Three-Dimensional Core−Shell Hybrid Solar Cells via Controlled In Situ Materials Engineering

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Supporting Information

ABSTRACT: Three-dimensional core−shell organic−inorganic hybrid solar cells with tunable properties are demonstrated via electropolymerization. Air-stable poly(3,4-ethylenedioxythiophene) (PEDOT) shells with controlled thicknesses are rapidly coated onto periodic GaAs nanopillar arrays conformally, preserving the vertical 3D structure. The properties of the organic layer can be readily tuned in situ, allowing for (1) the lowering of the highest occupied molecular orbital level (|ΔE| ∼ 0.28 eV), leading to the increase of open-circuit voltage (VOC), and (2) an improvement in PEDOT conductivity that results in enhanced short-circuit current densities (JSC). The incorporation of various anionic dopants in the polymer during the coating process also enables the tailoring of the polymer/semiconductor interface transport properties. Systematic tuning of the device properties results in a JSC of 13.6 mA cm−2, VOC of 0.63 V, peak external quantum efficiency of 58.5%, leading to a power conversion efficiencies of 4.11%.

KEYWORDS: Nanowire, electrophoresis, materials engineering, hybrid, solar cell, conducting polymer

Organic/inorganic hybrid solar cells (HSCs) are a compelling research field as they merge the desirable features of solid-state physics and organic electronics, offering a potential solution to low-cost, efficient photovoltaics. To date, semiconductor-based solar cells have higher efficiencies due, in part, to advantageous material characteristics such as extremely high carrier mobility. Furthermore, mature materials engineering practices allow exquisite control of doping concentrations, band-offsets, and interface abruptness down to the atomic level. Polymer solar cells, on the other hand, are inexpensive per square foot and have large absorption coefficients in the visible range. However, the most commonly used polymers such as poly(3-hexylthiophene) are often unstable in air and possess inferior transport properties. Major obstacles to advancing HSC device design have been the limited control over the organic layer features along with interfacial issues. Thus, a more sophisticated approach to materials engineering of HSCs remains an open challenge.

The hybrid interface represents the heart of any HSC devices. Tuning the energy levels in the polymeric conductor component for an optimal band arrangement is therefore one of the most important factors to rationally enhance the HSC performance potentially. By raising or lowering the energy levels or tuning the optical and electrical properties of the organic conductors, the band-to-band realignments between organic and inorganic layers can be altered, and thus maximizing the charge transfer and overall device efficiency. Such elegant materials engineering is typically achieved by modern synthetic chemistry. However, applying the as-synthesized polymer to a three-dimensional (3D) inorganic component such as nanowire arrays is challenging partly due to (1) the extremely specialized expertise required to prepare the functionalized polymers, (2) the multistep synthesis/processing procedures, and (3) the lack of a reliable and reproducible method to produce conformal coatings over the vertical 3D inorganic structures. In particular, common processing methods including spin-coating, inkjet printing, or doctor blading used to apply the organic layer to inorganic nanostructures of silicon, metal oxides, II−VI compound semiconductors or III−V nanowires result in intimately mixed hybrid...
films or interdigitated, blocklike HSC active layers.\textsuperscript{15,16} Using these techniques to coat individual vertical nanowires faces the challenge of nonconformal coatings or thickness gradients. Such coverage limitation diminishes the purpose of having well-oriented, high mobility, inorganic arrays that possess both the advantages of directional charge transport and light trapping properties. Hence, these obstacles have hindered materials engineering from being exploited in hybrid photovoltaics.

This report discusses in details a new, simple approach that combines rapid polymerization directly and conformally onto the inorganic nanostructure surface, and in situ materials engineering to optimize the properties of the organic layer, such as the highest occupied molecular orbital (HOMO) energy levels and the conductivity, that eventually allows for the tuning of the interface properties and performance of 3D nano-structured core–shell HSCs. In brief, periodic GaAs nanopillar arrays are fabricated via a fast, catalyst-free, bottom-up approach.\textsuperscript{17} The GaAs nanopillars are coated with poly(3,4-ethylenedioxythiophene) (PEDOT) that is synthesized with different anionic dopants incorporated during an electrochemical deposition process in order to tailor its physical properties to better match the charge transfer/exchange with respect to the inorganic semiconductor counterpart. The hybrid interface is explicitly tuned by (1) enhancing the in situ transport properties of PEDOT by using different dopant anions, (2) shifting the HOMO level of PEDOT downward to increase the $V_{OC}$, and (3) designing a PEDOT shell that balances out the short exciton diffusion length and the required thickness for light absorption. Furthermore, electropolymerization constitutes a low cost and selective technique that yields conformal radial shells around individual GaAs nanopillars to preserve the 3D features of the patterned array. A radial core–shell geometry is desirable because it allows for a shorter pathway for photogenerated carriers, thereby enhancing the charge collection efficiency. Ensuring a conformal coating of well-defined 3D inorganic semiconductor patterns, such as oriented nanopillars, with an organic conductor allows for a large surface/interface area as well as enhanced absorption from nanostructuring, which is difficult to achieve for all-organic cells due to the current scarcity and limitations in their patterning techniques. In addition, the selected conducting polymer here, PEDOT, unlike the readily photo-oxidizable P3HT,\textsuperscript{21} is well-known for its remarkable air stability,\textsuperscript{22,23} which is essential for a practical device.

Figure 1a,\textsubscript{b} illustrates the resulting device schematic and relevant energy levels in the hybrid device. As a first step, n-type GaAs nanopillars are grown on a masked n$^+$-GaAs substrate via selective area epitaxy (SAE). The growth is carried out using a metal organic chemical vapor deposition reactor (MOCVD, vertical-flow) with a hydrogen carrier gas at 60 Torr. The n-doped GaAs nanopillars are grown at 740 °C using trimethylgallium (TMGa) and tertiary-butyl-arsine (TBA) as the primary precursors and tetra-ethyl-tin (TESn) as the dopant. The SAE is a catalyst-free alternative that does not introduce any contamination into the nanopillars,\textsuperscript{17,24} and allows lithographic control of nanopillar diameter, center-to-center pitch, tiling pattern, and periodicity. The process requires only a few minutes for growing a complete array of nanopillars. Several previous studies reported enhanced optical absorption\textsuperscript{25,26} of nanopillar arrays in comparison with planar architectures despite the low fraction of material utilized. Theoretical calculations (Lumerical FDTD Solutions) show that a 600
nm center-to-center pitch in a square lattice arrangement yields the maximum absorption (see Supporting Information).

Ohmic gold–germanium/nickel/gold (200 nm/40 nm/100 nm) back metal contacts on the as-grown nanopillar arrays are electron-beam evaporated onto the dies and thermally annealed at 400 °C for 30 s. Subsequently, the samples undergo a 90 min de aqueous solution with various electrolytes. Electropolymerization selectively grows PEDOT on the conductive GaAs while leaving the BCB layer intact, thus allowing for a highly controllable thickness and uniform radial coating. Electropolymerization is carried out under potentialdynamic conditions with potential applied by a VersaSTAT 3-400 potentiostat/galvanostat (Princeton Applied Research) using a standard one compartment, three-electrode setup with the GaAs nanopillars as the working electrode. Finally, indium tin oxide (ITO, Kurt J. Lesker) is deposited by RF magnetron sputtering as a top transparent electrode at a rate of 18 nm min⁻¹ at room temperature at 5 mT of deposition pressure and 30 sccm of argon gas.

Figure 1b depicts the band diagram of the final HSC. PEDOT is a hole-injecting conducting polymer and because of its positive temperature coefficient of resistivity, it manifests a metallic signature. For this reason, electrical conductivity is one of the main factors that affect the electronic transport of the photocarriers in the organic component of the junction. Upon illumination, the incoming photons generate electron–hole pairs in the GaAs layer, which then diffuse to the PEDOT/GaAs interface where they dissociate. Subsequently, free carriers (e⁻ and h⁺) can travel to their respective electrodes to be collected. The charge diffusion process in the organic material is typically limited by the inherent short exciton diffusion length (5–30 nm), so controlling the polymer thickness minimizes the distance from the hybrid interface. In addition, the physical properties for the GaAs arrays such as nanopillar diameter and doping concentration are kept constant to facilitate the investigation and comparison of different energy levels/conductivities of PEDOT on the device performance.

Controlling the HOMO level of PEDOT is central to intimately correlate the physical properties of the polymer with that of the inorganic semiconductor at the active hybrid interface. Regarding the structural analysis of the electropolymerization, the deposition of PEDOT is evaluated in terms of thickness and coating morphology as a function of oxidation–reduction cycles applied to the GaAs nanopillar arrays as shown in Figure 2a–c. The arrays are standardized for equal center-to-center pitch (600 nm), height (∼1.2 μm), and radius (190 nm). Figure 2a shows a collection of scanning electron microscope (SEM) images captured at the end of 0, 10, and 25 scanning cycles. The thickness of the coating increases as a function of the number of cycles, as illustrated by the near linear trend shown in Figure 2b, of 0, 20, and 55 nm, respectively. The deposition rate is pattern-dependent and related to the edge-to-edge distance among the nanopillars (see Supporting Information); stronger electric fields enable larger nanopillars to pull in a greater amount of EDOT monomers and dopant anions from the electrolyte, translating into a faster deposition rate. The average deposition rate calculated for 190 nm diameter nanopillars is ~24.0 Å/cycle. The nanometer precision is a crucial degree of freedom for control of polymer thickness. Figure 2c shows a cross-sectional transmission electron microscope (TEM) image of hybrid nanopillars prepared by means of focused ion beam milling. The image confirms the high selectivity and uniformity of the organic coating (80 nm) of the exposed body of the GaAs nanopillars. A sputtered ITO anode (Figure 2d) preserves the 3D morphology and completes the HSC fabrication.

During electrodeposition, the negatively charged electrolyte anions bind to the positively charged PEDOT backbone, thus becoming part of the final polymer shell. This enables the
analysis of several promising dopants for use in the GaAs-based structure. Analysis of material composition, conductivity and HOMO levels are shown in Figure 3a–c. Dopant incorporation is confirmed by X-ray photoelectron spectroscopy (XPS) (AXIS Ultra DLD, Kratos Analytical) as shown in Figure 3a. The XPS also indicates a sulfur (S) elemental composition of 20% of oxidized sulfur (S\(^{+}\)) (peak area ratio of S\(^{+}\) 2p\(/2\) to S 2p\(/2\))\(^{31,32}\) suggesting a 20% doping concentration for all three kinds of dopant anions. Thus, one in every five EDOT monomers is oxidized regardless of the dopant type (see Supporting Information), resulting in an estimated hole concentration \(n_{h} \sim 2 \times 10^{20} \text{ cm}^{-3}\).

Figure 3b depicts the conductivity values with respect to different dopant incorporations into the PEDOT backbone. The general definition of conductivity \(\sigma\) for a p-type material is expressed in eq 1 as

\[
\sigma = q(\mu n_{p})
\]

Consequently, increasing conductivities will result in easier percolation paths for the photogenerated charges to travel to the ITO anode. Five counteranions, PSS\(^{-}\) (poly(styrenesulfonate)), DS\(^{-}\) (dodecyl sulfate), ClO\(_{4}\)^{−} (perchlorate), BF\(_{4}\)^{−} (tetrafluoroborate), and PF\(_{6}\)^{−} (hexafluorophosphate), are investigated as suitable dopants (see Supporting Information); however, only the last three were chosen for device testing since they resulted in the highest conductivities of approximately 68, 90, and 116 S/cm, respectively (Figure 3b). In order to characterize the band positions of the materials, cyclic voltammetry (CV) was utilized. CV for each polymer was carried out in a solution containing 0.1 M of the corresponding electrolyte salt that matches the dopant anion for each PEDOT, scanned at a rate of 0.05 V/sec from \(-3.0\) to 1.5 V. Figure 3c shows three different cyclic voltammograms corresponding to PEDOT/ClO\(_{4}\), PEDOT/BF\(_{4}\), and PEDOT/PF\(_{6}\). All three types of PEDOT exhibit reversible oxidative p-doping processes in the positive potential regions, and a weak reductive behavior in the n-doping region when the reverse bias is applied. The oxidation potential onsets are highlighted by arrows in the plots. Using a silver/silver chloride (Ag/AgCl) electrode in 3 M NaCl solution as reference potential, HOMO levels of \(-4.81, -4.91,\) and \(-5.09\) eV, were calculated for PEDOT/ClO\(_{4}\), PEDOT/BF\(_{4}\), and PEDOT/PF\(_{6}\), respectively (see Supporting Information for theory and calculations\(^{33}\)). The most electro-negative anions, PF\(_{6}\)^{−}, pull away the largest amount of electron density from the PEDOT backbone, significantly lowering the HOMO levels with respect to the GaAs band-edge.

Figure 4a presents the measured \(J-V\) characteristics under 1-sun (AM 1.5G) in ambient atmosphere. AM 1.5 illumination is carried out with a 300 W xenon-lamp-based solar simulator (Newport Corporation, 67005) with an AM 1.5G filter mounted. The light intensity is calibrated using a 1-sun (1000 W m\(^{-2}\)) reference silicon photodiode. A short circuit current density \(j_{sc}\) of 5.2 mA cm\(^{-2}\) was obtained for the device with PEDOT/ClO\(_{4}\) as the organic shell, whereas \(j_{sc}\) of 9.8 and 13.6 mA cm\(^{-2}\) are measured for the more conductive PEDOT/BF\(_{4}\) and PEDOT/PF\(_{6}\) respectively (Figure 4a). Since the charge transport is directly related to the electrical properties of the polymer, enhancing the PEDOT conductivity by a simple change of dopant anion appears to be a feasible way to increase the current density step-by-step, which has been so far difficult to achieve in HSC. Furthermore, since the ultimate \(V_{oc}\) (\(\alpha l/qE_{CB} - E_{HOMO}\)) is related to the energy level alignment between the p- and n-type materials, a lower HOMO level \(E_{HOMO}\) of the p-type polymer allows for a more favorable alignment with the conduction band edge \(E_{CB}\) of the n-type GaAs. Note that the downward tuning of the HOMO level enhances the \(V_{oc}\) value: the \(V_{oc}\) for the HSC

Figure 4. Electrical and electro-optical characterization of the hybrid nanopillar solar cells. (a) \(J-V\) characteristics of hybrid photovoltaic arrays under AM 1.5G illumination (1000 W m\(^{-2}\)) with differently doped PEDOT. (b) EQE measurements (from 340 to 1000 nm) for solar cells based on n-GaAs NPs processed with PEDOT/ClO\(_{4}\), PEDOT/BF\(_{4}\), and PEDOT/PF\(_{6}\). (c) The short-circuit current density \(j_{sc}\) increases quasi-linearly with respect to the electrical conductivity of the polymer, whereas the fill factor (FF) increases only slightly with an increase in conductivity. (d) The open-circuit voltage increases by including different dopant anions and the power conversion efficiency scales almost linearly with the polymer conductivity achieving peak values of 4.11% under 1-sun illumination (100 mW cm\(^{-2}\)).
with the PEDOT/ClO$_4$, PEDOT/BF$_4$, PEDOT/PF$_6$ organic shell is 0.56, 0.60, and 0.63 V, respectively, as the HOMO level of the polymer coating is lowered from $-4.81$, $-4.91$, and $-5.09$ eV (Figure 4a). Hence, the incorporation of different dopant anions provides a simple way to deterministically increase the $V_{OC}$ of the heterojunction. Figure 4b shows a comparison of the external quantum efficiency (EQE) spectra with respect to the three different doping schemes. The monochromatic illumination step is 5 nm and an objective lens with a focal length of 100 mm is used to focus down the spot size. The EQE shapes are overall quite similar with increasing EQE values of $\sim27.9$, 45.0, and 58.5% observed with increasing polymer conductivity, thus suggesting an optimum photocarrier balance between the electrons in the GaAs nanopillar array and the holes in the polymer. Hence, a successful engineering of the band energy of PEDOT results in improved charge separation at the polymer/GaAs interface, translating into higher $J_{SC}$ and $V_{OC}$. The increased charge transfer at the interface is once again confirmed by the EQE spectra across the entire absorbing region. Figure 4c, along with Figure 4d, summarizes the standard figures of merit for $J_{SC}$, fill factor (FF), and $V_{OC}$ required to calculate the total PCE ($V_{OC}J_{SC}FF/P_{AM1.5G}$). In Figure 4c, both $J_{SC}$ and FF show increasing trends with respect to the polymer conductivity. Since the interface ITO/PEDOT is ohmic, the higher conductivity of the polymer lowers the specific series contact resistance, resulting in a higher FF of $\sim48\%$ compared to previous polymer/GaAs nanowire (epitaxially grown) reports. The overall PCE for the core−shell HSCs monotonicly increases from 1.07, 2.71, to 4.11% (Figure 4d). The explicit, stepwise tuning of the figures of merit and the efficiencies of the devices illustrates the importance and the potential opportunities that materials engineering can bring to a HSC.

Representative 3D theoretical simulations (Lumerical FDTD Solutions) are carried out to correlate the EQE spectrum (Figure 4b) with the photogeneration partitioned between the organic PEDOT shell and the inorganic GaAs core in the hybrid nanopillar (Figure 5a). Figure 5b illustrates the spectral evolution (2D cut-planes) of the photogeneration in the structure at different wavelengths varying from 400 to 900 nm for a 1.2 μm-high, 190 nm-diameter GaAs nanopillar, with 80 nm of PEDOT shell. Because of delocalized orbitals in the doped PEDOT, the polymer is fairly optically active over the entire region of interest. However, the simulations consider a 600 nm periodic boundary conditions to account for the enhanced absorption from an infinite array of nanopillars. Therefore, the optical field becomes highly confined within the nanostructure, as a result of the waveguiding and focusing of light by the periodic array; the photogeneration rates are concentrated to several lobes that form along the nanopillar, indicating strongly guided modes that arise from the nano-structuring of the 3D HSC. The simulations suggest that the final arraylike morphology still supports light-trapping effects. Above the bandgap (for $\lambda = 900$ nm), no optical generation is detected as confirmed from the EQE measurements.

In conclusion, this work demonstrates the importance of materials engineering for tuning the energy levels in the organic layer for optimizing the charge transfer at the hybrid interface. A facile electrodeposition approach is used as the delivering vehicle toward this goal by incorporating different anionic dopants in PEDOT and deterministically fabricate 3D hybrid core−shell PEDOT/GaAs pillars with a high degree of control over the radial thickness of the organic shells. The electrodeposition technique allows for the rapid formation of PEDOT, conformal coating of the PEDOT around the oriented GaAs nanopillar arrays, and the in situ engineering of the organic material properties in terms of feature size, thickness, conductivity, and energy levels. Adjusting the energy levels of PEDOT to more favorably align with the band structure of the inorganic semiconductor has led to the enhancement in the overall PCE of the final device, hence illustrating the great potential and the endless possibilities of molecular engineering via simple and rapid electrochemical synthesis.

**ASSOCIATED CONTENT**

* Supporting Information
Additional information and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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