Supplementary file

Mechanism of polarization and voltage generation in boron nitride nano-ribbon

1. Theoretical background

In general, materials used for energy storage applications are categorized into four kinds based on polarizability: ferroelectric (has spontaneous electric polarization, and the direction of the electric polarization can be reversed by applying an external electric field), pyroelectric (has spontaneous electric polarization and the direction of the spontaneous electric polarization can be changed by cooling or heating), piezoelectric (the direction of the electric polarization can be changed by applying an external force), and dielectric (has no spontaneous electric polarization; however, until existence an external electric field, dielectric has electric polarization) [1,2]. The relationships between these materials can be explained based on figure 1.
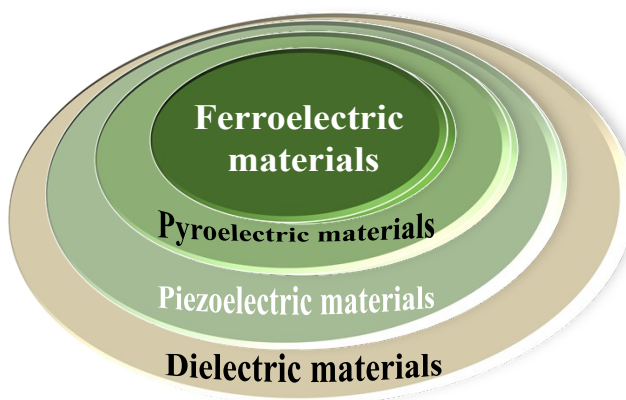

Figure 1. The relationships between ferroelectric, pyroelectric, piezoelectric, and dielectric materials

The total polarizability can be split into three parts: electronic, ionic, and dipolar polarizabilities [3,4]. In a solid crystal, the total polarizability of the particles (atoms, ions, and molecules) can be written as below [3,4]:

$$\vec{P}_{Total} = \vec{P}_{Electronic} + \vec{P}_{Ionic} + \vec{P}_{Dipolar} \tag{1}$$

Here, $\vec{P}_{Total}$ is the particles' total polarizability. $\vec{P}_{Electronic}$ represents the electronic polarizability and arises owing to the relative displacement between the shell (electrons) and core (protons). $\vec{P}_{Ionic}$ depicts ionic polarizability and occurs due to the relative separation between anions and

cations). $\vec{P}_{Dipolar}$ points the dipolar polarizability and happens when the molecules with a permanent electric dipole moment exist (for example H_2O).

2. Obtaining boron nitride nanoribbons polarization

Boron nitride nanoribbons (BNNRs) are classified as piezoelectric materials. The direction and magnitude of the electric polarization in these nanoribbons change when the external forces or stresses apply to the sample [5–7]. On the contrary, applying an external electric field to piezoelectric materials changes stress and creates strain [3]. These statements can explain why materials in a ferroelectric state are also piezoelectric (figure 1). To describe how the electric polarization vector creates in BNNR, the total polarizability of this material should be determined. In this respect, the share of $\vec{P}_{Electronic}$ can be neglected because the rigid ion approximation is used in the current study [8–10]. Thereby the contribution of the clamped ion term is zero, and there is no polarization between the shell and core. Moreover, the share of $\vec{P}_{Dipolar}$ is negligible because the frequency of BNNR is within the ultraviolet region [3,10–12]. Therefore, only $\vec{P}_{Ionic}$ remains, and the total polarizability of BNNR ($\vec{P}_{Total}^{BNNR}$) can be rewritten as below:

$$\vec{P}_{Total}^{BNNR} = \vec{P}_{Ionic} \tag{2}$$

For more clarification concerning how BNNR can obtain polarization, the effects of piezoelectric domains should be described. Figure 2 illustrates a relaxed (stress-free) BNNR with width×length $Å^2$ surface area (step 01) and the computation process of the total polarization vector (step 02-06). In each hexagonal cell (honeycomb cell), the cell ionic polarization vector is defined with respect to the relative distance between boron (B) and nitrogen (N) ions. It is worth mentioning that the polarization share of each B or N ion in each hexagonal cell is one-third (1/3). The sum of all ionic dipole moments in each hexagonal cell leads to creating the cell ionic polarization vector. The summation process performs using the principle of superposition of the vectors. Eq. (3) demonstrates how the cell ionic polarization vector obtains from ionic dipole moments in each cell (figure 2 step 02-03).

$$\vec{P}_{Ionic}^{cell,j} = \frac{1}{3}\sum_{i=1}^{3}\sum_{\alpha} \vec{P}_{Ionic}^{i,\alpha} \tag{3}$$

Here $\vec{P}_{Ionic}^{cell,j}$ is the cell ionic polarization vector, and the j represents the jth cell. $\vec{P}_{Ionic}^{i,\alpha}$ is the ionic dipole moment, i point to nitrogen ions in each hexagonal cell, and α containing a, b, and c represents the vector of ionic dipole moments for each nitrogen ion (step 03). The result of Eq. (3) for each stress-free BNNR hexagonal cell is almost zero because, based on the principle of

superposition of the vectors, all $\vec{P}_{Ionic}^{i,\alpha}$ remove each other (step 04). Therefore, the piezoelectric domain vectors obtained from summation on $\vec{P}_{Ionic}^{cell,j}$ are also negligible (step 05). The piezoelectric domain vectors calculate based on the below equation.

$$\vec{P}_{Ionic}^{domain,k} = \sum_{j=1}^{N} \vec{P}_{Ionic}^{cell,j} \tag{4}$$

Where $\vec{P}_{Ionic}^{domain,k}$ is the piezoelectric domain polarization vector, and the k represents the kth domain. N is the number of all hexagonal cells. Similarly, the total polarization vector of BNNR ($\vec{P}_{Total}^{BNNR}$) is almost zero because obtained from summation on $\vec{P}_{Ionic}^{domain,k}$ based on the below equation (step 06):

$$\vec{P}_{Total}^{BNNR} = \sum_{k=1}^{N^{'}} \vec{P}_{Ionic}^{domain,k} \tag{5}$$

Here $N^{'}$ is the number of all piezoelectric domains. Therefore, it can be concluded that for stress-free BNNR, the total polarizability is negligible.

Relaxed (stress-free) boron nitride nanoribbon (BNNR)

Step 01

Length (Å)

Width (Å)

Z: [001]
Y: [010]

Step 02

Nitrogen (N): negative ion (anion)

Boron (B): positive ion (cation)

Vector of ionic dipole moment

Step 05

The sum of all cell ionic polarization vectors ($\vec{P}_{Ionic}^{cell,j}$) lead to creating domain polarization vector ($\vec{P}_{Ionic}^{domain,k}$).

Step 06

The sum of all domain polarization vectors ($\vec{P}_{Ionic}^{domain,k}$) creates the sample polarization vector ($\vec{P}_{Total}^{BNNR}$).

Step 03

The sum of all ionic dipole moments ($\vec{P}_{Ionic}^{i,\alpha}$) in each hexagonal cell leads to creating the cell ionic polarization vector ($\vec{P}_{Ionic}^{cell,j}$).

The summation process performs using the principle of superposition of the vectors.

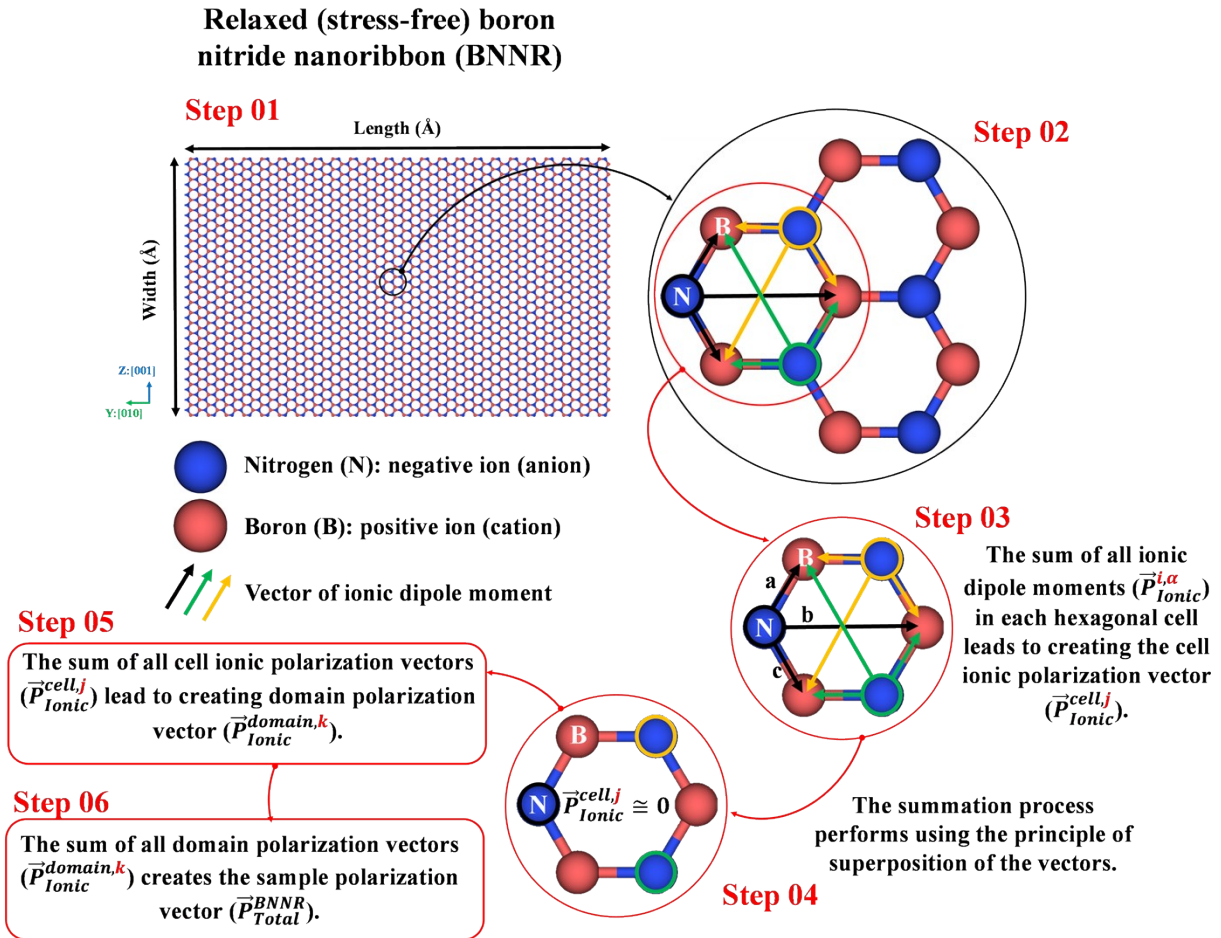$\vec{P}_{Ionic}^{cell,j} \cong 0$

Step 04

Figure 2. A relaxed (stress-free) BNNR with width×length Å² surface area and the computation process of the total polarization vector.

However, when the stress or strain is applied to the sample as a consequence of external forces, the situations are entirely different. When BNNR is strained or buckled or rotated, the polarization vectors differ from stress-free BNNR. Figure 3 illustrates a buckled BNNR. This structure has been obtained after applying buckling to stress-free BNNR in figure 2. It is clear from the figure that after applying buckling, the $\vec{P}_{Ionic}^{i,\alpha}$ cannot neutralize each other (step 02); thereby, each cell can earn $\vec{P}_{Ionic}^{cell,j}$ (step 03). The sum of all $\vec{P}_{Ionic}^{cell,j}$ leads to creating $\vec{P}_{Ionic}^{domain,k}$ (step 04 and 05), and by summation on the domain polarization vectors, the $\vec{P}_{Total}^{BNNR}$ is obtained (step 06). Therefore, it can be concluded that for buckled BNNR, both $\vec{P}_{Ionic}^{domain,k}$ and $\vec{P}_{Total}^{BNNR}$ have impressive values.
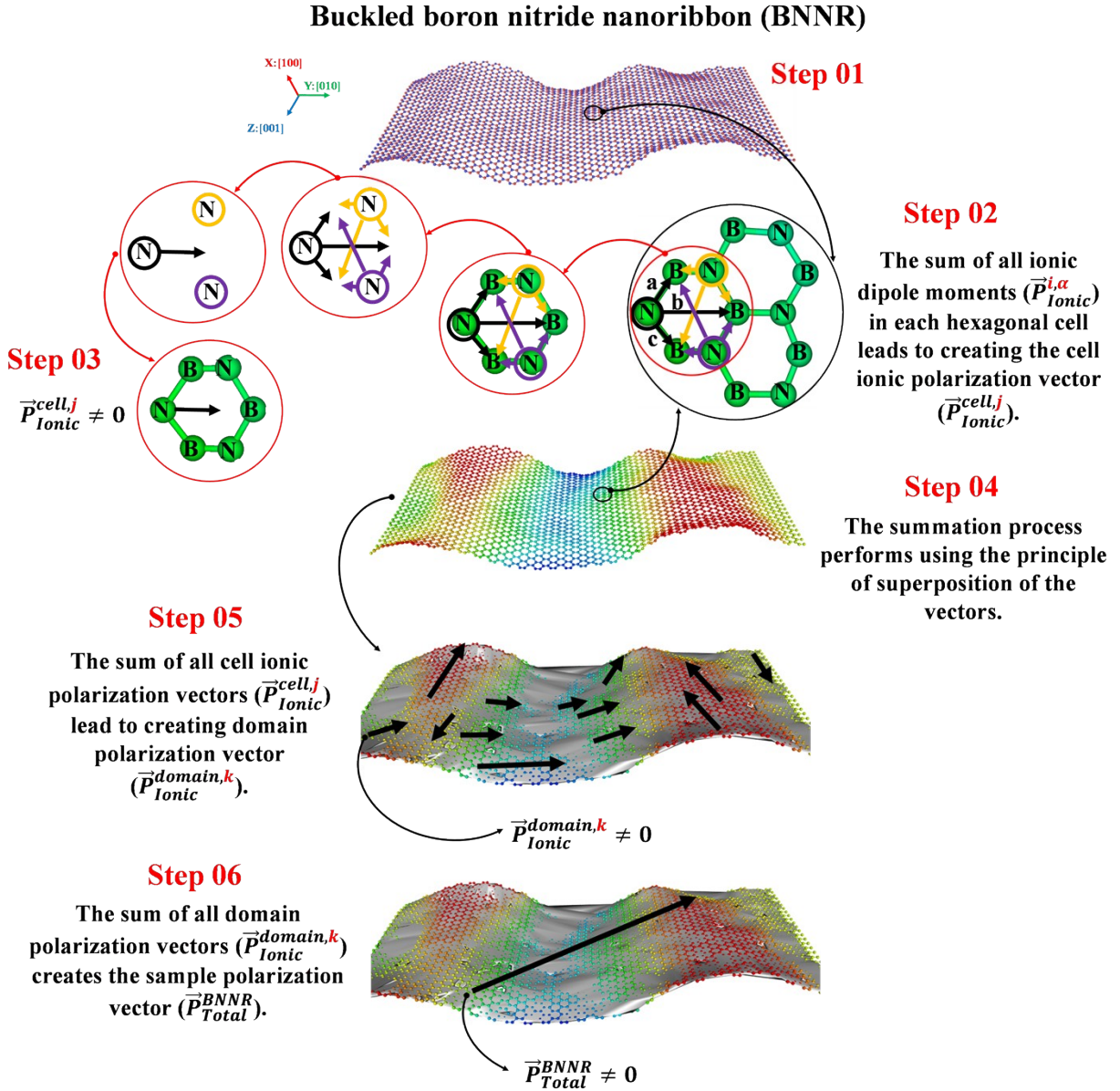
Buckled boron nitride nanoribbon (BNNR)

Step 01

Step 02

The sum of all ionic dipole moments ($\vec{P}_{Ionic}^{i,\alpha}$) in each hexagonal cell leads to creating the cell ionic polarization vector ($\vec{P}_{Ionic}^{cell,j}$).

Step 03

$\vec{P}_{Ionic}^{cell,j} \neq 0$

Step 04

The summation process performs using the principle of superposition of the vectors.

Step 05

The sum of all cell ionic polarization vectors ($\vec{P}_{Ionic}^{cell,j}$) lead to creating domain polarization vector ($\vec{P}_{Ionic}^{domain,k}$).

$\vec{P}_{Ionic}^{domain,k} \neq 0$

Step 06

The sum of all domain polarization vectors ($\vec{P}_{Ionic}^{domain,k}$) creates the sample polarization vector ($\vec{P}_{Total}^{BNNR}$).
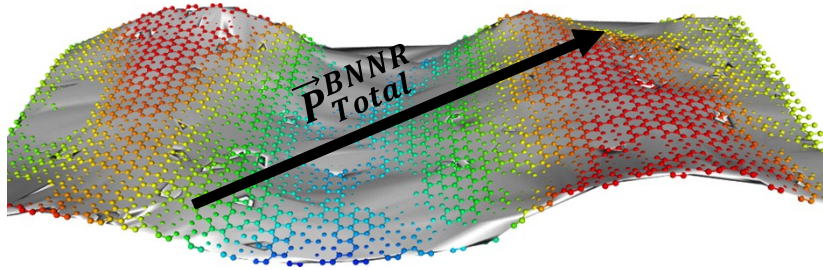
$\vec{P}_{Total}^{BNNR} \neq 0$

Figure 3. A buckled BNNR. This structure has been obtained after applying buckling to stress-free BNNR in figure 2. The computation process of the total polarization vector has been indicated from step 01 to 06.

3. Calculating voltage based on boron nitride nanoribbons polarization

The macroscopic electric field ($\vec{E}$) must be defined first to calculate the voltage. In BNNR as a piezoelectric material, the $\vec{E}$ arises from $\vec{P}_{Total}^{BNNR}$ in the absence of an external electric field. Using the famous theorem of electrostatics [3,13–16], it can be proved that the $\vec{E}$ caused by a uniform $\vec{P}_{Total}^{BNNR}$ is equal to the electric field in the vacuum of a fictitious surface charge density σ if the σ be equal to $\hat{n}.P_{Total}^{BNNR}$ where $\hat{n}$ is the unit normal to the surface. The $\hat{n}$ is drawn outward from the

polarized BNNR and is parallel with $\vec{P}_{Total}^{BNNR}$. Figure 4 depicts the polarized BNNR and two uniformly charged parallel plates. The provided $\vec{E}$ by both structures is identical.

(a)

(b)

$\sigma = +P$

$\sigma = -P$

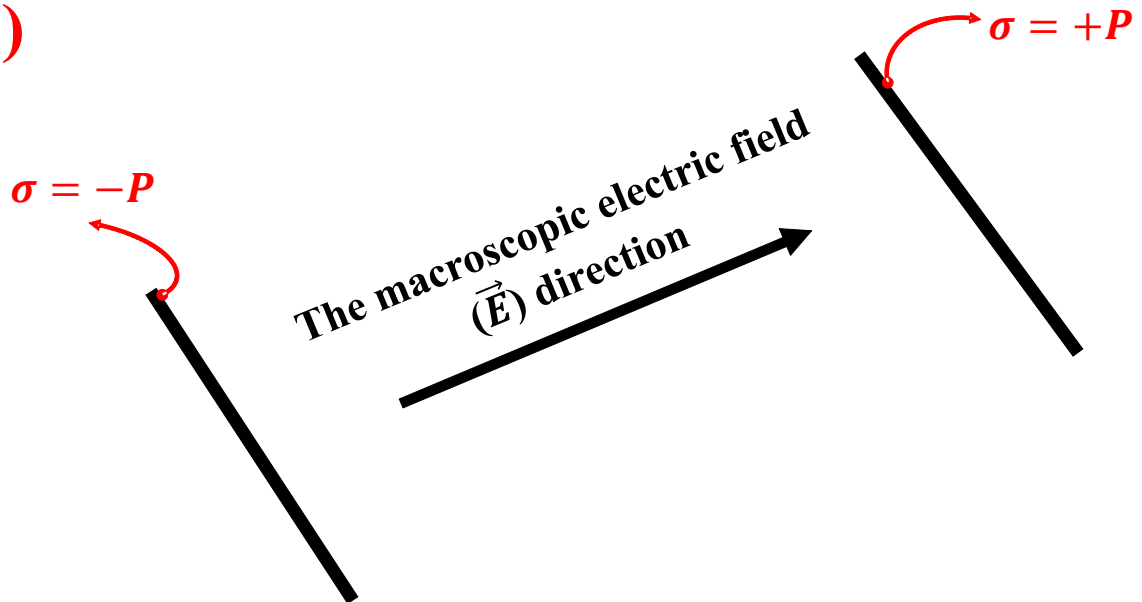The macroscopic electric field $(\vec{E})$ direction

Figure 4 (a) The polarized BNNR, and (b) two uniformly charged parallel plates. The provided $\vec{E}$ by both structures is identical.

Using Gauss's law [13,16], the $\vec{E}$ at each point between the plates is calculated as below:

$$\oint \vec{E} \cdot \vec{ds} = \frac{q_{enc}}{\varepsilon_0} \tag{6}$$

$$E = -\frac{q_{enc}}{\varepsilon_0 A} \rightarrow E = -\frac{\sigma}{\varepsilon_0} \xrightarrow{|\sigma| = |\vec{P}_{Total}^{BNNR}|} E = -\frac{|\vec{P}_{Total}^{BNNR}|}{\varepsilon_0} \tag{7}$$

$$\vec{E} = - \frac{|\vec{P}_{Total}^{BNNR}|}{\varepsilon_0} P_{Total}^{BNNR} \tag{8}$$

Here, ds is the element of the surface, q_{enc} is the total charge enclosed within Gauss's surface, and A is the Gauss's surface area. $\vec{E}$ is smoothly changing in space outside and inside the BNNR and satisfies Maxwell's rules [13–16] as written for the macroscopic electric field.

Now, the voltage can be obtained from $\vec{E}$. The relation between $\vec{E}$ and voltage (V) can be written as below based on electromagnetic theories.

$$\vec{E} = - \vec{\nabla}V \tag{9}$$

$$V = - \int \vec{E} \cdot \vec{dr} \tag{10}$$

Where $\vec{\nabla}$ and dr are gradient operator and the length element, respectively. The voltage can be obtained by replacing the $\vec{E}$ from Eq. (8) in Eq. (10).

$$V = \int - \frac{|\vec{P}_{Total}^{BNNR}|}{\varepsilon_0} P_{Total}^{BNNR} \cdot \vec{dr} \tag{11}$$

Here, dr is the length element of buckled (strained or rotated) BNNR. After any structure variation (such as buckling, strain, and rotation), the $\vec{P}_{Total}^{BNNR}$ gets a constant value and direction and can get out from the integral. Therefore:

$$V = |\vec{P}_{Total}^{BNNR}| \int \frac{|\vec{dr}|}{\varepsilon_0} (P_{Total}^{BNNR} \cdot \hat{dr}) \tag{12}$$

The above equation describes that the provided voltage by piezoelectric BNNRs is dependent on total polarizability ($|\vec{P}_{Total}^{BNNR}|$), length of BNNR ($|\vec{dr}|$), the direction of the polarization vector (P_{Total}^{BNNR}), and the direction of voltage harvesting ($\hat{dr}$). For $P_{Total}^{BNNR} \cdot dr = 1$, and the length of BNNR equal to L, the voltage can be rewritten as below:

$$V = |\vec{P}_{Total}^{BNNR}|L \tag{13}$$

The obtained value in Eq. (13) will change after each structure variation of piezoelectric; thereby, electrical consumers cannot use this produced voltage directly. In this respect, the electrical circuits containing the battery, capacitor, diode, resistance, et cetera, are required for increasing and storing voltage. Afterward, this stable voltage can be used by electrical consumers.

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