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Light-trapping in polymer solar cells by processing with nanostructured diatomaceous earth

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ABSTRACT

We demonstrate the use of fossilized diatoms (diatomaceous earth) as light traps in regioregular poly(3-hexylthiophene) (P3HT) and fullerene derivative [6,6]-phenyl-C_{60}-butyric acid methyl ester (PCBM) solar cells. Diatoms, the most common type of phytoplankton found in nature, are optimized for light absorption through millions of years of adaptive evolution. They are also an earth-abundant source of silica that can be incorporated into polymer solar cells without the need for complicated processing. Here we establish protocols dispersing the diatomaceous earth throughout the P3HT:PCBM active layer with characterization by optical and current-voltage measurements. We show that through the addition of diatomaceous earth, we can achieve the same power conversion efficiencies as standard thickness cells while using 36% thinner active layers. We find that adding the diatomaceous earth acts as a scattering center and textures the silver back contact, contributing to increases in the optical path length within devices. Results from this study open up pathways for incorporating hierarchical materials from nature into energy conversion devices.

1. Introduction

During the last decade, organic photovoltaics (OPV) have emerged as a promising technology for photon to electrical energy conversion [1]. They are seen as a low cost option due to their ease of fabrication at ambient temperatures. Although they offer advantages such as being lightweight, flexible and transparent, their power conversion efficiency (PCE) is low (11.5% current record [2]) compared to conventional silicon photovoltaics. One reason for the low PCE is the thickness limitation of the active layer to approximately 100–300 nm. In general, while thicker active layers provide more absorption, the low charge mobility of the organic semiconducting blend severely limits charge extraction for thick layers prior to recombination [3–5].

Promising strategies to enhance the active-layer absorption without increasing its thickness include active layer designs that improve energy transfer and morphology [6–9], enlarging the optical path length [10,11], or by light scattering [12,13]. While the former involves engineering the material system itself, the latter two focus on strategies that provide more opportunities for photons to be absorbed, thus increasing the photocurrent. These two approaches rely on light trapping schemes [14], by localizing the electromagnetic fields with the use of surface plasmons [10,15,16], photonic crystals [11] or by light scattering due to multiple reflections in the propagating medium [12,13]. Previously, Liu et al. used a photonic crystal to texture the active layer of thin OPV and observed a 10.5% enhancement of the short circuit current [12]. Other approaches to achieve light scattering include embedding nanospheres both in the active and buffer layers [17]. Recently, we have shown that microstructuring the substrate using periodically spaced fiber arrays significantly improves light trapping and enhances light absorption [18,19]. We note that other nano/microstructures have also demonstrated the ability to redirect or even trap light [20–26], such as the case of micro lens arrays [27] or even

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pyramidal rear reflectors [28]. Unfortunately, many of these approaches rely on expensive fabrication methods, which are too costly for large-scale production.

Through billions of years of adaptive evolution, nature has already designed unique but surprisingly elegant solutions enhancing light harvesting in low light intensity regimes. Diatoms, for example, are photosynthetic microorganisms (algae) that are abundant in nearly every water habitat, and even the bark of trees [29,30]. To survive in the carbon dioxide scarce environment of the early Jurassic period [31], they developed a silica skeleton, called a frustule, which has species-specific transparent cell walls with organized three-dimensional (3D) nanostructured porous silica.

There are several examples of diatom-based structures utilized for solar energy applications [32]. A recent patent by Sandhage and Bao proposes that diatom based structures can be used as diodes in silicon-based solar cells [33]. Expanding on the Sandhage group who pioneered the conversion of diatom SiO_2 into silicon [34], Chandrasekaran et al. have shown that diatom frustules can be converted into nanostructured silicon, gold plated, and employed as an electrode for solar energy conversion and photocurrent measurement [35]. Toster et al. used diatoms as photoanodes in dye sensitized solar cells (DSSCs), demonstrating a 30% increase in power conversion efficiency [36]. It has been suggested that improved light absorption is possible when diatoms are in close vicinity to the active layer [37]. Taking these observations into account, we embed diatoms in the active layer of a polymer solar cell to increase light absorption in thin film devices. Here, we utilize diatomaceous earth (DE), an assorted collection of the amorphous silica (fossilized remains of *Melosira Preicelanica*), as an additive to the active layer of regioregular poly(3-hexylthiophene) (P3HT) and fullerene derivative [6,6]-phenyl-C_{60}-butyric acid methyl ester (PCBM) polymer solar cells (PSCs). A great deal of attention has been given toward implementing complex silica based nanostructures into solar devices to achieve light trapping [17,38]. However, this work abstains from implementing processed nanostructures, opting instead to demonstrate a low cost, facile, earth abundant method to achieve enhanced light management. The DE was selected as an ample frustule source that does not need to undergo time-consuming treatments to remove organic matter before integration into the PSCs. Bulk heterojunction (BHJ) photovoltaic cells containing ternary mixtures of P3HT:PCBM:DE in the active layer are investigated to identify whether the presence of diatom frustules can improve the light harvesting efficiency of P3HT:PCBM solar cells. To the best of our knowledge this is the first demonstration using DE as an active layer additive for PSCs.

2. Materials and methods

2.1. General materials

P3HT was purchased from American Dye Source and PCBM was purchased from Nano-C and used without further purification. Diatomaceous Earth was purchased from Lumino and were ball milled to further reduce the particle size. Indium tin oxide (ITO) coated glass substrates were purchased from Zhuhai Kaivo Electronic Components Co., Ltd. (15 Ω sq^{-1}). Silver was purchased from Kurt J. Lesker Company (pellets, 99.99% pure). The ZnO layer was grown by sol–gel where the precursor solution was prepared according to literature preparation [39]. Dichlorobenzene and MoO_3 were purchased from Sigma Aldrich and used as received.

2.2. Device fabrication

ITO (Indium Tin Oxide) - coated glass substrates were sonicated, thoroughly cleaned in organic solvents, rinsed with water and dried with nitrogen. A UV-Ozone treatment of 10 min was performed immediately prior to deposition of the ZnO layer. ZnO was spin-coated in air at 5500 rpm and annealed at 150 °C for 30 min, yielding a 30 nm thick layer of ZnO. For the active layer, a 20 mg/ml solution of 1:1 P3HT- PCBM was dissolved in 1,2-dichlorobenzene (DCB) and previously treated DE particles were added to the DCB solution. An aliquot of this solution was then spin-coated onto the ZnO layer at 700, 900, 1100 or 1300 rpm (depending on the desired film thickness) under nitrogen. The substrate was taken from the spin chuck and immediately placed under an inverted Petri dish inside the glovebox for 10 min to encourage solvent annealing from the small amount of residual DCB on the substrate. Next, the solar cells were placed on a 150 °C hot plate and annealed for 2 min under nitrogen. Then samples were placed in evaporator to deposit a film of MoO_3 and Ag of 3.5 nm and 120 nm respectively.

2.3. Characterization

The current-voltage characteristics of the devices were measured using a Keithley 2400 sourcemeter. The devices were illuminated under 1 sun, AM1.5G from Abet Technologies using a calibrated silicon diode. Spectral mismatch was not corrected in these measurements. A commercially available system from Newport was used for external quantum efficiency measurements. In short, light from a broadband Xe arc lamp was coupled into a monochromator and chopped, and the solar cell response was measured using a current pre-amplifier and lock-in amplifier (Stanford Research Systems). A calibrated Si photodetector served as the reference cell. Reflection and transmission spectra were measured using a commercial integrating sphere setup (Labsphere). AFM measurements were performed on a Bruker Dimension FastScan AFM. SEM measurements were performed on ITO-coated glass and covered by blend with or without diatomaceous earth, depending on the sample. The SEM imaging system was a Hitachi SU-70.

3. Results and discussion

The most common species of the mixed diatom sample used for this work was cylindrically shaped *Melosira Preicelanica*. Scanning electron microscopy (SEM) reveals that the average frustule size is approximately 8 μm wide and 20 μm long (Fig. 1A, 1B). To incorporate the diatoms into photovoltaic cells without causing discontinuities or shorting the active layer, the DE was reduced in size both radially and laterally using ball milling (Fig. 1C). Briefly, the DE was placed into a ceramic jar containing ceramic balls and sealed in atmosphere for agitation at 3450 rpm for 3 h in a ball mill machine. Dynamic light scattering (DLS) was used to measure the particle size distributions, with spherical particle assumptions, of both pristine and ball-milled DE suspended in 1,2-dichlorobenzene (DCB) (Fig. S1). We observe that the average particle size of the milled DE integrated into these cells is reduced from ~1.4 μm to ~250 nm, and the polydispersity index (PDI) broadens from 0.16 to 0.43, after ball milling.

To assess the possibility of incorporating DE in realistic polymer solar cell structures, we measured the electrical characteristics of P3HT:PCBM solar cells of various thickness with and without the DE additive. Our control device architecture is: ITO(100 nm)/ZnO(30 nm)/active layer/MoO_3(3.5 nm)/Ag(120 nm). The thickness of the P3HT:PCBM (1:1) active layers was controlled by varying the spin parameters and the layer thicknesses were confirmed by atomic force microscopy (AFM). We show the current density versus voltage (*J-V*) characteristics under 1 sun illumination for these devices with active layers ranging from 128 ± 3 nm to 199 ± 8 nm (Fig. 2A) and a summary of their photovoltaic