# Single carbon nanotube photovoltaic device

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Here we present photocurrent measurements on a single suspended carbon nanotube p-n junction. The p-n junction was induced by electrostatic doping by local gates, and the E11 and E22 resonances in the nanotube could be probed using photocurrent spectroscopy. Current-voltage characteristics were recorded, revealing an enhanced optoelectronic response on resonance. The internal power conversion efficiency for the nanotube diode was extracted on and off resonance with the E11 and E22, and a large internal power conversion efficiency was observed. An internal efficiency of up to 23% is reported for the E11, showing the potential of carbon nanotubes to be used as the active element in photovoltaic devices. Finally, a photovoltaic device is proposed which exploits this enhanced efficiency. © *2013 AIP Publishing LLC*.
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## I. INTRODUCTION

Carbon nanotubes are one-dimensional materials with remarkable electrical and optical properties.[1,2] They have shown promise for photodetection[3] and solar cell applications;[4,5] however, the efficiency of the energy conversion has been very modest. Lately carbon nanotubes have been combined with Si p-n junctions[6] and composites[7] or integrated in organic solar cells,[8] in order to achieve high efficiency photovoltaic devices. In these hybrid structures the carbon nanotubes are typically used for efficient collection of the photogenerated current, and not as the active material for photovoltaic. Besides, studies carried out on networks of carbon nanotubes find that the device efficiency suffer from the coexistence of semiconducting and metallic nanotubes in the network.[8] Therefore, it is important to study the intrinsic efficiency of the carbon nanotube itself in order to evaluate its prospect for photovoltaic devices. Studies on carbon nanotube thin-films addressed the question of their potential as the active material in solar cells,[4,9] but this has not been investigated on the single nanotube level. Large efficiencies have been predicted in the photoresponse of carbon nanotubes near the band-edge,[10] and recently the energy harvesting potential of carbon nanotubes have been shown to be related to their resonances in the optical spectrum.[11]

Here we present photovoltaic measurements on a single carbon nanotube diode and compare the internal power conversion efficiency of the device for different excitation energies. We demonstrate an increased internal power conversion efficiency in the nanotube when excited on the E11 and E22 compared to off resonance excitation. We also found an optimal illumination power for the device, for when this is exceeded the diode becomes saturated and the electrons and holes recombine non-radiatively before they have time to escape the p-n junction.

## II. EXPERIMENT

The carbon nanotubes were grown using CVD[12] on a pre-fabricated device structure. The individual semiconducting carbon nanotubes are grown to bridge a 4 $\mu$m wide and 800 nm deep trench. On each side the suspended carbon nanotube makes an electrical contact to W/Pt electrodes. Details about the device fabrication has been reported elsewhere.[13,14] Two local gates at the bottom of the trench are used for electrostatic doping. A schematic representation of the device geometry can be found in the inset in Fig. 1(a). By applying a voltage to the trench gates, a p-n junction can be created in the carbon nanotube. This allows for a dynamic device with tunable doping levels.

Electrical and optical measurements were performed on the carbon nanotube diode at room temperature and under vacuum in a home-built scanning confocal microscopy setup. The diode was excited with a supercontinuum white light source (Fianium) in combination with an acousto-optical tunable filter (AOTF). Fig. 1(a) shows the dark current-voltage characteristic of the carbon nanotube device. With +8/−8 V applied to the two trench gates the carbon nanotube shows a rectifying behavior, characteristic of a diode.

The p-n junction was spatially located using scanning photocurrent microscopy,[13,15,16] where the excitation laser is raster scanned over the device and the photocurrent measured at every laser location. This generates the photocurrent image in Fig. 1(b) which shows the optical response from the carbon nanotube p-n junction to be located in the center of the trench.

## III. RESULTS AND DISCUSSION

After locating the position of the nanotube diode, we performed photocurrent spectroscopy[4,14,17] to identify the optical transitions in the carbon nanotube. Fig. 2(a) shows the E11 transition at 0.84 eV. The photocurrent spectrum was measured with the polarization aligned along the nanotube axis.[14,18] A plot of the photocurrent at E11 as a function of the polarization angle of the excitation laser can be found

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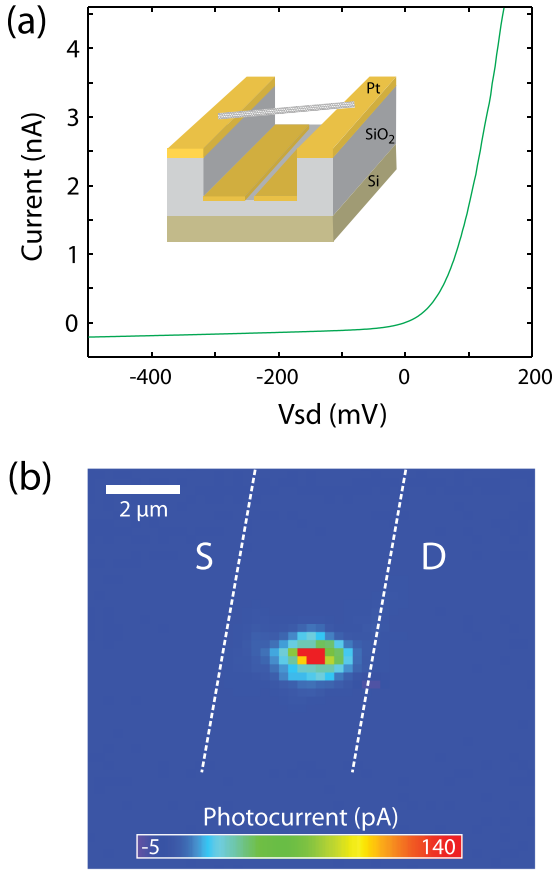


FIG. 1. Single carbon nanotube diode. (a) An I-V characteristic of the device without illumination, showing a rectifying behavior, characteristic for a diode. A schematic of the device geometry is shown in the inset. +8/−8 V was applied to the trench gates to create the p-n junction. (b) Scanning photocurrent microscopy image of the single carbon nanotube p-n junction. The excitation laser (532 nm) was raster scanned over the device, generating a spatial image of the location of the optical response. The scale bar is 2 $\mu$m.

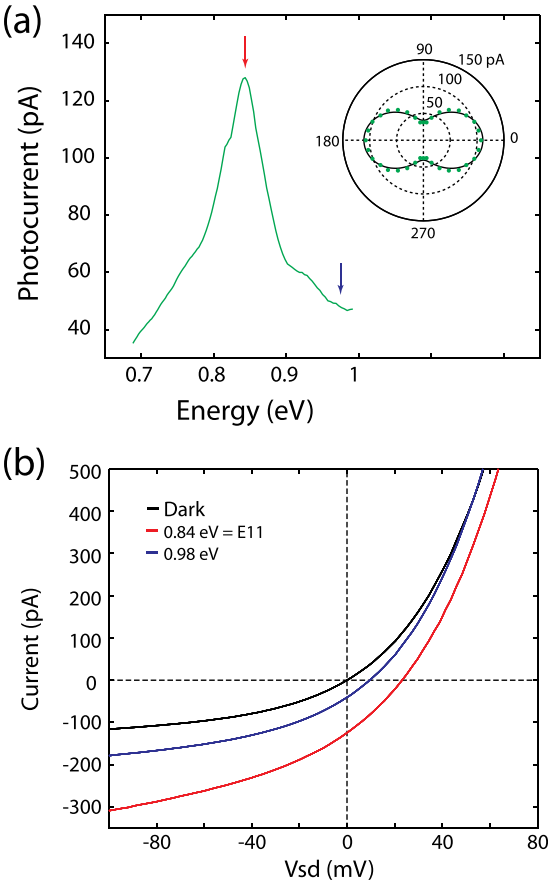


FIG. 2. Photoresponse in a single carbon nanotube diode. (a) Photocurrent spectroscopy on the carbon nanotube p-n junction, showing the E11 optical resonance at 0.84 eV with the polarization aligned along the nanotube axis. The inset shows the polarization dependence of the photocurrent at the E11 transition. (b) I-V characteristics recorded without illumination (black), with 0.84 eV excitation (red arrow in (a)) and 0.98 eV excitation (blue arrow in (a)). The incident laser power was 64 $\mu$W. We clearly see the increased photoinduced current in the device at the E11 energy (red) compared to off resonance (blue).

in the inset in Fig. 2(a), showing the polarization dependence of the photocurrent signal.

Thereafter we investigated the diode's response to illumination. The I-V characteristic of the carbon nanotube was measured for on resonance excitation on the E11 (0.84 eV), as well as for off resonance excitation at 0.98 eV, indicated by arrows in Fig. 2(a). The incident laser power was kept constant at 64 $\mu$W. Fig. 2(b) shows the I-V characteristics for excitation on E11 (red) compared to the case of no illumination (black), and the photoinduced current in the device under illumination can be observed. We also observe a larger photoinduced current in the device when excited on E11 (red) compared to off resonance excitation (blue).

The power conversion efficiency of a diode can be extracted using the open-circuit voltage ($V_{oc}$), the short-circuit current ($I_{sc}$), and fill factor (FF).[2,4] A $V_{oc}$ of 23 mV and an $I_{sc}$ of 119 pA could be extracted from Fig. 2(b), for on resonance excitation, and a fill factor of 29% was calculated. The fill factor both on and off resonance showed a very weak dependence on excitation power. This low fill factor and $V_{oc}$ are a result of the poor contact resistance of the device. The W/Pt electrodes make a good p-type contact to the carbon nanotube but work poorly for electron conduction. A device resistance in the order of 100 MΩ was measured, where the series resistance at the contacts is assumed to be dominating. The contact resistance could be improved by for example choosing a different contact metal; however, in our case the choice of metal was restricted by the elevated fabrication temperature.

The power conversion efficiency, $\eta$, can now be calculated according to $\eta = I_{sc}/(P_{in}T_{obj}A) \times V_{oc} \times FF$, where $P_{in}$ is the incident laser power (measured before the objective), $T_{obj}$ is the transmissivity of the objective, and $A = A_{nanotube}/A_{laser}$, which ensures that we only take into account the photons that are incident on the nanotube surface. We here consider the geometrical cross section of the nanotube, in order to evaluate the absorption efficiency, instead of using the optical absorption cross section per carbon atom.[19]

The calculated power conversion efficiency reaches 0.027 for excitation on the E11 and is one order of magnitude lower for off resonance excitation. In order to conclude that the difference in power conversion efficiency for the different excitation energies is not an effect of the increased absorption on the E11 resonance, the data were corrected for the absorption efficiency. The internal power conversion efficiency can be extracted by dividing the power conversion efficiency, $\eta$, with the absorption efficiency. A rough estimate of the lower limit of the absorption efficiency in the carbon

nanotube can be extracted from the external quantum efficiency, ensuring a conservative estimate of the absorption. The external quantum efficiency has been previously measured for this device geometry[14] and was found for approximately 6 $\mu$W excitation power to be 12% on the E11 and approximately 3% for off resonance excitation. These values agree with other reported quantum efficiencies for carbon nanotube devices.[3]

Fig. 3 shows the resulting internal power conversion efficiency in the nanotube. The power dependence of the internal power conversion efficiency shows a clear increased efficiency on the E11, showing that this increase is not a result of the larger absorption efficiency on the E11, but also related to the separation efficiency of electrons and holes and their conductivity to the electrical contacts. The enhanced energy conversion efficiency on the E11 has been reproduced on one additional device with similar results.

The internal diode efficiency exhibits a peak when excited on the E11. It increases for low optical powers, up to around 6 $\mu$W, which can be understood as the photogenerated current having a linear dependence on optical power, for low powers.[10] Thereafter, the efficiency decreases for larger excitation powers. This could be an effect of the increased density of charge carriers in the p-n junction at higher powers. When multiple electrons and holes are present in the junction, they might recombine non-radiatively before having time to escape the junction and reaching the contacts.[20] The decreasing efficiency could also be a result of exciton-exciton annihilation.[21,22] Fig. 3 clearly shows a proof of principle that the internal power conversion efficiency of the semiconducting carbon nanotube p-n junction is larger on the E11 than for off resonance excitation while the mechanism for exciton dissociation remains an open question in the field.

The internal power conversion efficiency of the E22 resonance at 1.36 eV was also investigated and found to (after compensating for the absorption efficiency in the nanotube, as described above) give a peak efficiency of 20%. Fig. 4 shows the internal power conversion efficiency of E22 and compares it to off resonance excitation. The increased efficiency also observed on the E22 supports our conclusion of enhanced energy conversion efficiency on resonance in our carbon nanotube diode.

Considering the vast selection of nanotube chiralities, a solar cell device based on different carbon nanotube species could be designed to operate across the solar spectrum. For wavelengths of 900 nm and longer a large selection of carbon nanotubes are available with E11 at these wavelengths. The FWHM of the E11 is typically of the order of 50 meV,[17,18] and the density of carbon nanotube chiralities with the E11 above 900 nm is sufficiently high, with respect to the absorption linewidth, to readily cover the infra-red part of the solar spectrum.

For the visible part of the solar spectrum one would need to rely on the E22 or higher resonances, as not enough nanotubes exist with the E11 in the visible range. It is also worth mentioning that although the nanotubes have an enhanced energy conversion efficiency at the resonances their efficiency at higher energies is not zero. The absorption coefficient for light off resonance is approximately 3%,[14] and the efficiency of converting this energy into electrical current is 5%–10% (see blue triangles in Figs. 3 and 4).

Different techniques could be used to tune the E11 to desired energy. For example strain has been demonstrated as a tool to tune the band gap of carbon nanotubes,[23] where 1% strain would alter the carbon nanotube band gap ~100 meV. Tuning the carbon nanotube band gap could aid in using the more efficient E11 for energy conversion across a larger energy range.

This points to the potential of using carbon nanotubes for photovoltaic. To realize a solar cell of a selection of chirality specific carbon nanotubes, cheaper chirality selection methods are needed. A deeper understanding of the exciton dissociation mechanism in carbon nanotubes would also be

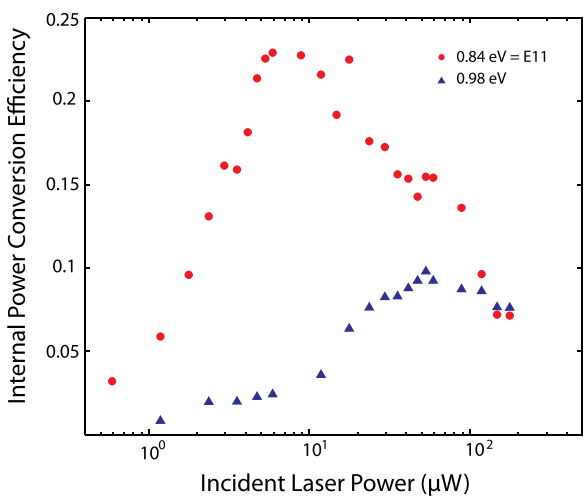


FIG. 3. Internal power conversion efficiency on and off resonance as a function of excitation power. The internal power conversion efficiency was extracted as a function of excitation power for 0.84 eV (red circles) and 0.98 eV (blue triangles). A clear enhancement in efficiency can be observed on the E11 as well as a peak efficiency around 6 $\mu$W. The decrease for large optical power is due to the fact that the junction becomes saturated and not all of the generated electrons and holes have time to escape the junction before recombining.

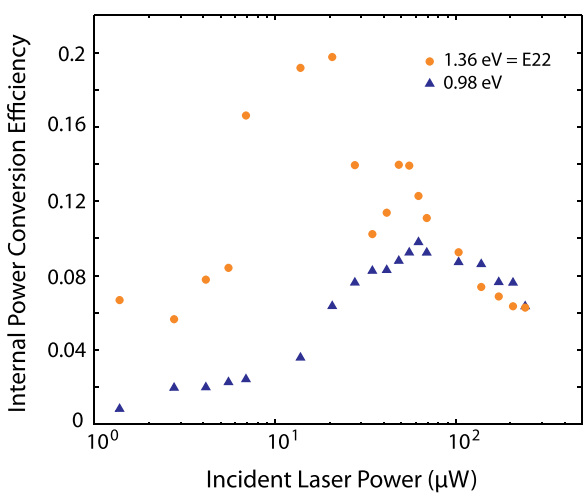


FIG. 4. Power dependence of the internal power conversion efficiency on the E22 at 1.36 eV (orange circles), compared to off resonance excitation at 0.98 eV (blue triangles). An increased internal power conversion efficiency of the diode can be observed also on the E22.

necessary in order to design efficient energy harvesting devices. In addition, chirality specific growth on a predetermined location would truly enable the design of a purely carbon based solar cell, covering the entire solar spectrum.

## IV. CONCLUSIONS

In summary, we have demonstrated an enhanced internal power conversion efficiency in a single carbon nanotube diode on resonance with the E11 and E22 optical transitions. Efficiencies of up to 23% were measured in this nanotube diode. This shows the potential of carbon nanotubes for photovoltaic applications and that the optical resonances not only enhance the light absorption in carbon nanotube diodes but also exhibit a larger intrinsic power conversion efficiency. By tailoring a carbon nanotube photovoltaic device such that the E11 coincides with wavelengths of interest, very efficient conversion between light and matter could be realized using carbon nanotubes.

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