Carbon nanostructures for solar energy conversion schemes

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Developing environmentally friendly, renewable energy is one of the challenges to society in the 21st century. One of the renewable energy technologies is solar energy conversion---a technology that directly converts daylight into electricity. This highlight surveys recent breakthroughs in the field of implementing carbon nanostructures---*fullerenes* (0D), *carbon nanotubes* (1D), *carbon nanohorns*, and *graphene* (2D)---into solar energy conversion schemes, that is, bulk heterojunction and dye-sensitized solar cells.

Of all the elements in the periodic table, only carbon provides the basis for life on earth. Carbon is also the key for many technological applications ranging from drugs to synthetic materials that have become indispensable in our daily life and have influenced the world's civilization for centuries. Importantly, the structural diversity of organic compounds and molecules results in sheer endless chemical and physical properties. Altering the periodic binding motifs in networks of sp^3-, sp^2-, and sp-hybridized C-atoms represents the conceptual starting point for constructing a wide palette of carbon allotropes. To this end, the past two decades have served as a test-bed for measuring the physico-chemical properties of carbon in reduced dimensions starting with the advent of *fullerenes* (0D), followed in chronological order by *carbon nanotubes* (1D), *carbon nanohorns*, and, most recently, by *graphene* (2D) and poised for wide-ranging applications—see Fig. 1.[1]

Expanding global needs for energy have led to a significant effort to develop alternatives to fossil fuels. While alternative sources for energy are already in use, they comprise a small percentage of the energy demands needed to carry us through the 21st century. No single source will solve the global needs, but the development of renewable sources based on photovoltaics has a vast potential as a point-of-use power source. The creation of a sustainable future and the increase of renewable energy sources

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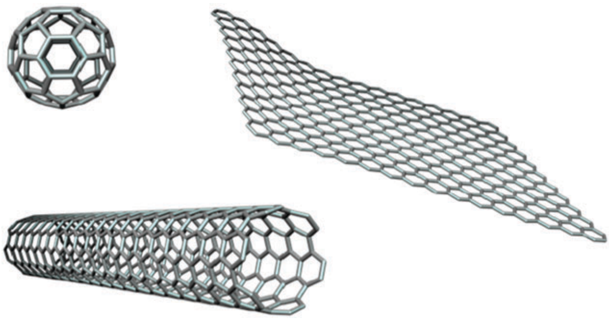

Fig. 1 Chemical structures of *fullerenes* (0D), *single wall carbon nanotubes* (1D), and *graphene* (2D).

are prominent means to improve quality of life and health and, in turn, are among the *14 Challenges the World Must Address to Ensure the Planet's Survival.*[2]

0D fullerenes

The first successful preparation of *0D fullerenes* in macroscopic quantities by the evaporation and recondensation of graphite was reported in 1990.[3] 0D fullerenes are now readily available and exhibit exciting characteristics. For example, the delocalization of charges within the giant, spherical carbon framework together with the rigid, confined structure of the aromatic π-sphere offers unique opportunities for stabilizing charged entities. Above all, the small reorganization energies of fullerenes in charge transfer reactions have led to a notable breakthrough in synthetic electron donor–acceptor systems by providing *accelerated charge separation and decelerated charge recombination*.[4]

In the context of *0D fullerenes*, organic photovoltaics (OPV) have gained extraordinary attention due to their immense potential in low-cost solar energy conversion devices. For typical bulk heterojunction solar cells—involving films of conjugated polymers and fullerenes or electron donor–acceptor conjugates—spin-coating has emerged as the number one choice to process them on electrode surfaces. In the photoactive layer, control over the interpenetrating network at the nanometre scale is considered to be the key step to ensure efficient charge separation/charge transport.[5]

Nevertheless, the power conversion efficiency of OPV technologies remains relatively low compared to other photovoltaic technologies. In fact, only a few reports document OPV device efficiencies over 5% employing [6,6]-phenyl-C_{61}-butyric methyl ester[6] and/or [6,6]-phenyl-C_{71}-butyric methyl ester.[7] Notable is in this context a dihydronaphthyl-fullerene benzyl alcohol benzoic ester derivative of C_{60} with an efficiency of 4.5%.[8] Nevertheless, the low efficiencies are in part due to the rather poor energy level offset between the available donor and acceptor materials.[9]

Novel acceptor materials with LUMO energies closer to that of the donor, such as the derivatives of metallo endohedral fullerenes $M_3N@C_{80}$ (M = Sc, Y, Gd, Tb, Dy, Ho, Er, Tm, Lu),[10] offer the possibility of dramatically increasing OPV power conversion efficiency by utilizing more of the energy associated with the exciton. We reported, for example, the influence that 1-(3-hexoxycarbonyl)-propyl-1-phenyl-[6,6]-$Lu_3N@C_{81,}$, a novel acceptor material, has on active layer morphology and performance of OPV devices using this material. Polymer/fullerene blend films with poly(3-hexylthiophene) donor material and 1-(3-hexoxycarbonyl)propyl-1-phenyl-[6,6]-$Lu_3N@C_{81}$ acceptor material were studied. Due to a smaller molecular orbital offset the OPV devices built with 1-(3-hexoxycarbonyl)propyl-1-phenyl-[6,6]-$Lu_3N@C_{81}$ display increased open circuit voltage over empty cage fullerene acceptors—see Fig. 2. The photovoltaic performance of these metallo endohedral fullerene blend films is found to be highly impacted by the fullerene loading. The findings indicate that the optimized blend ratio in a poly(3-hexylthiophene) matrix differs from a molecular equivalent of an optimized poly(3-hexylthiophene)/[6,6]-phenyl-C_{61}-butyric methyl ester active layer, a finding that was related to the physical differences of the C_{80} fullerene. Through properly matching the film processing and the donor/acceptor ratio, devices with power conversion efficiencies (η) greater than 4% were demonstrated.[11]

A similar approach, that is, utilizing the advantage of higher LUMO levels in bis-adducts of fullerenes—formed by two indene units covalently connected to C_{60}—offers a direct pathway to greater efficiency of OPV devices by reducing the energy loss of the photoexcited electrons. The presence of two indene groups improves the visible absorption compared to the parent [6,6]-phenyl-C61-butyric methyl ester, as well as its solubility and a 0.17 eV higher LUMO. An efficiency of 5.44% implies an outperforming of poly(3-hexylthiophene)/[6,6]-phenyl-C_{61}-butyric methyl ester cells, which afforded an efficiency of 3.88% under the same experimental conditions.[12]

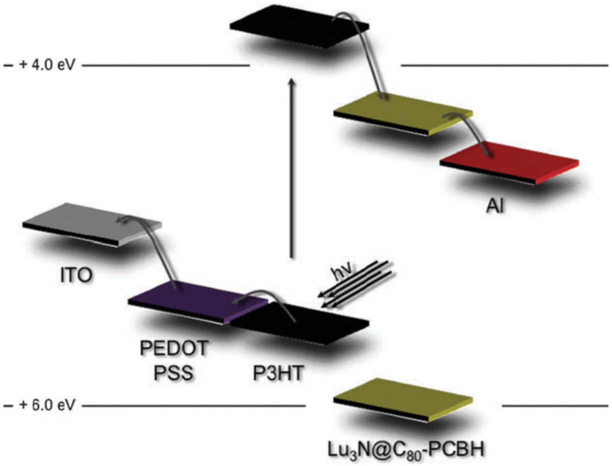

Fig. 2 Energy level diagram adjusted to the vacuum level for a ITO/PEDOT:PSS/P3HT:$Lu_3N@C_{80}$-PCBH/Al device.

Next to higher V_{OC}, higher I_{SC} should also be considered to increase the power conversion efficiency. One way to go is the use of low band gap polymers, which are loosely defined as polymers that absorb light with wavelengths longer than 620 nm. Importantly, lowering the band gap allows absorbing more photons and, in turn, generating higher currents. Examples are [6,6]-phenyl-C_{71}-butyric methyl ester blended with either poly[2,1,3-benzothiadiazole-4,7-diyl[4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-*b*:3,4-*b*']-dithiophene-2,6-diyl]] (PCPDTBT) or poly[4,8-bis-substituted-benzo[1,2-*b*:4,5-*b*0]-dithiophene-2,6-diyl-alt-4-substituted-thieno[3, 4-*b*]thiophene-2,6-diyl] (PBDTTT) that give rise to efficiencies of 5.5 and 6.77%, respectively.[7a,11, 13]

An intriguing approach to enhance light-harvesting efficiencies is dye-sensitized solar cells. Particularly promising is the electrophoretical deposition of fullerene clusters containing suitable electron donors onto semiconducting electrodes.[14] To this end, desirable phase-separated, interpenetrating networks are created that provide nanostructured pathways for charge carriers (*i.e.*, electrons and holes). Important is in this context the use of three-dimensionally preorganized systems. Leading examples are dendrimers, oligomers, and nanoparticles of porphyrins that have been combined with fullerenes.[15] For instance, dye-sensitized solar cells using composite clusters of porphyrin–peptide oligomers and C_{60} gave rise to remarkable device performances—η values of 1.6% (I_{SC} = 0.36 mA cm^{-2}, V_{OC} = 0.32 V, FF = 0.47) and IPCE values of 48% at 600 nm. Quite notably, an η of 1.6% is exceeding the 0.043% that was measured for devices using just monomers of porphyrins by a factor of 40.[16] Further performance improvement was achieved through the unique molecular arrangement of 5,10,15,20-(tetrakis(3,5-dimethoxyphenyl)porphyrinato zinc(II) and C_{60} on a SnO_2 electrode. The latter resulted in one of the highest IPCE values among this type of photoelectrochemical devices—60%. Rapid formation of composite clusters (~100 nm) and micro-cocrystals (~2 mm) is key to yield remarkably efficient photocurrent generations by the bicontinuous electron donor–acceptor network at the molecular level.[17]

1D carbon nanotubes (CNT)

Conceptually, *1D carbon nanotubes* (CNT) are considered as small strips of graphene sheets that have been rolled up to form perfect seamless single walled nanocylinders.[1d] The graphene sheets can be wrapped in a variety of ways that are denoted by a pair of indices (*n*,*m*), which define both the diameter and the chirality of SWCNTs. SWCNTs, for which the difference between *n* and *m* is a multiple of three, are metallic, in contrast to the rest, which are semiconducting. The small diameters and the large aspect ratios of SWCNTs render them ideal one-dimensional quantum wires. The *electrical transport in metallic* SWCNTs *is ballistic*, that is, electrons are not subject to any scattering events over a length scale of several micrometres or from any electromigration, even at room temperature. As a consequence, SWCNTs can carry current densities approximately 1000 times that of a typical copper wire. *Electron transport is also ballistic* for *semiconducting* SWCNTs, but only over distances of a few hundred nanometres.[18]

The overriding motivation to pursue the dispersion of CNT into photoactive layers is to combine the physicochemical properties of conjugated polymers with the long range charge transport characteristics of CNT in order to obtain efficiently performing OPV devices. In fact, initial reports revealed appreciable success in integrating CNT as an electron accepting material together with electron-donating conjugated polymer, such as poly(3-octylthiophene),[19] or poly(*p*-phenylenevinylenes),[20] into ITO based photovoltaic devices.

Spin coating leads, however, only to moderate maximum power conversion efficiencies of 0.22 regardless of the use of SWCNTs or multi wall carbon nanotubes (MWCNT).[21] Although the polymer CNT cells give rise to an exceptional V_{OC} between 0.75 and 1 V as well as an advantageous near-infrared light harvesting, their photocurrents are quite low. Please compare, for example, 0.25 to 0.5 mA cm^{-2} to 10.6 mA cm^{-2} measured for an optimized poly(3-octylthiophene)/[6,6]-phenyl-C_{61}-butyric methyl ester device.[6a] Owing to the fact that CNT are only randomly dispersed within the P3HT matrix leads to a myriad of charge recombination pathways.

More profitable are assembly strategies that follow the protocols of layer-by-layer (LBL)[22] and Langmuir–Blodgett (LB) depositions[23] as well as electrophoresis.[24] The LBL approach, namely, deposition of monolayer based stacks, is very universal and has been extended from SWCNT to double wall carbon nanotubes (DWCNT), MWCNT, and thin multi wall carbon nanotubes (thin-MWCNT), for example, together with water-soluble porphyrins[25] and polythiophene[22a] derivatives. Among all of the CNT that were tested, thin-MWCNT revealed by far the best photovoltaic performance. In particular, for this electron acceptor layer material a maximal IPCE of 1.9% was established.[25]

A viable alternative to the aforementioned is LB, which requires, however, stable SWCNT suspensions. Thus, we turned our attention to a poly(alkoxyphenylene-thiophene) derivative, poly(2,5-dioctyloxy-1,4-phenylene-alt-2,5-thienylene) (POPT), as a potent suspender for SWCNT. POPT is endowed with conjugated π-electrons, while being overall flexible. The POPT/SWCNT mixture was transferred onto solid substrates by the LB method and the morphology of the sample was investigated by means of AFM technique. A peculiar structure was observed: increasing the transferring surface pressure a tubular structure appears more and more clearly. AFM analysis was repeated after 5 hours exposure of the sample to soft X-rays. Here, highly organized structure, probably formed by bundles of nanotubes, originates. After the morphological studies, several photoelectrochemical cells were prepared using the LB film as photocathodes. 55 POPT/SWCNT stacks provided the optimal thickness and V_{OC} = 0.18 V, I_{SC} = 85.8 μA cm^{-2}, FF = 40.0%, and η = 6.23 × 10^{-3}% were recorded.[23]

Exposing SWCNT that were suspended with the assistance of tetraoctylammonium bromide in tetrahydrofuran to an electrophoretic field emerged as a valuable approach to deposit them. In fact, considerable photoconversion efficiencies were achieved when SWCNTs were deposited together with light harvesting CdS quantum dots and porphyrins with maximal values of 1.5%[26] and 13%,[27] respectively.

Single wall carbon nanohorns (SWNH)

Single wall carbon nanohorns (SWNH), conical tubules closed by cone-shaped caps that resemble horns, have emerged as a yet largely unexplored carbon allotrope.[1d] The cones are formed abstractly by cutting a wedge from graphite sheet and connecting the exposed edges in a seamless manner. SWNHs associate with each other to form "dahlia flowerlike structured assemblies" that have average diameters between 80 and 100 nm. X-Ray diffraction showed that the interhorn distance is 0.4 nm, which is slightly larger than the interlayer spacing of 0.335 nm in graphite.[28] Such considerations explain the *microporosity* and *mesoporosity* of SWNHs as well as their *n-type semiconductivity*.[29]

SWNH covalently functionalized at the conical tips with porphyrin moieties were used to construct photoelectrochemical solar cells. Electrophoretic deposition was applied to fabricate films of the modified SWNHs onto optically transparent electrodes, while nanostructured SnO_2 films were cast onto the OTE (OTE/SnO_2). The resulting films on nanostructured SnO_2 electrodes exhibited an incident photon to current conversion efficiency of 5.8% at an applied bias of +0.2 V *versus* SCE in a standard three-compartment electrochemical cell.[30]

2D graphene

The youngest representative of synthetic carbon allotropes is *2D graphene*. Single graphene layers were first prepared successfully in 2004 by simple mechanical exfoliation of graphite using Scotch Tape.[31] Other fabrication strategies, in particular epitaxial growth and solubilization from bulk graphite, have been demonstrated and are paving the way to systematic experiments and technological applications. Transport measurements show that graphene has remarkably high electron mobility at room temperature, with reported values exceeding 15.000 $cm^2\ V^{-1}\ s^{-1}$.[32] Additionally, the symmetry of the experimentally measured conductance indicates *high mobility for holes and electrons*. An ideal monolayer of graphene has an optical transmittance of 97.7%.[33] In summary, graphene should be a cost-effective and abundant source for transparent conductive electrode applications.

Organic solution-processed graphene material has been used as a new acceptor material in organic bulk heterojunction solar cell devices with poly(3-hexylthiophene) and poly(3-octylthiophene) as electron donor. The functionalized graphene material can be dispersed into organic solvent with donor materials P3OT and P3HT to form homogeneous solutions. The interaction between graphene and P3OT/P3HT makes this composite work well as the active layer in devices—see Fig. 3. Controlled annealing improves the OPV device performance considerably, and best power conversion efficiencies ranged from 1.1% to 1.4%.[34,35] Morphology investigations show that better performances are obtained at moderate contents of graphene, which keeps good dispersion, on one hand, and interconnection, on the other hand. Although the power efficiency of 1.4% is moderate, it is comparable with most of the best OPV devices using materials other than fullerenes as electron acceptors.

In the context of dye-sensitized solar cells, precleaned ITOs were coated with thin layers of graphene. The latter was accomplished by means of electrophoretic deposition from aqueous solution of chemically reduced graphene. Subsequently, a layer of CdS quantum dots was directly synthesized onto the predeposited graphene layers by sequential chemical bath deposition from their salt aqueous solutions. Devices with stacks of graphene/CdS were fabricated by repeating the aforementioned steps. When the number of stacks was two or higher, quite constant V_{OC} of 0.68 V was observed. The short-circuit photocurrent density (I_{SC}) increases with the number of stacks reaching a maximum of 1.08 mA cm^{-2} at 8 graphene/CdS stacks before decreasing as the number of stacks further increases. For I_{SC}, the value is more than 2.5 times the value found in analogous cells with SWCNT. Notably, the highest IPCE value (16%)[36] is far superior to that of other carbon/quantum dot solar cells reported to date (5%).[37]

Perspective

There is little doubt that nanocarbons offer a unique platform for exploring structural parameters, fine-tuning critical physico-chemical parameters, and gaining full control over the chemical components and their mutual interactions. The unprecedented charge transfer chemistry of *0D fullerenes*, the ballistic conductance of *1D carbon nanotubes*, the semiconducting features of *carbon nanohorns*, and the high mobility of charge carriers

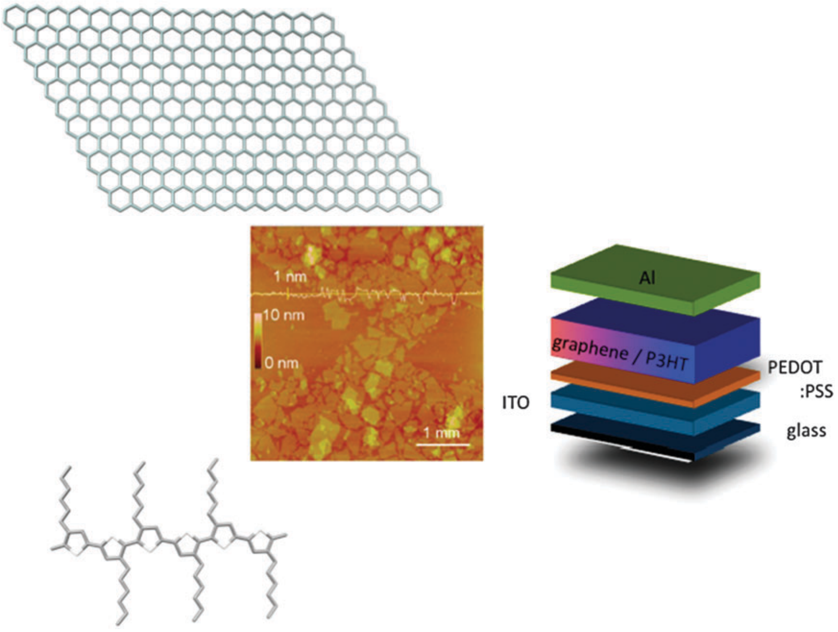

Fig. 3 Prototype of ITO/PEDOT:PSS/graphene:P3HT/Al solar cells.

in *2D graphene* bear great potential to solve a far-reaching challenge, that is, the efficient use of the abundant light energy around us. However, it is now our responsibility to seize such uniqueness to take full advantage of the potential, especially in the field of solar energy conversion schemes.

When considering *fullerenes*, exploiting the structure property relation will certainly be a high priority area of research, especially the control over the electronic properties of functionalized semiconducting materials. Likewise, the morphology in binary, ternary, and multicomponent blends and composites requires our attention.

Composites of *carbon nanotubes*, printed from solution, have been suggested as transparent electrodes for thin film applications like solar cells, lighting, batteries or super-capacitors.[38] There are many fundamental scientific challenges as well as practical challenges that need to be addressed.

With regard to *single wall carbon nanohorns* they will likely play a major role as tunable mesoporous material in the realization of n- or p-type semiconducting electrodes.

Finally, owing to the outstanding electron mobility of *2D graphene* at room temperature, most of the future applications will focus on its implementation as a transparent conducting electrode. Importantly, graphene based transparent films were found to be more flexible when compared with films based on the brittle inorganic benchmark material ITO. Moreover, graphene based films have lower surface roughness when compared with carbon nanotubes based films or metal grids. As a matter of fact, a low roughness is vital to reduce the possibility of leakage current and shorts.

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