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High angular-resolution automated visible-wavelength scanning angle Raman microscopy

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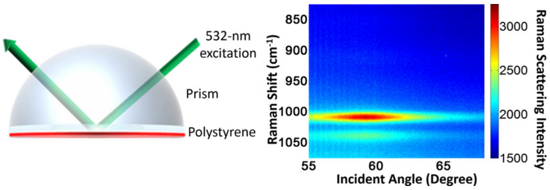
HIGHLIGHTS

- A scanning angle Raman microscope with improved instrumental design is reported.
- Improvements include large scanning angle range and low angular spread.
- Technique provides chemical content information with high axial spatial resolution.
- Benefits of visible excitation wavelengths in SA Raman measurements are discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

A scanning angle (SA) Raman microscope with 532-nm excitation is reported for probing chemical content perpendicular to a sample interface. The instrument is fully automated to collect Raman spectra across a range of incident angles from 20.50 to 79.50° with an angular spread of 0.4 ± 0.2° and an angular uncertainty of 0.09°. Instrumental controls drive a rotational stage with a fixed axis of rotation relative to a prism-based sample interface mounted on an inverted microscope stage. Three benefits of SA Raman microscopy using visible wavelengths, compared to near infrared wavelengths are: (i) better surface sensitivity; (ii) increased signal due to the frequency to the fourth power dependence of the Raman signal, and the possibility for resonant enhancement; (iii) the need to scan a reduced angular range to shorten data collection times. These benefits were demonstrated with SA Raman measurements of thin polymer films of polystyrene or a diblock copolymer of polystyrene and poly(3-hexylthiophene-2,5-diyl). Thin film spectra were collected with a signal-to-noise ratio of 30 using a 0.25 s acquisition time.

1. Introduction

Raman spectroscopy has been used in many fields to identify the chemical composition of diverse samples [1–7]. Several variants of Raman instruments have been developed, including portable units [8–10] and imaging systems [11,12]. Another variant of Raman instruments has the capability to probe interfaces using total internal reflection (TIR) illumination [13–26]. For these measurements the incident laser is directed at an interface with an incident angle (θ_i) at or above the critical angle (θ_c) as given by Snell's law: $\theta_c = \sin^{-1}(\eta_{\text{sample}}/\eta_{\text{prism/objective}})$, where η_{sample} and $\eta_{\text{prism/objective}}$ are the indices of refraction of the interfacial layers. A

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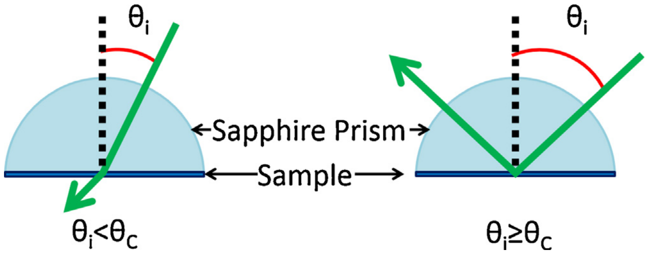

Fig. 1. Sapphire/sample interface showing transmission and reflection of the incident excitation light (left) below and (right) at or above the critical angle, respectively.

typical sample setup for a TIR experiment is shown in Fig. 1. Two layouts to achieve TIR are through the objective and through a high index of refraction prism [16–21,24,26,27]. TIR through the objective has the benefit of ease of implementation, but is limited to samples with a low index of refraction (e.g., aqueous) and the exact incident angle is rarely known. In addition, the incident angle for a typical TIR objective is limited to a maximum value in the 67° range [28]. The use of a prism generally presents a greater alignment challenge; however, a high index of refraction prism allows a much wider range of samples to be measured and the angle of incidence is easily determined.

We have previously reported a variation of Raman spectroscopy termed scanning angle (SA) Raman spectroscopy [20–23,25]. SA Raman instruments have a controlled and variable incident angle upon a prism/sample interface in the range of around 25–75° with a resolution of a tenth of a degree or less. Three distinct regions in the scanned angular range are below, at, and above the critical angle for total internal reflection. The Raman signal is enhanced by as much as a few orders of magnitude at the critical angle. At angles greater than the critical angle, the penetration of the evanescent wave into the sample decreases and these angles are suitable for selectively probing the interface [14–19]. When the sample meets conditions required for a waveguide, spectra collected at angles below the critical angle provide simultaneous information on chemical content and sample thickness [22,23]. The pattern of the Raman signal as the incident angle is changed upon a waveguide interface can be correlated to sample thickness.

Excitation wavelength is an important experimental parameter for any Raman spectroscopy experiment. The Raman intensity scales with the excitation frequency to the fourth power, making shorter excitation wavelengths desirable. However, considerations of the spectral background often make longer excitation wavelengths necessary for many Raman experiments. In addition to these considerations, for SA Raman spectroscopy the excitation wavelength affects the predicted angular dependence of the signal. Under TIR, 98% of the Raman scattering is generated in the sample within a distance D_{RS} (Eq. (1)), which is another important parameter that is dependent on the excitation wavelength (λ) and incident angle (θ_i) [26].

$$D_{RS} = \frac{\lambda}{4 \times \pi} \frac{1}{\sqrt{[(\eta_{prism}^2 \times \sin^2\theta_i) - \eta_{sample}^2]}} \quad (1)$$

For a sapphire/polystyrene interface, the calculated D_{RS} at a 68° incident angle for 785 and 532-nm excitation wavelengths are 148 and 123 nm, respectively. The D_{RS} at 78° is close to the minimum value that can be achieved with many optical schemes and is 90 nm (785-nm excitation) and 65 nm (532-nm excitation). SA Raman measurements with visible excitation wavelengths are predicted to produce better surface sensitivity with smaller D_{RS} values at large incident angles.

In this study we report a newly developed 532-nm SA Raman instrument that has the benefits of improved design, increased signal due to the short excitation wavelength and resonant enhancement, and decreased experimental times. The incident angular range, spread and uncertainty have been characterized, and comparisons of excitation wavelength on the SA Raman signals for several polymer interfaces have been conducted. The instrument will be of use in a variety of fields where interfacial characterization is needed, particularly in applications that benefit from measurements at ambient laboratory conditions.

2. Experimental methods

2.1. Instrumentation

The developed instrument can be used for SA Raman imaging or epi-illumination (Fig. 2). A single frequency 532-nm laser (Sapphire SF 532 nm 150 mW, Coherent, Santa Clara, CA) set to s-polarization was used for the excitation source. For epi-illumination imaging, the light was directed via a flip down mirror to a 10× beam expander (59-127, Edmund Optics, Barrington, NJ) then the rear port of a DM IRBE microscope (Leica,

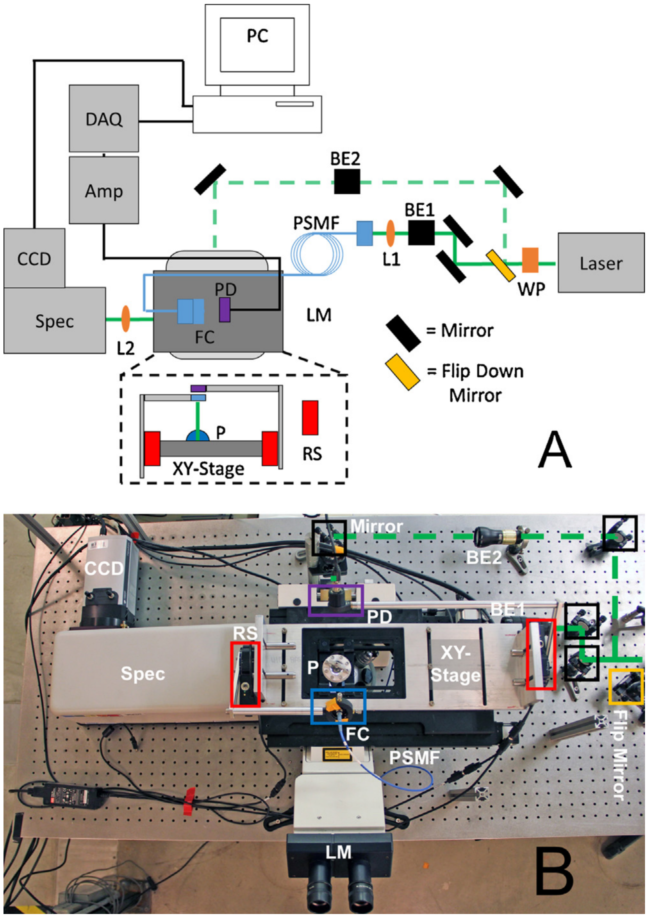

Fig. 2. (A) Instrument schematic for a 532-nm SA Raman microscope: half waveplate (WP), beam expanders (BE1, BE2), Leica microscope (LM), aspheric focusing lens (L1), polarization-maintaining single-mode fiber optic (PSMF), fiber collimator (FC), high index of refraction prism (P), photo-diode (PD), rotational stages (RS), amplifier (Amp), data acquisition device (DAQ), computer (PC), collection lens (L2), spectrometer (Spec), and charged-coupled device (CCD). The dashed view is perpendicular to the optical table. (B) Picture of the 532-nm SA Raman microscope. The laser is not shown. Selected items are highlighted in the picture with color-coded boxes to match the schematic. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)