Research paper

Organometallic compounds for photovoltaic applications

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A B S T R A C T

Organometallic compounds could be an excellent alternative to the organic active layers for solar cells due to several better properties like thermal and chemical stability. These organometallic compounds are electron donor materials which are easily used in donor-acceptor heterojunctions in these solar cells. One of the main problems for the active media in the solar cells is connected with the exciton diffusion length which limits the thickness of the donor layer in these donor-acceptor heterojunctions. A way to improve the exciton diffusion length is better charge transfer between the donor and acceptor facilitating the exciton diffusion towards the electrodes of the solar cells. The adding of electronegative ions or chemical groups could also influence the band alignment between the donor and acceptor smoothing the charge transport across the solar cells.

1. Introduction

Photovoltaic devices (OPVs) enter now in a new era in which the limits of silicon structures become crucial for increasing the external quantum efficiency of the solar cells. This classical c-Si bulk material is mainly used as crystalline structure and can be prepared as ingots, ribbons, and wafers [1]. In this category of crystalline silicon solar cells, a special class of materials was developed also known as p-n junction [2]. The c-Si based solar cells exhibit a limited efficiency at around 20%.

More recently, the newest OPVs are based on donor-acceptor heterojunctions employing new organic materials like perovskites for which the efficiency was busted from 3% to more than 20% starting with 2009 [3]. These new solar cells, based on perovskites as active layers, have the main disadvantages of the long-term stability, also saying a quick degradation after a few working days [4]. The replacement of the organic-inorganic structure, which includes the perovskite crystals, with more stable chemical compounds becomes a significant issue in this field. The stability problem could be overcome by using other compounds like the organometallic compounds which are very interesting from the scientific and technological point of view due to their long stability as they were already used in the OLED's technologies for a long time. The advantages of organometallic compounds are connected with the presence of the ionic metals in molecules which induces some exciting properties like:

a) architectural templates- extended molecular architectures could be developed which induces better electrical conductivities.

b) active redox centers- modify the electronic properties influencing the electrical conductivity of the molecules

c) tuning of the HOMO-LUMO bandgap- the molecular orbitals resulted after metal-ligand hybridization together with the adding of functional groups can tune the bandgap of these compounds.

The usage of organometallics in the field of photovoltaic devices was started, up to now, only in the form of electrochemical cells having as working electrode nanoporous TiO_2 substrate and a counter electrode graphite in *N*-methylpirolidone and poly(vinylidene fluoride) [5].

The efficiency of the solar cells are drastically influenced by two main parameters: a) photoconductivity which produces the photo generated charges and b) exciton diffusion length which limits the thickness of the active layer, while charge transport depends on the exciton diffusion length at the interfaces in those configurations. The question which arises is connected with the efficiency of exciton diffusion in these interfaces between donor/acceptor layers.

The main objective of this paper consists in developing of a new donor-acceptor material as the active layer for OPVs, composed from an Alq_3-5Cl organometallic as donor and graphene oxide (GO) acceptor in a bilayer structure. The presence of chlorine ions allows a better charge transfer between the donor Alq_3 with the acceptor GO layer.

2. Material and methods

The Alq_3-5Cl organometallic compound was synthesized from 5-chloro-tris- 8-hydroxyquinoline (5Cl-8HQ) and $Al(OH)_3$, while graphene oxide was obtained by graphite oxidation. The 5Cl-8HQ, Al

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(OH)$_3$, *mer*-Alq$_3$ and graphite powder were purchased from Sigma Aldrich and were used without any further purification.

The XPS spectra were recorded on Thermo Scientific K-Alpha equipment, fully integrated, with an aluminum anode monochromatic source. Survey scans (0–1200 eV) were performed to identify the composition of the compounds.

The Voltalab PGZ 100 potentiostat was used for cyclic voltammetry measurements. The photoluminescence (PL) spectra have been recorded at room temperature, in the UV-VIS region by using Edinburgh F900 spectrophotometer. The current-voltage characteristics were measured in the transverse mode using a Keithley 2400 source meter.

3. Experimental

3.1. Synthesis of Alq3-5Cl compound

5-chloro-tris- 8-hydroxyquinoline organometallic compound was prepared by reacting the 5-chloro-8-hydroxyquinoline ligand (5Cl-8HQ) with the Al^{3+} cation using the corresponding metal hydroxide in similar conditions described previously [6]. Briefly, 0.005 mol of Al(OH)$_3$ in deionized water was gradually dropped into a solution which contains 0.01 mol of 5Cl-8HQ. The solutions were stirred under reflux at 95 °C for 8 h. The synthesized Alq$_3$-5Cl powder was filtered and washed with double distilled water and dried at 110 °C.

3.2. Synthesis of GO

The oxidation of graphite was made using a modified Hummers method. Briefly, 200 ml H$_2$SO$_4$ and 10 g of graphite powder were placed in an iced bath at 0 °C. After mixing for 30 min, 1.5 g of KMnO$_4$ was added in small portions to keep the temperature less than 10 °C. In the final stage, 450 ml of distilled water were added slowly to avoid effervescence. The suspension was then further treated with a mixture of hydrogen peroxide (30%) and distilled water to reduce the residual permanganate. Upon treatment with the H$_2$O$_2$, the suspension turned yellow. The warm suspension was filtered and washed 3 times with 3% HCl solution at 45 °C. The filter cake was dispersed in distilled cold water and separated by centrifugation (20 min at 4000 rpm). The obtained suspension was dispersed in distilled water and centrifuged under the same conditions. The obtained graphite oxide was dried at 45 °C, and the obtained films were milled in a ball mill at 400 rpm.

To obtain graphene oxide (GO), 100 mg of the graphite oxide previously obtained were sonicated in 100 ml distilled water using a sonication bath for 2 h and then filtered and dried at vacuum oven for 24 h [7].

3.3. Donor-acceptor heterostructures fabrication

The donor-acceptor heterostructures were fabricated using spin coating deposition technique for GO layer, thermal evaporation for the Alq$_3$-5Cl layer and Magnetron Sputtering for the aluminum cathode. To obtain these heterostructures, we started with Indium Tin Oxide (ITO) substrates from Ossila. These substrates were cleaned before use, applying few steps described previously [8]. The substrates after drying with nitrogen stream were subjected to oxygen plasma treatment to form a hydrophilic surface state. A solution of graphene oxide (5 mg/ml) was spin-coated onto ITO substrate at 3000 rpm for 30 s resulting thin films with a thickness between 180 and 200 nm. The GO thickness has been kept constant and different layers of Alq3-5Cl were deposited onto this layer at different thicknesses by thermal evaporation. This concept is necessary for determining the exciton diffusion length of the layers. The Alq$_3$-5Cl layers were deposited by thermal evaporation at 1.3x10^{-6} mbar for 1, 3 and 5 min and the obtained thicknesses were 40, 70 and 90 nm measured by x-ray reflectometry. On top, an aluminum cathode (140 nm) was deposited through a shadow mask by using Magnetron Sputtering technique. The thicknesses of the layers were

measured with Thetametrisis FR-pOrtable profilometer for the organometallic compounds and Mitutoyo profilometer stepscan for the metallic cathodes.

4. Theory/calculation

Theoretical considerations are connected with the evaluation of donor/acceptor charge transfer excitations (CT). Under sunlight irradiation, the resulted exciton leads to photocurrent generation. The CT can be estimated by considering the difference between the electron affinity (E$_a$) of the acceptor and ionization potential (I$_p$) of the donor, to calculate the open circuit voltage, defined as:

$$V_{OC} = 1/e(E_a - I_p) - 0.3(eV) \tag{1}$$

The 0.3 eV energy shift arises from disorder within the phase separated organometallic and graphene oxide domains [9].

The ionization potential and electron affinity can be calculated by using Density Functional Theory (DFT) determining the energy of the system, organometallic for I$_p$ and carbon-based material for E$_a$. I$_p$ can be evaluated as the difference between the energies of the organometallic in cationic and neutral states, while the E$_a$ can be evaluated as the difference between the energies of the carbon-based material in anionic and neutral states [10]. The calculations for the ground states were performed using the B3YLP functional and 6-31G* basis sets for both donor and acceptor materials (Supplementary Information).

5. Results

5.1. Theoretical band alignments

The active layer of OPVs should deal with so-called band alignments which represent the driving force for the charge transport towards electrodes (Fig. 1). In the case of the Alq$_3$-5Cl organometallic compound, ionization potential is given by the HOMO level compared with the vacuum one. Following DFT calculations, the ionization potential was estimated at -4.25 eV considerably higher than −5.24 eV for the classical mer-Alq$_3$.

For the GO, the electron affinity is largely dependent on the number of *sp^3* groups induced by the oxidation process of graphene substrate. Theoretical determinations for the GO HOMO state are around −5.22 eV (Fig. 2). The electron affinity can be subtracted as being the LUMO state of graphene oxide and was estimated as −2.36 eV. So far, the open circuit voltage can be estimated to 0.99 V.
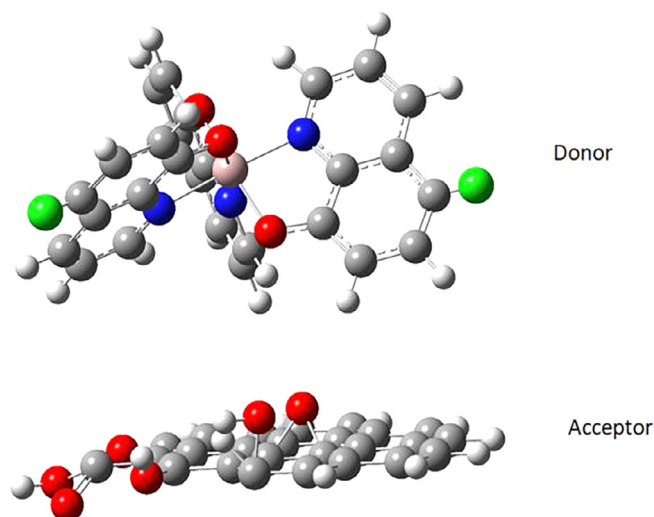

Fig. 1. Donor-acceptor configuration.