Type-II InSe/g-C3N4 Heterostructure as a High-Efficiency Oxygen Evolution Reaction Catalyst for Photoelectrochemical Water Splitting

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Supporting Information

ABSTRACT: We propose a conceptual design of InSe/g-C3N4 van der Waals heterostructure to achieve highly efficient and spontaneous water splitting. InSe/g-C3N4 possesses a direct band gap of 2.04 eV with type-II band alignment, which is beneficial to the separation of electrons and holes and exhibits proper valence and conduction-band positions for the redox reactions of H2O. In addition, the adsorption of multiple water molecules and the changes of free energy on InSe/g-C3N4 have been calculated to understand the oxygen evolution reaction (OER) process of water splitting. The free energies of reaction on three sides are all downhill, and the values of ΔG reduce to about −0.406 eV, indicating that the OER of water splitting is a thermodynamically permissible reaction without the aid of any other substance. Therefore, the water-splitting reaction could be thermodynamically continued using InSe/g-C3N4 as a photocatalyst, which indicates that InSe/g-C3N4 is an excellent candidate for photocatalyst or photoelectronic applications.

The development of renewable solar energy in the form of an effective storage chemical has been widely recognized as a promising and sustainable development strategy to meet the future global energy demand.1,2 Taking advantage of a photocatalyst and solar energy, water splitting to generate oxygen and hydrogen is a low cost and a promising and appealing way to resolve the environmental issues and energy crisis.3,4 On the basis of the definition of a photocatalyst, a desired water-splitting photocatalyst should have a narrow band gap for sunlight utilization, an excellent carrier separation for efficient surface activity, and suitable redox potentials for the sufficient driving force of the redox reaction, besides nontoxicity, economic viability, and photochemical stability.5,6 Recently, great efforts have been made toward the development of photocatalysts, and the photocatalytic activity of a series of semiconductors has been extensively demonstrated, such as ZnO, WO3, Bi2WO6, and CdS.7−10 However, low absorption in visible light and high electron−hole recombination greatly limit the practical application of semiconductor photocatalysis. Therefore, it is a challenging task to search for active semiconductor photocatalysts that can split water directly under visible-light irradiation and improve its catalytic efficiency.

In recent years, polymeric graphite-like carbon nitride (g-C3N4), as a 2D layered semiconductor material with excellent chemical stability, nontoxicity, simple production procedure, low cost, and earth abundance, has been proved to be a promising candidate for water splitting.11−13 Interestingly, the band gap of this metal-free material is 2.7 eV, which is suitable to generate hydrogen and oxygen through water splitting under light irradiation.14 However, the low quantum efficiency, which originates from the inefficient separation and transportation of the photogenerated electrons and holes for g-C3N4, still hinders the application of g-C3N4 as a water-splitting photocatalyst.15−17 On the contrary, indium selenide (InSe) nanosheet exhibits a low formation energy with Eg of 1.4 eV and much larger carrier mobility compared with transition-metal dichalcogenides.18 InSe nanosheet is analogous to that of black phosphorus and may be suitable for photocatalytic water splitting.19 Moreover, the photodetectors based on few-layered InSe nanosheets also present a broadband from the visible to near-infrared region with a high photoresponsivity.20 However, monolayer InSe presents indirect band-gap characteristics, which will prevent more applications in high-performance optoelectronic devices.21 Also, the effort to extract the photocurrent has been hampered by the need to separate the electron and hole pairs created by the incoming photons.22 To date, the construction of heterojunction structures is considered to be an effective way to modify the atomic and electronic structures of photocatalysts to accelerate the separation and transmission of electron holes.23,24 van der Waals (vdW) heterostructures with different 2D ultrathin functional nanosheets (e.g., MoS2/graphene and SnSe2/WSe2)
have been successfully applied to suppress the photoexcited electron–hole recombination in bulk materials in an attempt to simultaneously promote charge transfer.25 To further extend the applications of the 2D InSe nanosheet, several researchers have worked on InSe-based vdW heterostructures, such as InSe/graphene and InSe/black phosphorus, so far.26,27 Because of the similar properties between monolayered InSe and g-C3N4, we design and predict InSe/g-C3N4 vdW heterostructures for highly efficient visible-light photocatalysts that can effectively prevent the recombination of the photoinduced electrons and holes and eventually facilitate the charge separation.

In our study, we have systematically investigated the structural and electronic properties, the band alignment, as well as the water adsorption and decomposition of the InSe/g-C3N4 heterostructure by using first-principles calculation. A typical type-II band alignment forms between InSe and g-C3N4 monolayers, and both the valence band maximum (VBM) and the conduction band minimum (CBM) of InSe are lower than those of g-C3N4. Furthermore, the structural and thermodynamic performances during the oxygen evolution reaction (OER) of water splitting on three sides of the InSe/g-C3N4 heterostructure have been systematically studied. It is meaningful to find that the InSe/g-C3N4 heterostructure is an excellent candidate for photocatalyst or photoelectronic applications, which provide theoretical guidance for applications in next-generation nanoelectronic devices.

The first-principles calculations were performed by the Vienna ab initio simulation package (VASP) with the projector-augmented wave (PAW), based on the density functional theory (DFT).28,29 The Perdew–Burke–Ernzerhof (PBE) scheme within the generalized gradient approximation (GGA) was used to treat the exchange-correlation interaction of electrons.30,31 Considering the underestimation of the PBE functional on the band gap of the semiconductor, the HSE06 hybrid functional was also applied for more accurate electronic structure and optical properties calculations.32 Because the weak interactions were not well described by the standard PBE functional, the empirical correction scheme of the DFT-D2 (D stands for dispersion) approach within the Grimme scheme was adopted for the nontrivial vdW interaction.33 A kinetic energy cutoff was set to be 600 eV for the plane-wave expansion. The convergence tolerances for energy, force, and maximum displacement on each atom during structural relaxation were set to $10^{-4}$ eV, 0.01 eV/Å, and 0.005 Å, respectively. A Monkhorst–Pack k-point mesh of $7 \times 7 \times 1$ was respectively used to calculate the properties of all of the studies in the 2D Brillouin zone. To avoid the interaction
between neighboring layers and its periodic impact, a vacuum spacing of 25 Å was added along the direction perpendicular to 2D nanosheet. Moreover, a well-known fact is that relativistic effects (of which spin–orbit is a part) grow approximately as \( Z^7 \), where \( Z \) is the atomic number, and they are definitely important for compounds of elements in the fifth period. Spin–orbit coupling (SOC) is included in our calculation to examine the influence of SOC on the splitting of the electronic bands.\(^{32}\)

The InSe/g-C₃N₄ heterostructure is achieved by InSe and g-C₃N₄ monolayers stacked in the vertical direction with consideration of vdW interactions.\(^{33,35}\) The calculated lattice parameters of the InSe (\( a = b = 4.07 \text{ Å} \)) and g-C₃N₄ (\( a = b = 7.06 \text{ Å} \)) monolayers are in good agreement with experimental and other theoretical calculations.\(^{36,37}\) A \( \sqrt{3} \times \sqrt{3} \) InSe supercell and a \( 1 \times 1 \) g-C₃N₄ supercell are adopted to construct the InSe/g-C₃N₄ heterostructure to minimize the lattice mismatch to 0.78%. In Figure 1a, according to the relative position of the InSe and g-C₃N₄ monolayers, we have constructed six stacking patterns: C atoms of g-C₃N₄ locate in the hexagonal ring center of InSe (labeled as \( H_{C1}, H_{C2}, \) and \( H_{C3} \)), and N atoms of g-C₃N₄ locate in the hexagonal ring center of InSe (labeled as \( H_{N1}, H_{N2}, \) and \( H_{N3} \)). To check the stability of the heterostructure and quantitatively characterize the interlayer interaction intensity, the binding energy (\( E_b \)) per unit cell is calculated by the following formula

\[
E_b = E_{\text{InSe/ C N₄}} - E_{\text{InSe}} - E_{\text{g-C₃N₄}}
\]

where \( E_{\text{InSe/ g-C₃N₄}} \), \( E_{\text{InSe}} \), and \( E_{\text{g-C₃N₄}} \) represent the total energies of the InSe/g-C₃N₄ heterostructure, the isolated InSe, and the g-C₃N₄ monolayer, respectively. According to the definition, the negative value of \( E_b \) indicates that the heterostructure system is energetically stable.

<table>
<thead>
<tr>
<th>stacking patterns</th>
<th>InSe/g-C₃N₄</th>
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</thead>
<tbody>
<tr>
<td>( d_0 ) (Å)</td>
<td>( H_{N1} )</td>
</tr>
<tr>
<td></td>
<td>2.604</td>
</tr>
<tr>
<td>( E_b ) (eV)</td>
<td>-2.315</td>
</tr>
<tr>
<td>( E_b ) (eV)</td>
<td>1.581</td>
</tr>
</tbody>
</table>

\( d_0, E_b \), and \( E_b \) are the values of lattice parameters, the binding energy, and the band gap.

<table>
<thead>
<tr>
<th>type</th>
<th>( H_{N1} )</th>
<th>( H_{N2} )</th>
<th>( H_{N3} )</th>
<th>( H_{C1} )</th>
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\( H_{C1} \) and \( H_{C3} \) are optimized to \( H_{N1} \) due to the instability of the three structures. It can be seen that pattern \( H_{N1} \) has the smallest binding energy of \(-2.315 \text{ eV}\) with the interlayer distance of 2.604 Å, which indicates that \( H_{N1} \) should be chosen as the heterostructure's stacking model in the following calculations.

The band structures of monolayer g-C₃N₄ monolayer InSe, and InSe/g-C₃N₄ heterostructure with and without SOC are shown in Figure 1b. The SOC causes an additional slight splitting of the bands with a value of \(<0.1 \text{ eV}\). Hence, it will not be discussed in the following studies. It can be seen that both InSe and g-C₃N₄ monolayers are indirect semiconductors, with \( E_g \) values of 1.372 eV (2.29 eV) and 1.182 eV (2.63 eV) at the GGA-PBE (HSE06) level, respectively. After contacting, the InSe/g-C₃N₄ heterostructure has a direct band gap, where CBM and VBM are both located in the \( G \) (G) point. Because of the influence of vdW interactions between InSe and g-C₃N₄ monolayers, \( E_g \) of the InSe/g-C₃N₄ heterostructure is reduced to 2.06 eV at the HSE06 level, which is less than \( E_g \) of InSe and g-C₃N₄ monolayers. VBM is mainly contributed by g-C₃N₄, whereas CBM is mainly provided by InSe, which indicates that InSe/g-C₃N₄ is a typical type-II vdW heterostructure, and the excited electrons and holes are, respectively, localized in InSe and g-C₃N₄ layers, facilitating the effective separation of the photogenerated holes and electrons. To gain more insights into the electronic structures of the InSe/g-C₃N₄ heterostructure, the electron density of states (DOS) and partial density of states (PDOS) are plotted in Figure S1 and are discussed in Supporting Information.

To further study the interaction mechanism of InSe/g-C₃N₄, the planar average charge density difference \( \Delta \rho (z) \) is calculated, which is given as

\[
\Delta \rho (z) = \rho (z)_{\text{InSe/g-C₃N₄}} - \rho (z)_{\text{InSe}} - \rho (z)_{\text{g-C₃N₄}}
\]

where \( \rho (z)_{\text{InSe/g-C₃N₄}} \), \( \rho (z)_{\text{InSe}} \), and \( \rho (z)_{\text{g-C₃N₄}} \) are the planar average charge densities of the combined InSe/g-C₃N₄ system, the InSe monolayer, and the g-C₃N₄ monolayer, respectively. In Figure 1c, vertical bars indicate the positions of InSe and g-C₃N₄ monolayers. Here negative values of \( \Delta \rho (z) \) areas highlight the regions of charge accumulation, whereas positive values of \( \Delta \rho (z) \) areas mark the regions of charge depletion. The change at the interfaces indicates that the electrons transfer from g-C₃N₄ to the InSe side across the interface, and thereby the holes remain in the g-C₃N₄ side. To further understand the interfacial electronic properties, we have calculated the interface dipole moment \( \mu (z) \) as follows

\[
\mu (z) = \int z \Delta \rho (z) \, dz
\]

A dipole moment \( \mu (z) \) of +0.086 D is found, thus confirming the formation of a heterostructure-induced interface dipole, where a positive value of \( \mu (z) \) suggests an inward pointing dipole,\(^{38}\) that is, from the InSe layer (with electrons) to the g-C₃N₄ layer (with holes). Furthermore, we have also checked the direction of the interface dipole by comparing the electrostatic potentials of the interface and those of isolated InSe and g-C₃N₄ (vacuum level shift). It is found that the work function of monolayer g-C₃N₄ (\( \Phi = 4.34 \text{ eV}\)) is smaller than that of monolayer InSe (\( \Phi = 5.38 \text{ eV}\)), as seen in Figure S2. If the work functions of the two materials forming the heterojunction are different, then the interface dipole will be present, which directs toward the layer with a smaller work function.\(^{39}\) Therefore, the direction of the interface dipole of the InSe/g-C₃N₄ heterostructure is directed toward the g-C₃N₄ layer, which is consistent with the above results of \( \mu (z) \).

Finally, we explore whether the InSe/g-C₃N₄ heterostructure could be a better candidate in photocatalytic reactions, especially water splitting. It should be noted that the water redox potential also depends on the pH value.\(^{40,41}\) The standard oxidation potential of \( \text{O}_2/\text{H}_2\text{O} \) can be calculated by \( E_{\text{O}_2/\text{H}_2\text{O}} = -5.67 \text{ eV} + \Phi \times 0.059 \text{ eV} \), and the reduction potential for \( \text{H}^+/\text{H}_2 \) is determined by \( E_{\text{H}^+/\text{H}_2} = -4.44 \text{ eV} + \Phi \times 0.059 \text{ eV} \). The unique feature of chalcogenides is their high stability in an acidic environment, especially in combination with other transition metals.\(^{42}\) Hence, the redox potential in a
neutral environment (pH 7) is also studied, as seen by the blue dotted lines of Figure 2a. From the VBM and the CBM of the InSe and g-C₃N₄ monolayers presented, Eₜ of InSe spans from −6.20 to −4.01 eV, whereas Eₜ of g-C₃N₄ spans from −5.88 to −3.23 eV. Both InSe and g-C₃N₄ monolayers satisfy the conditions of photocatalytic water splitting. However, the calculated band-edge positions of InSe and g-C₃N₄ are their potentials before contact. After g-C₃N₄ monolayer comes into contact with InSe monolayer, the electronic properties of the constituents could be changed. Because the work function of g-C₃N₄ (4.34 eV) is lower than that of InSe (5.67 eV), the electrons flow from g-C₃N₄ to InSe to align the Fermi energy, thus causing the change of relative band-edge position, as shown in Figure 2a. The VBM band is mainly composed of g-C₃N₄ states with a value of −5.84 eV, which is more negative than the oxidation potential (−5.67 eV at pH 0) of H₂O/O₂ for water splitting, whereas InSe contributes to the bottom part of the lowest conduction band (CB) with a value of −3.90 eV, which is less negative than the oxidation potential (−4.44 eV at pH 0 and −4.03 eV at pH 7) of H⁺/H₂. Consequently, the valence band offset (VBO) between InSe and g-C₃N₄ is −0.2 eV, whereas the conduction band offset (CBO) between them is ∼1.1 eV. In the photocatalysis process, the electrons could be photogenerated from the CB of monolayer InSe when the InSe/g-C₃N₄ heterostructure is illuminated by incident light. The existence of CBO induces the photogenerated electrons in the CB of g-C₃N₄ to inject into the CB of InSe. Simultaneously, the existence of the VBO induces the photogenerated holes in the valence band (VB) of InSe to drift to the VB of g-C₃N₄ which results in the separation of the electron and the hole on InSe and g-C₃N₄ monolayers, respectively. The separation in space could restrain the recombination of electron–hole pairs and prolong the lifetime of photogenerated carriers, which improves the photocatalytic bands of monolayer InSe, and the oxidation of water on the VBs of monolayer g-C₃N₄ could be conducted.

Strain engineering has been known as an effective method in controlling the electronic, transport, and optical properties of semiconductors for decades.⁴⁻⁵ This tool is particularly useful in engineering 1D and 2D crystals because these reduced-dimensional structures can sustain much larger strains than the corresponding bulk crystals. Therefore, we explore how strain affects the band edges and the band gap of the InSe/g-C₃N₄ heterostructure. The in-plane strain has been applied by biaxially stretching the hexagonal cell, and the biaxial strain is defined as ε = Δa/a₀, where a₀ is the lattice constant of the InSe/g-C₃N₄ heterostructure in its equilibrium state and Δa is the difference between the strained lattice constant and the unstrained lattice constant of the InSe/g-C₃N₄ heterostructure. Our results in Figure 2b suggest that the InSe/g-C₃N₄ heterostructure could ensure a suitable band alignment when applying a biaxial strain from −6 to +2% without damaging its structure. The position of VBM (CBM) increases (decreases) linearly when the strain changes from −6 to +2%. The band edges of all of the compressed strain systems are proper for initializing the photocatalytic redox reactions of water, whereas the reduction reaction becomes energetically impossible for the stretched strain systems. Such a desirable band-edge alignment of the InSe/g-C₃N₄ heterostructure indicates a strong compressed strain tolerance of the photocatalytic water-splitting abilities.

In addition, the adsorption and reaction of H₂O on the surface or in the interface of InSe/g-C₃N₄ heterostructure is another important parameter to characterize its activity in the photocatalytic water-splitting application. Figure S3 shows the most stable adsorption structures of H₂O on three sides of InSe/g-C₃N₄ with a 2 × 2 supercell. After the adsorption of the water molecule on the InSe/g-C₃N₄ heterostructure is studied, it is used as the basis to investigate the catalytic decomposition of the water molecule. Relative to the total reaction of the water molecule, there are two half-reactions: OER in anode: H₂O → 1/2O₂ + 2H⁺ + 2e⁻; hydrogen evolution reaction (HER) in cathode: 2H⁺ + 2e⁻ → H₂. However, OER is recognized as a much more complicated process that involves four-electron transfer. In our model, we assume that the OER proceeds through one-electron transfer steps according to the following pathway

\[
\text{H}_2\text{O} + * = \text{OH}^* + \text{H}^+ + e^- \quad (4a)
\]
\[
\text{OH}^* + \text{H}^+ + e^- = \text{O}_2^* + 2(\text{H}^+ + e^-) \quad (4b)
\]
\[
\text{O}_2^* + \text{H}_2\text{O} + 2(\text{H}^+ + e^-) = \text{OOH}^* + 3(\text{H}^+ + e^-) \quad (4c)
\]
\[
\text{OOH}^* + 3(\text{H}^+ + e^-) = \text{O}_2 + 4(\text{H}^+ + e^-) \quad (4d)
\]

where * indicates the active site on the surface of the substrate. The absorption states of OH*, O₂*, and OOOh* intermediates on catalysts are particularly important to understand the water-splitting process. Detailed configurations of them are shown in Figure S3 and Table S1, and the corresponding adsorption energies are calculated. The change of free energy (ΔG) is calculated using the following equation

\[
\Delta G = \Delta E + \Delta ZPE - T\Delta S - \Delta G_U - \Delta G_{PH} \quad (5)
\]
where $G$, $E$, $ZPE$, and $TS$ are the free energy, the total energy from the DFT calculation, the zero-point energy, and the entropic contribution ($T$ is set to be 298.15 K), respectively. $ZPE$ could be derived after the frequency calculation by

$$
ZPE = 1/2 \sum \hbar \nu
$$

The $TS$ values of adsorbed species are calculated after the vibrational frequencies are obtained

$$
TS_i = k_B T \ln \left( \frac{1}{1 - e^{-\hbar \nu/k_B T}} \right) + \sum_k \frac{\hbar \nu}{k_B T} \ln \left( \frac{e^{\hbar \nu/k_B T} - 1}{e^{\hbar \nu/k_B T} - 1} \right)
$$

(6)

$\Delta G_i = -eU$ represents the effect of a potential bias on all states involving one electron in the electrode, where $e$ is the elementary positive charge and $U$ is the potential measured against the normal hydrogen electrode. When $pH$ does not equal 0, the $G$ values of $H^+$ ions are corrected by $\Delta G_{ph} = -k_B T \ln 10 \times pH$. Here $pH 0$ and $pH 7$ are considered. Using the standard hydrogen electrode (SHE) as the reference, the reaction $G$ of $1/2H_2 \rightarrow H^+ + e^-$ is zero at pH 0, $p = 1$ bar, and $T = 298.15$ K. Therefore, the $G$ of $(H^+ + e^-)$ is equal to the $G$ of $1/2H_2$ under standard conditions.

The calculated free-energy changes of the OER process on the InSe/g-C$_3$N$_4$ heterostructure for the proposed four reaction steps at the equilibrium potential of 1.23 V (pH 0) are plotted in Figure 3 and are listed in Table S2. Clearly, the rate-determining steps are the step of $O^*$ to OOH*, with the largest $\Delta G$ of 0.433 eV on the g-C$_3$N$_4$ side, and the dissociation of H$_2$O to OH*, with the largest $\Delta G$ values of 1.057 and 0.596 eV on the InSe side and the interface of InSe/g-C$_3$N$_4$, separately. Increasing $\Delta G$ on three sides for the step of H$_2$O to OOH* shows that the InSe/g-C$_3$N$_4$ catalyst exhibits a high activated water adsorption energy on the three sides, which hinders the dissociation of water to OH* intermediates and leads to sluggish OER kinetics. For the dissociation of OH* to O*, the $G$ of the reaction on the g-C$_3$N$_4$ (InSe) side decreases from 0.232 (1.057) eV to $-0.036$ (0.855) eV but increases on the interface of InSe/g-C$_3$N$_4$ from 0.596 to 0.890 eV. Next, O* reacts with another H$_2$O molecule to generate the OOH* group. In this step, $\Delta G$ is positive for the g-C$_3$N$_4$ side, with a value of 0.434 eV, and negative for another two sides, with values of $-0.438$ and $-0.365$ eV. For the final step, the OOH* group dehydrogenates and converts to O$_2$. The $G$ values of the reactions on the three sides are all downhill, and the values of $\Delta G$ reduce to about $-0.406$ eV, indicating that the OOH* peroxo species easily breaks down to generate oxygen. It can be shown that the OER process on the g-C$_3$N$_4$ side is more energetically favorable than that on the other two sides and leads to a reduced energy barrier of the initial water dissociation step and subsequent dehydrogenation of OH*. Therefore, we mainly discuss the corresponding $\Delta G$ of the OER on the g-C$_3$N$_4$ side with different potentials under pH 0 and 7.

The difference between the photodehydration reduction potential and the potential corresponding to the InSe/g-C$_3$N$_4$ VB is considered to be the driving force for photooxidation of water under illumination conditions. The potential of the VB edge ($U_{VB}$) of the InSe/g-C$_3$N$_4$ heterostructure relative to the SHE is $U = \sim 1.40$ V at pH 0 and $U = \sim 1.81$ V at pH 7. Figure 4 shows the corresponding $\Delta G$ at external potential ($U = 0$ V), equilibrium potential ($U = 1.23$ V), and corresponding potential of the VB under the extreme conditions of pH 0 and 7. It is shown that at $U = 0$ V, the $G$ for every step increases at pH 0 and 7, which means that the reactions need to overcome a large energy barrier ($\Delta G = 4.514$ eV at pH 0 and $\Delta G = 4.099$ eV at pH 7). At the equilibrium potential $U = 1.23$ V at pH 0 and 7, the free energies of the dehydrogenation steps of OH* and OOH* decrease, but for the other two steps, they still increase. At an operating potential of 1.40 V (pH 0), $\Delta G$ for the dehydrogenation of H$_2$O and generation of OOH* turns out to be less positive, and $\Delta G$ for the dissociation of OH* and OOH* is more negative. This indicates that the OER becomes easier under the driving force of the InSe/g-C$_3$N$_4$ VB edge. When an external potential $U = 1.81$ V is applied at pH 7, the $G$ of all steps involved in the reaction is reduced, and the reaction is thermodynamically sustainable.

![Figure 3](image1)

**Figure 3.** Free-energy ($\Delta G$, eV) profiles of the OER (pH 0, $U = 1.23$ V) on the InSe surface, the g-C$_3$N$_4$ surface, and the interlayer of InSe/g-C$_3$N$_4$. The surface structures of the g-C$_3$N$_4$ surface in different stages are shown in the inset.

![Figure 4](image2)

**Figure 4.** Free energies of the intermediates on g-C$_3$N$_4$ surface at pH 0 and 7 at different potentials.
Therefore, by using the InSe/g-C3N4 heterostructure as a photocathode, the photocatalytic decomposition of water is a thermodynamically permissible reaction without the aid of any other substance.

**CONCLUSIONS**

We have explored the potential of the InSe/g-C3N4 heterostructure for oxygen evolution electrocatalysis of water splitting by DFT calculations. The InSe/g-C3N4 heterostructure is a typical type-II semiconductor with a direct band gap of 2.04 eV, where CBMs and VBMs are separately contributed by InSe and g-C3N4, respectively. Furthermore, the calculated E_{ads} values for H2O-InSe/g-C3N4, InSe/g-C3N4-H2O, and InSe/H2O/g-C3N4 are −0.376, −0.778, and −0.991 eV, respectively, which are beneficial for water-splitting reactions. The G values of the reactions on three sides are all downhill, and the values of ΔG reduce to about −0.406 eV. When an external potential U = 1.81 V is applied at pH 7, the driving force provided by the InSe/g-C3N4 and the values of external potential respectively, which are beneficial for water-splitting reactions.

**ASSOCIATED CONTENT**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcl.9b00909.

Calculated DOSs and electrostatic potentials for InSe monolayer, g-C3N4 monolayer, and InSe/g-C3N4; stable adsorption structures of H2O, OH*, O*, and OO*; and specific data of ΔG calculation (PDF)

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**


(42) Vante, N. A.; Jaegermann, W.; Tributsch, H.; Honle, W.; Yvon, K. Electrocatlysis of Oxygen Reduction by Chalcogenides Contain-