



Value-adding to grape waste: Green synthesis of gold nanoparticles



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ARTICLE INFO

Article history:

Received 7 January 2014

Received in revised form 30 May 2014

Accepted 8 June 2014

Available online 26 June 2014

Keywords:

Grapes

High resolution transmission electron microscope (HR-TEM)

Response surface method

Catechin

Gold nanoparticles

ABSTRACT

In this study we report the potential use of food waste such as grape skin, stalk and seeds obtained after grape processing to produce gold nanoparticles (AuNP). The gold nanoparticles were synthesized according to the rules of green chemistry and integrating the goals of green nanotechnology. Results from the present work establish that AuNP were synthesized in a single step method using water at room temperature. The growth of AuNP was instantaneous within 5 min and was found to be highly stabilized. Thus produced AuNP were characterized using UV–Vis spectrophotometer, high resolution transmission electron microscope (HR-TEM) and energy-dispersive X-ray spectroscopy (EDX). The mean particle size for the green synthesized gold nanoparticles from grape waste ranged from 20 to 25 nm. Furthermore, a central composite design was used to determine the influences of the concentrations of catechin (0.5, 1, 1.5 mM) and HAuCl₄ (0.5, 1, 1.5 mM), and of temperature (10, 25, 45 °C) on the green synthesis of AuNP. Their interactions were determined by response surface methodology (RSM).

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1. Introduction

Researchers in nanotechnology are turning towards 'Nature' to provide inspiration, for exciting and innovative methods of nanosynthesis. Synthesizing novel nanoparticles based on the concept of green nanotechnology is gaining momentum. Green nanotechnology integrates the principles of green chemistry and green engineering to produce eco-friendly, safe, nanoparticles that do not use toxic chemicals in their synthesis protocol (Castro et al., 2011; McKenzie and Hutchison, 2004; Philip, 2009). The progressive development of 'nanotechnology' towards 'green nanotechnology' is shown in Fig. 1.

The production of nanoparticles of noble metals, such as gold nanoparticles (AuNP), is of great interest due to their unique characteristics. Manipulations of their size and shape produces unique properties which have potential applications in semiconductors (Schmid and Corain, 2003) and spectroscopy (Mulvaney, 1996), and in biomedical applications such as drug delivery (Mahal et al., 2013; Paciotti et al., 2004; Singh et al., 2013), tissue/tumor imaging (Jain et al., 2006) and cancer therapy (Peng et al., 2009). Current chemical and physical methods for the synthesis of AuNP use hazardous compounds such as hydrazine, sodium borohydride, and dimethyl formamide (DMF) as reducing agents, and may also require the use of expensive instruments. These methods produce

AuNP efficiently, however downstream processing to separate them from the toxic substances is expensive and time consuming. Presence of even a small trace of hazardous compounds makes these AuNP incompatible for biomedical applications.

On the other hand, waste management represents an important challenge in the agri-food based industries. It demands an integrated approach in the context of recycling, reuse and recovery (Pfaltzgraff et al., 2013). Grapes (*Vitis vinifera* L.) is one of the world's largest fruit crop with a global production of 68 million tonnes (2009) of which, 38 million tonnes is processed. Annually around to 2.5 million tonnes of grape waste is generated (FAOSTAT, 2012). This huge challenge in the management of grape waste must be addressed.

Since 2000, the synthesis of nanoparticles using bacteria (Kalishwaralal et al., 2009), fungus (Du et al., 2011; Gade et al., 2010) and plant extracts such as rose (Ghoreishi et al., 2011), tea (Nune et al., 2009), honey (Philip, 2009), lemongrass leaf (Shankar et al., 2005) and tansy fruit (Dubey et al., 2010) for nanoparticle synthesis are under intense exploration (Nadagouda et al., 2009). This can be a viable substitute to the conventional physico-chemical methods of synthesizing nanoparticles (Karn, 2008; Schmidt, 2007; Schwarz, 2009).

In the present study, the use of agricultural wastes materials such as grape seed, grape skin and grape stalk was investigated individually for the production of gold nanoparticles. Earlier studies used grape wine and grape pomace extract to reduce gold nanoparticles using 50 W of microwave power (Baruwati and Varma,

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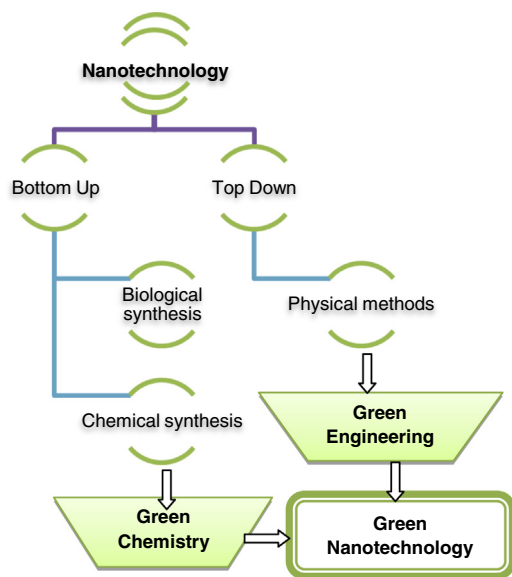


Fig. 1. Flow chart showing the progressive transition towards green nanotechnology.

2009). But in this study we have isolated individual components of grape pomace like the grape seed, skin and stalk and have found that individual components have the potential to form gold nanoparticles without much agglomeration in water at room temperature, following the principles of green engineering. Recent studies has shown remarkable *in vitro* stability and affinity of gold nanoparticles synthesized from grapes towards human breast cancer cells (HBL-100) biocompatibility (Amarnath et al., 2011). Grapes and grape wastes like seed, skin and stalk contain proanthocyanidins. Proanthocyanidins are a rich source of natural antioxidants and have many health benefits such as protection against cardiovascular disease and radiation (Castillo et al., 2000), prevention of cataract (Yamakoshi et al., 2002), anti-hyperglycemic effects (Pinent et al., 2004), protection against oxidative DNA damage in mouse brain cells (Guo et al., 2007), and neuroprotective effects by crossing the blood–brain barrier (Prasain et al., 2009).

In this paper we report a simple, cost-effective procedure to produce gold nanoparticles that are stable with extended shelf life. Recent reports have shown an increased use of water as solvent in chemical reactions instead of organic solvents (Li and Chen, 2006). The water dispersible nature of gold nanoparticles from grape byproducts along with its inherent health benefits can revolutionize the impact of nanotechnology on drug/nutraceutical delivery.

Flavan-3-ols are the most complex subclass of flavonoids ranging from the simple monomer catechin to oligomeric and polymeric proanthocyanidins (Crozier et al., 2008). The plant matrix (grape seed, skin and stalk) used was too complex to identify individual compounds responsible for the bio-reduction, hence catechin, a simple monomeric unit of proanthocyanidins, a powerful polyphenolic compound present in grapes was used as a reference compound to study its influence on the green synthesis of AuNP. The use of catechin would thus be a first step to help us understand the mechanism of formation of gold nanoparticles from grape products.

In this study, the response surface method (RSM) was used to assess the relationship between green synthesized AuNP and independent variables such as the concentration of catechin (5,7,3',4'-tetrahydroxyflavan-3-ol), the concentration of hydrogen tetrachloroaurate (III), and temperature. Central composite design, the most widely used approach of RSM, was employed to

determine the effect of our operating variables (Myers et al., 2009) since it is highly efficient, providing sufficient information on the effect of process variables for process optimization with a reduced number of total experimental runs.

2. Materials and methods

2.1. Sample preparation –synthesis of AuNP using grapes seed, skin and stalk

The seed, skin, and stalk of grapes were freshly collected and washed with deionised water. Grape skins and stalks were cut finely while whole grape seeds were used. For each biomaterial, three grams were mixed with 50 ml deionised water and were heated at 60 °C for 2 min (Fig. 2). Heating leads to the rupture of plant cells and aids in the release of intra-cellular materials into the solution. The clear supernatant was cooled to room temperature and filtered using 11 µm Whatman filter paper (Whatman filter paper, Grade 1). Hydrogen tetrachloroaurate (III) (HAuCl₄·3H₂O) was obtained from Sigma–Aldrich Chemicals Co., (St. Louis, MO), and 1 mM HAuCl₄ solution was prepared using deionised water. Five ml of each plant extract was added to 12 ml of HAuCl₄ solution and the total reaction volume was made up to 30 ml by addition of deionised water.

2.2. Synthesis of AuNP using catechin

(+) Catechin hydrate was obtained from Sigma Aldrich Chemicals Co., (St. Louis, MO). The effects of three different concentrations (0.5, 1, 1.5 mM) of catechin on the synthesis of AuNP at three different concentrations (0.5, 1, 1.5 mM) of HAuCl₄ at 10 °C, 25 °C, and 40 °C was investigated.

2.3. Apparatus and measurements

The maximum surface plasmon resonance (SPR) was measured by wave scan from 400 to 800 nm range using a UV–Vis spectrophotometer (Ultrospec 2100 pro, Biochrom Ltd., Cambridge, UK). The time of addition of plant extract or catechin solution to the HAuCl₄ solution was considered to be the start of the reaction. The color of the HAuCl₄ changed from light yellow to pink (Fig. 2), which indicated the formation of AuNP.

A drop of the sample solution was applied to a carbon coated TEM grid. The sample was allowed to stand for 1 min on the TEM grid and excess solution was carefully removed using Whatman grade 1 filter paper. This allows the formation a thin film of sample on the TEM grid. The sample was left at room temperature until a dried film was obtained. 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) operated at 120 kV. Images were analyzed with TEM image analysis platform and the mean diameter was calculated from the measurements of at least 50 particles from the series of experiments. Each experiment was performed three times. The TEM images of AuNP were selected from one of the replicate samples.

The elemental analysis of chemical constituents were determined by energy-dispersive X-ray spectroscopy (EDX) using FEI Tecnai G² F20 operated at 200 kV with a Cryo-S/TEM Gatan UltraScan 4000 4k × 4k CCD Camera System, Model 895 with EDAX Genesis EDS (FEI Company, Oregon, USA). Olympus LEXT OLS4000 3D laser microscope, was used to capture three dimensional images. A drop of gold nanoparticles solution was smeared on a glass slide and was used to view the green synthesized gold nanoparticles under the microscope.

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