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Potential Applications of Fullerenes in Photovoltaics

Surendra K Pandey
Dept. of Physics, Govt. Science College, Jabalpur (MP) – 482001 India

***Abstract*– In recent years, zero–dimensional carbon nanomaterials such as fullerenes have attracted significant attention from the scientific community due to their unique photovoltaic properties. Due to advances in synthesis, sorting, and assembly techniques, fullerenes are experiencing renewed interest as the basis of numerous scalable solar energy technologies. We present an extensive review of the usefulness of fullerenes in photovoltaic devices with a particular focus on the latest examples based on the highest purity samples. This review paper reports and explores the recent progress and prospects of fullerenes for solar energy applications. Furthermore, it will articulate the remaining research challenges confronting this field.**

***Key Words*– Fullerenes, Photovoltaics, Solar Cells, OPVs.**

I. INTRODUCTION

Fullerenes are the zero–dimensional form of graphitic carbon that can be visualized as an irregular sheet of graphene being curled up into a sphere by incorporating pentagons in its structure. Fullerenes come in various forms and sizes ranging from 30 to 3000 carbon atoms. The family is named after buckminsterfullerene (C_{60}), the most famous member, which in turn is named after Buckminster Fuller. The closed fullerenes, especially C_{60}, are also informally called buckyballs for their resemblance to the standard ball of association football (soccer).

As a fullerene is elongated in one dimension, it approaches the structure of a carbon nanotube (CNT). Conceptually, CNTs are seamless cylinders of single or few layered graphene with a high aspect ratio (length to diameter ratio) that ranges from 10^2 to 10^7. The mechanical flexibility, chemical stability, and elemental abundance of fullerenes promises excellent opportunities for solar technology. Fullerenes are effective electron transport materials in organic photovoltaics (OPVs). Fullerenes–based photovoltaics is thus an emerging applications area which has attracted the attention of scientists and engineers in recent years [1].

II. SYNTHESIS AND GROWTH

The first carbon nanomaterial to be successfully isolated was C_{60} using laser ablation of graphite in a high flow of helium by Kroto et al. in 1985 [2]. Although reports of even numbered carbon clusters existed prior to the landmark C_{60} paper, these clusters were produced in large size distributions and thus were unsuitable for characterization. Fullerenes have since been synthesized by many groups using a variety of processes which include electric arc discharge, electron beam ablation, and sputtering [3]. Most of these processes use graphite electrodes or targets as the carbon source. In some cases, composites of graphite and metal oxides are employed as targets to generate endohedral fullerenes where a metal atom is encapsulated inside the fullerene carbon cage [4]. Fullerenes have been detected in common combustion flame soot and have also been synthesized using bottom–up chemical methods [5–6].

III. SORTING AND PURIFICATION

Synthetic methods for carbon nanomaterials tend to lack control over all structural parameters, resulting in raw materials that possess considerable polydispersity in their physical and electronic structure. Since most applications require uniformity and reproducibility, methods for sorting and purifying carbon nanomaterials to improve their monodispersity are of critical importance. Fullerene production methods commonly yield mixtures of C_{60}, C_{70}, and many higher homologues, necessitating the use of high performance liquid chromatography (HPLC), column chromatography, or selective chemistry, to isolate monodisperse fullerene populations [7–8].

IV. SOLAR ENERGY APPLICATIONS

In solar technology, fullerenes and their derivatives are among the most important electron acceptor materials in OPVs. OPVs are solar cells fabricated from conjugated organic small molecules or polymers.

The low temperature, solution–based processing of organic materials makes OPVs a promising option for large–area, mechanically flexible solar technology. Fullerenes were recognized as strong electron acceptor materials for OPVs with the first report of charge transfer from MEH–PPV polymer (Poly [2–methoxy–5–(2–ethylhexyloxy)–p–phenylenevinylene]) to C_{60} by Sariciftci et al. in early 1992 [9]. Thereafter, the same group reported the first photovoltaic cell from bilayer heterojunctions of MEH–PPV (donor) and C_{60} (acceptor) [10]. Other donor polymers were later reported in a follow up study [11]. However, the efficiency values of bilayer devices were limited to about 0.05% due to the limited surface area of the bilayer heterojunction and the short diffusion length of photogenerated excitons.

To address the limitations of bilayer OPVs, the bulk heterojunction concept was introduced in which the donor and acceptor were incorporated into an interpenetrating network. Due to the poor miscibility and solubility of C_{60}, it is challenging to form bulk heterojunctions from pristine fullerenes. Consequently, Hummelen et al. [12] developed a chemically modified form of C_{60} popularly known as PCBM ([6,6]–phenyl–C_{61}–butyric acid methyl ester), that improved solubility in many organic solvents. PCBM was subsequently combined with MEH–PPV to form a phase–segregated, interconnected bulk heterojunction with large junction area. These bulk heterojunction OPVs had efficiencies that were approximately 60x higher (2.9%) than bilayer heterojunction devices [13]. PCBM has since become one of the best performing fullerene derivatives and is often cited as a benchmark for new acceptor materials. Recent PCBM analogues include $ThC_{61}BM$ (1–(3–methoxycarbonyl) propyl–1–thienyl–[6,6]–methano–fullerene) and $PC_{71}BM$ ([6,6]–phenyl–C_{71}–butyric acid methyl ester) [14] as depicted in Fig. 1. Since $PC_{71}BM$ absorbs a significantly larger proportion of incident solar light, it is a promising candidate for higher efficiency OPVs, although significantly more expensive. Correspondingly, metalloendohedral fullerenes have shown improved efficiency values [15–16]. Additional developments in fullerene–based acceptor materials for OPV devices are well abridged in popular reviews by He et al. [17] and Delgado et al. [18].

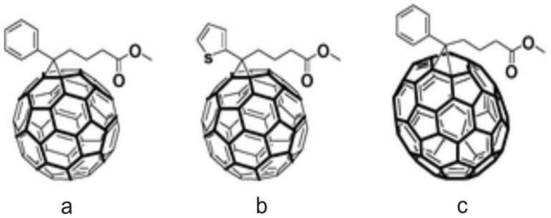

Fig. 1: Molecular structures of fullerene–based acceptors [18]. (a) $PC_{61}BM$ (b) $ThC_{61}BM$ (c) $PC_{71}BM$

V. CONCLUSIONS

Fullerenes have significant promise for photovoltaic applications. The unique strengths of fullerenes imply that they will have disproportionate representation in devices that play to their individual advantages. The solution processability of functionalized fullerenes has led to their dominance as electron acceptors in organic photovoltaics.

While significant progress has been achieved, additional challenges must be addressed before the full commercial potential of fullerenes is realized. Although advances in growth and post–synthetic separation methods have dramatically improved the monodispersity of fullerenes, device–to–device variability remains an issue. These variations can be partially addressed by further improvements in the purity and monodispersity of the same. Chemical methods for controlling and passivating carbon fullerenes surfaces and interfaces are also of paramount importance. Similarly, strategies for chemically enhancing and tuning the properties fullerenes are critical to further improvements in device characteristics. For these reasons, fullerenes will continue to be a subject of intense and fruitful research in solar energy technology.

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