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Radical scavenger for the stabilization of gold nanoparticles

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Abstract

In this contribution, we report the photo-catalytic synthesis of gold nanoparticles using poly(vinyl alcohol) as a radical surfactant stabilizer. Small Au nanoparticles were prepared depending on the concentration of the stabilizer. Both particle size and surface plasmon band are dependent on the concentration of poly(vinyl alcohol) and irradiation time. Transmission electron microscopic image and dynamic light scattering measurement shows that particles are spherical and monodispersed, respectively. This approach provides a simple route to fabricate gold nanoparticles that hold much promise for use in catalysis, chemical sensing, and biolabeling.

Keywords: Scavenger; Self-assembly; Gold nanoparticles; Colloids

1. Introduction

Metal nanoparticles are particularly attractive building blocks of individual atoms, which hold promise for use as advanced materials with new electronics, magnetic, optical, thermal, and catalytic properties [1–6]. Among the metal nanoparticles, gold nanoparticles gained considerable attention owing to their biocompatibility, bioinertness, and excellent interactivity with biomolecule [7–9]. The combining properties of gold nanoparticles with a biomolecule can open a number of new diagnostic applications in medicine. Gold nanoparticles have been used for detecting specific snippets of DNA with a simple color change test. The researchers attached gold nanoparticles to single stranded DNA, designed to home on target DNA sequence [7]. In addition, they have also been used as a contrasting agent for the biospecific labeling of tissues and transmission electron microscopic (TEM) observations [8,9]. In the future, these tiny inorganic nanoparticles are beginning to replace organic fluorescent dyes in a wide range of applications. Recently, gold nanoparticles have been used for destroying tumor cells [10]. They have also been widely used in photography [11], catalysis [12], biological labeling [13], photonics [14], optoelectronics [15], information storage [16], and surface enhanced Raman scattering (SERS) [17,18]. Also it has been widely used as a crystallization template for the in-vitro control synthesis of hydroxyapatite as a possible application of bone tissue engineering [19,20].

The main hurdle in the widespread application of metal nanoparticles is their agglomeration due to high surface energy. These unique properties mainly arise from the quantum-confinement effect and their large surface areas. The intrinsic properties of a metal nanoparticle are mainly determined by its size, shape, composition, crystallinity, and structure (solid versus hollow). In principle, one could control any one of these parameters to fine-tune the properties of these nanoparticles. In the future, successful fabrication of these structures may provide a new tool to integrate them into functional device and circuitry. All known preparative methods [21–30] lead to polydispersed metallic nanoparticles. However, the present challenge is to develop a system that is biologically acceptable and non-toxic.

Several preparative strategies, chemical [30,31], radiolysis [23], as well as photolytic [24,25], have been reported for the preparation of gold nanoparticles. Among these, the most popular one is the chemical reduction in the presence of capping

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agents [30,31]. Chemical reduction being a fast process rapid aggregation of nanoparticle results in the formation of aggregates, which is the present challenge in the field of nanotechnology. Whereas, photolysis being a slow and steady process, could be an excellent method to achieve monodispersed gold nanoparticles. Hence, to provide a general means for the controlled self-assembly of nanoparticles, we herein demonstrated the study of the photo-chemical reduction of tetrachloroaurate in the presence of polyvinyl alcohol (PVA) in aqueous medium. We have made a systematic investigation on how the SPB changes with UV-irradiation. In practice, the shapes of the nanoparticles were determined by TEM and DLS, and optical absorption spectra as a function of polymer concentration and irradiation time.

2. Materials and methods

2.1. Materials

All reagents used in this experiment were purchased from Aldrich Co., and used without further purification. Polyvinyl alcohol (Mw = 65,000) was purchased from Dong Yang Chem. Co., (POLINOL®-P-17), Korea. Water used was purified through a Milli-Q Plus system.

2.2. Methods and characterizations

Chemical and photo-catalytic reduction of $HAuCl_4$ was carried in the presence of PVA as a stabilizer. In a typical photocatalytic reduction, to 5 ml of 0.1% PVA aqueous solution, a calculated amount of $HAuCl_4$ was added in order to make a final concentration of 1.0×10^{-3} M, and kept constant in all the experiment. The solution was irradiated with UV-light ($\lambda \sim 365$ nm, Vilber Lourmat (VL)-6.LC, France) for specific intervals (20, 40, 60, 120, and 180 min) with continuous stirring, 50 rpm. During UV-irradiation, it was clearly noticed that the solution becomes pink in color indicating the formation of gold nanoparticles. On the other hand, in the chemical reduction process, samples were reduced by dropwise addition of 1.0 ml of 0.01 M cold aqueous $NaBH_4$ solution under rapid stirring. The rapid change in color from pink to dark red hue indicates the formation of gold nanoparticles. In order to study this change in color of chemically and photo-chemically formed gold nanoparticles, we prepared gold nanoparticles in the absence of PVA, where the color of gold colloids was fairly pink but unstable. Under these conditions the surface plasmon band of gold colloids was monitored by Varian Cary 3E UV–vis spectrophotometer in the range of 300–800 nm. The particle size distribution was determined by dynamic light scattering (DLS) measurement in Microtrac-UPA150, and the size distribution histogram is presented along with the respective transmission electron microscopic image. The gold nanoparticles thus prepared were characterized by JEOL JEM 2010 transmission electron microscopy (TEM) operated at 200 kV accelerating voltage. The sample for TEM measurement was prepared by dipping the TEM copper grid (400 mesh) in a solution of nanoparticle.

2.3. Mechanism of the reaction

The mechanism of the photolysis of the aqueous solution is carried out by the hydrated electrons and organic radical formed. The electron transfer step is important because there may be a large redox potential difference between the donor and acceptor, a situation which may restrict the passage of electrons. In the present study, the first stage seems to be originated from excitation of halogen in the complex aurous ion that results in the formation of chloride free radical, Eq. (1).

$$[AuCl_4]^- \rightarrow [AuCl_2]^- + 2Cl^\bullet \tag{1}$$

Thus a chain process of $[AuCl_4]^-$ decomposition starts, which is facilitated by the reaction with PVA, Eqs. (2) and (3).

$$R + Cl^\bullet \rightarrow R^\bullet + HCl \tag{2}$$

$$R^\bullet + Cl_2 \rightarrow RCl + Cl^\bullet \tag{3}$$

where R is a chain unit of PVA molecule [–CH_2–CH(OH)–] and $R^\bullet$ is its radical.
Eqs. (2) and (3) propagate as, Eqs. (4) and (5).

$$R^\bullet + [AuCl_4]^- \rightarrow RCl + [AuCl_2]^- + Cl^\bullet \tag{4}$$

$$RCl + [AuCl_4]^- \rightarrow R^\bullet + [AuCl_2]^- + Cl^\bullet + Cl_2 \tag{5}$$

Thus formed radicals may propagate into two different ways: firstly various modes of both cross-linking and destruction of polymer molecules, including carbonyl groups formation, while the interaction of PVA with chlorine and hydrochloric acid can result in the formation of double bonds, oxygen bridges and halogenated polymer molecules as describe earlier [32,33]. Finally, the reaction may be controlled by the disproportionation reaction, Eq. (6), or a secondary radical [–CH_2–$C^\bullet$(OH)–] efficiently reduces the precursor ion, Eq. (7).

$$3[AuCl_2]^- \rightarrow 2Au + [AuCl_4]^- + 2Cl^- \tag{6}$$

$$[AuCl_2]^- + R^\bullet \rightarrow Au + RCl + Cl^\bullet \tag{7}$$

3. Results and discussions

The reduction of $HAuCl_4$ forms well dispersed Au colloids under UV-irradiation in the presence of organic stabilizers such as PVP, PEG, sodium alginate or other surfactants [21–35]. In the present study PVA, that contains secondary alcohol which facilitates the reduction of gold salt, was used as a stabilizer to monitor the formation of particles under different conditions [34]. These colloids exist in a reduced state, as exceedingly fine particles, and these divided metals are responsible for their color [35]. The colors of the nanoparticle of noble metals in terms of strong absorption in the visible region are often referred as surface plasmon band (SPB). This absorption results when the incident photon frequency is resonant with the collective oscillation of the conduction electrons [36] and is absent in the bulk metal. Due to this property of the nanoparticle, UV–vis spectroscopy is an excellent method to monitor its formation and agglomeration. Because, on aggregation the