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Reduction of silver (I) using defatted cashew nut shell starch and its structural comparison with commercial product

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ABSTRACT

In this current study, we report on the reduction of noble metal silver into silver nanoparticles using defatted cashew nut shell (CNS) starch as both the reducing and capping agents. Furthermore, it was compared with commercially available silver nanopowder for the first time. Color changes, ultraviolet–visible spectra (433.76 nm), X-ray diffraction peaks (2θ = 37.8, 46.3, 66.2, and 77.92) revealed the face-centered cubic (fcc) geometry of silver nanoparticles, scanning electron microscopy–energy dispersive spectroscopy confirmed the presence of elemental silver nanoparticles and the defatted CNS starch silver nanoparticle structures was in accordance to commercial silver nanopowder. The size of both the nanoparticles was found to be similar in the range of 10–50 nm as analyzed using high resolution-transmission electron micrographs. The FT-IR spectroscopy revealed the shifting of N—H and O—H of defatted CNS starch, starch based silver nanoparticle and commercial silver nanopowder has parallel functional groups. The use of environmentally benign and renewable materials like defatted CNS starch offers an alternative to large scale synthesis of silver nanoparticle and includes numerous benefits like eco-friendly and compatibility for pharmaceutical and biomedical applications.

1. Introduction

In the emerging field of nanobiotechnology, various metal nanoparticles such as platinum, palladium, gold, silver, zinc and copper obtained by plant extract is the best eco-friendly alternative against physical and chemical methods and are playing an important role in the fields of pharmaceuticals, organic catalysis and bioelectronics (Velmurugan et al., 2014; Yuvakkumar, Suresh, Nathanael, Sundrarajan, & Hong, 2014). Green chemistry principles drive researchers to develop synthetic strategies using biological methods, whereas microorganisms (Velmurugan et al., 2014), enzymes (Konishi et al., 2007) and plant extracts (Velmurugan et al., 2015) play a major role in the formation of nanoparticles. In concern with increasing environment problems by chemical synthesis (Jiang et al., 2006a, Jiang, Zhou, Li, Wang, & Xie, 2006) of metal nanoparticles, attempts have been routinely made to develop nanoparticle synthesis using defatted cashew nut shell (CNS) starch. It is an environmental begins method for nanoparticle synthesis, without using any toxic chemicals during the synthesis protocols. Moreover, it plays an alternative way to obtain industrially required nanoparticles. Stable silver nanoparticles (size range ca. 10–34 nm) have been synthesized using soluble starch as both reducing and stabilizing agents (Khan et al., 2013); and silver and gold nanowires were synthesized using monosaccharide (β-D-glucose) and polysaccharide (soluble starch) was already reported by Shervani and Yamamoto (2011). Isolation and characterization of starch from defatted cashew nut shell (CNS) was previously reported by Yulian, Huynh, Ho, Truong, and Ju (2012), with starch containing of 85 wt.%. In this present article, an attempt was made to extract starch from defatted CNS, reduction of metal silver to silver nanoparticles and compared with commercially available silver nanopowder.

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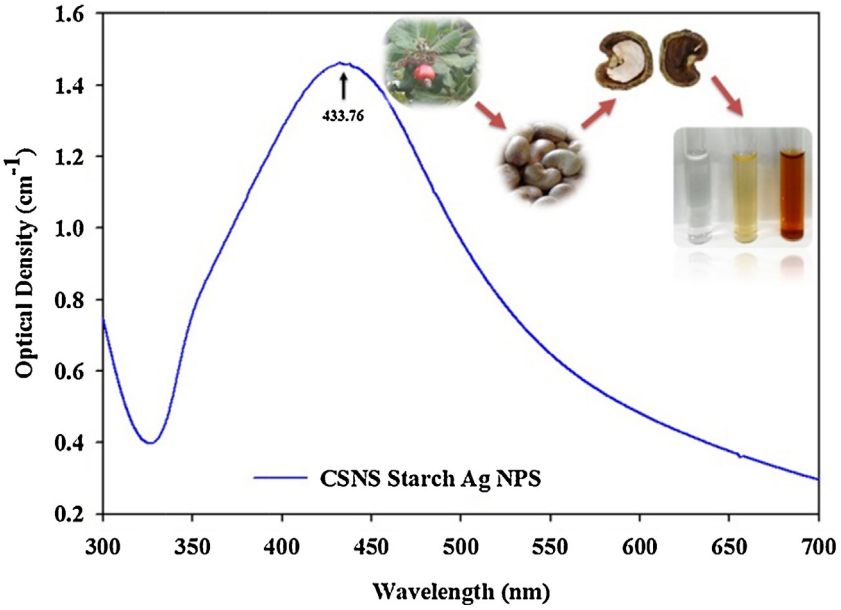

Fig. 1. UV–vis spectra showing the silver nanoparticle peak and the insert shows cashew nut shell, Ag^+ solution, starch solution and colloidal silver.

2. Materials and methods

2.1. Preparation of starch from defatted CNS

Defatted cashew nut shell starch (DFCNSs) were obtained from the waste of cashew nut processing factory in banrooty, Tamilnadu, India. Isolation and purification of starch from defatted CNS was followed according to Fabian, Ayucitra, Ismadji, and Ju (2011) and Yulian et al. (2012). In brief, defatting was done using methanol (95% purity, DaeJung Chemicals, Seoul, South Korea) at 65 °C for 10 h followed by n-hexane (95% purity, HPLC grade, DaeJung Chemicals, Seoul, South Korea) at 69 °C for another 10 h in a soxhlet extractor. CNS (10 g) was soaked in water for 3 h at 30 °C. The mixture was blended (Hanil blender) for 5 min and passed in a 60-mesh sieve for screening and re-blended with 50 ml 70% ethanol for 5 min, followed by screening and then the residue was re-blended with 50 ml 0.1 M NaOH for another 5 min, and screened. The obtained filtrates were centrifuged at 11,000 × *g* for 15 min. The supernatant was decanted and the residue was re-slurried, re-filtered and then washed with 0.1 M NaOH. The residue restrained at the filter paper was washed with deionized water several times in order to eliminate any unsolicited material followed by drying in freeze drier. The obtained pure starch was used for subsequent experiments.

2.2. Reduction of silver in to silver nanoparticles

DFCNSs (0.2 g) were added to 45 mL of nanopure water (conductivity = 18 μΩ/m, TOC <3 ppb; Barnstead, Waltham, MA, USA) followed by addition of 10^{-3} M silver nitrate ($AgNO_3$ –; Sigma-Aldrich, St. Louis, MO, USA). A reduction of silver ions was confirmed by the color change in the reaction mixture from light yellow to dark brown with a yellow shade. To separate the reaction product, it was subjected to centrifugation at 13,000 × *g* rpm for 15 min, purified by re-dispersion of the pellet in nanopure water, and repeated several times in order to ensure better separation of the free entities from the species. The obtained material was freeze dried at −80 °C and used for characterization.

2.3. Characterization of reduced metal silver

The obtained silver nanoparticles were scanned after the color change using a UV–Vis spectrophotometer (UV-1800, Shimadzu, Kyoto, Japan) within a working wavelength range of 300–800 nm using a dual beam operated at 1 nm resolution. The elemental composition of the synthesized silver nanoparticle and commercial available silver nanopowder, <100 nm, 99.5% metals (Sigma–Aldrich, USA) were confirmed by scanning electron microscopy–energy-dispersive spectra (SEM–EDS) (JEOL-64000; Tokyo, Japan). High resolution transmission electron microscopy (HR-TEM; HRTEM, JEM-2010HR, JEOL, USA) was then used to examine the surface morphologies and sizes of the particles for both the nanoparticles, respectively. X-ray powder diffraction of the samples was obtained using a Rigaku X-ray diffractometer (XRD; Rigaku, Japan) for both the nanoparticles, respectively. The scanning was done in the region of 2θ from 30 to 80° at 0.04°/min within a time constant of 2 s. Fourier transform infrared spectroscopy (FTIR) spectra of the DFCNS starch, DFCNSs silver nanoparticle and commercial silver nanopowder were obtained with a Perkin-Elmer FTIR spectrophotometer (Norwalk, CT, USA) in the diffuse reflectance mode at a resolution of 4 cm^{-1} in KBr pellets.

3. Result and discussion

The present study is an attempt to reduce the silver ion using DFCNSs. The color of reaction mixture turned from light yellow to dark brown in a short reaction time 30 min after addition of DFCNSs to the reaction mixture (10^{-3} M silver nitrate + 0.2 g DFCNSs), indicating $AgNO_3$ reduction as a colloidal silver nanoparticles and the starch acts as stabilizing and/or capping agent. As described by Khan et al. (2013), water soluble, amylose and water insoluble, amylopectin are the main constituents of the starch could be responsible for the reduction of silver with very minimum quantity of starch. According to Lee et al. (2013), the color change in the reaction mixture shows the presence of surface plasmon vibrations in metallic nanoparticles. UV–vis spectroscopy is an important technique to ascertain the formation and stability of metal nanoparticles in aqueous solution. The absorbance band