n-ZnO/p-NiO Core/Shell-Structured Nanorods for Piezoelectric Nanogenerators

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Recently, nanogenerators (NG) have attracted considerable attention due to the practical applications of converting mechanical energy to electrical energy from various sources.[1-5] Piezoelectric nanogenerators (PENGs) based on piezoelectric materials have attracted much attention due to their high energy-conversion efficiency, capability for miniaturization, and light weight. Zinc oxide (ZnO), which has a wurtzite crystal structure, is a representative piezoelectric material. The defects that are inevitably present in ZnO nanorods (NRs), however, generate excessive free electrons, which reduce the piezoelectric potential and thus reduce the output characteristics. Herein, ZnO–NiO core–shell structure–based PENGs are designed to enhance their piezoelectric output performance by reducing excess electrons in the ZnO NRs using a p-type semiconducting NiO layer. The thickness and structure of the NiO coated on the ZnO NRs are observed and analyzed by adjusting the molar concentration of solution for the NiO layer coating, and the effects of these on the piezoelectric output are discussed.

Energy-harvesting technologies, which can generate electrical energy from various energy sources, such as solar, thermal, and mechanical movement that are commonly found in the local environment, supply permanent and environmentally friendly energy. In addition, related research has been in the spotlight because it provides power by harvesting and converting a naturally occurring energy source without a charging process through external power. Piezoelectric nanogenerators (PENGs) based on piezoelectric materials have attracted much attention due to their high energy-conversion efficiency, capability for miniaturization, and light weight. Zinc oxide (ZnO), which has a wurtzite crystal structure, is a representative piezoelectric material. The defects that are inevitably present in ZnO nanorods (NRs), however, generate excessive free electrons, which reduce the piezoelectric potential and thus reduce the output characteristics. Herein, ZnO–NiO core–shell structure–based PENGs are designed to enhance their piezoelectric output performance by reducing excess electrons in the ZnO NRs using a p-type semiconducting NiO layer. The thickness and structure of the NiO coated on the ZnO NRs are observed and analyzed by adjusting the molar concentration of solution for the NiO layer coating, and the effects of these on the piezoelectric output are discussed.

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Recently, nanogenerators (NG) have attracted considerable attention due to the practical applications of converting mechanical energy to electrical energy from various sources.[1-5] Piezoelectric materials generate electricity by generating dielectric polarization when a physical force is applied. A piezoelectric nanogenerator (PENG) based on piezoelectric materials can convert various mechanical energy sources into electrical energy without generating contaminants, and they can be easily miniaturized and are light in weight, so they can be installed where vibration and pressure energy exist.[6,7] Various non-centrosymmetric piezoelectric materials such as lead zirconate titanate (PZT),[8-12] quartz,[13] zinc oxide (ZnO),[14-16] barium titanate (BaTiO$_3$, BTO),[17-21] zinc sulfide (ZnS),[22-24] polyvinylidene fluoride (PVDF),[25,26] etc. are widely used for PENGs. Among them, wurtzite structured ZnO nanorods (NRs) have undergone numerous studies due to their unique features, such as their piezoelectricity, semiconducting property, transparency, biocompatibility, and low manufacturing cost.[3,13-16]

ZnO NRs are an intrinsic n-type semiconductor due to native defects such as zinc (Zn) interstitials and oxygen (O) vacancies. Excessive free electrons from the defects in ZnO NRs limit their harvesting performance due to the screening of piezoelectric potential when mechanical stress is applied. To solve this issue, several approaches have been reported, for example, thermal annealing,[27] O$_2$ plasma treatment,[28,29] and p-type semiconducting layer coating[30,31] to reduce native defects or modulate carrier concentration.

In a previous work, NiO was used as a p-type semiconductor in connection with doping materials research to enhance the output performance of ZnO-based PENGs.[30] The oxidation temperature of Ni for making NiO is very high, however, from 500 to 900 °C, so there is a disadvantage in that its use on a...
transparent or flexible substrate is limited. Other work suggested phosphorus (P)-doped ZnO homojunction formation for reasons of mechanical durability, chemical stability, and improved piezoelectric power generation. Therefore, the process of doping P to make p-type ZnO is an added step, however, which is troublesome.

In this study, the ZnO–NiO core–shell-structure based PENGs were fabricated using NiO coating, as a representative p-type metal oxide. As NiO is a semiconducting transparent oxide, it is used widely in various applications. Therefore, it was used as a p-type material to reduce the screening effect of excess electrons in ZnO NRs and improve the piezoelectric effect. Compared with the previous work, our work proposes a wider application field because the NiO growth process temperature is relatively lower than that of the previous report. It is an individual coated core–shell structure, not a layer-by-layer thin-film structure, and has a wide surface area, which has a wide range of strains and thus has a wide range of p–n junction formations. Therefore, the ZnO–NiO core–shell structure with improved piezoelectric properties that is suggested in this study will also be applicable to various fields such as windows and displays that have to be transparent and flexible.

A core–shell structure was created using a simple process of immersing and withdrawing a ZnO NR-grown substrate using nickel(II) sulfate hexahydrate (NiSO₄·6H₂O), potassium persulfate (K₂S₂O₈) powders, and ammonium hydroxide (NH₄OH) solution. The method proposed in this study has the advantage that the thickness of the NiO coated on the ZnO NRs can be easily controlled by the number of moles of p-type NiO solution. In addition, by varying the molarity of the solution, changes in the core–shell structure and its output were also observed. NiO coatings on ZnO NRs form p–n junctions at the interface and reduce excess electrons in the ZnO NRs, resulting in improved piezoelectric output voltage and current density.

Figure 1a shows the device structure of a ZnO–NiO core–shell NR-based PENG. The ZnO–NiO core–shell NRs were formed by coating NiO flakes on ZnO NRs grown on fluorine doped tin oxide (FTO) glass substrate using a solution process, and Au/polyethylene naphthalate (PEN) substrate was placed above the ZnO–NiO core–shell NR arrays to form a Schottky formation between the Au and the ZnO–NiO core–shell. The Au/PEN substrate was used as the upper electrode, and piezoelectric power was measured by applying a vertical pushing force. The morphology and microstructure of the bare ZnO (B-ZnO) and the ZnO–NiO core–shell-structured NRs were observed by electron microscopy. Figure 1b shows a field-emission scanning electron microscopy (FE-SEM) image of the aligned B-ZnO and ZnO–NiO core–shell NRs on the FTO-coated glass substrate. Growth of the core–shell structure coated with NiO flakes is described in detail in Experimental Section and Figure S1, Supporting Information. Figure S2 and S3, Supporting Information, shows X-ray diffraction (XRD) results and top-view SEM images of the morphologies of B-ZnO NRs and ZnO–NiO NRs on the FTO/glass, respectively. The B-ZnO sample shows a typical hexagonal-shaped NR morphology. The average length and diameter of the B-ZnO NRs were ≈1 μm and ≈30 nm, respectively. The thickness of the NiO shell layer on the ZnO NRs was controlled by the molar concentration of the precursor solution of nickel (II) sulfate hexahydrate (NiSO₄·6H₂O) powder.

With the increasing molar concentration of the NiO precursor solution, the shell layer deposited on the ZnO NRs became thicker. The NiO particles grown on ZnO NRs showed a flake shape, as shown in the inset images of Figure 1b.

Figure 2 shows the high-resolution transmission electron microscope (HRTEM) images of the B-ZnO NRs and the ZnO–NiO core–shell NRs with different molar concentrations. Figure 2a shows an HRTEM image of B-ZnO NRs without the NiO shell layer. Based on the HRTEM image, the measured lattice spacing of 0.26 nm was assigned to the (001) plane of the hexagonal ZnO phase [space group: P6₃mc (186)]. The HRTEM image of a ZnO–NiO core–shell NR grown using a 5 mM solution (expressed as ZnO–NiO [5 mM]) is shown in Figure 2b. It was observed that the lattice spacing of the NiO region was ≈0.24 nm, corresponding to the (111) planes of the cubic NiO phase [space group: Fm3m (225)]. For the ZnO–NiO core–shell NRs with coatings grown using 10 mM and 20 mM solutions (represented as ZnO–NiO [10 mM] and ZnO–NiO [20 mM], respectively) (Figure 2c,d), the shell layers exhibited the lattice spacing of 0.24 nm and/or 0.21 nm, which are in good agreement with the NiO (111) and Ni (200) planes, respectively.

The voltage and current output performance of B-ZnO and ZnO–NiO core–shell NR-based PENGs grown with various molar concentrations of the NiO precursor are shown in Figure 3. Previous research showed that a thermal annealing
The process improved the crystal quality of ZnO, and oxygen vacancy-related defects are significantly reduced, resulting in reduced carrier density and improved output performance. The voltage and current characteristics of the B-ZnO NR-based PENG were 25 mV and 10 nA and those of the annealed ZnO (A-ZnO) NR-based PENG were 90 mV and 15 nA, respectively. (Figures 3 and Figure S3, Supporting Information) After annealing, it was clear that the output performance improved, so all the ZnO–NiO core–shell NRs structures were also annealed.

The output performance of the ZnO–NiO (5 mM) NR-based PENG was 300 mV and 75 nA. It was confirmed that the voltage improved by 12 times and the current by 7 times or more compared with the B-ZnO-based PENG. Due to the p-type semiconducting property of NiO, it is proposed that NiO and ZnO formed p–n junctions, so the piezoelectric potential screening effect caused by free electrons in the piezoelectric semiconducting ZnO NRs greatly reduces by the holes at the surface of NiO. The PENG based on ZnO–NiO (10 mM) core–shell
NRs exhibited voltage and current characteristics of 100 mV and 30 nA, whereas the PENG based on ZnO–NiO (20 mM) core–shell NRs showed 10 mV and 15 nA, respectively. Compared with the output characteristics of the PENG based on B-ZnO NRs, the ZnO–NiO (5 mM) core–shell structure was shown to have the best performance. When NiO flakes were coated by increasing the number of moles of the solution, the output performance gradually decreased. As shown in the TEM results in Figure 2, a thicker NiO layer is coated on the surfaces of the ZnO NRs when there are a higher number of moles in the solution. The fundamental role of NiO is to suppress the transportation of carriers across the ZnO–NiO interface. As the thickness of the NiO layer increases, the voltage drop at the ZnO–NiO interface improves, which causes a decrease in piezoelectric performance. The NiO layers in the ZnO–NiO (10 mM) NR-based PENG and in the ZnO–NiO (20 mM) NR-based PENG are too thick and interfere with the transfer of the piezoelectric potential of the ZnO NRs to the electrodes, leading to a reduction in the output voltage and current.

The detailed mechanisms of piezoelectric power generation for B-ZnO and the ZnO–NiO core–shell-based PENGs are shown in Figure 4. When vertical stress is applied to the vertically grown ZnO NR-based PENGs and the NiO-coated ZnO NR-based PENGs, a negative and positive piezoelectric potential is created at the top and bottom side of the ZnO NRs, respectively. From the Au electrode to the FTO electrode through an external circuit, the induced piezoelectric potential drives the electron flow, which is detected as a positive voltage and current pulse signal in the forward connection. Immediately, the piezoelectric potential declines, when the applied stress is released. The accumulated electrons caused by the piezoelectric potential near the FTO electrode flow back through the external circuit to the Au electrode, which is detected as a negative pulse signal. In the case of the B-ZnO NR-based PENG, the output voltage and current that are produced are reduced by the screening effect, resulting from the free carriers and surface defects in ZnO NRs, as shown in Figure 4a,b.

On the other hand, in the case of the NiO-coated ZnO NR-based PENG, the power output is greatly improved because holes near the interface from the NiO tend to diffuse into the ZnO NR layer at the ZnO–NiO interface. NiO reduces the surface defects in the ZnO–NiO interface where NiO can increase free carriers inside ZnO NRs. So it reduces carrier transport through the ZnO–NiO interface and consequently reduces leakage current to improve output. The free electrons of ZnO NRs begin to diffuse into NiO, and the combination of electrons and holes forms a p–n junction in an interface charge-depletion region. Therefore, the improvement in the output voltage is due to the increase in the piezoelectric potential through passivation of the free electrons presented in the ZnO NRs, which causes the screening effect and reduction of piezoelectric potential, by attracting holes from the NiO and p–n junction formation (Figure 4c,d). Furthermore, the surfaces of ZnO NRs are very rich in oxygen vacancy defects, predominantly, and these defects act as electron donors and also the binding sites for chemical adsorption. Therefore, surface passivation by NiO can eliminate these defects and make the surface chemically inactive, thereby increasing resistance to hydrogen (H) atom adsorption, for
example. In addition, band modulation is caused by potential generated across the ZnO NR layer, which leads to band bending at the ZnO–NiO and Au–ZnO junctions. Therefore, this band bending modulates the Schottky barrier, and piezoelectric signals are generated. Additional carriers from the NiO and the shift in the Fermi level help to increase the power output.

Furthermore, numerical simulations of ZnO NRs and the ZnO–NiO core–shell structure were conducted to demonstrate the suggested mechanism of the enhanced piezoelectric potential by electron–hole recombination and modification of the energy band using COMSOL multiphysics. The details of simulation are given in Experimental Section. The length and diameter of the ZnO NR used in our model parameter were 500 and 30 nm, respectively, and the thickness of the NiO flake was 10 nm. The ZnO–NiO core–shell structure forms a p–n junction.

Figure 5a,b shows the electrical potential along the z-axis of ZnO NR and ZnO–NiO core–shell NR at various strengths of compressive vertical pressure. In case of the bare ZnO NR, the electrical potential is constantly 0 without applied pressure. As the force increases in 2 MN m⁻² steps to 10 MN m⁻², the potential at the end of the ZnO NR drops from ~0.01 to ~0.07 V due to the negative piezoelectric charges at the top surface of the ZnO. In case of the ZnO–NiO core–shell NR, the electrical potential at the end of the ZnO NR reaches 2.2 V without applied pressure, which is the so-called built-in potential (ψ₀) because of the p–n junction between the n-type semiconductor ZnO and the p-type semiconductor NiO. As the force increases by 2 MN m⁻² steps to 10 MN m⁻², the potential drops from 2 to 1.9 V. The comparison of the calculated piezoelectric potential between ZnO NRs and p–n junction ZnO–NiO core–shell NRs is shown in Figure 5c. To calculate the exact piezoelectric potential (ψ_piezo) in the p–n junction NR, the initial potential (ψ₀) due to the p–n junction without applied pressure is subtracted from the total electrical potential using the following equation.

$$\psi_{\text{piezo}} = \psi - \psi_0$$

The obtained result shows a five-fold enhancement of the piezoelectric potential for the p–n junction ZnO–NiO core–shell NR, compared with the ZnO NR. The calculated enhancement by simulation is lower than the experimental measurement because of inaccurate material parameters, but it corresponds to the suggested mechanism of enhancement.

In summary, to reduce the screening effect of ZnO NR, a NiO layer, a p-type semiconductor, was coated in a straightforward way to immerse and withdraw the solution. The thickness and structure of the NiO coated on the ZnO NR were observed and analyzed by adjusting the molar concentration of the solution for the NiO layer coating, and the effect on their piezoelectric output performance was discussed. The output performance of the ZnO–NiO core–shell NR with a thickness of NiO layer at about 5 nm coated by a 5 mM solution was most improved. It was confirmed that the thick NiO layer did not affect the improvement of piezoelectric properties, by alleviating the stress applied to the ZnO–NiO core–shell NR. Therefore, the ZnO–NiO core–shell structure with improved piezoelectric properties proposed in this study can be applied to various fields of ZnO NR-based piezoelectric devices such as windows and displays that should be transparent and flexible.

**Experimental Section**

_Growth of ZnO NRs:_ Fluorine-doped tin oxide (FTO)/glass substrates with a size of 20 mm × 20 mm were ultrasonically cleaned using acetone, ethanol, and distilled (DI) water in sequence. The seed layer was deposited on FTO/glasses by spin coating a 0.05 M solution composed of Zn acetate.
The NiO flakes were grown on ZnO NRs by a chemical bath deposition, to fabricate ZnO–NiO core–shell-structured NRs. Nickel(II) sulfate hexahydrate (NiSO$_4$$\cdot$6H$_2$O) and potassium persulfate (K$_2$S$_2$O$_8$) powders were dissolved in DI water in an equivalent molar ratio to make growth solutions with molar concentrations of 10–40 mM. After immersing the ZnO NRs grown on the FTO/glass substrate in the NiO growth solution, an appropriate amount of ammonium hydroxide (NH$_4$OH, 28–30%) solution was slowly added under gentle magnetic stirring. After 5 min of growth time, the substrate was taken out and washed with DI water. Finally, the samples were subjected to heat treatment at 400 °C for 1 h at argon (Ar) atmosphere.

Characterizations: The morphology of the samples was observed by field-emission scanning electron microscopy (FE-SEM) with a JEOL JSM-7500FA microscope. The nanoscale microstructure of the samples was observed by TEM) with a JEOL JEM-2010 microscope.

Simulation Details: Numerical simulations were conducted using COMSOL multiphysics software. The height and diameter of a typical ZnO NR were 500 and 30 nm, respectively, and the thickness of the NiO layer was 10 nm. Each material was doped with donor concentration (N$_{D}^{+}$) of 1 $\times$ 10$^{16}$ cm$^{-3}$ in ZnO and acceptor concentration (N$_{A}^{-}$) of 2.6 $\times$ 10$^{18}$ cm$^{-3}$ in NiO. The electric potential in the material is described as follows.

\[ \varepsilon \psi \varepsilon = -q(p - n + N_{D}^{+}) \text{ for } n\text{-type ZnO} \] (2)

\[ \varepsilon \psi \varepsilon = -q(p - n - N_{A}^{-}) \text{ for } p\text{-type NiO} \] (3)

where $\varepsilon$, $\psi$, $q$, $p$, and $n$ are the permittivity of each material, electrical potential, electron charge, hole density, and electron density, respectively.

The governing equation of the piezoelectric effect is described by the coupled equations for strain (S) and electric displacement (D).

\[ S = cT + dE \] (4)

\[ D = dT + \varepsilon E \] (5)

where $c$, $T$, $d$, and $E$ are the compliance tensor, the stress tensor, the piezoelectric tensor, and the electric field, respectively. The piezoelectric tensor with superscript $t$ is the transformation of $d$. The piezoelectric polarization $dT$ is denoted by $\rho_{\text{piezo}}$ generated in the ZnO NR can be coupled to Equation (2) and, finally, the coupled equation is

\[ \varepsilon \psi \varepsilon = -q(p - n + N_{D}^{+} + \rho_{\text{piezo}}) \] (6)

Based on the coupled Equation (6), the electrical potentials of ZnO NR and ZnO–NiO NR were calculated under compressive pressure from 0 to 10 MN m$^{-2}$, and the piezoelectric potential was calculated by subtracting the initial potential at zero pressure from the electrical potential calculated by Equation (6).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.
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