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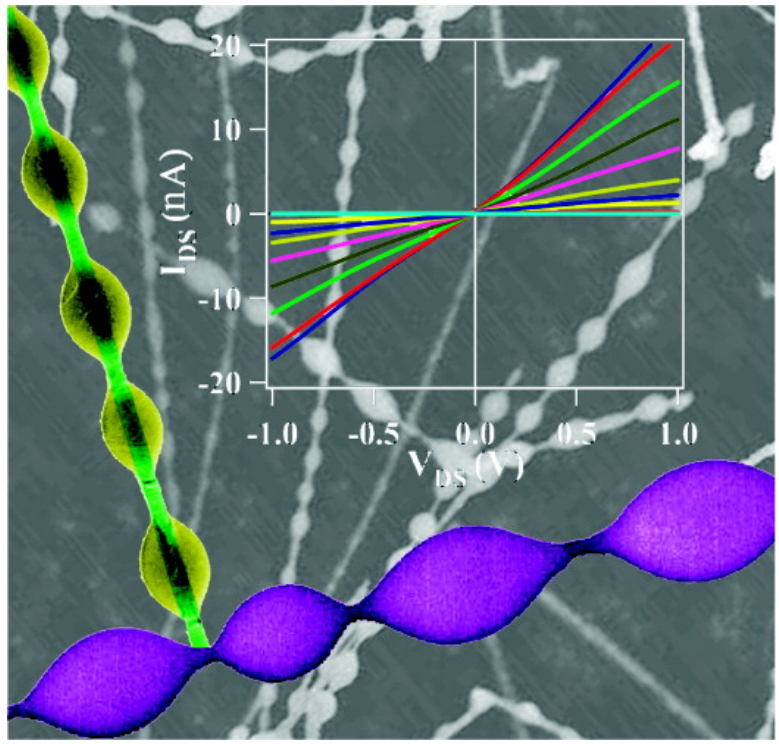


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# Pearl-Like ZnS-Decorated InP Nanowire Heterostructures and Their Electric Behaviors

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One-dimensional semiconductor heterostructures with modulated compositions and interfaces have become of particular interest with respect to potential applications in nanoscale building blocks of future optoelectronic and nanoelectronic devices and systems. In this paper, we reported the synthesis of pearl-like heterostructures, which are composed of ZnS-decorated on InP nanowires via a one-step thermochemical method. Field-effect transistors were fabricated on the basis of a single pearl-like InP/ZnS heterostructure, which exhibited p-type transistor performance and a decent response to UV light exposure. Electronic transport properties of the devices at different temperatures were finally investigated, revealing a thermal activation behavior.

## Introduction

In recent years, one-dimensional (1D) nanostructures with special compositions and morphologies have received prime attention because of their exceptional properties and potential applications in optoelectronic and electronic devices such as field-effect transistors, chemical and biosensors, Li-ion batteries, solar cells, etc.[1−8] Among them, 1D semiconductor heterostructures with modulated compositions and interfaces have become of particular interest with respect to potential applications in nanoscale building blocks of future optoelectronic and nanoelectronic devices and systems.[9−14] These kinds of heterostructures also provide the opportunities for enhancing the functionality of 1D nanostructures and may find applications in nanoscale heterostructured electronic devices.[9]

Inspired by the interesting properties and potential applications in fiber optical communications, electronics, and optoelectronics devices, researchers have shown great interest in 1D indium phosphide (InP) structures (nanowires, nanotubes and nanobelts) in recent years.[15−20] For example, isolated InP nanowires can be used to create polarization-sensitive nanoscale photodetectors,[17] which may be valuable for integrated photonic circuits, optical switches, and high-resolution detectors. InP nanowires with selective doping can show either p-type or n-type characteristics and may be assembled into highly integrated electronic devices.[16] Though many methods have been developed to synthesize 1D InP nanostructures,[15−24] few efforts have been paid to the controlled synthesis of 1D InP-based heterostructures[25,26] and much is left to be explored, especially with respect to the

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fabrication of nanodevices and investigation of their electrical transport properties.

In this paper, we reported a new interesting heterostructure based on InP nanowires, i.e., the pearl-like ZnS-decorated InP nanowires, prepared via a one-step thermochemical method using InP and ZnS powders as the source materials. Studies found that the trunk InP nanowires are single crystals with the preferred growth directions along the ⟨111⟩ orientations, whereas the wrapped ZnS bulbs are polycrystalline. Field effect transistors were fabricated based on single pearl-like InP/ZnS heterostructure, which exhibited p-type transistor performance and a decent response to UV light exposure. Electronic transport properties of the devices at different temperatures were finally investigated, revealing a thermal activation behavior.

## Experimental Section

Pearl-like ZnS-decorated InP nanowire heterostructures were synthesized in an induction furnace[27] using InP and ZnS powders as the source materials. The furnace consisted of a fused quartz tube and an induction-heated cylinder made of high-purity graphite coated with a carbon-fiber thermoinsulating layer. Two inlet graphite pipes and one outlet graphite pipe were set on its top and base, respectively. In a typical process, a graphite crucible containing InP powders was loaded in the center of the heating zone and another graphite crucible containing ZnS powders was put ahead about 4 cm away from InP. After evacuation of the quartz tube to approximately 20 Pa, two flows of pure Ar were introduced into the furnace and maintained through the top and base inlets at flow rates of 20 standard cubic centimeters per minute (sccm) and 50 sccm, respectively, at ambient pressure. The crucible was rapidly heated to 1250 °C within 10 min and kept at this temperature for 2 h before being cooled to room temperature.

The products were collected for characterization using a field-emission scanning electron microscope (SEM, JEOL JSM-6700), and a high-resolution transmission electron microscope (HRTEM, JEOL JEM-3000F) equipped with an energy-dispersive X-ray spectrometer (EDS).

## Results and Discussion

After the synthesis, a gray-black wool-like product was found deported on the inner wall of the crucible where the temperature was around 950 °C. Field-emission scanning electron microscopy (FE-SEM) was used to examine the morphologies of the products. Figure 1a shows a SEM image of the as-synthesized products. All the products display an interesting pearl-like morphology with length ranging from several to several tens of micrometers. Images b and c in Figure 1 show magnified SEM images of several synthesized nanowires. They clearly reveal that, within the pearl-like heterostructures, the diameter of the trunk part is smaller than 50 nm, and the maximum diameters for bulb parts are in the range of 100−400 nm.

An X-ray diffraction (XRD) pattern of the product is shown in Figure 2. All the strong diffraction peaks can be indexed to those of a cubic structure of InP (JCPDS no. 32−0452; $F\bar{4}3m$, $a = 5.869$ Å). Besides those peaks of InP, another weak peak around 28.3° was also detected, which can be indexed to the (002) plane of hexagonal phase of ZnS (JCPDS no. 36−1450).

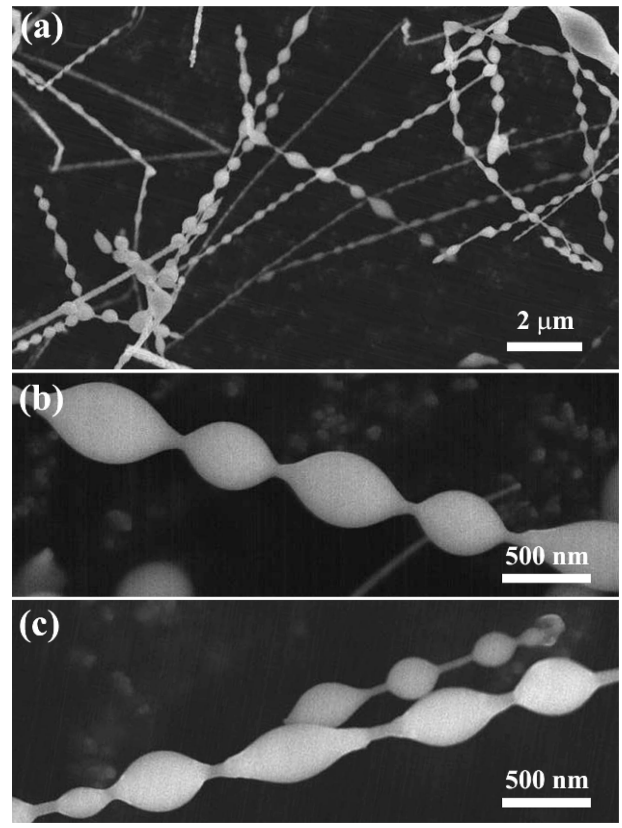


**Figure 1.** SEM images with different magnifications of the InP nanowires with ZnS decoration, showing unusual pearl-like morphology.

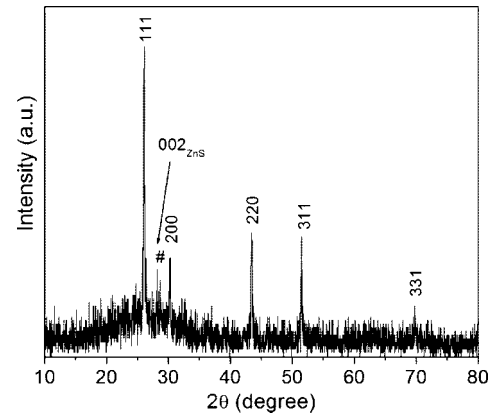


**Figure 2.** XRD pattern of the InP nanowires with pearl-like ZnS decoration.

The pearl-like nanowires were further characterized with TEM equipped with EDS. Figure 3a shows a low-magnification TEM image of a product, that clearly displays the pearl-like morphology. TEM images of a single pearl-like nanowire are depicted in images b and c in Figure 3, which reveal that the nanowire is actually consisted of a straight nanowire (trunk part) with diameter of about 50 nm wrapped almost periodically with olive-shaped bulbs along the whole length. EDS spectra of the inner nanowire and the wrapped bulbs are demonstrated in panels d and e in Figure 3, respectively.

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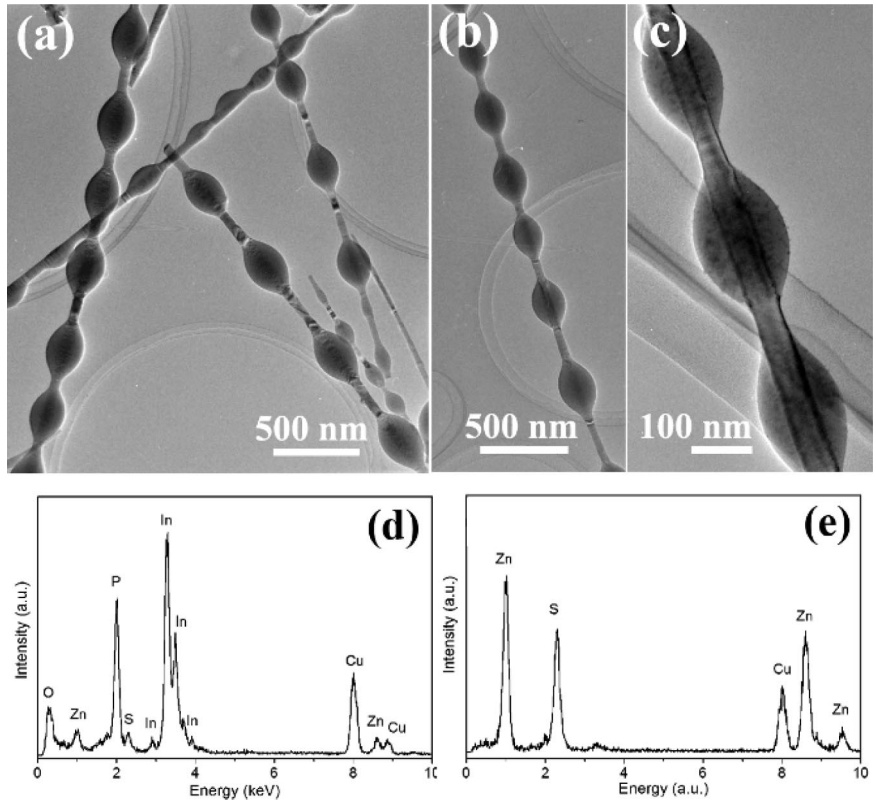


**Figure 3.** (a−c) TEM images of typical pearl-like ZnS/InP nanowires. (d, e) EDS spectra taken from the outer ZnS and inner InP nanowires, respectively.

Figure 3d suggests that the trunk nanowire is composed of In and P elements with an In/P ratio (atomic) close to the stoichiometry of InP. For the bulb part, the EDS spectrum shown in Figure 3e indicates that the bulb is composed of Zn and S with a composition of ca. 1:1, the stoichiometry close to ZnS. No other impurity elements could be detected. The EDS data confirm that the products are actually heterostructures made of InP nanowires decorated with ZnS, forming the pearl-like structures.

Detailed microstructural information on the pearl-like nanowires was obtained using high-resolution transmission electron microscopy. Figure 4a is a TEM image of a pearl-like nanowire with two bulbs. The trunk InP nanowire has a diameter of 50 nm, whereas the maximum diameter of the bulb is about 170 nm. A selected-area electron diffraction (SAED) pattern taken from the trunk InP nanowire is shown in the inset, which verifies its single crystal nature. The spots on the pattern can be easily attributed to the [110] zone axis of a cubic InP crystal. The single crystal nature of the trunk InP nanowire is further confirmed from a high-resolution TEM (HRTEM) image in Figure 4b. Figure 4c is a lattice-resolved HRTEM image of the trunk InP nanowire. The marked interplanar *d*-spacings perpendicular and parallel to the nanowire are 0.34 and 0.21 nm, corresponding to the [111] and [220] lattice planes of cubic InP, respectively. The HRTEM result suggests that the trunk InP nanowire has preferred growth direction along the ⟨111⟩ orientation. For the bulb ZnS part, TEM observations reveal that it is composed of polycrystalline ZnS domains. Figure 4d is the lattice-resolved HRTEM image taken from the bulb. The

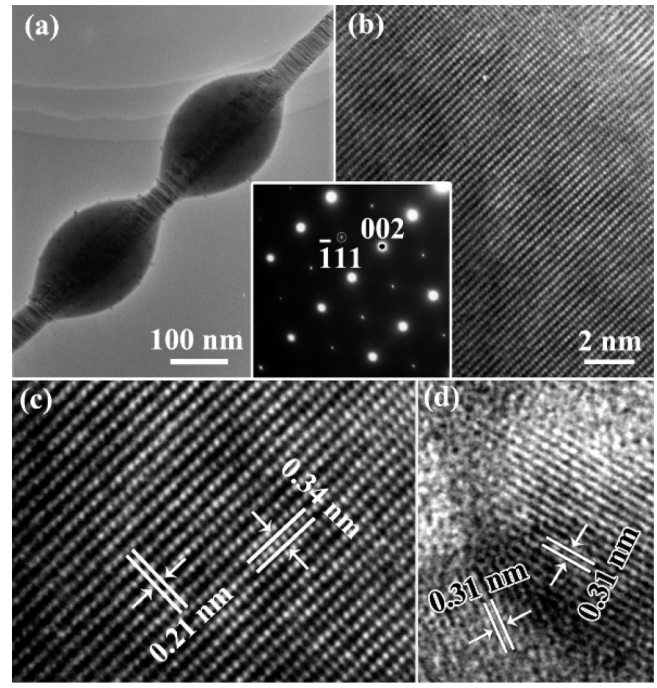


**Figure 4.** (a) TEM image of a single pearl-like ZnS-decorated InP nanowire and its SAED pattern; (b) HRTEM image; (c, d) lattice-resolved HRTEM image taken from the InP and ZnS, respectively.

marked interplanar *d*-spacing is 0.31 nm, corresponding to the [002] plane of hexagonal ZnS.

During the growth of pearl-like InP/ZnS heterostructure, no catalyst was used, so the vapor−liquid−solid (VLS) mechanism can be excluded and a vapor−solid (VS) mech-

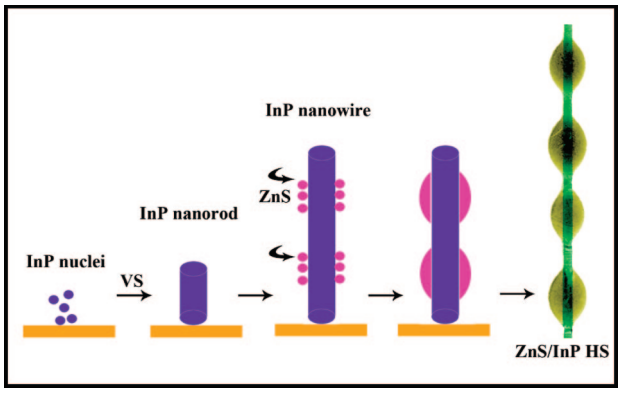


**Figure 5.** Schematic diagrams of the growth of pearl-like ZnS/InP heterostructures.

anism can be proposed to explain the growth of nanowires structures. The whole growth process can be expressed as shown in Figure 5. At a high reaction temperature, InP powder evaporates spontaneously, and the InP vapors are transferred by the carrier Ar gas to a low-temperature region, where they deposit and aggregate on the inner wall of a crucible as nuclei for further nanowire growth via a VS process. At the same time, ZnS powders are also evaporated to generate ZnS vapors, which are transferred by the Ar gas to the low-temperature region, deposit and aggregate on the surface of the newly formed InP nanowires. Driven by the surface tension, these newly formed ZnS nanoparticles tend to minimize their surface free energy by forming into sphere shapes.[28,29] With the increase of reaction time, the present pearl-like ZnS-decorated InP nanowire heterostructures are formed.

Single-nanowire-based FETs were then fabricated according to our previous reported technique.[30] Briefly, the pearl-like InP/ZnS heterostructure were first sonicated into a suspension in isopropanol and then deposited onto a degenerately doped silicon wafer covered with 500 nm $SiO_2$. Photolithography was then performed, followed by Ti/Au deposition to pattern the source and drain electrodes on both ends of the nanowires. Figure 6a inset shows a top view SEM image of the fabricated device. The channel length between the source and drain electrodes of the device is 2 $\mu$m and the silicon substrate was used as a back gate. Figure 6a shows the typical gate-dependent current−voltage ($I-V$) curves obtained from an individual pearl-like nanowire measured in a vacuum. The nanowire device exhibited good gate dependence and was rather conductive, reaching a current of 0.487 $\mu$A with a drain-source voltage of 1 V and a gate voltage of −30 V. The transport data clearly show decrease in conductance for $V_g > 0$, whereas the conductance increases for $V_g < 0$, indicating that the present pearl-like ZnS-decorated InP nanowires are of p-type. For the ZnS-decorated InP nanowire devices, positive gate voltages deplete holes in the nanostructures and thus reduce the conductance of the nanostructures. Intrinsic InP is an n-type semiconductor. Its electronic properties can be easily tuned

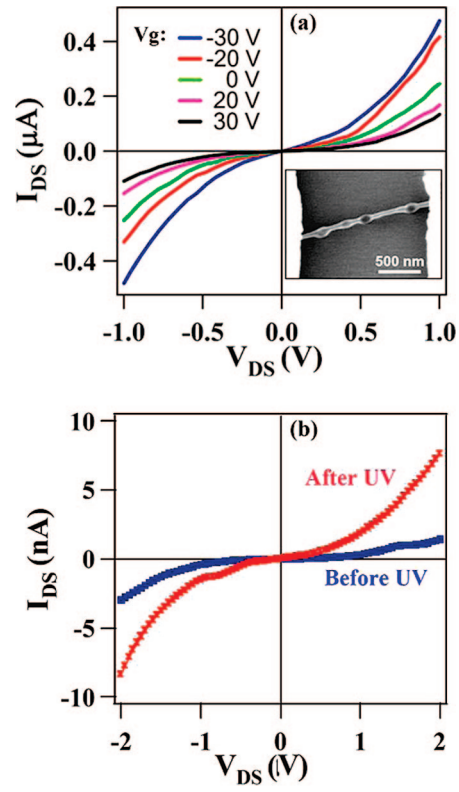


**Figure 6.** (a) Current vs source-drain ($I-V_{sd}$) curves at different gate voltages for an individual ZnS-decorated InP nanowire FET. (b) Current vs source-drain ($I-V_{sd}$) curves before and after UV exposure.

using different dopants, thus make it show either n- or p-type behavior. Many reports can be found on the electronic behaviors studies of InP films or bulk InP crystals.[30−32] However, the electronic transport of 1D InP nanostructures was seldom investigated. Previously, Lieber et al. reported the n- or p-type tuning of InP nanowires by introducing different dopants.[16] In this work, by forming heterostructures, instead of the introduce of dopants, p-type semiconducting behavior is also fulfilled. It was believed that the electronic behavior of current heterostructure is greatly influenced by the formation of special structures, surface areas, and interface structures within the heterostructures.

The UV response of the ZnS-decorated InP nanowire devices was also studied and the result is illustrated in Figure 6b. The experiment involved a UV lamp of 254 nm in wavelength fixed at a distance of approximately 5 cm away from the nanowire transistor. The measurement was conduced under practical conditions as in air, room temperature and under indoor incandescent light. Figure 5b shows two $I-V$ curves measured with and without UV irradiation. Enhanced conduction was clearly observed. The zero-bias conductance before and after the exposure to a 254 nm light is calculated to be 70 and 813 nS, respectively. For the UV light with wavelength of 254 nm, each photon has energy of 4.9 eV. The energy is sufficiently high to excite electrons directly from the valence band into the conduction band, which leads to enhanced carrier concentrations and signifi-

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cantly increases the conduction of the nanowire device. On the other hand, under UV exposure, oxygen and moisture species absorbed on the surface of the nanowire could be desorbed, which also may result in the enhancement of conduction.[33,34]

Comparing the data in panels a and b in Figure 6, it can be seen that the device measured in vacuum (Figure 6a) are much more conductive than measured in air (Figure 6b, before UV exposure). This effect is strongly related to $O_2$ in air absorbed on the surface of nanostructures as mentioned in many reports.[5,33,34] Once measured in a vacuum, $O_2$ molecules absorbed on the surface were pumped away, which resulted in higher carrier concentration and higher conduction. Finally, we studied the electronic properties of the device at different temperatures ranging from 300 to 100 K in a vacuum. Figure 7a shows the $I-V$ curves of a typical ZnS decorated InP nanowire device measured at different temperatures. At 300 K in vacuum, the $I-V$ curve appears to be linear, indicating ohmic contacts formed between the metal electrodes and the nanowire. It is therefore reasonable to assume that the two-terminal resistance is dominated by the nanowire. From the $I-V$ curves, it can be found that the conductance of the device progressively reduces with the decrease of temperature. The zero-bias conductance was measured to decrease from 17.27 nS at 300 K to 0.011 nS at 190 K, as indicated in the figure. Figure 7b shows a plot of the zero-bias conductance in a logarithmic scale as a function of 1000/$T$. Basically, electrical conductivity is strongly dependent on temperature. In semiconductor, the electrical conductivity increases with increasing temperature. The conductance versus temperature can be fitted into the formula $G \approx \exp(-E_\alpha/K_B T)$, where $G$ is the conductance, $E_\alpha$ is the thermal activation energy, $K_B$ is the Boltzmann constant, and $T$ is the measured temperature. The calculated $E_\alpha$ is about 236.7 meV. The results suggested that the thermal activation of carriers is the dominant transport mechanism according to previous reports.[35,36]

## Conclusion

In conclusion, pearl-like ZnS decorated InP nanowires consisted of InP trunks wrapped with ZnS bulbs were synthesized via a simple vapor-solid method. The core InP nanowires are single crystals whereas the wrapped ZnS are polycrystals. Field-effect transistors were fabricated based on the pearl-like ZnS-decorated InP nanowires, which show p-type characteristics. The devices show a clear response to UV irradiation. Electronic transport properties of the devices were also investigated at different temperatures, and the results suggested that the thermal-activated transport as the dominating transport mechanism with an activation barrier of 236.7 meV. Our results show that the pearl-like ZnS-decorated InP nanowires may be used as UV detectors as well as building blocks for nanoscale electronics and optoelectronics.

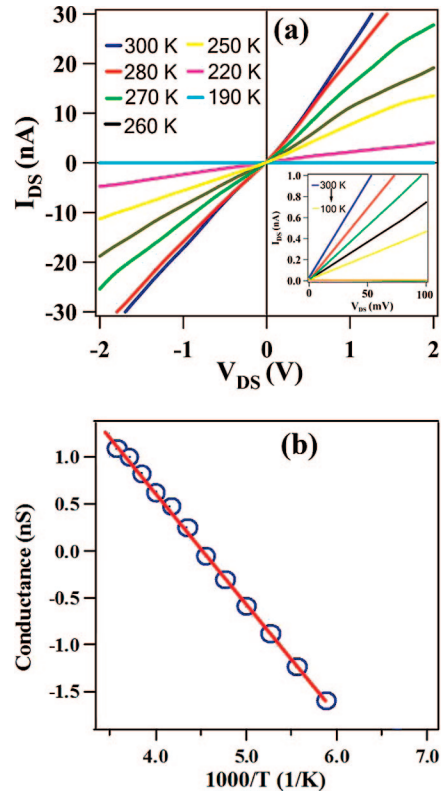


**Figure 7.** (a) Temperature dependence of $I-V$ characteristics of the nanowire transistors. (b) Plot of the zero-bias conductance in a logarithmic scale as a function of 1000/$T$.

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