



Nondestructive detection of the freshness of fruits and vegetables using gold and silver nanoparticle mediated graphene enhanced Raman spectroscopy

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ARTICLE INFO

Article history:

Received 19 June 2015

Received in revised form 27 August 2015

Accepted 29 August 2015

Available online 5 September 2015

Keywords:

GERS

Raman spectroscopy

Gold nanoparticles

Silver nanoparticles

Graphene

Fruit vegetables freshness

ABSTRACT

Raman spectroscopy and surface enhanced Raman spectroscopy (SERS) are expanding their horizons into widespread applications as analytical tools with immense potentials. In the current work, we demonstrated the use of a portable Raman system conjugated with graphene enhanced Raman spectroscopy (GERS) for assessing the freshness of fruits and vegetables. Dual nano-platforms have been used involving the use of gold/silver nanoparticles seeded graphene sheets (Au@G and Ag@G, respectively) as the SERS system for probing the freshness of fruits and vegetables. The data showed that Au@G offered high sensitivity, high resolution and high biocompatibility. A novel and simple GERS method based on a microdrop of Ag@G or Au@G on the fruit surface was used for the evaluation of the freshness of the fruits/vegetables. Fruits and vegetables like Wax apple, Lemon, Tomato, Red Pepper and Carrot were investigated. Market fresh and refrigerated fruits and vegetables were probed at various time intervals ranging from 1 day to 2 weeks. The results signify that some of the Raman signals increase with storage and certain peaks were found to appear with long term storage in the refrigerator. This study demonstrates that the quality of fruits and vegetables under short term (1 week) and even under cold storage conditions are impacted and should be avoided as much as possible. The changes effected on the fruits and vegetables under refrigeration and the applicability of using Au@G enabled GERS as a successful and novel platform for assessing the freshness of fruits and vegetables is elaborated.

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1. Introduction

Fresh fruits and vegetables are important and pivotal for the human beings and their healthy diet. When it comes to testing the quality of foods, people use all senses such as sight, smell, taste, touch and hearing. These natural sensors are very important but lack sensitivity and are affected through human bias. Thus, sensors and related technologies have experienced a significant increase in the recent years [1–7]. Artificial sensors or electronic noses are ultra-sensitive, selective and rapid having an unequivocal edge over natural sensors such as appearance, aroma,

flavor and touch. Many technologies and electronic noses have been reported for this purpose including: optoelectronic system [1], hyperspectral imaging (HSI) [7], cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) [2], surface acoustic wave (SAW) sensor [3], infrared multispectral imaging technique [5,6] and others [4]. These techniques provide direct and indirect assessments. These technologies depend on measuring the volatile organic vapors (VOCs) or detection of some toxins that may be considered harmful for human health. Among these techniques, Raman spectroscopy is promising for assessing quality of fruits and vegetables [8], since it can be used for detection of adulteration, contamination and testing the authenticity of meats, fruits and vegetables safely. Raman spectroscopy is vibrational spectroscopy and complementary to infrared spectroscopy [9,10]. It is a simple, sensitive, non-destructive and selective technique. Raman signals can be increased by rough metal nanoparticles such as

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gold and silver nanoparticles. This was coined as surface enhanced Raman spectroscopy (SERS). The amplification of Raman signal is due to the interactions of analyte molecules with a roughened noble-metal surface. These amplifications increase the limit of detection of the target analyte. New Raman systems were also reported such as tip enhanced Raman spectroscopy (TERS) [11] and handheld Raman scattering ‘portable techniques’. Its applications include fruits and vegetable quality control [8], and for detection of metals [12–14], dyes [15], explosives [16], for drug delivery [17], and cancer cell detection [18]. Thus, SERS, has been applied for identification, quantification, differentiation between the different analytes and for real-time monitoring of food products.

Graphene and their derivatives are a new carbon allotrope that consists of 2D carbon nanosheets [19]. It was awarded the Nobel Prize in physics for 2010 [19]. It has been applied for energy and analytical applications [20,21], cancer and pathogenic bacterial treatment [22–24], protein [25–27], lipodomics [5], heavy metal detection [25–28] and other applications as reviewed earlier [12–14]. Graphene and their derivatives were also used for SERS application. Recently, it was coined ‘Graphene enhanced Raman spectroscopy’ (GERS) [5,6]. GERS was applied for cancer cells [18], dyes [15], ions [12–14] and pesticide monitoring [29]. GERS offers higher sensitivity that can reach an improvement factor of 400% for fluorescence species that consider the main drawbacks of Raman spectroscopy [15]. It has been also proposed for ultrasensitive detection of explosive material [30].

Herein, a portable Raman spectroscopy unit conjugated with GERS has been used for the non-destructive evaluation of the freshness of fruits and vegetables. A novel and simple nanocomposite (silver and gold nanoparticles at graphene nanosheet, Ag@G and Au@G) based micro-drop was used to evaluate the freshness of fruits. The fruits and vegetables bought fresh from the market were investigated before and after refrigeration up to 2 weeks. The results show that the Au@G platform can successfully differentiate market fresh and stored fruits and vegetables. Since the Raman system used is a portable one and also the technique is a surface-based technique which does not require the destruction of the fruit or vegetable sample, this is deemed a non-destructive technique.

2. Experimental methods

2.1. Materials and samples

Unless otherwise specified, reagents were used as received without further purification. Sulfuric acid, nitric acids were purchased from J.T. Baker (India). KMnO_4 was purchased from Riedel-de Haën (Seelze, Germany). HAuCl_4 , AgNO_3 and natural graphite (–20+84 mesh, 99.9%) were purchased from Alfa Aesar (Great Britain). Methanol (HPLC grade) and potassium permanganate were purchased from Merck. Co (USA). Trisodium citrate was purchased from Show chemical Co. LTA, Japan. Poly(N-vinyl-2-pyrrolidone) (PVP) was purchased from Sigma, USA. The de-ionized water obtained from a Milli-Q Plus water purification system (Millipore, Bedford, MA, USA) was used for all experiments.

Five representatives of fruits and vegetables were tested. Tomato (*Lycopersicon esculentum* Mill.), Carrot (*Daucus carota* L.), Lemon (*Citrus limetta*, Risso), Wax apple (*Syzygium samarangense* (Blume) Merrill & L. M. Perry) and Red pepper (*Capsicum annum* L.) were studied. Fruits were purchased from the fresh market, the first condition is thus termed as ‘market fresh’. This is the condition which is available to the consumer and hence we use this to depict the fresh fruit/vegetable used in the study.

2.2. Instruments and methods

2.2.1. UV-vis absorption, fluorescence, FT-IR and TEM measurements

The UV measurements were conducted using a UV spectrophotometer (Perkin Elmer 100, German). The fluorescence spectra were obtained using a fluorescence spectrophotometer (F-2700 Hitachi Co., Japan), equipped with a xenon arc lamp (150 W). The scan speed was set at 120 nm min^{-1} . All spectra were drawn and fitted using the Raman instrument software. The Fourier transform infrared (FT-IR) spectra of nanomaterials were recorded on a FT-IR spectrometer (Spectrum 100, Perkin Elmer, USA). The size distributions of the nanoparticles were determined by a transmission electron microscope (TEM, Philip CM-200, Switzerland).

2.2.2. Preparation of graphene oxide

Graphene oxide was prepared using Hummers method with minor modification [31,32]. Briefly, a round flask containing natural graphite (1.0 g) and nitric acid (10.0 mL, 69–72%) was placed in an ice-bath, stirred for about 30 min (Ciramec). After that, sulfuric acid (15.0 mL, 96.0%) and potassium permanganate (3.0 g, $\geq 99\%$) were added gradually into the mixture (temperature was kept at $<0^\circ\text{C}$ using ice-sodium chloride bath). After removing the ice-bath, the hydrogen peroxide (30–32%, 15.0 mL) was added drop wise to remove the excess permanganate (till bubbles stop). After magnetic stirring (2 h), distilled water (200.0 mL) was poured slowly into the mixture. Further stirred for another 30 min, and then the dispersion was filtered and then washed several times with a 5.0 wt% HCl solution to remove the metal ions.

2.2.3. Preparation of graphene (G) aqueous dispersion

Aqueous solution of graphene oxide (GO, 0.5 mg/mL) was ultrasonicated (Sunway Scientific Corporation, LC30H) for 30 min, followed by centrifugation at 4000 rpm for 1 h. The GO colloidal dispersion (10.0 mL) mixed with hydrazine solution (5.0 μL , 35.0 wt% $\text{NH}_2\text{-NH}_2$) and ammonium hydroxide solution (35.0 μL , 28–30 wt%, J.T. Baker) was added into the flask. The mixture was subjected to magnetic stirring in an oil-bath at 100°C for 2 h to reduce GO to graphene nanosheets. The synthesized graphene nanosheets were characterized using transmission electron microscope (TEM), FT-IR, UV-vis absorption and fluorescence spectroscopy.

2.2.4. Preparation of gold nanoparticles

Citrate-stabilized gold nanoparticles were prepared according to the Frens procedure with minor modification [33]. Briefly, trisodium citrate solution (0.75 mL, 1%) was added to HAuCl_4 aqueous solution (100 mL, 2.43 mM) with boiling under vigorous stirring. The mixture was kept boiling for 15 min and then allowed to cool to room temperature with continuous stirring. The resultant Au nanoparticles were separated by ultracentrifugation ($18,000 \times g$, 20 min) and washed several times (3–5 times). Gold nanoparticles (2.9 mg/mL) were re-suspended into 50 mL sterilized deionised water and stored up to use.

2.2.5. In situ synthesis of Au nanoparticles on graphene nanosheets (Au@G)

Gold nanoparticles were prepared by reduction of the gold precursor in the presence of graphene. In a typical process, 2.5 mL of graphene aqueous suspension (1 g/50 mL) was added to 50 mL of HAuCl_4 solution (0.01%) and heated to 80°C . Sodium citrate (0.85 mL, 1%) was subsequently added drop wise to the reaction. The resultant nanocomposite was washed with deionised water using centrifugation (3000 rpm). Au@G nanocomposite (0.4 mg/mL) was re-suspended into 50 mL sterilized deionised water and stored.

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