Nanoparticles for organic electronics applications

Zhengran He\(^1\), Ziyang Zhang\(^2\) and Sheng Bi\(^3\)

\(^1\) Department of Electrical and Computer Engineering, The University of Alabama, Tuscaloosa, AL 35487, United States of America
\(^2\) Department of Electrical Engineering, Columbia University New York City, NY 10027, United States of America
\(^3\) Key Laboratory for Precision and Non-traditional Machining Technology of the Ministry of Education, and Institute of Photoelectric Nanoscience and Nanotechnology, Dalian University of Technology, Dalian, Liaoning 116024, People’s Republic of China

E-mail: zhe3@crimson.ua.edu

Keywords: nanoparticles, crystal growth, charge-carrier mobility, dielectric constant, organic thin film transistors

Abstract

Recently, the research in solution-based, small-molecule organic semiconductors has achieved great progress, although their application in organic electronics devices is still restricted by a variety of issues, including crystal misorientation, morphological nonuniformity and low charge-carrier mobility. In order to overcome these issues, hybrid material systems that incorporate both organic semiconductors and additives have been successfully demonstrated to control crystal growth and charge transport of the organic semiconductors. In this work, we first review the recent advances in the charge-carrier mobility of the organic semiconductors, followed by a comparison of the different additives that have been reportedly blended with the semiconductors, including polymeric additives, small-molecule additives and nanoparticle based additives. Then we will review the important nanoparticles employed as additives to blend with solution-based, organic semiconductors, which effectively improved the semiconductor crystallization, enhanced film uniformity and increased charge transport. By discussing specific examples of various well-known organic semiconductors such as 6, 13-bis(triisopropylsilyl)ethynyl) pentacene (TIPS pentacene), we demonstrate the essential relationship among the crystal growth, semiconductor morphology, dielectric properties, and charge-carrier mobilities. This work sheds light on the implementation of nanoparticle additives in high-performance organic electronics device application.

1. Introductions

The research of solution-processed organic semiconductors has achieved unprecedented progress in recent years [1–7]. Specially, they have been demonstrated with properties that would greatly benefit application in organic thin-film transistors (OTFTs), which include improved charge-carrier mobilities and expanded solubility in organic solvents [8–11]. Despite these advantages, their implementation in organic electronics devices still has many restrictions, which can be attributed to problems including crystal misorientation, morphological nonuniformity and low charge-carrier mobility [12, 13]. These issues would further cause problems such as substrate poor coverage and inferior device performance consistency [14–17]. As a result, various hybrid material systems that incorporate both organic semiconductors and additive materials have been successfully demonstrated, which can take advantages of the merits from both components and contribute to the enhanced performance of organic electronics devices [18–20].

In the first section of this article, we will review the recent efforts made to advance the charge-carrier mobilities of the solution-processed, small-molecule, organic semiconductors. Then we will discuss the various issues of random crystal orientation and charge transport, which challenge the implementation of the organic semiconductors in organic electronics device fabrication. In the second section, we will compare the advantages of each type of additives, i.e. polymeric additive, small-molecule additive, and nanoparticle based additive. We will continue on to provide an in-depth review of the benefits of using nanoparticles as additives to effectively control the crystal growth, film morphology, substrate wettability, and charge carrier mobilities, which facilitate
the application of the organic semiconductor in thin-film transistor and other electronics device fabrication. Throughout the discussion of these specific examples that mainly involve small-molecule organic semiconductors, we showcase that this work can be used to control the crystallization and electrical performance of other newly-discovered, high-performance, semiconducting materials.

1.1. Advances in organic electronics

In this section, we will review the various advances in charge-carrier mobilities and device application that have been recently achieved in the field of organic electronics. The following discussion will be mainly focused on various solution-processed, small-molecule, organic semiconductors.

The mobilities in solution-processed, small-molecule, organic semiconductors have been reported to be compared to or even far surpass the mobility of amorphous silicon. For example, Asare-Yeboah et al developed a temperature-based method which exposed the substrate to a gradient temperature and induced a solubility difference of a \( p \)-type small-molecule semiconductor \( 6,13 \)-bis(triisopropylsilylethyl) pentacene (TIPS pentacene) [18]. TIPS pentacene crystals grew from the lower temperature side of the substrate towards the higher temperature side, forming well-aligned ribbons across the whole substrate. A mobility of up to 0.5 cm\(^2\) V\(^{-1}\) s\(^{-1}\) has been reported from the TIPS pentacene OTFTs based on an ITO/PET flexible substrate by using the temperature-based alignment technique. Wade et al demonstrated a zone casting method to control the crystal alignment of both TIPS pentacene and \( 6,13 \)-bis(triisopropylsilylethyl) pentacene (TES pentacene) semiconductors [21]. Single crystalline crystals were obtained based on 50 \( \mu \)m s\(^{-1}\) zone-casting speed, yielding a mobility of 0.67 cm\(^2\) V\(^{-1}\) s\(^{-1}\) and 0.037 cm\(^2\) V\(^{-1}\) s\(^{-1}\) from TIPS pentacene and TES pentacene crystal based OTFTs, respectively. Lee et al demonstrated a tilting method to align the crystal growth of TIPS pentacene and obtained excellent alignment of the crystals with an average mobility of 0.3 \( \pm \) 0.08 cm\(^2\) V\(^{-1}\) s\(^{-1}\) [22]. Zhang et al reported the crystal alignment of TCNQ crystals with a brush writing method, resulting in both polycrystalline and single crystalline microstructural arrays with a mobility of 1.83 \( \times \) 10\(^{-3}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) [23]. Becerril et al reported the growth of \( db \)-P2TP, \( dbo \)-P2TP, \( dho \)-P2TP, \( dho \)-P3TP, TMS-P2TP and TMS-4T semiconductors and obtained highly aligned crystalline ribbons, with a mobility of 0.129 cm\(^2\) V\(^{-1}\) s\(^{-1}\) from elongated TMS-4T crystal based OTFTs [24]. Panidi et al reported a simple method to greatly enhance the charge-carrier mobilities in organic semiconductors via mixing a molecular Lewis acid, namely \( B(C_6F_5)_3 \), which results in effective p-doping in the organic semiconductors [25]. A mobility of 11 cm\(^2\) V\(^{-1}\) s\(^{-1}\) and 8 cm\(^2\) V\(^{-1}\) s\(^{-1}\) were demonstrated from the 2,7-dioctyl[1]-benzothieno[3,2-b][1]benzothiophene:poly(indacenodithiophene-co-benzothiadiazo[le] (C\(_{6} \)-BTBT:C\(_{16} \)-IDTBT) and 2,8-difluoro-5,11-bis(triisopropylsilylethyl) anthradithiophene:poly(triarylamine) (diF-TESADT:PTAA) based OTFTs, respectively.

More recently, researchers have devoted to the development of solution shearing based methods to control the crystal growth of solution-based, small-molecule, organic semiconductors. The application of the solution shearing technique has reportedly yielded even higher mobilities in the organic semiconductors including TIPS pentacene \[26, 27\], diF-TES-ADT [28], and 2,9-di-decyl-dinaphtho-[2,3-b:2′,3′-f]-thieno[3,2-b]-thiophene (C\(_{10} \)-DNTT) [29], which can far supersede the electrical performance of amorphous silicon. Specially, Peng et al reported a mobility of 10.4 cm\(^2\) V\(^{-1}\) s\(^{-1}\) from aligned single-crystalline, millimeter-scale C\(_{10} \)-DNTT crystals grown with a solution shearing method [29]. Rocha et al combined the solution shearing method with the addition of a polystyrene polymer additive in order to align the crystal growth of TIPS pentacene, resulting in the formation of highly crystalline ribbons and spherulitic film [30]. An average mobility of 8.3 cm\(^2\) V\(^{-1}\) s\(^{-1}\) and a highest mobility of 12.3 cm\(^2\) V\(^{-1}\) s\(^{-1}\) were demonstrated from TIPS pentacene with confined crystal growth and continuous crystalline ribbons.

In addition to the implementation of solution-processed, small-molecule, organic semiconductors in the device fabrication of OTFTs, the semiconductor materials have also been used in application of other electronics devices, such as gas sensors. For example, Lee et al reported that TIPS pentacene organic semiconductor was used for the fabrication of gas sensor [31]. By allowing an optimum residual solvent amount, the fine-tuned spin coating time in this work led to two-dimensional (2D) growth of TIPS pentacene and the formation of 2D spherulite structure of TIPS pentacene. Its high surface coverage and porous structure further results in improved charge-carrier mobilities and an easy penetration of gas molecules into the charge transport channel, which enhances its gas sensing capability.

1.2. Challenges in organic electronics

As mentioned in the previous section, the application of solution-processed, small-molecule, organic semiconductors in the field of organic electronics has encountered various challenges. In this section, we will briefly discuss these restrictions, which include the misoriented semiconductor crystals, morphological nonuniformity and low charge-carrier mobility.
The crystal growth of many solution-processed, small-molecule, organic semiconductors is intrinsically anisotropic via typical solution deposition methods such as drop casting \cite{32, 33}. This essentially leads to considerable variations in the measured mobilities of the organic semiconductor based OTFTs, which has been previous reported in many semiconductor material systems including TIPS pentacene \cite{34–37} and other semiconductors. In particular, Bi et al reported that p-type semiconductor 2,5-di-(2-ethylhexyl)-3,6-bis(5″-n-hexyl-2,2′,5′,2″-terthiophen-5-yl)-pyrrolo[3,4-c]pyrrole-1,4-dione (SMDPPEH) (molecular structure shown in figure 1(a)) based OTFTs exhibited crystals with random directions and large gaps, as shown in the microscopic picture of figures 1(b), (c), after SMDPHEH was drop casted in a single solvent of pure chloroform without applying any external alignment method \cite{38}. The measured mobilities in SMDPPEH ranged from $5.7 \times 10^{-5}$ $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ to $5.4 \times 10^{-4}$ $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, which indicated variations of one order of magnitude. He et al reported that when a p-type semiconductor 5,6,11,12-tetrachlorotetracene (molecular structure shown in figure 1(d)) was drop casted in a single solvent of chloroform, it formed misoriented needles without neither long-range alignment nor continuous coverage on substrate (figure 1(e)) \cite{15}. The 5,6,11,12-tetrachlorotetracene based OTFTs exhibited mobilities that largely ranged from 0.006 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ to 0.39 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, indicating mobility variations of almost three orders of magnitude. Chen et al reported the TIPS pentacene based OTFTs can exhibit mobilities that vary by one order of magnitude, depending on the angle between the crystal orientation and the source-to-drain direction \cite{12}. A mobility of 0.004 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ was measured from OTFTs which had TIPS pentacene crystals bridging the source-to-drain contact electrodes perpendicularly. In comparison, a 10-fold higher mobility was obtained when the TIPS pentacene crystals connected the electrodes in a parallel direction. The molecular structure of TIPS pentacene is shown in figure 1(f), and its typical randomly-located crystals via drop casting is shown in figures 1(g), (h), according to previous report \cite{39}.

### 2. Nanoparticles as additives

In order to address these aforementioned problems such as crystal misorientation, morphological nonuniformity and low charge-carrier mobility of the solution-processed, small-molecule organic
The study of polymeric materials employed as additives to blend with the solution-processed, small-molecule organic semiconductors can be primarily divided into amorphous polymers and conjugated polymers. First, polymeric additives have been reported to generally enhance the film uniformity of organic semiconductors. Second, the amorphous polymers can introduce both lateral and vertical phase segregation between the polymers and semiconductors. For example, various polymers have been reported to cause vertical phase segregation with the organic semiconductors, including poly(methyl methacrylate) (PMMA) [46–48], poly(alpha-methylstyrene) (PαMS) [49–56], polystyrene (PS) [57–59], and poly(triarylamine) (PTAA) [60–64]. A group of polymers, including poly(ethyl acrylate) (PEA), poly(butylacrylate) (PBA), and poly(2-ethylhexyl acrylate) (P2EHA), were reported with the capability to switch between lateral phase segregation and vertical phase segregation [45]. Multi-functional benefits can occur as a result of vertical phase segregation. The addition of PαMS can facilitate the semiconductor TIPS pentacene to move towards the semiconductor/dielectric layer interface. This led to the formation of a highly concentrated semiconductor layer and benefited charge transport. Third, the addition of conjugated polymers provides a special pathway to control the crystallization and charge transport via the intermolecular interactions with the solution-processed, small-molecule organic semiconductors. Two types of intermolecular interactions were reported in a study that involved the organic semiconductor TIPS pentacene and conjugated polymers of poly(3-hexylthiophene) (P3HT) and regiorandom pentacene-bithiophene polymer (PnBT-RRα) [66]. Distinctive polymorphism, crystal arrangement and charge-carrier mobilities were discovered depending on the extent of hydrophobic interactions and π–π interactions.

Small-molecule additives have been employed to effectively tune the crystal growth of solution-processed, small-molecule, organic semiconductors. In particular, the loading of small-molecule additives can have the following benefits on the charge-carrier mobilities and device performance of OTFTs. First, the small-molecule additives have been reported to increase the crystallinity of the organic semiconductors and improve the orderliness of crystal structures, which is advantageous for charge transport. Second, small-molecule additives can be utilized to modify the wettability of the organic semiconductor on the substrate, which leads to the formation of continuous crystalline film and is significant for the application in organic electronics device fabrication on large-scale substrates. Third, previous study showed that small-molecule additives that exhibit similar molecular structure but different length of side group can modify the crystal growth of organic semiconductor. For example, a series of small-molecule additives, including 4-butylbenzoic acid (BBA), 4-hexylbenzoic acid (HBA), and 4-octylbenzoic acid (OBA), were blended with TIPS pentacene. The small-molecule additives formed an interfacial layer on the gate dielectric, which further facilitated the uniform deposition of seeds and allowed TIPS pentacene to become well oriented. Fourth, some small-molecule additives have also been reported to enhance the device stability of OTFTs. This was reported to be related to their ability to repel the water molecules from being absorbed into the semiconductor active layer, which consequently enhanced the stability of the semiconducting OTFTs.

The addition of nanoparticle based additives impacted the semiconductor growth, crystal orientation, substrate wettability and dielectric properties of the transistor device, resulting in enhanced charge-carrier mobilities. First, nanoparticle were reported to be blended with organic semiconductors such as TIPS pentacene, which could effectively modify the crystallization of the organic semiconductor. As a result, well-oriented TIPS pentacene crystals were formed across the substrate. One benefit from such improved crystal orientation is the reduction of mobility variations, since crystals are aligned in an orientation that more closely overlaps with the direction from the source to drain contact electrodes. Second, various nanoparticles were added to the dielectric layer, which led to enhanced dielectric constant and higher measured mobility of the small-molecule organic semiconductor based OTFTs. Third, nanoparticles were reported to be capable of modifying the surface energy of the substrate. Enhanced wettability of the semiconductor can lead to more uniform coverage on the substrate, which is specially significant for application for large-scale, organic electronics device on flexible substrates.
substrate. Fourth, the addition of nanoparticle based additives can find application in other organic electronic devices such as biosensors [78, 79].

2.2. Overview of nanoparticle based additives

In this section, we review the various nanoparticle-based additives that were reported to blend with both small-molecule and polymeric organic semiconductors. These nanoparticles were added to tune the crystal growth, the semiconductor wettability, charge-carrier mobility, the dielectric constant of dielectric layer and other properties of organic electronics devices such as OTFTs and gas sensors.

He et al utilized silicon dioxide nanoparticles (SiO2 NPs) to manipulate TIPS pentacene crystallization in an effort to improve device performance consistency [77]. By blending TIPS pentacene with SiO2 NPs at different weight ratios, the crystal misorientation and poor film coverage of the pristine TIPS pentacene film can be largely mitigated (figure 2(e)). Specifically, an average hole mobility of $0.13 \pm 0.04$ cm² V⁻¹ s⁻¹ and $0.04 \pm 0.04$ cm² V⁻¹ s⁻¹ was obtained with 10% SiO2 NPs and without SiO2 NPs loading, respectively, indicating a great increase in both average mobilities and performance consistency of TIPS pentacene OTFTs. The distribution of SiO2 NPs in the vertical profile of the TIPS pentacene active layer was investigated, and a very small portion of SiO2 NPs were found to be located at the interface between the active layer and insulator layer. Since most SiO2 NPs are away from the interface, it would not adversely impact the charge transport of TIPS pentacene at the interface. Bright-field Transmission Electron Microscopy (TEM) was utilized to analyze the microstructural arrangement in the SiO2 NPs/TIPS pentacene films, and results were presented in figures 2(a)–(c). The darker regions (i.e., smaller gray value in figure 2(d)) represent TIPS pentacene films or SiO2 NPs, whereas the lighter ones (i.e., higher gray value in figure 2(d)) refer to amorphous-carbon supporting films. TIPS pentacene films with 10% SiO2 NPs (figure 2(a)) are distinctly darker and have broader edge when compared to that of the neat TIPS pentacene films (figure 2(b)). The TEM image of SiO2 NPs is presented in figure 2(c), with an average diameter of $18 \pm 4$ nm based on 12 different measurements. The SiO2 NPs/TIPS pentacene film has uniform electron contrast but shows gray value gradient only at the film edge, which can be attributed to the nanoparticle aggregations at the grain boundaries. Finally, a grayness plot is presented in figure 2(d) in order to quantitatively compare the width of the film edges. The two triangles in figure 2(d) correspond to the triangle in figures 2(a) and (b), respectively, allowing the calculation of the film edge width: 1.5 μm with 10% SiO2 NPs and only 0.2 μm for the pure TIPS pentacene film. The aggregations of SiO2 NPs at the grain boundaries of TIPS pentacene crystals attributed to the oriented crystal growth with improved alignment.

Afsharimani et al reported the addition of SiO2 NPs into the polymer PVA in order to modify its dielectric properties, for application in $\alpha$-$\omega$-dihexylquaterthiophene (DH4T) based transistor fabrication [80]. Two types of dielectric layers were used in this study including the pure PVA film and PVA/SiO2 NPs hybrid film. The PVA/SiO2 hybrid film was found to exhibit a higher a root-mean-square (RMS) roughness of 3.8 nm as well as an elevated water contact angle of 52°, leading to a reduced surface energy of 12.8 mJ m⁻². The reduced surface energy is considered to be beneficial for the device stability of the DH4T based OTFTs since it can repel the adsorption of water molecules. When measured at 800 kHz, PVA film and the PVA/SiO2 NPs hybrid film

![Figure 2. Bright-field TEM images of (a) TIPS pentacene film with 10% SiO2 NPs and (b) the neat TIPS pentacene film. The TEM image of freestanding SiO2 NPs is shown in (c). (d) Grayness curves of TIPS pentacene film with 10% SiO2 NPs and neat TIPS pentacene film, which are based on the dotted line shown in (a) and (b), respectively. Triangles in (d) correspond to these in (a) and (b). (e) Polarized optical images of TIPS pentacene films with different concentrations of SiO2 NPs, including 0%, 5%, 10%, and 15%. All images in (e) share the same scale bar of 50 μm. Reproduced from [77] with permission from Wiley VCH.](image-url)
SiO2 NPs led to more structural defects and larger leakage current. 

exhibited a capacitance value of 0.2 and 4.9 nF/cm², which caused more charge carriers to accumulate in the channel of the hybrid devices and resulted in higher drain currents. Electrical characterization of the DH4T based OTFTs demonstrated ambipolar behavior, which was attributed to the reduced trap density from the hydroxyl group 'neutralization' of PVA. Slightly higher electron and hole mobilities were obtained in the range of 10⁻⁴ cm² V⁻¹ s⁻¹ for devices with the hybrid film. Despite these improvements, however, the addition of the SiO₂ NPs led to more structural defects and larger leakage current.

Yamazaki et al reported the addition of silica nanoparticles (SNPs) into TIPS pentacene in order to improve the semiconductor coverage in the charge transport channel by tuning the wettablity on the hydrophobic surface of poly(methylsilsesquioxane) (PMSQ) polymer gate dielectric [75]. The sol-gel synthesized colloidal SNPs were blended with TIPS pentacene at varied weight ratios including 0%, 0.1%, 0.1%, and 1%. The blend solution was then spin-coated onto a hydrophobic surface of PMSQ dielectrics, and the resultant morphology indicated that the wettability was greatly improved with NPs weight ratio at 0.1% and 1%. The enhanced wettability was due to the anchoring effect of TIPS pentacene onto the phenyl-modified SNPs. TIPS pentacene/ SNPs based OTFTs were fabricated by both spin coating and inkjet printing of the blends on the PMSQ polymer gate dielectric. Electrical characterization results indicated an improved mobility of up to 1.2 × 10⁻² cm² V⁻¹ s⁻¹ (spin coating) and 2.6 × 10⁻² cm² V⁻¹ s⁻¹ (inkjet printing) with 0.1% of NPs additive, which was accredited to the enhanced molecular ordering of the self-organized TIPS pentacene.

Similarly, Nagase et al reported the addition of SNPs into P3HT in order to improve the charge-carrier mobility of OTFTs by modifying the semiconductor wettability [81]. The surface of the SNPs was modified with phenyl surfactants (Ph-SNPs) and with methyl surfactants (Me-SNPs). Different average diameters of the SNPs were studied. The photographs of figure 3 show different wetting conditions of the P3HT film, which had a molar ratio of 5:10, 10:90, and 20:80 between Si-HEMA and polymer. As shown in figure 3(c), Electrical characterization of the P3HT/SNPs based OTFTs on ODTS-treated substrates revealed higher mobility with the addition of larger-diameter SNPs, and correspondingly higher crystallinity was noted from X-ray diffraction spectra. In particular, a hole mobility of over 0.1 cm² V⁻¹ s⁻¹ was demonstrated from P3HT/SNPs based OTFTs with a 5:3 weight ratio and an average 38 nm diameter of the SNPs. The device configuration of P3HT/ SNPs based OTFTs was shown in the graphical representation figure 3(f).

Wang et al reported the hybrid layer of polymer/silicon nanoparticles (Si NPs) in application of organic transistor fabrication [82]. Specially, the Si NPs were modified with 2-hydroxyethyl methacrylate (HEMA) in order to facilitate their dispersion within the organic polymer layer of P-HEMA-&-GMA. Four different dielectric films were studied in this work: Si–5, Si–10, Si–15, and Si–20, which had a molar ratio of 5:95, 10:90, 15:85 and 20:80 between Si-HEMA and polymer. As shown in figure 4(a), para-exaphenyl (p-6P)/vanadyl-phthalocyanine (VOPc) semiconductor based OTFTs were fabricated with a dielectric bilayer incorporating both SiNxs and polymer/Si NPs blend film. The morphology of the Si-HEMA was presented in the TEM image of figure 4(b), which showed that these modified NPs exhibited good dispersion and narrow dimension distribution. The dielectric thin film was found to exhibit increased dielectric constant, which ranged between 3.5 and 5.2. The enhanced dielectric constant with adding Si NPs was much higher than that of the organic dielectric films. As the AFM images of figure 4(c) shows, the addition of the Si NPs can facilitate the continuous growth of p-6P material. Also, the crystal grain size was found to increase with the increased molar ratio of the

![Figure 3](image-url)
additive, which was considered to be beneficial for the device performance of OTFTs. The p-6P/VOPc based transistors demonstrated a mobility of up to 0.7 cm² V⁻¹ s⁻¹ based on the Si-10 film.

Park et al reported the utilization of gold nanoparticle (Au NPs) for application in TIPS pentacene based OTFTs and organic memory devices [83]. The device diagram was presented in figure 5(a). Negatively charged Au NPs were adsorbed onto a 3 nm multilayer-structure layer of polyelectrolytes (PEs) via a dipping process. The Au NPs array was presented in the Scanning Electron Microscopic (SEM) images of figure 5(b), which shows a uniform deposition and an average diameter of 16 ± 3.2 nm. Then, 15 nm layer of HfO₂ was deposited as a tunneling oxide layer, followed by the deposition of TIPS pentacene as active layer and silver as source and drain contact electrodes via inkjet printing (figure 5(c)). Characterization of the memory devices indicated both large

Figure 4. (a) A schematic of the thin film transistor which incorporates p-6P/VOPc as the active layer and a polymer/Si NPs hybrid dielectric layer. (b) TEM picture of Si-HEMA. (c) AFM images showing the surface morphology of the pristine p-6P layer and p-6P on different dielectric layers including Si-5, Si-10, Si-15, and Si-20, respectively. Reproduced from [82] with permission from ACS Publications.

Figure 5. (a) A schematic showing the device structure of organic memory devices. (b) SEM images of Au NPs arrays. (c) Photograph and (d) optical microscope image showing the memory device: both silver (Ag) source and drain contact electrodes and TIPS pentacene active layer were deposited via inkjet printing. Reproduced from [83] with permission from AIP Publishing.
memory windows and decent data retention. In addition, the organic memory devices incorporated with Au NPs were found to exhibit good reliability with repeated cycles of programming/erasing. This work sheds lights on application in nanofloating gate memory devices printed on flexible substrates.

Hou et al reported the blending of BaTiO3 nanoparticles (BaTiO3 NPs) into the polymer matrix of P(VDF-TrFE)/PMMA in order to enhance its electrical property [76]. While the pristine polymer matrix of P(VDF-TrFE)/PMMA exhibited a rod-like structure, the loading of BaTiO3 NPs at the weight ratios of 9%, 16% and 23% led to the formation of more compact crystal structure and reduced rod diameter, as shown in the Atomic Force Microscopy (AFM) images of figures 6(a)–(d) and SEM image of figures 6(e), (f). The dielectric constant of P(VDF-TrFE)/PMMA was found to increase with increased weigh ratio of the BaTiO3 NPs. In particular, a dielectric constant of 9.3 was obtained with 23% weight ratio of BaTiO3 NPs. TIPS pentacene OTFTs were fabricated with the P(VDF-TrFE)/PMMA/23% BaTiO3 film as the dielectric layer. Electrical characterization demonstrated a mobility of 0.01 cm² V⁻¹ s⁻¹ and reduced leakage current under high bias condition, which was attributed to the good miscibility property of the nanoparticle with the P(VDF-TrFE)/PMMA polymer matrix.

Jang et al reported the addition of barium strontium titanate (BST) NPs into the dielectric layer of polyvinylphenol (PVP) polymer in order to improve the mobility of pentacene based TFTs [84]. The BST NPs have a diameter of less than 50 nm. The digital images of PVP and BTS NPs solutions were presented in figure 7(a). The existence of abundant OH groups from the PVP polymer facilitated the dispersion of the BST NPs within the dielectric layer. A higher weight ratio of NPs loaded to the dielectric layer led to a higher dielectric constant, which resulted in an increase of charge density located at the charge transport channel and higher mobilities. However, as the AFM images of figure 7 show, the increased weight ratios of BST NPs at the same time led to increased surface roughness. In order to reduce the increased surface roughness, a thin polystyrene (PS) layer was formed on top of the PVP/BTS NPs blend dielectric layer. The highest mobility of 1.2 cm² V⁻¹ s⁻¹ was demonstrated from pentacene OTFTs based on the PVP/8% BST NPs/PS blend layer, which was attributed to the combined outcome of reduced surface roughness and increased dielectric constant.

Wang et al studied the effect of different thickness of silver (Ag) NPs on the charge-carrier mobility and memory property of pentacene based TFTs [85]. Ag NPs with a different thickness, including 1 nm, 5 nm and 10 nm, were embedded between two layers of organic semiconductor pentacene, as shown in the device configuration of figure 8(e). Electrical characterization results (figures 8(a)–(c)) demonstrate that the bottom-gate, top-contact pentacene TFTs only exhibited saturation behavior in the output currents with a 1 nm and 5 nm thickness of Ag NPs, whereas no saturation behavior was observed for TFTs with 10 nm of Ag NPs. A hole mobility of 0.34 cm² V⁻¹ s⁻¹ and 0.1 cm² V⁻¹ s⁻¹ was obtained with 1 nm and 5 nm thick layer of Ag NPs. By applying a cyclic sweeping gate voltage, the devices showed a memory window that increased with an increase in

![Figure 6. AFM images of P(VDF-TrFE)/PMMA polymer matrix loaded with different weight ratios of BaTiO3 NPs: (a) 0%, (b) 9%, (c) 16% and (d) 23%. Cross-sectional SEM images of P(VDF-TrFE)/PMMA polymer matrix on Al foil with BaTiO3 NPs loaded at (e) 0% and (f) 23%. Reproduced from [76] with permission from Elsevier.](image-url)
the thickness of the Ag NPs film, as shown in figure 8(d), which was attributed to the larger trap density from Ag NPs. Also, the on/off current ratio was found to be $10^5$, $10^4$, and 10 with a thickness of 1 nm, 5 nm and 10 nm of the Ag NPs film. The significant drop in on/off current ratio was related to the connected Ag NPs as their size increased, as observed in the SEM images of figures 8(g), (h). This created a low-resistance path for current flow and led to increased off current.

Kim et al reported the employment of alumina nanoparticles (Al$_2$O$_3$ NPs) to modify the dielectric property and to passivate defects on the gate layer for application in P3HT based OTFTs [86]. The silane-terminated polystyrene (PS) was grafted onto the core-shell Al$_2$O$_3$ NPs via an Al–O–Si bond, leading to the formation of Al$_2$O$_3$–PS NPs. The Al$_2$O$_3$–PS NPs were further mixed with a polymer polystyrene (PS) or poly (methyl methacrylate) (PMMA) to serve as a hybrid dielectric layer for transistor application. Depending on composition of the nanoparticle component, the hybrid layer exhibited a dielectric constant that ranged from 2.59 to 7.79. When P3HT was used as a benchmark semiconductor, bottom-gate, top-contact OTFTs were fabricated with a
| Author          | Materials      | Additive                  | Process                                                                 | Result                                                                 | Mobility                                      |
|-----------------|----------------|---------------------------|--------------------------------------------------------------------------|-------------------------------------------------------------------------|-----------------------------------------------|
| He et al        | TIPS pentacene | SiO₂ NPs                  | Add SiO₂ NPs to improve TIPS pentacene crystal orientation              | TIPS pentacene aligned due to SiO₂ NPs aggregating at grain boundaries   | 0.13±0.04 cm² V⁻¹ s⁻¹ with 10% SiO₂ NPs     |
| Afsharimani et al | DH4T          | SiO₂ NPs                  | Add SiO₂ NPs to modify the dielectric properties of PVA                 | DH4T based OTFTs showed ambipolar behaviors and larger drain currents   | 10⁻⁴ cm² V⁻¹ s⁻¹ based on the PVA/SiO₂ NPs hybrid dielectric                        |
| Yamazaki et al  | TIPS pentacene | SNPs                     | Add SNPs to improve TIPS pentacene wettability on hydrophobic gate dielectric | Wettability improved with TIPS pentacene anchoring onto the phenyl-modified SNPs | 2.6 × 10⁻² cm² V⁻¹ s⁻¹ from inkjet printing with 0.1% SNPs |
| Nagase et al    | P3HT          | SNPs                     | Add surfactant modified SNPs to improve P3HT wettability                | Wettability depends on the average diameter and weight ratio of SNPs, and on the surfactant | 0.1 cm² V⁻¹ s⁻¹ from P3HT/SNPs based OTFTs |
| Wang et al      | p-6P/ VOPc    | Si NPs                    | Add Si NPs to modify dielectric property and crystal growth             | More continuous film formed with larger grain size                      | 0.7 cm² V⁻¹ s⁻¹ based on the Si-10 film     |
| Park et al      | TIPS pentacene | Au NPs                    | Negatively charged Au NPs adsorbed onto polyelectrolytes via a dipping process | Large memory windows, decent data retention and good reliability due to adding Au NPs | Mobility not reported                        |
| Hou et al       | TIPS pentacene | BaTiO₃ NPs                | Blend BaTiO₃ NPs with P(VDF-TrFE)/PMMA to improve electrical property   | Increased weight ratio of the BaTiO₃ NPs led to enhanced dielectric constant of P(VDF-TrFE)/PMMA | 0.01 cm² V⁻¹ s⁻¹ based on dielectric constant of 9.3 with 23% BaTiO₃ NPs |
| Jiang et al     | Pentacene     | BST NPs                   | Add BST NPs to increase PVP dielectric constant                        | Higher weight ratio of NPs increased the dielectric constant of PVP      | 1.2 cm² V⁻¹ s⁻¹ from the PVP/8% BST nanoparticles/PS blends                        |
| Wang et al      | Pentacene     | Ag NPs                    | Add Ag NPs to tune charge-carrier mobility and memory property          | Increased memory window but reduced current on/off ratio with increased Ag NPs thickness | 0.34 cm² V⁻¹ s⁻¹ with 1 nm of Ag NPs        |
| Kim et al       | P3HT          | Al₂O₃ NPs                 | Add Al₂O₃ NPs to modify dielectric property and passivate charge trap centers | Al₂O₃ NPs addition increased dielectric constant and passivated silanol groups | 1.4 × 10⁻³ cm² V⁻¹ s⁻¹ with Al₂O₃-PS-NPs |

Table 1. A summary of the various nanoparticle based additives reviewed in this section, along with the related semiconductor materials, the experimental process, result and charge-carrier mobility.
Si/SiO₂/Al₂O₃-PS-NPs configuration, yielding a 6.3 nF/cm² capacitance at 1 kHz. The Al₂O₃-PS-NPs provided an effective passivation of the silanol groups on the SiO₂ substrate, which would otherwise serve as trap centers of charge carriers. The P3HT OTFTs with the Al₂O₃-PS-NPs showed a hole mobility of $1.4 \times 10^{-3}$ cm² V⁻¹ s⁻¹, which was 10-fold higher than the value from devices without the additive. This work sheds lights on a new surface treatment for the charge trap centers on the oxide gate dielectrics.

The various semiconductor materials, nanoparticle based additives, experimental process and result, and charge-carrier mobility were summarized in table 1.

3. Conclusions and outlook

In this article, we have reviewed the various nanoparticle based additives that have been reported to successfully blend with solution-processed organic semiconductors to control crystal orientation, increase substrate wettability, enhance dielectric properties and improve electrical performance of the semiconducting devices. Overall, these nanoparticle based additives can have the following benefits on the film morphology, charge transport and device performance. First, the nanoparticle based additives can control the crystallization of the small-molecule semiconductors, which further leads to enhanced crystallinity, improved crystal orientation and reduced mobility variation of the organic semiconductor based OTFTs. Second, the nanoparticle based additives can be employed to modify the wettability of the semiconductor on the substrate, which has significant application in large-area, high-performance organic electronics on flexible substrate. Third, the nanoparticle additives, when added into the dielectric layer, can enhance the dielectric constant, increase values of the measured mobility and improve the performance of memory devices. Besides the works that we have covered in this review article, there are still issues that need to be addressed in order to fully unlock the potentials of solution-processed, small-molecule organic semiconductors, such as degradation in air. Research efforts are still needed to enhance the stability of the organic semiconductor based devices when exposed to the ambient environment. We hope that the nanoparticle based additives as we reviewed in this work may shed lights on future endeavors in this field.

ORCID iDs

Zhengran He https://orcid.org/0000-0002-6853-0265
Sheng Bi https://orcid.org/0000-0003-0369-0572

References

[1] Bi S, Li Q, Yan Y, Asare-Yeboah K, Ma T, Tang C, Ouyang Z, He Z, Liu Y and Jiang C 2019 Hys. Chem. Chem. Phys. 21 2540
[2] Amer K, Elsaba A M, Anas M and Ebrahim S 2019 J. Mater. Sci., Mater. Electron. 30 391
[3] Shi Y Q, Guo H, Qin M C, Zhao J Y, Wang Y X, Wang H, Wang Y L, Facchetti A, Lu X H and Guo X G 2018 Adv. Mater. 30 1705745
[4] Bi S, Li Y, He Z R, Ouyang Z L, Guo Q L and Jiang C M 2019 Org. Electron. 65 96
[5] Demir A, Ali S, Ali A and Kosemen A 2019 J. Mater. Sci., Mater. Electron. 30 11034
[6] He Z R, Shaik S, Bi S, Chen J H and Li D W 2015 Appl. Phys. Lett. 106 133501
[7] da Rocha C T, Haase K, Zheng Y C, Loffler M, Hambos M and Mannsfeld S C B 2018 Adv. Electron. Mater. 4 1800141
[8] Chu M, Fan J X, Yang S J, Liu D, Ng C F, Dong H L, Ren A M and Miao Q 2018 Adv. Mater. 30 1803467
[9] Bi S, Li Q, He Z, Guo Q, Asare-Yeboah K, Liu Y and Jiang C 2019 Nano Energy 66 104101
[10] Haase K, da Rocha C T, Hauenstein C, Zheng Y C, Hambos M and Mannsfeld S C B 2018 Adv. Electron. Mater. 4 1800076
[11] Yuan Y B, Giri G, Ayzen A L, Zoombelt A P, Mannsfeld S C B, Chen J H, Nordlund D, Toney M F, Huang J S and Bao Z N 2014 Nature Comm. 5 4005
[12] Chen J H, Tee C K, Shtein M, Martin D C and Anthony J 2009 Org. Electron. 10 696
[13] Chen J H, Martin D C and Anthony J E 2007 J. Mater. Res. 22 1701
[14] Asare-Yeboah K, Frasier R M, Sušičková G and Li D 2014 J. Vac. Sci. Technol. B 32 052401
[15] He Z R, Lopez N, Chi X L and Li D W 2015 Org. Electron. 22 191
[16] He Z, Chen J and Li D 2019 Soft Matter. 5790–803
[17] He Z, Chen J and Li D 2019 J. Vac. Sci. Technol. A 37 040801
[18] Asare-Yeboah K, Bi S, He Z R and Li D W 2016 Org. Electron. 32 195
[19] Ohe T, Kuribayashi M, Tsbohi A, Satori K, Itabashi M and Nomoto K 2009 Appl. Phys. Express 2 121502
[20] Kang J, Shin N, Jang D Y, Prabhut V M and Yoon D Y 2008 JACS 130 12273
[21] Wade J et al 2014 J. Mater. Chem. C 2 10110
[22] Lee W H, Kim D H, Jung Y, Cho J H, Hwang M, Park Y D, Kim Y H, Han J I and Cho K 2007 Appl. Phys. Lett. 90 132106
[23] Zhang P, Tang Q X, Tong Y H, Zhao X L, Wang G R and Liu Y C 2016 J. Mater. Chem. C 4 433
[24] Bicerri H A, Roberts M E, Liu Z H, Locklin J and Bao Z N 2008 Adv. Mater. 20 2588
[25] Panidi J, Paterson A F, Khim D, Fei Z P, Han Y, Tsetseris L, Vourlias G, Patsalas P A, Heeney M and Anthopoulos T D 2018 Adv. Sci. 5 1700290
[26] Giri G, Verplaegen E, Mannsfeld S C B, Atahan-Evenk S, Kim D H, Lee Y S, Bicerri H A, Aspuru-Guzik A, Toney M F and Bao Z A 2011 Nature 480 504
[27] Diao Y et al 2013 Nat. Mater. 12 665
[28] Niaz M R et al 2015 *Nature Comm.* 6 8598
[29] Peng B Y, Huang S Y, Zhou Z W and Chan P K L 2017 *Adv. Funct. Mater.* 27 1700999
[30] da Rocha C T, Haake K, Zheng Y C, Löffler M, Harmbsch M and Mannsfeld S C B 2018 *Adv. Electron. Mater.* 4 1800141
[31] Lee J H, Seo Y, Park Y D, Anthony J E, Kwak D H, Lim J A, Ko S, Iang H W, Cho K and Lee W H 2019 *Sci. Rep.* 9 21
[32] Headrick R L, Wo S, Sansoz F and Anthony J E 2008 *Appl. Phys. Lett.* 92 3
[33] He Z R, Chen J H, Sun Z Z, Szulczewski G and Li D W 2012 *Org. Electron.* 13 1819
[34] He Z, Zhang Z and Bi S 2019 *Appl. Nanosci.* (https://doi.org/10.1007/s13204-019-01668-4)
[35] Akkerman H B, Li H Y and Bao Z N 2012 *Org. Electron.* 13 2056
[36] James D T, Kjellander B K C, Smaa W T T, Gelinck G H, Combe C, McCulloch I, Wilson R, Burrowes J H, Bradley D D C and Kim J S 2011 *ACS Nano* 5 9824
[37] Hwang D K, Fuentes-Hernandez C, Kim J B, Potscavage W J and Kippelen B 2011 *Org. Electron.* 12 1108
[38] Bi S, He Z R, Chen J H and Li D W 2015 *AIP Adv.* 5 077170
[39] He Z, Zhang Z, Asare-Yeboah K and Bi S 2019 *J. Mater. Sci., Mater. Electron.* 30 14355–43
[40] He Z, Zhang Z and Bi S 2019 *J. Polym. Res.* 26 173
[41] Hamilton R, Smith J, Ogier S, Heeney M, Anthony J E, McCulloch J, Veres J, Bradley D D C and Anthopoulos T D 2009 *Adv. Mater.* 21 1166
[42] He Z, Zhang Z and Bi S 2019 *J. Sci. Adv. Mater. Devices* 42 467–72
[43] Kim Y H, Anthony J E and Park S K 2012 *Org. Electron.* 13 1152
[44] He Z, Asare-Yeboah K, Zhang Z and Bi S 2019 *Ipn. J. Appl. Phys.* 58 061009
[45] He Z R, Li D W, Hensley D K, Rondoniane A J and Chen J H 2013 *Appl. Phys. Lett.* 103 113301
[46] Park J H, Lim H, Cheong H, Lee K M, Sohn H C, Lee G and Im S 2012 *Org. Electron.* 13 1250
[47] Park J H, Lee Y T, Lee H S, Lee Y J, Lee K, Lee G B, Han J, Kim T W, Im S and Appl A C S 2013 *Mater. Inter.* 5 1625
[48] Park J H, Lee K H, Mun S J, Ko G, Heo S J, Kim J H, Kim E and Im S 2010 *Org. Electron.* 11 1688
[49] Kwon J H, Shin S J, Kim K H, Cho M J, Kim K N, Choi D H and Ju B K 2009 *Appl. Phys. Lett.* 94 013506
[50] Sim K, Choi Y, Kim H, Cho S, Yoon S C and Pyo S 2009 *Org. Electron.* 10 506
[51] Cho S Y, Ko J M, Lim J, Lee J Y and Lee C 2013 *J. Mater. Chem. C* 1 914
[52] Madec M B, Crouch D, Lorette G R, Whittle T J, Geoghegan M and Yeates S G 2008 *J. Mater. Chem.* 18 3230
[53] Hwang D K, Fuentes-Hernandez C, Berrigan J D, Fang Y N, Kim J, Potscavage W J, Cheun H, Sandhage K H and Kippelen B 2012 *J. Mater. Chem.* 22 5531
[54] Park B, Jeon H G, Choi J, Kim Y K, Lim J, Jung J, Cho S Y and Lee C 2012 *J. Mater. Chem.* 22 5641
[55] Kjellander B K C, Smaa W T T, Anthony J E and Gelinck G H 2010 *Adv. Mater.* 22 4612
[56] Michels J J 2011 *ChemPhysChem* 12 342
[57] Li X R et al 2011 *Org. Electron.* 12 1319
[58] Moonen P F, Vraztov B, Smaa W T T, Gelinck G H, Peter M, Meinders E R and Husken S 2011 *Org. Electron.* 12 2207
[59] Madec M B, Smith P J, Malandraki A, Wang N, Korvink J G and Yeates S G 2010 *J. Mater. Chem.* 20 9155
[60] Smith J, Hamilton R, McCulloch I, Heeney M, Anthony J E, Bradley D D C and Anthopoulos T D 2009 *Synth. Met.* 159 2365
[61] Intaniweit A, Keddie J L, Shikunov M and Sellin P J 2011 *Org. Electron.* 12 1903
[62] Kwon J H, Shin S J, Choi J, Chung M H, Oh T Y, Kim K H, Cho M J, Kim K N, Choi D H and Ju B K 2009 *Org. Electron.* 10 729
[63] Hwang D K, Fuentes-Hernandez C, Kim J, Potscavage W J, Kim S J and Kippelen B 2011 *Adv. Mater.* 23 1293
[64] Chung M H, Kwon J H, Oh T Y, Lee S J, Choi D H and Ju B K 2010 *Thin Sol. Films* 518 6289
[65] Obe T, Kuriyayashi M, Yasuda R, Tsuibo A, Nomoto K, Satoki K, Itabashi M and Kasahara J 2008 *Appl. Phys. Lett.* 93 3
[66] Chen J H et al 2013 *Chem. Mater.* 25 4378
[67] Park Y J, Seo J H, Elsway W, Walker B, Cho S and Lee J S 2015 *J. Mater. Chem. C* 3 5951
[68] Chae G J, Jeong S H, Baek J H, Walker B, Song C K and Seo J H 2013 *J. Mater. Chem. C* 1 4216
[69] Bharti D and Tiwari S P 2016 *Synth. Met.* 215 1
[70] He Z, Zhang Z and Bi S 2019 *J. Mater. Sci., Mater. Electron.* 30 20899–20915
[71] Treat N D, Malik J A N, Reid O, Yu L, Shuttle C G, Rumbles G, Hawker C J, Chabinyc M L, Smith P and Stingelin N 2013 *Nature Mater.* 12 628
[72] He Z R, Chen J H, Keum J K, Szulczewski G and Li D W 2014 *Org. Electron.* 15 150
[73] Nikolka M a et al 2017 *Nature Mater.* 16 356
[74] Li H, He Z, Ouyang Z, Palchoudhury S, Ingram C W, Harruna I I and Li D D 2020 *J. Nanosci. Nanotechnol.* 20 2611
[75] Yamazaki S et al 2010 *Appl. Phys. Express* 3 091602
[76] Hou X Y, Ng S C, Zhang J and Chang J S 2015 *Org. Electron.* 17 247
[77] He Z R, Xiao K, Durant W, Hensley D K, Anthony J E, Hong K L, Kilbey S M, Chen J H and Li D W 2011 *Adv. Funct. Mater.* 21 3617
[78] Lin C, Huang B R and Yang Y K 2013 *Sens. Actuat. B-Chem.* 184 27
[79] Chou J A, Chung C L, Ho P C, Luo C H, Tsai Y H, Wu C K, Kuo C W, Hsiao Y S, Yu H H and Chen P L 2019 *Front. Chem.* 7 281
[80] Afsharimani N and Nysten B 2019 *Bull. Mater. Sci.* 42
[81] Nagase T, Yoshikawa M, Yamazaki S, Kobayashi T, Michiwayi Y, Watase S, Watanabe M, Matsukawa K, Naito H and Polym J 2016 *Sci. Pol. Phys.* 54 509
[82] Wang X S, Wang H, Li Y, Shi Z S, Yan D H and Cui Z C 2018 *J. Phys. Chem.* 122 11214
[83] Park Y S, Chung S, Kim S J, Lyu S H, Iang J W, Kwon S K, Hong Y and Lee J S 2010 *Appl. Phys. Lett.* 96 3
[84] Yang Y, Lee W H, Park Y D, Kwak D, Cho J H and Cho K 2009 *Appl. Phys. Lett.* 94 183301
[85] Wang S M, Leung C W and Chan P K L 2010 *Adv. Appl. Phys.* 97 023511
[86] Kim K, Park M S, Na Y, Choi J, Jeneke S A and Kim J S 2019 *Org. Electron.* 65 305