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ARTICLE

Photocatalytic Splitting of Water on s-triazine based Graphitic Carbon Nitride: An *ab initio* Investigation

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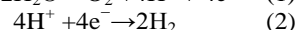
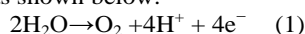
Density functional theory based investigations have been carried out to understand the reaction mechanism of the overall photocatalytic water splitting reaction on s-triazine based carbon nitride (g-CN) and to calculate the overpotentials for both oxygen and hydrogen evolution reactions. The calculated free energy changes for different possible intermediate reactions show that at the equilibrium potential of 1.23 V (against NHE), the oxygen evolution reaction is not completely downhill indicating that the photo-generated holes at 1.23 V cannot oxidize water to oxygen. The oxygen evolution reaction on the g-CN surface is however found to be completely downhill at and above a potential of 2.16 V. As the valence band of g-CN is shown to be located at a potential of 2.64 eV, the photo-generated holes in the valence band can oxidise water to oxygen without the aid of any co-catalyst. However, the hydrogen evolution reaction is found to have an overpotential of around 1.1 V and the photo-generated electrons in the conduction band of g-CN are placed at around 0.26 V above the water reduction potential indicating that the hydrogen evolution is possible only in the presence of a co-catalyst.

Introduction

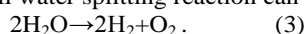
Hydrogen generation through photocatalytic water splitting using solar energy is an important strategy in advancing towards a sustainable energy system.¹⁻³ Apart from being renewable in nature, energy production through hydrogen generated in this manner is also environmentally clean as it does not lead to release of any hazardous gas to the earth's atmosphere.⁴ The main challenge in this process lies in finding an effective photocatalyst which can efficiently utilize solar energy to split water and generate hydrogen.⁵⁻⁸ Along with the tremendous experimental efforts to develop a potential photocatalyst, computational chemistry has also shown to play an important role in screening a large number of catalysts which can give valuable inputs to the experiments.⁹⁻¹³ An efficient photocatalyst should have both chemical and photochemical stability, efficient visible light absorption capability, appropriate electronic band structure for overall water splitting and also economic viability. Following the pioneering work by Honda and Fujishima¹⁴ on developing the photo-electrochemical cell using TiO₂ as an anode, enormous number of semiconductor photocatalyst materials have been tested for solar water splitting which include metal oxides, metal sulphides, metal nitrides, metal oxinitrides etc.¹⁵⁻²⁰ In spite of the intensive research work carried out throughout the world, finding an efficient photocatalyst for solar water splitting is still a challenging problem and computational design

of new catalysts is thus very important.

When a semiconductor photocatalyst with proper band gap is irradiated with light, electrons in the valence band can be excited to the conduction band leaving holes in the valence band. These photogenerated electrons and holes travel to the surface of the catalyst where oxidation of water by the holes leads to oxygen evolution and the electrons can reduce protons to hydrogen as shown below.



and the overall water splitting reaction can be written as



The theoretical minimum band gap required for this process to occur is 1.23 eV and the conduction band minima (CBM) of the catalyst should be above the water reduction potential and the valence band maxima (VBM) should be located below the oxidation potential of water. However, in practice, these conditions are not just sufficient due to associated overpotentials with the redox processes, especially in case of the oxygen evolution reaction. In most of the catalyst materials investigated, though the VBM and CBM satisfy the thermodynamic conditions for overall water splitting, a co-catalysts is required.¹⁵⁻¹⁸ Oxidation of water to dioxygen is found to have very high overpotentials as compared to the hydrogen evolution reactions and demands sacrificial reagents.

Computational studies have been found to be highly useful in understanding the underlying mechanism, estimating the overpotential associated with each half-cell reaction and also predicting whether the particular reaction requires a co-catalyst. Using density functional theory (DFT) calculations, Rossmeisl et al.²¹ have studied the electrolysis of water on different metal surfaces, and shown that it is feasible only on partially oxidized metal surfaces. They have also proposed a linear relation between the oxygen adsorption energy and the catalytic reaction rate. They have also studied the photo-oxidation of water on different metal oxide surfaces like TiO₂, RuO₂ and

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IrO₂ and predicted that the overpotential in TiO₂ is higher as compared to the other two catalysts.²² Wirth et al.²³ studied water splitting on rutile RuO₂ where they have shown that the rate limiting step is the formation of hydroxyl radical and calculated the overpotential as 0.64 eV. Recently, polymeric carbon nitride based semiconductors attained great research interest for making photocatalyst because of their high stability and the possibility of tuning their electronic structure through functionalization and doping.²⁴ Tris-s-triazine based graphitic carbon nitride (g-C₃N₄) has been reported to be a metal-free photocatalyst for solar water splitting.²⁵ However, initial studies indicate that this material shows poor quantum yields and requires a sacrificial reagent. A number of strategies have been attempted to improve its activity through non-metal doping, metal decoration, structure control through different precursors etc.²⁶⁻³¹ Wirth et al.³² have investigated the photocatalytic splitting of water on g-C₃N₄ using first principles based method as well as semi-empirical methods. Their results indicate that the O₂ evolution reaction requires a minimum potential of 2.28 V whereas the potential of the holes in valence band is 1.85 V (with respect to NHE). This shows that the material requires a cocatalyst for O₂ evolution. Liu et al.³³ reported a new catalyst based on carbon nitride- carbon nanodot composite as metal-free photocatalyst with a solar to hydrogen conversion efficiency of 2.0 % and without requiring any sacrificial reagent. Here, the reaction is shown to follow a step wise 2e⁻/2e⁻ reduction through the formation of H₂O₂ intermediate.

In our recent study, we have proposed s-triazine based carbon nitride (g-CN) as possible photocatalyst for water splitting.³⁴ The proposed g-CN has been found to have highly dispersed valence and conduction bands and no isolated states were present indicating the possibility of high carrier mobilities. Very recently, based on the nature of the electronic band structure, Wang et al.³⁵ have proposed that the charge carriers in g-CN can act like massless Dirac Fermions. These observations indicate that the mobility of the photo-generated charge carriers in g-CN can be very high and is expected to lead to better photo catalytic activity as well. In the present study, we are interested in understanding the mechanism of photocatalytic splitting of water on g-CN surface and estimating the overpotentials associated with both oxygen and hydrogen evolution reactions. We have considered a supercell of g-CN and studied the adsorption of all the possible intermediates proposed.

Computational Details:

All the periodic first principles calculations were carried out using the spin-polarised density functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP).³⁶⁻³⁷ Kohn-Sham equations of the valence electrons were expanded using plane-wave basis sets with a kinetic energy cutoff of 550 eV. The interaction between the core and valence electrons was treated by using the projector augmented wave (PAW) potentials.³⁸⁻³⁹ The exchange-correlation energy density functional was treated through the Generalized Gradient Approximation (GGA) of Perdew-Burke-Ernzerhof (PBE).⁴⁰ To take care of the weak van der Waals interactions, the dispersion corrections to the total energies were incorporated through the Grimme's semi-empirical method.⁴¹ Electronic optimization was carried out through self-consistent field iterations with an energy cutoff of 1×10^{-6}

eV. For the ionic optimization, both unit cell and atomic positions were relaxed at constant volume by setting a force cut-off of 0.01 eV Å⁻¹ on each atom. The Brillouin zone has been sampled through an automatically generated Γ -centered $5 \times 5 \times 1$ Monkhorst-Pack set of k-points.⁴² Sufficient vacuum (~ 20 Å) has been considered along the z-direction to avoid the interactions between images. The graphical software VESTA has been used for generating the reported figures.⁴³

For calculating the free energy change in the proton coupled electron transfer reactions in the oxidation/reduction reactions considered, we have used the method developed by Nørskov et al.⁴⁴ which has been extensively used for estimating the free energy changes in many electrochemical reactions.⁴⁵⁻⁵⁰ From these free energy differences calculated for different intermediate states involved, the energy barriers associated with the formation of intermediates can be measured but it does not involve the calculation of kinetic barrier for the formation of the intermediates. The free energy change of a reaction is calculated as the difference between the free energies of the initial and final states as shown below

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_U + \Delta G_{pH} \quad (4)$$

where, ΔE corresponds to the DFT calculated reaction energy, ΔZPE is the difference in zero point energy, ΔS is the change in entropy, $\Delta G_U = -eU$ (U is potential of the photogenerated hole in the valence band with respect to the normal hydrogen electrode (NHE)) and $\Delta G_{pH} = 2.303 k_B T \text{ pH}$. Here, k_B is the Boltzmann constant, the temperature T has been taken as 300 K and $\text{pH} = 0$ has been used. The vibrational frequencies were calculated through density functional perturbation theory to obtain the zero point energy correction and entropies. The entropies of the species in gas phase were taken from the NIST database.⁴⁹ The free energy of the ($\text{H}^+ + \text{e}^-$) pair at standard conditions of $\text{pH}=0$, $p=1$ bar and $U=0$ is taken as that of $1/2(\text{H}_2)$ in the gas phase. As it has been discussed in our earlier study,⁴⁵ the free energy of O₂ calculated from DFT methods is incorrect and hence its free energy has been taken from the free energy change of the reaction $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ which is 4.92 eV.⁴⁴⁻⁴⁷

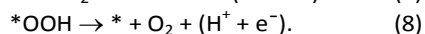
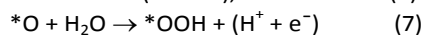
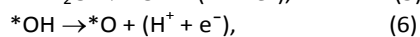
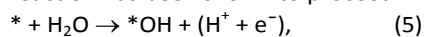
Results and discussion

To study the adsorption of different intermediates involved in photocatalytic splitting of water on g-CN surface, we have considered the supercell of the g-CN with 24 carbon atoms and 24 nitrogen atoms. The optimized supercell structure using the PBE method is reported in Figure 1(a) and the measured C-C and C-N bond distances are found to be 1.51 Å and 1.34 Å respectively which are matching well with earlier reported results.³⁴⁻³⁵ Band decomposed charge density of the valence band maximum (VBM) and conduction band minimum (CBM), are calculated and the corresponding isosurface plots are shown in Figures S1. The plots indicate that the VBM is mainly contributed by the nitrogen 2p states and the CBM is originating from the pz states of both C and N. The atomic charges calculated through Bader charge density analysis⁵²⁻⁵⁴ indicate that there is a charge transfer of around 1.1 e⁻ from carbon to nitrogen due to the difference in electronegativity.

Before discussing the adsorption of different intermediates, we start the discussion with the adsorption of water on the g-CN surface. We have considered different possible sites for water adsorption such as above the C-C bond, above the C₃N₃ ring and above the N₆ cavity. From the optimized energetics, the minimum energy structure is found to be above the N₆ cavity as shown in Figure 2(b). The adsorbed water molecule is found to orient in such a way that it forms two hydrogen bonds with the two opposite nitrogen atoms of the s-triazine rings and the plane of water molecule is found to be perpendicular to the g-CN plane. The measured N...H bond distances are found to be 2.24 Å and 2.14 Å and the NHO bond angle is found to be 165.38° and 167.01°. The calculated adsorption energy of the water molecule on g-CN using the PBE method is found to be -0.56 eV.

Oxygen evolution reaction (OER)

To study the overall water splitting on g-CN we have used the model proposed by Nørskov^{21-22,44} which has been used extensively in many recent studies.⁴⁵⁻⁵⁰ The oxygen evolution reaction has been shown to proceed in four steps as



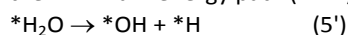
where *X refers to species X adsorbed on g-CN surface

All the intermediates adsorbed on the g-CN surface (*OH, *O and *OOH) have been subjected to energy minimization and the resulting optimized structures are reported in Figure 2. The free energy changes for all the elementary reaction steps were calculated as specified in the computational details section. In the first elementary reaction step, the water molecule on g-CN surface is converted to *OH by releasing one (H⁺+e⁻). In the case of OH adsorbed on g-CN (*OH), the oxygen atom is chemically bonded to the nitrogen of triazine ring with a bond length of 1.37 Å and the hydrogen atom of OH forms hydrogen bond with the nitrogen of the neighbouring C₃N₃ ring as shown in Figure 2. The OH...N distance is found to be 1.62 Å and the corresponding distance with the next neighbouring nitrogen is found to be 2.95 Å with NHO angle in the range of 145-147°. The calculated free energy for this reaction step (5) is found to be +2.15 eV. In the next reaction step, the adsorbed OH releases one (H⁺+e⁻) and converts into *O. In the optimized structure of *O which is shown in Figure 2, the N-O bond distance is found to decrease to 1.26 Å from 1.37 Å in *OH which is expected. The calculated free energy change for this reaction step is found to be +0.23 eV. In the third step of the reaction, a second water molecule interacts with *O and results into *OOH by releasing the third electron-proton pair. For the *OOH geometry, it is found that the geometry with OOH placed above the N₆ cavity (as shown in Figure 2) without any N-O chemical bond is found to be energetically preferred as compared to the one with the N-O bond (Figure S2). Here also, the hydrogen of OOH is found to be bonded to nitrogen of C₃N₃ ring through hydrogen bonding and the measured OOH...N distance is 1.89 Å. The O-O bond distance is found to be 1.34 Å and the O-H distance is 1.02 Å. The free energy change for this reaction is calculated to be +2.16 eV. In the

final reaction, *OOH will release the fourth pair of electron-proton along with di-oxygen leaving the g-CN surface. The calculated free energy change for this process is calculated to be +0.38 eV.

From all the free energies discussed above, it can be seen that all the reaction steps are uphill at U=0 V with a total free energy change of +4.92 eV and the reaction (7) will be the limiting step with +2.16 eV free energy change. The free energy plot at different potentials is shown in Figure 3, from which it can be seen that at equilibrium potential of U=1.23 V, the reactions (6) and (8) are found to be downhill whereas reactions (5) and (7), where proton is extracted from water, are uphill in nature. This shows that the holes in the valence band positioned just at the water oxidation potential cannot really oxidize water to O₂. The free energy profile at U= 2.2 V shows that none of the reactions is associated with uphill energy and the reaction can occur. Hence, holes in the valence band with potential of 2.16 V and above can oxidize water to oxygen and the overpotential for this reaction will be 2.16-1.23=0.93 V. In our earlier study,³⁴ we have shown that the valence band of g-CN is placed at a potential of 2.64 eV with respect to the NHE. This indicates that the photo-generated holes in the valence band of g-CN can oxidize water without any cocatalyst. An earlier study³² on g-C₃N₄ has shown that the corresponding OER has very high overpotential as compared to the position of the valence band and it requires a cocatalyst. Our results on g-CN indicate that this material is superior to g-C₃N₄ in this regard.

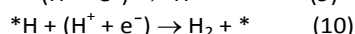
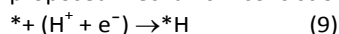
As it is found from the calculated free energy differences, that the reactions (5) and (7), where proton is extracted from water, are more energy demanding steps, we have evaluated the minimum energy path (MEP) for the following reaction



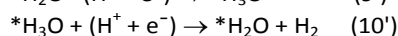
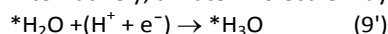
where the proton is adsorbed to the g-CN surface instead of getting transferred to the water medium. MEP calculations have been carried out using the climbing image nudge elastic band (CI-NEB) method⁵⁵ as implemented in Quantum Espresso.⁵⁶ The geometries of the initial, final and transition states along with the energy profile of the MEP are shown in Figure 4 and complete details are given in supporting information. It can be seen from Figure 4, that the barrier for the reaction (5') is 2.12 eV which is just comparable to the free energy changes for the reactions (5) and (7) and hence the effect of the barrier on the measured overpotentials can be expected to be minimum.

Hydrogen evolution reaction (HER)

We have also investigated the HER on g-CN surface and the proposed mechanism consist of the following steps²¹⁻²²



Alternatively, a water molecule may be involved



We have studied both the cases shown above. The optimized structures of both *H and *H₃O are reported in Figure 5. From the optimized structures it can be observed that in the case of

*H, the hydrogen atom is chemically bonded to one of the nitrogen of C_3N_3 ring with a N-H bond distance of 1.03 Å, whereas in the case of $*H_3O$, even if we place the hydrogen near the N atom of C_3N_3 initially, in the optimized structure the hydrogen is bonded to water molecules forming H_3O adsorbed on g-CN surface through hydrogen bonding as shown in Figure 5. The free energies were calculated for both the processes and are reported in Table 1. It can be observed that for the H adsorbed case, the adsorption free energy is found to be -0.82 eV indicating that the overall H_2 evolution will have an overpotential of 0.82 V. In presence of an extra water molecule, the free energy is found to further increase to -1.15 eV and hence the overpotential will be 1.15 V. From our previous study,³⁴ the conduction band of g-CN is found to be located just 0.26 eV above the water reduction level. This indicates that the hydrogen evolution on g-CN cannot proceed without the aid of a co-catalyst. Otherwise, to facilitate the hydrogen evolution without a cocatalyst, the electronic band structure of g-CN has to be tuned in such a way that the conduction band is elevated above the estimated overpotential.

Although the material, g-CN considered here is found to have little higher overpotential for HER and requires a co-catalyst, the OER is found to proceed here without any cocatalyst, which is in contrast to many other catalytic systems investigated for which the OER demands a co-catalyst or sacrificial reagent. Hence, g-CN based photocatalyst can be a good choice for photocatalytic water splitting. As g-CN is showing good activity for OER and g- C_3N_4 is known to show good activity for HER, we propose that the composite of these two materials can be investigated further to design a better photocatalyst and studies in this direction are in progress. As the synthesis of the material considered has already been reported,⁵⁷⁻⁵⁸ it is possible to design the g-CN based photocatalyst. Our computational results reported here will definitely provide better understanding of the underlying mechanism and useful insights in designing new g-CN photocatalyst and modification of its electronic structure to facilitate the overall water splitting on g-CN surface

Conclusions

In summary, we have investigated the overall water splitting reaction mechanism on s-triazine based graphitic carbon nitride surface. The calculated binding energy of a water molecule on g-CN surface is found to be -0.56 eV and the driving force is the hydrogen bonding between the water hydrogen atoms and nitrogen atoms of g-CN. A systematic study of different intermediate reaction steps involved in both OER and HER has been carried out. The calculated overpotential for OER is found to be ~0.93 V and the holes in the valence band are at a potential of 2.64 eV (with reference to NHE). These results on OER mechanism indicate that g-CN can facilitate the reaction without the aid of any co-catalyst which is highly desirable for designing an active photocatalyst. The study of HER on g-CN reveals that the reaction is having an overpotential of around 1.0 eV. As the photogenerated

electrons in conduction band are located just 0.26 eV above the water reduction level, the reduction reaction requires a cocatalyst.

Acknowledgements

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Table 1: Calculated free energy changes for hydrogen evolution reaction under different conditions

	Calculated free energy change (eV)	
	Isolated H atom	In presence of H ₂ O
ΔG (9/9')	+0.82	+1.15
ΔG (10/10')	-0.82	-1.15

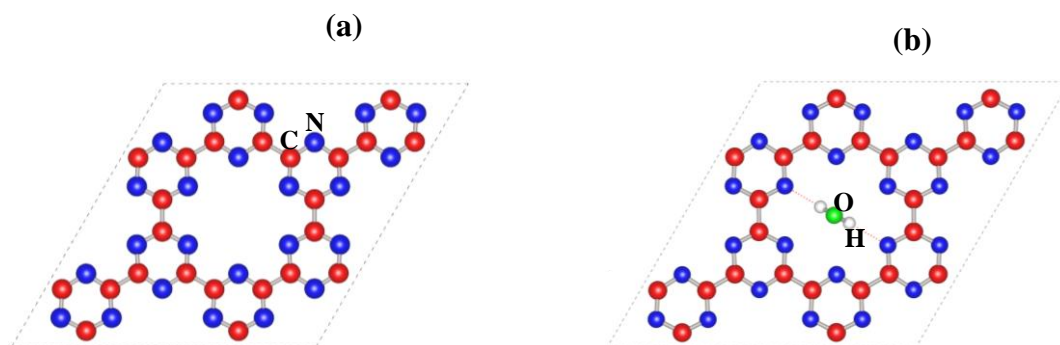


Figure 1: Optimized geometry of (a) g-CN supercell and (b) water adsorbed g-CN supercell

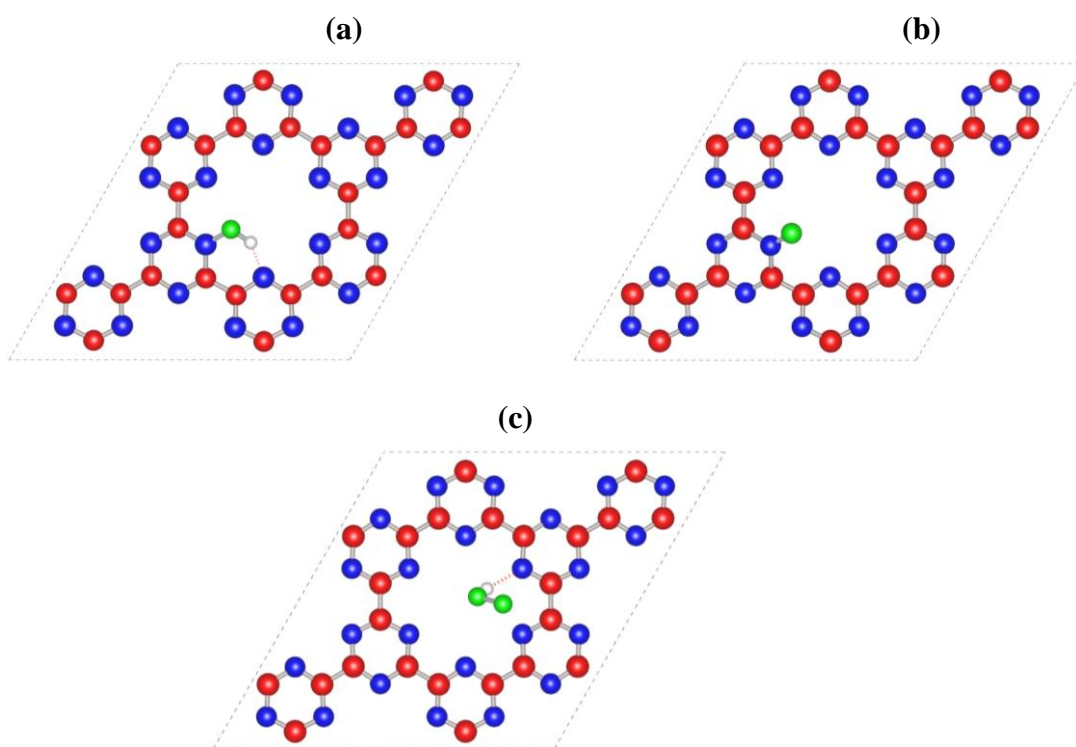


Figure 2: Optimized geometries of possible intermediates of OER (a) $*OH$, (b) $*O$ and (c) $*OOH$

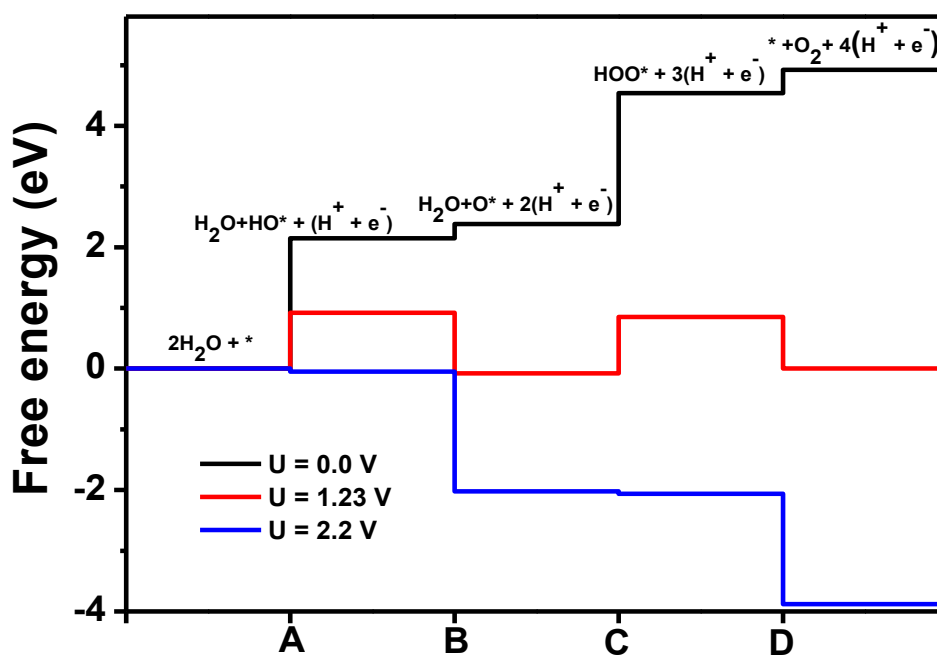


Figure 3: Calculated free energy changes for the different intermediated reaction steps involved in the oxygen evolution reaction at different potentials.

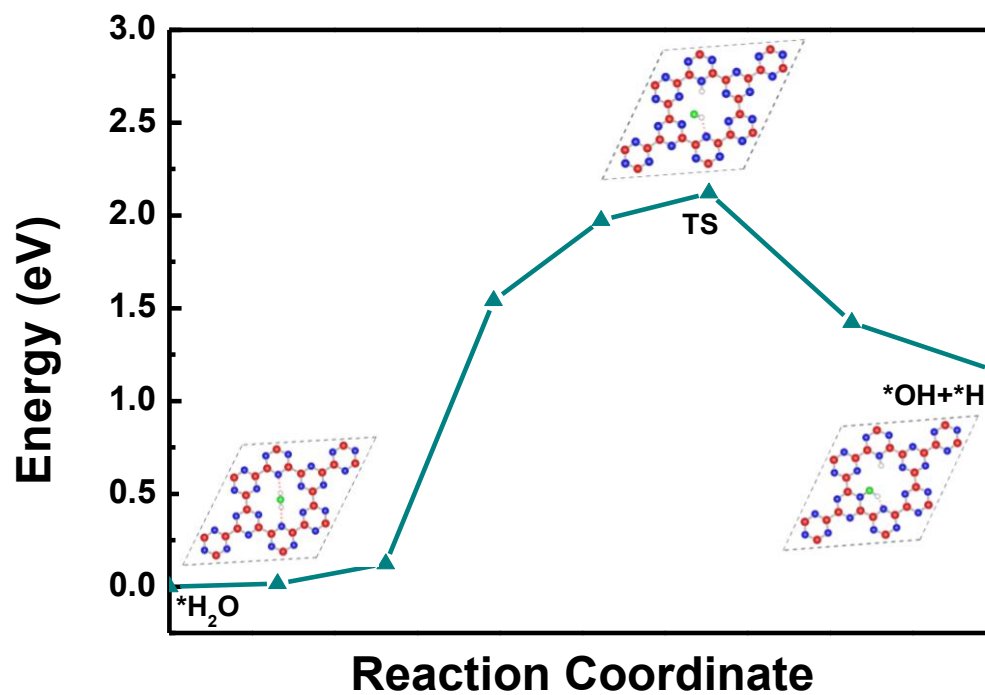


Figure 4: Minimum energy path for the dissociation of water molecule on g-CN surface with the optimized geometries of the *H₂O, transition state (TS), and *OH+*H.

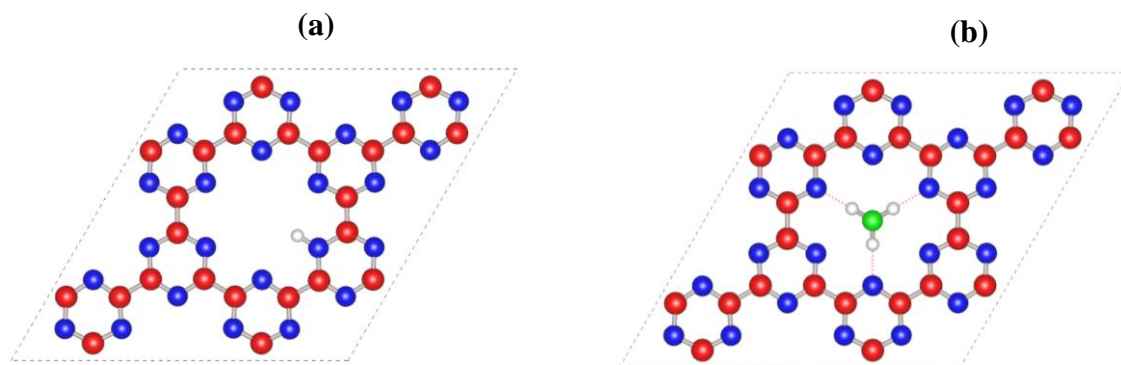
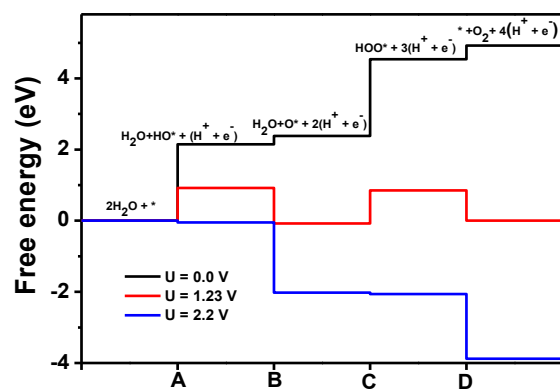
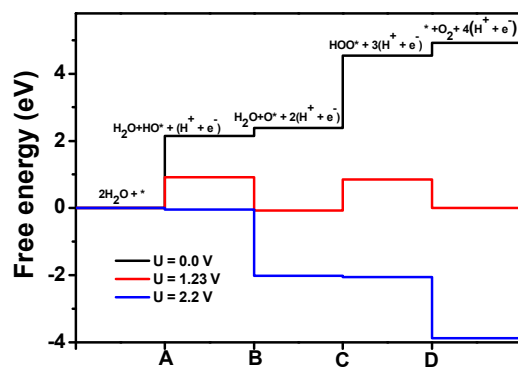


Figure 5: optimized geometries of (a) *H and (b) *H_3O

TOC

Ab initio investigations have been carried out to understand the mechanism of photocatalytic water splitting on the g-CN based semiconductor photocatalyst.

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