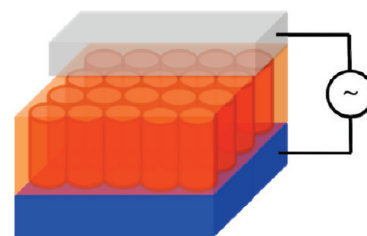


One-Dimensional Nanostructured Semiconducting Materials for Organic Photovoltaics

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ABSTRACT Bulk heterojunction solar cells with highly ordered one-dimensional (1D) nanostructured components of semiconducting conjugated polymers, dyes, and metal oxides are reviewed in terms of device structure and performance. The morphologically controlled semiconducting materials show characteristic features of the light-harvesting and photocurrent generation. We highlight the recent progress and improvement of self-assembling 1D materials for a donor–acceptor active layer as well as an electron-transporting layer in organic solar cells. Strategies of the fabrication procedures and origin of the photophysical properties are summarized. 1D nanostructured semiconducting materials that are vertically phase-separated with respect to a transparent conducting electrode facilitate efficient carrier transportation and collection.



Recently, solar cells have attracted much attention relevant to global environmental issues. In particular, organic photovoltaics (OPVs) such as dye-sensitized solar cells (DSSCs) and organic thin-film solar cells have made remarkable progress in terms of power conversion efficiency (PCE) and durability.^{1,2} The maximum PCEs of DSSCs (11 %)³ and organic thin-film solar cells (7 %)⁴ are still lower than those of silicon-based solar cells. Nevertheless, such organic materials are superior to silicon in light of lightness, flexibility, color tunability, and facile processability and thus are highly promising for ubiquitous utilization.^{5,6} The external quantum efficiency (EQE) of a OPV based on exciton dissociation at a donor–acceptor (D–A) interface is represented as follows:⁷ $\eta_{\text{EQE}} = \eta_{\text{A}} \times \eta_{\text{ED}} \times \eta_{\text{CT}} \times \eta_{\text{CC}}$, where η_{A} is the optical absorption efficiency, η_{ED} is the exciton diffusion efficiency, η_{CT} is the charge-transfer efficiency, and η_{CC} is the carrier collection efficiency. In OPVs, the short exciton diffusion length of donors (less than 10 nm),⁷ which is much shorter than the optical absorption length (~ 100 nm)⁸ for sufficiently high η_{A} , has limited the EQE, and a large fraction of the photogenerated excitons remains unused for photocurrent generation. Therefore, it is crucial to control the morphology and mixing state of the D–A heterojunction, which would influence on the efficiencies of η_{ED} , η_{CT} , and η_{CC} . Even though morphology control of the bulk heterojunction by treatments of solvents, annealing, and/or additives attained a high EQE over 70 %, overall PCEs reported are still low due to the inferior charge-transport properties and limited spectral absorption range of the devices. Kayes et al. reported that the use of low diffusion length materials such as the absorbing base in a conventional planar p–n junction solar cell geometry results in devices having a carrier collection limited by minority carrier diffusion in the base region.¹⁰ In this context, they proposed an improved semiconductor device consisting

of arrays of “radial p–n junctions” of densely packed nanorods (Figure 1), which would enable good optical absorption and carrier collection into orthogonal spatial directions (namely, parallel to the incident light direction).

Although such a well-organized nanostructure is difficult to be constructed, attempts have been made to achieve the highly efficient charge-transport property (namely, reduced recombination under forward bias) and effective optical absorption by tailoring the functionality through molecular design and chemical synthesis of 1D nanostructured semiconducting materials. This Perspective will focus on recent advances in self-assembling 1D materials for a D–A active layer as well as an electron-transporting layer in OPVs including both DSSCs and organic thin-film solar cells. Such morphologically controlled semiconducting materials are highly promising to reveal characteristic features of the light-harvesting and photocurrent generation. Strategies of the fabrication and origin of the photophysical properties of 1D nanostructured semiconducting materials are discussed and addressed with outlooks for the future.

Morphologically controlled semiconducting materials are highly promising to reveal characteristic features of the light-harvesting and photocurrent generation.

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Supramolecular 1D Nanostructured Donor–Acceptor. Conjugated polymers (poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene (MDMO-PPV), poly(3-hexylthiophene) (P3HT), and poly(9,9'-dioctylfluorene-co-bis-N,N'-(4-butylphenyl)-1,4-phenylenediamine) (PFB)) and fullerene derivatives ([6,6]-phenyl- C_{61} -butyric acid methyl ester and [6,6]-phenyl- C_{71} -butyric acid methyl ester) have been widely utilized as p-type (donor) and n-type (acceptor) components of the bulk heterojunction layer in polymer/fullerene solar cells. Inspired by the developments, Coakley et al.¹¹ and Günes et al.¹² proposed that high-performance bulk heterojunction solar cells possess an interpenetrating network of D–A molecules in the p–n blend film sandwiched between two electrodes bearing different work functions as an “ordered bulk heterojunction” that is analogous to a “radial p–n junction”.¹⁰ Various strategies have been suggested to create such a desirable D–A bicontinuous network in p–n blend films, which exhibit efficient charge

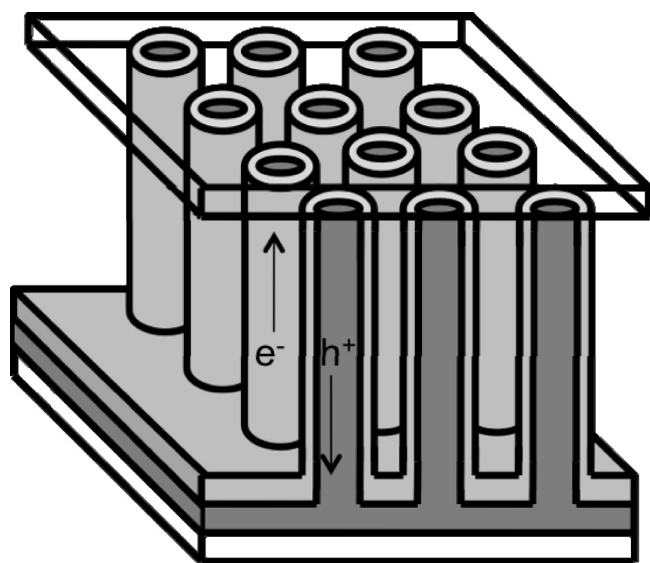


Figure 1. Schematic cross section of the radial p–n junction nanorod cell. (Reprinted from ref 10. Copyright 2005, American Institute of Physics.)

separation as well as hole and electron transportation through the network.

Bicontinuous D–A arrays in liquid crystalline oligothiophene- C_{60} had been formed by Li et al.¹⁵ Synchrotron radiation small-angle X-ray scattering (SAXS) analysis disclosed that liquid crystalline oligothiophene- C_{60} arrays showed the head/tail orientation in the nonuniform lamellar structure and exhibited periodic conductive character under illuminate/dark conditions. Fang et al. reported a three-point hydrogen bonding assembly between a conjugated PPV and a functionalized C_{60} containing a 2,6-diacylamidopyridine moiety.¹⁴ Remarkable quenching of the PPV moiety by the addition of C_{60} was observed with the Stern–Volmer constant of $5.8 \times 10^4 \text{ M}^{-1}$, though further investigation of the construction of photovoltaic devices is still underway. Imahori et al. reported continuous hydrogen-bonded porphyrin–fullerene composites using ZnP–acid and C_{60} –acid (Figure 2) on a SnO_2 electrode, which exhibited efficient photocurrent generation compared to the reference system without hydrogen bonding.¹⁵

They also succeeded in preparing a molecular crystalline system using electrophoretically deposited nanoarrays of porphyrin–fullerene on a SnO_2 electrode, which led to an incident photon-to-current efficiency (IPCE) of up to $\sim 60\%$.¹⁶ Such self-assemblies of D–A small molecules have difficulty in achieving vertical arrangement of bicontinuous D–A arrays on an electrode. On the other hand, Snaith et al. developed a polymer brush/ CdSe nanocrystal composite for photovoltaic devices and attained an IPCE of $\sim 20\%$,¹⁷ though the difficulty in incorporating the acceptor into the polymer brush uniformly at a molecular level still remains. Morisue et al. designed 1D vertical donor arrays on the electrode by self-assembly of porphyrin arrays through coordination and the metathesis reaction.¹⁸ However, they only prepared well-organized directional and oligomeric porphyrin arrays without forming bicontinuous D–A arrays. Therefore, the relationship between the molecular structures, the film structures, and the photoelectrochemical properties of D–A assemblies on electrodes remains elusive due to the difficulty in achieving vertical arrangement of bicontinuous D–A arrays on electrodes. Recently, Kira et al. successfully prepared vertical alignment of porphyrin–fullerene nanoarrays by coordination bonding and π – π interaction on a flat SnO_2 electrode (Figure 3).¹⁹

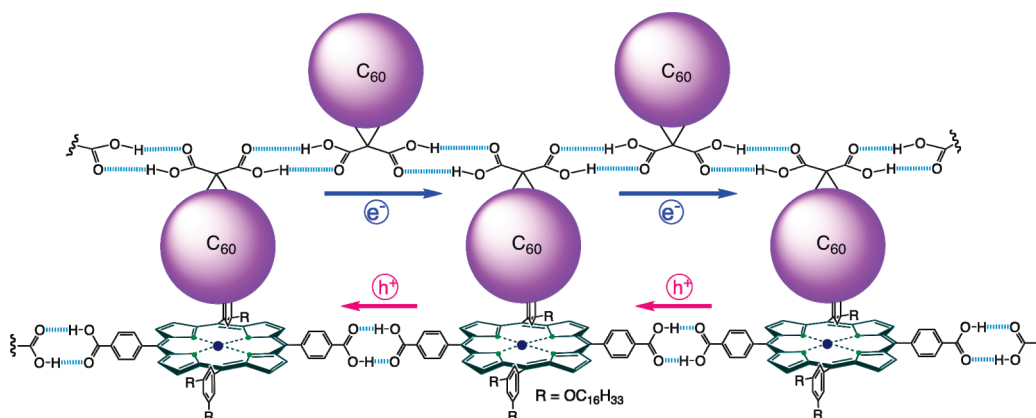


Figure 2. Hydrogen-bonded porphyrin–fullerene composites on SnO_2 electrodes (from ref 15).

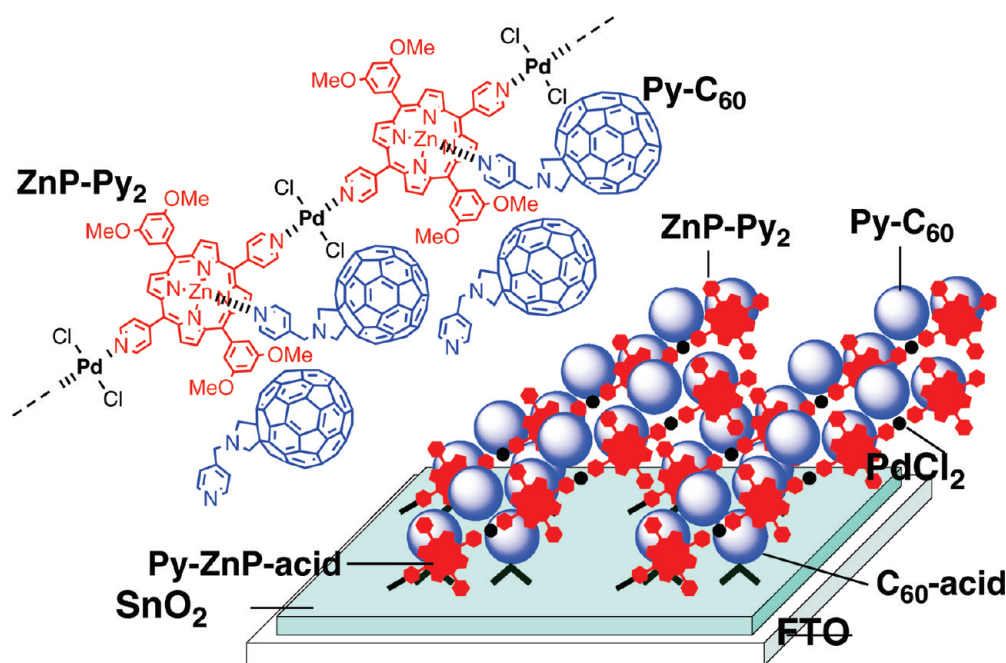


Figure 3. Schematic porphyrin–fullerene arrays on a SnO_2 electrode (from ref 19).

The photocurrent generation efficiencies were found to correlate well with the length of porphyrin arrays and the nature of C_{60} derivatives. This system exhibited a maximum IPCE of 21 %, which is comparable to the corresponding value reported by Snaith et al.¹⁷ Li et al. fabricated multilayer assemblies by consecutive absorption of poly{(2,5-bis(3-bromotrimethylammonio)propoxy)phenylene-1,4-divinylene}alt-1,4-(2,5-bis(2-(2-hydroxyethoxy)ethoxy))phenylenevinylene} (BH-PPV) and the sodium salt of hexa(sulfobutyl)fullerenes ($\text{C}_{60}\text{-HS}$).²⁰ A steady and rapid cathodic photocurrent response of $5.5 \mu\text{A cm}^{-2}$ was measured as the irradiation of the multilayer film was switched on and off. The SAXS pattern of a seven-bilayer film of BH-PPV and $\text{C}_{60}\text{-HS}$ revealed a series of Kiessig fringes, which suggested that the D–A layer-by-layer film was uniform and flat (namely, bicontinuous). They found that the photocurrent increases with increasing bilayer number until the sixth bilayer. As the film becomes thicker, the photocurrent shows no steady increase and even decreases since the probability of charge recombination and the film's electrical resistance increase with increasing film thickness. Self-organization of bicontinuous D–A arrays can also be introduced by diblock copolymers, as shown by Charvet et al.²¹ Characteristic ambipolar charge transport in 1D nanostructured films was observed by the current-mode time-of-flight (TOF) measurement. Desirable “ordered bulk heterojunctions”^{11,12} were partially achieved by Matsuo et al. They formed a columnar structure ($\sim 60\%$) of a tetrabenzoporphyrin precursor and silylmethyl C_{60} on a glass/indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS) substrate.²² SEM observation revealed that tetrabenzoporphyrin molecules were assembled to yield the columnar structure with a height of 65 nm and a diameter of 26 nm. Each column was estimated to contain 30 000–100 000 molecules of benzoporphyrin. The three-layered p–i–n structured photovoltaic device afforded a PCE

of 5.2 % with an open circuit voltage (V_{oc}) of 0.75 V, a short circuit current (J_{sc}) of 10.5 mA cm^{-2} , a fill factor (FF) of 0.65, and a maximum IPCE of 50 %. There is still room for improvement with regard to the diameter and regularity of the columnar structure.

1D Nanostructured Electron-Transporting Layer. Novel hybrid solar cells have been made from a combination of both organic and inorganic semiconducting materials. Huynh et al. reported hybrid CdSe nanorod–P3HT solar cells.²³ They prepared three different types of CdSe nanocrystals, with the aspect ratios ranging from 1 to 10. A photovoltaic device consisting of $7 \text{ nm} \times 60 \text{ nm}$ CdSe nanorods (namely, the aspect ratio was ~ 10) and P3HT showed a best EQE of 54 % and a PCE of 1.7 %. Kang et al. tried to improve the alignment of the CdTe nanorod vertically through electrodeposition, though the resulting EQE was 18 % and the PCE was 1.1 %.²⁴ Therefore, further optimization is still required for the improvement of the nanocrystal–polymer interface to remove nanorod surface traps and for alignment of the nanorods perpendicular to the substrate completely and adjustment of their length. Coakly et al. reported that the hole mobility of P3HT can be enhanced 20 times by the vertical alignment through infiltrating it into straight nanopores of anodic alumina.²⁵ To rectify electron flow to the ITO side, ZnO (work function $\sim 4.3 \text{ eV}$, LUMO $\sim 4.1 \text{ eV}$) and TiO_x (work function $\sim 4.3 \text{ eV}$, LUMO $\sim 4.4 \text{ eV}$)²⁶ are particularly suitable as electron-transporting layers (namely, hole-blocking layers), considering the large band gaps and good energy level matching. In this context, various types of inverted polymer solar cells with nanostructured ZnO and TiO_x have been developed and evaluated. Mor et al. presented an efficient hybrid solar cell with vertically oriented TiO_2 nanotube arrays formed by anodization.²⁷

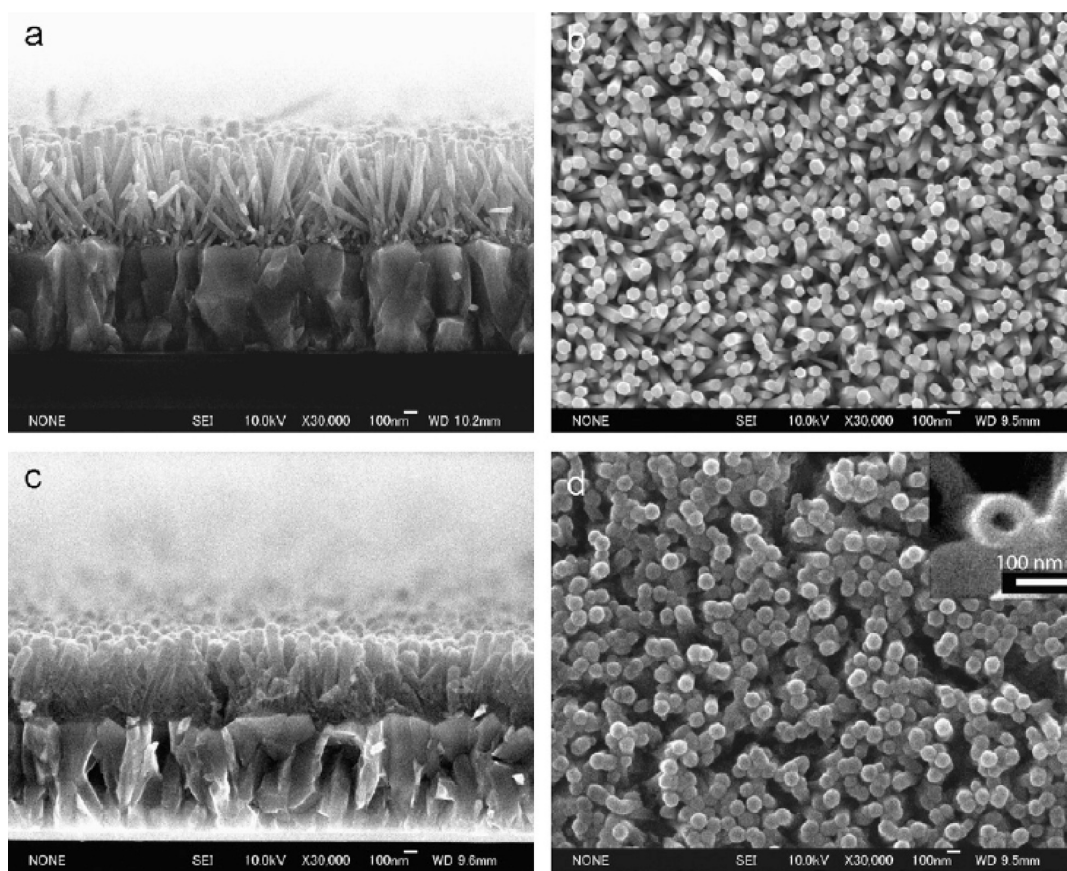


Figure 4. SEM images of ZnO nanorod arrays (a, b) and TiO₂ nanotube arrays (c, d) grown on a FTO substrate; cross-sectional views and top views, respectively (from ref 32).

The device exhibited a PCE of 4.1 % with a maximum EQE of 80 % and an excellent J_{sc} of 12.4 mA cm⁻². They claimed that the double heterojunction structures of P3HT-PCBM and P3HT-TiO₂ were responsible for efficient charge separation. On the other hand, stepwise electron transfer from the P3HT excited state to PCBM, followed by electron injection from the reduced PCBM to a conduction band of the nanocrystalline ZnO electrode, has been described²⁸ in analogy to ZnO/P3HT-PCBM bulk heterojunction solar cells. Taking into account the high electron mobility of 1D ZnO,²⁹ Takanezawa et al. developed hybrid devices composed of P3HT-PCBM/ZnO nanorod arrays, which exhibited a PCE of 2.7%.³⁰ Hayashi et al. applied 1D ZnO to “dye-sensitized bulk heterojunction” solar cell with zinc porphyrin and fullerene (C₆₀-acid), possessing characteristics of both dye-sensitized and organic thin-film devices.³¹ Despite a larger surface area of the ZnO nanoparticle electrode by a factor of 3 relative to that of the corresponding ZnO nanorod electrode, they noted similar photocurrent generation efficiencies. Rattanaoravipha et al. coated ZnO nanorod arrays with TiO₂ (Figure 4) to fabricate P3HT-PCBM devices resulting in a PCE of 0.7 % because of the low crystallinity and small surface area of TiO₂ nanotubes.³²

Further improvement of the hybrid electron-transporting layers would be required for enhancing charge separation and preventing charge recombination. For instance, the cell

performance of DSSC can be improved by treating the TiO₂ nanotube arrays with TiCl₄.³³ After TiCl₄ treatment, the TiO₂ nanotubes were covered with a small amount of TiO₂ crystals. Both the J_{sc} and the PCE were ~2 times larger than those without the TiO₂ treatment. A similar trend can be seen in ZnO nanorod-P3HT solar cells prepared with and without TiO₂ coating; through TiCl₄ treatment though, the TiCl₄-treated device resulted in a low PCE of 0.07%.³⁴ Recently, Guo et al. prepared the single p-n junction nanowire composed of polypyrrole/CdS by an electrochemical method through an anodic aluminum oxide template.³⁵ The nanowire exhibited a PCE of 0.018 % under an illumination intensity of 6.05 mW cm⁻².

Versatile 1D nanostructures of semiconducting conjugated polymers, dyes, and metal oxides have been explored for applications to a D-A active layer as well as an electron-transporting layer in OPVs. In addition, recent progress of the molecular design of novel donors^{4,9} and acceptors^{36–38} with respect to the band gap tuning is outstanding, and the energy level diagram is also tunable by doping or other surface treatment of the electrode.^{39,40} The active layer structure shown in Figure 1 is the ideal one for efficient organic solar cells. It provides effective exciton dissociation if the size of each donor and acceptor section is within an exciton diffusion length and greatly reduces charge losses by recombination because of the independent and straight pathways for hole

and electrons. Although further tailoring is still required, such 1D nanostructured organic/inorganic semiconducting materials, which are vertically phase-separated with respect to a transparent conducting electrode by rational design and strategy, will allow us to achieve excellent optical absorption and efficient carrier transport and collection, resulting in remarkable improvement of the device performance.

Versatile 1D nanostructures of semiconducting conjugated polymers, dyes, and metal oxides, have been explored for applications to a donor–acceptor active layer as well as an electron-transporting layer in organic photovoltaics.

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