Stable H-Terminated Edges, Variable Semiconducting Properties, and Solar Cell Applications of C₃N Nanoribbons: A First-Principles Study

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ABSTRACT: Motivated by the recent synthesis of the graphene-like C₃N nanosheet, the geometrical structures and electronic properties of its ribbon form, that is, C₃N nanoribbons (C₃NNRs), are investigated by first-principles calculations. It is found that there are five types of energetically favorable H-terminated edges in the C₃NNRs. Different from graphene nanoribbons, the corresponding stable C₃NNRs are all non-magnetic semiconductors regardless of the edge shape and termination. However, their band feature and gap size can be modulated by the ribbon width and edge termination, which brings direct-, quasi-direct-, and indirect-band-gap semiconducting behaviors in the nanoribbons. Comparing to the C₃N nanosheet, the work function is reduced in the C₃NNRs with fully di- and monohydrogenated edges, which results in a type-II band alignment with SiC and silicane nanosheets. More interestingly, the combined hetero-nanostructures will be promising excitonic solar cell materials with high power conversion efficiencies up to 17–21%. Our study demonstrates that the C₃NNRs have distinct edge stabilities and variable semiconducting behaviors, which endow fascinating potential applications in the fields of solar energy and nanodevices.

1. INTRODUCTION

Carbon nitride nanomaterials have attracted abundant scientific attention because of their variable chemical composition and promising electronic properties for wide-range applications.²⁻³ Two-dimensional (2D) C₃N₈,⁴ C₃N₁₂,⁵ and C₃N₁₅ nanosheets have already been synthesized in the experiments, which are nitrogenated holey honeycombs with different nanopore sizes. Versatile electronic and magnetic properties are found in these carbon nitrides, which are related to the holey geometrical characteristic.⁶⁻⁹ Besides that, porous C₃N₁₂,¹⁰ C₃N₁₄,¹¹ C₃N₁₅,¹² and C₃N₁₃ nanosheets have also been theoretically proposed, which possess unique electronic and topological properties as functional carbon nitrides. The hole-free structure is found to be dynamically unstable in the CN honeycomb,¹⁴ which only appears in the C-rich case. Starting from the N-doped graphene, 2D C₋₋₋₋Nₓ alloy can maintain the hexagonal lattice up to the N concentration of δ = 1/3.¹⁵ Interestingly, for δ = 1/4, an ordered CₓN arrangement is predicted to be the ground state structure of the graphene-like C₋₋₋₋Nₓ system.¹⁶⁻¹⁸ This CₓN structure is isostructural to the CₓB,y,²⁰⁻²¹ and CₓSi,y,²²⁻²⁴ nanosheets, where C atoms compose the separated Cₓ hexagons that are interconnected by N atoms. Very recently, utilizing the direct solid-state reaction of organic molecules, experimenters have synthesized this theoretically predicted CₓN nanosheet.²¹⁻²³ Such a graphene-like CₓN nanostructure is an indirect narrow-band-gap semiconductor with a high hole carrier mobility up to 10⁴ cm²/V s.²⁴⁻²⁶ The electronic structure of CₓN nanosheet can be tailored by vacancy defects and surface decorations, which would convert it into a metal or a magnetic semiconductor.²⁷⁻³⁰ Compared to the monolayer CₓN nanosheet, the band gaps of bi- and trilayer ones are pronouncedly reduced because of the strong interlayer interaction.³¹⁻³² When stacked with arsenene monolayer, the CₓN nanosheet can form a type-II van der Waals heterostructure, whose band gap is well modulated by the vertical strain and external electric field.³³ For the CₓB/CₓN hetero-bilayer, it even exhibits a Dirac fermion behavior akin to the bilayer graphene.³⁴ Besides that, the phononic thermal transport property has also been systematically studied in the CₓN nanosheet, whose lattice thermal conductivity is found to be much lower than the value of graphene but still higher than the ones of BN, MoS₂, MoSe₂, and phosphorene systems.³⁵⁻³⁸

Because the 2D nanosheet can be regarded as a precursor of one-dimensional (1D) nanomaterials, which would be cut into nanoribbons or rolled into nanotubes,³⁹⁻⁴¹ the discovery of...
C₃N nanosheet brings interests into its 1D-forms, that is, C₃N nanoribbons (C₃NNRs) and nanotubes. In the literature, the electronic properties and adsorption abilities of C₃N nanotubes have been widely investigated, which exhibit potential applications in chemical sensors and hydrogen storage. With respect to the C₃NNRs, although there is a report on the NC₃ nanoribbons, the investigated structure does not correspond to the experimentally synthesized C₃N ordered arrangement. It would be noted that the properties of nanoribbons are significantly dependent on the edge structures. For example, in the graphene and graphyne nanoribbons, versatile magnetic and electronic behaviors can be introduced by the mono- and dihydrogenated edges, oxidized edges, as well as metal-terminated edges. So far, fundamental information about the structural and electronic properties of C₃NNRs is still unknown. What kind of stable edges will appear in these C₃NNRs? How about their electronic properties? Do these C₃NNRs have peculiar applications? To address these issues, we perform a first-principles calculation to explore the structural and electronic properties of C₃NNRs.

2. RESULTS AND DISCUSSION

2.1. Stable H-Terminated Edges in C₃NNRs. Figure 1a depicts the geometrical structure of the 2D C₃N nanosheet, C₃N nanosheet brings interests into its 1D-forms, that is, C₃N nanoribbons (C₃NNRs) and nanotubes. In the literature, the electronic properties and adsorption abilities of C₃N nanotubes have been widely investigated, which exhibit potential applications in chemical sensors and hydrogen storage. With respect to the C₃NNRs, although there is a report on the NC₃ nanoribbons, the investigated structure does not correspond to the experimentally synthesized C₃N ordered arrangement. It would be noted that the properties of nanoribbons are significantly dependent on the edge structures. For example, in the graphene and graphyne nanoribbons, versatile magnetic and electronic behaviors can be introduced by the mono- and dihydrogenated edges, oxidized edges, as well as metal-terminated edges. So far, fundamental information about the structural and electronic properties of C₃NNRs is still unknown. What kind of stable edges will appear in these C₃NNRs? How about their electronic properties? Do these C₃NNRs have peculiar applications? To address these issues, we perform a first-principles calculation to explore the structural and electronic properties of C₃NNRs.

2. RESULTS AND DISCUSSION

2.1. Stable H-Terminated Edges in C₃NNRs. Figure 1a depicts the geometrical structure of the 2D C₃N nanosheet,
which is a flat honeycomb sheet akin to graphene. Its lattice constant is 4.856 Å, and the C–C and C–N bond lengths are 1.403 and 1.400 Å, respectively. The band structure of C3N nanosheets is displayed in Figure 1b, which shows an indirect-band-gap semiconducting behavior. The valence band maximum (VBM) is located at the M point, while the conduction band minimum (CBM) is doubly degenerated at the Γ point. The Perdew–Burke–Ernzerhof (PBE) calculation obtains a band gap of 0.405 eV, and the gap size is raised to 1.006 eV in the Heyd–Scuseria–Ernzerhof (HSE) calculation. The density of states (DOs) and partial DOSs of C and N atoms are depicted in Figure 1c, which indicate that the top valence states are dominated by the C and N atoms, while the bottom conduction states are mainly from the C atoms. This is consistent with the partial charge densities of valence and conduction band edges in Figure 1d, which show that the VBM is composed of C and N p orbitals along the C–N dimers and the CBM is originated from the C p orbitals in C6 hexagons. All the obtained structural and electronic properties agree well with previous results.24,25,32

Table 1. Parameters for the $E_{\text{form}}$ Calculations of Different Types of Edges

| edge type | $L$ (Å) | $\Delta E_{\text{form}}$ (eV/Å) | $\rho_{C,N}$ (Å$^{-1}$) | $\rho_{H}$ (Å$^{-1}$) |
|-----------|--------|-------------------------------|-----------------------|---------------------|
| AC0C0     | 8.394  | −0.973                        | 0.238                 | 0                   |
| AC0N0     | 8.381  | 2.736                         | −0.238                | 0                   |
| ZC0C0     | 4.837  | 1.140                         | 0                     | 0                   |
| ZC0N0     | 4.843  | 0.758                         | 0                     | 0                   |
| A-C1C1    | 8.430  | −3.193                        | 0.237                 | 0.474               |
| A-C1N1    | 8.434  | 0.905                         | −0.237                | 0.474               |
| Z-C1C1    | 8.458  | −0.931                        | 0                     | 0.411               |
| Z-C1N1    | 8.461  | −1.115                        | 0                     | 0.411               |
| Z-C1N0    | 8.482  | −0.476                        | 0                     | 0.206               |
| Z-C2N0    | 8.487  | −0.109                        | 0                     | 0.206               |
| A-C1N2    | 8.399  | 1.952                         | −0.238                | 0.238               |
| A-C1N3    | 8.396  | 1.541                         | −0.238                | 0.238               |
| Z-C1C2    | 4.862  | −1.994                        | 0                     | 0.822               |
| Z-C1N2    | 4.860  | −1.701                        | 0                     | 0.822               |
| A-C1C2    | 8.448  | −4.445                        | 0.236                 | 0.946               |
| A-C2N2    | 8.429  | 0.249                         | −0.237                | 0.949               |
| Z-C2N1    | 4.864  | −1.477                        | 0                     | 0.616               |
| Z-C2N2    | 4.859  | −1.137                        | 0                     | 0.617               |
| A-C2N1    | 8.427  | 0.202                         | −0.237                | 0.711               |
| A-C2N0    | 8.428  | 0.833                         | −0.237                | 0.711               |
| Z-C2C2    | 8.416  | 0.981                         | −0.237                | 0.475               |
| Z-C2N3    | 8.458  | −0.530                        | 0                     | 0.411               |

The L is the edge length, and the $\Delta E_{\text{form}}$, $\rho_{C,N}$, $\rho_{H}$ are the used factors in the formula of $E_{\text{form}}$, the definition of which can be found in the Method section.

Analogous to the graphene nanoribbons, 1D regular C3N nanoribbons (C3NNRs) can be formed by cutting the 2D nanosheet along the armchair and zigzag directions. As shown in Figure 1a, in the binary C,N system, there are two kinds of edges, that is, the pure C edges (CC) and the CN edges with alternated C and N atoms. Following the convention of nanoribbons,51 the AC0N0 and AC1N0 edges under the H-poor and H-rich conditions, respectively. While under the C-rich condition, the CN edges will be formed under H-poor and H-rich conditions, respectively. This indicates that all these C3NNRs will possess good thermal stability and the corresponding $E_{\text{form}}$ are provided in Table 1. Utilizing these data, the energetically favorable edges are determined by comparing their $E_{\text{form}}$ under different chemical potentials.

Figure 2b depicts the phase diagram of most stable edges in the C3NNRs. It can be seen that only five H-terminated edges are present in the phase diagram. Under the C-rich condition, the CC edges are preferred, for which the AC1C1 and AC2C2 edges will be formed under H-poor and H-rich conditions, respectively. While under the C-poor condition, the CN edges become more favorable, which conduces to the formation of AC0N0 and AC1N2 edges under the H-poor and H-rich surroundings, respectively. The ZC1N1 edge is also present in the phase diagram, but it only appears in a small area with particular $\Delta \mu_{H}$ and $\Delta \mu_{C}$ values. In Figure 2b, the horizontal and vertical lines correspond to the special chemical potentials of H2 and N2 molecules, which are $\Delta \mu_{H} = E_{H}/2 - E_{H} = -2.296$ eV and $\Delta \mu_{C} = ((E_{H} - E_{N}/2)/3 - E_{N}) = -8.641$ eV. The corresponding $E_{\text{form}}$ variations of different edges along these lines are depicted in Figures 2c,d, respectively. It shows that the case of in the fact of $\Delta \mu_{H} = -2.296$ eV, the edge C atoms prefer saturated H-hydrogenation. For large $\Delta \mu_{H}$ values, the AC2C2 edge is the most stable one in the C3NNRs. As $\Delta \mu_{H}$ is decreased, the $E_{\text{form}}$ of this CC edge is raised while the ones of CN edges are declined. As a result, when $\Delta \mu_{C} < -8.332$ eV, the A2C1N1 edge becomes the most favorable edge structure. While in the case of fixed $\Delta \mu_{H} = -8.64$ eV, Figure 2d indicates under the H-poor condition, the 2D C3N nanosheet is preferred to the C3NNRs. When $\Delta \mu_{H} > -2.713$ eV, the C3NNRs become more energetically favorable than the 2D nanosheet. The ZC1N1 edge is preferred in a small $\Delta \mu_{H}$ range of $[-2.713, -2.413]$ eV, and the AC2C2 edge becomes the favorable one when $\Delta \mu_{H} > -2.413$ eV. Thus, similar to graphene nanoribbons,31 enough H potential will benefit the formation of C3NNRs, which not only stabilizes the edge structures but also tunes the electronic properties of nanoribbons. Besides that, we have also performed ab initio molecular dynamics (AIMD) calculations on the C3NNRs with these stable edges. The AIMD calculations are conducted on C3NNRs with a Nose thermostat of 500 K for 10 ps, that is, 104 steps with a time step of 1 fs. As shown in Figure 3, after the AIMD simulations, although there are noticeable distortions in the C3NNRs, the whole structures still keep integrated for the ZC1N1, AC1C1, AC2C2, A2C1N0, and A2C1N1 ones. This indicates that all these C3NNRs will possess good thermal stabilities, whose structural integrity can be well maintained under room temperature.

2.2. Electronic Structures of C3NNRs. Now, we pay main attention to the electronic structures of stable C3NNRs with the above finding edges. First, the zigzag C3NNRs with ZC1N1 edges (ZC1N1–C3NNRs) are investigated, whose geometrical structure is displayed in Figure 4a. Here, the ribbon width is measured by the number (NZ) of integral C6 hexagons across the nanoribbon. It is found that all the investigated NZC1N1–C3NNRs are semiconductors as shown in Figure 4b. Unlike the zigzag graphene nanoribbons with an antiferromagnetic ground state,34 the ZC1N1–C3NNRs are nonmagnetic as confirmed by the spin-polarized calculations. Figure 4c,d depicts the band
alternated C and N atoms along the edge, which corresponds to localized flares resemble the ones of the C3N nanosheet folded along the band dispersions of bottom conduction and top valence bands. As semiconductors, whose band gaps are larger than the 2D gap of Z C1N1 nanosheet. Although these Z C1N1 fragments have not been synthesized so far, the zigzag-shaped edge has been observed in the quantum conduction band structures of (c) 5-ZC1N1−C3NNRs, and (d) 5-AC2C2−C3NNRs. It is found that for these armchair C3NNRs, the band gaps and band features are strongly dependent on the edge terminations. As shown in Figure 5c, the AC1C1−C3NNRs are indirect-band-gap semiconductors, whose band gaps are larger than the value of C3N nanosheet. Contrarily, the AC2C2−C3NNRs have not been investigated. The geometries of A-AC1C1−C3NNRs and A-AC2C2−C3NNRs are depicted in Figure 5a,b, where the NAc is also the number of integral C6 hexagons across the nanoribbon. It is found that for these armchair C3NNRs, the band gaps and band features are strongly dependent on the edge terminations. As shown in Figure 5c, the A-AC1C1−C3NNRs are indirect-band-gap semiconductors, whose band gaps are larger than the value of C3N nanosheet. Contrarily, the AC2C2−C3NNRs have similar dispersions for the bottom conduction bands, but the dispersions of top valence bands are noticeably different. In the 5-AC2C2−C3NNR, the HOVB at the Γ point is lower than the one at the X point, resulting in an indirect band gap of 0.600/1.258 eV by the PBE/HSE calculation. While in the 5-AC1C1−C3NNR, one valence band is up-shifted, which reduces the PBE/HSE band gap to 0.294/0.925 eV. In order to understand the discrepancy between 5-AC1C1− and 5-AC2C2−C3NNRs, the partial charge densities of their band edges are depicted in Figure 6. It can be seen that for the monohydrogenated 5-AC1C1−C3NNR, one valence band is up-shifted, which reduces the PBE/HSE band gap to 0.294/0.925 eV. In order to understand the discrepancy between 5-AC1C1− and 5-AC2C2−C3NNRs, the partial charge densities of their band edges are depicted in Figure 6. It can be seen that for the monohydrogenated 5-AC1C1−C3NNR, the lowest unoccupied conduction band (LUCB) at the Γ point comes from the C p orbitals along the C−C dimers in the whole nanoribbon, while the HOVB at the X point is composed of N p orbitals at the same row, for which the edge atoms make noticeable contributions. On the other hand, in the dihydrogenated 5-AC2C2−C3NNR, the LUCB at the Γ point stems from the C p orbitals in the interior region, and the HOVB at the Γ point is composed of N p and C p orbitals along the N−C dimers. It should be noticed that there are no edge contributions in the CBM and VBM of 5-AC2C2−C3NNR. This is consistent with the previous study on the dihydrogenated armchair graphene nanoribbons, which shows that the sp3-hybridized edge C atoms will not participate in the states around the Fermi level. This is equivalent to reducing the effective width of nanoribbon, which would raise the energies of delocalized states. Thus, one top valence band is remarkably up-shifted in the AC2C2−C3NNR, which significantly reduces the band gap. It would be noted that for the narrowest 2-AC2C2−C3NNR, the PBE calculation even obtains a metallic behavior. However, the HSE calculation still predicts a semiconducting property with a small band gap of 0.482 eV as shown in Figure 5d. Thus, it can be concluded that all these armchair C3NNRs with hydrogenated CC edges are semiconductors.

Figure 3. Geometrical structures of (a) 5-ZC1N1−, (b) 5-A-AC1C1−, (c) 5-A-AC2C2−, (d) 5-AC2C2−, and (e) 5-A-AC1N1−C3NNRs after the 10 ps AIMD simulations.

Figure 4. (a) Geometrical structure of N2ZC1N1−C3NNRs, and (b) variations of band gaps vs the ribbon width N_z. The PBE and HSE band structures of (c) 5-ZC1N1− and (d) 6-ZC1N1−C3NNRs.
Now, we investigate the armchair C₃NNRs with AC₁N₀ and AC₂N₁ edges. The geometrical structures of Nₐ-AC₁N₀−C₃NNRs and Nₐ-AC₂N₁−C₃NNRs are depicted in Figure 7a,b. As shown in Figure 7c, all the investigated AC₂N₁−C₃NNRs are semiconductors, whose band gaps are larger than the value of C₃N nanosheet. While for the AC₁N₀−C₃NNRs, they possess smaller band gaps and the narrow nanoribbons are even metals. Figure 7d depicts the band structure of 2-AC₁N₀−C₃NNR, which shows the bottom conduction and top valence bands are quite dispersive. Both the PBE and HSE calculations indicate that there are two bands crossing the Fermi level, which leads to the metallic feature of nanoribbons. However, for wider nanoribbons, such as the 5-AC₁N₀−C₃NNR in Figure 7d, these bands become flat and open a sizeable PBE/HSE gap of 0.130/0.600 eV. While for the C₃NNR with AC₂N₁ edges, the band gap variation is analogous to the nanoribbons with AC₁C₁ edges. As shown in Figure 7d, the band structure of 5-AC₂N₁−C₃NNR resembles that of 5-AC₁C₁−...
C3NNR, which is also an indirect-band-gap semiconductor with a PBE/HSE gap of 0.707/1.390 eV between the X−Γ point. This similarity can be understood that because of the saturated hydrogenation, the next-to-edge atoms, instead of the out-side edge ones, will participate in the states of AC2N1−C3NNRs around the Fermi level. Because the next-to-edge atoms are pure C−C dimers in the AC2N1−C3NNRs, just like the AC1C1 ones, it thus can be expected that the electronic behaviors of AC2N1−C3NNRs are quite similar to those of AC1C1 nanoribbons.

2.3. Potential Solar Cell Applications of C3NNRs.

Finally, the work functions (W) of C3NNRs are investigated, which are calculated as the energy difference between the vacuum level and Fermi level. Here, the vacuum level is adopted to the zero point and the Fermi level is set at the middle of band gap. Thus, the work function W equals to (Evbm + EcBM)/2, where Evbm and EcBM are the absolute energies of VBM and CBM. To avoid the underestimation of EcBM, the W values are calculated from the HSE data. As shown in Figure 8a, comparing to the C3N nanosheet, the C3NNRs with A1C1C1, A1C2C2, Z1C1N1, and A2C2N1 edges have smaller work functions, while the ones with A2C1N1 edge have bigger W values. Such a phenomenon is related to the edge dipole in the nanoribbons, whose work function can be lowered (raised) by the edge dipole pointing outward (inward) the ribbon. Here, for the fully H-terminated edges, the H atoms are positively charged while the C and N edge atoms are negatively charged. Thus, there are edge dipoles pointing outward the nanoribbons, which reduces the work function of C3NNRs with AC1C1, AC2C2, ZC1N1, and A2C2N1 edges in Figure 8a. On the other hand, in the A2C1N0−C3NNRs, the bare N edge atoms are still negatively charged, which leads to edge dipoles pointing inward the nanoribbon. As a result, the work function is raised in the A2C1N0−C3NNRs. Because the edge dipole effect is weakened with the increase of ribbon width, the work function of wide C3NNRs will approach the value of C3N nanosheet as shown in Figure 8a.

For the C3N nanosheet, our HSE calculations indicate that the CBM (−2.831 eV) and VBM (−3.838 eV) are both located in the band gap of SiC nanosheet, which leads to a type-I band alignment as shown in Figure 8b. Considering that the C3NNRs with A1C1C1, A1C2C2, Z1C1N1, and A2C2N1 edges have smaller work functions, their band edges will be up-shifted relative to the C3N nanosheet. As shown in Figure 8b, our HSE calculations obtain the EcBM values of 8−12−A1C1C1−C3NNRs and 7−11−A2C2N1−C3NNRs as −1.943 to −2.123 and −1.925 to −2.209 eV, respectively, which are all higher than the CBM (−2.217 eV) of SiC nanosheet. Meanwhile, the Evbm values of

Figure 8. (a) Work functions of five types of stable C3NNRs with different widths. (b) Band alignment between SiC nanosheet and Na−A12C2C2−C3NNRs (Na = 8−12), Na−A1Z1C1N1−C3NNRs (Na = 7−11), as well as C3N nanosheet. (c) Corresponding band alignment between the silicane nanosheet and C3NNRs, Na−A1C1C1−C3NNRs (Na = 8−12), Na−Z1C1N1−C3NNRs (Na = 6−10), as well as C3N nanosheet. (d) Optical absorptions of 12−A1C1C1−, 12−A1C2C2−, 11−A1Z1C1N1−, and 10−Z1C1N1−C3NNRs. (e) Calculated power-conversion efficiency as a function of the donor band gap and CBO, in which the data of different C3NNR−SiC/silicane heterostructures are marked and the maximum values are listed.
these C₃NNRs are also higher than the VBM of SiC nanosheet, thus forming a type-II band alignment. It means that when the AC₂C₁⁻/AC₂N₁⁻C₃NNRs are superimposed on the SiC nanosheet, the SiC layer will be the acceptor while the C₃NNRs will be the donor. Simultaneously, the AC₂C₂⁻/C₃NNRs exhibit a strong adsorption ability for the solar-light around the 2–4 eV in Figure 8d. Thus, the combined AC₂C₂⁻/AC₂N₁⁻C₃NNRs-SiC heterostructures will be utilized as an excitonic solar cell, whose power conversion efficiency (PCE) can be estimated as

\[ \eta_{PCE} = \frac{J_{sc} V_{oc} \beta_{FF}}{P_{solar}} \]

where \( J_{sc} \), \( V_{oc} \), \( \beta_{FF} \), and \( P_{solar} \) are the short circuit current, the open-circuit voltage, the band-fill factor, and the incident solar radiation, respectively.58,59 Following previous work,58,59 the \( \beta_{FF} \) value is set to 0.65, \( V_{oc} \) is adopted to \( E_{g} - E_{CBO} - 0.3 \), where \( E_{g} \) is the band gap of donor part, \( E_{CBO} \) is the conduction band offset (CBO) between the acceptor and donor materials, and 0.3 is an empirical factor for energy conversion kinetics. The \( J_{sc} \) is calculated by the integral in the numerator in the limit external quantum efficiency of 100%, and the \( P_{solar} \) in the denominator is the integrated AM 1.5 solar energy flux, which amounts to 1000 W/m². As shown in Figure 8b, the CBO values between the 8 and 12 AC₂C₂⁻C₃NNRs and SiC nanosheet are 0.274–0.093 eV, while the \( E_{g} \) values of these AC₂C₁⁻C₃NNRs are 0.956–0.97 eV. These values meet the requirement for a high PCE in Figure 8e. Therefore, the \( \eta_{PCE} \) values of these AC₂C₁⁻C₃NNRs/SiC heterostructures will be as high as 12.5–18.7%. Similarly, the AC₁C₁⁻C₃NNRs/SiC ones also possess a \( \eta_{PCE} \) of 15.7–21.9% for the \( N_x = 7–11 \) case. For the ZC₁N₁⁻ and NH₁₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋_-21%. Our study demonstrates that the C₃NNRs have distinct edge stabilities and variable semiconductor behaviors, which enable fascinating utilization in the fields of solar energy and nanodevices for them.

3. CONCLUSIONS

In summary, we have investigated the geometrical structures and electronic properties of C₃NNRs. Five types of H-terminated edge structures are found as the energetically favorable edges in the C₃NNRs, which are monohydgenated zigzag CN edge (ZC₁N₁⁻), mono- and dihydrogenated armchair CC edges (AC₁C₁⁻ and AC₂C₂⁻), partially N-bare armchair CN edge (AC₁N₀⁻), and mixed di-/monohydgenated one (AC₂N₁⁻). Different from graphene nanoribbons, the C₃NNRs with these stable edges are all nonmagnetic semiconductors, whose band features and gap sizes are determined by the edge termination and ribbon width. The ZC₁N₁⁻C₃NNRs can be direct- or quasi-direct band gaps depending on the ribbon width, while the AC₁C₁⁻ and AC₂N₁⁻C₃NNRs possess robust indirect band gap feature. The band gaps of these three C₃NNRs are all larger than the 2D value, but for the AC₁C₁⁻ and AC₂N₁⁻ones, they have smaller gap sizes and will be direct- or indirect-band-gap semiconductors depending on the edge H-terminations. Comparing to the C₃N nanosheet, the full H-terminations on the edges will reduce the work function of C₃NNRs, which causes the dihydrogenated AC₁C₁⁻ and AC₂N₁⁻C₃NNRs (monohydgenated AC₁C₁⁻ and ZC₁N₁⁻C₃NNRs) to form a type-II band alignment with the SiC (silicane) nanosheet. The combined hetero-nanostructures will be promising excitonic solar cell materials, which possess high power conversion efficiencies up to 17–21%. Our study demonstrates that the C₃NNRs have distinct edge stabilities and variable semiconductor behaviors, which enable fascinating utilization in the fields of solar energy and nanodevices for them.

4. METHOD

The first-principles calculations are performed by the Siesta code,67 which adopts a double-ζ plus polarization basis set with norm-conserving pseudopotentials. The grid cutoff is set to 200 Ry, and the PBE exchange–correlation functional is used. During the AIMD calculation, a small single-ζ basis plus polarization orbitals basis set with a low grid cutoff of 150 Ry is used to reduce the required computational resource. The k-meshes of 25 × 25 × 1 and 1 × 12(15) × 1 are used for the 2D nanosheet and 1D armchair (zigzag) nanoribbons, respectively. To simulate the isolated nanostructure, a vacuum layer of 15 Å is added in the nonperiodic directions. All the geometrical structures are fully optimized until the maximum residual force is less than 0.02 eV/Å. The hybrid HSE calculation is further performed to check the obtained band structures by the FHI-aims code,68,69 which utilizes the HSE06 form with a screening parameter of 0.25 bohr⁻¹ and a mixing parameter of 0.5 for the short-range exchange.70

To compare the energetic stability of different edges, the formation energies (\( E_{form} \)) are calculated as \( E_{form} = (E_{NRN} - n_{C} \mu_{C} - n_{N} \mu_{N} - n_{H} \mu_{H})/2L \). Here, the \( E_{NRN} \) is the total energy of the C₃N nanoribbon, \( n_{C}/n_{N} \) are the numbers of C/N/H atoms in the nanoribbon, and \( \mu_{C}/\mu_{N} \) is the corresponding chemical potential. \( L \) is the edge length and the factor 2 comes from the two edges of nanoribbons. To obtain converged energy values, wide nanoribbons with the width of more than 25 Å are used in the \( E_{form} \) calculations. Considering the thermodynamic equilibrium condition of C₃N nanosheet, it requires \( 3 \mu_{C} + \mu_{H} = E_{2D} \), where \( \mu_{C} \) and \( \mu_{H} \) are the respective chemical potentials of C and N elements, and \( E_{2D} \) is the total energy of the 2D C₃N nanosheet per formula unit (f.u.). Here, 1 f.u. corresponds to three C atoms and one N atom. Thus, the
where

\[
\Delta \mu_n = E_k^N - E_k^C - (nC - 3nN)E_a - n\Delta \mu \rho L \rho_n - (nC - 3nN)2L, \quad \rho_n = n\chi/2L \text{ as shown in Table 1.}
\]

Following this definition, the more negative the \(E_{ion} \) value, the more energetically favorable the corresponding edge structure.

![AUTHOR INFORMATION](image)

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