Fluctuation imaging of nanoscale disorder in monolayer semiconductors

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Two-dimensional materials have great potential in the fields of electronics, optoelectronics, and photonics. Monolayer semiconductors are particularly interesting because they host excitons that dominate the optical properties even at room temperature. The electric field of the excitons extends outside the monolayer, making them sensitive to the surroundings of the monolayer. Disorder in these surroundings can thus cause instability in the excitonic fluorescence over time, which is generally detrimental for devices. Here, we adapt a fluctuation-based super-resolution technique to image localized exciton fluctuations in monolayer semiconductors. Fluctuation imaging enables localization of fluctuating spots on an otherwise continuous monolayer with constant fluorescence. The fluctuating spots correspond with interface disorder measured by atomic force microscopy (AFM). We investigate the role of different material combinations and interfaces on the fluctuations by comparing different substrate materials. Hyperspectral imaging provides additional insight into the disorder behind the fluctuations. Our results show that fluctuation imaging can detect similar features to AFM and hyperspectral imaging, while being faster and simpler to implement. Therefore, it is a promising method for quickly evaluating the quality of monolayer semiconductors and their interfaces with other materials, including nanostructures such as metasurfaces or nanophotonic devices.

1. Introduction

Two-dimensional semiconductors, in the form of transition-metal dichalcogenides (TMDs), are layered materials. The bulk crystals of these materials consist of two-dimensional layers bonded together by van der Waals bonds. These layers can be separated by exfoliation, reducing the crystal to a single layer with a thickness below one nanometer. Monolayers of TMDs have a wide range of applications, including optoelectronic applications such as detectors or emitters [1], [2]. The ultrathin character of these materials can be exploited for downsizing components and imparts them interesting properties in some areas of electronics. For example, the high spin-orbit coupling of these materials can be utilized in spintronics, where the spin state of electrons is used as an extra degree of freedom beyond conventional electronics [3]. Additionally, with the direct bandgap at the K and K' point for a monolayer TMD, an extra degeneracy is available, which is exploited in the field of valleytronics that uses the valleys as an additional degree of freedom similar to the electron spin in spintronics [4].

The two-dimensional nature of TMD monolayers results in confinement of the excited electrons and holes, leading to strongly enhanced Coulomb interactions and the formation of stable excitons, even at room temperature. The excitons inside a monolayer consist of an electric field that is not confined to the monolayer itself but can probe its nanoscopic surroundings. Although this sensitivity is useful in sensing applications, the effect of disorder, such as residue, strain, crystal defects, or doping, can be significant. A schematic of a monolayer in the presence of different types of disorder is shown in Figure 1. These sources of disorder can locally induce effects such as band bending, charge trapping, or exciton funneling, which affect the stability of the excitons and, consequently, the performance of devices [5], [6].

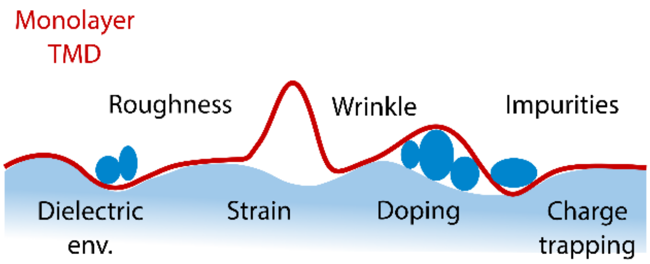

Figure 1: Schematic of different origins of disorder in a monolayer and their influence on the monolayer.

Several methods are available to evaluate the quality of monolayers and their interfaces, including atomic force microscopy (AFM) and scanning electron microscopy (SEM). Optical techniques like exciton lifetime imaging, excitonic fluorescence spectral analysis, or Raman mapping also exist[7]. However, these techniques are slow and not scalable, which limits their use on the device and wafer scales.

Here, we demonstrate a novel method based on measuring excitonic instability directly utilizing exciton fluorescence fluctuations. Previous work has shown that the fluorescence of a TMD monolayer fluctuates in intensity, similar to quantum dot blinking [8]. Here, we present a rigorous method to quantify and image the strength of these fluctuations and correlate the fluctuations with AFM, resulting in the localization of the same disordered areas. This fluctuation imaging technique only requires fluorescence videos of a few minutes taken with a commonly available widefield microscope, making it a more scalable quality-control method for monolayer semiconductors and their heterostructures as found in electronic, optoelectronic, and nanophotonic devices.

2. Fluctuation imaging

Within the field of super-resolution imaging, fluctuations are commonly used to extract finer spatial information about the imaged object, allowing for an increase in resolution beyond the diffraction limit. Similar methods can be employed for the use case of monolayer TMDs, resulting in the mapping of fluctuations. Our method is based on a super-resolution method called super-resolution optical fluctuation imaging (SOFI) [9], which involves video data-processing based on autocorrelations at different time delays of every pixel. Furthermore, additional virtual pixels are added by cross-correlations between neighboring pixels. The method yields a measure for the fluctuation strength. To quantitatively compare fluctuations across the full image, which can contain different fluorescence intensities, we divide the results by the time-averaged intensity. In its most basic form, this method is the same as the standard deviation divided by the mean.

The fluorescence of a monolayer TMD (WS_2 in Figure 2) clearly fluctuates more compared to a stable fluorescent film used as a reference to measure system noise. It is evident that the standard deviation divided by the mean is much larger for the WS_2 monolayer than for the stable reference. A potential drawback of this approach is that regions with insufficient illumination may exhibit fluctuations entirely dominated by detector noise. Furthermore, dividing by the mean fluorescence results in a divergence of the computed fluctuations for dark areas like the background. To circumvent this problem, we employ fluorescence intensity thresholding.

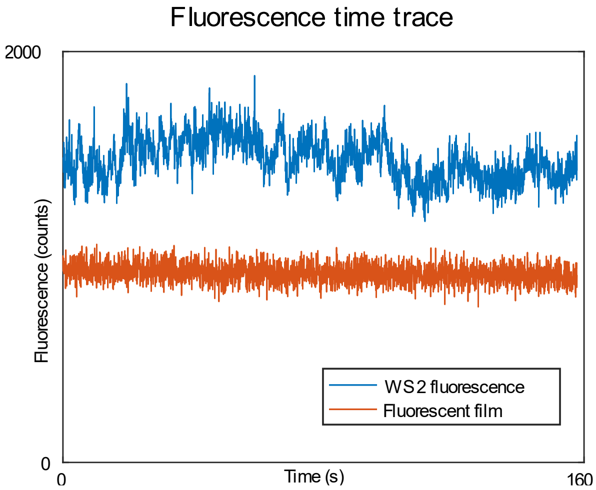

Figure 2: Fluorescence fluctuations on a WS_2 monolayer compared to a reference stable fluorescent dye

3. Results

The fluorescence of a WS_2 monolayer was analyzed using the fluctuation imaging technique, as shown in Figure 3. Upon comparing the time-averaged fluorescence and the fluctuation map, it is clear that fluctuation imaging resulted in improved contrast, revealing additional spots that were initially buried in the background. The same spots are also identified in AFM measurements of the same monolayer area. It is worth noting that AFM can detect disorder caused by impurities, bubbles, or substrate roughness by measuring height variation. In contrast, the fluctuations depend on exciton instability, which can be a more direct indicator of the optical and electronic quality of the monolayer sensitive to other effects such as charge trapping or changes the dielectric environment under the monolayer.

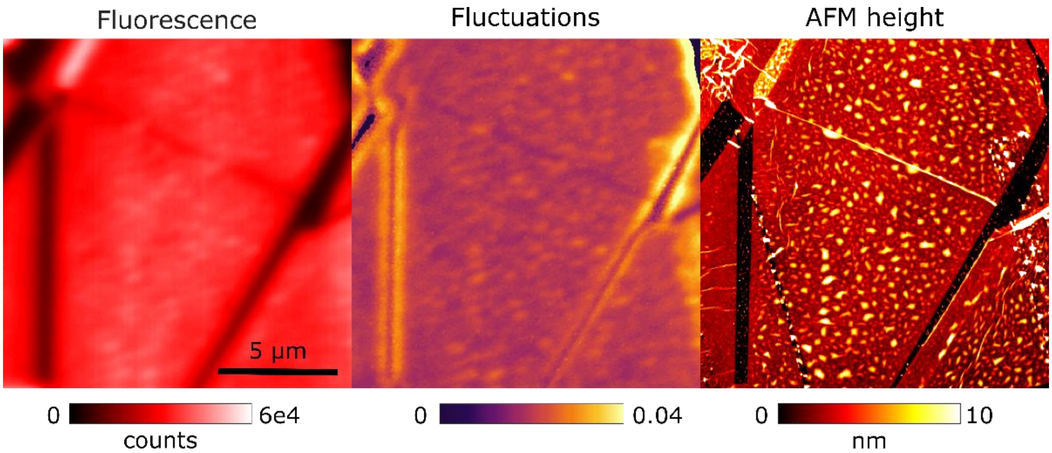

Figure 3: Fluctuation imaging identifies disorder in a WS_2 monolayer. Comparison between time-averaged fluorescence, fluctuation imaging, and AFM for a monolayer WS_2

4. Conclusion

Monolayer semiconductors, such as TMDs, have numerous applications. However, their two-dimensional nature makes them vulnerable to disorder in the surroundings and material, which often limits their performance. Although several methods can be used to measure the quality of a monolayer TMD, most of them are poorly scalable to large-area monolayers or devices. Fluctuation imaging, on the other hand, is a simpler technique that only requires a camera-based fluorescence microscope. Our results show that fluctuation imaging can quickly detect features that would take longer to characterize using more complex equipment, such as AFM or hyperspectral imaging. Therefore, it is a promising method for fast evaluation of the quality of monolayer semiconductors and their interfaces with other materials.

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