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Communication – Feature Article**Supramolecular Structure through Epitaxial Growth of
Semiconducting Poly (3-hexylthiophene)
on Carbon Nanotubes as Building Blocks for Nanoscale Electronics**

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Abstract

Semiconducting conjugated polymers such as (3-hexylthiophene) (P3HT) and carbon nanotubes are attractive for applications that include field-effect transistors and photovoltaic devices. In these applications, the control of structure, morphology, and alignment of polymer chains is important from the perspective of charge transport and optical properties. In this regard, a novel solution-based nucleation approach involving direct epitaxial nucleation of nanofibers of poly(3-hexylthiophene) (P3HT) polymer on carbon nanotubes (CNTs) leading to supramolecular structure is demonstrated. The supramolecular structure of P3HT on CNTs is characterized by nucleation of oriented precursors of P3HT on CNTs by epitaxial mechanism, onto which a high density of transcrystalline ~800-1000 nm long nanofibrils of P3HT with thickness of ~2-3 nm are nucleated in a periodic manner. The nanoscale structure of epitaxially grown P3HT nanofibrils exhibit optical and photoluminescence characteristics. The UV-vis spectroscopy study of the fabricated structure suggests combination of π - π electronic transition and a strong lattice vibration in the conjugated polymer chains. Furthermore, the supramolecular structure is envisaged to comprise of an accumulating thread for charge transport, onto which nanometer thick long fibrils are assembled in a periodic configuration with strong potential for organic-inorganic optoelectronic devices. In conclusion, the described approach enables fabrication of supramolecular structure on carbon nanotube-based electrodes, making it attractive for functional devices.

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1. Introduction

Poly(3-hexylthiophene) (P3HT), a π -conjugated semiconducting and semicrystalline polymer, is a key material of significant interest in applications that include field-effect transistors and organic photovoltaic devices because it inherently exhibits high carrier mobility (1-4). The underlying reason for high carrier mobility of P3HT is related to controlled regioregularity and the fact that thiophene rings of the main chain maintain their coplanar position. Furthermore, the π -electron-conjugated structure along the main chain can be developed without any steric hindrance between side chains in head-to-tail regioregularity (5,6). The alkyl group in P3HT with two different regioregularities, notably, head-to-head (HH) and head-to-tail (HT) play an important role, where the HT-regioregularity is preferred over HH-regioregularity because it enhances electrical conductivity, optical non-linearity, and magnetic properties (7).

Moreover, the controlled regioregularity of P3HT allows its molecules to form a highly ordered structure via π - π interaction between the thiophene rings. In a manner similar to other macromolecular crystals, P3HT forms ~ 10 nm wide crystalline regions separated by amorphous interlayers (8). Considering that the performance of any device is primarily governed by the structure and morphology of the polymer in the active layer, the crystallization process that governs the structural morphology, is of utmost significance (9-17) in the design and fabrication of organic photovoltaics. The fundamental reason is that the nanoscale architecture (or morphology and crystalline packing of electron donor and acceptor materials) within the device is tunable via manipulation of crystallization parameters and is a challenge (18-20). The challenge of crystallization is further complicated by the unique structure of P3HT that is characterized by a rigid-main-chain backbone and flexible side chains, influencing their

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interactions. This characteristic is envisaged to influence the crystallization of P3HT in contrast to linear polymers. In summary, the aforementioned aspects have a role in influencing the crystallization behavior and consequent structural morphology, with direct impact on charge transport properties and device performance. It is therefore important to understand the crystallization process with the aim that the understanding of crystallization will facilitate future efforts in improving device performance and in the design of new semiconducting polymers with high charge mobility (21-23).

The motivation to fundamentally understand crystallization of P3HT from solution on CNTs is the advantage of combining the unique properties of P3HT and CNTs to promote efficient transfer from the conjugated polymer to CNTs under visible light in the fabrication of photovoltaic devices (24). CNTs are attractive as active components both in photovoltaic devices and field-effect transistors because of intriguing optoelectrical and physical properties (25-28), while controlled alignment of P3HT chains provides intrinsic one-dimensional (1D) carrier transport path (29,30). Thus, combining the two constituents, P3HT and CNTs, is expected to result in high charge mobility with superior device performance (31-33).

Motivated by the need to understand relationship between opto-electronic properties (charge transport, photovoltaic activity) in organic devices with structure and morphology of π -conjugated polymers, we describe here initial studies on a novel method for nucleation and growth of P3HT from solution on to carbon nanotubes (CNTs) of different diameters. The process results in oriented and periodic superstructure consisting of several hundred nanometers long crystalline nanofibrils made of folded polymer chains, obtained through epitaxial mechanism. Furthermore, the process described here overcomes the challenge of dispersion of CNTs and interfacial adhesion between the constituents (polymer and CNTs) at the molecular

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scale through fostering of direction nucleation and growth of polymer crystals along the long tube axis of CNTs. In our case, the control of dispersion of CNTs does not involve (a) covalent functionalization of CNTs or (b) non-covalent functionalization via surfactant absorption, such that the intrinsic properties of CNTs are retained because of the undisturbed structure of CNTs. The oriented morphology results in optical absorption and photoluminescence characteristics.

The envisaged nanoscale-hybrid architecture will most likely enable formation of conductive networks suitable for fabrication of complicated and efficient devices. Based on previous studies of π - π interactions between CNTs and π -conjugated polymers (34-36), we hypothesize that CNTs are effective nucleants in inducing crystallization of P3HT.

In the present study, we address the fundamental challenge of dispersion and command at the interface between the constituents (polymer, CNTs) in the resultant hybrid architecture at the molecular scale. The process involves a novel approach that fosters direct nucleation and growth of polymer crystals along the long tube axis of the CNTs. The important advantage of direct crystallization of polymer on CNTs is that it culminates in interfacial adhesion, which is derived from electrostatic and van der Waal's interaction in the polymer-CNT hybrid nanoscale architecture.

Using this method, we are able to exploit the tremendous potential of CNTs which have a tendency to agglomerate because of strong intertubular interactions (37-39). Attempts to covalently functionalize CNTs to secure good dispersion leads to disruption of π -conjugation in CNTs and scattering of electrons from each covalent functionalized site. This aspect is detrimental to electrical and transport properties, while non-covalent functionalization of CNTs renders a weak CNT-polymer interface (37-39). Covalent and non-covalent functionalization of CNTs is generally carried out to facilitate dispersion in polymers. However, they have inherent

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disadvantages. For instance, covalent functionalization converts sp^2 hybridization to sp^3 hybridization of carbon atoms, which alters trigonal-planar local bonding geometry to a tetrahedral geometry (37, 40, 41).

An accompanying objective is to fundamentally understand the principles and mechanism of crystallization of P3HT on CNTs. The various reaction parameters such as CNT diameter and the crystallization time were studied to explain the interaction between the CNT and the polymer and that becomes a part of the novelty of the work.

2. *Experimental*

2.1 *Materials*

Poly(3-hexylthiophene) (P3HT) of molecular weight 50-70 kDa, was obtained from Acros Chemicals, USA and decahydronaphthalene (decalin) was obtained from Sigma-Aldrich. The H-T regioregularity of P3HT used in the present study was 91-94%, as determined by NMR. Single-walled carbon nanotubes (SWCNTs) of diameter in the range of ~2-5 nm were obtained from Global Nanotech, Mumbai. Prior to conducting the experiments, the structure and diameter of SWCNTs were ascertained by transmission electron microscopy and Raman spectroscopy.

Decahydronaphthalene (decalin) was used as a solvent for P3HT. The polymer:CNT ratios studied were 4:1, 10:1, 50:1, and 200:1. The crystallization of polymer on CNTs involved the following steps: First, 0.1 mg CNTs were dispersed in 10 mL of decahydronaphthalene using a combination of ultrasonication for 3 h, followed by 30 min of probe sonication. Next, P3HT was dissolved in 10 mL decalin and heated at 150°C for 1 h in an oil bath. After dispersion of CNTs in decalin and separately dissolving P3HT in decalin, the dispersion of CNTs was added to the P3HT solution drop-wise and quenched to the crystallization temperature of 80°C for 8 h.

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After crystallization, the resulting purple colored solution was filtered using a Teflon filter (0.45 μm pore size) and washed with decalin.

The resulting polymer-CNT nanoscale architecture (P3HT-CNT) was examined using a combination of field emission scanning electron microscopy (SEM) (JEOL JSM 6300) and/or transmission electron microscopy (TEM) (Hitachi H-7600). Fourier transform infrared spectroscopy (FTIR) (Jasco-480) was used to study changes in vibration bands induced by crystallization, while optical spectra was obtained using UV-vis spectroscopy (Jasco V6300). Photoluminescence spectrum was recorded for the sample by exciting with an argon ion laser or frequency-doubled Yb-tungstenate laser (400 fs, 10 MHz : t-pulse, $\lambda_{\text{excitation}} = 515 \text{ nm}$). The laser beam entered a Nikon inverted microscope and was focused on to the back plane of the objective, so that the excitation laser passed through the sample as a parallel beam, thus promoting wider-field excitation. The excitation power was $\sim 1 \text{ W/cm}^2$.

3. Results and Discussion

It is appropriate to first outline the reasons underlying dispersion of CNTs in decalin and not directly dispersing CNTs in polymer. The two chemical approaches that have been used to disperse CNTs in polymer are covalent and non-covalent functionalization. However, these two methods are not viewed as appropriate methods to obtain the desired success. The covalent functionalization is governed by the transformation of sp^2 to sp^3 hybridization of carbon atoms and is accompanied by a change from trigonal-planar local bonding geometry to a tetrahedral geometry (42-44). Important examples of covalent functionalization are oxidation (42,44,45), fluorination (42,47-49), polymer chain attachment (42,50,51), and in-situ polymerization (42,52,53). While covalent functionalization does not impact thermal and mechanical properties, but has an adverse effect, involving, disruption of extended π -conjugation in CNTs. This effect

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negatively influences the electrical properties because electrons are scattered from each covalent functionalized site (42,54,55). More importantly, when functionalized CNTs react with pre-formed end-functionalized polymer molecules, the chemical binding of polymer chains sterically prevents diffusion of additional polymer molecules to the surface, leading to reduction in graft density. In contrast, the non-covalent functionalization approach via surfactant absorption and helical wrapping with polymers produces a weak interface, even though the intrinsic properties of CNTs are retained because of the undisturbed structure (47,56,57).

The approach of dispersing CNTs in a solvent in which the polymer is also soluble overcomes the challenge of dispersion and command of the interface between the constituents (polymer, CNTs) at the molecular scale through fostering of direct nucleation and growth of polymer crystals along the tube axis of the CNTs (see results). A similar process was adopted for crystallization of polyethylene (PE) on CNTs (58). The approach culminates in interfacial adhesion, coming from electrostatic and van der Waal's interaction in the hybrid polymer-CNT nanostructure. Direct crystallization of polymers from solution was first proposed in 1974 (59) but it involved shear flow and moreover the crystallization was carried out in the absence of nanoparticles. In contrast, in our case shear flow is not involved and the solution is stationary or motionless. Thus, the proposed approach can be considered as a natural alternative to crystallization under shear flow conditions.

3.1 Structural Morphology of P3HT on CNTs: Hybrid Nanoscale Architecture

Figure 1 illustrates the nucleating ability of P3HT on CNTs. We note a supermolecular structure characterized by combination of oriented and transcrystalline growth of nanosized fibrils several hundred nanometers long that are connected in a periodic manner. The figure which represents edge on view provides a strong support that CNTs are a viable medium for

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nucleation of an oriented growth of P3HT along the entire long axis of the CNTs on to which P3HT subsequently crystallizes in a periodic and transcrystalline manner. Also presented is a low magnification micrographs illustrating numerous CNTs with P3HT nanofibers (Supplementary Figure S2).

The morphology of P3HT is not smooth, but it indicates a hybrid superstructure, similar to that observed during crystallization of P3HT in a mixture of 1,3,5-trichlorobenzene (TCB) on pyridine (60). The length of the transcrystalline P3HT fibrils is in the range of ~800-1000 nm and the average periodicity, and thickness of transcrystalline branching measured by Fast Fourier Transformation (FFT) of the TEM micrographs was <1 nm and ~2 nm, respectively. The periodicity of transcrystalline fibrils of P3HT values is significantly small such that the transcrystalline nanofibrils of P3HT are closely and tightly packed side-by-side along the entire long axis of CNTs. There is near absence or no distinct evidence of amorphous zone or tie molecules bridging the successive crystalline lamellae nanofibrils through the amorphous constituent and may well be related to the high molecular weight of studied P3HT. It also leads us to suggest that the nanofibrils are primarily crystalline consisting of folded P3HT chains that form fibrils without significant presence of extended amorphous part or tie molecules bridging successive nanofibrils. While one does not expect folding of chains in regioregular polymers, however, in recent years evidence of folded chains was obtained via high-resolution TEM and scanning tunneling microscopy (STM) (61,62). The oriented P3HT nanofibrils (please see section 3.3) observed in the study described here can be viewed as another testimony of the occurrence of folding of chains of stereoregular polymer. As regards, the amorphous constituent bridging the fibrils, it is expected that the decrease in molecular weight would induce structural changes, notably, the disorder in the crystalline packing of polymer chains and increase

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connectivity between the crystalline fibrils via tie-molecules (63). We are currently studying the effect of molecular weight.

In summary, the ability of CNTs to enable oriented growth of P3HT along the entire long axis of CNTs was high. This kind of superstructure provides a large contact area between nanoscale crystalline domains in the hybrid architecture and makes the hybrid potentially valuable for photovoltaic device fabrication.

Interestingly, when the polymer concentration was increased from 4:1 to 200:1, there was no noticeable or apparent change in the morphology or dimensions of nanofibrils (Figure 1). Similarly, no change in the behavior of nucleation of needle-like crystals was observed when the diameter of CNTs was increased from 2-5 nm to 200-300 nm (not presented). This is again believed to be related to the high molecular weight of P3HT and the ongoing study with low molecular weight P3HT is expected to clarify and provide greater insight.

3.2 The Epitaxial Growth Scenario

In the epitaxial growth scenario characterized by the combination of oriented and transcrystalline P3HT nanofibrils along the long axis of CNTs, we identify the following two stages: First, CNTs with large surface area are effective nucleating agent or template with high length/width aspect ratio of ~ 1000 with length close to a micrometer or greater. The high specific area (500 times more surface area per gram on the basis of equivalent volume fraction of a typical carbon fiber) makes them ideally suitable for crystallization of polymers on CNTs. Thus, in the first step, the polymer chains orient themselves along the CNTs by a mechanism involving surface-mediated stretching of polymer chains on the surface of CNTs. Unlike the ‘coil-stretch’ transition of polymer chains which is commonly induced by shear flow (60,64), in our case the

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solution is stationary or motionless, thus, the oriented growth of P3HT is mediated by epitaxial CNT/P3HT interface interaction.

It is reasonable to envisage that multiple oriented nuclei can occur on CNTs and merge, consistent with the appearance of non-uniform growth of P3HT along the long axis of CNT (Figure 1). It is pertinent to indicate that an identical behavior was confirmed with other polymer systems, high density polyethylene and nylon 6,6 (65,66), where the oriented growth was significantly thicker than that observed here with P3HT. The first step is presumably an autocatalytic process involving “self-orientation” of the P3HT chains at the growth front of initial oriented growth (60,67) on CNTs. In the second step, periodic nucleation of P3HT occurs.

The near-absence of individual nanofibrils of P3HT between transcrystalline nanofibrils implies that nucleation is the rate limiting step in the crystallization of P3HT (54) and is consistent with the view point that the periodic nucleation of crystalline lamellae can be activated through the availability of stretched polymer chains (60,68). Furthermore, computational modeling of molecular systems (Langevin dynamics) indicated that oriented polymer elicits or initiates subsequent nucleation of periodic crystalline lamellae (68). Consistent with the crystallization of stereoregular polymer in trichlorobenzene (TCB), it is believed that the anisotropy of the interchain interactions in P3HT crystal, i.e., π -stacking along the b-axis and the weak van der Waals interactions between the planes of π -stacked polythiophene backbones along the axis, is conducive to the configuration or arrangement of long transcrystalline fibrils as compared to the 2-D lamellar structure.

The approach described here provides an avenue for the fabrication of polymer-CNT hybrid architecture for photovoltaic applications. The orientation of P3HT chains can be explained in terms of epitaxial deposition of P3HT on CNTs, onto which nucleation and growth

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of lateral crystalline nanofibrils comprising of folded P3HT chains, closely connected in a periodic manner. Epitaxial growth of the crystallizing polymer develops lowest possible energy state at experimental conditions. An important condition of epitaxially coordinated interface is that the degree of registry, Δ_{epitaxy} for the dimensions involving polymer nucleation on a substrate surface is less than 10% and is given by (69,70):

$$\Delta_{\text{epitaxy}} = 100(d_{\text{overgrowth}} - d_{\text{substrate}})/d_{\text{substrate}} \quad (1)$$

Table 1 summarizes the data illustrating epitaxial match between P3HT and the basal plane edges of CNT. The potential dimensional match is within 10% and is nearly perfect, thereby accommodating favorable low-energy positioning of P3HT's crystal structure.

Table 1. Epitaxial match between carbon and P3HT.

Substrate (Carbon-CNT)		Over growth (P3HT)	
Spacing (nm)	Multiple x Spacing	Multiple x Spacing	Spacing (nm)
Niched 0.7145 0.4263	1 x (0.7145) 4 x (0.4263)	2 x (100) 1 x c	d(100) = 0.38 ± 0.1 d(011) = 1.6

Figure 2 depicts the orientation and dimensions of basal planes in CNTs (equivalent to these present in graphitic carbon). The niched and zig-zag terms refer to the configuration of the carbon atoms along the edges of each basal plane, while the pitched and alternating terms refer to the manner and stacking of each plane could have when adjacent to neighboring, parallel basal planes (69,70). Figure illustrates how a carbon-plane could epitaxially nucleate oriented P3HT onto CNTs. It is believed that nucleation occurs upon basal plane edges or steps rather than flat basal plane surface because ordered nucleation of polymer has greater possibility of nucleation at basal plane edges.

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The epitaxial relationship envisaged involves crystallization or placement of main chain of P3HT across the ‘steps’ at the ends of the basal plane of CNT.

3.3 Effect of Orientation of P3HT on Optical Properties

The oriented character of P3HT was evident from the selected area diffraction pattern presented in supplementary Figure S1. The electron diffraction pattern indicated highly intense and arc-shaped reflection at 0.385 nm. This closely corresponded to the π -stacking distance between the P3HT chains, pertaining to (020) reflection. The (020) reflection was normal to the long axis of the P3HT nanofibrils and interestingly only this reflection was observed normal to the axis of P3HT fibrils.

The evolution of UV-vis adsorption spectra of P3HT with CNTs as a function of selected crystallization time is presented in Figure 3. At the start of crystallization, an adsorption band corresponding to P3HT was observed at 442 nm. This adsorption band, which corresponds to individual or isolated P3HT chains in the solution, continued to exist until approximately 30 min of crystallization time. However, after ~60 min of crystallization, low energy adsorption bands at 514, 555, and 604 nm were observed. After ~3h, no change in the intensities of the low energy peaks was observed implying that the crystallization process was completed in less than 3 h. These low energy peaks correspond to the combination of π - π -electronic transition and a strong lattice vibration in the conjugated P3HT chains. The presence of an obvious isosbestic point at 555 nm (Figure 3c) in the UV-vis spectra suggesting a direct transformation from dissolved individual polymer chains to ordered nanofibrils without evidence of an intermediate state (71,72). A comparative analysis of optical spectra of a simple mixture of P3HT + CNT and P3HT crystallized on CNTs is presented in supplementary Figure S3. The optical spectra of P3HT and CNT mixture shows a broad band of P3HT at 442 nm. During the course of

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crystallization, these isolated chains interact with CNTs and are crystallized on CNTs and additional low energy peaks emerge.

The PL spectrum shows two peaks (Figure 4), the smaller peak at 515 nm corresponds to the residual excitation peak, whereas the peak with maxima at 592 nm corresponds to the crystalline P3HT nanofibrils. Consistent with UV-vis with TEM discussion, the evidence of a broad amorphous peak expected at ~560 nm (65) was not observed in Figure 4. Based on analysis of UV-vis absorption spectrum and PL spectrum, we can attribute these measurements to the homogenous nature of the hybrid nanoscale architecture and to their predominantly crystalline nature. Moreover, a comparative analysis of PL spectra of pure P3HT and P3HT crystallized on CNTs is presented in supplementary Figure S4. The PL spectra of pure P3HT exhibits a high intensity emission maximum at 513 nm and low intensity peak at 592 nm. On the other hand, the PL spectra of the hybrid P3HT-CNT exhibits a relatively low intensity peak at 515 nm and a high intensity 592 nm peak. This is due to the photoluminescence quenching and lower degree of phase separation of P3HT after crystallization on CNTs.

To extend our understanding of the chemical interaction, FTIR spectroscopy studies were carried out and the data is presented in Figure 5. The peaks at 2855, 2927 and 2950 cm^{-1} in pristine P3HT are assigned to CH_2 out-of-plane mode, CH_2 in-plane mode and CH_3 asymmetry mode, respectively. The peak at 1410 cm^{-1} represents the symmetric ring stretching mode of P3HT and the peak at 821 cm^{-1} corresponds to the C-H out-of-plane mode (Figure 5). In P3HT-CNT hybrid composite system, on crystallization of P3HT on CNTs, the C-H out-of-plane mode peak that was previously present in pristine P3HT at 821 cm^{-1} , shifted to 812 cm^{-1} , which implies chemical interaction between CNT and P3HT.

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When the thiophene rings of P3HT come in close contact with CNTs, which is a sp^2 hybridized arrangement of carbon atoms, where a single layer of graphene is rolled to obtain one-dimensional carbon nanotube, they both interact via π - π - stacking. This is in addition to the CH- π interaction between the pendant hexyl group and graphitic walls of CNTs (73). The hexyl side chains of P3HT are hydrophobic in nature and are attracted towards the hydrophobic walls of CNTs and envisioned to be chemically bonded via van der Waals force, providing strong adhesion between the constituents.

The hierarchical superstructure of epitaxially grown P3HT can be imagined as comprising an accumulating thread for charge transport properties, onto which nanofibrils of \sim 2-3 nm thickness and \sim 800-1000 nm length are assembled in a periodic manner. We are currently studying charge transport properties of the novel structures and will be reported later. Additionally, we are exploring the impact of reducing the molecular of P3HT such that there is significant content of tie molecules forming a bridge between the crystalline fibrils.

4. Conclusions

The study illustrates direct epitaxial crystallization of semiconducting P3HT on CNTs from solution. It is envisaged that the first step in epitaxial crystallization involves formation of an oriented structure along the long axis of CNTs such that surface-mediated stretching of P3HT chains occurs on the surface of CNTs. This is followed by periodic nucleation of a row of transcrystalline P3HT fibrils that are characterized by near absence of amorphous content between the nanocrystalline fibrils. From a generic sense, the solution-based approach of epitaxial crystallization of P3HT on CNTs as nanoscale superstructure characterized by highly oriented fibers of P3HT onto which transcrystalline nanofibrils comprising of folded polymer chains are nucleated in a periodic manner. The nucleation of oriented P3HT precursors by

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epitaxial crystallization of P3HT chains on CNTs can be considered to be an alternative to the classical growth under shear flow conditions. The photoluminescence (PL) and optical absorption characteristics are attributed to the homogenous and highly crystalline nature of oriented epitaxial superstructure.

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