

Effect of metal cathode reflectance on the exciton-dissociation efficiency in heterojunction organic solar cells

Ajay K. Pandey,^{1,2,a)} Paul E. Shaw,² Ifor D. W. Samuel,² and Jean-Michel Nunzi^{1,3}

¹*Equipe de Recherches Cellules Solaires Photovoltaïques Plastiques, Laboratoire POMA, UMR-CNRS 6136, Université d'Angers, 2 Bd Lavoisier, 49045 Angers, France*

²*Department of Physics and Astronomy, Organic Semiconductor Centre, North Haugh, University of St. Andrews, Fife KY16 9SS, United Kingdom*

³*Department of Chemistry and Department of Physics, Queen's University, Kingston, Ontario, Canada*

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Effects of different cathode metals, such as aluminum, calcium, and silver, and difference in their reflectivity on the photocurrent generation in pentacene-C₆₀ heterojunction solar cell are presented. Using optical transfer matrix calculations, we find that metal reflectivity has a profound impact on the electrical field confinement within the multilayer device structures. Silver as cathode offers better optical-field confinement close to the pentacene-C₆₀ interface over generally preferred aluminum cathode. External quantum efficiency measurements confirm higher exciton dissociation efficiency and high photocurrent generation ability of silver over aluminum cathode making the choice of cathode metal an important parameter in device optimization. © 2009 American Institute of Physics. [DOI: 10.1063/1.3098472]

Donor-acceptor (DA) based organic solar cell (OSC), in its simple geometry, is often made up with one or more organic layers sandwiched between two metal electrodes where organic layers are responsible for the light capture and charge generation while metallic layers are used to transmit or reflect the incident light and also to collect the charges generated within the device structure. Hence electrode transmittance and reflectance are important parameters for optimal performance of an OSC. The most commonly used transparent electrode (anode) in OSC is indium tin oxide (ITO) owing to its excellent transmittance and conducting properties. For cathode, aluminum (Al) is commonly favored because of its low work function, which matches well with the energy-level alignment required for exciton diffusion/dissociation and charge collection in OSC.

Recently, much attention has been paid on improving efficiency of OSC through optimizations at different scales with major thrust on optimization of DA morphology and phase separation in the so called bulk-heterojunction OSC with treatments such as thermal annealing at core of it.¹⁻⁴ For heterojunction solar cells, such treatments often work with limited advantage as exciton dissociation in such devices occur at the well defined interface of donor and acceptor, control of light confinement close to this interface remains the key for their efficient performance. One way to have this is through use of high absorption coefficient materials with large exciton diffusion length. With average values for exciton diffusion length in the range of 10–30 nm, efficient performance can only be achieved by avoiding optical and recombination losses.⁵ Such low exciton-diffusion length often puts restriction on the overall thickness of photoactive layers in the heterojunction devices. Keeping these restrictions in mind, the performance of such heterojunction devices can still be increased through addressing the optical field confinement within the device structures. There have been few attempts on addressing this through electrode and material

optimization with different light trapping strategies.⁶⁻⁸ With ITO fixed as widely used transparent anode not much attention has been paid on optimization of light trapping in OSC devices using reflecting cathodes and their overall influence on photocurrent generation ability. In this letter, we present our studies associating metal cathode reflectivity to exciton dissociation efficiency in OSC, showing that choice of cathode metal should not be made constant while optimizing an OSC structure.

Pentacene-C₆₀ heterojunction solar cells with different metal cathodes were prepared on transparent ITO as common anode with sheet resistance 15 Ω/□. A 40 nm thin layer of PEDOT was spin coated on top of sequentially cleaned ITO substrates in acetone, ethanol, and de-ionized water. Then 55 nm pentacene, 45 nm C₆₀, and 8 nm BCP layers were sequentially deposited before evaporating 60 nm thin Al, Ca, or Ag metallic layers. All depositions were performed inside a vacuum chamber, internally connected with an argon filled glove box, at base pressure lower than 2 × 10⁻⁷ mbar. Pentacene and C₆₀ were deposited at a substrate temperature of 80 °C. All other depositions were performed at room temperature. Devices thus fabricated have an active area of 0.03 cm². Current-voltage (*J-V*) characterization devices were illuminated through transparent ITO side at illumination intensity of 80 mW cm⁻² using a AM 1.5 spectrally matched solar simulator (KHS 150). *J-V* and external quantum efficiency measurements were performed inside the same glove box with oxygen and moisture presence <0.1 ppm.

Figure 1 shows the optical absorption spectra of C₆₀ and pentacene thin films. *J-V* response of pentacene-C₆₀ heterojunction devices with different metal cathodes is shown in Fig. 2(a). For reference, energy-level alignment at cathode level using silver, aluminum, and calcium metals is shown in the inset. As evident from Fig. 2(a), by varying cathode metal, performance parameters of pentacene-C₆₀ differ not only in terms of open-circuit voltage (*V*_{OC}) but also for the short-circuit current (*J*_{SC}). Also, Fig. 2(a) (inset) associates

^{a)}Electronic mail: akp6@st-andrews.ac.uk.

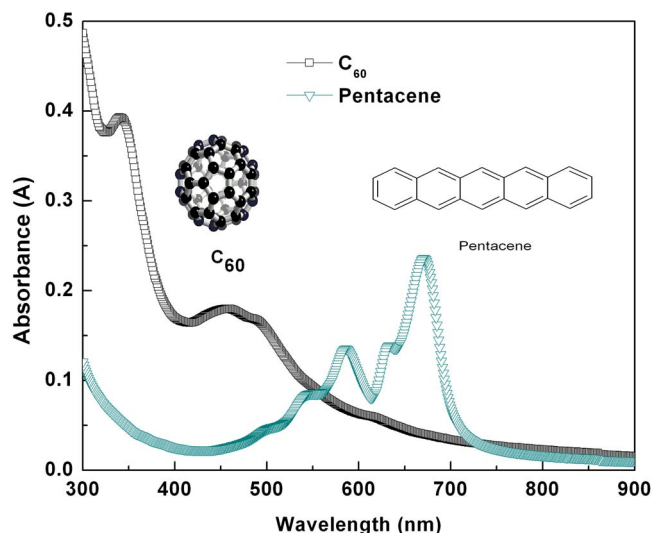


FIG. 1. (Color online) Absorption spectra of 50 nm thin pentacene and C_{60} films. Also shown is their chemical structure.

different metal work functions with allowed V_{OC} in pentacene- C_{60} heterojunction. Following the classical metal-insulator-metal picture, 0.7, 0.8, and 2.1 V of V_{OC} is expected with Ag (4.3 eV), Al (4.2 eV), and Ca (2.9 eV) cathodes, respectively,⁹ though observed V_{OC} here varies from 278 to 304 mV. This observation suggests that metal work function has a weaker effect on the experimentally measured V_{OC} . Such discrepancy in measured and expected values of V_{OC} occurs because of the “Fermi-level pinning” mechanism in OSCs, where the metal work function is pinned to the Fermi level of the semiconductor making metal work function less dominating parameter than the highest occupied molecular orbital and lowest unoccupied molecular orbital offset at the DA interface behind the observed V_{OC} .^{10,11} In agreement with this the energy offset of 400 meV at pentacene/ C_{60} interface seems to control the measured V_{OC} here.

Table I summarizes the performance parameters of pentacene- C_{60} solar cell with different cathode metals. As evident from this table, although different values for V_{OC} and fill factor (FF) are observed the difference is not more than 10% for all three devices. A strong difference in J_{SC} is observed illustrating effectiveness of Ca, Al, and Ag cathodes on the device performance. With FF values greater than 50% for all three devices, we can certainly rule out possibility of any fabrication related defects and variations behind different J_{SC} observed in these devices. Also, going by previously shown energy-level alignment Ag, Al, and Ca as low work function metals essentially form Ohmic contacts with C_{60} , hence no barrier for charge (electrons) collection exists at C_{60} -metal interface.

Henceforth the difference observed in J_{SC} may originate from difference in magnitude of light absorbed/confined inside these device structures. Absolute optical reflection spectrums of 60 nm thin Ag, Al, and Ca films on glass substrate shown in Fig. 2(b) supports this observation. At around 670 nm (peak absorption of pentacene) and at normal incidence, Ag reflects 96%, Al reflects 90%, and Ca reflects 68%. This explains why lowest J_{SC} is observed when Ca serves as cathode. Although the reflection from Al differs by 6% only to Ag, the J_{SC} variation is significant.

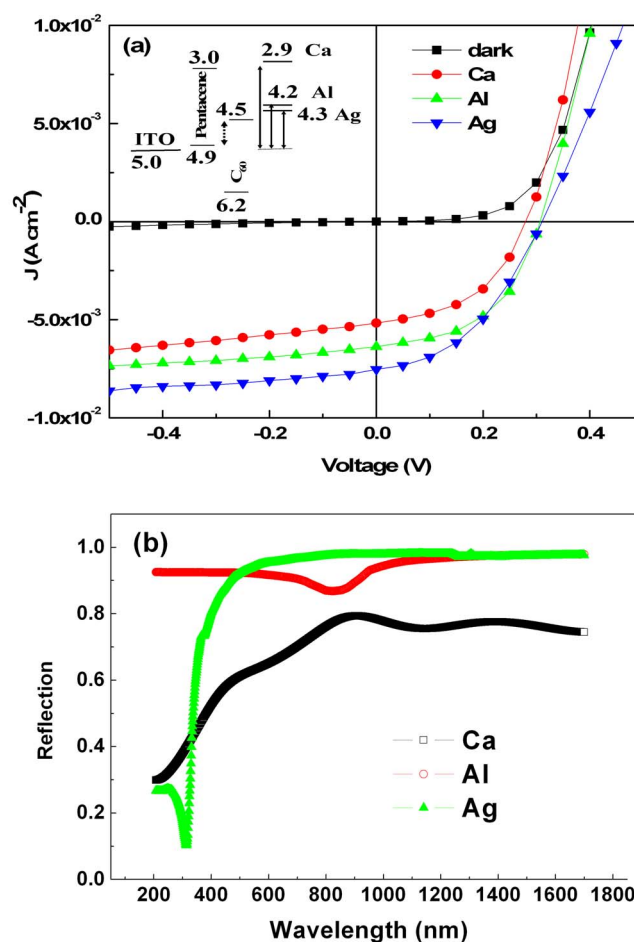


FIG. 2. (Color online) (a) J - V response of pentacene/ C_{60} heterojunction device with calcium, aluminum, and silver cathodes, in dark and under illumination intensity of 80 mW cm^{-2} . Inset shows energy level positioning and theoretically allowed V_{OC1} (dashed arrow) and V_{OC2} (solid arrows). (b) Optical reflection spectrum of 60 nm Ag, Al, and Ca thin films on glass substrate for quantitative analysis of photocurrent variation observed in the J - V curves.

Above reflectance values can be used as indicative to the different amounts of light trapped in our devices but, to establish the difference observed in J_{SC} , it is imperative to look at the light confinement and resulting exciton distribution particularly created by interference effects known in such thin film devices. We used the transfer matrix method initially presented by Pettersson *et al.*¹² to quantify the electric field intensity within the multilayered devices. The complex indices of refraction for ITO, pentacene, C_{60} , BCP, Ca, Al, and Ag at peak absorption of pentacene at 670 nm were determined from ellipsometry. The simulated field distribution for our multilayered devices at 670 nm with Ca, Al, and Ag cathodes on glass substrates is presented in Fig. 3(a), which remains in good agreement with calculations reported

TABLE I. Pentacene- C_{60} solar cell performance parameters under 80 mW cm^{-2} illumination intensity for different metal cathodes.

Metal cathode	V_{OC} (mV)	J_{SC} (mA cm^{-2})	FF (%)	η (%)
Calcium	278	4.91	55.3	0.94
Aluminum	302	6.38	52.3	1.25
Silver	304	7.53	57.1	1.63

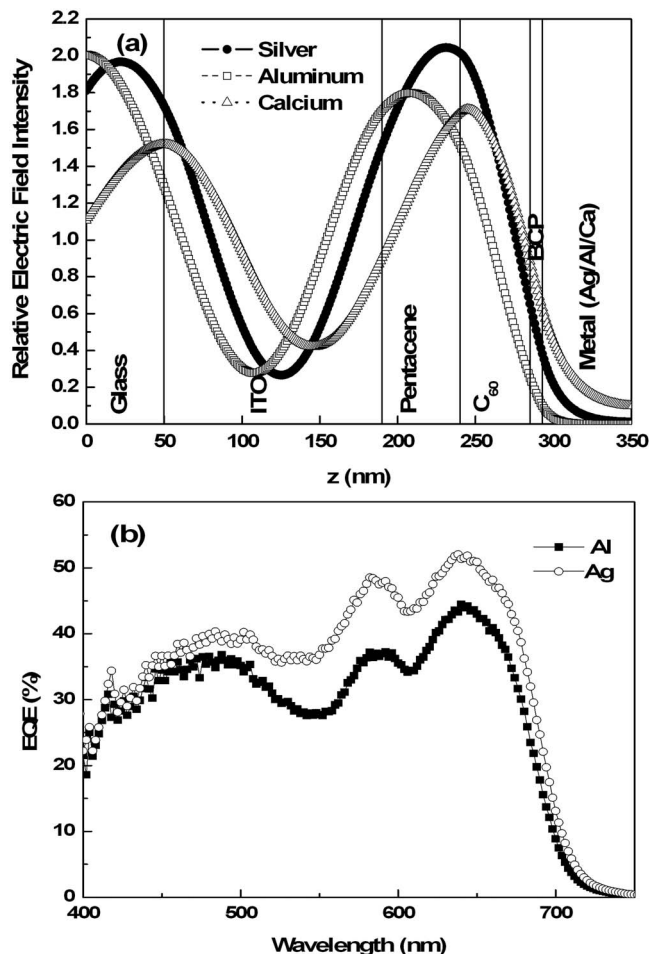


FIG. 3. (a) Calculated distribution of normalized electric field intensity, at 670 nm, inside the pentacene- C_{60} heterojunction device for Ca ($n=0.688, k=2.63$), Al ($n=1.598, k=8.0$), and Ag ($n=0.14, k=4.28$) metals with glass ($n=1.52, k=0$), 50 nm/ITO ($n=1.77, k=0.01$), 140 nm/pentacene ($n=1.50, k=0.43$), 55 nm/ C_{60} ($n=2.10, k=0.01$), 45 nm/BCP ($n=1.70, k=0$), 8 nm/metal 60 nm. Effect of PEDOT layer here is not taken into account. (b) Photocurrent action spectra with Al and Ag cathodes showing different EQE due to difference in optical field confinement inside these device structures.

by Yoo *et al.*¹³ on similar heterojunction using Al cathodes. It is seen that electric field intensity is strongly influenced by interference effects giving rise to different confinement for different cathode metals. In line with our previous discussions over absolute reflectance from Ca, Al, and Ag metals, here too the calcium device appears *leaky* over Al and Ag, hence performs poorly.

For clarity of presentation, we compare the performances of Al- and Ag-based devices from hereon. Although Al seems to give better confinement, it does confine the electric field far from the pentacene- C_{60} interface. With Ag, we get superior confinement that too at the pentacene- C_{60} interface, allowing more excitons to dissociate. Also, following this confinement, the exciton distribution seems to scale up quite impressively throughout the pentacene layer allowing maximum exciton to reach the interface, whereas for Al, the maxima occurs close to the ITO-pentacene interface making the probability of the far end exciton to reach pentacene- C_{60} interface difficult. Such observation is supported from the

fact that lower FF values are measured in Al devices compared to Ag devices (refer to Table I).

For further confirmation, we compare photocurrent action spectra of Al and Ag devices. Figure 3(b) shows comparative external quantum efficiency spectra of pentacene- C_{60} devices with Al and Ag cathodes. Very first evidence comes from the region of EQE spectra, where pentacene absorbs more and C_{60} has a weaker absorption. Quite interestingly and in agreement with Fig. 2(b), we can see that devices with Al and Ag have identical conversion ratios in the wavelength regime of 400–450 nm, where maximum absorption takes place in C_{60} . As we move beyond 450 nm the EQE values from Al device starts lagging behind by $\sim 10\%$ in absolute terms as pentacene absorption picks up. At 670 nm the maximum EQE from Al devices is 36.4%, whereas for Ag devices, it is as high as 44.4% making choice of reflecting metal cathode vital to exciton dissociation efficiency in such heterojunction OSC. Hence Ag as cathode metal increases the overall device efficiency of pentacene/ C_{60} heterojunction solar cells over generally preferred Al cathode. The overall efficiency of 1.63% achieved with silver cathode here is certainly an improvement over commonly reported efficiency of $\sim 1.5\%$ from similar pentacene/ C_{60} heterojunction solar cells with aluminum cathode.^{13–15}

To summarize, we have shown the effect of metal cathode on the exciton dissociation and photocurrent generation ability of pentacene- C_{60} heterojunction solar cells. It has been clearly established that the metal reflectance plays an important role in confinement of optical field distribution within such multilayer device structures. Hence performance optimization of OSC should include energy harvesting/management not only at material scale but also at electrode level.

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