APPLICATION OF ALUMINIUM NANOSTRUCTURES FOR 355 nm SURFACE-ENHANCED RAMAN SPECTROSCOPY OF COCONUT MILK

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Abstract

Less than two decades ago aluminium plasmonics emerged and attracted great interest. Aluminium nanoparticles were produced on fused silica substrates by the direct picosecond laser deposition technique. The as prepared active substrates were used for the first time to 355 nm surface-enhanced Raman spectroscopy to detect coconut milk as a probe analyte. The μ-Raman spectrum was also applied for comparison and the transmission spectrum of the aluminium nanoparticles array was checked.

Key words: aluminium nanostructures, picosecond laser deposition, 355 nm surface-enhanced Raman spectroscopy, coconut milk

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Introduction. Raman spectroscopy has been widely applied to detect and analyze different chemicals. It is expressed by an enormous enhancement of the Raman signal, when the material is in close vicinity of the metal nanostructure.

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However, the application of Raman spectroscopy has some drawbacks when studying some samples, for instance which have fluorescence. This can be overcome when excitation wavelength is in the ultraviolet (UV) or better in the deep ultraviolet (DUV) region [1, 2]. Other advantages when using UV excitation are stronger and more defined Raman peaks, since the Raman signal is proportional to the fourth power of the light frequency [3].

Less than two decades ago aluminium (Al) plasmonics emerged and attracted great interest [2, 4], instead of Raman studies based on gold and silver nanoparticles, in which plasmon resonance is situated in the visible region of the electromagnetic spectrum. On the contrary, the plasmon resonance of Al is situated in the ultraviolet part of spectrum and thus it can be used for studying organic, biological systems and those, which have strong fluorescence, absorptions and photocatalysis in this region. Aluminium is a relatively cheap metal, stable and easy to work with. However, it is self-limiting oxidizing and consequently, the preparing and storing of the nanostructures must be done in vacuum environment.

Raman spectroscopy is one of the rapid, sensitive, non-destructive, and relatively inexpensive techniques that can detect contaminants [5–7]. Compared to other spectroscopy-based methods such as fluorescence and infrared spectroscopy, Raman spectroscopy allows multiplex detection of different analytes due to their higher spectral resolution and narrower bandwidths. Furthermore, quantitative analysis of analytes can be achieved based on the proportional relationship between Raman signal intensity and analyte concentration [8].

The possibilities of 355 nm Raman spectroscopy to detect molecules using Al NSs is a subject of the present study. Coconut milk was chosen as a probing analyte due to its importance in nutrition and medicine. It is a milky-white liquid extracted from the grated pulp of mature coconuts. The opacity and rich taste of coconut milk are due to its high oil content, most of which is saturated fat. Coconut milk is a fully natural plant protein opaque liquid, which presents an emulsion of natural oil in water. It is extracted from shredded coconut endosperm (*Cocos nucifera* L.) with or without the addition of water. Nowadays, there are varieties of commercial coconut milks, which are prepared at different temperatures of pasteurization, sterilization or spray drying method [9]. It is one of the richest natural plant sources of nutritional and medicinal components with broad applications in treating tumours, inflammation and attacks of microbes and insects [10]. During these processes, the physico-chemical, sensory, and aromatic properties as well as the consumer acceptance properties have been changed. The importance of studying this product can be understood since the global market of coconut products reached $1.1 billion in 2019 and is anticipated to reach $2.9 billion by 2027.

Among the coconut products, the coconut milk is one of the least studied. In the advanced study [11], new method for measuring fat content in the coconut milk was developed. Additionally, the reflection spectrum was also measured.

Two peaks of fat in coconut milk were measured in the infrared region, i.e. at 1060 and 1250 nm, respectively. The reflection in the ultraviolet region drops dramatically below 400 nm reaching minimum at about 270 nm and being 62% at 355 nm. Generally, coconut oil and coconut water are the most intensively investigated [12].

The non-destructive spectroscopic techniques such as nuclear magnetic resonance and dielectric spectroscopy that employ radio frequency, UV-VIS spectroscopy, IR spectroscopy, Raman spectroscopy, Fourier transform infrared (FTIR) spectroscopy and spectroscopic imaging such as hyperspectral imaging (HSI), have been employed for studying various food products [13, 14].

The purpose of the present study is to produce aluminium nanoparticles (Al NPs) arrays using picosecond (ps) laser on fused silica substrate. The Al nanoparticles were investigated by transmission electron microscopy (TEM). The as produced active substrate was applied for advanced UV (355 nm) SERS of the coconut milk as probing analyte for the first-time. Additionally, μ-Raman spectrum of coconut milk was also applied for the first time for comparison. The possibilities of the proposed technique for analyses are discussed.

Materials and methods. Samples of aluminium nanostructures (NSs) were fabricated by direct pulsed laser deposition on fused silica substrates using 1 KHz repetition rate picosecond (ps) Nd:YAG laser (Model: CNI Laser, PS-A1-1064). It generates 20 ps pulses at 1064 nm. The aluminium target, which was situated at about ≈ 3 cm from the substrate, was ablated by laser pulses with a fluence of 2 J$\cdot$cm^{-2} in an ambient pressure of 9.5×10^{-4} Torr at room temperature. The deposition time was 5 min. Prior to processing the substrates were cleaned with alcohol, washed with deionized water and dried.

Canned coconut milk (Chaokoh, Thailand) with concentration of 99.98% and 0.02% antioxidant (sodium metabisulphite) was purchased from the store. It was diluted in distilled water in order to produce liquid solutions with concentrations of 0.1 M. It is important to note that the purpose in this study is not to detect the lowest possible quantity or to evaluate the lowest detection limit of the analytes, but to prove the ability of SERS study, when excitation at 355 nm is applied using Al nanostructured array.

The optical property of the nanostructured array was obtained via a spectrometer (Ocean Optics HR 4000–$200 \div 1000$ nm). The Raman spectra were achieved using μ-Raman spectrometer (Photon Design, Tokyo, Japan) supplied with optically pumped semiconductor laser (Genesis CX) generating at $\lambda = 355$ nm. The beam was focused using a confocal microscope with $90\times$ objective lens and various laser excitation powers of 0.5, 1.0 and 2.0 mW have been applied. In order to avoid irregularities, each Raman spectrum was obtained on the basis of averaging of at least two scans taken from different points of the samples and an acquisition time of 10 min.

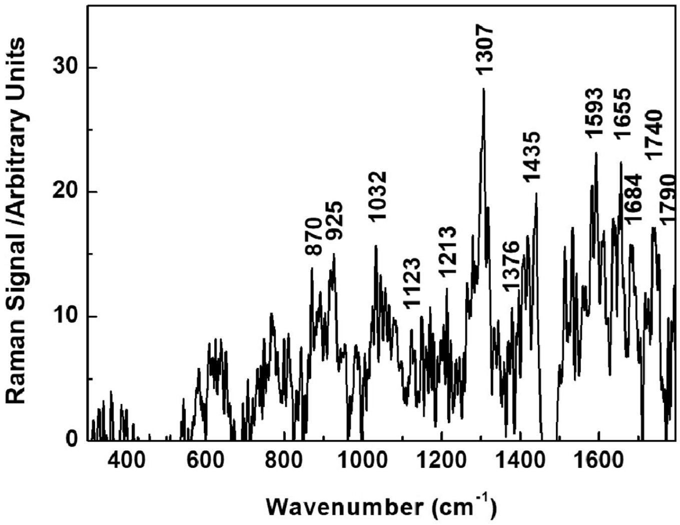

Fig. 1. μ-Raman spectrum of liquid coconut milk as purchased deposited on glass plate. The Raman excitation power was 2.0 mW

The transmission electron microscopy (TEM) study was accomplished by JEOL JEM 2100 at an accelerating voltage of 200 kV and Al NPs were visualized in order to evaluate their shape and size distribution.

A drop of the as purchased analyte of about 10 μL was deposited on a glass plate in order to check its μ-Raman spectrum for reference (Fig. 1). The most prominent seven peaks are situated at 925, 1032, 1307, 1435, 1593, 1655, and 1740 cm^{-1}, respectively. Moreover, the vibrations at 870, 1123, 1213, 1376, 1684, and 1790 cm^{-1} can also be distinguished.

Results and discussion. The transmission spectrum of the aluminium nanoparticles array in Fig. 2 was achieved directly by ps pulsed laser deposited of Al on quartz substrates. As is seen, the optical resonance of the sample is situated at 287 nm. However, at 355 nm (the Raman excitation wavelength) the transmission is still noticeable compared to the optical plasmon resonance value. It is about 12% less, but is still enough to ensure enhancement of the Raman signals. It is worth noting that the position of the plasmon resonance strongly depends on the size of the Al nanoparticles [15], which is a very promising way to improve the properties of the samples to coincide with this excitation wavelength of the Raman spectrometer.

The samples for TEM analysis were deposited at the same conditions as mentioned above on TEM copper grid for 2 min in order to avoid accumulation of material that would hamper evaluation of the nanoparticles' characteristics (Fig. 3(a)). As is seen it is composed of spherical nanoparticles. The size distribution of the Al NPs is also presented in Fig. 3(b). Here, data from five TEM

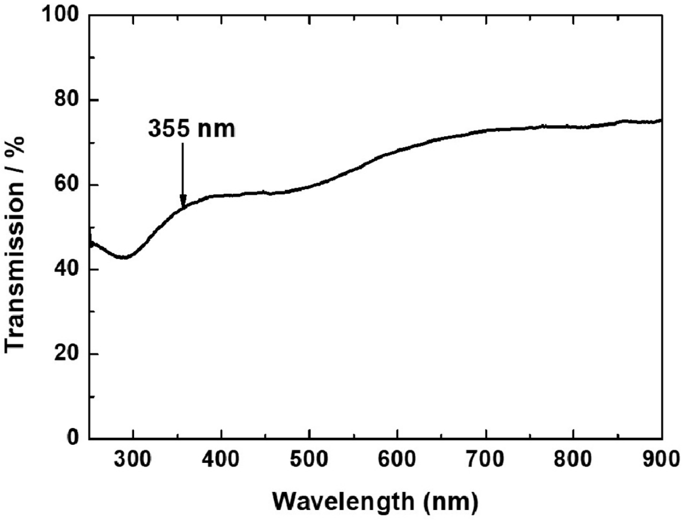

Fig. 2. Optical transmission spectrum of aluminium nanostructure array. The point of the ultraviolet Raman excitation at 355 nm is indicated

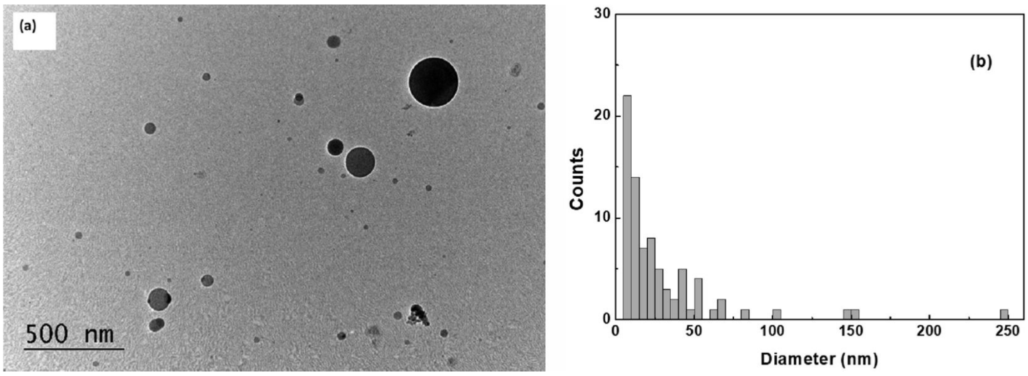

Fig. 3. (a) Transmission electron microscope image of the deposited material at picosecond laser deposition of aluminium in vacuum. The laser fluence is 2 J/cm² and the deposition time is 2 min. (b) Size distribution of the deposited nanoparticles. Five images (in total 90 particles) are used to construct the dependence

images were used in order to present better statistics. The most probable particles diameter is 7.5 nm, as single particles with size of several hundreds of nanometers are also present.

The SERS spectrum of 0.1 M coconut milk, deposited on Al NPs arrays produced on quartz substrate is shown in Fig. 4. As it is seen, the peaks having most prominent intensity are situated at 1307, 1434, 1593, 1213, and 1684 cm^{-1}. They were also obtained from the undiluted with distilled water liquid coconut milk (Fig. 1, Table 1). They coincide with the vibrations of the coconut milk

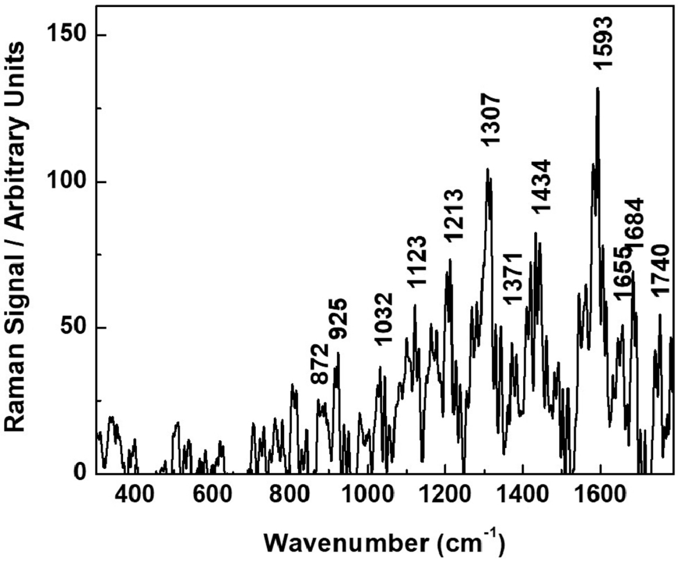

Fig. 4. Surface-enhanced Raman spectroscopy spectrum of 0.1 M coconut milk, deposited on aluminium nanoparticles arrays produced on quartz substrate. Sample 3-C2. The Raman excitation power was 2.0 mW

(Table 1). The peaks at 1300 and 1440 cm^{-1} belong to the coconut oil and are close to the first two most intensive SERS peaks [16].

It is worth mentioning that the intensity of the peaks in the SERS spectrum are more than six times higher than those of the coconut milk deposited on glass (Fig. 1, Fig. 4), regardless of an order of magnitude lower concentration. In this respect, it is very important to evaluate the highest enhancement factor (EF) and lowest detection limit (LOD) of the Al active substrates, which is out of the scope of this study. Additionally, the normal coconut milk is very rich in coconut oil. This was confirmed by the near infrared spectroscopy measurements [17], when 100 samples have been investigated and evaluated that the mean value of the fat in the coconut milk is about ≈ 32–34%. Thus, several vibrations, which were observed to coincide or are very near [18, 19] can be assigned to the coconut oil (see Table 1). Furthermore, the peak at 872 cm^{-1}, which exactly matches with our observations, comes from the functional group of =CH_2 of the bending (wagging) vibrational modes or from –$(CH_2)n$– of the stretching (C–C) vibration [15]. The SERS peak with middle intensity at 1123 cm^{-1} can be assigned to –$(CH_2)n$– stretching (C–C) vibration and this at 1440 cm^{-1} – to –$(CH_2)n$– of stretching (C–C) or (C=O), absorption of aldehyde, respectively [19]. Finally, the peak at 1740 cm^{-1} can be connected, to the –C=O functional group of the (carbonyl ester) stretching mode, or to the (C=O) stretching mode of absorption of aldehyde [19].

In summary, half of the peaks in the SERS spectra at 1593 and 1684 cm^{-1} with very strong intensity and these at 925, 1032, 1213, 1655, and 1790 cm^{-1}

Table 1

The vibrational modes (in cm^{-1}) of coconut milk. Peak strengths – vs: very strong; s: strong; m: medium; w: weak. The vibrational modes (in cm^{-1}) and functional groups of coconut oil are given for reference

Coconut milk			Coconut oil, [16]	Virgin coconut oil, [18]	Coconut oil, [19]
μ-Raman Glass, as purchased	SERS Quartz (3-C1) as purchased	SERS Quartz (3-C2) 0.1 M	Raman	FTIR	FTIR
870, m	871, w	872, w	868; $-(CH_2)n-$; stretching (C–C)	872; $=CH_2$ bending (wagging)	
925, m	924, m	925, m			
1032, m	1031, m	1032, m			
1123, w	1121, m	1123, m	1125; $-(CH_2)n-$; stretching (C–C)		
1213, m	1212, m	1213, m			
1307, vs	1308, vs	1307, s	1300; $-CH_2$; bending (C–H)		
1376, w	1372, m	1371, w		1377; $-C-H$ ($-CH_3$) symmetrical bending	1375; (CH_3) methyl bending
1435, s	1440, s	1434, m	1440; $-CH_2$; bending (C–H)		
1593, s	1594, vs	1593, vs			
1655, s	1655, w	1655, w			
1684, s	1684, s	1684, m			
1740, m	1739, m	1740, m		1743; $-C=O$ (carbonyl ester) stretching	1740, (C=O) stretching, absorption of aldehyde
1790, m	1790, s	1790, w			

having middle intensity, came from some species into the coconut milk and were observed and described for the first time here.

Conclusion. In summary, the ability for μ-Raman and SERS studies of coconut milk at 355 nm excitation was demonstrated for the first time. Moreover, the active aluminium nanostructures used for the SERS investigations were prepared on quartz substrates directly using picosecond laser pulses. The experimental results obtained are very promising. With a view to increase the sensitivity of the samples and to improve the method some more work is needed in order to shift the position of the plasmon resonance to match with 355 nm excitation wavelength of the Raman equipment used by tailoring the size of the Al nanoparticles.

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