Sub-Micron Spatial Resolution in Far-Field Raman Imaging Using Positivity-Constrained Super-Resolution

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Abstract
Raman microscopy is a valuable tool for detecting physical and chemical properties of a sample material. When probing nanomaterials or nanocomposites the spatial resolution of Raman microscopy is not always adequate as it is limited by the optical diffraction limit. Numerical post-processing with super-resolution algorithms provides a means to enhance resolution and can be straightforwardly applied. The aim of this work is to present interior point least squares (IPLS) as a powerful tool for super-resolution in Raman imaging through constrained optimization. IPLS’s potential for super-resolution is illustrated on numerically generated test images. Its resolving power is demonstrated on Raman spectroscopic data of a polymer nanowire sample. Comparison to atomic force microscopy data of the same sample substantiates that the presented method is a promising technique for analyzing nanomaterial samples.

Keywords
Super-resolution, digital image restoration, Raman spectroscopy, nanomaterials

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Introduction
Super-resolution image reconstruction (SRIR) uses signal processing techniques to overcome the resolution limitation of conventional (optical) imaging apparatus, usually by combining multiple images of the same scene. A multitude of numeric SRIR methods based on different philosophies are available in the literature and various super-resolution algorithms have been employed for SRIR in Raman spectroscopy mapping over the last decade. The application of SRIR to Raman spectroscopy is a promising method that allows distances and objects below the diffraction limit to be resolved using far-field instrumentation, without the added experimental complexity of near-field techniques such as near-field Raman spectroscopy (NFRS) or tip-enhanced Raman spectroscopy (TERS). While the concept of SRIR is already very powerful in itself, it still takes adequate optimization algorithms to unleash its full potential.

A promising approach to SRIR is constrained optimization, which has been successfully applied in image inpainting, non-negative matrix factorization, and achieved great resolution enhancements in digital image restoration, whether the constraint was used explicitly or implicitly by the choice of regularization function.

In this work, a primal-dual method for interior point least squares (IPLS) was used for constrained optimization SRIR. Interior-point least squares was applied to Raman spectroscopic data acquired from a bundle of nanowires made of poly-(3,4 ethylenedioxythiophene) here referred to as PEDOT. Atomic force microscopy (AFM) images were obtained from the same sample area. Atomic force microscopy imaging is not affected by the optical diffraction limit and hence provides a means to evaluate the quality of the super-resolved Raman images.

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The discussion of the results focuses on the resolving power if SRIR, a point that was sometimes ambiguous in related work. The ambiguity arises from the two research disciplines overlapping in Raman SRIR, digital image restoration and microscopy, having slightly different notions of resolution. In digital image restoration, resolution is usually seen as the level of detail contained in an image and often characterized by the sharpness of features in the image, a point of view that has been adopted in previous work on SRIR in Raman imaging. Resolution in microscopy, on the other hand, is defined by the minimal separation between two objects necessary to observe them as distinct objects. Super-resolution image reconstruction results in Raman imaging have not been analyzed from that perspective and while the two points of view are somewhat related, they are not strictly identical.

The aim of this paper is to highlight the difference between these two interpretations of resolution and to demonstrate that Raman SRIR is capable of resolving distances smaller than the diffraction limit in the strict microscopist's sense.

Materials and Methods

Sample Preparation

PEDOT nanowires were synthesized by the hard template method described in a previous paper. The template was an anodic aluminum oxide membrane of (50 ± 1) μm thickness and (100 ± 10) nm pore diameter (Synkera Unikera SM 100-50-13). The pore diameter constrains the diameter of the synthesized nanowires. The sonicated PEDOT nanowires were dispersed in water and drop cast on a silicon substrate.20 The dispersion, as most dispersions of nano-objects in water, is incomplete and the nanowires tend to stick in bundles of different sizes, shapes and numbers of nanowires, although some of them were found isolated (see Fig. 3a).

Instrumentation

Raman spectroscopic measurements were performed using a confocal Raman microscope (Renishaw inVia) with a 532 nm frequency doubled neodymium-doped yttrium aluminum garnet (Nd:YAG) laser as the excitation source. A 100 × 0.85 NA objective lens was used to focus the laser onto the sample and to collect the Raman back scattered light. The laser was linearly polarized along the vertical image axis. Laser power on the PEDOT sample was 0.1 mW with an acquisition time of 0.5 s per spectrum. With these parameters, no bleaching or other photo-induced modification of the sample was observed. The system was operated in high confocal mode to ensure the best lateral resolution was achieved. Raman mapping was conducted under the microscope using a motorized piezo-electric stage (Physikinstrumente Hera P621.2CD XY) in closed loop operation (0.4 nm resolution, 2 nm repeatability). Data were collected by point mapping in a raster scanning fashion and each Raman spectrum is acquired under identical conditions. For this work a 20 nm step size was used.

The Raman system with the piezo stage rests on an optical table that is passively damped; any environmental vibrations were not seen to be a significant issue. Measurement parameters were optimized to reduce measurement times to avoid artefacts originating from other environmental factors such as thermal drift.

Atomic force microscopy was performed with a scanning probe microscope (Bruker Innova) operated in tapping mode. AFM tips used were Olympus AC160TS-10 (OTESPA) AFM tips in visible apex geometry with a side and back angle of 35° ± 1° each, a front angle of 0° ± 1°, and a maximum tip radius of 10 nm. Atomic force microscopy imaging is a high-resolution imaging technique and served as validation of the results obtained using SRIR from the Raman data. For samples with high aspect ratios, and heights exceeding the tip curvature radius, the lateral resolution of the AFM is adversely affected by the tip geometry. Since the diameters of the studied PEDOT nanowires were well in excess of the tip radius, tip geometry effects were visible in the AFM images obtained. Tip geometry effects, however, only broaden the apparent width of objects, while position, height, orientation, and alignment are imaged faithfully and the obtained lateral resolution was still significantly better than that of the diffraction limited Raman microscope.

Super-Resolution Image Restoration

Super-resolution image restoration relies on inverse problem resolution and thus needs three ingredients to work properly: an observation model; an optimization criterion; and a powerful optimization algorithm.

The observation model describes how an ideal high-resolution image transforms into a blurry and noisy image through the distortions imposed by the imaging apparatus and the imaging process. Observation models in digital optical imaging can be written in the compact linear form:

\[ y = \mathbf{H} \mathbf{x} + \eta \]  

Each index of column vector \( y \) corresponds to one of the \( M \) pixels in the low-resolution image. Likewise, each index of the column vector \( \mathbf{x} \) corresponds to one of the \( N \) pixels in the high-resolution picture. The \( M \times N \) matrix \( \mathbf{H} \) is the forward operator which describes the weights with which each pixel intensity in the high-resolution picture \( \mathbf{x} \) affects each pixel intensity in the low-resolution image \( y \). The additive term \( \eta \) accounts for any non-deterministic process during imaging and is usually modelled as independent and identically distributed (i.i.d.) Gaussian noise.
For the present case, the linear degradation $H$ is factored into two terms:

$$H = H_2 H_1$$

(2)

$H_1$ corresponds to a two-dimensional (2D) convolution with the microscope’s point-spread function (PSF) and $H_2$ represents downsampling. The former is ubiquitous in microscopy and gives rise to the well-known diffraction limit in conventional optical microscopes. The PSF depends on the specifications of the instrument and will be determined experimentally below.

If the high-resolution image $x$ has more pixels than the observed low-resolution image $y$, a decimation or downsampling operation $H_2$ has to be included in the observation model. Conversely, its transpose $H_2^T$ is known as upsampling and describes the manner in which pixels are added to the low-resolution image. The upsampling operation $H_2^T$ is dependent on the pixel dimensions of the high-resolution image which in most cases can be chosen as desired. The corresponding downsampling operation $H_2$ is found by transposition. Additional pixels can be added with equal spacing along each dimension between existing pixels in the low-resolution image $y$. The point mapping nature of the confocal imaging process means that there is a one-to-one correspondence between the low-resolution image pixels and a subset of the pixels in the high-resolution image. Figure 1 shows the case where two high-resolution pixels are inserted between each two low-resolution pixels along each dimension.

Super-resolution image restoration in this paper is performed using IPLS. The optimization criterion solved is

$$\hat{x} = \arg \min_x (y - Hx)^T (y - Hx)$$

(3a)

$$s.t. \ x \geq 0$$

(3b)

The positivity constraint on the pixel intensities, Eq. 3b, reflects the natural assumption that abundances of scattering sources can only be non-negative. Given $y$ and $H$ are known, Eq. 3 can be solved by a primal-dual optimization method for IPLS. Super-resolution image restoration via Eq. 3 on numerically generated test data with known degradation $H$ is demonstrated in the supplemental material.

**Point-Spread Function Measurement**

The instrument’s PSF enters the forward operator $H$ through $H_1$ (Eq. 2). Because $H$ must be known for solving Eq. 3, the PSF of the instrument has to be determined before any SRIR. The Raman microscope used in this work probes the sample with an excitation laser. It can be reasoned from the beam shape of lasers in resonators, the subsequent optics, and the response function of optical microscopes that the intensity profile of the PSF is approximately Gaussian. A general 2D Gaussian takes three independent parameters, but from the symmetry of the instrument’s configuration, it can be assumed that its functional dependency factorizes along the stage axes. Thus, the PSF is sufficiently described by

$$p(r_x, r_y) \propto \exp \left( - \frac{r_x^2}{2 \sigma_x^2} - \frac{r_y^2}{2 \sigma_y^2} \right)$$

(4)

where $r_x$ and $r_y$ are the coordinates along the stage axes. This is supported by the data shown in Fig. 2. The parameters $\sigma_x$ and $\sigma_y$ in Eq. 4 were determined experimentally using the step-edge criterion.

The laser was scanned over the edge of a gold pad deposited on a silicon substrate (Fig. 2a and 2b). Raman scattering only occurs when laser light falls on the silicon and not on the metallized region. The resulting intensity profile is a one-dimensional line integral of Eq. 4 that can be modelled by:

$$\phi(r, a, b, \mu, \sigma) = a + \frac{b}{2} \left( 1 + \text{erf} \left( \frac{r - \mu}{\sqrt{2}\sigma} \right) \right)$$

(5)

For horizontal and vertical step edges, $\sigma$ in Eq. 5 is equal to $\sigma_x$ and $\sigma_y$ in Eq. 4, respectively. Figure 2 shows the peak area profile of the principal silicon Raman peak across a horizontal and vertical step-edge. The peak area was calculated by integrating the Raman signal from 480 cm$^{-1}$ to 562 cm$^{-1}$ in the wavenumber domain, which contains the principal Raman peak of silicon (found at 520.7 cm$^{-1}$). Before integration, a linear background was subtracted from each spectrum to remove any interfering fluorescence signal. Equation 5 is fit to each of the profiles and the values obtained for $\sigma$ are:

$$\sigma_x = (202.2 \pm 4.9) \text{ nm}$$

(6a)
These correspond to a full width half-maximum (FWHM) of

\[ \text{FWHM}_x = (476.1 \pm 11.5) \text{ nm} \]  

(7a)

\[ \text{FWHM}_y = (362.9 \pm 15.8) \text{ nm} \]  

(7b)

which can be used as a measure for the minimum resolvable distance of the instrument in the respective direction (see Supplemental Material for more details). The Raman data for PSF measurement were acquired with 20 mW laser power at 532 nm, 0.2 s acquisition time per spectrum, and 20 nm step size.

Raman and Atomic Force Microscopy Mapping of PEDOT Nanowires

An optical image of the PEDOT nanowire sample area is shown in Fig. 3a. A map of 1.2 \times 1.2 \mu m is collected from within the red rectangle displayed. The Raman data of PEDOT nanowires are acquired with 0.1 mW laser power at 532 nm, 0.5 s acquisition time per spectrum, and a step size of 20 nm along each stage axis. Figure 3b shows a PEDOT Raman spectrum. The two main peaks at 1437 cm\(^{-1}\) and 1518 cm\(^{-1}\) are attributed to the symmetric and anti-symmetric vibration modes of the aromatic C=C bond, respectively.\(^{19}\)

The Raman intensity of the spectral channel centered at the peak position of the dominant C=C peak (1437 cm\(^{-1}\)) is plotted as a heat map over the sampling area in Fig. 4a. An AFM map of size 3 \times 3 \mu m covering the area probed by Raman spectroscopy was acquired for comparison. The number of sampling points was 512 \times 512, resulting in a pixel size of approximately 6 \times 6 nm. The measured height across the Raman probed area is shown in Fig. 4b. Two nanowires separating from each other at the top of the mapping area, as visualized in Fig. 4b, cause the spatial broadening of the Raman signal perpendicular to the direction of the wire observed in Fig. 4a. However, the separation of the two wires within the sampling areas is smaller than any of the minimum resolvable distances of the Raman microscope, Eq. 7, and hence they cannot be directly observed as individual wires.

Image Restoration Results

With knowledge of the PSF parameters in Eq. 6, \(H_1\) in Eq. 2 is fully specified and Eq. 3 can be solved for the Raman map data of Fig. 4a for different choices of \(H_2\). The first choice was identity, resulting in a pixel size of 20 \times 20 nm (20 nm' for brevity, Fig. 5a), identical to that in the observed Fig. 4a. The second choice was such that the resulting pixel size was 10 \times 10 nm (10 nm' for brevity, Fig. 5b).

The properties of the SRIR results can be examined along the sections S1 and S2 shown in Fig. 5. The corresponding line profiles obtained by linear interpolation are shown in Fig. 6. The super-resolved Raman images in Fig. 5 do not match perfectly with the AFM image in Fig. 4b, but they illustrate the position, alignment, and orientation of the nanowires in good agreement with this image. They are much sharper.
Discussion

Sharpness and Resolution

Downsampling in the forward operator of single-frame super-resolution renders the unconstrained optimization problem Eq. 3a ill-posed. In multi frame super-resolution, this is compensated by the acquisition of multiple low-resolution images resulting in a total number of observed pixels that is equal to or larger than the number of pixels in the super-resolved image, thus reinstating well-posedness. In the present work, lost high spatial frequency information was recovered by the positivity constraint (Eq. 3b) and its implementation through primal-dual ICLS. This allowed for the reconstruction of the sharp high-resolution image (Fig. 5b) with a 10 nm pixel size from just a single observation in Fig. 4a with a 20 nm pixel size. Comparison of Fig. 5a and 5b, as well as the line profiles of Fig. 6, show that the super-resolved image with the 10 nm pixel size is much sharper than that with the 20 nm pixel size. While this is a very exciting result from an image restoration point of view, detailed analysis reveals the gain in sharpness does not necessarily correspond to a gain in resolution.

The edges in the line profiles shown in Fig. 6a and 6b have widths well below 50 nm for both high-resolution images shown in Fig. 5. However, this does not mean that the obtained resolvable distance is 50 nm or smaller in each case. This is illustrated along the area A1 in Fig. 5, where the SRIR results only show one nanowire with high intensity, while the corresponding AFM image in Fig. 4b clearly shows 2–3 wires in the same area. The SRIR results show two separate nanowires only in areas where the two wires are separated further than the SRIR minimum resolvable distance, which can be estimated from the line profiles along the section S1 in Fig. 6a. The two peaks observed correspond to two different nanowires that can be distinguished as two different objects. The peak-to-peak distance between their maximum intensities is 189.8 nm and 186.0 nm for 20 nm and 10 nm pixel sizes, respectively. For point-like objects, this would give a
measure of the spatial resolution. However, as known from the fabrication process and confirmed by AFM in Fig. 4b, we are dealing with objects of finite size and a more suitable measure would be their edge separation. Since their edges are not sharp, the edge positions were chosen to be at $1/e$ times the peak intensities. The resulting edge separations are 113.2 nm and 126.6 nm for 20 nm and 10 nm pixel sizes, respectively, which is much larger than the observed width of edges for both cases. Although the width of edges and other features, which determines the sharpness of an image, puts a lower bound on the minimum resolvable distance, resolution and sharpness are two distinct properties and thus should be treated as such. Further, the apparent increase in sharpness in the 10 nm pixel size super-resolved image compared to the 20 nm pixel size one is not reflected in the achieved minimum resolvable distance.

This, however, should not obscure the satisfying result that the larger minimum resolvable distance, 126 nm, is about a factor of three smaller than $FWHM_\lambda = 362.9$ nm, the smallest value obtained for the instrument’s minimum resolvable distance.

**Comparison to Atomic Force Microscopy Image**

Despite the enhanced resolution, SRIR images still mismatch with the AFM image for a number of reasons. The minimum resolvable distance in AFM is well below 10 nm (for objects of similar height), i.e., much lower than the one achieved by SRIR. And even though AFM has much higher intrinsic resolution than optical microscopy, it cannot serve as a ground truth as AFM images can be blurred by tip geometry effects.\textsuperscript{24–26} Furthermore, Raman spectroscopy and AFM measure fundamentally different material properties, so even if both techniques had indefinite resolution, identical images would not be expected (AFM, for instance, would not reveal any embedded nanoheterogeneity).

**Resolution Enhancement and Regularization**

Resolution enhancement in SRIR is often achieved with the help of regularization, which is simply adding a term of the form $\lambda \phi(x)$ to the optimization criterion (Eq. 3a). Initially used as a heuristic to suppress noise artefacts in the
restoration process, Bayesian analysis has managed to connect the regularization function \( \phi(\cdot) \) to prior knowledge about the super-resolved image. The regularization parameter \( \lambda \) is usually chosen depending on the noise level in the observed low-resolution image. It has been recognized early that a large amount of prior information can be used to increase the resolution by a large amount. An excellent example from fluorescence imaging demonstrates the power of aptly chosen regularization while simultaneously hinting at the difficulties involved in arriving at such an apt choice. The drawback of using regularization is that prior information may not always be available to a sufficient degree; even if it is, the choice of corresponding regularization function \( \phi(\cdot) \) and parameter \( \lambda \) may not be straightforward.

In the present paper, regularization was incorporated by the positivity constraint rather than by a choice of regularization function \( \phi(\cdot) \). Noise suppression and high spatial frequency estimation were achieved by the positivity constraint (Eq. 3b) and primal-dual IPLS alone. This allows for SRIR of images for which no information about the super-resolved image is available a priori, apart from the generic assumption that the resulting pixel intensities should be positive. Simultaneously, if any additional prior knowledge about the super-resolved image is available, it can be straightforwardly implemented via a regularization term in Eq. 3a. This makes constrained optimization via primal-dual IPLS a powerful and flexible tool for SRIR.

Below the Sampling Step Size

The information received from a scanning stage microscope is band limited with the cut-off frequency given by the inverse of the sampling step size. This means that by utilizing the information received from the imaging process only, it is impossible to resolve objects separated by less than a step size. By choosing appropriate constraints and regularization, we are no longer restricted by the information theoretic limit as these provide a mean to estimate Fourier coefficients above the cut-off frequency which, when aptly chosen, can push resolution enhancement even further.

In the case of the present experiment, this can be observed in the line profile along section S2 (Fig. 6b). The profile of the 20 nm pixel size super-resolved image shows one peak whereas two peaks are clearly distinguishable for the 10 nm pixel size, indicating additional information might have been recovered. The nature of the variation remains uncertain, but we consider two likely explanations. The presence of additional nanowires is ruled out by the AFM image, which clearly shows one wire in the corresponding area. However other features are possible that would reduce the Raman intensity in this area. These include local contamination, defects, and potentially cracking. It also must be taken into consideration that this gap could be an artefact generated by the restoration method. Artefacts occur in high-resolution images if there is insufficient noise suppression in the restoration algorithm or if there are any effects impacting on the observed image, such as thermal drift or micro-mechanical oscillations, that are unaccounted for in the forward model (Eqs. 1 and 2).

The primary aim of this work was only to go beyond the intrinsic diffraction limit of the confocal Raman microscope. The occurrence of sub-step size separations in the super-resolved image (Fig. 5b) should only give an idea of the possibilities when the full power of SRIR is unleashed. However, when going to smaller scales, especially below the sampling step size, one needs to consider that the forward model accounts for all imaging relevant processes occurring at the scale of the desired resolvable distance.

Conclusion

We have successfully applied SRIR to Raman data of PEDOT nanowires. A conservative estimate suggests an enhancement in spatial resolution of about a factor 3 relative to the confocal Raman microscope’s intrinsic resolution. The minimum resolvable distances of 360 nm and higher in the raw data have been reduced to 125 nm and lower by application of SRIR. The gain in resolution through SRIR constitutes true super-resolution in the microscopist’s sense of resolution as it has been demonstrated on objects that are unresolved in the raw data. The high-resolution images obtained through the proposed SRIR method, primal-dual IPLS, show satisfactory agreement when compared to AFM data of the same scene.

The raw data were acquired using a conventional Raman microscope equipped with a motorized piezo stage. No near-field spectroscopic techniques such as NFRS or TERS were involved, thus adding no complexity to the experimental setup and avoiding any kind of electronic interaction with the sample material.

In addition, we demonstrated and discussed the potential of primal-dual IPLS to resolve distances below the raw data sampling step size of 20 nm. Faithful SRIR at such small scales would require thorough thermal and mechanical stabilization during the measurement process and will be the subject of a future investigation.

Further, the SRIR results of this paper were generated by processing data from only one spectral channel of the Raman microscope. Data from multiple channels would allow for the retrieval of chemical information with high spatial resolution and perhaps for further reduction of the minimum resolvable distance through SRIR with primal-dual IPLS. These would be desirable results as they would not require any additional measurements or experimental complications and will be addressed in future publications.

Conflict of Interest

The authors report there are no conflicts of interest.
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Supplemental Material

All supplemental material mentioned in the text is available in the online version of the journal.

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