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Short communication

Insight into the nanodielectric properties of gold nanoparticles synthesized from maple leaf and pine needle extracts

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ABSTRACT

This study reports on the use of maple leaf (*Acer saccharum*) and pine needle extracts for the green synthesis of gold nanoparticles (AuNP). The gold nanoparticles were formed within 10 min using distilled water as the solvent following green nanotechnology approach. This is the first study reporting the use of maple leaves and pine needles for synthesizing gold nanoparticles. Characterization using transmission electron microscope (TEM) indicated the presence of quasi-spherical to triangular prisms of AuNP; nanodielectric properties were studied using dielectric spectroscopy which provides information about dielectric constant (ϵ') and dielectric loss factor (ϵ''); thermal properties of the nanoparticle solution where studied using differential scanning colorimeter (DSC). This information on the physical characterization of green synthesized AuNP will be useful in designing applications for hyperthermal treatments using radiofrequency waves and for microwave based tumor therapy.

1. Introduction

Efficient use of natural resources and the development of innovative green synthesis methods are key to sustainable advancements in nanotechnology. Green nanoscience integrates nanotechnology with the emerging field of green chemistry for developing greener products, processes and applications (McKenzie and Hutchison, 2004). The last decade has seen a tremendous growth in the use of biomaterials for the synthesis of nanoparticles and in particular gold nanoparticles as carriers for targeted drug delivery. Using a green chemistry approach for the synthesis of nanoparticles is competitively and environmentally a better solution than using harmful chemicals as reducing agents or surfactants.

In this study, we report the use of plant materials, namely maple leaves and pine needles for the green synthesis of gold nanoparticles. The maple tree being deciduous sheds off its leaves during the fall season; which is generally considered as a waste product and is at best used for composting. This paper proposes an alternative use for this biomass. This is the first study stating that maple leaves and pine needles can be used as prospective bio-reducing agents to produce gold nanoparticles. Thus formed gold nanoparticles are considered eco-friendly as they do not use toxic chemicals during their synthesis and can be better substitutes to chemically synthesized gold nanoparticles in a variety of applications.

Song and Kim (2009) studied the biological synthesis of silver nanoparticles using five different plant leaves extract such as Pine (*Pinus desiflora*), Persimmon (*Diopyros kaki*), Ginkgo (*Ginko biloba*), Magnolia (*Magnolia kobus*) and Platanus (*Platanus orientalis*). They found that there was rapid reduction of silver nanoparticles using magnolia leaf broth within 11 min at 95 °C. A very recent report by Vivekanandhan et al. (2014) stated the use of maple leaf extract for the functionalization of ZnO powders with silver nanoparticles. There are a growing number of reports available in the literature for the reduction of gold nanoparticles by different plant materials, but till date there is no data available demonstrating the use of maple leaves and pine needles for the synthesis of gold nanoparticles following a green chemistry approach along with their physical characterization.

"Nanodielectrics" is the study of dielectric phenomena of nanoscale materials and fabrication of structures, devices and systems that have novel dielectric properties because of their nanometric size (Cao et al., 2004; Lewis, 1994). The concepts of nanodielectrics were mentioned in the landmark theoretical paper by Lewis (1994) that went unnoticed until the experimental works published by an eminent UK/US team in 2002 (Nelson et al., 2002). Since then, there is an increase in the reports being published in the field of nanodielectrics (Fothergill, 2007; Green and Vaughan, 2008). Dielectric spectroscopy involves the study of a material's

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response to an applied electric field. The dielectric data provides information on how materials react to an applied electromagnetic field. This information will be of great use for the development of a variety of applications, such as new semiconductor devices, identification of new electrical insulators, for cancer detection since cancer cells have different permittivity than healthy cells, for monitoring chemical reactions, etc.

2. Experimental details

The maple leaves and pine needles were collected between 8 and 9 am in mid-July on the Macdonald campus, McGill University, Ste-Anne-de-Bellevue, Canada. During this period, the maple leaves are generally green in color. Three grams of each plant material were weighed, cut into fine pieces and were placed individually into two Erlenmeyer flasks containing 50 mL of deionized water. The flasks were heated at 60 °C for 2 min, the extracts were cooled to room temperature and filtered using 11 μm pore size Whatman filter paper (Grade 1). The above mentioned steps were completed within 30 min of sample collection from the trees to avoid any post-harvest degradation of chemical compounds present in the plant matrix. Hydrogen tetrachloroaurate(III) ($HAuCl_4 \cdot 3H_2O$) was obtained from Sigma–Aldrich Chemicals Co. (St. Louis, MO), and 1 mM $HAuCl_4$ solution was prepared using deionized water. Five mL of each plant extract was added to 12 mL of $HAuCl_4$ solution and the total reaction volume was made up to 30 mL by addition of deionized water. Gold nanoparticles were also synthesized using Turkevich method (Li et al., 2011; Turkevich et al., 1951), 95 mL of cholorauric acid solution (0.25 mM) was heated in an Erlenmeyer flask and 5 mL of 1% sodium citrate solution was added. The temperature of the AuNP solution was maintained at 100 °C with magnetic stirring for 5 min. The AuNP solution from Turkevich method was used as a standard for nanodielectric properties analysis.

UV–visible spectrophotometer (Ultrospec 2100 pro, Biochrom Ltd., Cambridge, UK) was used for this study. The maple leaf and pine needle extract synthesized AuNP were analyzed through a transmission electron microscope (TEM) by placing a drop of the sample solution on a carbon coated TEM grid. Transmission electron microscopy (TEM) analyses were performed using a FEI Tecnai 12 TEM equipped with an AMT XR-80C CCD Camera System (FEI Company, Oregon, USA) which was operated at 120 kV. Thermal properties of the nanoparticle solution were analyzed using a differential scanning calorimeter (DSC Q-100, TA Instruments, Texas, USA). Aluminum pans containing 25 μL of nanoparticle solution were hermetically sealed and used for analysis. Indium was used for calibration of the system and 25 μL Millipore water was used as reference. The temperature ranged from −30 °C to 400 °C with the heat flow increasing at 10 °C/min. Reproducibility was checked by running the sample in triplicates and the data was processed using DSC Q-100 V9.8 built-in software.

The dielectric measurements were performed using an open ended coaxial probe, ideal for measuring liquids. A network analyzer (Agilent S Parameter Network Analyzer, 8722ES, Agilent Technologies, USA) with slim form probe was used to record the dielectric data. The probe was immersed into the solution containing the gold nanoparticles. The broadband frequency range from 200 MHz to 20 GHz was selected for this study.

3. Results and discussion

The maple leaf and pine needle extracts were green in color following filtration. Upon the addition of the $HAuCl_4$ solution to each of the plant extracts, appearance of a ruby red color was observed within 10 min (Fig. 1). This indicated the formation of gold nanoparticles. Fig. 2 shows the UV–visible spectra for the maple leaf extract

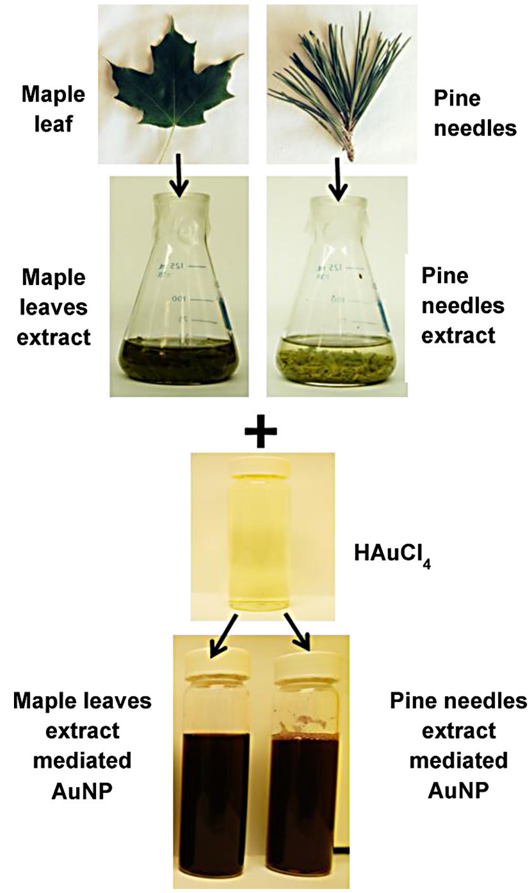

Fig. 1. Schematic flow diagram for green synthesis of gold nanoparticles mediated through maple leaf and pine needle extracts.

reduced gold nanoparticles indicating a maximum absorbance at 534 nm when analyzed with a UV–visible spectrophotometer.

The UV–visible spectra obtained for maple leaf extract reduced gold nanoparticles after a period of one month showed a decrease in the absorbance from 1.792 to 0.779 at 532 nm. Settling of gold nanoparticles was observed at the bottom of the bottle, this might be due to the agglomeration of gold nanoparticles synthesized by maple leaf extract. The pine needle extract-synthesized gold nanoparticles showed a maximum absorbance at 552 nm within first 10 min as can be seen in its UV–visible spectra shown in Fig. 2(b). The AuNP solution containing pine extract remained the same without significant agglomeration after one month storage when compared to maple leaf extract.

The transition electron microscope (TEM) results indicate the presence of spherical to triangular prism of gold nanoparticles synthesized by maple leaf extract as shown in Fig. 3(a). The TEM images of pine needles extract mediated AuNP showed the presence of spherical to quasi-spherical shaped gold nanoparticles shown in Fig. 3(b). A distinctive layer of the organic plant material was found surrounding the pine needle extract AuNP which was absent in the maple leaf extract AuNP. The pine needle mediated AuNP under observation have shown to be stable for a year without much agglomeration. This is an interesting result as this naturally available plant source has the potential not only to reduce the gold nanoparticle but also act as a stabilizing agent.

It can be clearly seen that beautiful triangular prism of gold nanoparticles were produced by the maple leaves extract (Fig. 3(a)). The shape of the nanoparticle plays a significant role in modulating the electronic properties of nanoscale materials. Shankar et al. (2004) reported gold nanotriangles synthesized using