RESEARCH ARTICLE

Exploiting plasmonic enhancement with light-emitting diode excitation in surface-enhanced Raman scattering

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Abstract

Surface-enhanced Raman scattering (SERS) is a well-established technique that enables the detection of very low molecular concentrations down to single molecules. Typical applications of SERS are the consistent identification of various samples used in chemistry, biology, and physics among others. In contrast to common SERS setups, where lasers are used as excitation source, we exploit SERS to perform Raman spectroscopy with a light-emitting diode (LED). We demonstrate the applicability of our approach on four different Raman reporters. We unambiguously distinguish two similar designer molecules 4-nitrothiophenol (p-NTP) and 5,5-dithio-bis-(2-nitrobenzoic acid) (DTNB) that are often used in SERS experiments. Additionally, we probe Rhodamine 6G that is used in many different applications and carbon nanotubes as a one-dimensional solid state nanosystem. The LED excited surface-enhanced Raman spectra reproduce the characteristic Raman modes of the different samples. We compare the LED spectra to Raman spectra excited with a laser at the same wavelength. We envision the combination of LED sources with SERS substrates in the next generation of handheld devices and low-cost Raman setups.

KEYWORDS

LED, Raman, SERS

1 | INTRODUCTION

The very first Raman spectrum was measured with focused sun light,[1,2] since then the laser has become the standard excitation source due to its monochromatic emission and high optical power. Recent advances in surface-enhanced Raman scattering (SERS) lift the necessity of high-power sample irradiation by enhancing the Raman signal by several orders of magnitude.[3,4] This can allow an application of alternative more efficient photon sources such as light-emitting diodes (LEDs), but first the ability of LED based Raman setups need to be tested for identification of molecules and crystals.

SERS is a well-known technique that uses plasmonic near fields to enhance the Raman scattering intensity.[3,4] Light interacting with metallic nanoparticles or rough metal surfaces excites strong plasmonic near fields in the vicinity of the metal.[5–8] SERS achieves enhancement

factors of up to 10^{11} and even enables the detection of single molecules.[9–11] The strong enhancement of SERS is used in a wide variety of applications for example in biosensing, analytics, and the observation of chemical reactions.[12] Further, possible applications are DNA sequencing, explosive detection and the preservation of artworks.[13–15]

In SERS, the incoming light excites a localized surface plasmon in the metal which itself generates an enhanced and localized electromagnetic near field. The specific design of SERS substrates enables the tunability of the plasmonic resonance by varying the size, shape, and separation of the plasmonic nanoparticles.[16] Gold and silver nanoparticles are commonly used because their plasmonic resonance is located in the visible range of light. Arrangements of nanoparticles are used to provide strong enhancement over large areas. The SERS substrates are designed to show the plasmonic resonance at a specific wavelength matching the excitation wavelength.

In conventional Raman scattering, lasers are used as excitation sources. High-power LEDs were previously reported as excitation sources for Raman scattering in combination with liquid samples.[17,18] In SERS, however, high excitation light powers are superfluous and can even be disadvantageous because of sample damage due to the very strong near fields.[19] Typical laser powers in SERS experiments are in the order of microwatts that can be easily provided by commercial available LEDs. To the best of our knowledge, no experiments were performed to prove the feasibility of Raman identification of molecules with a combined LED-SERS setup. These setups will be interesting for the next generation of hand-held SERS devices and low-budget Raman setups.

Here, we show that the combination of an LED with a SERS substrate opens a new way of Raman spectroscopy.[20] We use a commercially LED and SERS substrate with different Raman probes to show the applicability of our approach. For comparison, we show Raman spectra recorded with a helium–neon (He-Ne) laser at the same wavelength. We investigate four different samples showing the wide range of possible applications for our approach. The variety of samples ranges from different molecules, namely, 5,5-dithio-bis-(2-nitrobenzoic acid) (DTNB), Rhodamine 6G (R6G), and 4-nitrothiophenol (p-NTP), often used in SERS experiments, to carbon nanotubes (CNTs), a one-dimensional solid state system.

2 | EXPERIMENTAL SECTION

Figure 1a shows a sketch of the experimental setup using an LED as excitation source for Raman measurements.
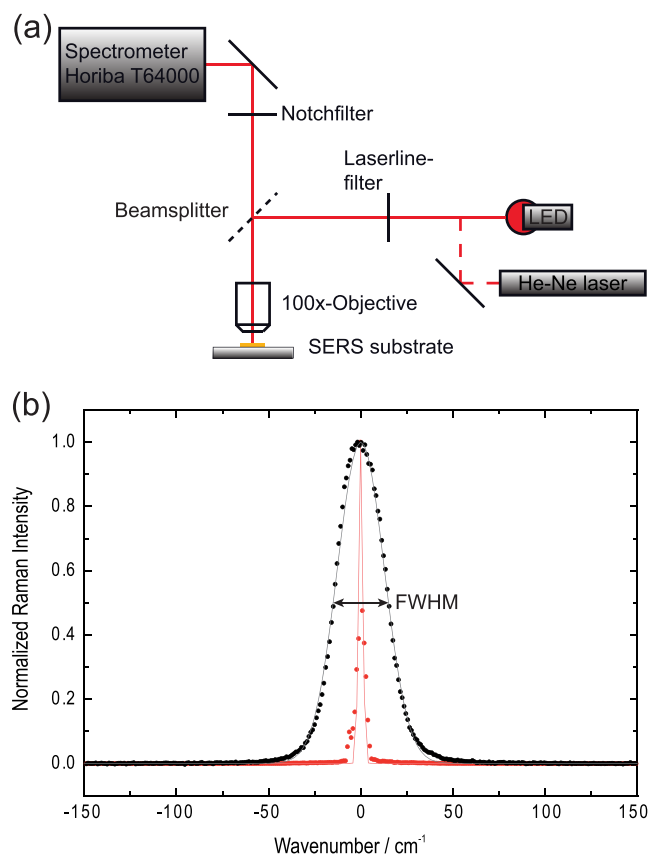

FIGURE 1 (a) Sketch of the used experimental setup. The different samples were measured with a He–Ne laser and an light-emitting diode (LED). (b) Spectra of both excitation sources. Dots are experimental data and lines the Gaussian fits of the laser (red) and LED (black). Central wavelength corresponds to 632.1 nm [Colour figure can be viewed at wileyonlinelibrary.com]

The four different samples were measured with an LED (Thorlabs M625L3, 700 mW with collimator, nominal wavelength 625 nm, bandwidth 17 nm) and with a He–Ne laser (Coherent, 12 mW). The Raman spectra measured with the LED were acquired with 2 µW power on the sample and 30 s acquisition time, whereas the laser provided 14 µW power on the sample with 10 s acquisition time. The power of the laser was reduced by neutral density filters to be comparable to the LED power on the sample. The light passed through a bandpass filter (632.1 nm; full width at half maximum [FWHM] $= (1 \pm 0.2$ nm) and was focused through an $100\times$ objective (NA = 0.9) on the sample. The chosen band pass filter was used in front of both excitation sources. In case of the laser, it suppresses plasma lines. For the diode, it defines the center wavelength and the width of the excitation because the LED emission profile is much broader than that of the laser (see Figure 1). The spot size for the laser is assumed to be less than 1 µm in diameter,[21] although it is larger for the LED because the

LED has inherently a larger divergence than the laser.[1] The setup was used in backscattering configuration. The elastically scattered light was blocked by a notch filter. The inelastically scattered light was dispersed in a Horiba T64000 Jobin Yvon spectrometer (900 gr/mm) used directly in single spectrometer mode and detected with a silicon CCD (Horiba DU420A-OE-323). In Figure 1b, we show the excitation profiles of both sources. The Gaussian fit yields a line width of $FWHM_{LED} = 1.2$ nm (30 cm^{-1}) for the LED and $FWHM_{laser} = 0.1$ nm (3 cm^{-1}) for the He–Ne laser.

For SERS, we used the commercially available Silmeco SERS substrate. It is built up of nanostructured silicon covered with gold. We acquired Raman spectra of DTNB, R6G, p-NTP, and CNTs. The different probes were prepared in solution and dropcasted on the SERS substrate. The concentration of DTNB was $c_{DTNB} = 100$μM, of p-NTP was $c_{p-NTP} = 10$ mM, and of $c_{R6G} = 1.4$ mM. The concentration of the CNTs (ComoCat) is 0.1 g/L. The tubes were debundled and sonicated before deposition.

p-NTP and DTNB are often used as SERS reporter molecules.[22] p-NTP is a designer molecule used in SERS to investigate the plasmonic enhancement of SERS substrates.[22,23] It is often chosen in SERS experiments because it can easily functionalize gold and can therefore report the SERS enhancement. DTNB is another organic molecule that inhibits two Raman modes with the same origin as in p-NTP but in a different chemical environment leading to a different Raman shift therefore both can be distinguished by Raman spectroscopy. One mode originates from the NO_2 group ($\sim$1380 cm^{-1}) and the second from the C–C stretch vibration ($\sim$1600 cm^{-1}) present in both molecules. The third sample is the dye molecule R6G that is often used in SERS experiments as a probe to investigate different chemical reactions and as a biomarker. The last probe system in this work is CNTs. They stand as an example of a one-dimensional solid state system. CNTs are built up of rolled up graphene. Their physical properties depend strongly on their chirality that is visible in differences in their Raman spectrum.[24]

3 | RESULTS AND DISCUSSION

We performed Raman measurements on four different Raman probes on a SERS substrate with an LED and a

He–Ne laser as reference. Figure 2 shows the Raman spectra of the different investigated samples excited with the LED (black) and laser (red) in comparison. The spectra shown in Figure 2 were accounted for the different excitation power and acquisition time. We were able to unambiguously identify the different probes with both excitation sources. The dashed lines in Figure 2 specify the Raman modes whose fit parameters are listed in Table 1. To avoid oversampling in the LED spectra because of the broader excitation profile, we applied pixel binning of four pixels leading to a better signal to noise ration without losing spectral resolution. The Raman peaks were fitted by Lorentzians.

First, we will discuss the peak positions of the different Raman modes. For both excitation sources, we find the modes at the same Raman shift within the uncertainty of the measurement ($\Delta\omega_{pos} = 2$ cm^{-1}) with two exceptions: The N–O mode of DTNB and the C–S mode of p-NTP. Taking a more detailed look at the spectral range of these two modes, we find multiple Raman peaks near them (especially in the spectra recorded with the laser). These additional modes lead to a broadening and shift of the discussed modes in the fitting process. We were able to distinguish the N–O mode of DTNB and p-NTP despite them having the same origin and only differing in Raman spectroscopy because of the different chemical environment of each mode influencing the Raman shift. The best resolution we obtained under LED excitation is between the CNT G$^-$ and G$^+$ mode with 41 cm^{-1}.

Now, we want to discuss the FWHM of the different Raman modes. Generally, broader Raman peaks are observed under LED excitation. The FWHM is larger by a factor that lies between 1.7 (R6G C–C mode at 1309 cm^{-1}) and 3.1 (p-NTP C–S mode at 1083 cm^{-1}). The width of the peaks is determined by the width of the excitation source. In case of the LED, it is limited by the bandpass filter (FWHM = 1 nm), whereas for the laser, it is limited by the laser bandwidth itself. In Figure 1b, the excitation profiles of both sources are shown. The width of the LED (30 cm^{-1}) is resembled in several of the measured peaks, although some Raman modes appear much broader. This might be due to a superposition of more than one Raman mode. A bandpass filter with an even narrower linewidth would lead to an improvement of the resolution.

Finally, we compare the intensities of the different Raman peaks. There are two main observations. The intensity of the Raman spectra measured with the LED are all in the same order of magnitude, whereas there are large differences in the laser excitation (one order of magnitude difference between DTNB and p-NTP). A possible explanation to the relatively large difference between

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[1]We characterized the beam diameter (FWHM) of both excitation sources with a 10× (NA = 0.26) objective. They show a Gaussian profile; Laser: $Laser_x = 6$μm, $Laser_y = 5$μm; $LED_x = 232$μm, $LED_y = 288$μm. The experimental data were acquired with a 100× objective with which we were not able to image the focus of the excitation sources due to the short working distance.
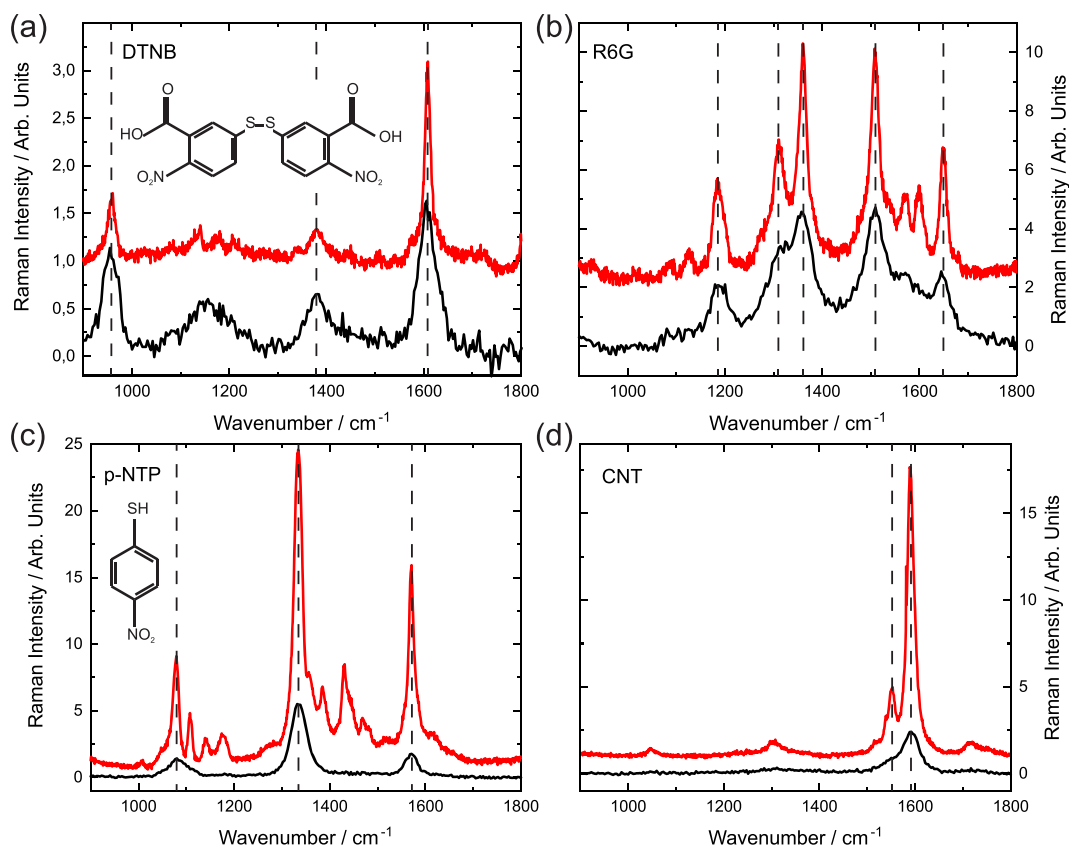
FIGURE 2 Raman spectra of (a) 5,5-dithio-bis-(2-nitrobenzoic acid) (DTNB), (b) Rhodamine 6G (R6G), (c) 4-nitrothiophenol (p-NTP), and (d) carbon nanotubes (CNTs) on the surface-enhanced Raman scattering (SERS) substrate measured with the light-emitting diode (LED) (black) and with the He–Ne laser (red). The spectra are normalized for power and acquisition time. The dashed lines indicate the Raman modes discussed in Table 1. The insets in (a) and (c) show the chemical structures of DTNB and p-NTP, respectively. Spectra are offset for clarity. [Colour figure can be viewed at wileyonlinelibrary.com]

laser and LED excitation is the lower power density in case of LED excitation. The bandpass filter blocks a large part of the spectrum of the LED leading to small power after the bandpass. Additionally, the size of the focus spot might differ for both excitation sources because of a higher divergence of the LED compared to the laser. These two factors lead to a decrease in Raman intensity. The overall similar Raman intensities in case of LED excitation are an indicator that mostly plasmonic-enhanced Raman scattering is observed although in case of laser excitation, additional conventional Raman scattering is observed leading to generally higher intensities.

We compared the four different samples and showed that the Raman spectra measured with the LED reproduce the Raman spectra measured with the laser at the same wavelength reasonably well. The peak positions are the same except for small deviations. The FWHM shows a large difference between the two light sources. The LED spectra show broader peaks in a range between 36% and 59%. The width of the Raman modes of the LED spectra is defined by the used bandpass filter. In the applications requiring high spectral resolution, the width can be reduced by using a filter with smaller bandwidth or other optical techniques to provide a narrower bandwidth.

In order to achieve larger Raman intensities with the proposed LED excitation of a SERS substrate, multiple parameters are important. Although the presented results only use a light intensity on the sample on the order of microwatts, we unambiguously identify the different samples. However, the light intensity on the sample can be improved by downsizing the LED beam diameter with a respective lens or telescope in order to match the size of the input aperture of the objective. A possible way to further enhance the intensity of the Raman signal excited by the LED would be to increase the light power on the sample or to improve the focusing of the light, for example, by using an objective with a higher NA. Further, it would be possible to achieve higher Raman intensities by using spectrometers with higher sensitivity optimized for the used

TABLE 1 Comparison of the Lorentzian fitting parameters of the DTNB, R6G, p-NTP, and CNT Raman spectra measured with the LED and the laser shown in Figure 2

	Mode		Position (cm^{-1})	FWHM (cm^{-1})	Amplitude (cts)
DTNB	C–N	LED	956	38	66
		Laser	958	18	89
	N–O	LED	1385	70	34
		Laser	1379	35	41
	C–C	LED	1606	43	93
		Laser	1608	16	277
R6G	C–C	LED	1188	45	112
		Laser	1186	22	427
	C–C	LED	1309	61	133
		Laser	1311	36	530
	C–C	LED	1360	55	220
		Laser	1361	23	958
	C–C	LED	1508	58	235
		Laser	1509	28	932
	C–C	LED	1648	36	108
		Laser	1650	15	580
p-NTP	C–S	LED	1083	44	82
		Laser	1078	14	1119
	N–O	LED	1336	36	346
		Laser	1336	20	3360
	C–C	LED	1570	33	104
		Laser	1571	12	1757
CNT	G$^-$	LED	1551	48	28
		Laser	1550	18	439
	G$^+$	LED	1592	37	140
		Laser	1591	17	2327

Abbreviations: CNT, carbon nanotube; DTNB, 5,5-dithio-bis-(2-nitrobenzoic acid); FWHM, full width at half maximum; LED, light-emitting diode; p-NTP, 4-nitrothiophenol; R6G, Rhodamine 6G.

wavelength. A grating with lower gr/mm would also increase the Raman intensity significantly. We foresee that using white light LEDs combined with tunable bandpass filters will pave the way for cheap, simple, and fast tools for LED-based resonant Raman scattering.

4 | CONCLUSION

We showed that it is possible to use LED light for micro-Raman measurements. With the combination of a SERS substrate with an LED, we were able to acquire Raman spectra of four different samples comparable with laser excitation. The Raman modes of four different samples DTNB, R6G, p-NTP, and CNTs were unambiguously identified. The LED has a broader excitation profile yielding broader FWHM of the Raman peaks. This article shall point out the applicability of the proposed measurement setup.

In the future, we foresee the possibility to vary the excitation energy by simply changing the LED or use multi color LEDs, with ultranarrow bandpass filter. We envision the use of the combination of LED and SERS substrates for handheld devices and analytics using SERS in a compact low-budget setup providing fingerprint-type information, which will be of high interest for sensing applications.

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