Full paper

Self-powered nanodevices for fast UV detection and energy harvesting using core-shell nanowire geometry

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Developing multiple functionalities in nanodevices is a desirable objective in current nanotechnology, where the self-powered capability is one of the most demanded functions—without the need of external batteries, nanodevices can be operated independently and maintenance-free for a long period of time. In this study, we fabricated the core-shell nanostructured device employing multi-walled carbon nanotubes (CNTs) as inner cores and ZnO as outer shells, and demonstrate their multiple functionalities of fast UV detection and self-powered capability. The device features high photoconductive gain of 800 and short response time of 0.48 ms in air and 29 ms in vacuum. For energy harvesting, the device shows photovoltaic (PV) capability to drive a conventional liquid crystal display (LCD) with a Voc of 0.85 V and Jsc of 5 nA. Those features demonstrate that our CNT-ZnO core-shell nanostructured device, performing both high photoresponsivity and PV capability, can be operated in different functionalities with or without external bias.

1. Introduction

The developing of hierarchical structures by combining materials of different scales, classes, and electrical/optical properties has paved the way for tunable performance of nano-optoelectronics [1–4]. In the view of optics, performance of nano-optoelectronics can be enhanced by employing hierarchical structure which supports a sophisticated management of light. For example, a combination of microgroove and NW structure can effectively reduce the reflection loss of monocrystalline Si solar cells [5], and three-dimensional dual-diameter nanopillars have shown improved light absorption [6,7]. From the electrical viewpoint, carrier transports as well as photon-electron couplings within materials can be facilitated through the heterojunctions introduced by hierarchical structures. For example, Hsu et al. reported the integration of carbon nanotubes and TiO2 shells to form radial Schottky barriers in a core-shell fashion to enhance the sensitivity and speed of the NW photodetectors (PDs) [8]. Lieber et al. and Yang et al. created the core-shell nanowires as a platform to explore PV applications in nanoscale [9,10]. Implementation of hierarchical structures also helps to eliminate the detrimental effects caused by the scaling down of the device, such as device integration difficulties and the scarification of device performance. For example, in this study, through appropriate design of hierarchical structures, the PD device can be powered by itself without integrating additional power supply. The hierarchical structures also provide a way to reinforce the performance of nanoelectronics. Taking ZnO as an example, although their nano-enabled PDs exhibit superior optoelectronic properties (e.g., the photoconductive gain can be up to ~108) [11], the temporal resolution (on timescales of a few seconds to minutes) is still unsatisfactory due to an inevitable compromise between sensitivity and speed [12,13]. Those faulty features limit the opportunities of nanodevices for real-time sensing and preclude their applications for various tasks. To improve the response speed, decorations of metallic or dielectric nanoparticles on metal-oxide NWs to form Schottky or pn junctions have shown remarkable effects [14]. Hierarchical structure, such as size selection [15], network schemes [16], biaxial [17], and core-shell structures [18], provide promising routes for enhancing the sensitivity as well as the response/recovery speed. However, despite all of these achievements, beating the sensitivity-speed tradeoff remains a challenge.

Harvesting renewable energies from environments to realize a self-powered nanosystem has drawn significant attention in recent years due to the energy and global warming issues. Such nanosystems are composed of energy-harvesting devices, such as solar cell, thermoelectric generator and nanogenerators to provide power, coupling with functional devices, like LEDs, PDs and various types of sensors to support functionality [19–21]. However, although the integration between...
devices enables the nanosystem to operate independently, power matching, efficiency and scaling are still challenging. To get around the mismatch, a current trend is to adapt active nanodevices that not only detect the signals but also capable of being powered by these detected signals. For example, Chen et al. have fabricated an active vibration sensor able to be powered by the detected vibrations [22]. Wu et al. demonstrated an piezotronic strain sensor able to be powered by the exerted forces [23]. To develop the active PDs, it is important to exploit the PV effect so as to realize a self-powered active sensor because it does not need an external power source to drive.

In this study, we design the core-shell nanostructures employing CNTs as inner cores and ZnO as outer shells (Fig. 1a) to realize the fast UV detection and self-powered capability. The employment of the core CNT provides two key advantages: (i) providing additional conduction path and reducing the need of ZnO thickness, and (ii) creating additional junction with Schottky contacts. We show that those advantages can greatly promote the response speed, enabling fast detection even in vacuum conditions, which is not achievable for conventional ZnO-based PDs without hierarchical structures. Due to the existence of radial depletion region extending along the NW, the device also exhibits PV characteristic and thus the UV energy can be converted to electricity. Owing to its small dimension and the use of asymmetric metal contacts (one side Ohmic and the other Schottky), the PD also features a very low dark current, can work at zero bias, and is expected to have very high operation speed. Furthermore, we show an example of how to apply this device to drive a LCD as a UV cell. This work demonstrates a possible scheme to function and harvest energy by an individual device.

2. Materials and experiments

2.1. Preparation of CNT-ZnO core-shell nanostructured materials

To achieve the self-powered PV device, ZnO with wide bandgap (3.3 eV), excellent thermal and chemical stability as well as optical properties [24], was introduced to construct the hierarchical structure on high conductive CNT. As illustrated in Fig. 1a, ZnO as a shell was partially deposited along the surface of the core CNT. The core-shell NWs were synthesized using an atomic layer deposition (ALD) technique. First, multiwalled CNTs were grown on a silicon wafer at 1400 K from a ferrocene-dissolved xylene solution (1:50, 100 c.c.). After the CNTs were synthesized, an ALD treatment was performed at 300 K to deposit ZnO onto nanotubes to achieve uniform shell layers, using diethylzinc and water as precursors. The as-grown CNT/ZnO core-shell structures were then annealed under a nitrogen-rich atmosphere at 1000 °C for 5 min by a rapid thermal annealing system to improve the crystalline quality. Due to the limited diffusion depth (~ 60 µm) of the ALD, only the upper part of the CNT along the tube axis was coated as shown in the scanning electron microscope (SEM) image in Fig. 1b. The diameters of the CNTs are 40–60 nm and the core-shell structures are 80–100 nm. The thickness of the coated ZnO shell-layer is 30–40 nm, agreeing well with the synthesis parameters of the ALD. The morphology of the CNT/ZnO nanostructure is verified by transmission electron microscopy (TEM), as displayed in Fig. 1c. The stripe fringes (0.34 nm) within the structures represent the walls of the multi-walled CNT. The outer shell is the aggregation of ZnO nanocrystals, whose crystallinity can be confirmed by the lattice spacing ~ 0.52 nm of ZnO (0001) [25]. The low-magnification TEM image in Fig. S1 in the Supplementary material shows that after the ALD deposition, ZnO crystal covering on CNTs to form a rod-like morphology. By having the TEM and SEM observation, the ZnO/CNT core-shell geometry can be confirmed.

2.2. Device fabrication

The ZnO-coated CNT PD device was fabricated in the following procedure. CNT/ZnO nanotubes were dispersed in isopropyl alcohol and then transferred onto a thermally oxidized Si substrate (300 nm SiO_2) with prepatterned electrodes. Nanotubes were observed under a SEM and contact electrode patterns connecting nanotubes with pre-patterned electrodes were defined by electron beam lithography.
followed by electron beam evaporation of Ti/Au (30 nm/70 nm) electrodes.

2.3. PD measurement

$I-V$ properties of the CNT/ZnO core-shell nanotube PD were characterized using a Keithley 4200-SCS semiconductor characterization system. UV light was emitted from a 325 nm UV He-Cd laser (KIMMON Koha Co., Ltd. Model: IK3552R-G). Time-resolved measurements were achieved with the assistance of a mechanical shutter to regularly switch on/off the UV laser. Spectral response of the PD device was performed with an EQE-R3011 spectral response system (Enli Technology). The photoconductive gain is calculated using the following equation:

$$G = \frac{\Delta I_{ph}}{\epsilon \Delta P_{ph}/h\nu}$$

where $\Delta I_{ph}$ is the difference between photo and dark current, $P_{ph}$ is the absorbed light power, $\epsilon$ is electron charge, and $h\nu$ is the photon energy, respectively.

3. Results and discussion

We first highlight the importance of the electrode contacts with relation to the device behaviors. The Ti/Au (30 nm/70 nm) electrodes were defined by electron beam lithography to selectively deposited onto a target region of the nanostructure. Two control experiments are presented here (see Fig. S2): (i) both electrodes contacting to the core CNT and (ii) both electrodes contacting to the ZnO shell. For the first case, since the multi-walled CNTs are typically metallic, the measured conductance is relatively high ($\sim 10^{-14}$ A at 1 V) and no obvious photoreponse is observed, demonstrating the CNT is insensitive to light. While connecting both electrodes to the ZnO shell, the $I-V$ curves exhibit symmetrical behaviors and only unsatisfactory photoreponse is observed because the back to back Schottky contacts sufficiently prevent collecting photo-carriers [26]. Note that the selective illumination to only one Schottky contact will prevent the current offset, resulting in the boost of the photoreponse [27].

To fully activate the functionality of the core-shell nanowires, it is required to fabricate electrode contacts selectively to the CNT core and the ZnO shells (Fig. 1d). According to the SEM image, 2/3 of the CNT core coated with the ZnO shell leads to a large difference in Schottky/Ohmic contact area dominating the transport behavior of the devices. Due to the rectifying nature of the Schottky contact, the CNT/ZnO core-shell nanodevices exhibit asymmetrical $I-V$ characteristic (Fig. 2a and an equivalent circuit is shown in the inset of Fig. 1a). The large reverse dark current, as a result of the unique core-shell geometry, can be attributed to the large Schottky contact areas [28]. Upon illumination, the device shows evident photoreponse to the UV light (325 nm UV He-Cd laser). Interestingly, the device performs different functionalities as operated at indifferent bias regions. At reverse bias region, the device exhibits pronounced photoreponse and works as PDs. At forward bias region, the device possesses the PV effect that is able to harvest energy from the detected signals. Those features demonstrate that our CNT-ZnO core-shell nanostructures, performing both high PD and PV capability, can be operated in different functionalities with or without external bias.

The photoconductive gain of a CNT-ZnO core-shell PD was investigated under various-powered UV light illumination. In Fig. 2b, the photoconductive gain at reverse bias ($-2$ V) is about ten times higher than that at forward bias (2 V) regardless of the UV intensity, showing obvious bias polarity. The origin of photogain as well as its polarity is explained as follows. Under illumination, the electron-hole pair is generated, and the separation of the photo-carriers is initiated by a built-in potential at the interface between cores and shells and the band bending at the surface of ZnO shells. The photo-generated hole will be trapped because of the oxygen-desorption process occurring at ZnO surface [29], leading to the circulation of electrons in circuit measured as the photogain. When the external output is applied, the voltage is directly exerted upon ZnO shells in the radial direction. Specifically, for $V < V_{oc}$, the built-in potential is enhanced by the external voltage and leads to an acceleration of the separated photo-carriers. This significantly reduces the carrier transition time, resulting in an amplification of photogain. For $V > V_{oc}$, the built-in potential is reduced, thereby lessening the photogain of the device. To find the optimum sensitivity of the core-shell nanodevice, we have characterized the dependence of photogain on UV intensity, as shown in Fig. 2c. A feature characteristic of our device is the increase of photogain at low incident power, which could be an evidence of Schottky barrier forming at the interface. Under higher light intensity, the spatial carrier separation is weakened due to significantly increased photo-carriers, lowering barrier height at radial Schottky junction and surface band bending; this would increase carrier recombination rate due to highly overlapped electron-hole wave functions, reducing the electron lifetime and therefore the gain [30,31]. On the other hand, barrier height at radial Schottky junction and surface band bending at low illumination intensities is not reduced significantly and retards the electron-hole recombination, resulting in a high-photogain behavior, suggesting the capability to achieve low-intensity and even a-single-photon detection. In addition, the wavelength dependence of the photogain (Fig. 2d) shows a sharp cutoff at 390 nm, confirming the superior photodetection capability of the device in UV wavelength region. This wavelength dependent photogain matches the absorption spectrum of ZnO (Fig. S3), indicating that the polycrystalline ZnO dominates the light absorption of the device. As a result, while CNT features polarization dependent optical absorption [32,33], the polarization dependent photoresponse is not obtained on the ZnO/CNT core-shell device. Furthermore, because both ZnO and CNT feature high thermal resistance and long-term stability in the air [34,35], the device can work more than three months and bear high UV light intensity up to 1000 mW/cm², which equals to 10 times of solar light intensity.

The temporal response was measured using a data acquisition system (DAQ 2214, ADLINK) with a resolution of 10 μs to highlight the fast speed of ZnO/CNT core-shell UV detectors and gain insights into photo-carrier dynamics. In Fig. 3a, the time-resolved response curves reveal a response time of 0.48 ms and a recovery time of 0.65 ms at a bias of $-2$ V in atmosphere. The response time is defined as the time needed to rise to (1−1/e) of the dark current and the recovery time is (1/e) of the maximum photocurrent. The core-shell CNT/ZnO PD was also operated in vacuum to both demonstrate their capability for outer-space use and to further elucidate the underlying mechanisms. It is well known that the adsorption/desorption of the oxygen molecules is the origin of high sensitivity of the metal-oxide sensors [36], and thus the deficiency of the oxygen molecules will significantly degrade the functionality of those sensors. For example, Molina-Mendoza et al. has reported a TiO₂ nanofibres-based UV sensor featuring much better performance in both responsivity and response time in air than in vacuum [37]. Generally, the response and recovery times of ZnO nanowire (NW) PDs are several seconds to minutes, and the delayed phenomenon becomes even worse in vacuum due to the suppression of oxygen readesorption [38]. Such environment-dependent factor has been found in various types of ZnO-based optoelectronics, which could be detrimental as applying them in oxygen-deficient environments [39-41]. In Fig. 3b, it shows that our devices can still detect with fast speed even in vacuum conditions. In contrast to the reported PDs whose response/recovery times prolongs for a very long time ranging from several thousand seconds to several hours [36], our device exhibits a fast response time of 29 ms and a recovery time of 30 ms in vacuum ($10^{-5}$ Torr). This improvement of photodetection speed enables many useful applications in outer space, for example, inter-satellite communication, missile early warming and global positioning [42]. It is also useful components as biosensors for in-vivo applications, used to resolve the luminescence characteristic of the biomedical agents, whose
lifetime could be detectable by the improved speed. Another thing should be noted is that both dark current and photocurrent of the device in vacuum are a little higher than that in air as shown in Fig. 3. Because the oxygen molecules adsorbed on the ZnO surface can trap free electrons and form a depletion layer near the ZnO surface, the conductivity of device slightly decreases in the oxygen-rich environment.

The observed fast response/recovery speed of CNT-ZnO core-shell nanowires can be attributed to two main advantages arising from the unique geometry of the core-shell structures: (i) the thin thickness of ZnO layer and (ii) Schottky barrier built at the radial interface of the core and shell. The shorter distance of charge transport can lead to fast charge collection, and the strong internal field at Schottky junction interface help the photogenerated electron-hole pair be separated quickly. Furthermore, CNT with extraordinary high mobility (> 10^5 cm^2 V^{-1} s^{-1}) enables the separated carrier arriving electrode at short time [43], which efficiently facilitates the response speed. Under illumination, the increase of photo-carrier density leads to a reduction of the barrier height, enabling the access of the photo-induced conducting path within the depleted ZnO, and thus the conductivity is increased. Due to the thin thickness, the photo-carriers separated within the fully-depleted shell ZnO will be quickly collected by core CNT and electrodes, giving rise to a rapid response speed. Since the process of the light-induced Schottky barrier modulation is rather fast, the response/recovery time can be effectively reduced.

Implementation of nanodevices benefits from the employed nanomaterials with improved properties as compared to their bulky counterparts. However, following those advantages, scaling down of the structure also brings some detrimental effects that obstruct the nanodevices to practical uses. Here, our CNT/ZnO core-shell nanodevice beats the challenge by fulfilling high photogain and fast detection at the same time as well as multiple functionalities. Upon illumination, the device shows a pronounced PV response due to the built-in potential from the Schottky junction. The short length of the nanowire device and the large depleted region by the built-in potential enable the nanowire PD to operate at zero bias. Moreover, the I-V characteristic also exhibits several notable features. First, the nanodevice shows pronounced photoresponse to the UV light when the external bias voltage is applied. The measured responsivity is ~ 200 A/W (at ~ 2 V; UV intensity = 100 mW/cm^2), corresponding to a high gain of 800, originating from the hole trapping activated by the oxygen desorption at the ZnO surface and the high carrier mobility of CNT. Compared to other recently developed nanoscale or larger self-powered PDs (featuring responsivities from few mA/W to 68 A/W and response times from few
hundred μs to several s) [44–51], the device reported here shows even better responsivity and comparable response time of 480 μs, demonstrating the advantages of this core-shell hierarchical structures. Secondly, the device also exhibits PV behavior, where no external voltage is applied and short circuit conditions exist. Under 325 nm UV illumination (~1000 mW/cm²), the representative device yields an open-circuit voltage (\( V_{oc} \)) of 0.85 V, a short-circuit current (\( I_{sc} \)) around 5 nA, and a fill factor (FF) of ~25%.

Here we investigate the PV capability of the CNT-ZnO core-shell device as well as its applications as an UV PV cell. The representative core-shell UV cell was ~3 μm long and ~100 nm in diameter, yielding a \( I_{sc} \) higher than 5 nA under 1000 mW/cm² illumination of 325 nm UV light, as shown in the inset of Fig. 2a. Assuming that the core-shell nanostructure is a perfect cylinder, the active area, namely the junction between core and shell can be estimated to be 9.4 × 10⁻⁹ cm².

Accordingly, the corresponding conversion efficiency can be calculated to be 1.33%. This estimation does not consider the shadow effect from nanotube. Since the shadow part of nanotube is not covered by UV illumination, the light active area should be smaller and the calculated conversion efficiency is most likely due to a consequence of the large series resistance in the polycrystalline ZnO shell and the recombination lose at the interfacial defects, which is expected to be improbable by optimizing the thickness of ZnO layer and crystal quality of the nanostructures. This conversion efficiency and \( I_{sc} \), yet to be optimized, is comparable to the reported value achieved by single nanowire devices harvesting energy from visible solar region [52,53], indicating the feasibility of integrating those devices into one cell, namely, a nanoscale tandem cell.

Although the photodetection performance in the PV self-powered mode is not as good as in external bias-powered mode (responsivity of 200 A/W), the core-shell nanodevice still demonstrates superior UV detection capability with a high responsivity of 27.5 A/W (at 0 V; UV intensity = 100 mW/cm²), corresponding to a photogain of 110. More importantly, in terms of power consumption, the PV mode is advantageous as it is self-powered. In addition, the ZnO/CNT core-shell device can be integrated with conventional electronics or other nanodevices to provide energy for low power applications, in which the core-shell device acts as a pure PV cell. Here the PV cells and its ability to drive a LCD using UV illumination are demonstrated. One can see that the LCD can be lighted up with an output power, where the minimum required power is ~1 nW, corresponding to ~0.2 V in voltage and ~5 nA in current. A stability test of the PV cell has been performed, showing that the switching behavior and the fast response speed were well retained after each on/off cycle, as shown in Fig. 4a. In Fig. 4b, it shows a sequence of LCD images when turn on and off the laser. As the laser was turned on, the LCD could be immediately lit up. Since the LCD is a capacitive device, the screen gradually faded away as the laser was off. Note that during the demonstration the device was directly connected to the LCD screen without any output powers or measurement meters to avoid artifacts. This demonstration shows that our device can produce enough power to drive an LCD screen. Previously, the similar experiments have been demonstrated on triboelectric nanogenerator, which harvest energy from mechanical motion and exhibit the same order of output power [22]. The achievement of this study is to scavenge UV energy to drive a LCD screen by an individual core-shell NW.

4. Conclusions

In summary, we have demonstrated a nanodevice with core-shell geometry capable of UV detection and energy harvesting. A combination of the advantages from the extraordinary photoresponse of ZnO and conductive CNT and photogain of 110 makes it a promising candidate for UV detection (~0.5 ms) and energy harvesting (~0.5 ms). This device has proved to function with fast speed (~30 ms) even in vacuum conditions, which is not achievable for conventional ZnO-based devices without hierarchical structures. As for energy harvesting, the device exhibits a \( V_{oc} \) of 0.85 V and \( I_{sc} \) of 5 nA with a conversion efficiency of 1.33%, which is capable of driving a LCD screen. We believe such core-shell schemes will provide many possibilities not only to improve the performance of the nanodevices, but also to achieve multiple function capabilities.

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Competing interests

The authors declare no competing financial or non-financial interests.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2018.06.065.

References


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