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Dextrin-mediated synthesis of Ag NPs for colorimetric assays of Cu^{2+} ion and Au NPs for catalytic activity

Kalipada Bankura[a,b], Dipak Rana[c], Md. Masud Rahaman Mollick[a], Sutanuka Pattanayak[d], Biplab Bhowmick[a], Nayan Ranjan Saha[a], Indranil Roy[a], Tarapada Midya[a], Gadadhar Barman[e], Dipankar Chattopadhyay[a,*]

[a] Department of Polymer Science and Technology, University College of Science and Technology, University of Calcutta, 92 A.P.C. Road, Kolkata 700 009, India
[b] Department of Chemistry, Tamralipta Mahavidyalaya, Tamluk, Purba Medinipur 721636, India
[c] Department of Chemical and Biological Engineering, Industrial Membrane Research Institute, University of Ottawa, 161 Louis Pasteur St., Ottawa, ON K1N 6N5, Canada
[d] Department of Chemistry, West Bengal State University, Barasat, Kolkata 700126, India
[e] Department of Chemistry, Midnapore College, Midnapore 721101, India

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ABSTRACT

A facile one-pot approach for rapid synthesis of silver and gold nanoparticles (Ag NPs and Au NPs) with narrow size distribution and good stability was described by reducing silver nitrate and chloroauric acid with polysaccharide dextrin. Here, dextrin was used as both a reducing and stabilizing agent for synthesis of NPs. The as-synthesized Ag NPs and Au NPs were characterized by UV–visible absorption spectroscopy, transmission electron microscopy (TEM) and X-ray diffraction (XRD). The Ag NPs and Au NPs exhibited an absorption maxima at 404 and 547 nm respectively. TEM images showed NPs in the range of 8–28 nm. The crystallinity of the NPs was measured by XRD analysis. Furthermore, the as-prepared Ag NPs revealed colorimetric sensor property for detection of Cu^{2+} ions based on changes in absorbance resulting from metal ion-induced aggregation of NPs or direct deposition of metal ions onto NPs. The as-prepared Au NPs exhibited a notable catalytic activity toward the reduction of 4-nitrophenol to 4-aminophenol in the presence of $NaBH_4$.

1. Introduction

In recent years, there has been a great deal of interest and attention in the area of noble metal nanoparticles (NPs), especially silver and gold NPs (Ag NPs and Au NPs) due to their unique size dependent optical, electrical and magnetic properties [1]. The multipurpose utilities of silver and gold nanoparticles have been proven in various applications such as catalysis [2,3], biological sensing and imaging [4], optics [5], chemical sensor [6] and antimicrobial activity [7,8]. Because of such a wide range of application possibilities, the preparation and characterization of metal nanoparticles are becoming increasingly popular among researchers. Different chemical and physical methods such as chemical reduction [9], electrochemical reduction [10], photochemical reduction [11], laser ablation [12], laser irradiation [13], etc., have been reported for synthesis of metal NPs. In the case of chemical reduction, the synthetic processes involve the treatment of metal salts with either the use of borohydride [14], hydrazine [15], citrate [16], etc. or require rather complex procedures or vigorous conditions, or other organic compounds in the presence of a suitable stabilizer (surfactants, polymers, tri-block polymers and dendrimers). The chemicals used in the chemical reduction method, in most of the cases, are highly reactive and associated with environmental and biological hazards. Thus, there is a requirement to develop environmentally clean and sustainable synthetic protocols to prepare stable metal NPs.

Biosynthesis has received considerable attention compared to traditional methods used to reduce these problems. Biosynthesis offers many advantages by avoiding the use of toxic chemicals in the process and eliminating risks in industrial, pharmaceutical, and biomedical applications. Researchers have begun to use a broad range of biological materials including biomolecules [17], bio-organisms (bacteria, fungi and yeast) [18,19], proteins [20,21], peptides [22,23], plant extracts [24] and biopolymers [25] for the biosynthesis of metal NPs. Among the various biological materials, polysaccharides are used as an important natural resource

* Corresponding author.
E-mail address: dipankar.chattopadhyay@gmail.com (D. Chattopadhyay).

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for the synthesis of metal NPs. In such processes, polysaccharides usually act as reducing or capping agents because of their special structure and properties. Early research by Raveendram et al. [26] reported a completely green method for the preparation of silver nanoparticles using the biopolymer starch as a capping agent and D-glucose as the reducing agent. Many researchers have investigated the effects and mechanisms of various carbohydrates, such as glucose, sucrose [27], fructose, galactose, ribose and lactose as reducing agents and biopolymers [28] such as starch [29], cellulose [30], chitosan [31], pectin, agarose, cyclodextrin [32], levan [3], Glucomannan [25] and guar gum as capping agents for the preparation of metal NPs. Biopolymers can stabilize NPs via electrostatic interaction of their functional groups with the NPs.

The use of catalyst in any chemical reaction is of great importance. From an economic and environmental point of view, a catalyst with high activity is particularly desirable [33,34]. Reduction of nitrophenol is considered as the standard reaction to evaluate catalytic activity, because it is easy to monitor with simple spectroscopic techniques such as the UV–vis and only a single product is obtained in the solution [35]. In the case of a heterogeneous catalyst, reactants are adsorbed on the active sites of the catalyst. Adsorption, being the basis of many industrial heterogeneous catalytic reactions attracted immense interest among researchers. A group of researchers have evaluated the catalytic application of gold and silver dendrimer-encapsulated nanoparticles in the conversion of 4-nitrophenol (NP) to 4-aminophenol (AP) by sodium borohydride ($NaBH_4$). The reduction of 4-nitrophenol with sodium borohydride at the surface of the catalyst can be described by the Langmuir–Hinshelwood model. Au13-DENs showed greater catalytic activity toward nitrophenol reduction than its Ag13-DENs counterpart as evidenced by the greater surface activity [36].

Recently, cyclodextrin, dextrin, and glucose have been successfully used as aqueous capping agents in organic media reduction for the synthesis of stable Ag NPs and Au NPs [37,38]. In this article, we have reported an environmentally clean and sustainable methodology for the synthesis of Ag NPs and Au NPs using dextrin as a reducing and capping agent in an aqueous solution. It is observed that the reaction time for synthesis of silver and gold nanoparticles using dextrin is short compare to earlier reported literatures. The dextrin mediated silver and gold nanoparticles have good stability over a period of one month. The synthesized Ag NPs and Au NPs were characterized in detail by UV–vis absorption spectroscopy (UV–vis), transmission electron microscopy (TEM) and X-ray diffraction (XRD). Furthermore, we have investigated Ag NPs for colorimetric assays of Cu^{2+} ion detection and Au NPs for catalytic reduction of 4-nitrophenol. Although several reports for the synthesis of silver and gold nanoparticles using carbohydrates (monosaccharides and polysaccharides) have been established, our method for the synthesis of silver and gold nanoparticles using dextrin is suitable because this is carried out in an aqueous medium without addition of alkali.

2. Materials and methods

2.1. Materials

Silver nitrate ($AgNO_3$, Merck, Mumbai, India) and tetrachloroauric (III) acid ($HAuCl_4$, Sigma–Aldrich, Steinheim, Germany) were used as the metal precursor to prepare the Ag and Au nanoparticles. Dextrin [$(C_6H_{10}O_5)_n{\cdot}xH_2O$, Loba Chemie, Mumbai, India] was used as a reducing and stabilizing agent to prevent aggregation of nanoparticles. Sodium borohydride ($NaBH_4$, Merck, Mumbai, India) and 4-nitrophenol (O_2NPhOH, Merck, Mumbai, India) were used for catalytic reduction. Copper nitrate [$Cu(NO_3)_2$, Beijing Chemical Reagent Company, Beijing, China] was used for the detection of Cu^{2+} by sensing the colorimetric property. All of the chemicals used were of analytical grade and used without any further purification. Triple distilled water was used throughout the total experiments.

2.2. Preparation of silver and gold nanoparticles

All the glasswares were cleaned with chromic acid and subsequently with tap water. The cleaned glasswares were rinsed thoroughly with triple distilled water, and then acetone, followed by drying in a hot air oven at 80 °C for 3 h. A stock solution of dextrin was prepared by dissolving the dextrin in triple distilled water. Typically, 0.005 mg of dextrin was dispersed in 20 mL of triple distilled water. The suspension was allowed to stir at room temperature for 10 min and then heated to 80 °C to get a clear transparent solution. Silver nitrate solution (0.001 M) was prepared by adding $AgNO_3$ in triple distilled water. Then, the silver nitrate solution was mixed with the dextrin solution (1:9). The transparent colorless solution was converted to the characteristic yellow color when the solution was heated at 60 °C for 3 h indicating the formation of Ag NPs. Tetrachloroauric acid solution (0.001 M) was prepared by adding $HAuCl_4$ in triple distilled water. Then, the tetrachloroauric acid solution was mixed with a dextrin solution (1:9) at room temperature. In the case of formation of Au NPs, the transparent colorless solution was converted to the characteristic purple color when the solution was heated at 60 °C for 2 h. It was observed that the reaction time for the synthesis of Au NPs from tetrachloroauric acid solution is lesser than the synthesis of Ag NPs from silver nitrate solution. This is most likely due to the fact that the reactivity of tetrachloroauric acid is higher than silver nitrate.

2.3. Characterization of dextrin stabilized nanoparticles

The silver and gold nanoparticles were characterized by Ultraviolet–visible (UV–vis) spectroscopy, transmission electron microscopy (TEM) and X-ray diffraction analysis (XRD).

2.3.1. UV–vis absorption spectroscopy

Silver and gold are inorganic metals, showing characteristic absorption peaks that can be identified qualitatively by UV–vis absorption spectroscopy. All UV–vis spectra were recorded on a Shimadzu UV 1800 spectrophotometer in the range 200–700 nm. The absorption of the prepared colloidal solutions was obtained by being measured in a quartz cuvette with 1 cm optical path length. At different time intervals, aliquots of the solution were taken out and then tested immediately.

2.3.2. Transmission electron microscopy

The size, shape and particle size distribution can be examined using transmission electron microscopy. The images of transmission electron microscopy (TEM) were obtained using JEOL JEM 2010 (Japan) running at 200 kV. The samples for TEM analysis were prepared by placing a drop of suspension on a carbon coated copper grid and allowed to air dry at room temperature overnight.

2.3.3. X-ray diffraction

The crystallinity and phase composition of nanoparticles were investigated using X-ray diffraction. The diffractogram was recorded in a PANalytical, XPERT-PRO diffractrometer (Netherlands) operated at 40 kV, 30 mA, with graphite monochromatized Cu Kα radiation of wavelength $\lambda = 1.5406$ Å as X-ray source. The XRD pattern was recorded in the 2θ range from 0° to 90° at a scanning step of every one unit. The sample for XRD analysis was prepared by depositing the centrifuged sample on a microscopic glass slide and then air-dried overnight.