

Nanoscale Chemical Characterization of Novel Semiconductor Materials using Tip-Enhanced Optical Spectroscopy

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Advancement of next-generation optoelectronic devices and organic photovoltaic (OPV) technologies is underpinned by the development of innovative nanoanalytical tools. In this article, I discuss how our research tackles this challenge by focusing on nanoscale characterization of cutting-edge semiconductor materials including two-dimensional (2D) transition metal dichalcogenides (TMDs) and OPV devices with a unique combination of tip-enhanced optical spectroscopy (TEOS) and electrical-mode atomic force microscopy (AFM). For nanoanalysis of 2D TMDs, we successfully applied TEOS to visualize the distribution of exciton and trion quasiparticles in semiconductors like single-layer (1L) MoS₂, achieving 20 nm-resolution for the first time. Furthermore, by combining TEOS with Kelvin probe force microscopy, we delved into the behavior of grain boundaries in 1L WSe₂, uncovering how their orientation impacts electronic and excitonic properties. For nanoanalysis of OPV devices, we introduced a novel method called simultaneous topographical, electrical, and optical microscopy (STEOM) by combining TEOS with photoconductive-AFM. This allowed us to simultaneously study the surface topography, chemical composition, and electrical properties with sub-20 nm spatial resolution. By applying STEOM to an operating OPV device, we demonstrated direct correlations between surface morphology, nanoscale molecular distribution, and macroscopic device performance. The novel results presented in this article expand the capabilities of optical nanospectroscopy and nanoimaging, shedding light on excitonic processes, material heterogeneity, and device behavior, offering insights crucial for the development of next-gen semiconductor devices. We believe our research in nanoanalytical technologies will facilitate rapid advancements in this field.



Introduction

The field of semiconductor devices is rapidly advancing, driven by the demand for high-performance optoelectronic technologies. Two-dimensional (2D) transition metal dichalcogenides (TMDs) and organic photovoltaic (OPV) devices are at the forefront of this revolution. 2D TMD semiconductor materials are composed of a single layer of transition metal atoms (Mo, W, Ga) sandwiched between two chalcogenide atoms (S, Se, Te). They possess unique physical properties, including high electron mobility, large exciton binding energy, and substantial spin-orbit splitting energy. These characteristics make them highly promising candidates for applications in novel optoelectronic devices. Our research specifically focuses on two important members of the 2D TMD family: Single layer (1L) MoS₂ and 1L WSe₂. The exceptional electronic and optical properties of 1L MoS₂ have generated enormous interest for use in 2D optoelectronics, such as photodetectors, solar cells, and light-emitting devices^[1]. Unlike graphene, which is a zero band-gap material, MoS₂ exhibits a transition from an indirect band structure in bulk form to a direct band in its 1L structure. This transition results in strong photoluminescence (PL) through excitonic processes. However, the PL process is strongly influenced by various factors, including the local environment, substrate, capping layers, adsorbed molecules, and defects. These factors create non-uniformity within and on the surface of 1L MoS₂, leading to inhomogeneous charge transfer and significant impact on the local population of exciton (exciton) and trion (charged exciton) quasiparticles. To investigate and map these excitonic processes at the nanoscale, we utilized a powerful nanoanalytical tool

called tip-enhanced optical spectroscopy (TEOS) that surpasses the limitations of the conventional optical techniques.

Similarly, 1L WSe₂ has attracted significant attention in recent years due to its outstanding optoelectronic properties, positioning it as a promising candidate for various applications, including ultrafast photodetectors, spintronics, light harvesting, light-emitting diodes, and quantum light sources^[2]. However, the 1L WSe₂ sheets prepared using chemical vapor deposition are usually polycrystalline in which electronic and excitonic properties are critically influenced by grain boundaries (GBs). Moreover, visualization of the optoelectronic behavior of GBs in the TMDs at nanometer length-scales remains beyond the sensitivity and spatial resolution of the conventional analytical techniques.

Over the last two decades, TEOS, specifically tip-enhanced Raman (TER) and tip-enhanced photoluminescence (TEPL) spectroscopies, have emerged as powerful nanoanalytical tools^[3-5]. These techniques overcome the limitations of low sensitivity and spatial resolution of conventional optical analytical tools. By utilizing localized surface plasmon resonance (LSPR) at the apex of a metallic tip, TEOS enhances and confines the electric field to a nanoscopic volume as illustrated in Figure 1. This enhancement enables the observation of excitonic and phononic processes at the nanoscale through intensified local PL and Raman signals. In our first study of 2D TMDs, we employed hyperspectral TEPL imaging to map excitonic processes, including excitons and trions in 1L MoS₂^[6]. We achieved an unprecedented spatial resolution

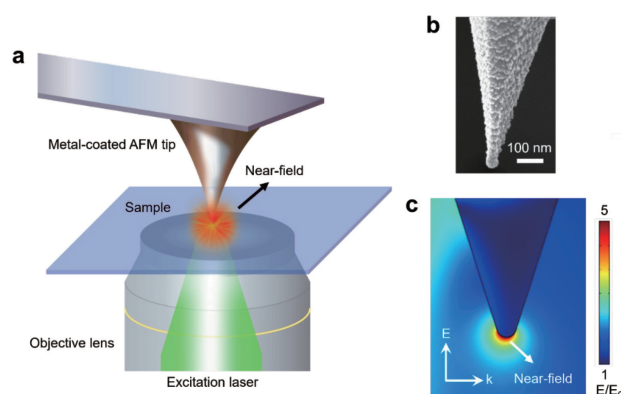


Figure 1 Principle of tip-enhanced optical spectroscopy. (a) A metallic atomic force microscopy (AFM) or scanning tunneling microscopy (STM) tip is placed in the excitation laser spot of an optical microscope. A highly intense electric field localized to a nanoscopic volume (also called near-field) is generated at the tip-apex via LSPR effect, which enhances Raman and PL signals from the sample underneath. By scanning the sample with the near-field, nanoscale Raman and PL images are generated. (b) Scanning electron microscopy image of a representative silver coated AFM TERS probe. (c) Simulated image of the electric field enhancement and localization at the apex of a silver tip. Excitation laser: 532 nm. Figure adapted from reference [8].

of 20 nm, surpassing the confocal optical resolution by a factor of 18. In our second study, we went a step further and demonstrated in situ multiparameter investigation of the optoelectronic behavior of GBs in 1L WSe₂ with 50 nm resolution using an innovative combination of light-sensitive Kelvin probe force microscopy (KPFM) and TEOS^[7].

In addition to 2D TMDs, our research also addresses the nanoscale characterization of OPV devices. OPV devices have experienced a significant increase in efficiency in recent years, driven by a growing recognition of the crucial role played by the nanomorphology of the active layer in determining device performance^[9]. An OPV device comprises two electrodes enclosing an active layer, which is a blend of organic semiconductor materials such as a conjugated polymer (Donor) and a fullerene derivative (Acceptor). Light absorption generates bound excitons that must be dissociated at the Donor-Acceptor heterojunction for efficient charge generation. However, the limited exciton diffusion length in organic semiconductors necessitates optimizing the domain structure within the Donor-Acceptor blend films. This optimization entails achieving efficient charge generation (via exciton dissociation) by controlling the domain structure while ensuring well-connected pathways for charge collection. Coarse phase-separated morphologies (>100 nm) in Donor-Acceptor blends yield low device efficiency due to inadequate charge generation. On the other hand, excessive intimate phase mixing hampers device performance due to inefficient charge collection.

Previous studies have utilized surface imaging techniques like AFM to correlate solar cell performance with the apparent size of observed phase-separated domains. However, the rationale behind relating domain size to device performance lacks consistency and is poorly understood due to the lack of correlative molecular information. Furthermore, conventional optical techniques are limited in their sensitivity and spatial resolution, making it challenging to achieve nanoscale characterization. To address these challenges, we introduced a novel methodology called “simultaneous topographical, electrical, and optical microscopy” (STEOM), which combines TEOS with photoconductive-AFM (PC-AFM) enabling simultaneous characterization of the topographical, electrical, and optical properties of OPV devices at the nanoscale^[10]. This innovative approach provides rich correlative information, enabling a comprehensive understanding of the intricate interplay between the local nanomorphology, chemical composition, and photocurrent generation.

Results and Discussion

Nanoscale Characterization of 2D TMDs

In our first study of 2D TMDs, we applied hyperspectral TEPL and TERS imaging techniques to investigate 1L MoS₂ (Figure 2(a)) at the nanoscale for the first time^[6]. In 1L MoS₂, light absorption generates exciton and trion quasiparticles, which are schematically depicted in Figure 2(b). The relative population and energy of the excitons and trions can be measured from the optical spectrum of 1L MoS₂, which is depicted in Figure 2(c). The optical spectrum also shows Raman bands, which provide fingerprint information about the vibrational modes. We first examined the effect of silver- and gold-coated AFM probes on the local excitonic processes and electronic population in 1L MoS₂. The silver-coated probes exhibited enhanced trion signals in TEPL measurements, while the gold-coated probes displayed enhanced neutral exciton signals. These disparate behaviors resulted from the lower work function of silver (4.3 eV) and the higher work function of gold (5.1 eV) compared to 1L MoS₂ (4.7 eV).

Using hyperspectral TEOS imaging, we demonstrated combined nanoscale Raman and PL imaging of a 1L MoS₂ sheet for the first time as shown in Figures 2(d) and (e). Furthermore, hyperspectral TEPL imaging allowed visualization of the spatial distribution of neutral excitons and trions in the 1L MoS₂ sheet. Intriguingly, excitons and trions exhibited distinct spatial characteristics at the nanoscale. While trions appeared uniformly distributed across the pristine 1L MoS₂ sheet (Figure 2(f)) excitons displayed significant spatial variations (Figure 2(g)). These results suggest that local environmental factors, including the substrate, adsorbates, and structural defects, contribute to non-uniform variations in exciton and trion populations in 1L MoS₂ that can potentially impact the performance of excitonic devices such as excitonic interconnects. Furthermore, we achieved an unprecedented spatial resolution of 20 nm in TEPL imaging, highlighting the capability of this powerful nanoanalytical tool to provide valuable insights into local changes in the distribution of excitons and trions within 1L MoS₂.

In our second study, we joined forces with Dr. Ophélie Lanery and Dr. Marc Chaigneau of Horiba Scientific, France to advance the current state-of-the-art in nanoscale characterization of 2D TMDs. We examined the in-situ light-sensitive electronic and excitonic behavior of GBs in merged 1L WSe₂ sheets with a unique combination of TEOS and KPFM using the experimental setup depicted in Figure 3(a)^[7]. An optical image of the 1L WSe₂ sheets grown using chemical vapor deposition (CVD) is shown in Figure 3(b). Using in-situ TEOS and KPFM imaging, we were able to obtain correlative TEPL, topography, surface potential and capacitance images of the same 1L

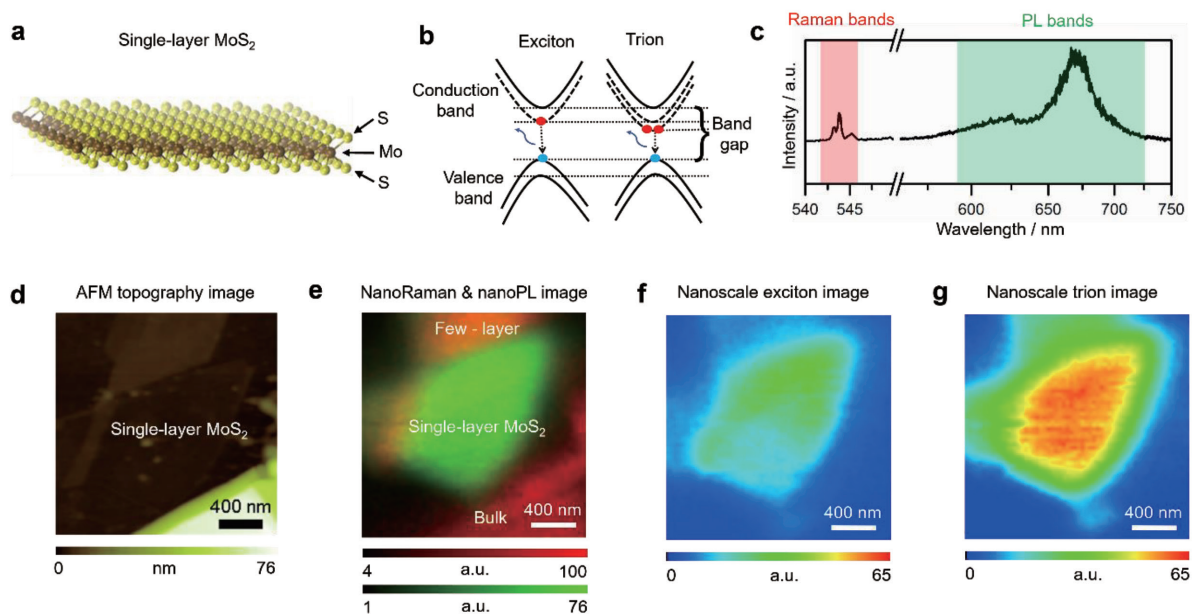


Figure 2 Nanoscale imaging of excitonic processes in 1L MoS₂. (a) Schematic illustration of a 1L MoS₂ sheet, which consists of a layer of Mo atoms sandwiched between two layers of S atoms. (b) Schematic illustration of the exciton and trion formation in 1L MoS₂. Exciton formation occurs when photon absorption generates an electron-hole pair in the conduction and valence bands of 1L MoS₂. Trion formation occurs when photon absorption generates a quasiparticle where two electrons in the conduction band are bound to one hole in the valence band. Trions are also called charged excitons and have lower energy than excitons. (c) Optical spectrum of 1L MoS₂ displaying Raman and PL bands. Raman bands provide fingerprint information about the vibrational modes, whereas PL bands provide information about the relative population and energy of excitons and trions in 1L MoS₂. (d) AFM topography image of a 1L MoS₂ sheet on glass substrate prepared via mechanical exfoliation. (e) Overlay of the TERS (red) and TEPL (green) images of the 1L MoS₂ region shown in Panel d. A strong PL signal is observed at the location of 1L MoS₂. TEPL images of the (f) exciton and (g) trion signals in the 1L MoS₂ region shown in Panel d. Figure adapted from reference [6].

WSe₂ sample as shown in Figures 3(c-f), respectively. A zoomed-in TEPL image of the 1L WSe₂ sample is shown in Figure 3(g). Through correlative topographical, TEPL and electrical imaging with 50 nm spatial resolution, we discovered that the optoelectronic behavior of GBs in 1L WSe₂ is governed by the orientation of the merged sheets. GBs exhibiting tilt angles of 14°, 18°, 38°, 40°, and 60° demonstrated different electronic and excitonic behaviors at the nanoscale. Specifically, the 14°, 38°, and 40° GBs exhibited a comparatively higher work function, lower capacitance, and greater PL quenching than the 18° and 60° GBs. To comprehend this intriguing behavior, density functional theory (DFT) calculations of the GBs' band structure and density of states were performed. The DFT calculations revealed that the 14°, 38°, and 40° GBs encompassed a larger number of midgap states between the valence and conduction bands (Figure 3(h)) compared to the 18° and 60° GBs (Figure 3(i)). These midgap states facilitate non-radiative recombination of excitons, leading to

PL quenching, and the entrapment of charges, resulting in a relatively higher work function in the 14°, 38°, and 40° GBs.

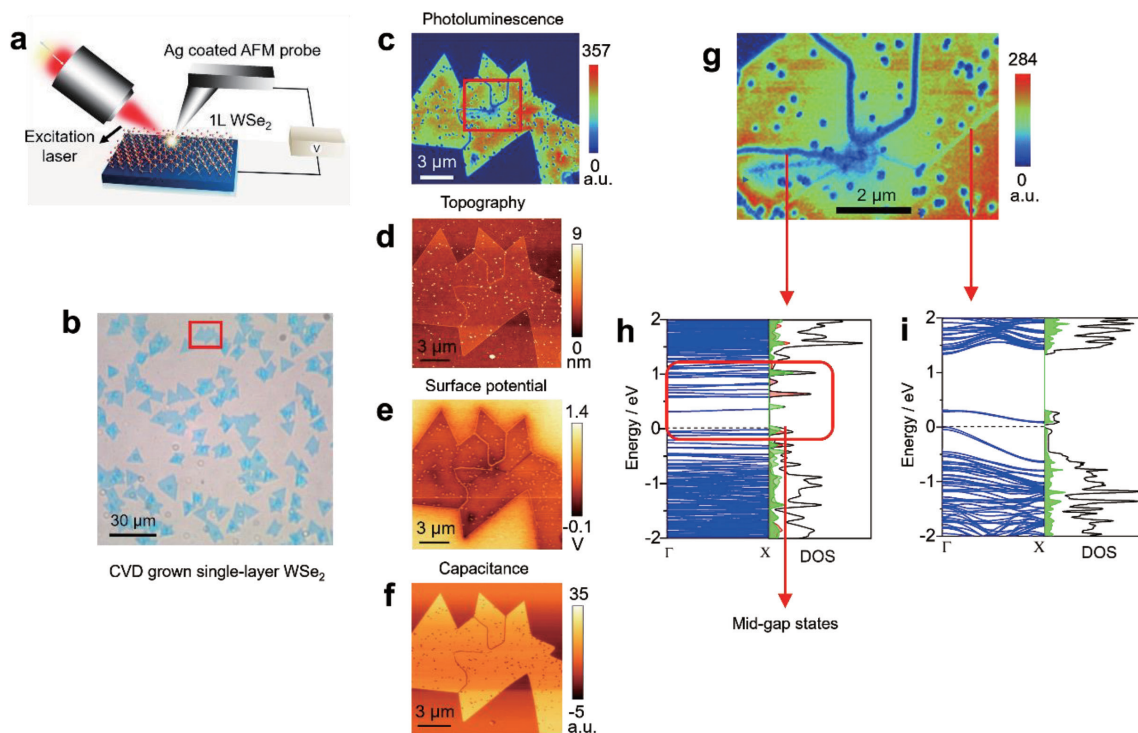


Figure 3 Nanoscale investigation of GBs in 1L WSe₂. (a) Schematic diagram of the experimental setup used to study optoelectronic behavior of GBs in 1L WSe₂. In situ KPFM and TEOS measurements performed in the same experimental setup enabled a direct correlation of topographical, excitonic, chemical, and electrical properties at the nanoscale. (b) Optical image of the CVD-grown 1L WSe₂ sheets. (c) TEPL, (d) AFM topography, (e) surface potential and (f) capacitance images of the 1L WSe₂ sheets measured in the region marked in Panel b. (g) Zoomed-in TEPL image of the region marked in Panel c. DFT calculated band structure (left panel) and DOS (right panel) of GBs with tilt angles of (h) 38° and (i) 60°, which are visible in the blue and green contrast in Panel g. The mid-gap states generated in the 38° GB are highlighted. Figure adapted from reference [7].

Nanoscale Characterization of OPV Devices

For nanoscale characterization of OPV devices, we introduced a novel non-destructive method called STEOM that combines plasmonic optical signal enhancement (TEOS) with electrical-mode scanning probe microscopy (PC-AFM) using the setup shown in Figure 4(a)^[10]. This novel technique enabled the mapping of morphology, chemical composition, and photoelectrical properties with sub-20 nm spatial resolution. We applied STEOM to investigate an operating OPV device based on the blend of poly[(2,1,3-benzothiadiazole-4,7-diyl)-alt-(4,9-dihydro-4,4,9,9-tetraoctylbenzo[1'',2'':4,5;4'',5'':4',5']bissilolo[3,2-b:3',2 b]dithiophene-2,7-diyl)] (C8SiIDT-BT) and 1',4'-dihydro-naphtho[2',3':1,2][5,6]fullerene-C60 (ICMA). The AFM topography image of the C8SiIDT-BT:ICMA solar cell active layer and the molecular structures of C8SiIDT-BT and ICMA are shown in Figures 4(b) and (c), respectively. In the active layer, the C8SiIDT-BT and ICMA molecules act as electron donor and acceptor, respectively. The optical spectrum of the solar cell is depicted in Figure 4(d), which shows Raman (yellow) and PL (green) signals of C8SiIDT-BT and PL (red) signals of ICMA.

STEOM allowed simultaneous imaging of the solar cell active layer topography, donor Raman, donor PL, acceptor

PL and photocurrent signals as shown in Figures 4(e-i), respectively. The rich information provided by these multi-parameter images revealed strong correlations between surface and subsurface molecular distribution of C8SiIDT-BT and ICMA, local photocurrent generation, and macroscopic device performance. Our simultaneous topographic, spectroscopic, and electrical measurements unveiled a hierarchical blend nanostructure in the C8SiIDT-BT:ICMA solar cell, with nanoscale photocurrent hotspots and larger islands of high efficiency dispersed within a low-efficiency blend background. Interestingly, the topographic islands displayed high photocurrent generation due to the presence of large ICMA (acceptor) aggregates surrounded by the C8SiIDT-BT (donor) molecules as illustrated in Figure 5. The donor: acceptor interface provided efficient charge separation, whilst the large ICMA aggregates provided well-connected pathways for efficient charge collection.

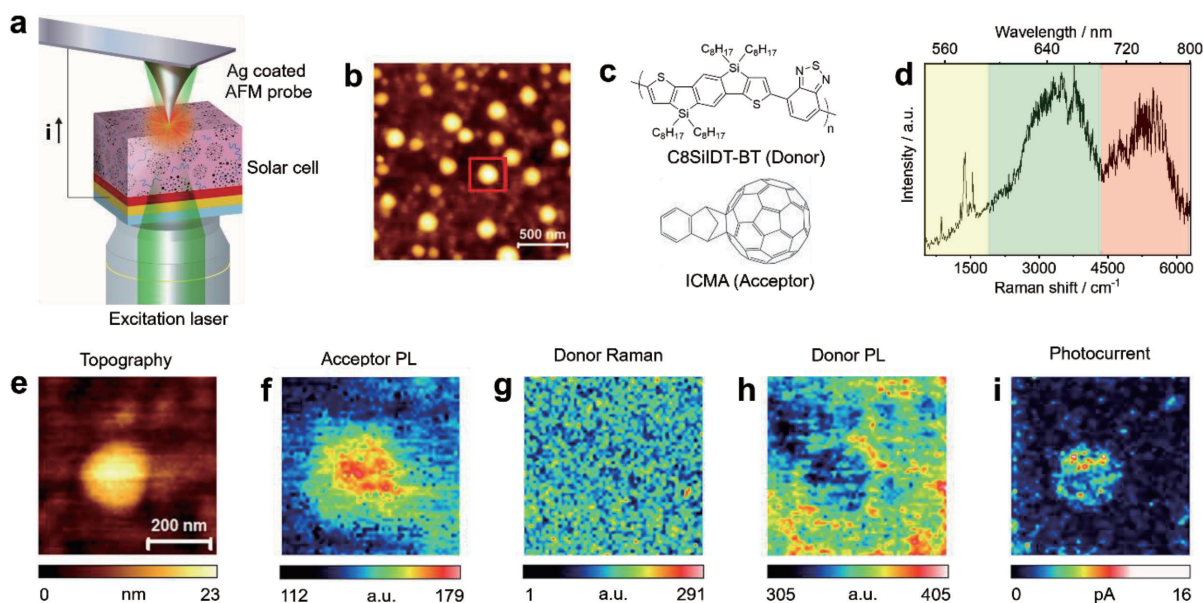


Figure 4 Simultaneous topographical, electrical, and optical microscopy. (a) Schematic diagram of the optical setup used to study operating C8SiIDT-BT:ICMA organic solar cell. (b) AFM topography image of the solar cell active layer containing phase-separated domains of C8SiIDT-BT and ICMA. (c) Structures of C8SiIDT-BT and ICMA molecules, which act as the donor and acceptor in the solar cell. (d) Optical spectrum of the C8SiIDT-BT:ICMA active layer. Raman (yellow) and PL (green) bands of C8SiIDT and PL (red) band of ICMA are highlighted. (e) Topography, (f) acceptor PL, (g) donor Raman, (h) donor PL and (i) photocurrent images measured simultaneously in the region marked in Panel b under operating conditions. Figure adapted from reference [10].

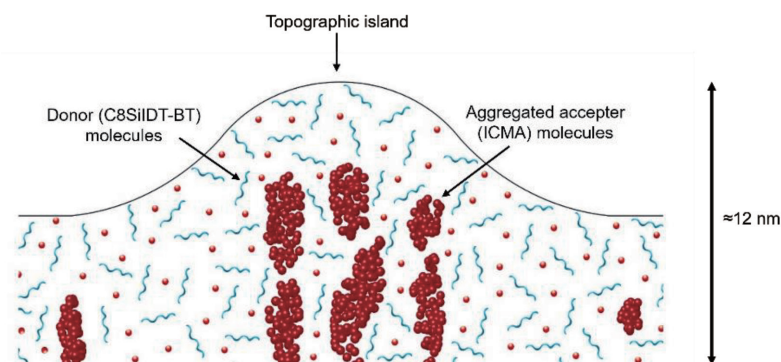


Figure 5 Schematic depiction of the chemical composition in and around a topographic island at the C8SiIDT-BT:ICMA active layer surface revealed using STEOM. Figure adapted from reference [10].

Furthermore, STEOM could distinguish between high purity and lower purity aggregates of ICMA, providing insights into their impact on photocurrent generation and collection. Importantly, we showed that the nanoscale multi-parameter measurements of C8SiIDT-BT:ICMA solar cell are consistent with and can successfully explain the macroscopic device performance. These results validated the ability of STEOM to directly correlate nanoscale characteristics with macroscopic device performance, thus providing a powerful tool for understanding and optimizing OPV devices.

Conclusions and Outlook

In summary, our work focuses on the nanoscale investigation of two classes of novel semiconductor materials, namely, 2D TMDs and OPV devices. As discussed in this article, through our research, we have discovered new insights into the nanoscale properties of these cutting-edge semiconductor materials and demonstrated a novel nanoscale characterization methodology that has the potential to contribute significantly to the advancement of next-generation semiconductor devices.

In 2D TMDs, our research has provided valuable insights into the nanoscale properties of semiconductor materials like 1L MoS₂ and 1L WSe₂. By utilizing TEOS, we have

overcome the limitations of conventional techniques and achieved unprecedented spatial resolutions, enabling the mapping of excitonic processes at the nanoscale. This breakthrough in understanding the behavior of excitons, trions, and grain boundaries in 2D TMDs paves the way for the development of high-performance optoelectronic devices. The ability to manipulate and control the excitonic behavior at the nanoscale opens new avenues for applications in areas such as photodetectors, solar cells, light-emitting diodes, and quantum light sources. The insights gained from our research will likely inspire further exploration and innovation in the field, leading to the design and fabrication of more efficient and advanced semiconductor devices.

Similarly, our research on the nanoscale characterization of OPV devices using STEOM has significant implications for the advancement of organic photovoltaic technologies. The ability to probe the morphology, chemical composition, and photoelectrical properties of OPV devices at the nanoscale provides a comprehensive understanding of the structure-property relationships crucial for device performance. This knowledge can drive the optimization of the active layer's nanomorphology, leading to improved charge generation and collection efficiency in OPV devices. By enabling a direct correlation between nanoscale characteristics and macroscopic device performance, STEOM offers a powerful tool for the rational design and development of high-efficiency OPV devices.

The perspectives resulting from our research contribute to the broader scientific community and semiconductor industry. The innovative methodologies and techniques we have demonstrated push the boundaries of nanoscale characterization and provide researchers with new tools for investigating the properties and behavior of semiconductor materials. The ability to visualize and understand excitonic processes in 2D TMDs and the nanoscale characterization of OPV devices offer critical insights for optimizing their performance and pushing the limits of their efficiency. We anticipate that these advancements will facilitate the development of environmentally friendly and sustainable energy solutions, such as high-performance solar cells and energy-efficient optoelectronic technologies.

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