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Research Paper

Development of a sustainable plasmon-enhanced spectroelectrochemical sensor using avocado pit (*Persea americana*) extract

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ABSTRACT

With the increasing popularity of nanotechnology, it is undoubtedly necessary to render the synthesis of nanomaterials more environmentally benign to allow for continued growth of the field. Natural extracts provide a green alternative to harsh chemical reducing and capping agents in noble metal nanoparticle synthesis. In this study, we not only report the first synthesis of silver nanoparticles (AgNPs) using avocado pit extract (APE), but also establish improved surface enhanced Raman spectroscopy (SERS) performance of these APE AgNPs over traditionally synthesized AgNPs. The exceptional size and shape monodispersity of these AgNPs is demonstrated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The excellent SERS performance of these particles is illustrated using both *para*-aminothiophenol (*p*-ATP) and 4,4′-bipyridine (4,4′-Bipy) as Raman probe molecules. Finally, efficient and cost effective plasmon-enhanced screen printed electrodes fashioned using these APE AgNPs is demonstrated for electrochemical SERS (EC-SERS) studies of adenine.

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1. Introduction

Noble metal nanomaterials have become increasingly utilized in areas such as diagnostic biosensing [1,2], antimicrobial applications [3,4], cosmetics [5], and medicine [6] over the last number of years. The upsurge in demand for metal nanoparticles can only be sufficiently met for future use if their production incorporates sustainable approaches, including greener synthetic routes. In the past, these green synthetic routes for nanoparticle synthesis have included the use of fruits [7], plants [8] and other biological organisms [9] as greener alternatives to commonly used reducing and capping agents. In many cases, these nanoparticles have also been used for surface-enhanced Raman spectroscopy (SERS) [10,11]. A central challenge with these green metal nanoparticles however is that the size and shape polydispersity is typically high [9], leading to non-uniform enhancement of the Raman signal and fairly inefficient SERS enhancement [12]. In addition, the nanoparticles are generally coated in a layer of biological material of thickness ranging from 3 to 15 nm [13], and such surface coatings have been shown to decrease the observed SERS signal [14]. In the case of green metal nanoparticles, this surface layer likely prevents a close association between the target analyte and the metal surface, resulting in adverse SERS performance.

In the present study, synthesis of spherical silver nanoparticles (AgNPs) using avocado pit extract (APE) is reported for the first time, to the best of our knowledge. Avocado pits have been reported to contain more phenolic compounds than the pulp itself [15–17], having several-fold greater antioxidant properties than raw blueberries [16]. For the purpose of this work, the plasmonic properties of the APE AgNPs were assessed. While past studies in this area have focused mainly on the formation of silver nanoparticles using green synthetic methods and their antibacterial capibility [18,19], this study aims to push the application of these more sustainable nanoparticles a step further. In order for traditional nanoparticle synthesis to be replaced with greener methods, the green strategies must produce highly functional nanoparticles, at least comparable to that which can be made using non-green routes. In order to demonstrate the value of using APE AgNPs over traditionally synthesized nanoparticles, the APE AgNPs were used to fashion SERS substrates for plasmon-enhanced spectroelectrochemical sensing and were directly compared to their non-green counterparts.

The field of plasmonics uses metal nanostructures to convert light into localized electrical fields, or to direct light to desired locations with nanometer precision. The powerful interaction between the free electrons in the metal and incident electric field of elec-

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tromagnetic radiation results in unique optical and electronic properties which can be exploited in plasmonic applications [20]. Although light manipulation has many applications in modern society such as in communication, biomedical testing and astronomy [21], this current study applies plasmonics to an enhanced variant of Raman spectroscopy, the now well-studied surface enhanced Raman spectroscopy (SERS) technique. SERS uses the strong electromagnetic field enhancement at the surface of the nanoparticles on the SERS substrate to intensify the fundamentally weak Raman signal [22]. SERS is therefore a highly sensitive technique that is able to provide valuable structural data for molecules at low concentration [23]. Since the SERS enhancement happens at the surface of the nanoparticles, size and shape control of the nanoparticles plays an important role with regards to the precise manipulation of incident light [20]. Size and shape control over nanoparticles produced via green strategies has been a major limitation in the field, greatly limiting the SERS performance of green nanoparticles.

Although many environmentally benign processes for metal nanoparticle syntheses using natural extracts as reducing agents have been reported, such green methods still fail to compare to traditional methods in terms of efficacy in plasmonic sensing applications. In order for green methods to be universally implemented to carry nanoscience into the future, natural methods of metal reduction and capping must result in materials that have at least equal, if not superior, performance to their chemical counterparts [24]. In this work, the SERS performance of the APE AgNPs is investigated and compared to AgNPs prepared using the commonly employed Lee-Meisel method [25].

A major limitation in the use of green-synthesized AgNPs for plasmonic applications is the presence of an organic layer covering the nanoparticles, termed the *biogenic corona* [26]. The biogenic corona, reported to be composed mainly of carbohydrate and protein [26], can be difficult to remove or displace even after several washings. The presence of this biogenic corona can also alter the nanoparticle functionality, making the particles less favourable than traditionally synthesized nanoparticles for some applications [26]. As a result of this biogenic corona, the vast majority of green synthetic methods for AgNP synthesis have shown successful application in the SERS detection of thiol-containing probe molecules only; non-thiolated molecules are typically unable to bind strongly enough to the nanoparticle surface to displace the biogenic corona. Unfortunately, this reality significantly limits the application of green-synthesized AgNPs for large scale SERS-based sensing applications. In this work, the application of APE AgNPs for use as plasmonic substrates to detect non-thiolated probe molecules will be explored.

Another issue that arises when natural products are used for this chemical synthesis is that the chosen products are often a food resource such as coffee and tea [27], fruits such as pineapple [28] and even honey [29]. Although plants and fruits are renewable resources, it is not environmentally or economically discerning to use such foodstuffs for green synthetic approaches. It is more insightful, rather, to incorporate the use of waste products from one process as a feedstock for another [24]. Avocado pits are considered to be a solid waste by-product of avocado processing, which is a growing problem given the worldwide increase in avocado consumption in recent years [30]. In Canada alone, avocado imports have nearly doubled from 2010 to 2014 according to Statistics Canada [31]. Avocado pits thus represent a waste material for which there is at present no defined use, despite their high reported antioxidant content.

Green synthetic methods for metal nanoparticle synthesis have been established as sustainable and robust, but little is known about the 'cocktail of phytochemicals' that are responsible for the metal ion reduction [32,33]. Phenolic compounds (comprised of hydroxycinnamic acids, flavonoids, flavonols and their derivatives) have been identified in wines [34,35], cocoa [36], fruit [37,38] and other foods, and are widely accepted as beneficial to health due to their antioxidant and free-radical scavenging properties [39]. It is therefore expected that the large concentrations of phenolic compounds in natural extracts must be responsible for their exceptional performance as green reducing agents. This is substantiated by the analysis of *Eucalyptus globulus* bark extract, where phenolic compounds were found to be the main reducing phytochemicals, along with sugars such as glucose and fructose to a lesser extent [40]. Reverse phase high performance liquid chromatography (RP-HPLC) is a powerful technique for the categorization of phenolic compounds [35,37–39] and was therefore used in this work for APE analysis in conjunction with diode array detection (DAD).

The focus of this research was to explore the extent to which avocado pit extract could be used in a facile, green synthesis of silver nanoparticles for use in electrochemical-SERS (EC-SERS) sensing. Since avocado pits are high in antioxidant content, it was hypothesized that their extract should function as an excellent reducing agent in metal nanoparticle synthesis. As such, the resultant silver nanoparticles were assessed for size and shape dispersion, the presence of any significant biogenic corona, and their ability to provide efficient SERS enhancement. Both thiolated and non-thiolated SERS probe molecules were explored in this work, and electrochemical SERS using the APE AgNPs was evaluated. In addition, the potential for APE AgNP use in quantitative SERS sensing is investigated. A characterisation of possible reducing agents in APE using HPLC-DAD is also discussed.

2. Materials and methods

2.1. Reagents and materials

4,4′-Bipyridine (4,4′-Bipy, 98%), silver nitrate ($AgNO_3$,>99%), potassium chloride (KCl, ≥99%), 4-aminothiophenol (*p*-ATP, 97%) and adenine (≥99%) were all purchased from Sigma Aldrich (St. Louis, MO, USA). Chromatographic standards quercetin (96%), luteolin (95%), caffeic acid (98%) and chlorogenic acid (96%) were purchased from Toronto Research Chemicals Inc. (Toronto, Ontario, Canada). Standards were all prepared in HPLC grade water. A 100 ppm mixed standard was used to optimize HPLC separation and detection while individual standards were used to identify retention times. All chemicals were used as received without further purification. All other solutions were prepared using Millipore water (solution resistivity ≥18.2 MΩ cm). Glassware was cleaned in neat sulfuric acid and thoroughly rinsed with Millipore water prior to use. Screen printed electrodes used to fashion the electrochemical SERS substrates and the WaveNow Potentiostat/Galvanostat system used for EC-SERS measurements were purchased from Pine Research Instrumentation (Durham, NC, USA). Hass avocados were purchased from a variety of local grocery stores.

2.2. Preparation of avocado pit extract (APE)

Several avocado pits were thoroughly washed and baked at 135 °C for two hours. The avocado pits were then allowed to cool for 15 min, and were then peeled and crushed into a fine powder using a mortar and pestle. Approximately 10 g of the powder was then blended in a commercial grade blender with 100.0 mL of Millipore water for 80 s at the lowest speed setting and for an additional 20 s at the highest speed setting. The resulting extract was filtered through three layers of cheesecloth and then gravity filtered using Whatman filter paper #1 and subsequently filtered through a Nalgene® PVDF 0.2 μm syringe filter. The extract was stored in the fridge at 4 °C prior to use. The extract was typically used within 48 h of preparation, as it was readily air-oxidized.

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