Published in final edited form as:

Appl Phys A Mater Sci Process. 2013 August ; 112(2): 305–310. doi:10.1007/s00339-013-7737-9.

Negative differential resistance in ZnO coated peptide nanotube

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Abstract

We investigate the room temperature electronic transport properties of a zinc oxide (ZnO) coated peptide nanotube contacted with Au electrodes. Current–voltage (I – V) characteristics show asymmetric negative differential resistance (NDR) behavior along with current rectification. The NDR phenomenon is observed in both negative and positive voltage sweep scans, and found to be dependent on the scan rate and humidity. Our results suggest that the NDR is due to protonic conduction arising from water molecule redox reaction on the surface of ZnO coated peptide nanotubes rather than the conventional resonant tunneling mechanism.

1 Introduction

There is a growing interest in the realization of negative differential resistance (NDR), a nonlinear transport phenomenon where current suddenly decreases with increasing bias voltage, in different material systems. The NDR constitutes an active component for building logic circuits, oscillator, diodes, memory, switches, and sensors [1–7]. Recently, bio-template methods of material synthesis have been exploited for the creation of multifunctional materials for electronic and optoelectronic applications. Different biological scaffolds such as virus, DNA, protein, and peptide have been used as templates due to their high degree of organization, ease of chemical modification, and self-assembly properties [8–

15]. In addition, their capabilities to self-organize and control assembly in different geometries make them an attractive candidate for fabricating various nanomaterial-based functional devices in one-, two-, or three-dimensions [8–11]. Some of the reports indicate that the function of the templates is not only to provide a backbone for organization of discrete nanomaterials, but also to create novel electronic effects while being integrated with nanomaterials [15]. Applications of these bio-templated nanostructures have been reported in photocatalysis, photovoltaics, battery, and memory devices [12–19]. For example, virus templated zinc porphyrins and iridium oxide hydrosol clusters have been used for visible light driven water oxidation [12]. Using M13 virus as a template, carbon nanotube–titanium oxide core shell nanostructures were fabricated for photo-anodes in dye sensitized solar cells [13]. Virus templated platinum nanoparticles showed bi-stable memory switch with on–off ratio greater than 10^3 [15]. DNA templated poly(3,4-ethylenedioxythiophene) (PEDOT) exhibited capacitance behavior with good charge/discharge reversibility [16]. DNA biopolymer templated silver nanoparticles have been used to fabricate a photoinduced write-once read-many-times (WORM) memory device [17]. Chaperonin protein has been used as a template to assemble cobalt nanocrystal array for flash memory fabrication [18]. In addition, peptide nanotube template has been used for synthesis of mono-dispersed Au nanoparticle where carrier hops from one nanoparticle to another [19]. However, the NDR, which is a building block for many electronic circuits, has not yet been demonstrated in any bio-templated systems.

In this paper, we report room temperature NDR behaviors on zinc oxide (ZnO) coated peptide nanotube contacted with Au electrodes by measuring current–voltage (I – V) characteristics. The NDR behaviors were found to be highly sensitive to successive voltage sweeps, voltage sweep rates, and humidity. With repeated voltage sweeps performed in very short time intervals, the NDR disappeared and current intensity decreased. However, it can be recovered when the time interval between successive sweeps is long enough (5 minute). The NDR behavior was observed at 45 % relative humidity (ambient condition) but it was not observed inside a nitrogen filled glove box with 11 % humidity or in vacuum. Control experiment on peptide nanotube without ZnO did not show any measureable conduction. Our results suggest that the origin of the NDR is protonic conduction arising from water molecule redox reaction on the surface of the ZnO coated peptide nanotubes rather than the conventional resonant tunneling mechanism.

2 Experimental

First, bis(*N*– α -amido-glycylglycine)-1,7-heptane dicarboxylate monomers were self-assembled into template nanotubes whose surface was programmed to bind synthetic peptides. Details for the monomer synthesis, the chemical structure, and the method for the cylindrical self-assembly of the nanotube were described in our previous report [20]. Next, the template nanotubes were treated with *N*-hydroxysuccinimide (NHS)/1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDAC) reaction in 2-(*N*-morpholino)-ethanesulfonic acid (MES) buffer (0.1 M, pH 5.5). Then, the nanotube was rinsed with de-ionized (DI) water to eliminate extra NHS, EDAC, and the remaining MES buffer. To immobilize sequenced peptide onto the template nanotube, we synthesized the ZnO-1 peptide (amino acid sequence of EAHVMHKVAPRP) by adding a five amino acid tail (GGGSC) to the C-

terminal. The resulting GGGSC-conjugated ZnO-1 peptide (whose amino acid sequence is EAHVMHKVAPRPGGGSC) was used for sequence peptide because it showed a high affinity to ZnO and was capable of mediating the mineralization of ZnO from Zinc hydroxide ($\text{Zn}(\text{OH})_2$) at room temperature [21]. The GGGSC-conjugated ZnO-1 peptide (2 mM) was incubated with NHS ester group decorated nanotubes in 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) buffer (0.1 M, pH 8). Zinc acetate ($\text{Zn}(\text{Ac})_2$) (0.5 mM) was added to the mixture after eliminating the extra peptide by rinsing with DI water, then incubated for 6 days. Next, NaOH (1.5 mM) was added and incubated for a day. Finally, unreacted NaOH was rinsed after incubation. After the growth, the media was washed and centrifuged for the removal of any residual materials grown in solution.

The resulting nanotube was then characterized using transmission electron microscopy (TEM), energy disperse spectroscopy (EDS), and photoluminescence (PL). Figure 1(a) shows a TEM image of three ZnO coated peptide nanotubes by using JEOL JEM-2100 with field emission gun operating at 100 kV. The images were visualized by the instrumental software. A mean diameter and length of ~ 500 nm and ~ 2 μm , respectively, of the ZnO coated peptide nanotubes are observed. The average diameter of the peptide nanotube without ZnO is about 400 nm [20]. Thus, we estimate that the typical thickness of the ZnO layer is around 50 nm. Figure 1(b) is a high resolution TEM (HRTEM) image of one of the ZnO coated nanotubes. This HRTEM image of ZnO coated peptide nanotube shows the internal cavity that is collapsed and creates multiple cavity domains around the center. In addition, there is no defined electron diffraction patterns on the surface of the coated nanotube, and no obvious crystalline lattice fringes on the surface was seen (Fig. 1(c)), indicating that the ZnO grown on the peptide nanotube is likely amorphous. This is confirmed by taking HRTEM images at several places. It should be noted that Zn and O elements are detected on the nanotube by EDS analysis (Fig. 1(d)). In order to further confirm the presence of ZnO on the peptide nanotube, we performed PL spectra of ZnO coated peptide nanotube using a Horiba Fluoromax 3 fluorescence spectrophotometer with an excitation wavelength of 325 nm. This is shown in Fig. 1(e) where we observed a strong characteristic near band edge emission of ZnO around 370 nm, and a weak emission near 500 nm. The peak intensity ratio of green (visible emission) to blue (UV emission) is only around 0.06. In general, in the PL spectra of ZnO, the oxygen vacancies affect visible emission [22]. The presence of water molecules in amorphous ZnO restrains the formation of oxygen vacancies and hence leads to decrease in intensity of visible emission. Such small ratio in our study is consistent with the PL properties of those reported in amorphous ZnO [23, 24].

The ZnO coated peptide nanotube devices were then fabricated on doped silicon (Si) substrates capped with a thermally grown 250 nm thick SiO_2 layer. Figure 1(f) shows a schematic diagram of the device and experimental measurement set up. Source and drain electrode patterns with interdigitated arrays of 1 μm were defined by electron beam lithography (EBL) and electron beam deposition of 3 nm Cr and 27 nm Au followed by lift off. A 1 μL of ZnO coated peptide nanotube solution was dropped on the electrodes and allowed to dry at room temperature. Figure 1(g) shows a scanning electron microscopy (SEM) image of a fabricated device with a ZnO coated peptide nanotube of diameter ~ 0.5 and length ~ 2 μm placed between Au source and drain electrodes. The image was taken by a

Zeiss Ultra-55 SEM operating at 2 kV. Room temperature current–voltage (I – V) measurements were performed using a Keithley 2400 source-meter and a current pre-amplifier (DL 1211) capable of measuring sub-picoampere signal interfaced with LABVIEW program. A total of nine devices were investigated.

3 Results and discussion

Figure 2(a) (solid lines) shows the room temperature current–voltage (I – V) characteristics of a representative ZnO coated peptide nanotube measured in an ambient condition. The relative humidity was ~45 %, measured with a humidity sensor. The voltage was swept from – 10 to + 10 V (forward sweep) and then back to – V (reverse sweep) with a voltage scan rate of ~500 mV/s. The resulting current was recorded. It can be seen from this figure that the I – V characteristics strongly depends on the voltage sweep direction. In the forward sweep, current linearly increased up to 0 V and then super-linearly increased to a peak value ~26 nA. The voltage corresponding to this peak (V_{peak}) is at 5.2 V for forward sweep. As the voltage increased further, current started to decrease sharply. This decrease of current with increasing voltage is a signature of NDR. The linear behavior at negative bias with small current and super linear behavior at positive bias is a reminiscent of diode type current rectification. In the reverse sweep (+10 to –10 V), the current did not follow the same path as that of forward sweep; an opposite behavior was observed with NDR occurring at $V_{\text{peak}} \sim -7$ V with a peak current of 30 nA. We also note that the current does not vanish at zero bias. A positive current (0.5 nA) at zero bias for forward sweep and a negative current (–0.6 nA) for reverse sweep were observed.

A recent report shows that the NDR can depend on the starting voltage when a scan is done [25]. In order to see whether NDR phenomenon in our device depends on the starting voltage, we started the sweep from zero bias instead of –10 or +10 V. This scan is presented in Fig. 2(b), where we show I – V curve for different sweep scan directions: (i) 0 to –10 V, (ii) –10 to 0 V, (iii) 0 to + 10 V, and (iv) +10 to 0 V. Again, asymmetric NDR behavior is clearly observed in both negative and positive scans. Most of our devices showed similar NDR behaviors although there were slight variations in the NDR peak positions and current intensities from device to device.

A peptide molecule or nanotube is commonly known as a non-conducting material, however, if a peptide chemically or biochemically reacts with foreign atoms or molecules, it can have electronic conduction paths [26–28]. Therefore, in order to confirm the role of peptide on conduction, we also measured a “peptide only” nanotube. Neither NDR nor any detectable current (down to pA) was measured (Fig. 2(a), dashed curve and inset). From this, we conclude that the peptide alone is not responsible for the observed behavior.

Since NDR was first discovered in Esaki tunnel diode [1], which is based on semiconductor p–n junction, many different materials systems such as p–n junction, quantum wells, nanowires and molecular junctions exhibited NDR behavior. Understanding the NDR behavior in nano- and molecular devices can be of a significant challenge as there are several mechanisms that can be associated with the origin of NDR. Among these are: (i) resonant tunneling [29–32], (ii) bistable interfacial contact [3, 33, 34], (iii) redox mediated

electron tunneling [4, 5], and (iv) proton exchange mechanism [35]. Resonant tunneling mechanism has been reported in several molecular junction based devices [29–32]. In this mechanism, when the Fermi level of the one of the electrode comes to the resonance of a molecular orbital of the device, the current peak appears. Upon further increases in bias voltage, the energy levels go off-resonance, resulting in a NDR behavior. In this mechanism, the current for both forward and reverse sweep is expected to follow the same path and the current peak is not expected to depend on the relaxation time between successive sweeps nor on the voltage scan rate [32, 33]. In our device, the NDR is highly dependent on voltage sweep direction implying that resonant tunneling is not responsible for NDR. Voltage sweep dependent asymmetric NDR and hysteresis can occur in bi-stable interfacial switching, redox reaction, and proton mediated mechanisms [3–5, 7, 33–35]. In a broad sense, all these mechanisms can be labeled as chemical reaction induced NDR. In all of these mechanisms, a chemical reaction is involved to create bistable conducting states. The difference among them is the nature (or origin) of this chemical reaction. For example, in bi-stable interfacial contact, NDR originates from the transition from strong to weak chemical bonding of the active material with contact [3, 33, 34]. In redox mediated mechanism, NDR occurs due to oxidation and reduction of a redox active molecule at a particular voltage [4, 5]. In proton exchange mechanism, a water layer is formed on the surface of the material [35]. Water is dissociated to oxygen and proton through electrolysis. The fast drift of protons to electrode and slow diffusion of water at the dissociation site create NDR.

In order to better understand the mechanism of NDR in our device, we examined whether the NDR depends upon the relaxation time of successive sweeps. This is done by performing continuous voltage scan on the device without any relaxation time. Figure 3(a) shows five consecutive I – V sweeps of the device from 0 to +10 V. The NDR peak current decreased in successive voltage sweeps. The NDR peak currents were ~26, 6, and 4 nA during the first, second, and third sweeps, respectively. After the fourth sweep, the NDR disappeared and current was stabilized. However, after a 5 minutes relaxation time the NDR fully recovered. This is shown in Fig. 3(b) where we present I – V curves with relaxation time of 1, 2, 3, 4, and 5 minutes. No NDR can be seen for relaxation of 1, 2, 3, and 4 minutes. We have also investigated the NDR by varying the scan rate. This is shown in Fig. 3(c), where we study NDR peak position with different sweep rates from 250 to 750 mV/s with 250 mV/s intervals. During these measurements, we allowed a 5 minute relaxation time between successive scans. The sweep rates have effects on the peak current positions and current intensities. As shown in the figure, the corresponding currents for V_{peak} in NDR were ~30, 63, and 86 nA when sweep rates were 250, 500, and 750 mV/s, respectively. When the sweeping speed increased, the peak current also increased. Our results suggest that the NDR is occurring due to a voltage driven modification of conducting pathways. An increase or decrease in current depends upon the construction and destruction of this pathway. Thus, the I – V curves are sweep history and direction dependent. With successive sweeps without any relaxation time, the pathway becomes less efficient resulting in a decrease in current without any NDR. Apparently, the 5 minute relaxation time is needed for the reconstruction of the maximum conducting pathway.

In order to further investigate what causes such a modification of conducting pathways, we measured the I - V curves in a nitrogen filled glove box with a relative humidity (RH) of 11 % as well as in a vacuum loaded cryostat (100 mtorr with RH of ~0 %). When the devices were measured at RH of 11 %, a significant decrease (over 20 times) in current was observed and the NDR effects were not observed, as shown in Fig. 4(a). The I - V hysteresis and nonzero condition at zero bias voltage were observed similar to measurement in ambient condition. A positive current (0.2 nA) at zero bias for forward sweep and a negative current (-0.25 nA) for reverse sweep were observed. However, unlike the device measured in ambient condition, I - V curves are symmetric and very reproducible. Nonetheless, when the devices were measured under vacuum condition (RH of 0 %), no measureable current (pA) was detected as shown in Fig. 4(b) (black line). Interestingly, after exposure to ambient condition with RH of ~45 % for 10 minutes, the NDR behavior reappeared. In a forward sweep, V_{peak} was 3.5 V with current intensity of 8 nA, whereas in a reverse sweep, V_{peak} was 3.8 V with current intensity of ~ 11 nA. Nonzero currents were also observed.

All of the results suggest that the NDR mechanism in our device is due to a proton conduction mechanism (Grotthuss mechanism) [35–37]. It is well known that ZnO can easily absorb water. The higher conductivity with increasing humidity signifies the role of water in conduction mechanism. At ambient condition, a water layer is formed at the surface of ZnO. With the application of a voltage, water gets dissociated into oxygen and proton at the positively charged anode. The proton then drifts to cathode through the water layer and is reduced to hydrogen gas. This drift process is fast. However, for continuous electrolysis, enough water needs to be available at the anode. Since water diffusion is slow, at some point (or at a finite voltage) water will be depleted from the anode, causing a slow production of proton and reduction of conductivity. This will result in NDR. After a NDR process, a relaxation time is needed so that enough water is available for the fast generation of protons. In our case, this relaxation time was 5 minutes. Therefore, in subsequent sweeps involving shorter than a 5 minute relaxation time, the NDR ceased to exist. For the same reason, no NDR was observed at low humidity. Since the peptide only device, which served as a control device, did not show any conduction, we concluded that the ZnO is a prerequisite to allow water molecules to absorb on its surface, generating the NDR.

4 Conclusions

We have demonstrated room temperature NDR in ZnO coated peptide nanotubes contacted with Au electrodes. The NDR behavior was observed only in ambient condition and disappeared when measured inside a glove box or in vacuum. The NDR disappeared in successive voltage sweeps without any relaxation time; however, it could be recovered again after a 5 minute relaxation time. We explained that the NDR mechanism as a result of fast protonic conduction through water layers absorbed at the surface of ZnO coated peptide tubes and slow diffusion of water rather than the conventional resonant tunneling mechanism.

Acknowledgments

This work for the part of electronic fabrication and electric measurement were supported by the US National Science Foundation under grant ECCS 0823902 (HM) and 0823973 (SIK). The material synthesis and the structural

analysis were supported by the US Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DEFG-02-01ER45935 (HM). The Hunter College infrastructure is supported by the National Institutes of Health, the RCMI program (G12-RR003037-245476).

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Fig. 1.

A TEM image of ZnO coated peptide nanotubes. A mean diameter and length of the tubes are ~500 nm and ~2 μm, respectively (Scale bar 1 μm). (b) A HRTEM image of a ZnO coated peptide nanotube (Scale bar =500nm). (c) A HRTEM image of the ZnO coated peptide nanotubes surface (Scale bar = 5 nm). (d) EDS analysis of the ZnO coated peptide nanotubes (e) PL spectra of ZnO coated peptide nanotubes at room temperature (λ_{ex} : 325 nm). (f) Schematic diagram of the device structure and measurement set up. (g) A SEM image of a typical device with 1 μm electrode separation (Scale bar = 400 nm)

Fig. 2.

(a) *I-V* characteristics of a typical ZnO coated peptide tube with full cycle sweep ($-10\text{ V} \rightarrow +10\text{ V} \rightarrow -10\text{ V}$) at ambient condition with a relative humidity of $\sim 45\%$ (*solid lines*). The *dashed line* and *inset* show *I-V* characteristics of a peptide only nanotube. (b) *I-V* characteristics for different sweep scan direction: (i) 0 to -10 V , (ii) $+10$ to 0 V , (iii) 0 to $+10\text{ V}$, and (iv) $+10$ to 0 V scan ranges. Sweep rate = 500 mV/s

Fig. 3.

(a) I - V characteristics of a ZnO coated peptide nanotube showing five consecutive sweeps without any relaxation time. (b) I - V characteristics of a time-course study with relaxation time of 1, 2, 3, 4, and 5 minutes. (c) I - V characteristics with different sweep rates from 250 to 750 mV/s

Fig. 4.

(a) I - V characteristics with full cycle sweep ($-10\text{ V} \rightarrow +10\text{ V} \rightarrow -10\text{ V}$) measured inside a glovebox with a relative humidity of $\sim 11\%$. No NDR have been observed. (b) I - V characteristics in vacuum (*black line*) showing no detectable current. *Blue* and *red curves* indicate full cycle sweep ($-10\text{ V} \rightarrow +10\text{ V} \rightarrow -10\text{ V}$) after exposure to ambient condition with a humidity of $\sim 45\%$ for 10 minutes