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Synthesis and characterization of biopolymer agar mediated gold nanoparticles

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ABSTRACT

Gold nanoparticles (AuNPs) were prepared by reducing $AuCl_3$ using agar as a reducing and stabilizing agent. The formation of AuNPs was evidenced by strong absorption peak at 534–543 nm caused by the characteristic surface plasmon resonance (SPR) of gold nanoparticle. Height of SPR peak increased with increase in the concentration of $AuCl_3$. The AuNPs observed with TEM were spherical in shape with particle size of 2–20 nm. The presence of elemental gold was also confirmed by EDX analysis. The XRD pattern of the AuNPs exhibited four characteristic peaks of gold at 38.2, 44.4, 64.6, and 77.8° of 2θ corresponding to the face centered cubic (fcc) structure of crystalline AuNPs with (1 1 1), (2 0 0), (2 2 0), and (3 1 1) planes of gold, respectively. These results confirmed that natural biopolymer agar had potential to be used as a reducing and stabilizing agent for AuNPs.

1. Introduction

With the advent of nanotechnology, various types of noble metal nanoparticles have also been utilized in various industrial and biomedical application [1] due to their unique superior functional properties such as optical, electrical, thermal, and catalytic properties [2,3]. Such nanomaterials are known to possess high surface area to volume ratio with increased surface reactivity and more heat stability [3,4]. Therefore, the application of nanostructured particles in different fields has been increased considerably in the last decades. Various preparation methods have been tested to synthesize metal or metallic oxide nanoparticles such as silver, gold, ZnO, and CuO nanoparticles. Physical methods such as sonochemical, electrochemical, photochemical, aerosol method, microwave assisted, lithography, gamma rays, solar irradiation, UV irradiation, sol-gel, hydrothermal, laser ablation, molecular beam epitaxy, etcetera, have been performed to produce metal nanoparticles [2,5,6].

Chemical methods using chemicals such as sodium borohydrate, trisodium citrate, ascorbic acid, gallic acid, sodium hydroxide, 3-thiopheneacetic acid, hydroxylamine, tetrakis (hydroxymethyl) phosphonium chloride (THPC), sodium dodecyl sulfate, N, N-dimethyl formamide, 2-mercaptobenzimidazole, etcetera, have been used to produce metallic nanoparticles [1,5,7]. Recently, a green method using biological reducing agents such as plant extract [8], bacteria [9], fungi [10], algae [11], natural biopolymer [1,12], and oils [13] have been tried to synthesize metallic nanoparticles. These biological resources are frequently used to fabricate silver nanoparticles (AgNPs) for various industrial applications since they are safe, nontoxic, eco-friendly, and biocompatible.

Among metallic nanoparticles, gold nanoparticles (AuNPs) are the potential candidates for various chemical and biological applications especially for bio-imaging, bio-sensing, drug delivery, etcetera, by exploiting their unique properties such as binding ability to various molecules, comparable size with biomolecules and optical properties in visible and NIR region [9]. The synthesis of nanoparticles in polymer solution is an ideal way because of their better solubility, non-toxicity, easy processing and compatibility. Agar, a polysaccharide extracted from marine red algae, such as *Gelidium* and *Gracilaria* spp, is a promising natural biopolymer. However, there have been no reports available for the production of AuNPs using biopolymer agar as a reducing and stabilizing agent. In this study, AuNPs were synthesized using natural biopolymer agar as a reducing and stabilizing agent, and the produced AuNPs were characterized by UV, TEM, EDX, XRD, and FT-IR spectroscopy.

2. Materials and methods

Materials: Agar for the preparation of AuNPs was purchased from Fine Agar-Agar Co., Ltd. (Damyang, Jeonnam, Korea). Gold (III) chloride trihydrate ($AuCl_3$) was procured from Sigma Aldrich (St. Louis, MO, USA). The ultra-filtered high purity deionized water was used to prepare all the solutions.

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Synthesis of AuNPs: Agar (1 g) was dissolved into 100 mL of water under stirring at 90 °C for 20 min. Different amount of $AuCl_3$ solutions (0.5, 1, 1.5, and 2 mL, which corresponds to 5, 10, 15, and 20 mg of AuNPs, respectively) were taken from the 1% $AuCl_3$ stock solution (100 mg/10 mL) and added drop-wise into the agar solution and boiled for 1 h with vigorous stirring. Color of the solutions was changed from transparent white to wine red color, indicating formation of AuNPs.

UV-visible spectroscopy analysis: Biopolymer agar mediated reduction of Au^{3+} ions in agar aqueous solution was determined by measuring UV–vis absorption spectrum of the solution using a UV–vis spectrophotometer (Model 8451A, Hewlett-Packard Co., Santa Alara, CA, USA) in the region of 300–700 nm.

Transmission electron microscopy and Energy dispersive X-ray microscopy: A drop of AuNPs solution was directly placed on carbon coated copper grid and allowed to dry at room temperature before analysis. The shape and size of the AuNPs were examined using a Transmission Electron Microscope (TEM, FEI Tecnai G2 F30, Eindhoven, Netherlands) at an accelerating voltage of 300 kV. The presence of elemental gold in the AuNPs was analyzed by energy dispersive X-ray microscopy (EDX) equipped with TEM microscopy.

X-ray diffraction: X-ray diffraction analysis was performed to analyze phase composition and crystal structure of the AuNPs using a PANanalytical Xpert pro MRD diffractometer (Amsterdam, Netherlands). A dried sample was prepared on a microscopic glass slide and scanned at diffraction angle $2\theta = 20–80°$ with a scanning rate of 0.5 °/min. The diffractogram was recorded using Cu Kα radiation and a nickel monochromator filtering wave at a voltage and current of 40 kV and 30 mA, respectively.

Fourier transform infrared spectra analysis: Fourier transform infrared (FT-IR) spectra of the agar-mediated synthesis of AuNPs were analyzed using FT-IR spectroscopy (TENSOR 37 spectrophotometer with OPUS 6.0 software, Billerica, MA, USA) operated at a resolution of 4 cm^{-1}. Samples were placed on the ray exposing stage and the spectra were recorded at wavelength ranges from 500–4000 cm^{-1}.

3. Results and discussion

3.1. UV-visible absorption spectroscopy

Fig. 1 shows UV–vis absorption spectra of the AuNPs. Although the control agar solution (without $AuCl_3$) didn't show any absorption peak at gold region, the agar solutions with $AuCl_3$ showed a characteristic sharp absorption peak at the red light absorption region of 534–543 nm. The absorption peak was attributed to the surface plasmonic resonance (SPR) effect of the AuNPs. Usually, AuNPs are known to exhibit characteristic SPR peaks in the range of 520–550 nm [14–16]. This indicates that Au^{3+} of the $AuCl_3$ solution was reduced into Au^o by agar to form AuNPs. Since agar contains reducing sugar and free hydroxyl groups which can act as a reducing agent for the metal ion. The SPR peak height increased slightly with increase in the content of AuNPs (Fig. 1). Jin et al. [17] also found that chitosan stabilized AuNPs showed strong SPR peaks in the range of 520–530 nm and the SPR peak increased as concentration of $HAuCl_4$ increased from 10 mM to 40 mM. Bai et al. [16] also found that AuNPs-included composite solution (β-cyclodextrin/poly(vinyl pyrrolidone) (PVP) exhibited strong SPR band at 530 nm. The UV–vis absorption spectrum of chitosan/AuNPs nanocomposite exhibited characteristic SPR peak at 542 nm [18]. In addition, Pucci et al. [19] synthesized AuNPs using poly (vinyl) alcohol (PVA) under UV irradiation with different time duration and found that the AuNPs showed characteristic SPR band at 550 nm. As can be seen in Fig. 1, the SPR peaks shifted to higher wavelength with increasing content of AuNPs. Similar results have been observed by Jin et al. [17] for chitosan/AuNPs nanocomposites. The peak shift of the AuNPs indicates that the shape and size of the formed AuNPs are changed with increase in the concentration of $HAuCl_4$.

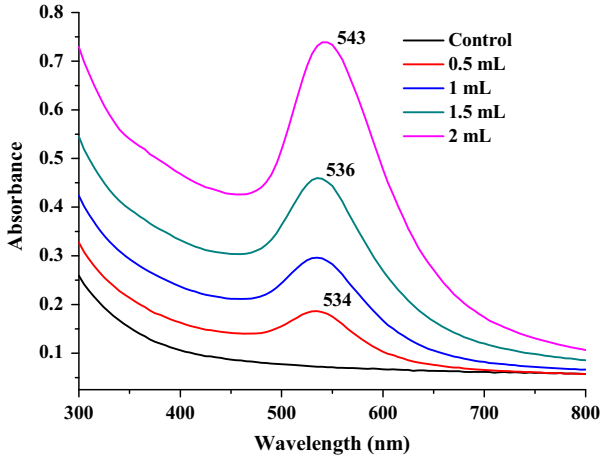

Fig. 1. UV–vis spectra of control and agar with various concentrations of AuNPs.

3.2. TEM and EDX analysis

Transmission electron microscopy (TEM) is frequently used to study morphology, size and shape of nanoparticles. Fig. 2(a, b, and c) shows TEM images of agar mediated AuNPs. The AuNPs formed were mostly spherical in shape with diameter ranges from 2–20 nm. As evidenced by TEM images, individual nanoparticles were uniformly distributed and well stabilized by biopolymer agar. These results are in good agreement with those reported by Huang and Yang [14], and Jin et al. [17] for chitosan/AuNPs nanocomposites. Pucci et al. [19] also found that TEM images of PVA-stabilized AuNPs showed spherical shape of nanoparticles with average size of 3–20 nm. The presence of elemental gold in the formed nanoparticles was examined by energy dispersive X-ray (EDX) analysis. Fig. 2d shows EDX spectrum of agar reduced AuNPs. The strongest signal appeared at gold region (~2 keV, 38%) confirms the presence of elemental gold in the solution. Due to the strong surface plasmonic effect, the metallic AuNPs are known to exhibit gold signals at ~2 keV [9,20]. In addition, various other peaks were observed presumably due to the presence of other atoms came from agar and the grid for sample holding for the TEM analysis.

3.3. Crystal structure analysis

The crystalline structure of AuNPs was confirmed by X-ray diffraction (XRD) analysis. Fig. 3 shows XRD diffraction pattern of the AuNPs. As expected, no specific diffraction peaks except minor one caused by agar at $2\theta = 28.2$ [7], were observed in the control agar solution. However, four distinctive diffraction peaks were observed in the AuNPs-included solutions at $2\theta = 38.2$, 44.4, 64.6, and 77.8 which were assigned to (1 1 1), (2 0 0), (2 2 0), and (3 1 1) planes of gold, respectively. These peaks indicate Bragg's reflection of face centered cubic (fcc) structure of crystalline metallic gold [9,21]. Especially, the peak at $2\theta = 38.2$ was found to be more intense than those of other peaks, which might be due to the predominant orientation of (1 1 1) plane. Lee et al. [15] and Wang et al. [22] observed similar pattern of diffraction peaks with composites of carbon nanotube/polyaniline/AuNPs and PVP/AuNPs, respectively.