Organic Semiconductors for Energy-Harvesting Applications and The Emergence of Novel 2D Layered Materials For Energy and Flexible Electronics

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ABSTRACT

Research in organic semiconductors has progressed steadily that has enabled commercial applications in areas such as organic light emitting diodes (OLEDs) for solid state lighting and displays, as well as organic field effect transistors (OFETs) for RFIDs, e-paper and flexible electronics. The use of organic semiconductors for photo-voltaics (PV) has also seen tremendous progress over the past decade with power conversion efficiencies that have risen from 1% to above 10% as reported recently. Organic PV provides advantages in its very low-cost manufacturing processes that utilize room temperature techniques, unlike crystalline Si and other inorganic PV technologies that are less cost-effective. In addition, the emergence of new classes of two-dimensional layered materials, similar to graphene, also appears to show promise for enabling applications in flexible electronics, as well as energy harvesting applications given the novel electronic and optical properties these two-dimensional layered materials exhibit.

Keywords: green electronics, organic semiconductors, organic photovoltaics, graphene, flexible electronics, 2D-layered materials

1 INTRODUCTION

Organic semiconductors offer advantages of low material cost, low temperature processes and the ability to engineer materials properties through chemical synthesis which has enabled a large number of potential applications for organic semiconductors in electronics and optoelectronics over the past several decades. Their compatibility with flexible substrates has created prospects for organic semiconductors to be spin coated onto light weight flexible substrates using high-throughput, low-cost roll-to-roll processing. Tremendous progress has been made in recent years that has enabled organic semiconductors to serve as effective light emitters in organic light emitting diodes (OLEDs),[1] logic and memory elements using organic field effect transistors (OFETs),[2] as well as photodetectors. As an example, in Fig. 1a, an OFET is shown (left), where source-drain currents are modulated in the organic semiconductor through the application of a gate voltage. Such devices have applications in flexible electronics (right) or for e-paper and smart textiles.

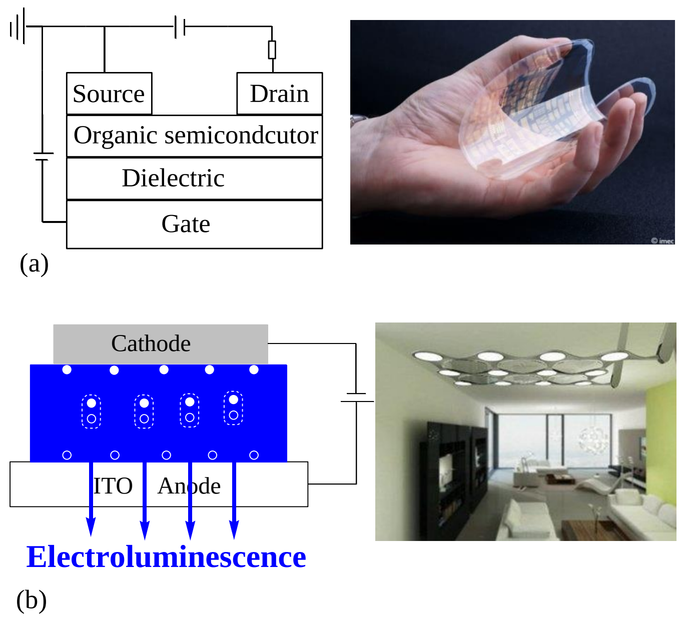

Figure 1. Organic semiconductors used in a) OFETs (left) which has applications in flexible circuits (right) in RFIDs, e-paper and memory; b) OLEDs (left) which have applications in solid state lighting (right) and displays.

In the OLED device architecture (Fig 1b, left), applying a voltage between the transparent anode and metallic cathode injects charge carriers from both electrodes within the organic semiconductor in the trilayer structure. These injected electrons and holes then create excitons which then emit light upon recombination at a wavelength that is determined by the choice of the active layer. The tremendous success in OLEDs has enabled commercial products from such devices in ultra-thin, full color, flat panel displays, as well as for solid state lighting (Fig. 1b, right).

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While tremendous progress has been made in organic semiconductors for OFETS and OLEDs, another potential application of organic semiconductors is in converting sunlight to electricity for photo-voltaics (PV).[3,4,5,6] The working principle of such a device is outlined in Fig. 2 where a photon from incoming light is absorbed and results in the formation of electron-hole pairs that generate bound excitons in the organic active layer. These excitons are then separated and collected as charges at the terminals, where they generate a photocurrent.[7] This is in contrast to an inorganic semiconductor,[8] where the absorption of a photon leads directly to the creation of free electrons and holes which are then driven away to the respective electrodes through the built-in potential. As with organic semiconductors, the advantage of organic PV lies in the very low-cost manufacturing process utilizing room temperature techniques. In current generation organic solar cells, the composite active layer can be prepared on large area substrates using techniques such as spin-coating, inkjet-printing, spray coating, gravure-coating, which are also compatible with roll-to-roll processing as shown in Fig 2b.

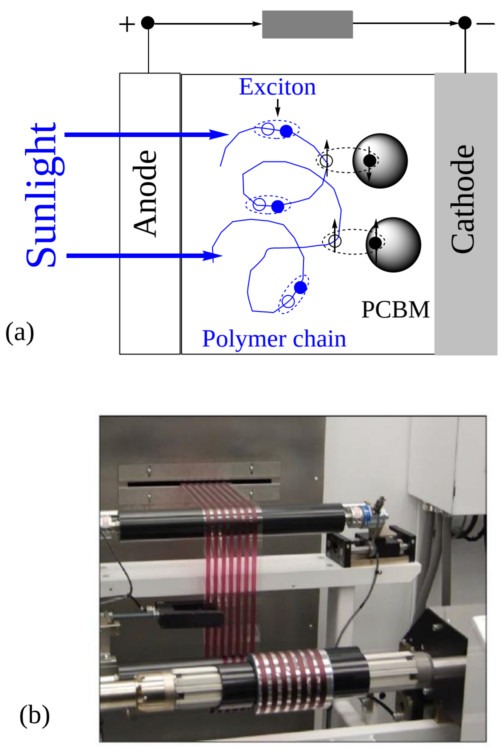

Figure 2. a) Working principle of an organic solar cell. b) Roll-to-roll processing can be used to create OPV cells.

2 ORGANIC PHOTPVOLTAICS & COMPARISON TO OTHER ENERGY HARVESTING TECHNOLOGIES

While crystalline silicon based PV cells and other inorganic materials such as CdTe and copper-indium/gallium-selenide/sulphide Cu(In,Ga)Se_2 (CIGS) account for 99% of the world production of solar cells, the need for high-temperature processing and high vacuum environments keeps the cost of these modules high. It is imperative that low cost alternative energy sources be found since fossil fuel reserves are limited and lead to CO_2 emissions, impacting global warming. In addition, worldwide demand for energy will be tripled by the end of the century, with current global energy usage at ~ 12 TW for 6.5 Billion people which is projected to reach ~ 20 TW for 8-10 billion people by 2050. The urgency for developing efficient renewable energies is even more pressing considering the demand arising from emerging economies, such as China, India and Brazil. In order to meet the DOE cost goal for achieving \$0.2/Watt, low cost, high efficiency PV technologies are being actively sought. Figure 3 surveys the various technologies that are currently in consideration for PV, from crystalline Si cells, multi-junction concentrators, thin-film technologies to emerging technologies which involves the use of nanomaterials,[9] and also includes organic PV technologies.

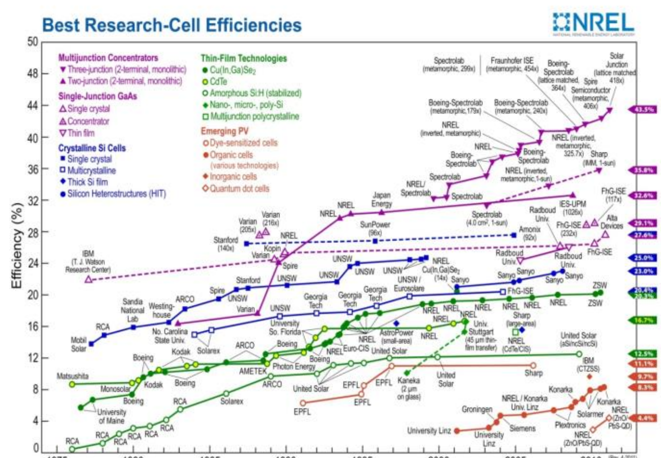

Figure 3: Comparison of OPV to other energy harvesting technologies. Source NREL.

Crystalline Si is considered a first generation (I) technology for PV, as exemplified in Fig 4a, where the power conversion efficiencies (PCEs) have reached ~ 25%. The second generation technologies (II) are based on thin films: amorphous Si, CdTe, and CIGS. While CIGS thin films have PCEs ~ 19 %, amorphous Si, although being cheaper than crystalline Si, has lower efficiencies ~ 12% and also suffers from stability issues which has limited its use in commercial applications. Third generation PV cells with ultrahigh efficiencies and/or ultra-low costs have been proposed, and if successful, would significantly reduce the cost-to-efficiency ratio and make solar electricity competitive against or even cheaper than fossil fuel generated electricity. Organic PV is a class of technologies that is considered to lie in this third generation PV cell technology (III)

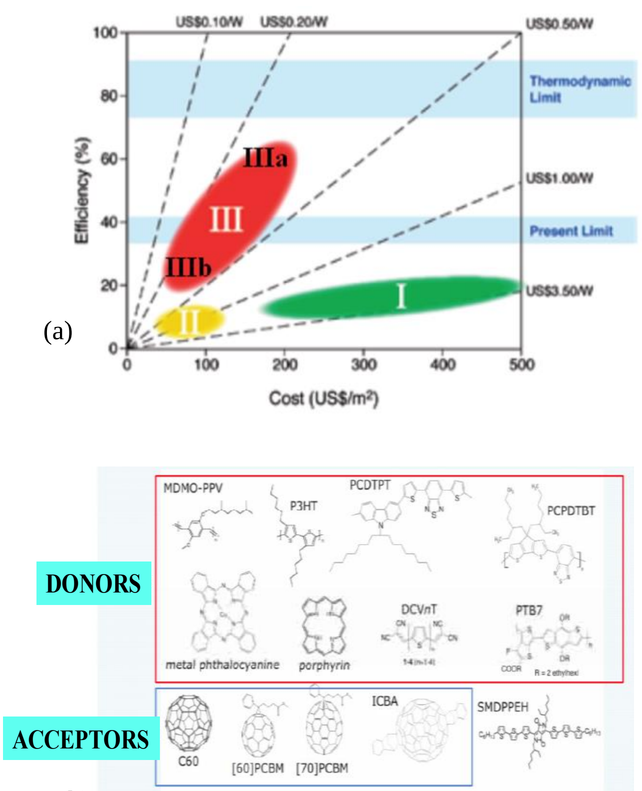

Figure 4. a) Generation I, II and III solar cell technologies. OPV is considered to lie in Generation III due to its prospects for high efficiency and low cost. b) Some representative materials used as p-type donors and n-type acceptors in organic solar cells.

A wide variety of new organic materials have now emerged,[10,11] as exemplified in Figure 4b; these include the development of conjugated p-type polymers such as regioregular poly(3-hexylthiophene) (P3HT) as the electron donors materials and fullerene derivatives, such as [6,6]-phenyl-C61-butyric acid methyl ester (PC61BM) or [6,6]-phenyl-C71-butyric acid methyl ester (PC71BM) as the n-type acceptors. Organic PV is also particularly attractive for integration with flexible materials such as clothes and tents. Considerable progress has been made in enhancing the PCE in OPV from less than 1% in the poly(phenylene vinylene) (PPV) system to 4–5% in the poly(3-hexylthiphene) (P3HT) system in 2005,[12] to 10.6% achieved recently.[13] The significant progress seen in PCE in OPV can also be elucidated by the steeper slope of the OPV technology line in Fig. 3 in recent years, when compared to other energy harvesting technologies that have remained largely flat during the past 10 – 15 years, such as CIGS and amorphous Si. Despite the progress, challenges still lie ahead in improving PCE's in OPV further to make them economically competitive with other commercial technologies, as well as enhancing their operational stability

3 PROSPECTS OF 2D LAYERED MATERIALS FOR ENERGY AND FLEXIBLE ELECTRONICS

The incorporation of novel low-dimensionality materials such as graphene in flexible and organic electronics continues to be an actively researched area. For example, due to its flexibility, strength, high conductivity, transparency and low cost, graphene has been proposed as a replacement for indium tin oxide for solar cells,[14] and organic light emitting diodes, as well as in touch screens.[15] Indium tin oxide is currently the leading material for transparent conductors but given its scarcity, the cost of this material is becoming prohibitively expensive.

Although graphene was the first class of a two-dimensional (2D) layered material to be isolated experimentally in 2004, recently, layered 2D crystals of other materials similar to graphene have been realized. These include insulating hexagonal-BN (band gap ~5.5 eV) and transition metal di-chalcogenides (TMDCs) which display properties ranging from metallic NbS_2 to semiconducting MoS_2. The TMDCs consist of hexagonal layers of metal M atoms sandwiched between two layers of chalcogen atoms X with stoichiometry MX2; e.g. for the case of MoS_2, M = Mo, X = S. As with TMDCs in general, the interatomic binding in MoS_2 is strong, arising from the covalent in-plane bonding, but the subsequent layers interact through the weaker van der Waals interlayer forces.

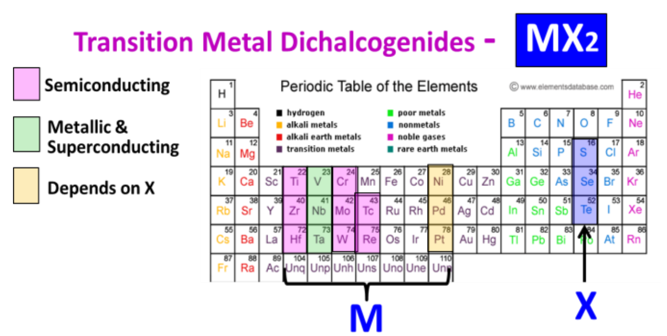

Figure 5. The transition metal di-chalcogenides are an example of 2D layered materials. Depending on the combination of the transition metal M, and the chalcogen atom X (S, Se, Te), a wide range of properties can arise.

Recently, it has been shown that bulk MoS_2 films are indirect band-gap semiconductors with a band gap of ~1.2 eV and a transformation takes place to a direct band gap semiconductor with a gap of ~1.8 eV. This behavior is similar to other 2D TMDCs such as WS_2. Given the tunable, direct band gaps of some of the 2D TMDCs and their relative earth abundance, they appear to be a promising choice for solar cells or light-absorbing components, photo detectors, in addition to light-emitting devices. Also, given the thinness of these materials, the devices could be made transparent, light and flexible, and could provide an alternative choice to organic semiconductors, given their degradation at ambient conditions. Recently, a bulk heterojunction solar cell made from TiO_2 nanoparticles, MoS_2 and poly(3-hexylthiophene) (P3HT) was recently demonstrated with 1.3% photo conversion efficiency.[16] TMDCs have also been utilized as electron-blocking layers in OLEDs.[17]

For flexible and transparent optoelectronics applications such as displays and wearable electronics, materials such as conductors, semiconductors, optical absorbers, light emitters and dielectrics are desired. Semiconducting 2D TMDCs, combined with other 2D materials such as conducting graphene and insulating BN, can enable 2D electronic circuits to be fabricated on flexible substrates. In addition, the mechanical properties of MoS2 appear to be very attractive, where it was found to be 30 times as strong as steel and could tolerate deformations of up to 11% before breaking.[18] Such mechanical properties makes MoS_2 one of the strongest semiconducting materials and very attractive for flexible electronics.

In conclusion, in this paper an overview of organic semiconductors was presented, with a focus on their use in OFETs, OLEDs and OPV. The emergence of novel 2D layered materials beyond graphene was also discussed in the context of the exciting applications they promise in flexible electronics as well as for energy harvesting applications.

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