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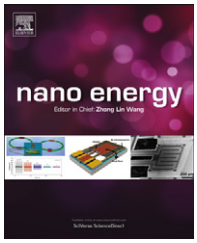

RAPID COMMUNICATION

Nanogenerator based on zinc blende CdTe micro/nanowires

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KEYWORDS
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Abstract
Nanogenerators (NGs) have been developed mainly using wurtzite and proviskite structured materials. Here, we demonstrate the first application of zinc blend structured nanowires (NWs) for NGs, opening a new materials system for harvesting mechanical energy. Free-standing cadmium telluride (CdTe) micro/nanowires (MW/NWs) were synthesized using a facile one-step hydrothermal approach. X-ray diffraction (XRD) analysis indicates that zinc blende is the major phase compared to wurtzite. Laterally packaged single MW generator can generate up to 0.3 V and 40 nA when a strain is applied on an individual MW. Stability test displays its robust piezoelectric performance. Based on these characteristics of NG, we have demonstrated that the CdTe nanomaterials have potential applications in high-output mechanical energy harvesting.
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Introduction

Harvesting energy, such as light, heat and vibration, from our ambient environment, has been a vital subject since the beginning of this century [1]. NW based solar cells can be used to convert light energy into electric energy [2]. ZnO NW array-based pyroelectric NGs can convert thermal energy into electric energy [3]. Recently, to meet the needs of powering mobile electronics, harvesting vibration/mechanical energy, like heartbeat, body movement, hydraulic energy, respiration [4], or air/liquid pressure [5], has been an active area of research for new energy technology. The powering of liquid crystal displays (LCD), light emitting diodes (LED), implantable biosensors and many portable personal electronics [6,7] have been demonstrated. In 2006, our group successfully developed the first piezoelectric ZnO NG. Later, different NGs based on ZnO's superior piezoelectric properties have been

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developed for various applications [8–12]. In addition to ZnO, NGs have been demonstrated using other piezoelectric nanomaterials, such as GaN [13], InN [14], lead zirconium titanate (PZT) [15] and $ZnSnO_3$ [16].

Among group II–VI semiconductors, CdTe is of particular interest because it has a direct band gap (E_g=1.44 eV at 300 K) [17] and high optical absorption coefficient in the visible spectrum [18], making it prominent in the fields of photovoltaics, LEDs, and infrared detectors [19,20]. However, reports focusing on the piezoelectric properties of CdTe are limited. Corso et al. have demonstrated nonlinear piezoelectricity in CdTe by performing first principle calculation with density-functional theory [21]. From structure point of view, both wurtzite and zinc blende structures are non-centrosymmetric [22] and thereby possess piezoelectric property. Here, we report the first application of zinc blende structured CdTe for NG. This study expands the choices of materials for NG and piezotronics from the wurtzite family to the zinc blende family, which can significantly enrich the field.

Experimental section

CdTe micro/nanowires synthesis and structural analyses

We adopted facile hydrothermal method similar to the approach used by Gong et al. [23] to synthesize CdTe MWs/NWs. 0.23 g cadmium chloride ($CdCl_2$, 99.99%, Aldrich) powder and 0.16 g tellurium dioxide (TeO_2, ≥99%, Aldrich) powder were added to an empty beaker. Then we added 15 mL, 10 mM cetyltrimethyl ammonium bromide (CTAB, ≥99%, Sigma) to the beaker as a surfactant during the reaction. After 3 min, 5 mL hydrazine hydrate solution ($N_2H_4 \cdot H_2O$, 78–82%, Sigma-Aldrich) was added into the above mixed solution. Stirring for 15 min, the final solution was put in a Teflon-lined stainless steel autoclave. The container was sealed and heated up in an oven for 48 h at 150 °C. The autoclave was then removed to naturally cool down at room temperature. A dark, black precipitation was collected by filtration and washed with distilled water 5 times. Finally, the precipitate was dried on a hot plate for 2 h.

The phase information was obtained with an X-ray diffractometer (Paralytical XRD-600), operated at 40 kV and 40 mA using filtered Cu Kα radiation of 0.154 nm. A field-emission scanning electron microscope (SEM, LEO 1550), operating at 10 kV, was used to investigate the surface morphology. In order to prepare the transmission electron microscopy (TEM) specimen, all samples were sonicated in ethanol and then dispersed on copper grid supported by an ultrathin carbon film. A field-emission TEM (FEI Tecnai-G2-F30) equipped with energy dispersion spectrometer (EDS) was used to characterize the microstructure and determine the chemical composition.

Fabrication of NG and electrical measurement

Single CdTe MWs (≥500 μm) were deposited onto a flexible polystyrene (PS) substrate with 40 mm in length, 10 mm in

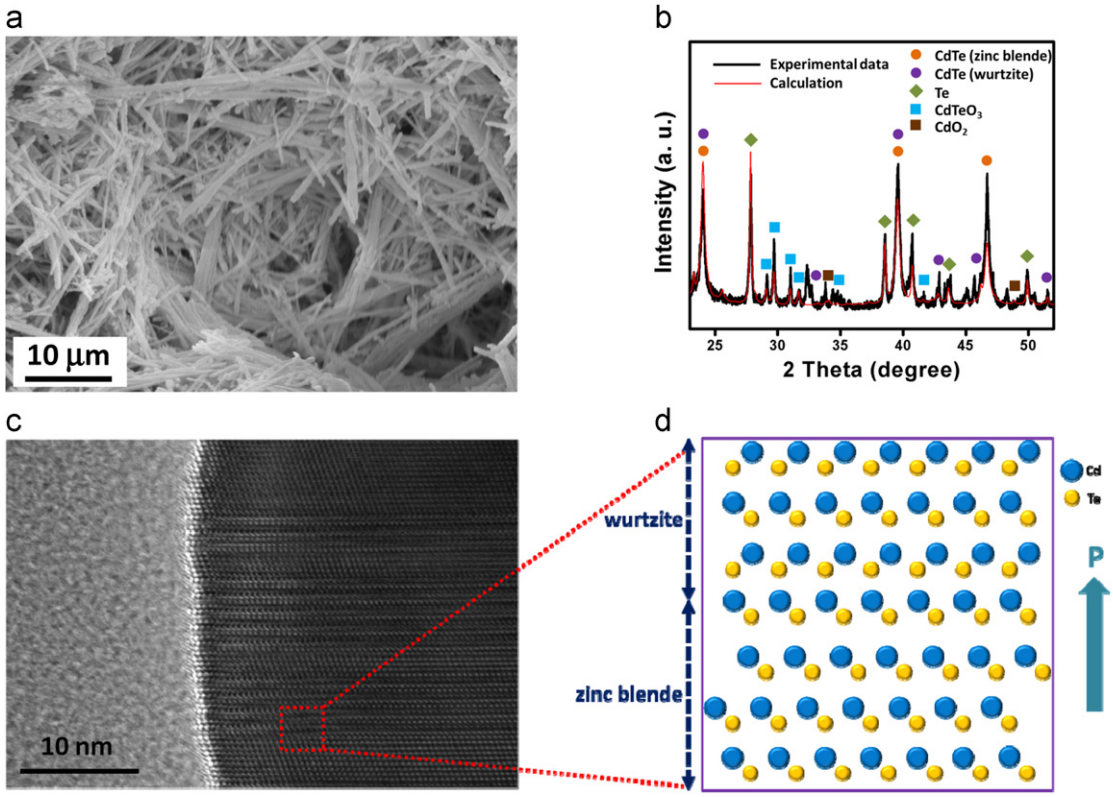

Figure 1 Structural analyses of CdTe NWs. (a) Top-view SEM image of the as-grown CdTe NWs, (b) XRD spectum of CdTe NWs, (c) and (d) HRTEM image of a single CdTe NW and the corresponding atomic model.

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width, and 1 mm in thickness. Then we applied silver paste at both ends of the CdTe MW to fix its two ends tightly; two metal wires were bonded to the each end of CdTe MW for electrical measurement. Afterwards, the whole NG was capped with a thin layer of polydimethylsiloxane (PDMS) to protect the device while under cyclical mechanical deformation and prevent moisture from penetrating into NG.

The NG was connected to the measurement system to detect the output signals. SR560 and SR570 low noise current amplifiers (Stanford Research Systems) were employed to acquire voltage/current, respectively. A mechanical linear motor (Labworks Inc.) was used to apply a bending force to the NG.

Results and discussion

We synthesized free-standing CdTe MW/NWs through a one-step hydrothermal method at 150 °C. Figure 1(a) shows a top-view scanning electron microscopy (SEM) image of synthesized long free-standing CdTe MWs, with lengths from 100 to 800 μm and widths ranging from 1 to 2 μm. The corresponding X-ray diffraction spectrum is shown in Figure 1(b). The major peaks are ascribed to wurtzite and zinc blende CdTe structures. In addition, peaks from minor contents of Te, $CdTeO_3$ phases are also identified, which may come from nanoparticles or residual precursors after the syntheses. Rietveld refinement technique was employed to quantify the proportion of each phase in the samples. The red line in Figure 1(b) represents the fitting curve based on the four primary phases, which are CdTe (zinc blende), CdTe (wurtzite), Te and $CdTeO_3$. The quantified results are shown in Table 1. We carried out the measurements and refinement fittings for 5 different batches of samples and found that CdTe (zinc blende) was the dominant phase. The numbers in parentheses are the quantities of CdTe (zinc blende) and CdTe (wurtzite) calculated when we did not consider other phases present in the material. It shows that among these two phases of CdTe, zinc blende structure (which is cubic) is still the predominant phase, which accounts for nearly 80% on average.

Table 1 XRD quantitative phase analysis results obtained by Rietveld refinement technique on different as-synthesized CdTe samples containing particles in addition to MW/NWs. The peaks from unidentified phases were not included in the refinement. The numbers in parentheses are the relative quantities of CdTe (zinc blende) and CdTe (wurtzite) calculated when other phases present in the material were not considered.

Sample	CdSe (Zinc blende)	CdSe (Wurtzite)	Te (%)	$CdTeO_3$ (%)
1	32.8% (67.2)	16% (32.8)	13.7	37.5
2	47.3% (84.3)	8.8% (15.7)	23.1	20.8
3	50.1% (78.5)	13.7% (21.5)	9.3	26.9
4	59% (92.5)	4.8% (7.5)	17.2	19
5	65.7% (77.6)	19% (22.4)	0	15.3

The coexistence of the two phases of CdTe MW/NW can be confirmed through high resolution transmission electron microscopy (HRTEM) as shown in Figure 1(c). Locally, the wire in Figure 1(c) consists of alternating zinc blend and wurtzite structures. Along the growth direction of the NW, alternating stacking order changes from ABC to AB, zinc blende (111) to wurtzite (0001), similarly to CdS NW [24]. Figure 1(d) depicts the corresponding atomic model of the two phases, which illustrates how the atoms stack as well as the direction of polarization in the NW. Since Cd atoms and Te atoms are positively and negatively charged, respectively, the polarization directions are identical in the zinc blende and wurtzite blocks in a single NW.

The schematic diagram (Figure 2(a)) demonstrates the working principle and measurement process of the NG. When the external force is applied on the top and bottom

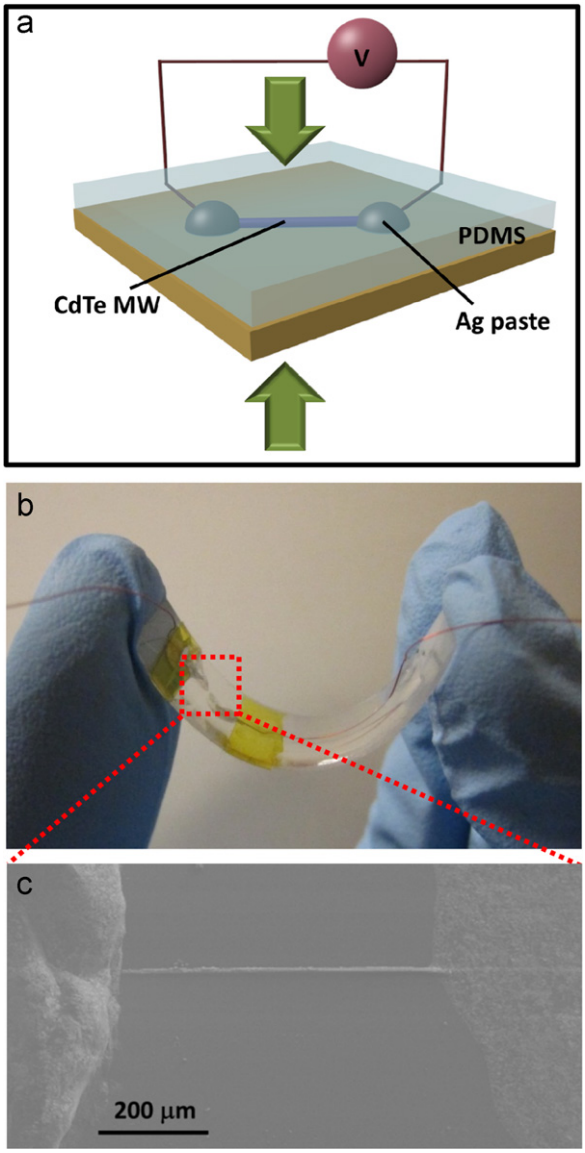

Figure 2 NG device. (a) Schematic diagram of the NG device, (b) Photograph of the NG device demonstrating its flexibility and (c) SEM image of the NG. The single CdTe NW is fixed with silver paste at the two ends. The distance between two electrodes is about 600 μm.

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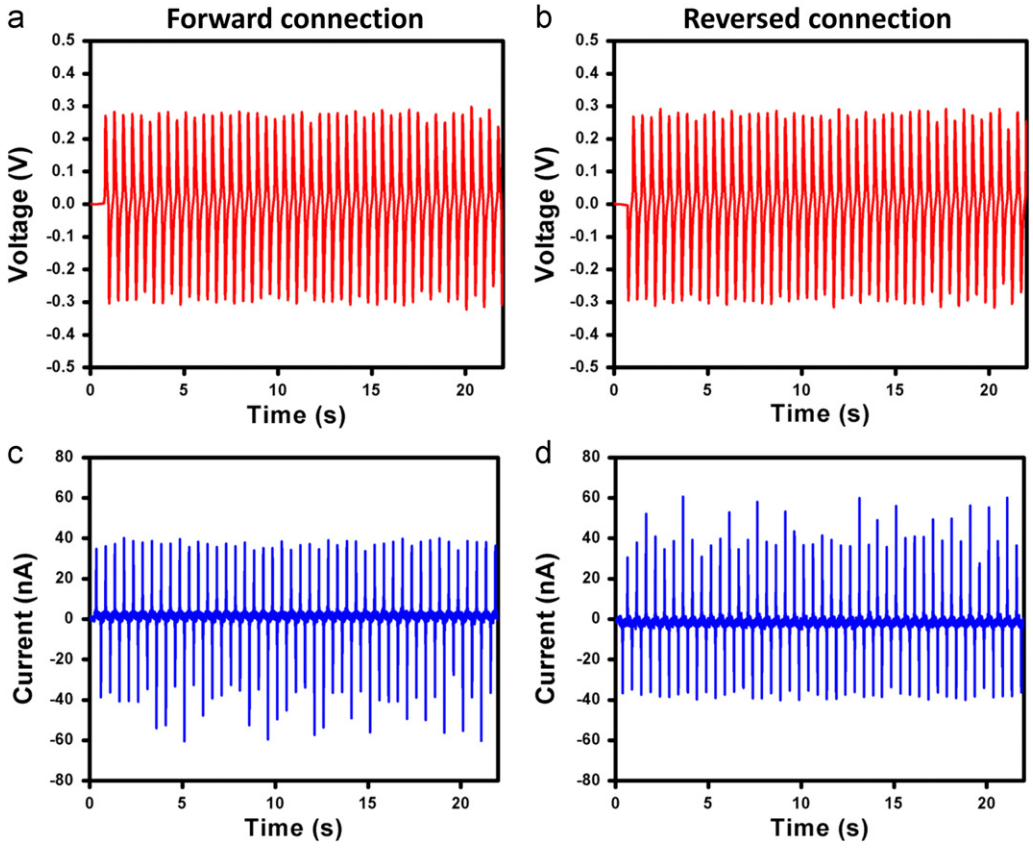

Figure 3 Electrical output performance of a NG when subjected to repeated cyclic force. (a) Open-circuit voltage under forward connection to the measurement system, (b) Open-circuit voltage under reverse connection, (c) Short-circuit current under forward connection to the measurement system and (d) Short-circuit current under reverse connection to the measurement system. All the data shown in this figure were obtained from the same NG.

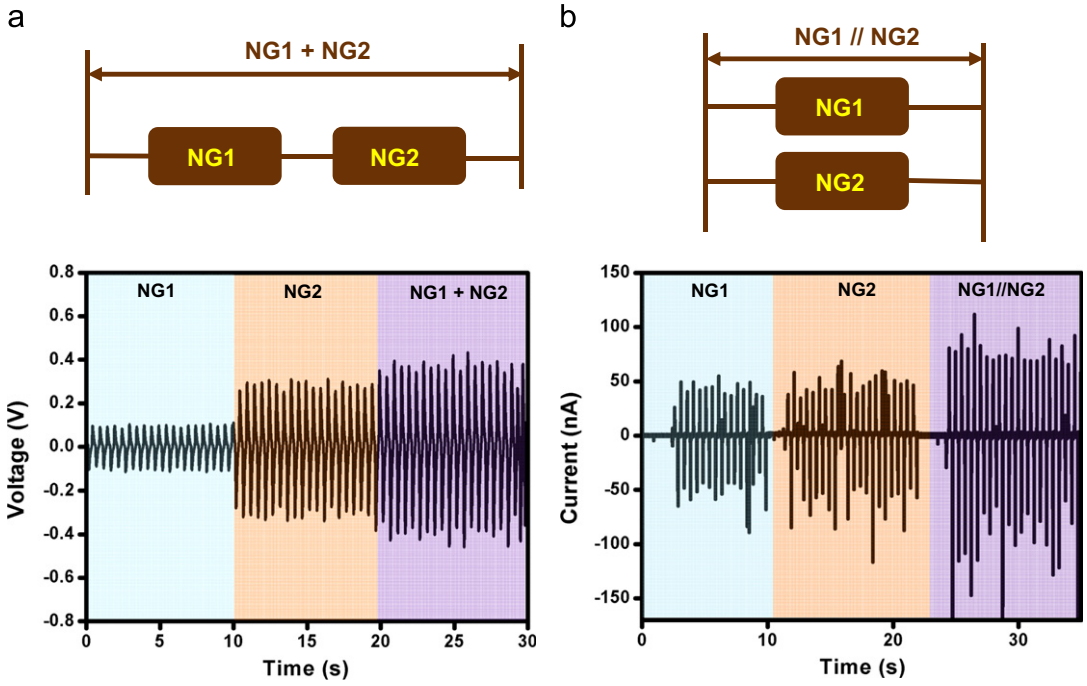

Figure 4 Linear superposition of two different NGs. Open-circuit voltage of NG1 and NG2 in (a) parallel and (b) series connection.

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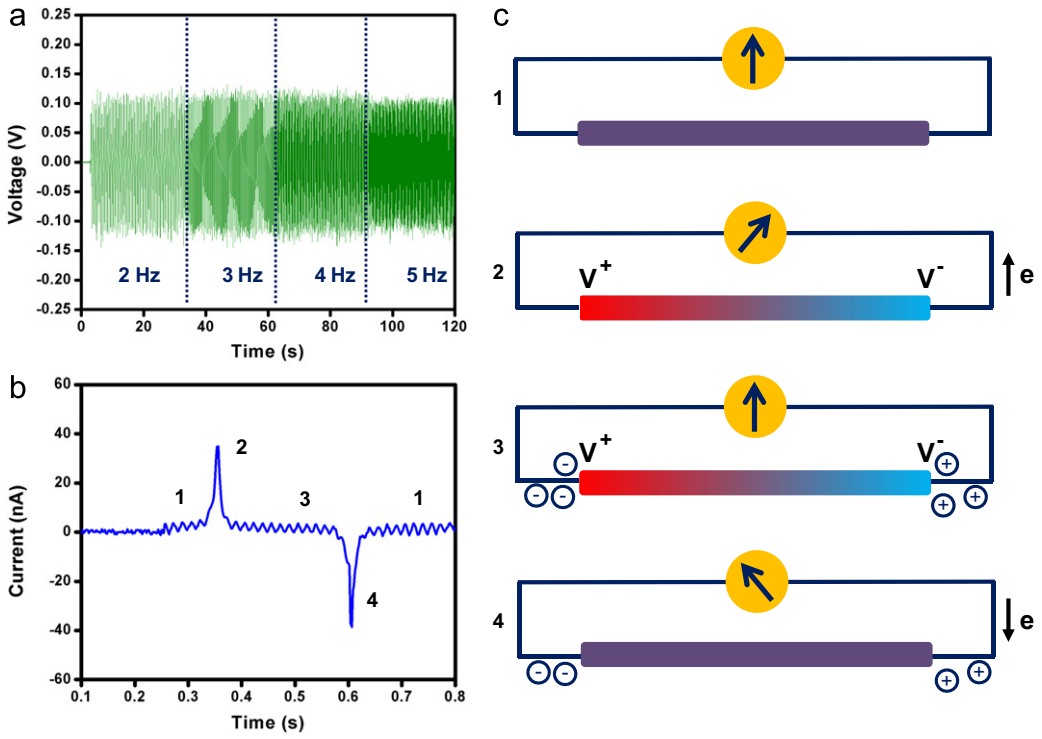

Figure 5 (a) Output voltage as a function of time with a driving frequency from 2 to 5 Hz, (b) experimentally measured output current from an NG and (c) Corresponding piezopotential diagrams at the four different stages marked in (b).

of the NG, the piezoelectric potential (piezopotential) is generated accordingly. Figure 2(b) displays the flexibility of the fabricated nanodevice. In order to make the wire manipulation process easier, we picked longer MWs ($\geq$500 μm) to fabricate NGs. A representative SEM image in Figure 2(c) depicts a smooth CdTe MW connected with silver paste at each end. The distance between the two electrodes is nearly 600 μm.

Electrical measurements reveal that the output open-circuit voltage of the NG is nearly 0.3 V (Figure 3(a)). In order to verify that the measured signal was generated by the CdTe MW rather than the measurement system, we switched the polarities of the electric configuration [11]. When the NG was reversely connected to the measurement unit, the output voltage remained roughly the same at 0.3 V, but the polarity was reversed (Figure 3(b)), indicating that the signal came from the NG. The short-circuit output current of the same NG is about 40 nA as shown in Figure 3(c), and it also follows the reversal test (Figure 3(d)). We successfully tested fifteen different CdTe NGs, and the output voltage and current ranged from 0.1 to 0.4 V and 20 to 70 nA, respectively. The variation depended on the size of the MWs as well as the distance between the two electrodes of the NGs. In terms of output voltage, this value is nearly ten times higher than that from a single ZnO fine wire [11] and four times higher than that from an individual $ZnSnO_3$ microbelt [16] NG. On the other hand, the output current is about one hundred times that of ZnO NG [11] and comparable with that of the $ZnSnO_3$ NG [16].

By integrating two different NGs in serial connection, the output voltage is approximately the sum of the output voltages of each NGs (Figure 4(a)). As shown in Figure 4(b), while connecting NG1 and NG2 in parallel, the output current can reach 100 nA. To test the stability of NG, we measured the NG with different working frequencies from 2 Hz to 5 Hz. Figure 5(a) shows the voltage as a function of time with a driving frequency from 2 to 5 Hz. The NG displays a steady output voltage when the frequency increases from 2 to 5 Hz. This result implies that the CdTe NG has robust and steady piezoelectric performance.

Both zinc blende and wurtzite have non-centrosymmetric structures, hence exhibiting piezoelectricity when subjected to a stress. We use the following diagram to explain the mechanism of the observed electricity output. Figure 5(b) and (c) show the experimentally measured output current from an NG and corresponding piezopotential distribution in the MW in four different stages marked in (b). In the first stage (Figures 5(c1)), without any stress, there is no piezopotential drop along the MW. Then, when the NG is subjected to a mechanical force, a spontaneous polarization is created in the crystal along the [111] direction. This process leads to the formation of dipoles, and charges are ionic induced at both ends, which cause a piezopotential [1] along the MW shown in Figure 5(c2). This piezopotential can last for an extended period of time without being depleted by free carriers as long as the strain is retained [11]. In this way, the induced electrons in the loading system will drift through the external load resistor and aggregate at the positively charged side (V^+), thus generate electricity accordingly. We can observe a positive peak current in Figure 5(b) in the second stage. In the third stage, when the electron flow accumulates at the positive potential side and balances the potential difference, there is no charge flow in the external measurement system. The reason that the electrons accumulate at the end is due to that the CdTe MW has little conductivity, possibly because that there is little doping inside the MW so that there is no free carrier. After

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the loading force in the NG is released, the piezopotential disappears immediately. Therefore, the accumulated electrons flow back to their original state through the external circuit so we see a reversed current (negative current peak) in Figure 5(b), which is the fourth stage in Figure 5(c).

Conclusions

In summary, we have successfully synthesized free-standing CdTe MW/NWs with a facile one-step hydrothermal method. The structural analysis show that the synthesized materials (which consist of wires and particles) are composed of multiple phases with much more CdTe (zinc blende) than CdTe (wurtzite). This coexistence of two phases was also confirmed using HRTEM. A laterally packaged NG can generate up to 0.3 V and 40 nA when strain is applied on the individual MW. Due to the high stability, the MW can be used in piezoelectric applications under various circumstances. Through these combined properties, we believe zinc blende-based CdTe material can open up a great opportunity in the future practical application in energy harvesting.

Acknowledgments

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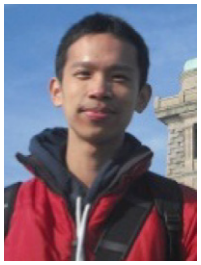

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