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Self-Powered Pendulum and Micro-force Active Sensors Based on ZnS Nanogenerator

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Abstract

We demonstrated a nanogenarator as a pendulum and micro-force active sensors which is first made from zinc sulfur (ZnS) nanowires. The ZnS nanowires were synthesized on Si substrate by carbonthermal evaporation process at 1050^{o} C. The length and diameter of the ZnS nanowires are around 20-50 μm and 50-100 nm, respectively. The x-ray diffraction (XRD) pattern shows that the ZnS belongs to a wurtzite structure. The TEM image shows that the nanowires were grown along [0001] axis, which is in spontaneous polarization direction. The ZnS nanowires can be packed into a nanogenerator either in-serial or in-parallel manner. Furthermore, on the basis of our theoretical calculation, as applied a compressive stress (1×10^{6} N/m^{2}) along the c-axis of ZnS nanowire, the corresponding output piezopotential can be reached ~2V. Because the output voltage and current of the ZnS nanogenerator is proportional to the momentum, it can detect various momentums from 0.077N s to 0.177N s. The latter can also be self-powered to trace a simple harmonic motion of a pendulum that is released from different heights or angle. The same device can therefore be used for pendulum and micro-force active sensors without applying an external power source.

KEYWORDS: Nanowires, Pendulum, Active Sensors, ZnS, Nanogenerator

1. Introduction

Since Wang's et.al., the first demonstrated nanowire-based piezoelectric generator in 2006[1], the nanostructure-based energy harvesting has headed towards an important milestone, making nanotechnology become a promising new way to harvest piezo-energy. This technological breakthrough has resulted in piezoelectric devices such as ZnO[1], GaN[2], polyvinylideneuoride (PVDF),[3, 4] $ZnSnO_3$,[5] $BaTiO_3$,[6] and lead zirconate titanate (PZT)[7] receiving enormous attention. The nanogenerator based sensors made from piezoelectric materials, which can convert the mechanical energy in our living environment into the electric output signals, which have successfully analyzed the mechanical motions to develop a heart-pulse[8], tire pressure[9], and bridge vibration sensors. This is also called self-powered nanotechnology that enables to make the sensor self-drive without batteries or external power sources, namely, an active sensor.[10] Therefore, the nanogenerator based on piezoelectric nanomaterials not only shows considerable potential for an energy harvesting application, but also can act in the capacity of a highly sensitive active sensor such as in health management and environmental monitoring applications. When considering these issues, it is extremely important to develop an infrastructure monitoring system and health care devices that prevent natural disasters or endanger human life. Therefore, a highly sensitive active force sensor is important for human security.

However, in a larger scale of sensors network system, due to the difficulty of tracking and recycling the batteries in the system, it is important to reduce the usage of batteries to minimize environmental impacts if such sensor have to be powered entirely by batteries.[11] To develop the energy harvesting device or active sensors, the wurtzite structures such as ZnO[1], GaN[12], CdS[13], and CdSe[14] have received intense attraction because such materials possess a unique noncentrosymmetric structures naturally created in a c-axis to form spontaneous polarization properties. Among the wurtzite structures, the noncentrosymmetric ZnS has a remarkable semiconducting property and can be used in many different applications, for instance UV nanolasers[15], optical devices[16], and sensors[17]. ZnS has superior piezoelectric properties,[18] but it is not as widely researched as ZnO, GaN, and PZT in piezotronic devices.[19]

This work, our theoretical calculation suggests that ZnS has a significant output piezopotential of ~2V while apply a compressive strain on the c-axis of the ZnS nanowire. Based on our calculation and experimental results, the ZnS exhibited significantly piezoelectric properties that enable to impose these results on the energy harvesting of nanogenerator. Motivated by these considerations, we have systematically investigated ZnS nanowire based nanogenerator as an active force sensor.

The wurtzite structure of ZnS nanowires were synthesized on Si substrate and packed as an active force sensor. The ZnS nanogenerator can generate an output current of ~ 60 nA and a voltage of 0.5 V. Because the output voltage and current of the ZnS nanogenerator is proportional to the momentum, it can detect various momentums from 0.077N s to 0.177N s. On the basis of our experimental results, the output voltage and current can linearly be superposed by a number of nanogenerators (ie., either in-serial or in-parallel manner). The ZnS nanogenerator can be regarded as a self-powered force sensor that enable to trace and detect a harmonic motion of pendulum[20] and various momentum in the range of 0.077 N s. to 0.117 N s., respectively. This is a first-time demonstration of a highly sensitive pendulum and force active sensor using a self-powered ZnS nanowire based nanogenerator.

2. Experimental detail

The synthesized process of the ZnS nanowires was prepared from source materials such as ZnS and carbon powder with a mole percentage ratio of 1:1. The combination of materials, heated to 1050^{o} C under an argon gas flow with a rate of 200 sccm (Ar purity 99.9 %) for three hours, created a carbonthermal reaction.[21,22] The working pressure of the system was maintained at 5×10^{-2} Torr. The thin-film X-ray diffractometer (Bruker, D8 SSS), a high-resolution transmission electron microscope (HRTEM, JEOL JEM-3000F, operated at 300 kV), and a field emission scanning electron microscope (FESEM, HITACHI S4800, operated at 3 kV) were used to investigate the material's compound, crystal structure, and morphologies. The output voltage and current of the nanogenerator were measured by using a low-noise voltage and current preamplifier (Stanford Research System Model SR560 and SR 570).

The fabrication process of the ZnS nanogenerator was as follows: First, the ZnS nanowires were grown on a Si substrate (001) with a resistance that ranged from 0.1 to 0.5 Ohm-cm). The Si substrate was used for a substrate and top electrode. The polydimethylsiloxane (PDMS) solution was created by a process of spinning a coating on the ZnS nanowires to protect the device from damage.[23] The other Si was attached to the top of the device as a top electrode. The nanogenerators can be in-serial and in-parallel packed into a tandem nanogenerator to investigate the linear superposition principle of output voltage and current.

3. Results and Discussion

Figure 1(a) shows the FESEM images of as-synthesized ZnS nanowires that were grown on the Si substrate. The length of the nanowires can be up to a few thousands micro meters (μm) and 100-200 nm in diameters. The inset of Figure 1(a) shows the nanowire's oblique direction, namely, on the Si (001) substrates, out-of-plane vapor-liquid-solid growth favors nanowires propagating in range of 45^{o} to 135^{o} from substrate's surface. This fact demonstrates that our nanowires could deform vertically from 45^{o} to 135^{o}. The XRD pattern of Figure 1b shows that synthesized nanowires belong to a single phase of wurtzite-type ZnS (JCPDS Card No. 36-1450) with lattice parameters of a = 3.82098 nm and c = 6.2573 nm. The synthesis temperature of ZnS nanowires was controlled at 1050^{o}C. Accordingly, the ZnS nanowires underwent a crystal structural phase transformation from the cubic zincblend to a hexagonal wurtzite structure. The HRTEM in Figure 1(c) reveals the lattice fringe ~0.619 nm of ZnS growing along the c-axis. Figure 1(d) shows the corresponding Fast Fourier Transformation (FFT) image and demonstrates a wurtzite structure with a growth direction of [0001], which is evidence of the spontaneous polarization of ZnS that is governed by the c-axis.

Figure 2(a) (left-hand-side) shows a schematic diagram of a ZnS wurtzite structure with the space group of P63mc. The grey spheres represent the S ions and the red spheres are the Zn ions. The unit cell of ZnS is stacked alternately along the c-axis; its structure consisted of tetrahedrally coordinated S^{2-} and Zn^{2+} ions.[24] Figure 2(a) (right-hand-side) shows a hexagonal close packed array of anions, with half the tetrahedral interstices filled by cations. Each anion and cation was surrounded by four cations and anions, respectively, and has formed tetrahedral coordinated geometry.

In this work, the growth orientations of the nanowires were randomly oblique and out-of-plane to the substrate. The Comsol software package was used to calculate the piezopotential distribution of ZnS nanowires.[25, 26] The theoretical calculation is based on an insulating assumption of the material. Figure 2(b) and 2(c) shows that the forces were applied to the different orientation. The maximum piezopotential is positioned on the c-axis, which is corresponding to ~2.1V (see Figure 2(b)). The calculated deformation and applying pressure of the ZnS nanowires are 1.14×10^{-9} m and

1×10^6 N/m^2, respectively. The output piezopotential depends on the size of ZnS nanowires and the strain's orientation. Moreover, when the nanowires were randomly lying in parallel to the substrate plane, its piezopotential was reduced to ~0.083V (see Figure 2(c)). The theoretical calculation of piezopotential distribution in ZnS nanowires has demonstrated that the c-axis of the nanowires indeed dominate the maximum output of the device. This is the source of piezoelectricity in ZnS nanowires. The theoretical calculation implies that the growth of ZnS nanowires is vertically out-of-plane, which is a key factor for governing the actual output of the piezopotential. Accordingly, we propose that the ZnS nanowires should be grown as perpendicularly and out-of-plane to the substrate, as shown in the schematic diagram in Figures 2(d) and 2(e), and this will produce a significant output signal. Figure 2 (e) shows that the ZnS nanowires were grown on planar Si substrate and affixed another one (Si substrate) to from a sandwich structure. The PDMS was then covered on the entire device to keep the nanogenerator in robust under the various mechanical collisions. Indeed, Figure 2(f) and its inset show that the ZnS nanowires growing obliquely on a substrate after coated by a PDMS layer.

The nanogenerator was applied with a constant collision of ~ 0.117 N.S. The definition of momentum is given by supporting information of S1. Figures 3(a) and 3(b) show that the output voltage and current of a ZnS nanogenerator can reach 0.8V and 40nA, respectively. The nanogenerator was reversely connected to the measurement system, the corresponding output voltage and current was 0.8V and 40nA, respectively, as given in Figures 3(c) and 3(d). This fact demonstrated that the nanogenerator made from ZnS nanowires indeed produce a significant and reliable voltage and current, which urged us to comprehensively investigate the output-power performance of the nanogenerators and its application on self-powered active sensor.

This work, we have developed the superposition principle by considering two to three independent nanogenerators in-serial and in-parallel connection to evaluate the linear superposition tests by using a constant collision of ~ 0.117 N.S. First, the output voltage of each nanogenerator are defined as V^{+}_{NG1}, V^{+}_{NG2}, and V^{+}_{NG3}. Next, the measured voltage of two and three nanogenetaror in-serial connections is defined as $V^{+}_{NG1+NG2}$ and $V^{+}_{NG1+NG2+NG3}$, which are shown in the upper and lower schematic diagrams of Figure 4(a), respectively. The linear superposition can be demonstrated by the following equations:

$$V^{+}_{NG1+NG2}=(V_{p-}-V_{p+})_{NG1}+(V_{p-}-V_{p+})_{NG2}=V^{+}_{NG1}+V^{+}_{NG2} \quad (1)$$

$$V^{+}_{NG1+NG2+NG3}=(V_{p-}-V_{p+})_{NG1}+(V_{p-}-V_{p+})_{NG2}+(V_{p-}-V_{p+})_{NG3}=V^{+}_{NG1}+V^{+}_{NG2}+V^{+}_{NG3} \quad (2)$$

$$V^{+}_{NG1-NG2}=(V_{p-}-V_{p+})_{NG1}+(V_{p+}-V_{p-})_{NG2}=V^{+}_{NG1}-V^{+}_{NG2} \quad (3)$$

$$V^{+}_{NG1+NG2-NG3}=(V_{p-}-V_{p+})_{NG1}+(V_{p-}-V_{p+})_{NG2}+(V_{p+}-V_{p-})_{NG3}=V^{+}_{NG1}+V^{+}_{NG2}-V^{+}_{NG3} \quad (4)$$

Where $V_{p-}-V_{p+}$ is a voltage drop between two ends of a nanogenerator. Figure 4(b) shows that NG1, NG2, and NG 3 is 0.7V, 0.5V, and 0.2V, respectively. Accordingly, it is logical that the output voltage of $V^{+}_{NG1+NG2}$ is ~1.2 and $V^{+}_{NG1+NG2+NG3}$ is 1.4 V. That is, when the polarities of the nanogenerator are connected in the same direction (see Figure 4(a)), which increased the total voltage of the circuit. By contrast, when the polarity of the nanogenerators is connected in opposite direction, as defined by $V^{+}_{NG1-NG2}$ and $V^{+}_{NG1+NG2-NG3}$ (see Figure 4(c)), the corresponding linear superposition of equations is presented in equations of (3) and (4). The output voltage is therefore decreased to ~0.3V for $V^{+}_{NG1-NG2}$ and 1.2 V for $V^{+}_{NG1+NG2-NG3}$ (see Figure 4(d)). On the basis of our experimental results, we conclude that if we apply the power sources (eg., nanogenerator) in the opposite polarity connection, thereby decreasing the total voltage of the circuit in the nanogenerator group. Conversely, the polarities of the power sources are connected in the same direction, thereby increasing the total voltage of the circuit.

Similarly, when evaluating the output current, the measured configurations are defined as the linear superpositions $I^{+}_{NG1+NG2}$ and $I^{+}_{NG1+NG2+NG3}$ (see Figure 5(a)). The $I^{+}_{NG1+NG2}$, $I^{+}_{NG1+NG2+NG3}$ are given by the equations of (5), (6), respectively. First, the individual measured output current of three nanogenerators as NG1, NG2, and NG3 are 40 nA, 30 nA , and 10 nA, respectively. Next, the corresponding output current of linear superposition $I^{+}_{NG1+NG2}$ is ~70 nA and $I^{+}_{NG1+NG2+NG3}$ is ~80 nA (see Figure 5(b)), that their amplitudes add linearly. To conduct a switching polarity tests, the polarities of the NG2 and NG3 are connected in an opposite direction, as shown the schematic diagram in the Figure 5(c). The linear superposition minus are defined as $I^{+}_{NG1-NG2}$ and $I^{+}_{NG1+NG2-NG3}$, which can be presented as the equations of (7) and (8), respectively. The measured output current of $I^{+}_{NG1-NG2}$ produced ~10nA while $I^{+}_{NG1+NG2-NG3}$ produces ~60 nA, as shown in Figure 5(d). On the basis of the experimental results, our nanogenerators are indeed consistent with a linear superposition principle. Moreover, the control sample has carefully been conducted by using PDMS without ZnS nanowires, which exhibited no output signal, as shown in supplementary information of S2. Therefore, we concluded that the linear superposition principle with the switching polarity tests have been demonstrated to rule out any artifact such as coupling effect with electrical measurement system.

$$I^{+}_{NG1+NG2}=(I_{p-}-I_{p+})_{NG1}+(I_{p-}-I_{p+})_{NG2}=I^{+}_{NG1}+I^{+}_{NG2} \tag{5}$$

$$I^{+}_{NG1+NG2+NG3}=(I_{p-}-I_{p+})_{NG1}+(I_{p-}-I_{p+})_{NG2}+(I_{p-}-I_{p+})_{NG3}=I^{+}_{NG1}+I^{+}_{NG2}+I^{+}_{NG3} \tag{6}$$

$$I^{+}_{NG1-NG2}=(I_{p-}-I_{p+})_{NG1}+(I_{p+}-I_{p-})_{NG2}=I^{+}_{NG1}-I^{+}_{NG2} \tag{7}$$

$$I^{+}_{NG1+NG2-NG3}=(I_{p-}-I_{p+})_{NG1}+(I_{p-}-I_{p+})_{NG2}+(I_{p+}-I_{p-})_{NG3}=I^{+}_{NG1}+I^{+}_{NG2}-I^{+}_{NG3} \tag{8}$$

To understand the relationship between the falling height and output signal, the 100g object was dropped from different heights of 3, 4, 5, 6, and 7 cm. This produced various forces of momentum, as demonstrated in Figure 6(a). The momentum for the vary height of 3, 4, 5, 6, and 7 cm are 0.077N s, 0.089 N s, 0.099 N s, 0.108N s, and 0.117 N s, respectively. Thus, the corresponding output voltages for various momentum of 0.077N s, 0.089 N s, 0.099 N s, 0.108N s, and 0.117 N s are 0.2 V, 0.4V, 0.6V, 0.7V, and 0.8V, respectively, as shown in Figure 6(b). Likewise, the corresponding output currents for such momentums are 12nA, 15nA, 25nA, 28 nA, and 32 nA, respectively, as shown in Figure 6(c). Figure 6(d) shows that the various momentums are proportional to the varied height.[27] The force is therefore proportional to the collision momentum. This is consistent with our previous findings in $ZnSnO_3$ nanogenerator.[23,28] The various momentums have high sensitivity to the corresponding output signal.

The ZnS nanogenerator was mounted on an object with a mass of 77g to conduct a pendulum experiment that undergo a simple harmonic motion as it swings forth and back. The equilibrium position of the pendulum is the location when the object is hanged downward. Figures 7(a)-7(d) shows that the harmonic motions of the pendulum are released at 15^o, 30^o, 60^o, and 90^o, respectively. The more angles the pendulum had, the more current it put out. The harmonic motions have amplitude for the sine (or cosine, depends on the phase angle) function. Thus, as increased the swing angle of the pendulum, the amplitude increased (see Figure 7(a)-7(b)). Subsequently, the amplitude exhibits an exponential decay with time. The results are in good agreement with a typical harmonic motion performs by a pendulum. There have slight variations in the output signals. This is attributed to a small swing frequency and directions difference.

On the basis of the superior performance of the ZnS nanogenerator and the simple demonstration, the results show that the ZnS nanogenerator can detect a various momentums and mechanical motions as a high sensitive active sensor. It can be argued this is the first unique demonstration of using a ZnS nanogenerator as a highly sensitive active sensor that without applied an external power source.

4. Conclusion

The ZnS nanowires with a wurtzite structure were synthesized by a carbonthermal evaporation process at 1050 ^{o}C. A spontaneous polarization direction [0001] of ZnS was revealed by a HRTEM image. Theoretical calculation demonstrated the piezopotential of the ZnS nanowires ~2V while applied a compressive or tensile strain on its c-axis. An output voltage and current of a ZnS nanogenerator can reach 0.8V and 40 nA. The nanogenertaors are consistent with a linear superposition principle. The output signals are proportional to the collision momentum. The ZnS nanogenerator can be self-powered to trace a simple harmonic motion of a pendulum that released from different angle (i.e, 15^{o}, 30^{o}, 60^{o}, and 90^{o}). This is a first demonstration that a highly sensitive active sensor made by a ZnS nanogenerator that enable to detect and/or harvesting energy from a various mechanical motions.

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Figure Captions

Figure 1. (a) FESEM image of ZnS nanowires. Inset image shows that the growth of nanowires propagating in range of 45^o to 135^o from substrate's surface. (b) The XRD pattern shows the nanowires belongs the wurtzite structure. (c) HRTEM image shows the ZnS nanowires with a lattice fringe ~0.619 nm. (d) Fast Fourier Transform (FFT) pattern shows the nanowires grows along [0001] direction.

Figure 2. (a) Atomic model of the structure ZnS. (b) Piezoelectric potential distribution obtain by theoretical calculation with applying directions along +z axis (c) Appling force at 90^o to the surface of the nanowire. (d) The schematic diagram of as-grown nanowires on the surface of the substrate. (e) A sandwich structure of ZnS nanogenerator (f) The ZnS nanowires with a PDMS layer.

Figure 3. Output power of a ZnS nanogenerator by a forward connection: (a) output voltage (b) output current; and reverse connection of (c) output voltage (d) output current

Figure 4. (a) Equivalent circuit of the nanogenerators in-serial package with the polarity in the same direction. (b) The corresponding output voltage. (c) Equivalent circuit of two and three nanogenerators in-serial package the polarity with a opposite direction. (d) The corresponding output voltage.

Figure 5. (a) Equivalent circuit the nanogenerators in-parallel package with the polarity in the same direction. (b) The corresponding output current. (c) Equivalent circuit of the nanogenerators in-parallel package the polarity with an opposite direction. (d) The corresponding output current.

Figure 6. A collision momentum test for different heights of 3, 4, 5, 6, and 7 cm. (a) A

schematic diagram of the nanogenerator testing stage. (b) The corresponding output voltage (c) The corresponding output current. (d) The experimental data and fitting curves for output voltage and current as function of a vary collision momentum.

Figure 7. The output current of a nanogenerator perform by a pendulum test. The harmonic motion of the pendulum is released at (a) 15^o, (b) 30^o,(c) 60^o, and (d) 90^o.

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Figure 1

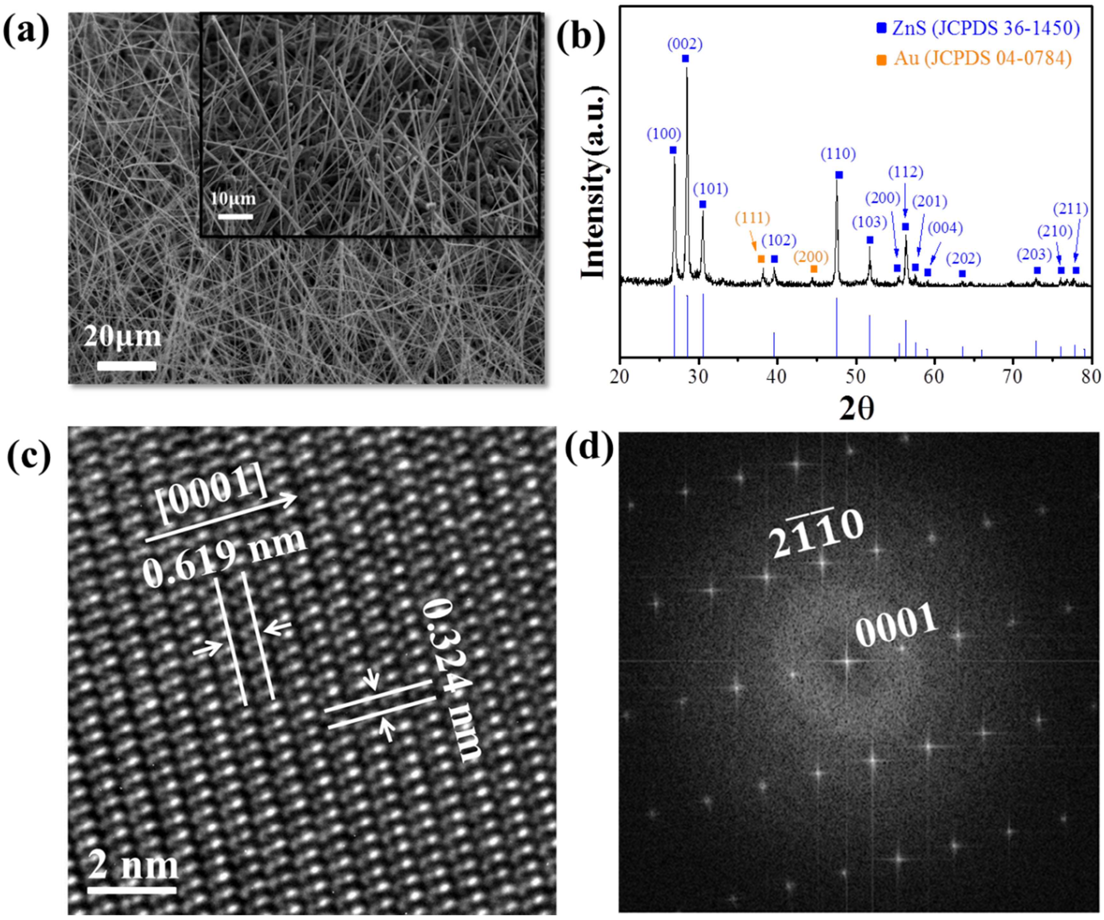
(a)
10μm
20μm
(b)
ZnS (JCPDS 36-1450)
Au (JCPDS 04-0784)
Intensity(a.u.)
(100)
(002)
(101)
(111)
(102)
(200)
(110)
(103)
(112)
(200)
(201)
(004)
(202)
(203)
(210)
(211)
20
30
40
50
60
70
80
2θ
(c)
[0001]
0.619 nm
0.324 nm
2 nm
(d)
2$\bar{1}\bar{1}$0
0001

Figure 2

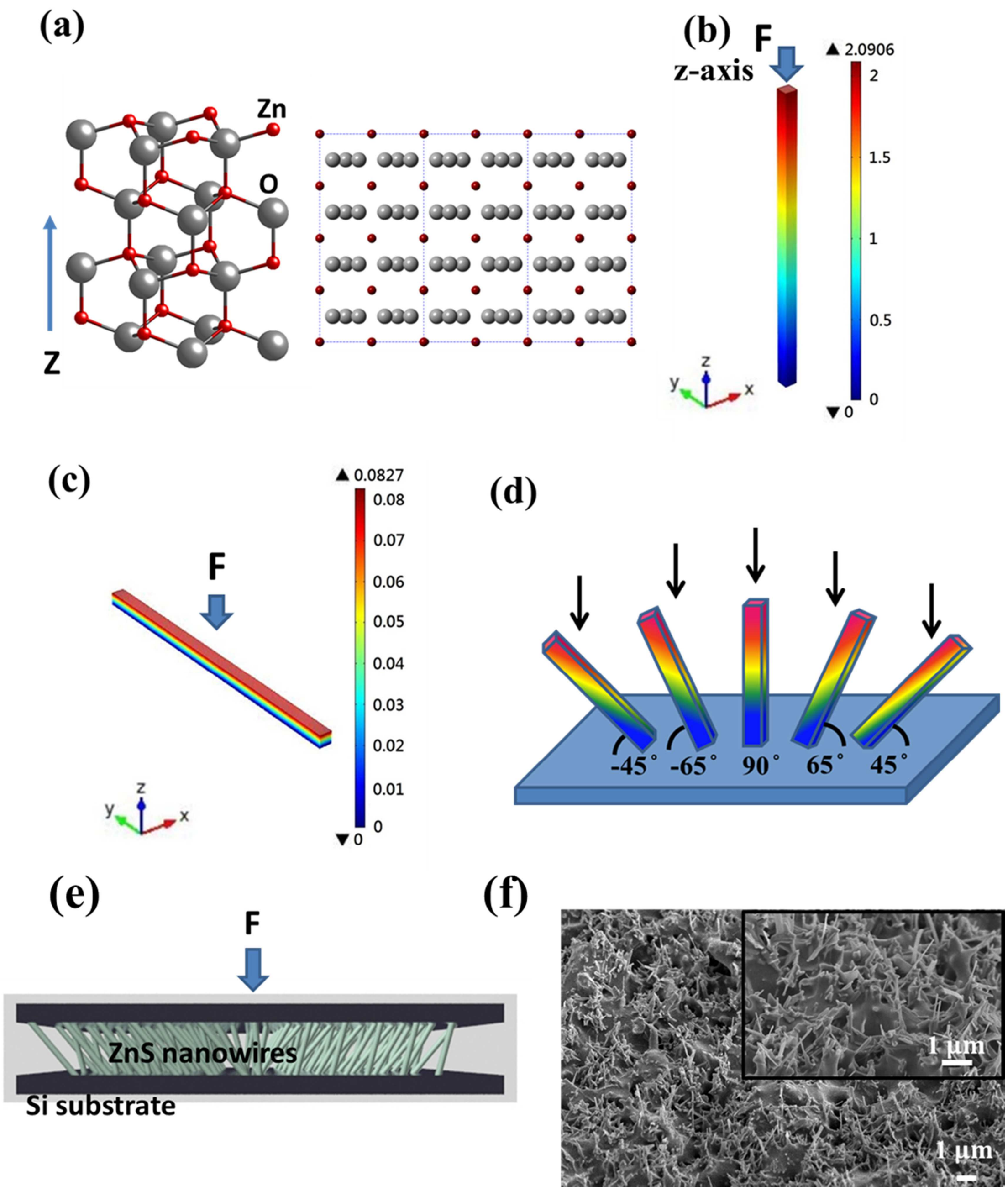
(a)
Zn
O
Z
(b)
F
z-axis
2.0906
2
1.5
1
0.5
0
0
(c)
F
0.0827
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0
(d)
-45°
-65°
90°
65°
45°
(e)
F
ZnS nanowires
Si substrate
(f)
1 μm
1 μm

Figure 3

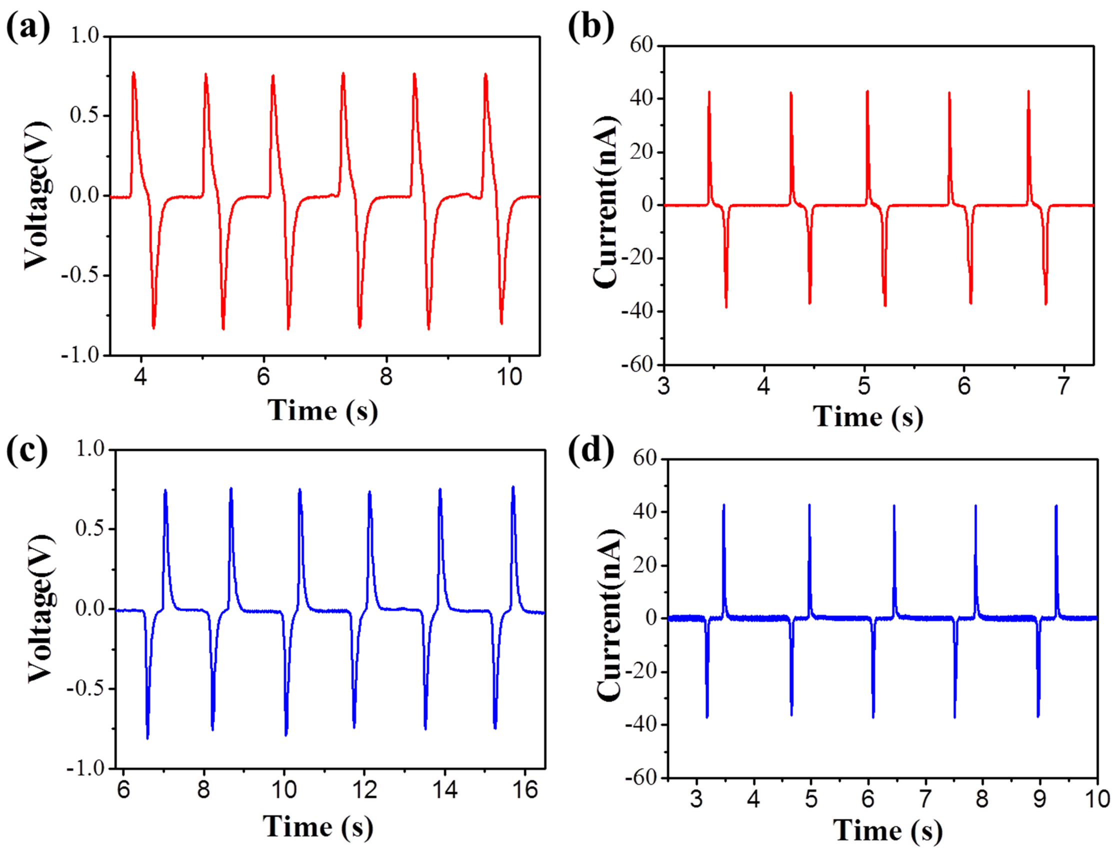
(a)
Voltage(V)
1.0
0.5
0.0
-0.5
-1.0
4
6
8
10
Time (s)
(b)
Current(nA)
60
40
20
0
-20
-40
-60
3
4
5
6
7
Time (s)
(c)
Voltage(V)
1.0
0.5
0.0
-0.5
-1.0
6
8
10
12
14
16
Time (s)
(d)
Current(nA)
60
40
20
0
-20
-40
-60
3
4
5
6
7
8
9
10
Time (s)

Figure 4

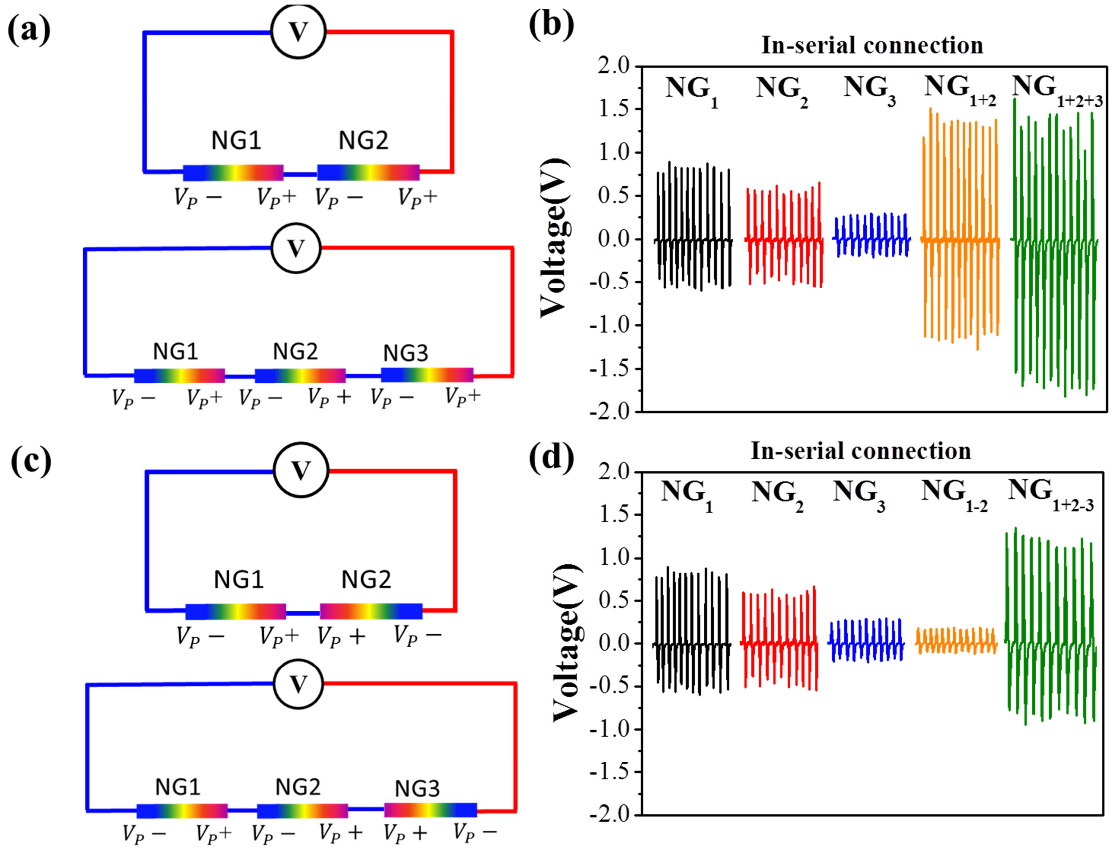
(a)
NG1
NG2
NG3
(b)
In-serial connection
Voltage(V)
NG1 NG2 NG3 NG1+2 NG1+2+3
(c)
(d)
NG1 NG2 NG3 NG1-2 NG1+2-3

Figure 5

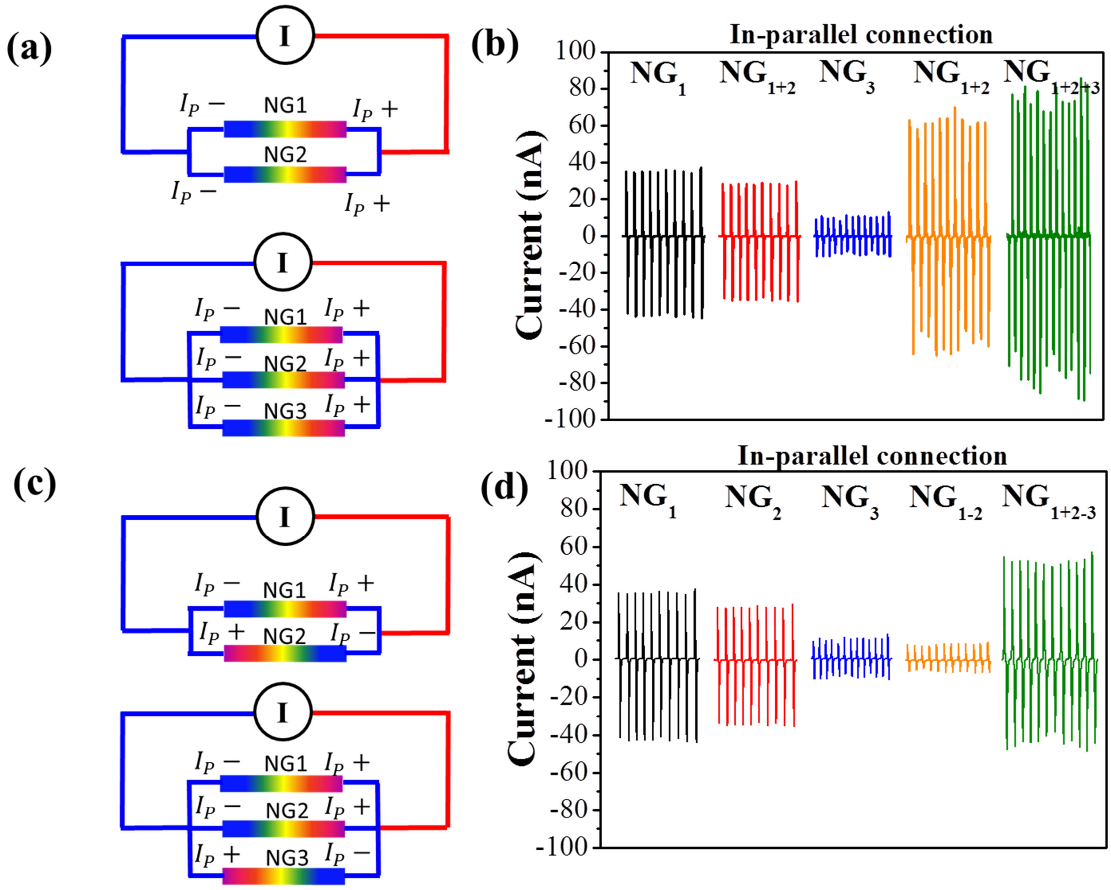
(a)
I
I_P − NG1 I_P +
NG2
I_P − I_P +
I
I_P − NG1 I_P +
I_P − NG2 I_P +
I_P − NG3 I_P +
(b)
In-parallel connection
NG1 NG1+2 NG3 NG1+2 NG1+2+3
Current (nA)
100 80 60 40 20 0 -20 -40 -60 -80 -100
(c)
I
I_P − NG1 I_P +
I_P + NG2 I_P −
I
I_P − NG1 I_P +
I_P − NG2 I_P +
I_P + NG3 I_P −
(d)
In-parallel connection
NG1 NG2 NG3 NG1-2 NG1+2-3
Current (nA)
100 80 60 40 20 0 -20 -40 -60 -80 -100

Figure 6

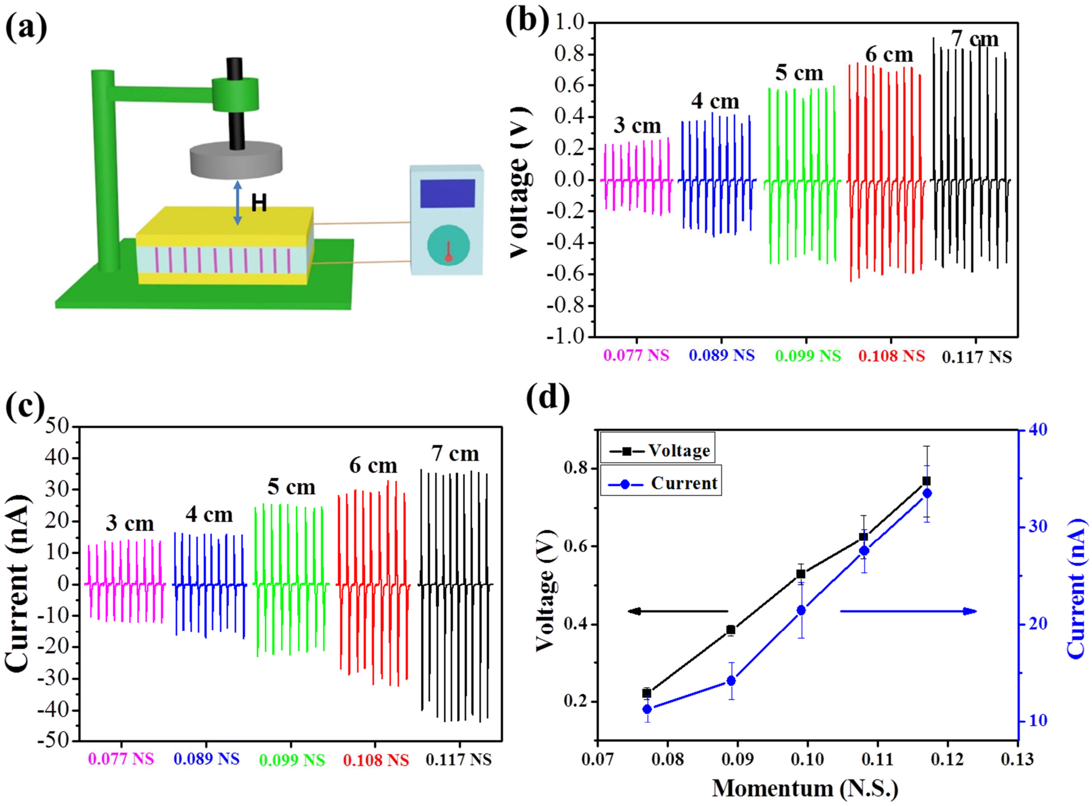
(a)
H
(b)
Voltage (V)
3 cm
4 cm
5 cm
6 cm
7 cm
0.077 NS
0.089 NS
0.099 NS
0.108 NS
0.117 NS
(c)
Current (nA)
3 cm
4 cm
5 cm
6 cm
7 cm
0.077 NS
0.089 NS
0.099 NS
0.108 NS
0.117 NS
(d)
Voltage
Current
Voltage (V)
Current (nA)
Momentum (N.S.)

Figure 7

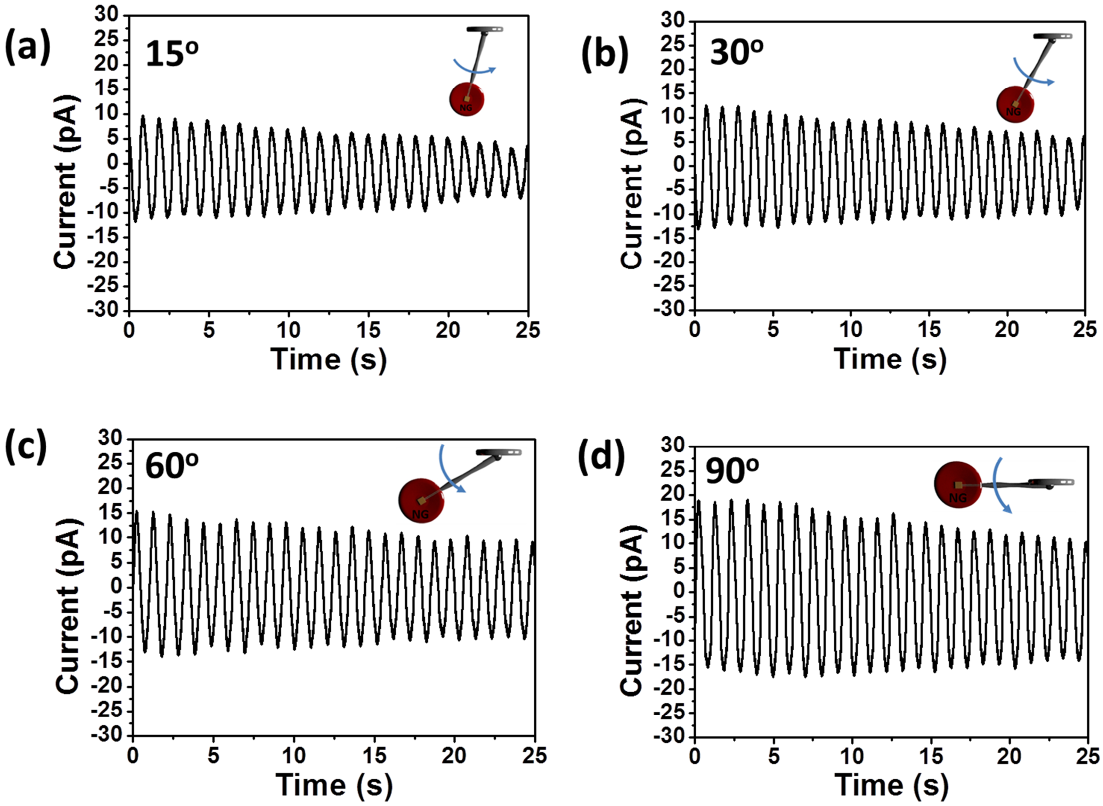
(a)
15°
Current (pA)
Time (s)
(b)
30°
Current (pA)
Time (s)
(c)
60°
Current (pA)
Time (s)
(d)
90°
Current (pA)
Time (s)

Table of contents graphic

A pendulum and micro-force active sensors have been first made from zinc sulfur nanowires based nanogenerator. The ZnS nanogenerator can be self-powered to trace a simple harmonic motion of a pendulum that released from different angle. A various momentums from 0.077N s to 0.177N s were able to detect owing to the output voltage and current of the ZnS nanogenerator were proportional to the momentum.