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Potential of fullerene-based materials for utilisation of solar energy

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This paper reviews the prospects of fullerene-based materials for photovoltaics. Device structure and parameters of inorganic and organic fullerene-based solat cells are presented. An additional promising direction of solar energy utilisation — production of fullerenes and carbon nanotubes by concentrated sunlight — is also discussed.

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Pristine solid C_{60} is known to exhibit semiconductor-like behavior in its optical and electronic properties while that of doped fullerenes can be "tuned" between semiconductors, conductors and even superconductors [1]. There are, accordingly, great expectations that fullerene-based materials will find practical applications is electronic and optoelectronic devices, and in particular in photovoltaic solar cells.

This paper reviews the prospects of fullerene-based materials for photovoltaics. However, we start with another promising direction of solar energy utilisation — production of fullerenes by concentrated sunlight.

1. Production of fullerenes and carbon nanotubes by concentrated sunlight

In 1990 Krätschmer et al. [2] discovered a simple technique to produce fullerenes. The method uses arc discharge between two graphite electrodes in a helium atmosphere to vaporise graphite and produce fullerene-containing soot, the subsequent extraction of soluble fullerenes from the insoluble species of the soot by an organic solvent (e. g., toluene) and final chromatographic separation of isolated fullerenes (C_{60}, $C_{70}, \ldots$). At present, the most effecient methods of fullerene production involve different modifications of thermal evaporation of graphite in an inert atmosphere (e. g. ac or dc arc discharge between graphite electrodes, laser ablation of graphite) [1].

The electric arc process requires using of high quality, electrically conductive graphite rods. On the other hand, the yield of fullerene production from the collected soot is low (5–10%) due to photodestriction of fullerene molecules by UV radiation of the electric arc [3]. Furthermore, because the yield is low, excessive amounts of toluene are required to separate the fullerenes from the soot. These factors present serious limitations on the minimum cost that can be obtained by this process.

Even though the yield from the laser ablation process can be high, it is generally accepted that this process will not be cost effective for scaling to large production levels [4]. The search for a more efficient and environmentally benign method led to the use of concentrated solar energy to evaporate the carbon and efficiently produce fullerenes [3–8] and carbon nanotubes [8–10].

In all reported solar techniques, concentrated ($\geqslant 1100\,\mathrm{W/cm^2}$) sublight is focused onto a graphite target resulting in its heating up to temperatures in excess of 3500 K. Controlling vaporization and condensation conditions leads to the formation of fullerene-rich soot or/and carbon nanotubes (if the target consists of a mixture of graphite and metal catalysts).

The UV component is sunlight is very small (compared with irradiation of an electric arc). Therefore, the photodestruction process is very weak and the yield of fullerenes is as high as 20% [8]. Increased yield leads to less solvent use, which reduces cost. Furthermore, the relaxation of the requirement to use conductive graphite rods opens the possibility to use less expensive forms of graphite, including mineral graphite powders. A preliminary cost analysis [5] suggested that solar production can be less expensive than the arc process by at least a factor of four.

Fullerenes were demonstrated to be purified and crystallised via differential sublimation [1]. These technological steps are certainly possible to perform in a similar solar furnace.

2. Fullerene-based photovoltaic solar cells

2.1. Why fullerenes are so promising for photovoltaics? We consider the following reasons that make C_{60} unique among all known semiconductors, and in particular, promising for photovoltaic applications.

1) There is probably no more environmentally benign semiconductor than C_{60} in that it can be sythesized from graphite using nothing more than a beam of concentrated solar energy, and subsequently purified and crystallised using the same energy source (as described above).

2) Early studies of C_{60} as a material for inorganic solar cells were instigated by the theoretical prediction [11] that a C_{60} crystal has a direct band gap of 1.5 eV. On one hand, this value is close to the experimental value of about 1.6 eV for the fundamental edge in the optical absorption spectra [12] and that of 1.7 eV for the photoconductivity spectra [13] of C_{60} thin films. On the other hand, this is the optimal value for high efficiency photovoltaic devices of the single

junction type [14]. Recent experimental studies [15,16] demonstrated that the electronic structure of a C_{60} crystal is more complicated. Specifically, the band gap value is suggested to be about 2.3 eV (the mobility gap) but the optical absorption extends from the gap energy to the lower energy side (the optical gap is of $\sim$ 1.6 eV). These experimental works stimulated new theoretical calculations of the band gap value of 2.15 eV using a "many-body" approach [17]. However, even if this is true, the electronic structure and optical properties of C_{60} thin films are suitable for using the material in efficient heterojunction solar cells (such as C_{60}/Si devices).

3) If one contrasts a C_{60} molecular crystal unit cell with the corresponding Si cell, the former has 240 atoms to the latter's 8. This allows the possibility of doping to a much greater percentage than would be possible with conventional semiconductors. Furthermore, unlike the case of conventional semiconductors for which doping is only possible via substitution of atoms (e. g. P or B for Si), fullerenes may be doped in three additional distinct ways: intercalation of dopants between the buckyballs, endohedral doping within the buckyballs themselves and adductive doping to the outside of the buckyballs [1]. The spectrum of resultant doping energy levels will naturally differ from each manner of doping, thus greatly increasing the probability of finding successful dopants for high efficiency photovoltaic devices.

4) For organic donor-acceptor solar cells, a C_{60} molecule is an ideal candidate for acceptor because of its high electron affinity (2.65 eV [1]). Such cells are now becoming a serious alternative to conventional inorganic photovoltaic devices due to a number of potential advantages, such as their light-weight, flexibility and low cost fabrication of large areas. The efficient photoresponse of the donor-acceptor cells consisting of conjugated polymers and fullerenes [18–22] originates from an ultrafast (sub-picosecond) photoinduced electron transfer from the conjugated polymer (as a donor) to a nearby C_{60} molecule (as an acceptor) [23]. Since this process is faster than any other relaxation mechanism in the conjugated polymer, the quantum efficiency of this process is estimated to be close to unity. Accordingly, the best photovoltaic parameters ever reported for organic solar cells — and in particular, energy conversion efficiencies of 2.5% [24] — were for bulk hetrojunction fullerene/polymer devices.

2.2. Inorganic photovoltaic devices. In 1992 Hebard et al. patented an idea for utilisation of photoconductivity of fullerides in the fabrication of fullerene-based solar cells [25]. A photovoltaic response of most device structures is originated from their rectifying properties. However, in that patent publication the authors described a symmetrical (non-rectifying) Ag/C_{60}/Ag device structure which exhibited photoconductivity but no photovoltaic effect.

For the first time, a fullerene-based device with remarkable rectifying effect in the dark and photoresponse under illumination was demonstrated with a sandwich cell consisting of a C_{60} thin film (of 100 nm thickness) and two Al electrodes [26]. The devices without any exposure of the front electrode to oxygen exhibited no rectification and photoresponse. The devices with a front Al electrode exposed to oxygen (before C_{60} film deposition) exhibited a rectification ratio of 66 (at ± 2 V) and greatly enhanced photocurrent (quantum yield of photocurrent for monochromatic irradiation of $\lambda = 400$ nm was about 53%). The observed excitation profile of photocurrent closely follows the optical absorption of C_{60} film. The authors interpreted the results by the formation of an oxide layer at the front Al electrode interface resulting in Metal-Insulator-Semiconductor (MIS) configuration rather than Schottky barrier device. The Schottky barrier solat cells based on C_{60} crystals and films were demonstrated later [27,28].

A heterojunction behaviour with a high rectifying ratio in the dark ($> 10^4$ at ± 2 V) [29] and photovoltage generation [30] were demostrated, firstly, for a C_{60}/p-Si interface. The properties of such a heterojunction were then extensively studied in the dark and under irradiation of various light sources [27–34]. Although different groups studied various device configurations (Nb/C_{60}/Si, Ti/C_{60}/Si [29,31], Au/C_{60}/Si, ITO/C_{60}/Si [30,34], Al/C_{60}/Si [27,28,32,33]), all authors seem to agree that potential barrier formation at the C_{60}/p-Si rather than metal/C_{60} interfaces is repsonsible for strong rectifying properties of the heterostructures.

The detailed study of the photovoltaic properties were performed for highly crystalline C_{60} thin film/p-Si heterojunction solar cells [28,32]. The dark $I-V$ curve is shown in Fig. 1 which exhibits strongly rectifying properties, the rectification ratio being approximately 10^4 at $\pm$ 2 V. Under sun irradiation (AM 1.5), the short-circuit current density, J_{sc}, was found to be 42 μA/cm^2, open-circuit voltage $V_{oc} = 322$ mV, fill-factor $FF = 0.3$. The low values of J_{sc} and $FF = 0.3$ are attributable to the high resistivity of pristine C_{60} films. SPV spectroscopy characterisation

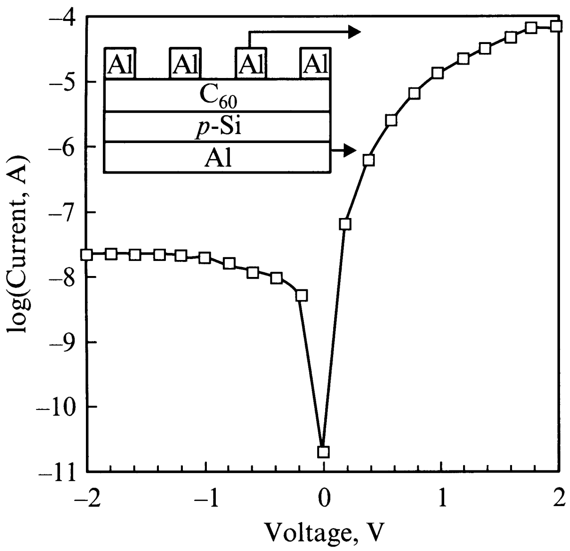

Figure 1. Dark $I-V$ curve of the Al/C_{60}/p-Si/Al heterojunction solar cell (inset shows a schematic diagram of the device) [32].

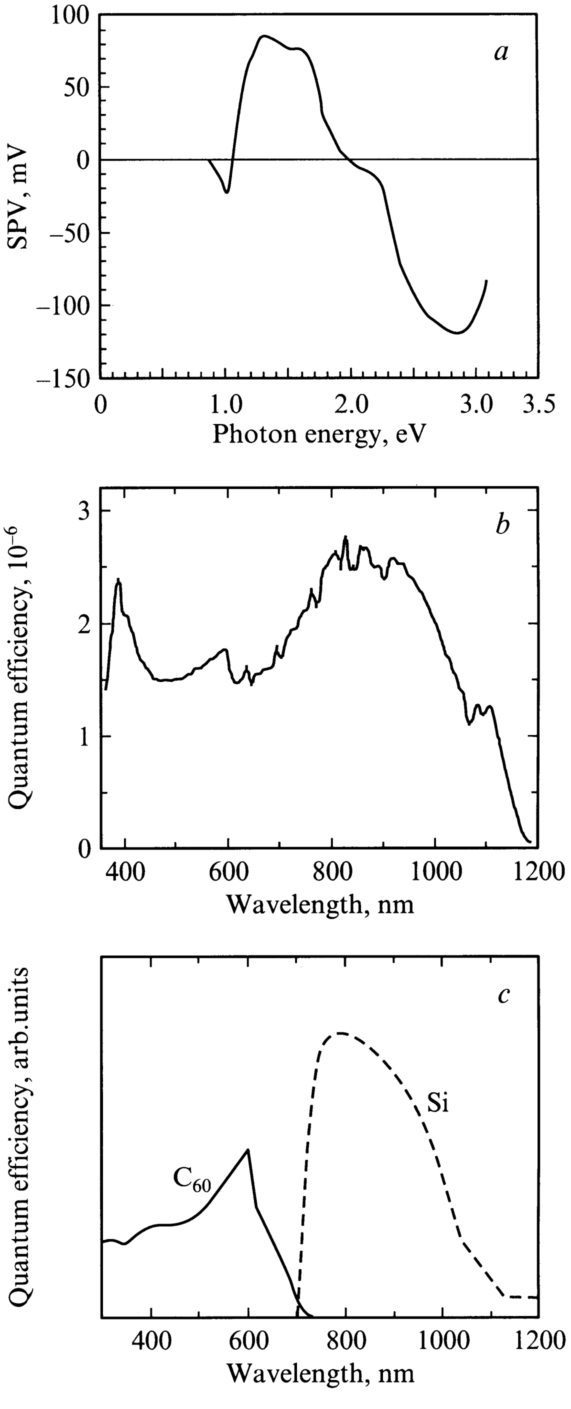

Figure 2. Spectral characteristics of the Al/C_{60}/*p*-Si/Al solar cells: Surface Photovoltage Spectrum [32] (*a*); experimental (*b*) and calculated (*c*) spectral response.

of the devices (Fig. 2, *a*) suggested that the C_{60} film acts as an active layer in the device, in particular for the conversion of short-wavelength components of sunlight. This conclusion is consistent with the spectral response of similar Al/C_{60}/*p*-Si/Al solar cells (Fig. 2, *b*) and one calculated using the published optical absorption coefficient values for C_{60} and Si (Fig. 2, *c*) [33].

The maximum V_{oc} of a heterojunction corresponds to its built- in potential, i.e., difference of the Fermi levels of both semiconductors forming the junction, C_{60} thin film and Si in this case. The Fermi level of Si can be controlled by changing the kind and concentration of dopant. The photovoltage generation by a C_{60}/Si heterojunction was studied with four different types of Si substrates: heavily doped *p*-Si ($8 \cdot 10^{18}\,\text{cm}^{-3}$ of B), lightly doped *p*-Si ($1.5 \cdot 10^{15}\,\text{cm}^{-3}$ of B), lightly doped *n*-Si ($5 \cdot 10^{14}\,\text{cm}^{-3}$ of P) and heavily doped *n*-Si ($5 \cdot 10^{18}\,\text{cm}^{-3}$ of P) [34]. The lightly doped *n*-Si/C_{60} junction was measured to have the highest V_{oc} (0.4 V) while the lightly doped *p*-Si/C_{60} junction was measured to have the lowest, 0.12 V (Fig. 3). This result implies that the Fermi level of C_{60} should be more than 0.4 eV below the Fermi level of lightly doped *n*-Si and more than 0.12 eV above that of lightly doped *p*-Si. The Fermi level of C_{60} was estimated to be at about 4.7 eV below the vacuum level. To our opinion, further research is needed to understand the frue electronic structure of such heterojunctions.

The very intrinsic conductivity of a C_{60} solid is considered by most authors as one of the main limiting factors for solar cell efficiency. Therefore, doping of C_{60} is one of the central challenges for high efficiency fullerene-based solar cell production. Photovoltaic cells based on doped C_{60} films were reported, for the first time, in [35]. *p*-type conductivity was observed for C_{60} films doped with Al by its simultaneous sputtering during the film deposition. Photovoltaic parameters of C_{60}/Si solar cells were found to be improved by doping. In the same paper, an ion implantation of P was demonstrated to result in an increase in *n*-type conductivity of C_{60} films.

The idea of ion implantation of P and B in C_{60} films was then developed and applied to solar cells production [36–38]. Implantation of B^+ (with energy of 50−80 keV and dose of $10^{14}\,\text{cm}^{-2}$) into C_{60} films, grown on an *n*-Si substrate, was shown to lead to structural changes from the crystalline

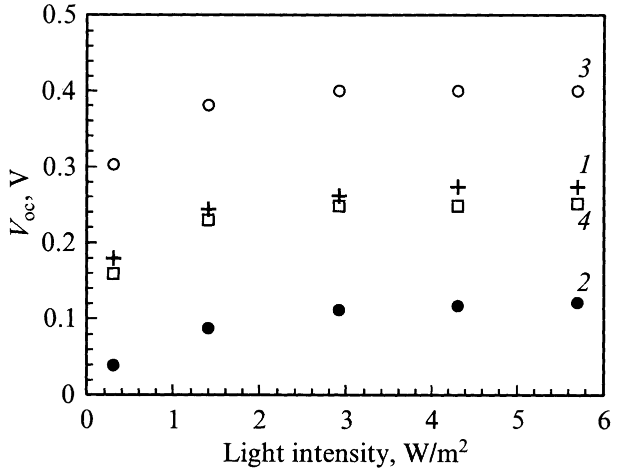

Figure 3. Irradiance dependence of open-circuit voltage of the solar cells based on a heterojunction between C_{60} thin film and different types of Si substrates [34] heavily doped *p*-Si (*1*), lightly doped *p*-Si (*2*), lightly doped *n*-Si (*3*) and heavily doped *n*-Si (*4*).

C_{60} to amorphous carbon, and a dramatic increase in the C_{60} film conductivity. The Hall effect measurements of the implanted films indicate *p*-type conduction. Boron implantation significantly improved the parameters of the resultant *p*-C/*n*-Si solar cells [36]. Especially, the cell series resistance R_s was improved by the implantation from $35\,\mathrm{k\Omega}$ to $370\,\Omega$. J_{sc} for the implanted cells was found to be $0.33\,\mathrm{mA/cm^2}$, $V_{\mathrm{oc}} = 0.17\,\mathrm{V}$, fill-factor $FF = 0.415$ and efficiency $\eta = 0.023\%$. (The latter is the highest value reported for inorganic C_{60}-based solar cells.)

The spectral response of these cells (not shown) includes two broad features: 370−600 nm due to α-C layers and 700−1150 nm due to Si [36]. This result is in agreement with the experimental finding that the optical gap of the C_{60} films decreased after B^+ implantation [37]. Furthermore, it is possible to control this value by variation of the implantation dose. The optical gap was found to decrease gradually with the ion dose. For example, the gap was reported to be reduced continuously from 1.6 eV for non-implanted C_{60} films to 0.8 eV after implantation with the dose of $8 \cdot 10^{14}\,\mathrm{cm^{-2}}$ [37]. The authors explained this effect by the structural transformation from C_{60} to α-C. We may attribute the intermediate optical gap values to a composite with various concentration of C_{60} and α-C. To our opinion, this result is even more important than the improvement of the solar cell parameters (which are still not high). Indeed, using this effect, together with the control of the depth-implantation profile by the ion energy variation [38], it might be possible to produce a C_{60}/α-C composite with a non-homogeneous depth-profile optimised for maximum sunlight absorption and cell efficiency. We may predict that the next step in this direction will be production of efficient multijunction C_{60}/α-C/Si solar cells.

2.3. Organic photovoltaic devices. Over the last decade, tremendous progress has been achieved in organic donor-acceptor solar cells, and fullerene/conjugated polymer devices in particular. A number of detailed reviews are devoted to this topic [20–22]. Thus, we will discuss it here very briefly.

Immediately after discovery of the photoinduced electron transfer from the conjugated polymer to C_{60} molecule [23], this molecular effect was used for the preparation of a heterojunction between methyl-ethyl-hydroxyl-polypropylvinyl (MEH-PPV) and C_{60} thin film [18]. The dark rectification ratio of 10^4 (at $\pm 2\%$) and the following photovoltaic parameters (measured under illumination of an argon ion laser with wavelength $\lambda = 514.5\,\mathrm{nm}$ and a light power of $1\,\mathrm{mW/cm^2}$) were reported: $J_{\mathrm{sc}} = 2\,\mu\mathrm{A} \cdot \mathrm{cm^{-2}}$, $V_{\mathrm{oc}} = 0.5\,\mathrm{V}$, $FF = 0.48$ and $\eta = 0.04\%$. The spectral response measurements revealed a clear minimun at the photon energy of 2.5 eV. This minimum corresponds to the region of maximum absorption in the polymer layer. Since the light was incident from the polymer side of the device this result implies that diffusion of charge carriers in the devices is limited and the photoactive region is a very thin layer adjacent to the heterojunction interface.

Significant improvement of the relatively low collection efficiency has been achieved using composite material with a network of internal heterojunctions between fullerene and conjugated polymer, forming so-called bulk heterojunctions. Using this principle of the material construction, a solar cell without any macro-junction (!) was demonstrated [19]. An electric field was created by asymmetric (with different work functions) metallic contacts one of which was transparent ITO. The photo-generation which results in separated charge carriers may occur over the whole depth of such a device. Very recently [24], a flexible and inexpensive bulk heterojunction fullerene/polymer solar cells (Fig. 4) with tremendously improved efficiency (2.5% under AM 1.5 sunlight) was reported. The other parameters were as $J_{\mathrm{sc}} = 5.25\,\mathrm{mA/cm^2}$, $V_{\mathrm{oc}} = 0.82\,\mathrm{V}$, $FF = 0.61$. These results strongly demonstrate that fullerene/polymer solar cells can be a viable technology for future power generation although further work is needed to improve stability of such devices.

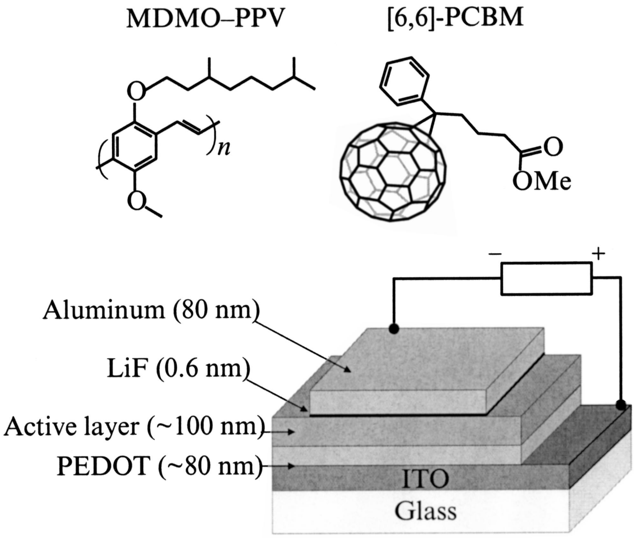

Figure 4. Schematic device structure of the bulk heterojunction fullerene/polymer solar cells, together with chemical structure of compounds used for the cell active layer [24]. Poly[2-methoxy, 5-(3′, 7′-dimethyl-octyloxy)]-p-phenylene-vinelyne (MDMO-PPV) was used as the electron donor while the electron acceptor was [6, 6]-Phenyl C_{61}-butyric acid methyl ester (PCBM). The enhanced solubility of PCBM compared to C_{60} allows a high fullerene-conjugated polymer ratio and strongly supports the formation of bulk donor-acceptor heterojunctions. As electrodes, a transparent indium-tin-oxide (ITO) film on one side and a LiF/Al bi-layer contact on the other side were used. For improvement of the ITO contact, the ITO was coaled with a thin layer of poly (ethylene dioxythiphene) (PEDOT).

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