Carbohydrate-directed synthesis of silver and gold nanoparticles: effect of the structure of carbohydrates and reducing agents on the size and morphology of the composites

Zameer Shervani [a,*], Yasushi Yamamoto [b]

[a] Department of Materials Science and Engineering, Faculty of Engineering, Iwate University, 4-3-5, Ueda, Morioka 020-8551, Japan
[b] Department of Life and Materials Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

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ABSTRACT

A monosaccharide (β-D-glucose) and polysaccharide (soluble starch) were used as structure directing and subsequently stabilizing agents for the synthesis of spherical nanoparticles (NPs) and nanowires of silver and gold. Homogeneous monodispersed Ag(0) nanoparticles (Ag NPs) of 15 nm diameter were obtained when 10^{-4} M AgNO$_3$ precursor salt was reduced in starch (1 wt %)–water gel by 1 wt % β-D-glucose. For a second preparation the effect of reducing agents on the synthesis of Au(0) metallic nanoparticles (Au NPs) of 2×10^{-4} M concentration prepared in a β-D-glucose (0.03 M)–water dispersion was studied first in detail. Different equivalent amounts of NaBH$_4$ and a number of pH values were evaluated for the reduction of the Au salt HAuCl$_4$·3H$_2$O to obtain Au NPs. The type and the amount of reducing agent, as well as the pH of the solution was shown to affect the size and morphology of the NPs. NaBH$_4$ (4 equiv) produced the smallest (5.3 nm (σ 0.7)) metallic particles compared to larger particles (10.0 nm (σ 1.4)) when the salt was reduced by 1 equiv of NaBH$_4$. Addition of excess NaBH$_4$ caused the NPs to settle out as a precipitate forming a mesh or wire structure rather than monodispersed particles. Low pH (pH 6) resulted in incomplete reduction, while at pH 8 the salt was completely reduced. When the salt was reduced by NaOH at pH 8, the particles were larger (14.2 nm) and less homogeneous (σ 2.8) compared to those from NaBH$_4$ reduction.

1. Introduction

Nanomaterials of different shapes and sizes have attracted considerable attention because of their unique physicochemical properties compared to the bulk materials.[1–4] The optical and electronic characteristics of these nanometer-sized materials dramatically change their behavior in favor of potential applications[5–7] as catalysts, semiconductors, photovoltaic devices, and most recently in medical diagnosis[8] and pharmaceutical products.[9] The synthesis of nanoparticles has been known for more than two decades. Lianos and Thomas[10] in 1986 successfully prepared stable CdS particles of 5 Å radius in inverted micelles. Lisieki and Pileni[11] synthesized in situ copper metallic nano-clusters (2–10 nm) using an aqueous core of reverse micelles as microreactors. The authors showed that the size of the material was controlled by adjusting the amount of water in the solution, that is, the size of the water core of micelles in which the metallic particles were formed. At low water content the smaller particles were formed since the size of aqueous core was smaller. By increasing the water content the size of metallic cluster increased from 2 to 10 nm. The monolayer of the surfactant AOT (sodium bis(2-ethylhexyl) sulfosuccinate) used in the preparation of reverse micelles compensated for the high surface energy of such smaller sized metallic particles that prevented the aggregation or bulk formation of the metal. In preparation of nanomaterials in reverse or inverse micelles toxic and expensive organic solvents, such as benzene, hexane, dodecane, or isooctane[12–15] are used as bulk solvents in which nanometer-sized water droplets surrounded by a layer of surfactants remained monodispersed.

To avoid the use of toxic organic solvents for the preparation of nanomaterials, researchers have explored the possibilities of preparing them in aqueous medium with the help of synthetic or commercial stabilizing or capping agents. We previously used a number of capping agents, PVP, poly(methyl vinyl ether) (PVE), ethylene glycol, and water-soluble starch, to obtain Ag NPs of different morphology and sizes.[16] The Ag salt was reduced in capping agent–water solution by NaOH or (+)-D-glucose by heating the solutions in the temperature range of 70–190 °C. The preparation of copper nanoparticles by electron beam irradiation of a metal salt in aqueous surfactant solutions has also been reported.[17] These workers demonstrated that one could vary the size of the copper particles in the range of 20–40 nm depending on the surfactant

* Corresponding author. Tel./fax: +81 19 621 6352.
E-mail addresses: shervani@iwate-u.ac.jp, shervani.chem@gmail.com (Z. Shervani).

employed. The surfactants polyvinyl alcohol, sodium dodecyl benzenesulfonate, gluten, and polyethylene glycol were used as stabilizing agents. High-temperature (200 °C) heating was used[18] to synthesize self-organized Au NPs when AuCl$_3$ was heated in oleyl amine in the presence of tri-octyl phosphine oxide (TOPO). Oleyl amine acted in multiple roles as a high-boiling point solvent, capping agent, and reducing agent. The monodispersed 10-nm Au particles so obtained were characterized by transmission electron microscopy (TEM) and X-ray powder diffraction (XRD) studies.

There is a considerable interest in colloidal transition nanometals Au and Ag since they exhibit different colors when they are in colloidal form depending on the shape, size, and the tendency of aggregation.[19] The synthesis of L-cysteine-capped Au NPs has been carried out[20] from the viewpoint of generating biological markers, and comparative studies have been conducted with the uncapped particles. UV–vis spectra showed a strong blue shift of 176 nm in the plasmon resonance band when the particles were covered with 2.0 mM L^{-1} of cysteine compared to the bare particles. The TEM measurement showed considerable reduction in size from 20 nm to 2 nm. Uncoated particles do not exhibit any luminescence when excited at 250 nm wavelength, whereas a strong emission peak was observed at 382 nm for coated particles. Immobilization of antibodies has been achieved[21] on an electrochemically synthesized polypyrrole(Ppy)–Au NPs composite. The device, a film of Au NPs immobilized on a microelectrode was shown to be an attractive platform for immunosensors as tested by electrode surface morphology, cyclic voltammetry, and immunosensor performance. In a recently published review article,[22] the authors cited in vitro diagnostic applications of Au NPs in immunoassays, immunohistochemistry, DNA diagnostics, bioseparation of specific cell populations, and cellular imaging. They mentioned that Au NP-based diagnostics may open new frontiers for detection of tumors, as well as infectious and neurological diseases. There are a considerable number of opportunities to fully utilize in modern clinical technology the new concepts and phenomena that have appeared in the field of NP research. In another review article[23] the authors demonstrated that Au NPs in drug and gene delivery are considered as essentially nontoxic carriers. The Au core imparts stability to the delivery assemblies, while the surface covering the particles can be tuned for charge and hydrophobicity. Au NPs are more attractive from a medical viewpoint as they interact with thiols that are important for effective and selective means of controlled intercellular release. The synthesis of nanomaterials as described above involved harmful and expensive organic solvents preparation media. If the synthesis was conducted in supercritical or subcritical conditions, then high temperature and pressure were required.

We describe herein the preparation of Ag and Au NPs in inexpensive, nontoxic, environmentally benign, aqueous media of biocompatible monosaccharides and polysaccharides under ambient conditions and at atmospheric pressure from the viewpoint of the mass production of materials for industrial applications. The reaction mechanism of carbohydrates responsible for tuning the morphology of materials has also been demonstrated in this work. The role of carbohydrate chemistry in the synthesis of nanomaterials has been described by the changes occurring in the molecular structures of carbohydrate in each preparation.

2. Experimental

2.1. Materials

The silver (AgNO$_3$) and gold precursor salts ((hydrogen tetrachloroaurate(III) trihydrate (HAuCl$_4$·3H$_2$O) and hydrogen tetrachloroaurate(III) tetrahydrate (HAuCl$_4$·4H$_2$O)) were from Wako

Pure Chemical Industries Ltd. Reducing agents NaBH$_4$ and NaOH were also procured from Wako Pure Chemical Industries Ltd. Soluble starch was from Sigma–Aldrich Chemical Co. (+)-D-Glucose and β-D-glucose were obtained from Wako Pure Chemical Industries Ltd and Tokyo Chemical Industry Co., Ltd, respectively. EtOH used to prepare NaBH$_4$ stock solution was obtained from Kanto Chemical Co., Inc. Ultra-pure double-distilled water was used for sample preparations.

2.2. Preparation of Ag and Au NPs

A 10^{-4} M solution of AgNO$_3$ was reduced in an aq gel of 1 wt % soluble starch by 1 wt % of β-D-glucose as the reducing agent. The preparation was heated at 70 °C and continuously stirred for 30 min. For preparation of Au NPs, a stock solution (0.05 M) of Au precursor salt stock was prepared in water, and the measured amount of stock solution was added to 0.03 M β-D-glucose–water dispersion solution to give a final Au salt concentration of 2×10^{-4} M. To reduce the Au salt a measured amount of fresh NaBH$_4$ stock solution (0.1 M) prepared in EtOH was added to the salt solution containing β-D-glucose as a capping or stabilizing agent. Similarly the pH-dependent preparation was carried out by adding a stock solution (0.05 M) of aq NaOH to the salt solution and the pH was adjusted using a pH meter. When preparing the glucose dispersion in water, or when dissolving the Au stock solution in the glucose–water dispersion, or when adding reducing agent, the preparations were continuously stirred at ambient temperature (25 °C). After adding the reducing agent, the preparation was stirred for 1 h before characterization.

2.3. Characterization

The extent of reduction of salt to metal was monitored visually and by recording the UV–vis spectra of the preparations where Ag and Au salt bands collapsed and the plasmon resonance band characteristic of monodispersed NPs appeared. The pH value and the equivalent of NaBH$_4$ necessary for the completion of the reduction were determined by comparing the Au NP UV–vis band intensity with the addition of an excess of NaBH$_4$ or NaOH stock solution at higher pH (pH 12.2), at which point no further increase in the UV–vis band occurred. A UV–vis spectrophotometer (Shimadzu UV-2550) was used to record the UV–vis spectra. Photos of the preparations were taken with a digital still camera (Sony Cyber-shot DSC-T1). The transmission electron microscopy (TEM) of the preparations was carried out using a TEM microscope (JEOL, JEM 2100F) operating at 200 kV by diluting the NP preparation with water and loading a drop of the diluted solution on the standard TEM carbon–copper grid and leaving the grid overnight to dry before loading the grid on the instrument holder before recording the TEM micrographs to determine the size, shape, polydispersity, and mesh or wire-like structures. Atomic force microscopy (AFM) images of the Au NPs prepared by addition of 4 equiv of NaBH$_4$ were recorded with a scanning probe microscope (JEOL, JSPM-5200). The sample for AFM was prepared by diluting the preparation in acetone, and a drop of the acetone diluted sample was put on the nonporous graphite sheet mounted on the AFM holder. The loaded holder was dried to evaporate acetone before conducting AFM observations. Apart from capturing the TEM and AFM photographs of the Au NPs, dynamic light scattering (DLS) based on the concept of laser light scattering by the particles was employed. A high-performance digital light scattering (DLS) particle size analyzer (Malvern Instrument Co., HPP 5001) was used for the size determination of the NPs. The average size of the NPs was found to be larger than that measured by TEM. The DLS apparatus is known to measure the shell thickness of a capping or stabilizing agent enveloping the metallic particles along with the actual size of the metallic core. This discrepancy is obvious in