Introduction of Graphene Oxide as Buffer Layer in Perovskite Solar Cells and the Promotion of Soluble n-Butyl-substituted Copper Phthalocyanine as Efficient Hole Transporting Material

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Abstract

Organometal halide perovskite solar cells have been constructed using soluble tetra-n-butyl-copper phthalocyanine as hole transporting material. Devices were constructed and characterized under ambient conditions of 50-60% ambient humidity. Soluble copper phthalocyanine gave a modest PCE of 7.3% but when a buffer layer of either Al_2O_3 or graphene oxide was introduced between the perovskite and the hole transporting layer the cell efficiency extensively increased and reached 14.4% in the presence of graphene oxide. Corresponding data obtained by employing the standard spiro-OMeTAD as hole transporter gave equivalent performance. Combination then of tetra-n-butyl-copper phthalocyanine with graphene oxide offers a very good alternative of simpler and stable materials for perovskite solar cell construction. The presently recorded data highlight the role of the buffer layer, especially graphene oxide, as the material which blocks shunt paths and facilitates hole transfer between the perovskite and the hole transporting layer.

Introduction

Organic-inorganic mesoscopic solar cells have followed a remarkable route that marked a very popular research field in materials science. It started with dye-sensitized solar cells, about 25 years ago [1] and instead of getting “old” it has led to a new and very promising domain with the introduction of organometal halide perovskites, following the seminal work of Miyasaka et al. [2]. Perovskite solar cells (PSCs) are solid state hybrid organic-inorganic devices where the standard structure follows a n-i-p scheme, i.e. a nanostructured n-type semiconductor, typically nanoparticulate titania (np-TiO₂), an intrinsic semiconductor, i.e. the perovskite, and an organic p-type semiconductor, i.e. the hole transporter. The n-i-p layers are usually deposited on a transparent electrode, for example, an FTO glass as electron collecting anode and they are completed by depositing a metal counter electrode on the top, typically, a thin layer of Au. The strong interest in PSCs is supported by the ease of device construction, the high charge carrier mobility in organometal halide perovskites [3,4] and the ensuing high photon-to-charge conversion efficiency (PCE), which currently overpasses 20% [5,6]. Even though, the efficiency of PSCs is now competing with the best of inorganic photovoltaics, there are still a lot to be learned about these interesting systems [7]. One of the main components of PSCs, which has raised some skepticism, is the standard hole transporting material (HTM), namely spiro-OMeTAD (2,2',7,7'-Tetrakis-(N,N-di-4-methoxyphenylamino)-9,9'-spirobifluorene). This material is expensive to synthesize or to acquire, it has a limited conductivity which necessitates the utilization of additives [8] and its stability is questioned [9,10]. Attempts to substitute spiro-OMeTAD by other HTM gave exploitable results [11-13], even though, no one has overpassed its records. A p-type material that has attracted particular interest is Cu and Zn phthalocyanine [14-19], which do not compete spiro-OMeTAD records either but they have other advantages. These molecules are very stable. Thus they may be deposited non-destructively by thermal evaporation. They have

the tendency to aggregate but this comes out to be an advantage, since they form crystalline phases offering high conductivity values necessary for their application as HTM. We are recently studying copper phthalocyanine (CuPc) molecules and we have gone through a successful process of material (and device) amelioration by developing alkyl substituted soluble CuPc. Thus it has been found that n-butyl-substitution of CuPc has not impeded but rather facilitated CuPc molecular packing and π - π interaction leading to progressive increase of PSC device efficiency [17,18].

A very important factor, which improves PSC performance, is the deposition of a buffer layer between the perovskite and the hole transporting layer. Al_2O_3 is a standard choice for this purpose [20]. Moreover, SiO_2 [21], montmorillonite [22], ZrO_2 [23], ZnO [24], glycerol-doped PEDOT:PSS [25], LiF and C_{60} [26] are further examples of buffer layer for solid-state solar cells. The buffer layer plays a multiple role in solar cell functionality. The simplest and most effective one is that its presence discourages the formation of shunt paths towards both electrodes, which may result in a decrease of shunt resistance and thus a drop in Fill Factor (FF) and open-circuit voltage V_{OC} of the cell [20-24,27]. The buffer layer also prevents any corrosive additives employed with spiro-OMeTAD to reach and destroy the perovskite layer [22]. Furthermore, it provides a porous framework, which organizes the formation of the upper HTM layer, facilitating proper film formation even in a case of a hardly soluble and hardly processable HTM [20,28]. By improving the formation of the HTM layer, it facilitates hole transfer and conduction and limits charge recombination [20-22,25]. It can also improve the stability of the PSCs [26]. Having these data in mind, in the present work we have successfully tried to improve CuPc performance as HTM in the presence of a buffer layer, using soluble n-butyl-substituted CuPc (CuBuPc) as functional component. We have tested standard Al_2O_3 but we have also studied graphene oxide (GO) for the same purpose. GO has been used as a buffer layer less frequently than Al_2O_3 [29-31]. We have

chosen GO because of its high band gap, its transparency and its mesoporous structure. GO has demonstrated itself as a very good choice for this purpose. It must be underlined at this point that carbon nanostructures in PSCs have been reported to improve stability of the cells [32]. This favorable behavior is probably due to their hydrophobicity and water-repelling capacity, as it has been observed in other cases [33-35]. Corresponding data have been recorded by also employing spiro-OMeTAD, as a reference HTM component.

Experimental

Materials

All materials were purchased from Aldrich, unless otherwise specified, and they were used as received. Commercial nanocrystalline titania Degussa P25 was used in all cell constructions and Millipore water was used in all experiments. $\text{SnO}_2\text{:F}$ transparent conductive electrodes (FTO, Resistance 8 Ω/square) were purchased from Pilkington.

Synthesis of n-butyl substituted CuPc (CuBuPc)

A mixture of 4-butylphthalonitrile (1.0 g, 5.4 mmol), copper(II) chloride (0.24 g, 1.8 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (0.2 mL), and 1-pentanol (2 mL) were stirred at reflux under argon for 2 h. The reaction mixture was cool to room temperature and petroleum ether (50 mL) was added to precipitate the product. The suspension was stirred for 5 min, filtered and the residue washed with CH_2Cl_2 (30 mL). The filtrates were combined and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography with $\text{CH}_2\text{Cl}_2/\text{ethanol}$ (v/v, 1/3) as the eluent to give a blue product. The product was further purified by repeated recrystallization from $\text{CH}_2\text{Cl}_2/\text{ethanol}$ to give CuBuPc (0.38 g, 35%). To fulfill the requirements of electronic applications, the product was further purified by vacuum sublimation in a sublimation machine (Technol VDS-80) operated

at 400 °C and $\sim 3 \times 10^{-3}$ Pa. Elemental analysis calcd (%) for $C_{48}H_{48}CuN_8$: C, 72.02; H, 6.04; N, 14.00; found: C, 71.89; H, 6.10; N, 13.89. ESI-MS: m/z (M^+) 799.33. UV-Vis ($CHCl_3$): $\lambda_{max} = 678$ nm ($195625 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), 611 nm ($43360 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$). IR (K_{Br}): $\nu = 2950, 2924, 2855, 1611, 1504, 1456, 1405, 1337, 1159, 1095, 1064, 819, 737, 720 \text{ cm}^{-1}$.

Preparation of Graphene Oxide (GO) dispersion

GO was synthesized from pre-oxidized graphite flakes by the Hummers and Offeman method [36]. Briefly, in the first step, 5 g of graphite flakes (99.95%), 3 g of $K_2S_2O_8$ and 3 g of P_2O_5 were dissolved in 20 mL concentrated H_2SO_4 (95 wt.%) and stirred at 80 °C for about 8 h. The resultant mixture was then diluted with 1 L deionized water and filtered using a porous membrane (0.45 micron). Washing procedure was carried out until achieving neutral pH. The pre-oxidized graphite flakes were obtained by drying the final product at 40 °C overnight. In a second step, the above oxidized graphite powder was added into 100 mL concentrated H_2SO_4 (95 wt.%) in an ice bath (0 °C) and were stirred until dissolution. 12 g of $KMnO_4$ and 4 g of $NaNO_3$ were then added gradually and successively into the mixture, controlling its temperature around 20 °C. The cooling bath was then removed and the solution was transferred to a 35 °C water bath for gas releasing under continuous stirring for about 1 h to obtain a thick green paste. Afterwards, 180 mL of deionized water was slowly added into the paste, causing violent effervescence and an increase of temperature up to 98 °C. The temperature of the diluted dark brown mixture was kept constant at 98 °C for 20 min with vigorous stirring in order to increase the oxidation degree of the GO product. Then 300 mL of warm deionized water was added to further dilute the mixture, which was treated with 30 mL of 30% H_2O_2 , drop by drop within 10 min, in order to reduce the residual permanganate and manganese dioxide to colorless soluble manganese sulfate. The color of the final solution turned to yellow-pale brown. To eliminate the residual metal ions, the filtered cake was

washed and filtered four times with warm deionized water and a 10% HCl solution in ethanol and water until the pH reached a neutral level (ca. 6.4). The product was further diluted to approximately 400 mL with deionized water and ultrasonicated at boost mode for 40 min. The yellow-brown GO dispersion was then subjected to dialysis to completely remove metal ions and acids. Finally, it was dehydrated in an air oven at 40 °C for 14 h to yield the GO powder. 10 mg of the GO powder was added in 2 mL isopropanol alcohol, then placed in an ultrasonic water bath for 1 h to ensure good exfoliation.

Preparation of Al₂O₃ dispersion

A colloidal dispersion of aluminum oxide (Al₂O₃) nanoparticles [<50 nm particle size (DLS), 20 wt. % in isopropanol] has been used. It was further diluted by sonicating 200 µL of this colloidal dispersion in 2 mL isopropanol.

Solar cell device construction

FTO-coated glass substrates were cut in pieces of dimensions 1 cm × 3 cm. One third of the conductive layer was removed using zinc powder and hydrochloric acid. Then they were washed with mild detergent, rinsed several times with distilled water and subsequently with ethanol and acetone in an ultrasonic bath, finally dried under air stream. A compact thin layer of TiO₂ was then deposited on this patterned and cleaned FTO electrode by aerosol spray pyrolysis using a solution of 0.2 M Diisopropoxytitanium bis(acetylacetonate) in EtOH. After spraying, the samples were heated for 1 hour at 500°C. Subsequently, a mesoporous TiO₂ layer composed of titania paste made of P25 nanoparticles was spin coated at 4000 rpm for 60 seconds and then dried at 100 °C for 20 min and calcined for 30 minutes at 500 °C. After that the samples were treated in TiCl₄ by dipping into a solution made of 0.04M TiCl₄ in H₂O for 30 minutes at 70 °C, then copiously rinsing and finally calcining at 500°C. Active

perovskite layer was deposited on the thus prepared titania film by the following procedure. A precursor solution was made by mixing 253 mg PbCl_2 and 507 mg PbI_2 with 270 mg methyl ammonium iodide in a mixture of 1 ml N-N-dimethylformamide (DMF) and 0.5 ml dimethylsulfoxide (DMSO). The solution was kept under stirring for about 2 hours at about 80 °C and then deposited by two consecutive spin-coating steps; first 1000 rpm for 10 s, then 6000 rpm for 30 s. During the second step, 1 mL chlorobenzene, as an anti-solvent, was gently dropped on the spinning substrate. The layer was then heated at 90 °C for about 45 min, which made the sample's color turn from yellow to black. Thereafter, thin mesoporous buffer layers were spin-coated directly on the annealed perovskite layer at room temperature. Both Al_2O_3 and GO layers were deposited at 2000 rpm for 60 s. The hole transporting material (HTM) was then deposited by spin coating at 3000 rpm for 60s. The HTM solutions were prepared by dissolving 36 mg of HTM powders (spiro-OMeTAD or CuBuPc) in 1 ml of chlorobenzene. In these solutions we added 28.8 μL of 4-tert-butylpyridine (TBP) and 17.5 μL of a stock solution of Lithium bis (trifluoromethane sulfonyl) imide (Li-TFSI) in acetonitrile (520 mg/1 mL). All of these procedures were carried out under ambient conditions of 50–60% relative humidity. The last step for preparing the solid state solar cell was the deposition of 90 nm thick gold electrodes by thermal evaporation under vacuum. The thickness of the subsequent layers forming the solar cells can be seen in the FESEM cross-sectional images of **Figure 1**. These unit devices had an active size of 15 mm² (10 mm×1.5 mm) as defined by the size of the gold electrodes.

Characterizations

Illumination of the solar cells was made with a PECCELL PEC-L01 Solar Simulator set at 100 mW/cm², through a mask of aperture size 1×6 mm². J–V characteristic curves were recorded under ambient conditions with a Keithley 2601 source meter that was controlled by

Keithley computer software (LabTracer). IPCE values were obtained with an Oriel IQE 200 system. X-ray diffraction (XRD) patterns were obtained with a D8 Advance Bruker diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Absorption and photoluminescence spectra using thin transparent perovskite films were recorded with a Cary 1E UV-Vis spectrophotometer and a Cary Eclipse Fluorescence spectrometer, respectively. FESEM/EDX measurements were made using a Zeiss SUPRA 35VP with a field emission gun equipped with an EDX system (QUANTA 200, Bruker AXS). Electrochemical Impedance Spectroscopy (EIS) characterization has been carried out on PSC devices with a potentiostat/galvanostat (PGSTAT128N, Autolab B.V., Netherlands) under both dark and AM-1.5G illuminated conditions.

Results and discussion

Construction of PSCs and materials characterization

As detailed in the experimental section, PSCs were constructed by successive layer deposition of the functional components. This is pictorially summarized in **Figure 1** showing a cross-sectional FESEM image of a device. Furthermore, **Figure 2** shows the FESEM top views of the subsequent layers. Thus **Figure 2a** shows the top view of the mesoporous titania film composed of commercial Degussa P25 nanoparticles. The perovskite film formed within the mesoporous titania structure and on its top is imaged in **Figures 2b** and **c** showing that it attained a fully-covered compact structure without voids. **Figure 2d** shows GO flakes on the top of the perovskite film and, finally, **Figures 2e** and **f** depict the top view of the CuBuPc film, without (**e**) and with an underlying GO layer (**f**). CuBuPc alone forms aggregated structures with voids. Obviously, the presence of the buffer layer may serve, among other functions, to block such voids and thus block shunt paths, a function, which is in agreement with the experimental findings on buffer layer reported by other works [20,21]. XRD patterns

of the perovskite/titania film shown in **Figure 3** revealed a well-defined crystallinity of the perovskite film with narrow and strong diffraction peaks. The peaks corresponding to the perovskite film appeared at approximately 14.24° (110), 20.16° (112), 28.59° (220), 31.81° (310), 40.67° (224), and 43.24° (330) crystal planes, which correspond to the reflections from the tetragonal phase of the perovskite [37-39]. There are no unidentified peaks besides those attributed to FTO, TiO_2 and perovskite, indicating that a pure phase of perovskite was grown on the mesoporous TiO_2 scaffold.

Photon to charge conversion efficiency (PCE) of the PSC devices

PSC devices of various compositions have been constructed and were characterized by recording their current-voltage data. **Figure 4** and **Table 1** report the obtained results. **Figure 4a** reports data on devices made with CuBuPc as HTM either alone or in the presence of Al_2O_3 or GO buffer layer. **Figure 4b** reports corresponding data obtained by using spiro-OMeTAD as reference HTM in the place of CuBuPc, for comparison. The beneficial effect produced in the presence of a buffer layer is more than obvious in **Figure 4a**. This effect is much more pronounced in the case of CuBuPc than in the case of spiro-OMeTAD. Thus, both FF and V_{OC} largely increased and this resulted in a dramatic increase of the cell efficiency, which changed from 7.3% to 14.4%. Increase of the fill factor and of the open-circuit voltage are standard indicators of blocking of the shunt paths across the cell [20,23,24]. Indeed, as seen in **Figure 2e**, CuBuPc films are composed of aggregates, possibly due to its lower solubility in chlorobenzene [40], and this results to the creation of voids that may become paths, for example, of Au penetration. Such paths are obviously blocked by the underlying buffer layer, as indicated by **Figure 2f**. This idea is supported by the smaller effect produced in the case of spiro-OMeTAD, which is known to form smoother films with less voids. We believe that the reason for this difference is the smoother films made by spiro-OMeTAD with

higher solubility in chlorobenzene and with less voids, particularly in the presence of Li-TFSI [41].

The current-voltage data of **Figure 4** demonstrate the superiority of GO as buffer layer. Most researchers have used metallic oxides as buffer layer [20,21,23,24], however, the present data highlight the importance and the superiority of GO. The nature of the effects caused by GO should not be different from that of metal oxides but we believe that the particularity of the GO structure may assist better film formation, especially in the case of CuBuPc.

It is interesting to also inspect the data of **Figure 5**, which shows the corresponding IPCE spectra for all the above device variants. In all cases, the prevalent functional species for light absorption and charge generation is perovskite. Therefore, the shape of the spectra is similar in all six cases. The maximum IPCE value is in line with the maximum current density produced in each case (*cf.* **Figures 4** and **5**).

The results of **Figures 4** and **5** present for the first time an important finding: n-butyl-substituted copper phthalocyanine (CuBuPc) can compete spiro-OMeTAD as HTM for perovskite solar cells. CuBuPc alone gave so far a modest efficiency [18] but apparently the introduction of GO as buffer layer was the crucial factor that repaired its deficiencies. We believe that the most serious of these deficiencies was the extended aggregation and the existence of voids in their films. The presence of GO apparently limits this disadvantage. At this point, it must be pointed out that the device was inactive in the presence of GO but in the absence of CuBuPc. This means that GO does function as buffer layer but not as HTM, at least under the present configuration.

Electrochemical Impedance Spectroscopy analysis

In order to get further insight on the impact of the GO buffer layer on hole transport characteristic of PSCs, EIS measurements have been additionally performed. **Figure 6** shows Nyquist and Bode-phase plots of the above PSC devices. The spectra are characterized by two major arcs at low-intermediate and high frequencies. The high-frequency part of the spectra contains information on the transport resistance and series resistance elements, as well as dielectric contributions [42]. The low frequency arc is attributed to recombination in the photoactive layer [43]. It is evident from **Figure 6** that the main characteristic frequency peak of the Bode plots of PSC devices containing CuBuPc/GO layer shifted towards lower frequencies and the corresponding central arc in the Nyquist plots became wider with respect to those containing neat CuBuPc layer, in particular for the measurements under illumination conditions. This means that the GO buffer layer not only can help to form a blocking layer, but also may retard the charge recombination, especially under illumination. In other words, charge recombination will be impeded when the photogenerated holes could be transported more efficiently from active perovskite layer via CuBuPc/GO layer.

Photoluminescence data

The benefits produced by the presence of the buffer layer are further highlighted by photoluminescence data, as seen in **Figure 7**. A perovskite film has been deposited on plain glass (without FTO or TiO₂ layer) and its absorption and photoluminescence spectra have been recorded. Interestingly, organometal halide perovskites emit substantial photoluminescence, which depends on halide composition [44]. Then on the top of the perovskite film a layer of CuBuPc was deposited with or without an intermediate Al₂O₃ or GO buffer layer. In the presence of CuBuPc, the luminescence was extensively quenched, suggesting efficient hole scavenging by CuBuPc. It is interesting to note that quenching was

even more extensive in the presence of a buffer layer, GO being again the most effective. The results of **Figure 7** highlight CuBuPc as efficient hole scavenger but they also highlight GO as a means to further facilitate this functionality. Thus, we can conclude that buffer layers, in particular, GO layer, can efficiently suppress charge recombination in the PSCs, a conclusion which is in line with previous reports [20-22]. The functionality of GO in PSCs comprising CuBuPc as HTM is pictorially summarized by the energy diagram of **Figure 8**.

Conclusions

Soluble copper phthalocyanine can be used as HTM in organometal halide perovskite solar cells with equivalent performance as the standard spiro-OMeTAD. Therefore, CuBuPc, which is a stable and rather simple molecule with lower commercial price than spiro-OMeTAD, can be a valuable substituent of the latter. High performance of CuBuPc was achieved in the presence of a buffer layer, especially graphene oxide, which seems to be particularly fit to the case of CuBuPc.

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Table 1. Current –voltage data extracted from **Figure 4.**

Hole-Transporting Layer	J_{SC} (mA/cm²)	V_{OC} (V)	FF	η%
CuBuPc (neat)	17.0	0.89	0.48	7.3
CuBuPc (Al₂O₃)	19.5	0.99	0.50	9.7
CuBuPc (GO)	20.9	1.04	0.66	14.4
Spiro (neat)	16.8	0.84	0.61	8.6
Spiro (Al₂O₃)	19.4	0.85	0.55	9.1
Spiro (GO)	21.7	0.87	0.66	12.5

Figure 1. Cross-sectional FESEM image of the subsequent layers of a PSC device

Figure 2. FESEM top views of the subsequent layers making the PSC device: (a) titania; (b) and (c) perovskite; (d) GO on the top of the perovskite film; (e) CuBuPc on the top of perovskite without buffer layer; and (f) CuBuPc with underlying GO buffer layer. The scale bar is 200 nm in (a) and (b), 1 μm in (c), 3 μm in (e) and 10 μm in (d) and (f).

Figure 3. XRD patterns of mesoporous TiO_2 film on FTO glass: (1) without and (2) with deposition of perovskite film on TiO_2 surface. Characteristic peaks associated with the perovskite structure are labeled and denoted with asterisks.

Figure 4. Current-voltage data for PSC devices made by employing CuBuPc (A) or spiro-OMeTAD (B) as HTM in the absence or in the presence of Al₂O₃ or GO buffer layer. Curves showing hysteresis by reverse plotting were not included to avoid confusion but they are included in the supporting information file.

Figure 5. IPCE% spectra for PSC devices made by employing CuBuPc (A) or spiro-OMeTAD (B) as HTM in the absence or in the presence of Al_2O_3 or GO buffer layer.

Figure 6. Bode-phase plots (a,c) and Nyquist plots (b,d) at $V_{app} = V_{OC}$ under (a,b) dark and (c,d) illumination conditions for PSCs employing CuBuPc as HTM: (1) in the absence and (2) in the presence of GO buffer layer.

Figure 7. Absorption (left) and luminescence (right) spectra of perovskite films deposited on plain glass without FTO or a titania film, with or without an intermediate buffer layer and a CuBuPc layer on the top,: (1) perovskite film alone; (2) CuBuPc /perovskite; (3) CuBuPc /Al₂O₃/perovskite; and (4) CuBuPc /GO/perovskite. Photoluminescence was recorded by excitation at 450 nm.

Figure 8. Placement of energy states and suggested charge transfer in PSCs based on CuBuPc as HTM. The diagram highlights the elimination of shunt paths across the cell.

Graphical Abstract

for the manuscript “Introduction of Graphene Oxide as Buffer Layer in Perovskite Solar Cells and the Promotion of soluble n-butyl-substituted Copper Phthalocyanine as Efficient Hole Transporting Material” by *Nouri et al.*