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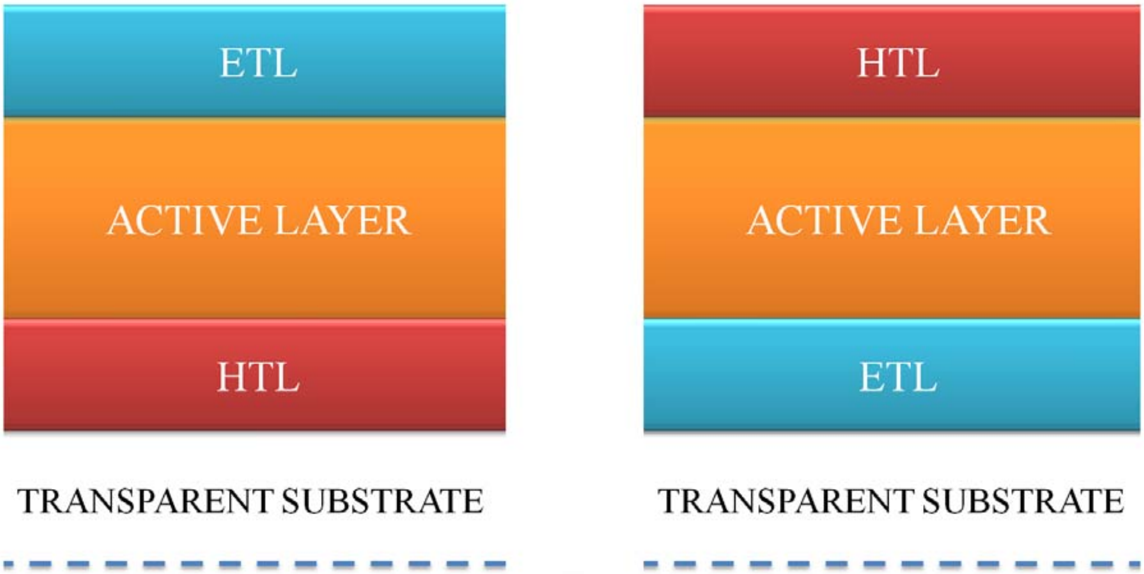
FLEXIBLE ORGANIC PHOTOVOLTAICS

State of the art

Organic photovoltaic cells (OPVs) become a promising alternative to the classical Si-based devices or at least tend to occupy their own niche in the field of photovoltaics. The principal advantages of the OPVs relate to wet processes of the constituent layers that can be grown from solutions. This makes them attractive as low cost devices compatible with flexible substrates (due to relatively low temperatures of the underlying processes).

This review outlines the possible solutions to overcome the remaining drawbacks of the OPVs: i) relatively low performance (some laboratory samples reach ~10 % efficiency [1–4]) and ii) short age of life [5; 6]. They both concern the nature of the layers used, in particular: the active layer is thin enough to ensure better light propagation (whereas the light absorption suffers) and some interfaces are degradable.

Modification of the technology including bulk heterojunction (BHJ) as active layer [3, 6–8] and inverted architecture (Fig. 1) [5, 9–12] improved the total performance of the OPVs: BHJ increases the light conversion, and the inverted structure avoids using degradable interfaces and low work function cathode contacting the air.

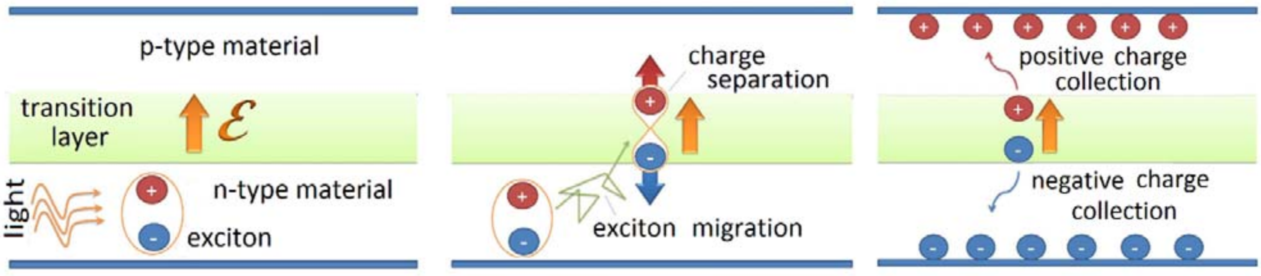


a *b*

Fig. 1. Schematic representation of typical actual architectures of the OPV cells:
a — conventional; b —inverted. The structures are irradiated through the transparent substrate which is usually glass or polyethylene terephthalate (PET) foil both covered with transparent conducting film of ITO (indium tin oxide)

Active layer (BHJ)

The active layer plays the role of the current source due to its specific ability to maintain three principal processes Fig. 2: *a* — light absorption (with formation of exciton); *b* — migration of the exciton to the transition layer with the built-in electric field $\mathcal{E}$ separating the charges; *c* — collection of the charges by the opposite electrodes. The process competing to the charge separation is the exciton annihilation due to charge recombination prior the charges reach the transition layer with built-in electric field.



a *b* *c*

Fig. 2. Stages of the photovoltaic process:
a — the exciton generation by light; *b* — the exciton migration to the transitional layer with built-in electric field separating the charges-constituents of the exciton; *c* — collection of the separated charges at the opposite electrodes

This is the idea of the bulk heterojunction that proposes the structure with the transition area penetrating through the whole space between two electrodes (Fig. 3, *b* and *c*), which enlarges the heterojunction area as to that for the flat junction (Fig. 3, *a*). There are two possibilities: i) two bicontinuous regions contacting only to its "own" electrode each; ii) random distribution of the constituents over the bulk. The former morphology is applicable in the case of hybrid organic-inorganic structures with nano species of low dimensional structures [9]. The other case (Fig. 3, *c*) needs further requirements to the contacts: each of them should be selective either hole-transporting (and electron-blocking) or vice versa.

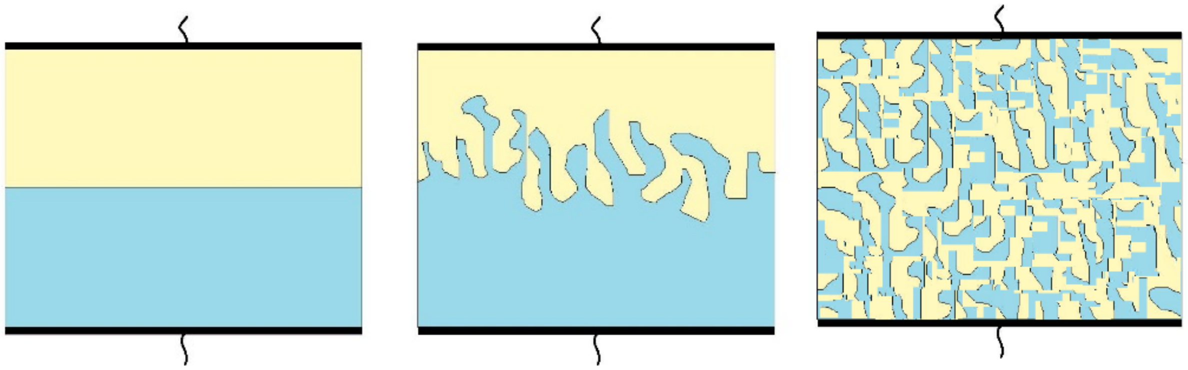
The most studied BHJ (commercially applicable) is the one of regioregular poly (3-hexylthiophene) (P3HT) with soluble fullerene of 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6) C61 C61 (PCBM) [6; 7].

Hole and electron transporting layers (HTL and ETL)

The hole and electron transporting layers (HTL and ETL, respectively) are important charge separating components of the BHJ-based OPVs since they conduct selectively only one type of charged carriers to correspondent electrode.

Their electronic structures determine the open circuit voltage [12], hereby making an influence on the overall performance.

The principal question addressing in this review concerns the specific fabrication of the ETL (low work function electrode — cathode) for an inverted OPV cell.



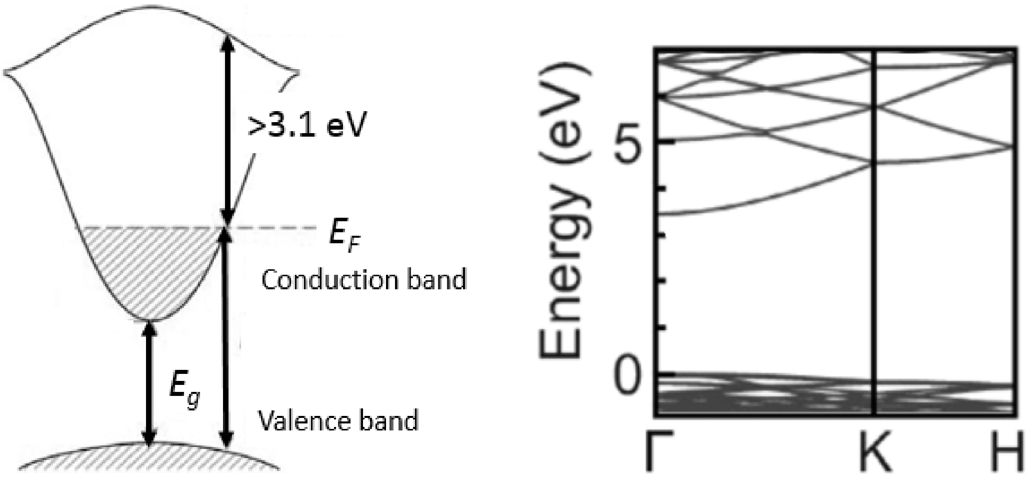
a *b* *c*

Fig. 3. Illustration to the evolution of heterojunction morphology for photovoltaics:
a — flat heterojunction; *b* — bulk HJ with separate contacts for each component;
c — bulk heterojunction with randomly distributed components

ZnO:Al is used as effective ETL, the doping concentration corresponding to Fermi level position not exceeding the value where intraband transitions are possible within the conduction band (Fig. 4, *a*). There is some contradicting data in the literature as to the energy of the intraband transitions (as follows from comparison of *a* and *b* diagrams in Fig. 4).

One of the possible ways to improve the performance is to increase the light absorption additionally to the active layer contribution. The latter is restricted mainly within 400–700 nm range for P3HT/PCBM BHJ.

One of the promising approaches for enhancing the light absorption is to use light harvesting materials like nano species placed both within the layers and at interfaces to "trap" the incident photons via plasmonic effects and additional scattering to increase the optical path [13–18].



a *b*

Fig. 4. Diagrams of ZnO electronic states:

a — schematic illustration of the intraband transitions associated with degenerate doping [23];
b — simulated by HSE hybrid functional method [24]

Nanoparticles as light harvesting components

The nanoparticles (NPs) of Ag and Au are used thoroughly at various combinations for conventional OPV structures.

These nanospecies have plasmon resonance spectrum overlapping with spectral sensitivity range of the active layer [19; 20]. The Al NPs with blue shifted plasmonic resonance (as compared to Ag and Au NPs) are promising as light harvesting component [21], and this role of Al NPs is evidenced in Si-based devices [22].

The main scientific and technological questions are whether light absorption beyond the sensitivity range of the active layer can be increased via:

1) Placing Al NPs at the interface of active layer/ETL in the inverted organic cell.

2) Increasing Al doping concentration in ZnO to shift the Fermi level to lower work function of the ETL.

The answer to this question is important for improving the inverted OPV cell performance owing to tandem structure [13] with broaden spectral range without screening the main sensitivity of the active layer. In conjunction with inverted geometry, the yield is twofold: better performance and longer life.

Technological aspects

The global objective relates to OPV cells both of enhanced performance and long life. One of the possible solutions is to fabricate the photocathode for the inverted OPV cell (see Fig. 1, *b*) with the following features: i) transparent in long wavelength range of visible; ii) with strong light absorption in short wave length edge of the visible and near UV; iii) acting as electron conducting and hole blocking layer; iv) having low work function.

The material chosen to meet these requirements is AZO — Aluminum doped ZnO (Fig. 4 presents the electron structure) with additional coverage of Al NPs.

The technological task can be divided into two steps: AZO layer preparation and synthesis of Al nanoparticles. The nanoparticles can be redistributed over the AZO layer or used in active layer. However, the latter is found to produce additional recombination centers as it was observed for Au NPs within the active layer.

AZO film preparation

The fabrication method is sol-gel described elsewhere [25–29] as low cost and reproducible technique in many instances. The basic technology of

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ZnO:Al film preparation uses the following precursors: $Zn(CH_3COOH)_2{\cdot}2H_2O$ — zinc acetate dihydrate (ZnAc) and Al salt ($Al(NO_3)_3$ is more preferred (provided the low cost technology is presumed) and $H_2NCH_2CH_2OH$ — monoethanolamine (MEA) as a stabilizer.

Some typical rout can be the following:

1. ZnAc is dissolved in ethanol (as a solvent with the highest solubility of ZnAc) in concentration of 0,4 mol/L and stirred till clear and homogeneous solution for approx. 30 min.
2. MEA is added drop by drop under intensive stirring at room temperature to MEA:Zn^{2+} molar ratio of 1:1.
3. The solution of ZnAc and MEA is stirred together at room temperature for ~2h.
4. Aluminum Nitrate, Nonahydrate — $Al(NO_3)_3{\cdot}9H_2O$ is added to the above solution in 1–5 wt% content for Al in ZnO, depending on the desired conductivity of the final film.
5. The solutions are refluxed for 1h at 80 ^oC under continuous magnetic stirring.
6. The final solution is spin-coated to a clean ITO-glass substrate at 3000 rpm for 30 s. Then the film is dried at 180 ^oC in inert atmosphere for 15 min.
7. The samples are annealed at 500 ^oC for 1 hour in an inert medium.

Al nanoparticles coverage over the AZO film

There are several approbated technological routes for the synthesis of Al NPs (as analyzed in the review article [30], for instance). Since the principal purpose is oriented toward low cost technology, the preferable methods are those based on the synthesis from the solutions [31–34]. Maziani method [31] is often used to produce Al NPs in testing OPV structures to check the influence of the Al NPs on the performance [21]. A prospective variant can be also the synthesis of Al/Au nanosystems [34; 35] due to twofold reason: i) Au NPs are successfully incorporated in OPV cells; ii) the Al/Au nanosystems are found to posses paramagnetic properties, which is promising for producing active layer with longer lifetime of the excitons due to generating triplet states under local field of the magnetic nanospecies.

Conclusion

Inverted organic photovoltaic structures are considered to be the most appropriate for flexible sources of electricity due to the following reasons: i) degradable interfaces can be avoided; ii) low work function electrode does not contact air, which allows one to minimize the related aging effects. The technological rout based on: $Zn(CH_3COOH)_2{\cdot}2H_2O$ — zinc acetate dihydrate (ZnAc) and Al salt ($Al(NO_3)_3$ as precursors is proposed for a possible low cost production of the transparent Al-doped transparent ZnO electrodes. Metal-containing nanoparticles are studied in view of their contribution to the overall performance of the final OPV cells. Along with Au- and Ag-based nanoparticles widely used by many researchers as an additional plasmonic harvesting element, the nanospecies containing aluminum are discussed as promising components for the performance improvement.

The inverted organic flexible photovoltaic cells can be used on transport, in particular at the cabin of airplanes as additional power supplies, while a passenger covers the window, the cover being equipped with the flexible solar battery. Low weight of the flexible substrate and low cost of their production are advantage as to the Si-based PV modules.

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ОРГАНІЧНІ ФОТОВОЛЬТАЇЧНІ ЕЛЕМЕНТИ НА ГНУЧКИХ ПІДКЛАДИНКАХ

У статті розглянуто сучасні проблеми у галузі створення фотовольтаїчних (ФВ) джерел електрики на гнучких підкладинках. На підставі багатьох експериментальних свідчень зроблено висновок про перспективність використання інвертованих органічних ФВ структур з прозорим електродом ZnO легованим алюмінієм для фотовольтаїчних перетворювачів з низькою собівартістю виготовлення. У інвертованих структурах ФВ елемент освітлюється через прозорий катод, який є матеріалом з низькою роботою виходу. На відміну від традиційної структури, в якій освітлення відбувається через анод, в інвертованій геометрії матеріал з малою роботою виходу не має прямого контакту з навколишнім середовищем, яке викликає його передчасне старіння. Допування ZnO алюмінієм дає можливість досягнути двох цілей: 1) підвищення електропровідності; 2) зменшення роботи виходу, що, в свою чергу, покращує ефективність ФВ елементу завдяки збільшенню напруги холостого ходу. Однак, при достатньо високому рівні допування можуть виникати внутрішньо зонні оптичні переходи, що є небажаним.

Додаткове підвищення ефективності таких ФВ елементів можливе завдяки використанню Al-вмісних наночастинок між прозорим електродом та активним шаром. Плазмонна смуга поглинання світла такими чатинками лежить на короткохвильовому краю області спектру фоточутливості активного шару, тому використання Al наночастинок не буде перекривати основного діапазону спектральної ефективності цих ФВ перетворювачів.

Вибрана технологічна послідовність виготовлення гнучких фотовольтаїчних джерел електрики на основі золь-гель методу дає можливість створювати шари прозорого електропровідного електроду з малою роботою виходу. Використання дешевої технології синтезу для створення легких та гнучких ФВ джерел електрики є перспективним для широкого їх використання на транспорті (наприклад, в салонах літаків) як додаткових джерел живлення.

Ключові слова: фотовольтаїчні елементи; прозорий провідний оксид; ZnO:Al; наночастинки.

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FLEXIBLE ORGANIC PHOTOVOLTAICS

The current issues in the field of flexible organic photovoltaic cells (OPVs) are reviewed. The inverted OPVs with conducting electrode of Al-doped ZnO electrode are argued on the basis of a numerous experimental evidences to be promising for low cost photovoltaic converters. Additional performance improvement of the OPVs is due to Al-containing nanospecies incorporated between the transparent electrode and the active layer. A technological rout is proposed for production of the low cost flexible power supplies promising for transport applications (e.g. airplanes) due to their light weight.

Keywords: photovoltaic cells; transparent conducting xide (TCO); ZnO:Al; nanoparticles.

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ОРГАНИЧЕСКИЕ ФОТОВОЛЬТАИЧЕСКИЕ ЭЛЕМЕНТЫ НА ГИБКИХ ПОДЛОЖКАХ

В обзоре рассмотрены актуальные проблемы в области создания фотовольтаических (ФВ) источников электричества на гибких подложках.

На основании анализа множества экспериментальных свидетельствований сделан вывод о перспективности использования инвертированных органических ФВ структур с прозрачным электродом из ZnO легированным алюминием для фотовольтаических преобразователей с низкой себестоимостью производства. Дополнительное повышение эффективности таких ФВ элементов возможно благодаря использованию Al-содержащих наночастиц между прозрачным электродом и активным слоем. Предложена технологическая последовательность изготовления гибких фотовольтаических источников электричества (малой себестоимости изготовления), которые являются перспективными для использования на транспорте (например, в салоне самолёта) из-за их малой массы.

Ключевые слова: фотовольтаические элементы; прозрачный проводящий оксид; ZnO:Al; наночастицы.

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