Functional Materials

Single-Wall Carbon Nanotubes as Integrative Building Blocks for Solar-Energy Conversion**

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Abundant clean energy is one of the greatest challenges facing the world in the 21st century. Solar energy conversion is one of the most natural and abundant ways to produce alternative energy to carbon fuels. Over the years, the use of inorganic semiconducting materials has dominated the solar energy conversion market. However, the production of organic or mixed organic/inorganic solar cells has visibly increased the potential of solar energy conversion and made an impact with a broad range of innovative technologies. Most promising approaches include dye-sensitized nanocrystalline solar cells,[1] polymer/fullerene blends,[2] small-molecule thin

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[**] This work was carried out with partial support from the EU (RTN networks "WONDERFULL" and "CASSIUSCLAYS"), MIUR (cofin prot. 2004035502), SFB 583, the National Science Foundation (grant EPS-0132543), and the Office of Basic Energy Sciences of the U.S. Department of Energy. This is document NDRL-4586 from the Notre Dame Radiation Laboratory.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200462416

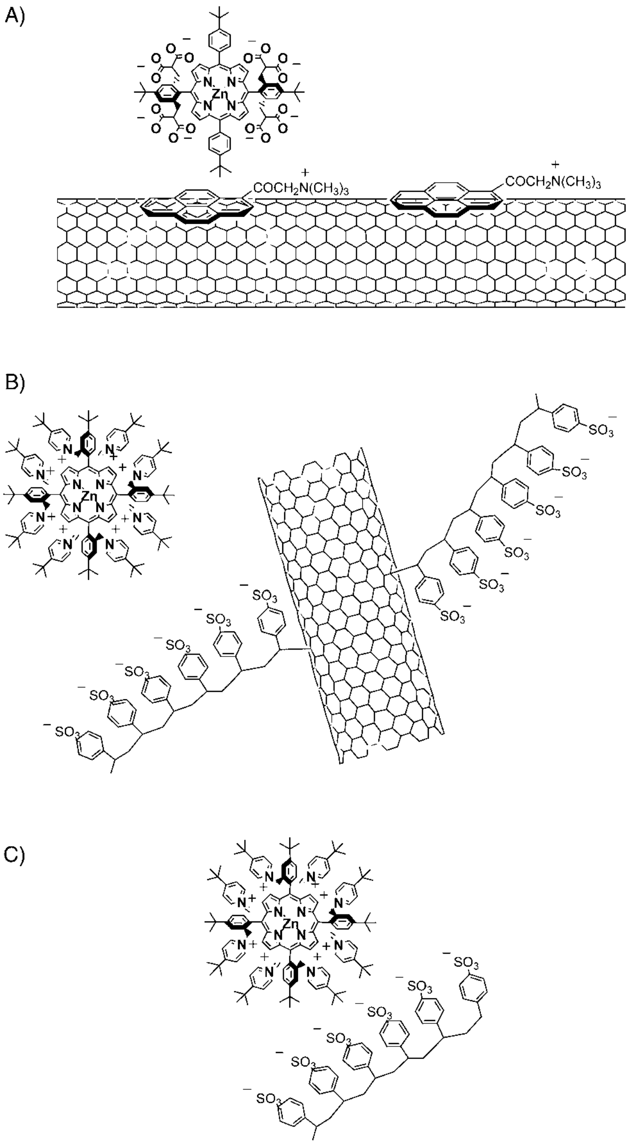
films,[3] and hybrid polymer/nanocrystal devices.[4] Small-area dye-sensitized solar cells have so far reached conversions of about 11 %,[5] whereas polymer-fullerene blends have been reported with 3 % efficiency.[6] Recently, discotic liquid crystalline materials have been successfully used in the construction of organic solar cells.[7]

Single-wall carbon nanotubes (SWNT), are attractive platforms for photovoltaic applications.[8,9] In principle, these innovative materials, which possess extended π-electron systems, in combination with photoexcitable electron donors, could be useful for novel, ultrahigh efficient photoelectrochemical cells for water splitting and reduction of CO_2 to fuels.[10] In fact, SWNT are good electron acceptors and, at the same time, one-dimensional nanowires.[10d,11,12] Therefore, they are ready to accept electrons, which are then transported with high efficiency. In light of this feature, the combination of SWNT with donor groups signifies an innovative concept to 1) harvest solar energy and 2) convert it into useful electricity. Based on these principles, a SWNT-based solar cell should work efficiently. The role and potential of SWNT photovoltaic hybrids has only been sparingly explored.[13] Herein we focus for the first time on the systematic and molecularly controlled integration/organization of SWNT, together with porphyrin systems, into nanostructured devices. The rich and extensive absorptions, typical of porphyrinoid systems, make an efficient use of light. The new system gives rise to promising monochromatic solar-energy conversion efficiencies—up to 8.5 % internal photoconversion efficiencies (IPCE).

The favorable charge-separation features of SWNT–PSS^{n-}/H_2P^{8+}[11] and SWNT/$pyrene^+/ZnP^{8-}$ nanohybrids[12b] (shown in Scheme 1) are promising for the construction of photoactive electrode surfaces.[14] The combination of the electron-accepting character of SWNT with ZnP, which acts as an excited state electron donor, is a fundamental design consideration.[15]

To test these novel SWNT architectures in photoelectrochemical devices, we take advantage of the electrostatic interactions, which govern the organization of SWNT-PSS^{n-}/ZnP^{8+} and SWNT/$pyrene^+/ZnP^{8-}$ in solution, to integrate them sequentially onto solid substrates.[11,12b] In particular, points of multiple interactions between poly(diallyl dimethylammonium) chloride ($PDDA^{n+}$) and sodium poly(styrene-4-sulfonate) (PSS^{n-}) base layers and SWNT-PSS^{n-} or SWNT/$pyrene^+$ are expected to secure strong and tight binding.[16]

Owing to the absorption features of the polyelectrolytes ($PDDA^{n+}$ and PSS^{n-}), SWNT (SWNT and SWNT-PSS^{n-}), and porphyrins (ZnP^{8+}, ZnP^{8-}), conventional spectrophotometry is a convenient tool to assess the adhesion of the individual building blocks to the surface (Figure 1). For example, on quartz substrates, $PDDA^{n+}$ and PSS^{n-} exhibit transitions that are mainly located in the UV region (mainly below 200 nm for $PDDA^{n+}$ and 260 nm for PSS^{n-}). SWNT, on the other hand, are strong UV/Vis-NIR absorbers, since the van Hove singularities extend up to 1500 nm. Finally, the porphyrin systems exhibit strong Soret- and Q-bands at around 435 nm and in the 550–600 nm region, respectively. Also the strong π–π* transitions of $pyrene^+$ can be observed at 235, 290 and 365 nm.



Scheme 1. Structure of A) SWNT/$pyrene^+/ZnP^{8-}$, B) SWNT-PSS^{n-}/ZnP^{8+}, and C) PSS^{n-}/ZnP^{8+} used in this work.[12]

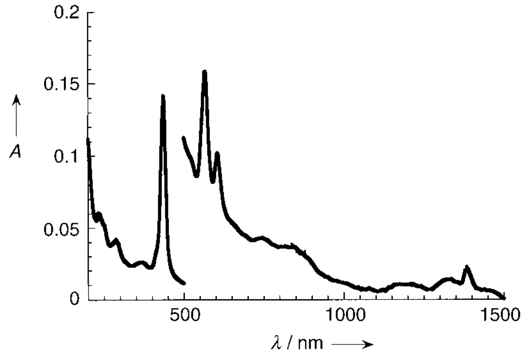


Figure 1. Absorption spectrum of a single SWNT/$pyrene^+/ZnP^{8-}$ stack on quartz. The 500–1500 nm region is amplified by a factor of 10.

The electrostatically driven deposition of SWNT and porphyrins onto the surface was also monitored by atomic force microscopy (AFM). (Figure S1 in the Supporting

Information shows randomly organized bundles of SWNT on a pretreated silicon wafer in the case of SWNT/pyrene$^+$. Layers of SWNT-PSS^{n-} behave similarly.)

Photoaction and photocurrent measurements with different sets of electrodes were performed in aqueous solutions containing 0.1 M Na_3PO_4.[17] Photoaction spectra with monochromatic light were measured (see Figure 2) which confirm the photoactivity of the porphyrin chromophores. Through photocurrent measurements, in which the entire solar spectrum was used, we probed mechanistic aspects. Upon addition of sodium ascorbate—an electron donor that restores the oxidized porphyrins—the photocurrents of the system increased markedly. Obviously, regeneration of the initial porphyrin state helps to close the photo-electrochemical circuit. In concentration-dependent assays between 0 and 10 mM sodium ascorbate, a maximum response was observed at 1 mM. At higher quencher concentrations, though, the currents stagnate. When monitoring several back-to-back intervals of light-on and light-off, exceptionally reproducible and stable photocurrents were obtained, which is illustrated in the inset to Figure 2.

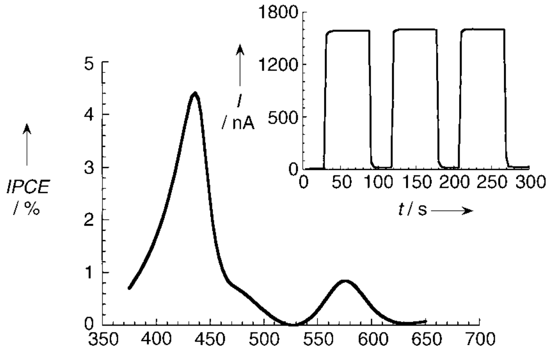
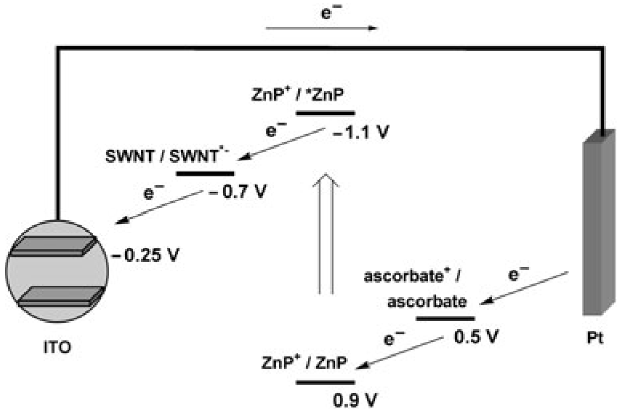


Figure 2. Photoaction spectrum of a single SWNT/pyrene$^+$/ZnP^{8-} stack: 0.1 M Na_3PO_4, 1 mM sodium ascorbate, N_2-purged, electrochemical bias of +200 mV. Insert several on/off cycles for a single SWNT/pyrene$^+$/ZnP^{8-} stack: 0.1 M Na_3PO_4, 1 mM sodium ascorbate, N_2-purged, electrochemical bias of +200 mV.

Another decisive set of data comes from biasing the indium tin oxide (ITO) electrode through electrochemical charging. With increasingly negative potentials, the photocurrents drop, while an opposite trend is observed in the positive region. In fact, changing the bias from −200 mV to 0 mV and to +200 mV versus Ag/AgCl leads to threefold and sixfold increase of the photocurrent, respectively. It is very likely that, at the minimum value of the bias, we reach equilibrium conditions between the ITO conduction band and the reduction of SWNT.[18]

Considering all the pieces of information together, we reach the following conclusion. Charge separation from the photoexcited porphyrin to SWNT generates electron-hole pairs at the SWNT surface.[10d,12b,19] While the energetic position of the ITO conduction band favors a thermodynamically driven electron transfer from the reduced SWNT, the sacrificial electron-donor sodium ascorbate reduces the oxidized porphyrins (Scheme 2).[20]



Scheme 2. Schematic illustration of photocurrent generation in ITO electrodes covered with a single SWNT/pyrene$^+$/ZnP^{8-} stack.[17]

The photoaction spectra (Figure 2) were further used to quantify the internal photoconversion efficiency. For SWNT-PSS^{n-}/ZnP^{8+} cells that contain single layers of PDDA^{n+}, SWNT-PSS^{n-}, and ZnP^{8+} monochromatic IPCE values of 0.25 % were determined. A lot more efficient is the SWNT/pyrene$^+$/ZnP^{8-} cell with 1.8 %. Next we replaced the electron-accepting SWNTs with C_{60}. In the corresponding C_{60} cells, namely, PDDA^{n+}/$C_{60}{}^{9-}$/ZnP^{8+} moderate IPCE values of 0.15 % were noted.[21] Finally, in the absence of any electron acceptor—neither SWNT nor C_{60} were present—the efficiencies for PSS^{n-}/ZnP^{8+} cells drop dramatically to 0.08 %.[22]

Repetition of the deposition steps allows modifying the PDDA^{n+} or PSS^{n-} baselayers with SWNT-PSS^{n-}/ZnP^{8+} and SWNT/pyrene$^+$/ZnP^{8-} stacks. The repetitive growth is monitored with absorption spectroscopy (a typical example is shown in Figure S2 in the Supporting Information). The transitions of pyrene$^+$ (that is, 235, 290 and 365 nm), ZnP^{8+} (435, 565, and 605 nm), and SWNT (685, 745, 815 and 880 nm) grow linearly up to 10 stacks, that is, 10 alternate layers of SWNT/pyrene$^+$ and ZnP^{8-}. Of note is that we see an overall increase in photocurrent generation up to at least 10 stacks (Figure 3). Greatly enhanced absorption cross-sections favor the photocurrent increase. In addition, strong electronic coupling between the stacks, which is augmented by the

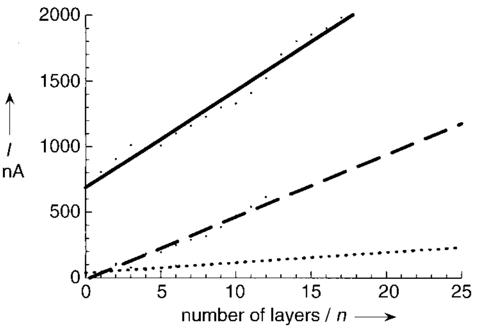


Figure 3. Photocurrent dependence for the different SWNT structures; *n* reflects the number of individual deposited layers: SWNT/pyrene$^+$ and ZnP^{8-} (solid line), SWNT-PSS^{n-} and ZnP^{8+} (dashed line), PSS^{n-} and ZnP^{8+} (dotted line); these three lines are the extrapolated fit of the experimental data (dots).

intriguing SWNT transport features within the individual layers, is believed to be critical for the observed trend. Translating the currents into IPCEs, maximum values for SWNT/pyrene^{+}/ZnP^{8-} and SWNT-PSS^{n-}/ZnP^{8+} are 4.2 % and 1.0 %, respectively. With a +200 mV bias the corresponding monochromatic efficiency is approximately 8.5 %. In the case of PSS^{n-}/ZnP^{8+} no significant current increase is seen owing to the insulating features of PSS^{n-}.

In conclusion, we have demonstrated that the successful incorporation of SWNT hybrids—noncovalently linked SWNT/pyrene^{+} and covalently linked SWNT-PSS^{n-}—onto semitransparent ITO electrodes leads to solar-energy conversion devices. Considering that a cell containing a single SWNT/pyrene^{+}/ZnP^{8-} stack, namely, a single layer of SWNT/pyrene^{+} and single layer of ZnP^{8-}, leads to monochromatic conversion efficiencies of up to 4.2 % (that is, with a +200 mV bias) this is a promising starting point.[23] The strategy illustrated herein is not optimized, but leaves ample room for improvement. Whereas other systems may have shown higher efficiency, the present method offers flexibility and can be considered as a complementary technique to those already existing. Since the problem of solar-energy conversion is so important, we believe that the high photocurrents found in our preliminary experiments deserve much further investigation, including studies of efficient ways of dispersing individual SWNT better into thin films.

Received: October 25, 2004
Revised: December 6, 2004

Keywords: carbon nanotubes · charge separation · porphyrinoids · solar-energy conversion · zinc

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