were mixed with constant stirring for 2 h at 20°C.

2.3. Procedure for the Reduction of Nitro Compounds

The catalytic activity of colloidal silver nanospheres was measured for the reduction of 4-NP, 3-NP and 2-NP. The reduction reaction was carried out in a standard cuvette (1-cm path length, room temperature, 303 K), 1 mL of ice-cold solution of NaBH₄ (8 × 10⁻² M) was mixed with 1 mL of water and 1 mL of nitro compound (5 × 10⁻⁴ M). 100 μL (0.4 × 10⁻¹ g Ag) of colloidal silver nanospheres were added in reaction mixtures and monitored by UV–vis spectra at different time interval.

2.4. Characterization Techniques

The absorption spectra of silver nanospheres were measured using a UV–vis spectrophotometer (HACH, Germany). Size of the colloidal nanospheres was investigated with transmission electron microscope (TEM), Philips Tecnai-20, operated at 200 kV provides 0.27 nm point resolution. X-ray diffraction (XRD) of nanospheres were carried out on a Philips, X' Pert–MPD equipped with a Ni filtered CuKα radiation source (λ = 1.542 Å) of 40 kV and 30 mA. Mean crystallite size of the silver nanospheres was calculated using the Scherrer equation. NPs size was obtained using dynamic light scattering (DLS) setup (Malvern Zetasizer, Nano ZS 90, U.K.). Stability of the colloidal nanosphere dispersion was analyzed using UV–vis absorption spectroscopy.

3. RESULTS AND DISCUSSION

3.1. Preparation of Colloidal Silver Nanospheres

The reaction mechanism for the synthesis of silver nanospheres can be drawn as follows:

\[
\text{AgNO}_3 + \text{NaOH} \rightarrow \text{AgOH} + \text{NaNO}_3, \quad (1)
\]

\[
2\text{AgOH} + (\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4 + 2\text{NaOH} \rightarrow 2\text{Ag} + \text{N}_2 + \text{Na}_2\text{SO}_4 + 6\text{H}_2\text{O}. \quad (2)
\]

Temperature of the reaction is a key factor for the production of silver nanosphere colloids. At lower temperature, the viscosity of the solution increased which reduced the diffusion rate of Ag⁺ ions and NH₂OH and the overall rate of reaction too. At low temperature (5°C), more nitrogen gas was produced and hollow Ag nanospheres were formed on the surface of nitrogen gas bubbles [23].

3.2. UV–vis Absorption Spectroscopy

UV–vis spectrum of the silver nanospheres exhibited a strong absorption band at 405 nm (Fig. 1),