Quantitative modeling, optimization and verification of 63Ni-powered betavoltaic cells based on three-dimensional ZnO nanorod arrays (Postprint)

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Abstract

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Full Text

Quantitative Modeling, Optimization, and Verification of 63Ni-Powered Betavoltaic Cells Based on Three-Dimensional ZnO Nanorod Arrays

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Abstract

Betavoltaic cells (BCs) are promising self-generating power sources with long lifetimes and high power density. However, their low energy conversion efficiency (ECE) limits practical engineering applications. Wide-bandgap semiconductors (WBGSs) with three-dimensional (3-D) nanostructures represent ideal candidates for enhancing the ECE of BCs. This paper proposes hydrothermally-grown ZnO nanorod arrays (ZNRAs) for 63Ni-powered BCs. A quantitative model was established for simulation using parameter values derived from experimental measurements of dark characteristics obtained from a simulated BC based on a Ni-incorporated ZNRAs structure. Monte Carlo (MC) modeling and simulation were conducted to determine the β energy deposited in ZNRAs with varying nanorod spacings and heights. Through simulation and optimization of both 3-D ZNRAs and 2-D ZnO bulk structures, the performance of 63Ni-powered BCs was evaluated using a quantitative model. The BCs based on 3-D ZNRAs and 2-D ZnO bulk structures achieved maximum ECEs of 10.1% and 4.69%, respectively, demonstrating the significant superiority of 3-D nanostructured WBGSs for increasing the ECE of BCs.

Keywords: Betavoltaic cells; Monte Carlo simulation; ZnO nanorod arrays; Quantitative model; Performance evaluation

1. Introduction

The rapid development of wireless sensor networks for harsh environments—including deep sea, deep ground, deep space, and polar and desert regions—has significantly increased demand for micropower sources. Compared with conventional cells (chemical cells, fuel cells, and solar cells), betavoltaic cells (BCs) offer longer lifetimes, stronger environmental adaptability, and higher energy density, making them highly promising for applications with remarkable market potential [1]. Recent reviews on BCs have been published by Olsen et al. [2], Prelas et al. [3], and Spencer et al. [4]. According to Olsen's calculation model, the possible efficiency cap can reach as high as 35% for BCs employing wide-bandgap semiconductors (WBGSs). However, the recorded energy conversion efficiency (ECE) reported for experimental betavoltaics falls far short of 35%

when using available WBGSs. Over the past decades, research on BCs has gained increasing attention, with related experimental studies reporting ECEs on the order of 6% when using available WBGSs (4H-SiC and diamond) [5–9]. To increase the output power (Pout) of BCs, multiple cells have been stacked modularly to generate microwatt-level output power [10]. Nevertheless, the issue of low ECE remains unresolved, hindering the practical engineering applications of BCs. New strategies are needed to further improve the loading and utilization efficiency of radioactive sources in energy conversion structures (ECSs).

It is well understood that ECSs with larger specific surface areas can load more radioactive sources, enabling BCs to generate higher output power. In conventional planar diode structures, ECE and output power density are limited by the low active area of the planar geometry. In contrast, three-dimensional (3-D) nanostructures with larger specific surface areas can significantly enhance β energy conversion through four fundamental mechanisms: (i) filling radioisotope material into the interspaces of 3-D nanostructures substantially increases the loading amount of radioisotope materials; (ii) combining a radioisotope source with 3-D nanostructures enables interaction of β particles with nanostructured ECSs in all directions, dramatically increasing β particle collection efficiency; (iii) self-shielding effects of the radioisotope source are eliminated due to the nanometer-level thickness of the radioactive structure; and (iv) the effective junction region area of the 3-D nanostructure is significantly extended.

Several evaluation studies considering 3-D nanostructures have been conducted based on theoretical analysis or experimental verification. For example, Sun et al. [11] developed a BC based on a 3-D porous silicon p-n diode structure loaded with tritium gas, achieving an ECE of 0.22%—ten times larger than that of a 2-D planar diode structure. Murphy et al. [12] designed a BC based on a 3-D silicon diode structure incorporated with a 147Pm source, which achieved an ECE of 5.8% and power density of 25 mW/cm^3. In our previous studies, WBGS TiO_2 (bandgap = 3.2 eV) and ZnO (bandgap = 3.37 eV) nanostructures were used to fabricate ECSs for BCs [13–19]. Cost-effective anodic oxidation and hydrothermal methods were employed to prepare highly ordered, free-standing nanotube and nanorod array structures, respectively. Using a Nickel-63 (63Ni) sheet as the radioisotope source and electrode, an enhanced betavoltaic effect was observed in the BCs.

Over the last decade, 3-D ZnO nanorod arrays (ZNRAs) have attracted extensive attention due to their large bandgaps, high aspect ratios, and large specific surface areas. Compared with TiO_2, ZnO exhibits longer electron lifetime and higher electron mobility [20], making it one of the most promising electrode materials for photoelectronic devices. For instance, in photodetectors using ZNRAs as photoelectrodes, electrons can be rapidly transported along ZnO nanorods, helping suppress recombination of electron-hole pairs (EHPs) [21]. Additionally, ZNRAs can be synthesized on a wide variety of substrates for versatile electrode preparation [22]. However, devices based on pure ZNRAs suffer from high carrier recombination due to the lack of an effective EHP separation mechanism.

For BCs using ZNRAs, an effective approach is to incorporate metal-based radioactive materials, such as 63Ni or 147Pm, into the interspaces of ZNRAs to form a core-shell structure with a Schottky junction that can efficiently separate EHPs. This approach also significantly increases the loading amount of the radiation source compared with using 63Ni sheets alone, thereby enhancing the Pout of BCs.

Recent studies on optimal design of BCs with 2-D bulk structures have shown that the size and structure of ECSs and the thickness of the radioactive source significantly influence BC performance [23–29]. However, few studies have investigated the influence of 3-D nanostructured ECSs combined with radioactive sources on BC performance. Therefore, an accurate theoretical model must be established to evaluate the performance of BCs based on 3-D nanostructured WBGSs.

This paper proposes a theoretical model for evaluating the performance of BCs based on 3-D nanostructured WBGSs. A freestanding ZNRAs structure combined with normal Ni was used to simulate the ECSs and obtain parameters for dark characteristics. A Monte Carlo (MC) model based on the MCNP code was established to investigate interactions between incident β particles and the ECSs. By combining the theoretical model with experimental data, BCs based on the 63Ni-incorporated ZNRAs structure can be accurately evaluated and further optimized.

2.1. MC Simulation for β Energy Deposition on 3-D Nanostructure

[Figure 1: see original paper] shows schematic diagrams of BCs based on (a) 2-D ZnO bulk structure and (b) 3-D ZNRAs structure.

To design an optimal BC structure, MC simulation [30] was conducted to investigate β radiation interactions with 3-D 63Ni-incorporated ZNRA structures. This study selected 63Ni as the β-emitting source, which has a half-life of approximately 100 years, average energy of 17.4 keV, and maximum energy of 66 keV. Two types of BCs were designed for energy deposition simulation comparison. As shown in [Figure 1: see original paper]a, a sandwich-type BC based on a 2-D ZnO bulk structure consisted of an Al-doped ZnO (AZO)/glass substrate, ZnO film, and 63Ni/Ni layer deposited on the ZnO film. In contrast, the 3-D nanostructured BC consisted of an AZO/glass substrate, 3-D ZNRAs combined with 63Ni, and a top Ni electrode ([Figure 1: see original paper]b).

[Figure 2: see original paper] presents MC modeling and simulation results for 2-D ZnO bulk and 3-D ZNRAs structures under β irradiation, showing scattering trajectories of β particles in (a) 2-D ZnO bulk structure and (e) 3-D ZNRA structure; energy deposition distributions of β particles in (b–c) 2-D ZnO bulk structure and (f–g) 3-D ZNRA structure on y–z and x–y planes; and dependence of energy deposition density and deposition ratio on depth in (d) 2-D ZnO bulk structure and (h) 3-D ZNRAs structure.

To qualitatively understand the interaction of incident β particles with ECSs, 2-D ZnO bulk and 3-D ZNRAs structures were modeled and simulated using the MC method. In this mode, the ZnO thickness was set to 3 m, and the diameter and length of the ZnO nanorods were set to 300 nm and 5 m, respectively. An electron beam with a diameter of 1.8 m and incident angle of 45° along the horizontal direction served as the excitation source, consisting of 1000 β particles with an average energy of 17.4 keV for the 63Ni β particles. The scattering trajectories and energy deposition distribution of β particles in both structures were simulated using CASINO software, as shown in [Figure 2: see original paper]. As shown in [Figure 2: see original paper]a, a fraction of incident β particles was reflected from the bulk ZnO surface, leading to certain energy loss in the 2-D ZnO bulk structure. The energy deposition distributions of incident β particles in the 2-D ZnO bulk exhibited an incident depth of approximately 1.47 m on the y–z plane ([Figure 2: see original paper]b) and an interaction radius of 2.9 m on the x–y plane ([Figure 2: see original paper]c). [Figure 2: see original paper]d shows the dependence of energy deposition density and deposition ratio on depth in the 2-D ZnO bulk structure. The maximum depth of energy deposition is approximately 1.47 m, with an energy deposition ratio reaching 32%. In contrast, the MC simulation yielded different results for the ZNRAs. The scattering behaviors of β particles in the ZNRAs imply higher structural trapping of β particles compared with the 2-D ZnO bulk structure ([Figure 2: see original paper]e). Moreover, simulation results for energy deposition distribution in the ZNRAs ([Figure 2: see original paper]f and 2g) reveal that incident energy can be deposited over a very deep range along the nanorod length due to multiple scattering and absorption of β particles. This is further verified by simulation results for the dependence of energy deposition density and energy deposition ratio on depth in 3-D ZNRAs structures, as shown in [Figure 2: see original paper]h. Compared with the 2-D ZnO structure, the energy deposition depth in the 3-D ZNRAs structure could reach approximately 4.5 m with an energy deposition rate of approximately 85%. This result indicates that 3-D ZNRAs can harvest more β energy in the ECSs compared with 2-D ZnO structures, resulting in higher ECE and Pout for BCs.

[Figure 3: see original paper] shows (a) a schematic energy band diagram of BC based on 63Ni@ZNRAs and (b) the transfer process of β-excited carriers in 63Ni@ZNRAs; (c) energy deposition and deposition ratio of incident β particles for devices based on 63Ni@ZNRAs with different nanorod spacings; (d) energy deposition distribution and deposition ratio of incident β particles for devices based on 63Ni@ZNRAs with different nanorod heights.

[Figure 3: see original paper] illustrates the working principle of BCs based on 63Ni@ZNRAs. A schematic energy band diagram is shown in [Figure 3: see original paper]a. An extended 3-D heterojunction of 63Ni/ZnO is formed with a Schottky contact (Φ_{SBH} = W_m –) at the 63Ni/ZnO interface and an ohmic contact at the AZO/ZnO interface. β particles emitted from the 63Ni source are incident on the ZnO lattice, where impact ionization results in energy deposition and generation of electron-hole pairs (EHPs). The EHPs are

separated by a built-in electric field in the depletion region of the 63Ni@ZnO Schottky junction. In this process, electrons migrate from the conduction band (with energy level E_C) of ZnO to the AZO substrate, while holes are transferred from the valence band (with energy level E_V) of ZnO to the 63Ni electrode [31]. [Figure 3: see original paper]b shows the horizontal EHP separation and longitudinal carrier transport.

To simulate β energy deposition in the ZNRAs with satisfactory accuracy, the MCNP software was used to establish the MC model of 63Ni@ZNRAs. This study employed 63Ni as an isotropic volumetric source integrated into the nanorod gaps, with the number of incident β particles set to 1$×10^{5}$. The β energy deposition in the ZNRAs from radiation emitted by the 63Ni source was simulated using the actual spectrum of emitted electrons. The energy deposition in the ZNRAs was calculated using F8 pulse counting in the MCNP program, and the deposited energy could then be employed to calculate the actual current density using Eq. (2), as described in Section 2.2. The dependence of energy deposition and deposition ratio of incident β particles on nanorod spacing and height is shown in [Figure 3: see original paper]c and 3d, respectively. As nanorod spacing increased, the loading amount of 63Ni increased, leading to higher total β-emitting energy. However, the number of nanorods per unit area decreased as spacing increased, consequently reducing the energy deposition rate. The trade-off reached equilibrium at a spacing of approximately 200 nm, where maximum energy deposition was achieved ([Figure 3: see original paper]c). As nanorod height increased ([Figure 3: see original paper]d), both deposited energy and energy deposition ratio increased, with the energy deposition rate exhibiting a slow increasing trend when height exceeded 4 m.

2.2. Quantitative Modeling for BCs Based on 3-D ZNRAs

A quantitative model must be established to accurately evaluate BC performance. Since the working principle of BCs is similar to that of solar cells, a conventional solar cell theoretical model can be adapted for 3-D nanostructured BCs. When high-energy incident β particles strike the ECSs, multiple electron-hole pairs (EHPs) are generated through impact ionization of β particles with the semiconductor. The EHPs are effectively separated and extracted as the theoretical maximum current density (I_{max}), which can be calculated as follows [32]:

$$I_{max} = \frac{eN_{\beta}\bar{E}_{\beta}}{\psi}$$

where is the ionization energy required to generate an EHP; E_g is the semiconductor bandgap; N_β is the β-emitting flux (N_β = A × 3.7 × 10^7); A is the activity (mCi) of the radioactive source; and $\bar{E}$_β is the average energy of β particles. The ionization energy is given by:

$$\psi = 2.8E_g + 0.5 \text{ eV}$$

The radiation-generated current (I_β) in BCs is given by:

$$I_\beta = I_{max}(1-\gamma)(1-\mu)(1-\sigma)\varphi = \frac{QeE_s}{\psi}$$

where γ is the reflection coefficient of β particles from the semiconductor surface; is the interaction coefficient between the external medium (air or electrode) and incident β particles; σ is the self-absorption coefficient of the radioactive source, related to the source thickness; and ϕ is the scattering angle coefficient of the radioactive source, defined as the ratio of incident particles on the semiconductor to the total number of emitted β particles. For 3-D ZNRAs, $\gamma = 0$, $= 0$, $\phi = 1$, e is the electron charge (e = 1.6$×10^{-19}$ C), and E_s is the β energy deposited in the semiconductors. Q is the collection efficiency, defined as the ratio between the number of effective carriers forming current in the devices and the total number of carriers produced by impact ionization of incident β particles with the semiconductors. Here, Q represents the collection efficiency of carriers in the space-charge region of the Schottky junction, which is approximately 100%; the collection efficiency of carriers outside the space-charge region can be calculated as follows [33]:

$$Q = \tanh\left(\frac{d}{L}\right)$$

where d is the distance the carrier travels to the depletion region boundary and L is the minority carrier diffusion length.

The width of the Schottky junction space-charge region can be calculated as follows [34]:

$$W = \sqrt{\frac{2\varepsilon_0\varepsilon_s(\Phi_{SBH} - V)}{eN_D}}$$

where $_0$ is the vacuum dielectric constant; _s is the semiconductor relative dielectric constant; N_D is the ZnO carrier concentration (approximately 2.1$×10^{15}$ cm^{-3}); and Φ_{SBH} is the height of the Ni@ZnO Schottky barrier (Φ_{SBH} = W_m - = 0.8 eV), representing the theoretical difference between the Ni work function (W_m = 5.15 eV) and ZnO electron affinity energy (= 4.35 eV).

From Eq. (5), the width of the depletion region for the Ni@ZnO Schottky barrier can be calculated as approximately 6.04$×10^{-1}$ m. Since the average diameter of ZnO nanorods grown using the hydrothermal method (approximately

0.3 m) is smaller than the depletion region width, Q is approximately equal to 1 for BCs based on the 63Ni@ZNRAs structure.

Figure S1 shows the equivalent circuit model of BCs (Supporting Information). The current density (I) delivered to the load resistor (R_L) at voltage V can be calculated as follows [35]:

$$I = I_\beta - I_0 \left[\exp\left(\frac{e(V + IR_s)}{nK_T} \right) - 1 \right] - \frac{V + IR_s}{R_{sh}}$$

where I_0 and n are the reverse saturation current and ideal factor of the Schottky diode, respectively; K_T is the thermal voltage; R_s and R_{sh} are the series and shunt resistances of the BC equivalent circuit, respectively. For the specific BC based on 3-D ZNRAs prepared for subsequent experiments, I_0, n, and R_s were extracted from its I-V curve measured under dark conditions, and the ideal R_{sh} was set to infinity. Since greater nanorod height and smaller nanorod density result in larger R_s, and both I_0 and R_s are variables related to structural parameters of 3-D ZNRAs—such as Schottky junction area (S), nanorod array density (D), and nanorod height (H)—two factors (δ and α) are combined with I_0 and R_s in Eqs. (6–7). Thus, H_0 and D_0 represent the structural parameters of the specific 3-D ZNRAs structure.

The maximum short-circuit current (I_{sc}) of BCs was calculated using Eq. (6). The open-circuit voltage (V_{oc}) of BCs can be calculated as:

$$V_{oc} = \frac{nK_T}{e} \ln\left(\frac{I_{sc}}{I_0} + 1 \right)$$

where k is the Boltzmann constant (k = 1.38×10^{-23} J/K), T is the thermodynamic temperature at room temperature (T = 300 K), I_0 is the reverse saturation current, and n is the ideal factor.

The maximum output power (P_{max}), fill factor (FF), and energy conversion efficiency ( ) can be expressed as follows [36]:

$$P_{max} = I_{mp} V_{mp}$$

$$FF = \frac{P_{max}}{I_{sc} V_{oc}} = \frac{I_{mp} V_{mp}}{I_{sc} V_{oc}}$$

$$\eta = \frac{P_{max}}{P_\beta} \times 100\% = \frac{eN_0 \bar{E}_\beta}{P_\beta} \times 100\%$$

where I_{mp} and V_{mp} are the current and voltage corresponding to P_{max}; P_β is the total power of the radioactive source; and N_0 is the

total number of β particles (N_0 = 3.7$×10^{7}$×Φ, where Φ is the activity of the radioactive source) emitted from the source.

2.3. Preparation of BCs Based on 3-D ZNRAs Nanostructure

The preparation process for the Ni-incorporated ZNRAs structure is shown in [Figure 4: see original paper]a. ZNRAs were grown on Al-doped ZnO (AZO) conductive glass (R $\leq$ 6 Ω, Nanotech, China) using a hydrothermal method [16]. First, the AZO conductive glass was cleaned in an ultrasonic bath using CH_3COCH_3, ethanol (C_2H_5OH), and deionized water for 15 min. After drying, the designated electrode region on the AZO glass substrates was covered with high-temperature tape, and the substrates were transferred to a reactor containing 10 ml of growth solution consisting of 0.05 M zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$], 0.05 M hexamethylenetetramine (HMTA, $(CH_2)_6N_4$), 0.02 M polyetherimide (PEI), and deionized water. The hydrothermal treatment temperature was maintained at 95 °C for 4 h. Next, the samples were cleaned with deionized water and dried at 150 °C for 10 min. Finally, the samples were soaked in 10% hydrogen peroxide (H_2O_2) for 1 min for surface passivation, then annealed in air at 400 °C for 2 h to obtain the ZNRAs [37]. H_2O_2 passivation treatment can reduce surface defects of ZnO nanorods, improving Schottky diode characteristics. Ni incorporation into the ZNRAs was performed using direct current (DC) magnetron sputtering. The vacuum chamber was evacuated to 5$×10^{-6}$ Pa, then Ar gas was introduced to reach a constant pressure of 0.6 Pa. Subsequently, Ni nanoparticles were deposited onto the ZNRAs using 400 W DC power at room temperature for 9 min. [Figure 4: see original paper]b shows a 3-D exploded diagram of the device based on the Ni-incorporated ZNRAs structure. For I-V measurements, a planar Ni sheet was mechanically compressed onto the sample surface to form a sandwich-type device with a Ni/Ni@ZNRAs/AZO/glass structure.

2.4. Material Characterization and Device Measurements

Scanning electron microscopy (SEM, ZEISS microscope, Germany) and energy-dispersive X-ray spectroscopy (EDS) were used to analyze sample morphology and chemical composition. Crystal structures were characterized by X-ray diffraction (XRD, D8 Advance, Bruker, Germany), and I-V measurements were performed in a Faraday cage using a Keithley Model 2450 source meter.

3.1. Experimental Results and Discussion

[Figure 5: see original paper] shows (a) XRD spectra of the Ni@ZNRAs structure; (b) cross-sectional and (c) top-view SEM images of ZNRAs; (d) cross-sectional and (e) top-view SEM images of the Ni@ZNRAs structure; and (f–h) EDS mappings of Zn, Ni, and O.

The XRD pattern of the Ni@ZNRA structure is shown in [Figure 5: see original paper]a. All diffraction peaks can be indexed to the hexagonal wurtzite structure of ZnO (JCPDS card No. 36-1451) and the cubic structure of Ni (JCPDS card No. 70-1849). The typical 2 peaks at 34.4° and 36.3° correspond to the (002) and (101) planes of ZnO, respectively. No new diffraction peaks were observed in the Ni@ZNRA structure, indicating that Ni introduction did not alter the ZnO nanorod crystal structure. The preferred growth direction of the ZnO (002) crystal plane is c-axis orientation perpendicular to the substrate, as verified by cross-sectional and top-view SEM images of the ZNRAs ([Figure 5: see original paper]b and 5c). The average nanorod diameter and height are 300 nm and 4 m, respectively. Cross-sectional and top-view SEM images of the Ni@ZNRAs are shown in [Figure 5: see original paper]d and 5e. Ni particles were uniformly filled into the gaps between ZnO nanorods and stacked to form a continuous Ni layer covering the ZNRAs surface. SEM-EDS mappings show that Ni was adequately distributed on the ZnO nanorod surfaces, forming a core-shell structure ([Figure 5: see original paper]f–h).

[Figure 6: see original paper] shows dark characteristics of devices based on the Ni@ZNRAs/AZO structure: (a) linear-scale I-V curve in the bias voltage range of -2.5–2.5 V; (b) logarithm-scale I-V curve in forward bias; (c) dV/d(lnI)-I curve.

[Figure 6: see original paper] presents the dark characteristics of devices based on the Ni@ZNRAs/AZO structure. A typical Schottky diode I-V curve is shown in [Figure 6: see original paper]a, confirming the existence of the Ni/ZnO Schottky junction. The reverse saturation current of the device is 4.2$×10^{-11}$ A/cm^2, determined by extrapolating the linear region of the logarithm-scale I-V curve in forward bias to zero bias voltage ([Figure 6: see original paper]b). The ideal factor n and series resistance R_s of the Schottky diode can be extracted from the dependence of dV/d(lnI) on current ([Figure 6: see original paper]c) [38]. The extracted n and R_s values are 6.96 and 248.45 Ω, respectively. This ideal factor n greater than 2 indicates that the Ni@ZNRAs junction quality is imperfect due to crystal defects or insufficient Ni filling in the ZNRAs [39–40]. Fig. S2 (Supporting Information) shows the I-V curve of devices based on the Ni@ZNRAs/AZO structure before H_2O_2 passivation, with a calculated n value of 11.2. The n value before passivation is significantly larger than after passivation, indicating that H_2O_2 passivation substantially improves diode quality. Large quantities of interface defects in ZnO nanorods may deteriorate Schottky device rectification characteristics, increasing reverse saturation current and ideal factor. This increase in reverse saturation current decreases open-circuit voltage, reducing output power as calculated using Eq. (8). This demonstrates that H_2O_2 passivation improves BC output power. To evaluate the electrical performance of BCs based on the 63Ni@ZNRAs structure, the aforementioned Schottky diode parameter values are used in the quantitative BC model described in Section 2.2.

lists the parameter values applied to the quantitative BC model. Notably, these

parameter values can be controlled and adjusted during ZNRAs growth using the hydrothermal method. Tao et al. [41] developed a combined lithography-assisted and hydrothermal growth approach to selectively control ZNRAs spacing and size on the ZnO seed layer. Sinem et al. [42] prepared ZNRAs with nanorod lengths exceeding 60 m by adjusting ammonium hydroxide and polyethyleneimine contents using a hydrothermal synthesis method. This means optimal nanorod parameter values—such as diameter, height, and density—can be prepared by adjusting process parameters including ZnO seed density, reactant concentration, reaction time and temperature, and pH values [43].

3.2. Simulated Results and Discussion

Using the fixed parameter values listed in and an average nanorod height of 4 m, the calculated I-V and P-V characteristics of BCs based on the 63Ni@ZNRAs structure with different nanorod spacings are shown in [Figure 7: see original paper]a and 7b, respectively. By extracting P_{max} from [Figure 7: see original paper]b and calculating ECE according to the total activity of 63Ni incorporated into the ZNRAs gaps, the dependences of P_{max} and ECE on variable nanorod spacing can be obtained, as shown in [Figure 7: see original paper]c. As nanorod spacing increases, the activity of 63Ni incorporated into the nanorod gaps also increases, resulting in rapid output power increase. However, as nanorod spacing increases further, nanorod density decreases, reducing energy deposited on the ZNRAs and thus decreasing output power. A maximum P_{out} of 875.4 nW/cm^2 was achieved, corresponding to I_{sc} = 676.2 nA/cm^2 and V_{oc} = 1.85 V, with FF = 0.699 and = 6.07%. In contrast, [Figure 7: see original paper]c shows a monotonic decline in the ECE curve as nanorod spacing increased. The ECE reached a maximum value of 9.3% when spacing was set to 40 nm.

The effects of nanorod height on ECE and P_{max} of BCs were investigated under optimal nanorod spacing. [Figure 7: see original paper]d and 7e show the calculated I-V and P-V characteristics of BCs based on the 63Ni@ZNRAs structure with different nanorod heights. I_{sc} increased with nanorod height, while V_{oc} remained constant at 1.62 V. [Figure 7: see original paper]f shows the dependence of P_{max} and ECE of BCs on nanorod height. The energy deposition ratio increased slowly when nanorod height exceeded 4 m ([Figure 3: see original paper]d), resulting in a slow approach to saturation of the energy conversion efficiency. As nanorod height increased, ECE tended toward a saturation value of approximately 10%, and a maximum P_{out} of 1185.9 nW/cm^2 was achieved at a height of 10 m, corresponding to a loading amount of 114.37 mCi, I_{sc} of 1081.2 nA/cm^2, and FF of 0.673. Although long nanorods are beneficial for increasing output power, fully depositing 63Ni into high-aspect-ratio ZNRAs structures is difficult in practical operation. Therefore, experimental investigation is required to determine the practical deposition depth of 63Ni on ZNRAs.

To verify the advantages of 3-D nanostructures in enhancing the betavoltaic effect, a BC based on a 2-D ZnO bulk structure was investigated for comparison with BCs based on a 3-D ZNRAs structure, as shown in [Figure 1: see original paper]a. According to MC simulation, the energy deposition depth of incident β particles in 2-D ZnO bulk is approximately 1.5 m. The dependence of energy deposition and deposition ratio of incident β particles on 63Ni thickness is shown in [Figure 8: see original paper]a. As 63Ni thickness increases, the self-absorption effect of the radiation source shields β particles emitted from deep within the source, reducing the deposition ratio. Energy deposition tended to saturate when thickness exceeded 1.5 m. The dependences of P_{max} and ECE of BCs based on 2-D ZnO bulk on 63Ni thickness were investigated, as shown in [Figure 8: see original paper]b. As 63Ni thickness increased from 50 nm to 150 nm, energy conversion efficiency increased from 4.05% to 4.69% due to increased deposited energy. As 63Ni thickness increased further beyond 150 nm, the self-shielding effect of the radiation source became significant, reducing the energy deposition ratio and thus decreasing energy conversion efficiency. P_{max} tended toward saturation (approximately 135.2 nW/cm^2) when 63Ni thickness reached 2 m. Beyond this thickness, the self-shielding effect of the radioactive source limits continued output power increase. The maximum ECE reached 4.69% at a 63Ni thickness of 150 nm, as expressed by Eq. S8 (Supporting Information).

compares performance between BCs based on 3-D ZNRAs and 2-D ZnO bulk. BCs based on 2-D ZnO film generated higher V_{oc} (1.87 V), attributed to lower reverse saturation current compared with 3-D ZNRAs. However, due to low radioactive source utilization efficiency, β energy deposited in the semiconductor decreased dramatically, resulting in lower I_{sc} (28.1 nA/cm^2) and P_{max} (36.8 nW/cm^2), leading to a low ECE of 4.69% compared with BCs based on 3-D ZNRAs. According to the Shockley–Queisser limit for photovoltaics [44], the efficiency cap of BCs is predicted to be as high as 13%, calculated by = V_{oc}·FF/ . This means that 3-D ZNRAs with optimal structural design are significantly superior and can be used to prepare BCs approaching their upper limits.

4. Conclusion

In summary, 3-D nanostructured WBGSs are ideal candidates for increasing the ECE and output power of BCs. To evaluate and verify their advantages as highly efficient β-energy-conversion structures, this study established a quantitative model for 63Ni-powered BCs based on freestanding ZNRAs and performed MC modeling and simulation to obtain deposited energy and maximum energy deposition depth. In experiments, a BC based on a Ni-incorporated ZNRAs structure grown using the hydrothermal method was simulated to obtain dark characteristic parameter values. By optimizing and simulating BCs based on both 3-D ZNRAs and 2-D ZnO bulk structures, the performance of 63Ni-powered BCs was evaluated using the quantitative model and experimen-

tal parameter values. This study found that the optimal nanorod spacing for BCs based on 3-D ZNRAs was 40 nm for maximum energy conversion efficiency and 200 nm for maximum output power. BCs based on 3-D ZNRAs achieved a maximum ECE of 10.1% and maximum output power of 1185.9 nW/cm^2. In contrast, BCs based on 2-D ZnO bulk achieved only 4.69% and approximately 135.2 nW/cm^2, respectively. These results confirm the significant superiority of 3-D nanostructured WBGSs for increasing the ECE and output power of BCs.

Author Contributions

All authors contributed to study conception and design. Material preparation, data collection, and analysis were performed by Zan Ding, Tong-Xin Jiang, Ren-Rong Zheng, and Na Wang. The first draft of the manuscript was written by Zan Ding. Writing-review and editing were performed by Hai-Sheng San. Project administration and source support were provided by Li-Feng Zhang, Shi-Chao Liu, Xin Li, and Hai-Sheng San. All authors read and approved the final manuscript.

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