Tailoring the Electronic Band Gap and Band Edge Positions in the C₂N Monolayer by P and As Substitution for Photocatalytic Water Splitting

M. R. Ashwin Kishore†,‡ and Ponniah Ravindran*,†,‡,§,∥

†Department of Physics, Central University of Tamil Nadu, Thiruvarur, Tamil Nadu 610101, India
‡Simulation Center for Atomic and Nanoscale Materials and §Department of Materials Science, Central University of Tamil Nadu, Thiruvarur, Tamil Nadu 610101, India
∥Center for Materials Science and Nanotechnology and Department of Chemistry, University of Oslo, Box 1033 Blindern, N-0315 Oslo, Norway

ABSTRACT: Exploiting earth-abundant and low-cost photocatalysts for high efficiency photocatalytic water splitting is of profound significance. Herein, we report an improved photocatalytic water splitting activity by P and As substitution at the N-site in the C₂N monolayer using state-of-the-art hybrid density functional calculations. Our results show that the band gap can be reduced in C₂N by increasing the concentrations of P and As substitution, and at the same time the obtained band gap value is higher than the free energy of water splitting except for As with concentrations of x = 0.333. This indicates that these new compositions of P/As substituted C₂N monolayers are thermodynamically suitable to drive hydrogen evolution reaction. The calculated effective mass of charge carriers illustrates that charge transfer to the reactive sites would be easier in the substituted system than the pure C₂N, and also our results suggest that the recombination rate would be lower in the substituted system, indicating the enhancement in the efficiencies of photocatalytic water splitting. The band edge position with respect to the redox potentials of water shows that P/As substituted C₂N monolayers are the potential photocatalysts for water splitting than the pristine C₂N monolayer. From the optical absorption spectra, we found that P/As substituted C₂N monolayer shows optical absorption extended more into the visible region, indicating enhanced energy harvesting. Our results reflect that the P/As substituted C₂N monolayer could be the potential visible-light photocatalyst for overall water splitting.

INTRODUCTION

Hydrogen production by photocatalytic water splitting using solar energy is an attractive and sustainable solution to solve the global energy problem and environmental issues.¹⁻³ Nanosized semiconductors, especially the two-dimensional (2D) materials, exhibit enhanced photocatalytic activity compared to their bulk counterparts due to the presence of more surface active sites, improved electron–hole separation, fast mobility of charge carriers, short diffusion length, and reduced recombination rate. Although, graphene, a single layer of carbon atoms of honeycomb-like layered material, possesses intriguing electronic and mechanical properties, its zero band gap makes it unsuitable to use in optoelectronic devices and photocatalysis. Therefore, great efforts have been made to open an appropriate band gap in graphene, and also the band gap shortcoming paves the way to search for other 2D materials with finite band gap and favorable carrier mobility. It has been realized experimentally and predicted theoretically that graphene-analogous materials such as BN, transition metal dichalcogenides, phosphorene, MXenes, g-C₃N₄, and so forth can significantly remedy graphene’s shortcoming in optoelectronic devices, photocatalysis, etc.⁴⁻⁸

Received: August 4, 2017
Revised: September 14, 2017
Published: September 18, 2017
In recent years, carbon-nitride-based nanostructures have attracted tremendous attention in the field of photocatalytic water splitting due to their earth-abundant nature, high thermal as well as chemical stability, tunable electronic structure, and economical affordability. The two-dimensional graphic phase of carbon nitride (g-C3N4) has been synthesized by Wang et al., and their results showed a good photocatalytic performance for hydrogen or oxygen production via water splitting. Its unique structure and exotic properties created interest among the researchers to search for other two-dimensional covalent triazine frameworks and have shown great promise for a wide variety of applications. C2N, another polymorph of carbon nitride composed of single-ring triazines, displays a ferromagnetic ground state and possesses an intrinsic half-metallicity. Srinivasu et al. reported that s-triazine-based porous graphitic carbon nitride (g-CN) is a potential photocatalyst for water splitting. Recently 2D C4N has been identified by first-principles calculations in combination with a swarm structure search, and it could be a promising material for applications in nanoelectronics.

Nitrogenated holey graphene (C3N) is a newly synthesized layered 2D network structure possessing evenly distributed holes. In the C3N structure, the benzene rings are bridged by pyrazine rings, which consist of a six-membered D3h ring with two nitrogen atoms facing each other. This material has a direct band gap, and the optically measured band gap value is 1.96 eV. The fabricated field effect transistor based on the C3N multilayer exhibits a high on/off ratio of 10^7. It is to be noted that the direct band gap, high on/off ratio, and porous nature of C3N is expected to exhibit desirable properties for electronics, optoelectronics, and energy conversion as well as storage, gas storage applications, etc.

It was reported by Sahin that the phonon modes of C3N monolayer are close to that of graphene, indicating the high structural stability of the C3N monolayer. Guan et al. demonstrated the effect of strain on electronic and optical properties on the C3N monolayer for optoelectronic device applications. Theoretical predictions have shown that the band gap and band edge positions of C3N can be tuned by varying their stacking order, layer number, and external electric field for optoelectronic and photocatalytic water splitting applications. An enhanced photocatalytic mechanism has been observed in g-C3N4/C3N heterostructures. C3N/MoS2 heterostructure has been reported as a potential photovoltaic material. Isovalent element-alloyed C3N monolayers have been predicted to have promising applications in optoelectronic and photocatalytic water splitting. Recently, it has been reported that C3N can be an ideal candidate for hydrogen storage material. Furthermore, earlier reports revealed its possibility in use for gas separation, HER catalyst, and OER catalyst.

Computational simulation and design play a great role in assisting experimental efforts in screening or identifying new potential photocatalysts. In many cases, it is necessary to modulate the electronic and optical properties of the material to broaden its widespread applications or improve the efficiency. There are several ways to achieve this, for example, doping, point/line defects, layer-by-layer or heterostructure mapping, chemical adsorption, strain, and external electric field. Herein, we demonstrate using density functional calculations that the isoelectronic substitution at the N site in the C3N monolayer improves the photocatalytic water splitting activity. We find that P/As substitutions reduce the band gap of the C3N monolayer and make it optimum for water splitting and thus enhance the optical absorption in the visible region of the solar spectrum. The low effective mass of charge carriers indicates an efficient charge separation in the P/As substituted system. More importantly, the band edge positions are even more favorable in the P/As substituted system than the pristine C3N for water decomposition.

### COMPUTATIONAL DETAILS

Total energy calculations were done using the projector augmented wave (PAW) method which is implemented in the Vienna ab initio simulation package (VASP). Geometry optimization is carried out by employing the generalized gradient approximation proposed by Perdew, Burke, and Ernzerhof (GGA-PBE) with van der Waals (vdW) correction proposed by Grimme. The Heyd—Scuseria—Ernzerhof (HSE06) hybrid functional was used to calculate electronic structures owing to the band gap underestimation of semiconductors by the PBE functional. The Brillouin zone was sampled using a Monkhorst—Pack scheme and employs a 9 × 9 × 1 k-mesh for geometry optimization and a 5 × 5 × 1 k-mesh for the more expensive HSE06 calculations. A plane-wave basis set with a cutoff energy of 520 eV was used. A large vacuum of ∼15 Å is used to avoid interlayer interaction due to the periodic boundary condition used in the present calculations. The convergence criterion for energy was set to be 10^{-5} eV between two consecutive SCF cycles, and the force is converged when the Helman—Feynman force acting on each atom was less than 0.01 eV/Å, upon ionic relaxation. The postprocessing of VASP calculated data was done by using VASPKIT code.

The positions of VBM and CBM of pristine and P/As substituted C3N monolayers are determined by the calculated band gap center energy (E_{BGC}) and the band gaps (E_g), using the following relation

\[
E_{\text{CBM/VBM}} = E_{\text{BGC}} = \frac{1}{2}E_{\text{HSE06}}
\]

where E_{BGC} is the band gap center energy calculated using the PBE functional. As E_{HSE06} is quite insensitive to the choice of exchange correlation functional, we have used the less expensive PBE functional. A more accurate HSE06 is used to calculate the band gaps. To align the energy levels for pristine and P/As substituted C3N monolayers, their vacuum levels are set to zero.

In order to study the optical absorption property of pristine and P/As substituted C3N monolayers, the frequency-dependent dielectric function \(\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)\) was calculated. The interband contribution to the imaginary part of the dielectric functions \(\varepsilon_2\) is calculated by summing transitions from occupied to unoccupied states with fixed k vector over the Brillouin zone, weighted with the appropriate matrix element giving the probability for the transition. To be specific, the components of \(\varepsilon_2\) are given by ref 40.
dielectric function, polarization vectors (along ϵ-frequency-dependent complex dielectric function Kramers).

The C1.336 Å for the C in-plane bond lengths were found to be 1.429 Å, 1.468 Å, and
wave functions at the ϵ
localized electrons, fully delocalized electrons, and very low
renormalized to the values between 0.00 and 1.00. The region
to the jellium-like homogeneous electron gas and is
chemical bond or the electron density distribution between
atoms can be described accurately by ELF.43

The relaxation lattice constant obtained from the present
gap. The relaxed lattice constant calculated using the HSE06 functional gives us
visualization of the electron localization function (ELF) and

Figure 1. Schematic structure of the C2N monolayer: (a) top view and (b) side view. The atoms are denoted as C (blue) and N (orange) in this picture. (c) The contour map of electron localization function (ELF) is viewed from the [0 0 1] direction. The reference bar for the ELF value is provided at the left and (d) band structure of the C2N monolayer calculated using the HSE06 functional.

\[ \epsilon_2(\omega) = \frac{4\pi^2}{\Omega} \lim_{\omega \to 0} \frac{1}{\hbar^2} \sum_{\mathbf{q},\mathbf{k}} 2\mu_{\mathbf{k}} \delta(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}} - \omega) \times \langle \mu_{\mathbf{k}+\mathbf{q}} \rangle^* \]

where the indices \( c \) and \( v \) refer to conduction and valence band states, respectively. \( \mu_k \) represents the cell periodic part of the wave functions at the k-point. The real part of the components of the dielectric tensor \( \epsilon(\omega) \) is then calculated using the Kramer–Kronig transformation. The absorption coefficient \( \alpha(\omega) \) was evaluated according to the following equation41

\[ \alpha(\omega) = \sqrt{2} \omega \sqrt{\epsilon_1^2(\omega) + \epsilon_2^2(\omega) - \epsilon_1(\omega)} \]

where \( \epsilon_1(\omega) \) and \( \epsilon_2(\omega) \) are the real and imaginary parts of the frequency-dependent complex dielectric function \( \epsilon(\omega) \), respectively. In order to account for the tensor nature of the dielectric function, \( \epsilon_{1x}(\omega) \) and \( \epsilon_{2x}(\omega) \) are averaged over three polarization vectors (along \( x \), \( y \), and \( z \) directions).

RESULTS AND DISCUSSION

Bonding Character and Structural Stability. The schematic structure of the C2N monolayer is shown as the top view and side view in Figure 1a and b, respectively. The visualization of the electron localization function (ELF) and band structure calculated using the HSE06 functional gives us insight into the character of the bonding and nature of the band gap. The relaxed lattice constant obtained from the present GGA-PBE calculation (\( a = 8.325 \) Å) is consistent with that reported from experimental and theoretical studies.15,17,18 The in-plane bond lengths were found to be 1.429 Å, 1.468 Å, and 1.336 Å for the C–C(1), C–C(2), and C–N bond, respectively. The C–N–C angle is 117.5°, slightly deviated from 120°, which is almost the same as the value of 117.4° by Liang et al.12 from similar calculations. The nature of the chemical bond or the electron density distribution between atoms can be described accurately by ELF.33–35 The ELF refers to the jellium-like homogeneous electron gas and is renormalized to the values between 0.00 and 1.00. The region with an ELF value of 1.00, 0.50, and 0.00 corresponds to fully localized electrons, fully delocalized electrons, and very low charge density, respectively. It can be seen from Figure 1c that the C and N sites are characterized by low charge densities. However, the ELF value close to 1.00 can be seen between carbon atoms and also between C and N, and the fact that the electrons are fully localized between these atoms confirms the presence of covalent bonding in the C2N monolayer. From this figure, it is also evident that the geometrical structure of C2N has pyrazine rings that contain nitrogen atoms having six lone-pair electrons. In order to tune the electronic band gap and band edge positions, we have done isoelectronic substitution at the N site with three different substitution concentrations such as \( x = 0.083, 0.167, \) and \( 0.333 \) to simulate C2N1–xMx (\( M = P \) and As) monolayers. We have used the supercell approach to simulate different substitution concentrations. For C2N1–xMx (\( M = P \) and As) monolayers, substitution concentrations \( x = 0.083 \) and 0.167 were obtained by replacing one N atom with one P/As atom in the 2 × 1 (36 atoms) and 1 × 1 (18 atoms) C2N cells, respectively. The substitution concentration \( x = 0.333 \) was obtained by replacing two N atoms with P(As) atoms in the C2N unit cell.

The cohesive energy per atom in a primitive unit cell was calculated (see Table 1) to evaluate the relative stability of C2N1–xMx monolayers using the formula

<table>
<thead>
<tr>
<th>System</th>
<th>Lattice constant (Å)</th>
<th>Cohesive energy per atom (eV)</th>
<th>Band gap (eV)</th>
<th>PBE</th>
<th>HSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2N</td>
<td>8.325</td>
<td>8.64</td>
<td>1.66</td>
<td>2.46</td>
<td></td>
</tr>
<tr>
<td>C2N0.667P0.333</td>
<td>8.426</td>
<td>8.63</td>
<td>1.33 (1.39)</td>
<td>2.22</td>
<td></td>
</tr>
<tr>
<td>C2N0.667As0.333</td>
<td>8.515</td>
<td>8.44</td>
<td>1.36</td>
<td>2.06</td>
<td></td>
</tr>
<tr>
<td>C2N0.833P0.167</td>
<td>8.771</td>
<td>8.22</td>
<td>0.94</td>
<td>1.47</td>
<td></td>
</tr>
<tr>
<td>C2N0.833As0.167</td>
<td>8.454</td>
<td>8.50</td>
<td>1.31 (1.35)</td>
<td>2.08</td>
<td></td>
</tr>
<tr>
<td>C2N0.917P0.083</td>
<td>8.570</td>
<td>8.37</td>
<td>1.30</td>
<td>1.89</td>
<td></td>
</tr>
<tr>
<td>C2N0.917As0.083</td>
<td>8.921</td>
<td>8.09</td>
<td>0.60</td>
<td>1.09</td>
<td></td>
</tr>
</tbody>
</table>

The calculated PBE direct band gap values for C2N0.667P0.333 and C2N0.833As0.167 are given in parentheses.
Table 2. Calculated Bond Strength from Integrated COHP\(^{16-18}\) for C\(_2\)N, C\(_2\)N\(_1\)-P\(_x\), and C\(_2\)N\(_1\)-As Monolayers

<table>
<thead>
<tr>
<th>composition</th>
<th>bond strength (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_2)N</td>
<td>C–C(1) −6.76</td>
</tr>
<tr>
<td>C(<em>2)N(</em>{0.833})P(_{0.167})</td>
<td>C–C(2) −5.75</td>
</tr>
<tr>
<td>C(<em>2)N(</em>{0.833})P(_{0.167})</td>
<td>C–N −6.91</td>
</tr>
<tr>
<td>C(<em>2)N(</em>{0.833})As(_{0.167})</td>
<td>C–C(1) −6.14</td>
</tr>
<tr>
<td>C(<em>2)N(</em>{0.833})As(_{0.167})</td>
<td>C–C(2) −5.85</td>
</tr>
<tr>
<td>C(<em>2)N(</em>{0.833})As(_{0.167})</td>
<td>C–N −6.67</td>
</tr>
<tr>
<td>C(<em>2)N(</em>{0.833})P(_{0.167})</td>
<td>C–C(2) −5.58</td>
</tr>
<tr>
<td>C(<em>2)N(</em>{0.833})As(_{0.167})</td>
<td>C–C(2) −5.90</td>
</tr>
<tr>
<td>C(<em>2)N(</em>{0.833})P(_{0.167})</td>
<td>C–N −6.67</td>
</tr>
<tr>
<td>C(<em>2)N(</em>{0.833})As(_{0.167})</td>
<td>C–N −6.79</td>
</tr>
<tr>
<td>C(<em>2)N(</em>{0.833})As(_{0.167})</td>
<td>C–C(2) −5.61</td>
</tr>
<tr>
<td>C(<em>2)N(</em>{0.833})P(_{0.167})</td>
<td>C–N −6.60</td>
</tr>
<tr>
<td>C(<em>2)N(</em>{0.833})As(_{0.167})</td>
<td>C–N −6.61</td>
</tr>
<tr>
<td>C(<em>2)N(</em>{0.833})As(_{0.167})</td>
<td>C–N −6.71</td>
</tr>
<tr>
<td>C(<em>2)N(</em>{0.833})P(_{0.167})</td>
<td>C–C(2) −5.82</td>
</tr>
<tr>
<td>C(<em>2)N(</em>{0.833})As(_{0.167})</td>
<td>C–C(2) −5.64</td>
</tr>
<tr>
<td>C(<em>2)N(</em>{0.833})As(_{0.167})</td>
<td>C–N −6.61</td>
</tr>
<tr>
<td>C(<em>2)N(</em>{0.833})As(_{0.167})</td>
<td>C–N −6.71</td>
</tr>
</tbody>
</table>

\[ E_{\text{coh}} = [N C + N M + N N - E_{\text{tot}}] / [2(N C + N M + N N)] \] (3)

where \( E_{\text{tot}} \) is the total energy of the model systems; \( N C \), \( N M \), and \( N N \) are the number of C, M (P and As), and N atoms per system, and \( E_{\text{CO}} \), \( E_{\text{AM}} \), and \( E_{\text{NN}} \) are the energies of the isolated C, M (P and As), and N atoms, respectively. From our cohesive energy calculations we have found that the cohesive energies of P/As substituted C\(_2\)N monolayers are slightly smaller than that of pristine C\(_2\)N indicating that stability will be reduced by substitution, but yet the higher values indicate that they can be stable. The cohesive energy of C\(_2\)N\(_{1-x}\)M\(_x\) monolayers shows a decreasing tendency with the increasing concentration of \( x \). The decrease in cohesive energy is due to weakening of bond strength and hence a decrease in optical band gap as seen from our band structure analysis. In order to substantiate this observation, we have calculated the bond strength between various constituents of C\(_2\)N and C\(_2\)N\(_{1-x}\)M\(_x\) monolayers using the Integrated Crystal Orbital Hamiltonian Population (ICOHP) as we have done earlier.\(^{19}\) The calculated ICOHP values are listed in Table 2. It is evident from the table that the bond strength of various constituents of C\(_2\)N\(_{1-x}\)M\(_x\) monolayers is decreasing when P/As substitution concentrations are increasing and thus the cohesive energy.

Electronic Properties. The calculated band structures using the GGA-PBE functional for C\(_2\)N and C\(_2\)N\(_{1-x}\)M\(_x\) are displayed in Supporting Information Figures S1 and S2, respectively. It can be seen from Figure S1 that the pristine C\(_2\)N monolayer is a direct band gap semiconductor, as the valence band maximum (VBM) and the conduction band minimum (CBM) both lie at the \( \Gamma \) point with the band gap value of 1.66 eV which is consistent with earlier reports.\(^{22}\) The obtained band gap value is much smaller than the value measured from optical measurements (1.96 eV)\(^{23}\) and the value calculated theoretically\(^{19}\) using the Heyd–Scuseria–Ernzerhof (HSE06) functional. The P/As substitutions also preserve the direct band gap nature for \( x = 0.083 \) concentrations, where indirect band gap behavior is observed with the VBM lying at the M point and the CBM lying at the \( \Gamma \) point. It is well-known that the PBE functional underestimates the band gaps of semiconductors,\(^{24}\) and also it may wrongly predict the nature of the band dispersion. Therefore, we carried out band structure calculations by the HSE06 hybrid functional which has been demonstrated to be more accurate in describing the exchange-correlation energy of electrons in solids.

The band structures of pristine and C\(_2\)N\(_{1-x}\)M\(_x\) (M = P and As) monolayers calculated with the HSE06 functional are depicted in Figure 1d and Figure 2, respectively. It can be clearly seen from the band structures of C\(_2\)N and C\(_2\)N\(_{1-x}\)M\(_x\) monolayers that all these systems belong to direct band gap semiconductors. As we mentioned earlier, the PBE functional may wrongly predict the nature of band dispersion. The band structure calculated using the PBE functional has two degenerate flat bands in the VBM (see Figure S1). However, in the band structure computed using the HSE06 functional, these two bands moved to lower energy, and the bands at \( -1 \) and \( -2.5 \) eV moved upward and form the VBM. Also, the band structures obtained using HSE06 functionals show that P/As substitution for \( x = 0.083 \) also has direct band gap nature which was wrongly predicted as an indirect band gap material by the PBE functional. It may be noted that the isovalent impurities do not induce deep defect energy levels in the band gap in semiconductors, and hence no localized states are present in the P/As substituted C\(_2\)N monolayers as evident from Figure 2. As a result, bands originating from substituents such as P/As in C\(_2\)N will not act as recombination centers for the photogenerated electron hole pairs. Also, from the figure, it is clear that the bands in the valence and conduction band edges of these materials are well dispersed. Hence, the lifetime of the photogenerated charge carriers in these systems is expected to be longer, which will result in better photocatalytic efficiency.

The calculated band gap values and the corresponding lattice constants are listed in Table 1 for C\(_2\)N and C\(_2\)N\(_{1-x}\)M\(_x\) monolayers. From this table, we can see that the increasing lattice constant due to the substitution of bigger size atoms may lead to a decrease of the band gap which is in agreement with a previous report.\(^{25}\) It is to be noted that the optimum band gap value for a semiconductor to be employed for water splitting application using solar radiation is between 1.8 and 2.2 eV.\(^{26}\) Interestingly, the band gap values for P/As substituted C\(_2\)N fall...
exactly in this optimum range (see Table 1) except for As substitution with $x = 0.333$ concentrations. The calculated band gap value for $x = 0.333$ is lower (1.09 eV) than the water redox potential of 1.23 eV, and hence this composition is not suitable to use for photocatalytic water splitting. Therefore, the photocatalytic properties of this composition are not analyzed further. The substitution of isoelectronic elements will preserve the electron per atom ratio which may stabilize the structure, and at the same time it distorts the structure due to strain introduced by variation in the atomic radii of the substituents; as a result the band gap as well as band edge positions may alter. The great advantage in substituting isoelectronic elements in C$_2$N is that it preserves direct band gap behavior, and more importantly, it allows us to tune the band gap from 0.24 to 0.99 eV and from 0.38 to 1.37 eV upon varying the concentration ($x = 0.083$ to 0.333) of P and As, respectively. This significant reduction in the band gap due to substitutions displays better light absorption performance and thus photoconversion efficiency than the pristine C$_2$N.

To gain a better insight into the orbital contributions to electronic bands, we present the orbital-projected band structure—so-called fat bands calculated using HSE06 in Figure 3. It is clear that the VBM and CBM of pristine C$_2$N are mainly occupied by C p$_z$ and N p$_z$ electrons, respectively. The bands present in the valence band at $-1$ eV and $-2$ eV are occupied by N s as well as p$_x$ + p$_y$ electrons of C and N s as well as p$_x$ + p$_y$ electrons of N, respectively. The whole CB is mainly occupied by p$_z$ electrons of N with little contributions from p$_x$ electrons of C. In the case of P/As substituted C$_2$N monolayers, the VBM and CBM are occupied by C p$_z$ and N p$_z$ electrons, respectively, for $x = 0.083$ and 0.167. On the other hand, for higher concentration of P (C$_2$N$_{0.333}$P$_{0.667}$), the VBM is occupied by P p$_z$ electrons, and the CBM is occupied by p$_z$ electrons of both C and N. It is interesting to note that the VBM of all compositions distinctly comprise the p$_z$ states of C/P, whereas the CBM is mainly contributed by p$_z$ states of N/C atoms. This implies that upon photoexcitation the holes will reside on the C/P site, and the electrons will reside on the N/C site. As a result, the electrons and holes will be well separated, and this extends the lifetime of the charge carriers. Hence, the probability of recombination rate would be lower, and this will further improve the photocatalytic water splitting efficiency.

In order to understand the bonding characteristics and the origin of the band gap reduction of P/As substitution in C$_2$N monolayers, we have analyzed the total and projected density of states (DOS) as shown in Figure 4. Here, we discuss the DOS for C$_2$N$_{0.833}$P$_{0.167}$ and C$_2$N$_{0.833}$As$_{0.167}$ only as the trend will be the same for the other compositions. DOS analysis shows that the VBM of the pristine C$_2$N monolayer is dominated by C-2p states with a noticeable contribution from N-2p states. Similarly the CBM is originating from hybridization of both C-2p and N-2p states. In the case of the C$_2$N$_{0.833}$P$_{0.167}$ monolayer, the VBM is mainly dominated by C-2p states with a noticeable contribution from N-2p as well as P-3p states, while the CBM is mainly originating from p states of C, N, and P. For the C$_2$N$_{0.833}$As$_{0.167}$ monolayer, the VBM is dominated by C-2p states with a noticeable contribution from As-4p and N-2p states, while the CBM is mainly originating from N-2p, C-2p, and As-4p states. The energetically degenerate nature of DOS distribution comes from C-2p and N-2p along with its broad dispersion in the whole valence band indicating a strong covalent character, which is typical for layered 2D materials. From the ELF analysis discussed above, there is a strong covalent bond present between C and N which is also evident from the degenerate nature of the band dispersion from C and N p states in the whole valence band range. Due to this strong covalent bonding, the broad band features are observed at the band edges that can reduce the effective mass of the charge carriers and thus increase their mobility that will be discussed in detail later. The observed band gap narrowing is attributed...
The pristine, and this can be understood from the band at the band shows a hole transfer along a specific C2N monolayer manifests lower electron band gap suitable for photocatalytic water splitting. monolayers are summarized in Table 3. P/As substituted broaden the band edges and significantly narrowed down the calculated total and partial density of states for C2N, Figure 4. The Journal of Physical Chemistry C is set to zero. functional are shown in (a), (b), and (c), respectively. The Fermi level Electronic Properties section. However, the P and As nitrogen atoms as evident from our fat band analysis in the Charge Mobility and Separation. The ability of electron/hole transfer along a specific direction is important to have efficient charge separation and thus reduced recombination rate which will improve the efficiency of water splitting activity. It is well-known that the carrier mobility is inversely proportional to the effective mass, and hence low effective mass of charge carriers results in high carrier mobility. Therefore, we pay attention to the carrier effective masses. The calculated effective masses of electrons and holes for C2N and C2N0.917M0.083 monolayers are summarized in Table 3. P/As substituted C2N monolayer manifests lower electron effective mass than the pristine, and this can be understood from the band structure. In C2N, the CBM has three bands that are degenerate at the Γ point, and among these three bands, the lowest energy band shows a flat band nature along Γ−M. This originates from the π state contributed by the localized p orbitals of the nitrogen atoms as evident from our fat band analysis in the Electronic Properties section. However, the P and As substitutions make the flat band along Γ−M more dispersive due to an increase in overlap interaction by the bigger size of the substituents and thus result in lower electron effective mass than the pristine C2N. Our results show that the electron and hole effective masses along the Γ−M direction are much heavier than those along the Γ−K direction. At least in one crystallographic direction, the effective mass of charge carrier should be lower than 0.5 m, to have an excellent mobility. In our case the effective mass of electrons and holes is lower than 0.5 m along the Γ−K direction for C2N0.833P0.167, C2N0.667P0.333, and C2N0.833As0.167. In the case of C2N0.917P0.083 and C2N0.917As0.083, the calculated effective masses are relatively smaller and are comparable with that of other known photocatalysts. Our effective mass analysis indicates that the charge carriers move faster to the reactive sites, and this results in efficient charge separation in these materials and hence the photoconversion efficiency.

Table 3. Calculated Effective Mass of Electron/Hole for C2N1−xMx (M = P and As) Monolayers

<table>
<thead>
<tr>
<th>system</th>
<th>effective mass of electron</th>
<th>effective mass of hole</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(m0)</td>
<td>(m0)</td>
</tr>
<tr>
<td>Γ−M</td>
<td>Γ−K</td>
<td>Γ−M</td>
</tr>
<tr>
<td>C2N</td>
<td>12.78</td>
<td>1.20</td>
</tr>
<tr>
<td>C2N0.667P0.333</td>
<td>3.51</td>
<td>0.90</td>
</tr>
<tr>
<td>C2N0.833P0.167</td>
<td>4.30</td>
<td>0.27</td>
</tr>
<tr>
<td>C2N0.833As0.167</td>
<td>2.53</td>
<td>0.24</td>
</tr>
<tr>
<td>C2N0.917P0.083</td>
<td>1.47</td>
<td>1.74</td>
</tr>
<tr>
<td>C2N0.917As0.083</td>
<td>3.10</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Figure 4. Calculated total and partial density of states for C2N, C2N0.833P0.167, and C2N0.833As0.167 monolayers obtained from HSE06 functional are shown in (a), (b), and (c), respectively. The Fermi level is set to zero.

charge mobility and separation. The ability of electron/hole transfer along a specific direction is important to have efficient charge separation and thus reduced recombination rate which will improve the efficiency of water splitting activity. It is well-known that the carrier mobility is inversely proportional to the effective mass, and hence low effective mass of charge carriers results in high carrier mobility. Therefore, we pay attention to the carrier effective masses. The calculated effective masses of electrons and holes for C2N and C2N0.917M0.083 monolayers are summarized in Table 3. P/As substituted C2N monolayer manifests lower electron effective mass than the pristine, and this can be understood from the band structure. In C2N, the CBM has three bands that are degenerate at the Γ point, and among these three bands, the lowest energy band shows a flat band nature along Γ−M. This originates from the π state contributed by the localized p orbitals of the nitrogen atoms as evident from our fat band analysis in the Electronic Properties section. However, the P and As substitutions make the flat band along Γ−M more dispersive due to an increase in overlap interaction by the bigger size of the substituents and thus result in lower electron effective mass than the pristine C2N. Our results show that the electron and hole effective masses along the Γ−M direction are much heavier than those along the Γ−K direction. At least in one crystallographic direction, the effective mass of charge carrier should be lower than 0.5 m, to have an excellent mobility. In our case the effective mass of electrons and holes is lower than 0.5 m along the Γ−K direction for C2N0.833P0.167, C2N0.667P0.333, and C2N0.833As0.167. In the case of C2N0.917P0.083 and C2N0.917As0.083, the calculated effective masses are relatively smaller and are comparable with that of other known photocatalysts. Our effective mass analysis indicates that the charge carriers move faster to the reactive sites, and this results in efficient charge separation in these materials and hence the photoconversion efficiency.

Our orbital projected band structure analysis in the Electronic Properties section indicates that the recombination rate will be lower in these systems due to different origins of CBM and VBM. We can also access the recombination rate of electron−hole pairs by evaluating the effective masses of charge carriers. Generally, in semiconductors the effective mass of electrons will be lower than that of holes. However, in these systems the effective mass of holes is lower than the electrons due to the well-dispersed bands in the VBM and relatively less dispersed bands in CBM. Therefore, the mobility of holes will be much higher than that of the electrons which results in a noticeable difference in electron−hole mobility.

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A higher value of relative ratio of the effective masses (D) indicates a large difference in the electron−hole mobility and thus reduces the recombination rate of electron−hole pairs. C2N1−xMx monolayers manifest higher D values along the Γ−M direction (ranging between 0.80 and 5.65) than that of the Γ−K direction (ranging between 0.66 and 2.35), and the values are comparable to other known photocatalysts. Hence, the iso-electronic-substituted C2N monolayers have lower electron−hole recombination rates which cater to enhance the photocatalytic water splitting efficiency.

Reduction and Oxidation Capabilities. An appropriate position of band edges relative to the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) potentials is necessary to identify the potential activity of a material for photocatalytic water splitting applications. The CBM has to lie above the reduction reaction potential, and the VBM has to lie below the oxidation reaction potential to drive
the redox reactions. It may be noted that the redox potential depends on pH value,\textsuperscript{4,5,7} and hence, the standard redox potentials with respect to the vacuum level for $\text{H}^+/\text{H}_2$ and $\text{O}_2/\text{H}_2\text{O}$ are calculated by using the following equations:

$$E_{\text{H}^+/\text{H}_2}^\text{red} = -4.44 \text{ eV} + \text{pH} \times 0.059 \text{ eV} \quad (5)$$

$$E_{\text{O}_2/\text{H}_2\text{O}}^{\text{ox}} = -5.67 \text{ eV} + \text{pH} \times 0.059 \text{ eV} \quad (6)$$

The band edge positions of C$_2$N, C$_2$N$_{1-x}$P$_x$, and C$_2$N$_{1-x}$As$_x$ monolayers with respect to the vacuum potential and to the HER and OER potentials at pH = 0 and pH = 7 are shown in Figure 5. From this figure one can see that the band edge position of P/As substituted C$_2$N monolayers has more favorable band edge position than the pure C$_2$N except for C$_2$N$_{0.667}$P$_{0.333}$ whose VBM is higher than the oxidation potential $E_{\text{O}_2/\text{H}_2\text{O}}^{\text{ox}}$ at pH = 0. Hence, this composition cannot split water into hydrogen and oxygen in acidic conditions. However, the band edge positions of all the other compositions straddling the HER and OER redox potentials at both pH levels indicate they are thermodynamically favorable for water splitting reactions to occur without any external bias.

**Optical Absorption.** Although there are other factors like appropriate band gap and suitable band edge positions which determine the efficiency of a photocatalyst, it is also important that a photocatalytic material should be able to absorb a significant fraction of incoming sunlight. Figure 6 shows the optical absorption coefficient of C$_2$N, C$_2$N$_{1-x}$P$_x$, and C$_2$N$_{1-x}$As$_x$ monolayers as a function of energy as well as wavelength. It may be noted that the PBE functional underestimates the calculated band gap values, and hence we have compensated them by using a so-called scissor operation with the correct band gap values obtained from the HSE06 functional that shifts the absorption spectrum rigidly to higher energy.\textsuperscript{22} From the estimated optical absorption spectra (see Figure 6), we have found that the optical absorption of the C$_2$N monolayer increases with photon energy over the range of visible light and reaches a maximum absorption at 3.2 eV with a maximum value as large as 10$^5$ cm$^{-1}$. This finding agrees well with previous results obtained from similar DFT calculations.\textsuperscript{17} This absorption peak at 3.2 eV is arising from the optical interband transition coming from a doubly degenerate flat band at $-1$ eV, which originates predominantly from the nonbonding (n) lone pair electronic states of N atoms to the localized $p_z$ orbitals of N in the CBM. In other words, the optical absorption is ascribed from the $n \rightarrow \pi^*$ electron transition involving lone pairs of the nitrogen atoms. However, C$_2$N$_{1-x}$P$_x$ and C$_2$N$_{1-x}$As$_x$ monolayers possess absorption edges that extended more into the visible region as evident from Figure 6. The observed notable red-shift of the absorption edge under P/As substitutions in C$_2$N is attributed by the band gap reduction. Hence, it is indeed that C$_2$N$_{1-x}$M$_x$ monolayers could efficiently utilize the maximum portion of the solar spectrum which improves the efficiency of photocatalytic water decomposition.

**CONCLUSIONS**

In conclusion, we have demonstrated using first-principles calculation that P/As substitution enhances the photocatalytic water splitting activity in the C$_2$N monolayer. Our results show that P/As substitutions decrease the bandgap of the C$_2$N with the increase in substitution concentrations, and at the same time it is still higher than the free energy of water splitting. Hence, these materials are thermodynamically suitable to drive hydrogen evolution reaction. Our effective mass calculations illustrate that charge transfer to the reactive sites would be easier, and also the rate of recombination would be lower which indicates that their photocatalytic efficiencies may be enhanced. The VBM and CBM of P/As substituted C$_2$N are distinctly comprised of different orbitals with well-dispersed valence and conduction bands, and hence longer carrier lifetimes are consequently expected. The band edge positions with respect to the redox potentials of water at pH = 0 and pH = 7 show that P/As substituted C$_2$N monolayers are potential photocatalysts for water splitting than the pristine C$_2$N monolayer. From the optical absorption spectra, we could find that P/As substituted C$_2$N monolayers show optical absorption extended more into the visible region, indicating that it could enhance the photoelectron conversion in the solar spectra. Optimum band edges to the redox potentials, enhanced optical absorption, low effective masses, and lower recombination rate reveal that P/As substituted C$_2$N monolayers are promising visible-light photocatalysts for overall water splitting.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b07776.

Band structure of pristine as well as P/As substituted C$_2$N monolayers using the GGA-PBE functional (PDF)

**AUTHOR INFORMATION**

*Corresponding Author

\textsuperscript{*}E-mail: raviphy@cutn.ac.in.

\textsuperscript{ORCID} ©

Ponniah Ravindran: 0000-0003-4611-011X

DOI: 10.1021/acs.jpcc.7b07776

J. Phys. Chem. C 2017, 121, 22216--22224
ACKNOWLEDGMENTS

The authors are grateful to the Research Council of Norway for computing time on the Norwegian supercomputer facilities. This research was supported by the Indo-Norwegian Cooperative Program (INCP) via UGC Grant No. F.No.58-12/2014(1C) and Department of Science and Technology, India, via Grant No. SR/NM/NS-1123/2013. The authors thank Helmer Fjellvåg and Anja O. Sjøstad for useful discussion.

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