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Green, microwave-assisted synthesis of silver nanoparticles using bamboo hemicelluloses and glucose in an aqueous medium

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ABSTRACT

A green, straightforward, microwave-assisted method of synthesizing silver nanoparticles in an aqueous medium was developed using bamboo hemicelluloses as stabilizer and glucose as reducer. The effects of irradiation time as well as initial concentrations of hemicelluloses, glucose, and $AgNO_3$ on the silver nanoparticle formation were studied. The silver nanoparticles were characterized by UV–vis spectroscopy, transmission electron microscopy (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The results indicated the formation of spherical, nanometer-sized particles. The reaction parameters significantly affected the formation rate, size and distribution of the silver nanoparticles. The average particle size was 8.3–14.8 nm based on TEM analysis. XRD analysis revealed that the particles calcined at 300 °C were face-centered cubic. XPS characterization showed that silver Ag(0) coexisted with silver Ag(I). The synthesis process of silver nanoparticles was rapid and eco-friendly.

1. Introduction

The stabilizing agent, reducing agent, and reaction medium are the three key factors for the efficient synthesis of metal nanoparticles. Stabilizing agents such as thiols (Zhou, Khoury, Qu, Dai, & Li, 2007), triphenylphosphine (Conte, Miyamura, Kobayashi, & Chechik, 2009), polyvinylpyrrolidone (Hou, Dehm, & Scott, 2008), and citrate (Zhang, Li, Goebl, Lu, & Yin, 2011) have been utilized to synthesize metal nanoparticles. However, stabilizers used in the chemical synthesis of metal nanoparticles are often toxic, difficult to dispose, and reduce the utilization of particles. On the other hand, the majority reducing agents reported include sodium borohydride ($NaBH_4$) (Conte et al., 2009; Hou et al., 2008) and hydrogen gas (H_2) (Saliger, Decker, & Prüβe, 2011). All of them are highly reactive and pose potential environmental as well as safety risks. Finally, most synthetic procedures reported rely heavily on organic solvents (Conte et al., 2009; Zhou et al., 2007), inevitably leading to serious environmental problems.

Over the past 10 years, studies have focused on the use of biological compound solutions in synthesizing and stabilizing metal nanoparticles. Biological syntheses of metallic nanoparticles that utilize plant extracts for green synthesis have been extensively carried out (Castro et al., 2011; Gangula et al., 2011; Li, Zhang, Xu, & Zhang, 2011; Vidhu, Aromal, & Philip, 2011). Vidhu et al. (2011) reported the green synthesis of silver nanoparticles using the aqueous seed extract of *Macrotyloma uniflorum*, and the obtained particles have anisotropic morphology and a size of about 12 nm. Some high-potential plant extracts are polyhydroxylated biomacromolecules, such as starch and plant polysaccharides. They present interesting dynamic supramolecular associations facilitated by inter- and intramolecular hydrogen bonding that result in molecular level able to act as templates for nanoparticle growth (Li et al., 2011; Raveendran, Fu, & Wallen, 2003; Vigneshwaran, Nachane, Balasubramanya, & Varadarajan, 2006). Li et al. (2011) developed a new method for constructing silver nanoparticles using triple helical polysaccharide (lentinan) dissolved in water as matrix. The binding interaction between polysaccharides and metal nanoparticles is weak compared with the interaction between typical thiol-based copulating agents and nanoparticles. Thus the stabilizing agent polysaccharides can be easily removed and separated (Raveendran et al., 2003). Several polysaccharides have been evaluated as protecting and capping agents for the preparation of metal nanoparticles (Bilgainya, Khan, & Mann, 2010; Kong, Wong, Gao, & Chen, 2008; Li et al., 2011; Raveendran et al., 2003; Vigneshwaran et al., 2006). However, studies describing the utilization of renewable biomass hemicelluloses are limited. Hemicelluloses are some of the most abundant polymers in plant cells. In a previous study, our laboratory confirmed that hemicelluloses from bamboo (*Phyllostachys pubescens* Mazel) exist as helical chains or random-coil chains in an aqueous solution (Peng, Wang, et al.,

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2012). The bamboo hemicelluloses consist of arabinoxylans, which are rich in hydroxyl groups (Peng, Wang, et al., 2012). Thus, particles are encapsulated by the special structure and the numerous hydroxyl groups.

In the present work, a green, microwave-assisted synthesis of silver nanoparticles was developed. Renewable biomass bamboo hemicelluloses were used as stabilizing agent, nontoxic biochemical glucose was utilized as reducing agent, and distilled water served as reaction medium. The effects of the reaction conditions on the synthesis of silver particles were studied. The obtained particles were analyzed by UV–vis spectroscopy, transmission electron microscopy (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The advantages of this methodology include the non-requirement of solvents as well as ability of both stabilizing and reducing agents to be produced from renewable biomass.

2. Materials and methods

2.1. Materials

Hemicelluloses were obtained from bamboo (*P. pubescens* Mazel) using the same separation method as that in our earlier paper (Peng, Hu, et al., 2012). The hemicelluloses were sequentially extracted and purified. The fully dried bamboo powder (100 g, 40–100 mesh) was first dewaxed with toluene–ethanol (2:1, v:v, mL/mL) for 6 h in a Soxhlet apparatus. The dewaxed bamboo powder was partially delignified with 0.6% $NaClO_2$ at pH 4.2–4.7 for 2 h at 75 °C under stirring, and holocellulose was obtained. The holocellulose was sequentially treated with hot water (85 °C) for 3 h under stirring. The obtained solid residue was extracted with 2% KOH at 55 °C for 3 h under stirring with the ratio of dry matter to liquor 1:20 (w/v, g/mL), and then filtrated. The pellet was further extracted with 5% NaOH at room temperature for 12 h, and the alkaline filtrate was obtained. The ratio of dry matter to liquor was also 1:20 (w/v, g/mL). After the alkaline filtrate was neutralized to pH 5.5 with acetic acid, the acid filtrate was concentrated at reduced pressure, and the solubilized hemicelluloses were isolated by precipitation in three volumes of 95% ethanol. Finally, the hemicellulose pellet was washed with 70% ethanol and freeze-dried for further use. Silver nitrate ($AgNO_3$) and glucose were analytical reagent grade. The bamboo hemicelluloses were used as stabilizer and glucose was used as reducing agent. All solutions were prepared with deionized water ($R = 18.2\ M\Omega$) that was prepared by ultrafiltration with a Milli-Q water purification system (Millipore, Bedford, MA, USA). All glass wares were thoroughly cleaned with water and dried in an oven.

2.2. Preparation of silver nanoparticles

In a typical preparation, the hemicellulose powder and glucose powder were dispersed in 20 mL aqueous solution containing $AgNO_3$ precursor in a 100 mL beaker. The solution was then irradiated by microwaves at a constant power of 40 W in a microwave oven (Sineo Microwave Chemical Technology Co., Ltd., China). After reaction completion, the solution was immediately cooled down to room temperature. Next, the solution was adjusted to 20 mL by adding a small amount of distilled water to compensate for the loss of water during microwave irradiation before analysis. The reaction dynamics for the formation of silver nanoparticles was systematically investigated by varying the irradiation time from 50 s to 140 s, initial hemicellulose concentration from 0.5 mg/mL to 6.0 mg/mL, glucose concentration from 1.0 mg/mL to 5.0 mg/mL, and $AgNO_3$ concentration from 0.001 mmol/mL to 0.007 mmol/mL.

Representative silver nanoparticles were prepared under the following conditions: 2.0 mg/mL hemicelluloses, 2.0 mg/mL glucose, 0.004 mmol/mL $AgNO_3$, 120 s microwave irradiation time, and calcination at 300 °C for 1 h in air after complete lyophilization. The obtained black powder containing silver and carbon was further characterized by XRD and XPS techniques.

2.3. Characterization

2.3.1. UV–vis spectra

UV–vis absorption spectra were obtained using a LabTech 300563 UV–visible spectrophotometer within the range of 200–600 nm. Before UV–vis measurements, the solutions obtained after irradiation for different times were diluted in five volumes of water (solution:water, 1:5, mL/mL); other solutions were diluted in 10 volumes of water (solution:water, 1:10, mL/mL).

2.3.2. TEM

The morphology and size of the silver nanoparticles were investigated by TEM using a JEM 2010 instrument at an accelerating voltage of 200 kV. The sample for TEM analysis was prepared by placing a drop of silver nanoparticle solution onto a carbon film supported on a copper grid, followed by water evaporation in air at room temperature.

2.3.3. XRD

XRD was recorded on a Bruker D-8 powder X-ray diffractometer using CuKα radiation ($\lambda = 0.15418$ nm) over a 2θ range of 20°–90° with a step size of 0.02°.

2.3.4. XPS

The exposed silver surface species were determined by XPS on an AXIS ULTRA DLD spectrometer with AlKα radiation ($h\nu = 1486.71$ eV) and a spectrometer resolution of energy of 0.48 eV. The peak positions were corrected for sample charging by setting the C 1s binding energy at 284.8 eV. XPS analysis was conducted at 150 W and a pass energy of 16 eV.

3. Results and discussion

Fig. 1A shows the preparations of silver nanoparticles in aqueous medium. After microwave treatment, the solutions became clear without any suspended solid material, indicating that the hemicelluloses were completely dissolved in water. When only hemicelluloses (2.0 mg/mL) or glucose (2.0 mg/mL) were added to the $AgNO_3$ solution (0.004 mmol/mL), the solution remained a colorless salt solution even after irradiation for 120 s. However, after microwave irradiation for 120 s, Ag^+ reduction was visually confirmed because the colorless $AgNO_3$ solution changed to yellow with the simultaneous addition of hemicelluloses (2.0 mg/mL) and glucose (2.0 mg/mL) (Raveendran et al., 2003; Vidhu et al., 2011; Zhang et al., 2011). Due to Mie scattering, the colloidal silver nanoparticles exhibited absorption from 390 to 420 nm (Kleemann, 1993). Thus, the observed typical surface plasmon resonance (SPR) band at about 415 nm (Fig. 1B) further confirmed the formation of silver nanoparticles when both hemicelluloses and glucose were added to the $AgNO_3$ solution (Raveendran et al., 2003). The symmetric plasmon band indicated that the solution did not contain many aggregated particles. The results indicated that hemicelluloses or glucose alone cannot reduce the Ag salt. These phenomena suggested that silver nanoparticles can be synthesized by the combination of bamboo hemicelluloses and biochemical glucose without externally added seed crystallites. Both hemicelluloses and glucose are involved in the reduction process to produce carbohydrate-conjugated silver nanoparticles. These carbohydrate-conjugated silver nanoparticles have potential uses