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Green synthesis of nanosilver as a sensor for detection of hydrogen peroxide in water

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ABSTRACT

Present “green” synthesis is an efficient, easy-going, fast, renewable, inexpensive, eco-friendly and non-toxic approach for nanosilver formation, which offers numerous benefits over physiochemical approaches. The X-ray diffraction (XRD) pattern suggests the formation and crystallinity of nanosilver. The average particle size of silver nanoparticles was 8.25 ± 1.37 nm as confirmed by transmission electron microscopy (TEM). The UV–vis absorption spectrum shows a characteristic absorption peak of silver nanoparticles at 410 nm. FTIR confirms Azadirachtin as reducing and stabilizing agent for nanosilver formation. In addition, the nanosilver modified electrode (Ag/GC) exhibited an excellent electro-catalytic activity toward the reduction of hydrogen peroxide (H_2O_2). The produced nanosilver is stable and comparable in size. These silver nanoparticles show potential applications in the field of sensors, catalysis, fuel cells and nanodevices.

1. Introduction

Nanosilver (NS) magnetizes a significant awareness because of its wide range of applications in emerging areas of nanoscience and technology [1]. Size, shape, and surface morphology play pivotal roles in controlling the physical, chemical, optical, and electronic properties of these nanoscopic materials [2,3]. Over the past decade there has been an increased emphasis on the topic of “green” chemistry and processes. These efforts aim at the total elimination or at least the minimization of generated waste and the implementation of sustainable processes through the adoption of 12 fundamental principles [4–6]. Any attempt meeting these goals must comprehensively address these principles in the design of a synthesis routes, chemical analysis or chemical process [4,6]. Utilization of nontoxic chemicals; environmentally benign solvents and renewable materials are some of the key issues that merit important consideration in a green synthesis strategy [7]. The three main steps in the preparation of nanomaterials that should be evaluated from a green chemistry perspective are the choices of the solvent medium used for the synthesis, the choice of an environmentally benign reducing agent, and the choice of a nontoxic material for the stabilization of the nanoparticles [8]. The great deal of efforts has been established for green synthesis of inorganic materials, especially noble metal nanoparticles using microorganisms such as bacteria, actinomycetes and fungi [9–11]. The main drawback of this method is the need to purify the sample and extract because pathogenic bacteria might contaminate nanoparticles.

On other hand, the use of various parts of plants in similar nanoparticles synthesis can be potentially eliminate this problem by making the nanoparticles more bio-compatible and non-toxic, as it eliminates the elaborate process of maintaining the microbial culture and often found to be kinetically favorable than other bio-processes. Jose-Yacaman and co-workers reported the formation of gold and silver nanoparticles using living plants. Recently silver nanoparticles have been synthesized using various plant products like green tea (*Camellia sinensis*), natural rubber, starch, aloe vera plant extract, lemongrass leaves extract leguminous shrub (*Sesbania drummondii*), latex of *Jatropha curcas*, neem leaf, etc. In this regard, Shankar et al. suggested that the reduction of aqueous $AuCl_4^-$ and Ag^+ ions using extracts from geranium and lemongrass plants were occur due to the ketones/aldehydes groups present in the extract which plays an important role in directing the shape evolution in these nanoparticles. Ankamwar et al. also synthesized gold nanotriangles using tamarind leaf extract as the reducing

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agent and identified that tamarind plant as a potential candidate for shape-controlled synthesis of gold nanoparticles due to tartaric acid (—COOH) [10–18].

The current approach involves totally green approach for formation and stabilization of nanosilver via neem kernel extract at room temperature. There are many advantages of using neem kernel for silver nanoparticles formation. Firstly, neem kernel is quite commonly available, stored and used up to 3–8 months, requires only one-fourth than that of neem leaf extract and the main constituents Azadirachtin was present in higher extent than that of neem leaves. Secondly, it excludes addition of external stabilizing agent during synthesis, gives faster reaction kinetics, provide better stability, offers better control over shape and size with higher crystallinity. In present study, the number of carboxylate groups available in neem kernel extracts facilitates the complexion of silver ions to the molecular mold. Analogously, it is plausible that neem kernel extracts can play a significant role in reduction and stabilization of nanosilver. Furthermore, there are several key advantages to the use of this renewable material as the protecting agent. First, it is possible to form a dispersion of the neem kernel extract in H_2O, and so one can completely avoid the use of organic solvents. Second, the binding interaction between neem kernel extracts and the metal nanoparticles is comparatively weak as compared to the interaction between the nanoparticles and typical thiol-based protecting groups. This implies that the protection should be smoothly reversible at passably higher temperatures, enabling the separation of these particles. Additionally, it is possible that the use of place exchange reactions [19] could be used to comfortably functionalize the nanoparticles. Finally, and perhaps most importantly, neem kernel extract-protected nanosilver can be readily integrated into systems relevant for pharmaceutical and biomedical applications.

Some authors also reported silver nanoparticles formation using neem leaf [17,18] and many of researchers points out what is the differentia between silver nanoparticles obtained using neem leaf and neem kernel extract. As we know that in nanotechnology, the control over particles shape and size is a real challenge and it play very important role to control the applications. Moreover, we also want to increase the reaction kinetics as well as greater stability of nanoparticles. We performed the experiment in similar fashion as we have already done with the neem leaf extract but the results in both the cases are very different. Silver nanoparticles in case of neem leaf extract were agglomerated, poly-dispersed as well as particle size are in the range of 5–50 nm (wide range), takes 2–24 h to complete reaction kinetics and shows UV–vis absorption spectra near 450 nm. On the other hand, formation of silver nanoparticles using neem kernel extract takes only 20 min to complete reaction kinetics, show particles in the range of 6–14 nm with spherical shape and crystalline in nature with UV–vis spectra occurs at 410 nm. Hence, a blue-shift occurs indicating toward smaller size of silver nanoparticles formation. During our experiment we can find that greater extent of Azadirachtin increases the reaction kinetics as well as greater control over the shape and size of silver nanoparticles than by using the neem leaves. The main reason for this is the biochemical difference between the silver precipitating neem kernel extract and neem leaf extract is the overall charge of the Azadirachtin biomolecules which is greater in neem kernel extract. Hence the use of neem kernel extracts offers improvement in all the sections of silver nanoparticles formation.

2. Experimental details

In a typical method, 10 g neem kernel was washed thoroughly with distilled water and dried in the air. These neem kernels were crushed it into small pieces and boiled in 50 ml distilled water for 10 min. The cooled filtrate was adjusted at pH 10 by adding 1 M NaOH. Now, 1.0 ml of above prepared extract was added drop by drop in 100 ml of 10 mM $AgNO_3$ (Merck) in a conical flask. The above solution was placed on a magnetic stirrer for 20 min and centrifuged at 10,000 rpm for 10 min. The residue was washed several times with double distilled water followed by ethanol (Fig. 1). Finally, the residue was kept in the vacuum oven at 40 °C for drying. For electro catalytic oxidation, Glassy Carbon (GS) substrates were cleaned with distilled water several times and air dried. The reaction mixture well vortexes and the substrate were put inside it. A thin Ag film was formed on the GS substrate. This Ag/GS electrode was washed with the buffer solution and used in three electrodes cell as working electrode for electro catalytic activity. Its electro catalytic activity was compared with the pure GS electrode.

3. Characterization

UV–vis absorption spectroscopy was taken on Perkin Elmer model L35 spectrometer. XRD was performed on Rigaku D/max-2200 PC diffractometer operated at 40 kV/20 mA, using Cu $K\alpha_1$ radiation with wavelength of 1.54 Å. FTIR spectroscopy measurements were carried out on a NICOLET-5700 (Thermo Electron Corporation) in the range of 3500–500 cm^{-1}. Transmission electron microscopy (TEM) was done on Technai 30 G^2 S-Twin electron microscope operated at 300 kV accelerating voltage. Cyclic voltammetry (CV) was performed on an electrochemistry workstation CHI 660A (Austin, USA). These measurements were performed in a conventional three electrode electrochemical cell using Ag/GS and pure GS as the working electrode, platinum wire as the auxiliary electrode, and Ag/AgCl (saturated with KCl) as the reference electrode.

4. Results and discussion

UV–vis absorption spectroscopy is a main tool to analyze the noble metal nanoparticles formation, which depends on surface plasmon resonance (SPR). The localized SPR's are collective oscillations of the conduction electrons confined to metallic nanoparticles. Excitation of the localized surface plasmons causes strong light scattering by an electric field at a wavelength where resonance occurs; this phenomenon results in the appearance of strong SPR bands. The optical absorption spectrum of metal nanoparticles is dominated by the SPR, which depends upon the particle size, shape, state of aggregation and the surrounding dielectric medium [20]. When the extract is mixed in the $AgNO_3$ solution, the solution first becomes yellowish after 3 min and then finally brownish after reaction completion (20 min), indicating the formation of nanosilver [21]. The UV–vis absorption spectrum of the sample shows reaction kinetics of 20 min, showing the surface plasmon absorption of nanosilver at 410 nm (Fig. 2A). The formation of the nanosilver starts with the addition of the neem kernel extract which increases rapidly after 2 min and starts stabilization after 14 min. No change in peak was observed after 20 min, i.e., all silver ions were consumed within 20 min. Since, the last three spectra of 16, 18 and 20 min are overlapped on each other in Fig. 2A, because there are very minute differences in these three spectra. Therefore, re-plot of the peak points of these three spectra is shown in Fig. 2B, so that one can grasp the whole spectra, i.e., 11 spectra clearly.

XRD pattern of synthesized nanosilver shows face-centered-cubic (fcc) lattice (JCPDS file no. 04-0783) with strong diffraction peaks at 37, 44, 66 and 77 degrees of 2θ corresponds to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) crystal planes (Fig. 3). The broadening of XRD peaks (i.e., Scherer's broadening) attributes nanosized