

Computational Modeling of Novel Materials for Hydrogen Energy Related Applications

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Abstract

Hydrogen is considered to be one of the best alternative, renewable and carbon-free energy carriers. However, its generation, storage and utilization are posing major challenges. Through *ab initio* investigations, we proposed s-triazine based graphitic carbon nitride as a possible metal-free photocatalyst for solar water splitting. We have also shown that the electronic band structure of graphitic carbon nitrides can be tuned through doping with non-metal elements as well as by metal decoration. The detailed mechanism of water splitting reaction on the photocatalyst surface has been studied and the associated overpotentials for each half-cell reactions were measured. For effective storage of hydrogen in molecular form, varieties of light metal decorated molecules and materials were modelled by using some of the elegant chemical concepts such as the electrostatic interactions, curvature of the carbon nanomaterials, aromaticity etc.

Introduction:

Energy is considered to be the key factor in deciding the social and economic development of any country. Worldwide, especially in the developing countries, energy sector has been given prime importance in view of rapidly increasing energy demands due to the day by day improved standards of living along with the industrial revolutions.¹ Gradually depleting fossil fuel resources and their adverse effects on environment are providing the motivation to search for a clean and sustainable energy system. Hydrogen has been accepted worldwide to be one of the best possible alternative renewable energy carriers.²⁻⁴ Though hydrogen is having very high energy density per unit mass, its energy density per unit volume is very less. At ambient conditions of 25 °C temperature and 1 bar pressure, 1 kg of hydrogen requires a volume of ~11 m³. Hence, developing effective hydrogen storage technology for transportation applications is highly challenging and one of the key factors in moving towards the hydrogen economy.

Though hydrogen is the most abundant element on the earth, less than 1% of it is present as the molecular hydrogen and majority of it is in chemically bonded state like water and hydrocarbons. Hence the generation of molecular hydrogen from the other forms requires breaking those molecules which is energetically intensive. The overall water splitting reaction is thermodynamically an uphill reaction with a positive free energy change of $\Delta G = +237.12$ kJ/mol. The hydrogen production from water can be carried out through different means such as thermal, electrical, photonic and biochemical methods. The primary energy needed for different methods to produce hydrogen can be obtained from different green energy sources like thermal and electrical energy from solar, wind,

geothermal, tidal, wave, ocean thermal, hydro, biomass, nuclear energy, etc.⁵ An ideal way for achieving sustainable energy is through the use of solar energy to convert water into hydrogen and oxygen. Solar water splitting using semiconductor photocatalyst has attracted immense research interest after the original work by Honda and Fujishima⁶ using a semiconductor anode such as TiO₂ and a metal cathode like platinum. To be a good photocatalyst for water splitting, the materials should satisfy several requirements, viz. (i) suitable bandgap for efficient absorption of solar visible-light (ii) appropriate band edge potentials for overall water splitting (iii) ability to separate photo generated electron-hole pairs (iv) stability towards chemical and photo corrosion in aqueous environments etc.⁷ For a photocatalyst to complete the overall water splitting, its conduction band bottom should be more negative than the proton reduction potential (0 V vs. NHE) and the top of the valence band should be more positive than the oxidation potential of water (+1.23 V vs. NHE). Apart from the conventional materials such as transition metal oxides, nitrides, oxinitrides etc, polymeric semiconductor materials like graphitic carbon nitride (g-C₃N₄) materials are found to have great potential as photocatalyst. In a recent study, Wang et al.⁸ have reported the melem-based polymeric graphitic carbon nitrides (g-C₃N₄) as a metal-free photocatalyst for visible-light driven hydrogen production through water splitting. g-C₃N₄, with appropriate band structure for overall water splitting along with its high thermal and chemical stability gained lot of interest in designing a metal-free catalyst. However, this material is reported to have a very poor quantum yield of ~0.1% which is attributed to the high recombination rate of electron-hole pairs generated. To overcome this problem, many methods are proposed to tune the properties viz. doping, metal decoration, introducing porosity, making

graphene/C₃N₄ composites etc.⁹⁻¹¹ Pan et al.¹² have shown that the g-C₃N₄ nanotubes have delocalised valence top states unlike sheet which is having strongly localized valence top states indicating the larger mobilities in nanotubes. They have also shown that functionalization of these tubes with metals like Pt and Pd can enhance the photocatalytic properties of these nanostructure materials.

Developing efficient hydrogen storage technology for transportation applications at ambient conditions is another key challenge in hydrogen economy. A good hydrogen storage material should satisfy certain operating requirements such as: (i) hydrogen absorption and desorption enthalpies should be in-between that of chemisorption and physisorption, (ii) fast kinetics at ambient conditions for quick uptake and release of hydrogen, (iii) high gravimetric and volumetric densities for effective hydrogen storage, (iv) effective heat transfer, (v) Long recyclable lifetime of the material for hydrogen absorption/desorption, (vi) high mechanical strength and durability, and (vii) safety at operational conditions.¹³ Currently, hydrogen is usually stored through two technically well-understood technologies, high pressure compression of the gas and cryogenic storage of liquid hydrogen and both these methods are neither safe nor cost effective. Another important way of storing hydrogen is by absorbing it either physically or chemically in the form of metal or chemical hydrides or adsorbing it on the surfaces and inside the pores of a porous solid matrix. In physical adsorption, hydrogen is bound to the substrate through weak van der Waals forces of interaction between the hydrogen and the substrate. As the binding interactions between hydrogen molecules and the substrate are very weak, physisorption typically takes place at low temperature. Doping with light metal atoms like alkali and alkaline earth metals is found to be effective in improving the hydrogen binding energies and varieties of metal decorated materials have been explored for hydrogen storage.

Computational Methods

In all our studies, we have employed different quantum mechanical methods, viz. wave function based Hartree-Fock and MP2 methods and also the density functional theory (DFT) based methods for all the studies carried out. In principle, the molecular level calculations are carried out by using the localised Gaussian basis sets (using GAMESS), while the plane-wave basis sets were used for the periodic solid state calculations (using VASP).¹⁴⁻¹⁶ Within the framework of DFT, we have used several exchange-correlation energy functionals, such as the local density approximation (LDA), generalized gradient approximation (GGA), Becke's three-parameter exchange functional and Lee-Yang-Parr correlation functional (B3LYP), and also the recently developed Minnesota functionals. As it is known that the band gaps calculated from PBE functional are underestimated, we have also used the more accurate

hybrid functional, developed by Heyd, Scuseria, and Ernzerhof (HSE).

Graphitic Carbon Nitride Based Photocatalyst for Solar Water Splitting

Through *ab initio* electronic structure studies, we explored the s-triazine based polymeric graphitic carbon nitride with CN stoichiometry (g-CN) for its photocatalytic activity towards water splitting.¹⁷ The optimized cell parameter from PBE method is found to be 7.127 Å with the C-C and C-N bond distances of 1.510 Å and 1.341 Å respectively. From the PBE calculations, g-CN is found to have a direct band gap of 1.54 eV along the k-vector **K**. However, as it is well known that the band gaps calculated from pure DFT functionals like PBE are underestimated and the hybrid functionals like HSE06 can deliver reasonably good results, we have also calculated the band structure of g-CN using HSE06 method. The band gap of g-CN calculated from HSE06 method is found to be 3.18 eV which is more than double the corresponding value from PBE functional. The conduction band minimum (CB_{min}) calculated from HSE06 method is found to be -3.37 eV which is above the proton reduction potential and the valence band maximum (VB_{max}) is found to be -6.55 eV which is below the water oxidation potential. As the band edge potentials are suitable for the overall water splitting to generate hydrogen, the g-CN can be expected to be a good photocatalyst material for hydrogen generation.

To verify the effect of stacking on the electronic structure of g-CN, we have also studied the bilayer as well as the trilayer of g-CN. For the bilayer, we have considered two different stacking modes, AA and AB. From the optimized structures, the AB stacking mode is found to be energetically more favourable as compared to the AA mode. The optimized inter layer separation from the PBE method is found to be 3.088 Å indicating the strong coupling between the two g-CN layers. The interlayer interaction energy per unit cell is found to be -0.57 eV. The calculated band gap is found to be 2.81 eV which is 0.08 eV less as compared to that of the single layer. This indicates that the band gap is reduced due to the interlayer coupling in g-CN.

To see any further effect of inter-layer coupling on the electronic structure, we have also studied the electronic structure of trilayer g-CN. For trilayer, we have added one more g-CN sheet above the bilayer in two different ways, ABA and ABC. It has been found that the ABC mode of stacking is energetically more favourable with interlayer separation of 3.029 Å and the corresponding inter-layer interaction energy per unit cell is calculated to be -1.19 eV. The calculated band gap is found to be 2.75 eV which is 0.14 eV less as compared to the single layer band gap. We have studied the effect of doping with different non-metal elements like boron, oxygen, sulphur, and phosphorous. The results on non-metal doping reveal that the phosphorous doping will be more

suitable to bring down the band gap of g-CN without creating any undesirable mid gap states. The calculated optical absorption spectra show significant enhancement in visible light absorption efficiency on phosphorous doping. The positions of band edges in pure g-CN as well as phosphorous doped counterpart with respect to water redox levels are found to satisfy the thermodynamic criteria for overall water splitting.

To understand the detailed mechanism of overall water splitting reaction mechanism we have investigated both the oxygen evolution reactions (OER) and hydrogen evolution reactions (HER) on the g-CN surface.¹⁸ The calculated binding energy of a water molecule on the 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 the OER and HER has been carried out. The calculated overpotential for the 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 the NHE). These results on the 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 the HER on g-CN reveals that the reaction has overpotential of around 1.0 eV. As the photogenerated electrons in the conduction band are located just 0.26 eV above the hydrogen reduction level, the reduction reaction requires a cocatalyst. Our computational studies will definitely provide better understanding of the underlying mechanism and useful insights into designing new g-CN photocatalysts and modification of its electronic structure to facilitate the overall water splitting on the g-CN surface.

Hydrogen Adsorption on Light Metal Decorated Molecules and Materials

Carbon nanomaterials are found to be one of the promising candidates for hydrogen storage because of their low molecular weight and high surface area. To understand the effect of charged surface and nature of substrate, we have investigated varieties of organic molecular systems, such as, cyclo-butadiene (C_4H_4), cyclopentadienyl radical (C_5H_5), benzene (C_6H_6) and cyclo-octatetraene (C_8H_8) and their alkali metal-doped complexes for hydrogen adsorption.¹⁹⁻²⁰ We have demonstrated that creating a charged surface on the model system by doping the alkali metal cations can improve the hydrogen adsorption energy significantly. Among the alkali metal cations (Na^+ and Li^+), it is observed that Na^+ can interact with more number of hydrogen molecules as compared to Li^+ . Introduction of a functional group in the model system also affects the binding of the alkali metal cation to the organic system and the hydrogen adsorption significantly due to the electronic induction effects. It can be mentioned that the model studies considered in the present investigation can provide a detailed insight into the adsorption of hydrogen molecules in carbon nanomaterials, metal

organic frameworks and other materials where benzene derivatives are the building blocks. We have also shown that the binding of sodium atom, especially, with the π electron deficient systems like C_4H_4 , C_5H_5 and C_8H_8 is observed to be energetically feasible and there is a charge transfer from the sodium atom to the organic molecules. Such interactions are not possible with benzene molecule due to its exceptional aromatic stability. Among all the alkali metal atom doped complexes, C_5H_5-Na is found to be the most stable and the interaction of molecular hydrogen is also found to be very strong. The aromaticity in such molecular systems plays a very important role in stabilizing the ionized organometallic complex doped with alkali metal atoms. Similar to carbon systems, we have also studied different boron hydrides alkali metal complexes for their hydrogen adsorption characteristics.²¹⁻²²

We have demonstrated the important role of the curvature exhibited by different carbon nanomaterials on the molecular hydrogen adsorption. In order to represent the curvature effects in more realistic manner, we have considered different sizes of fullerenes, C_{20} , C_{28} , C_{32} , C_{36} , C_{60} , and C_{70} .²³ The high reactivity of the surface with the maximum curvature has been attributed to the weakening of the π -conjugation due to the bending of the carbon surface which makes the system have quasi sp^2 - sp^3 hybridization with substantial s-orbital character. Based on our results, it can be mentioned that the metal doped nanotubes with smaller radius will be a better candidate for hydrogen adsorption. We have also shown that the truncated doping of carbon with nitrogen in C_{60} can generate porphyrin-like porous fullerene, $C_{24}N_{24}$ that can bind with transition metal atoms with high interaction energies which are nearly double the cohesive energies of the corresponding metals.²⁴ Hence the clustering problem associated with the transition metals can be avoided. These transition metal sites are found to trap molecular hydrogen through Kubas type of interaction, and the hydrogen adsorption energies are also found to be suitable for ambient temperature hydrogen storage.

We have explored two-dimensional carbon materials graphyne, graphdiyne and conjugated microporous polymers for their energy storage applications.²⁵⁻²⁶ Lithium metal binding to these carbon materials is found to be enhanced considerably and is more than the cohesive energy of lithium which can be attributed to the presence of more electronegative sp carbon in the framework. This strong metal binding energy will ensure the stability of the materials towards recyclability. We have also Due to the electron transfer from lithium metal to the carbon surface in these materials, the lithium sites are found to be cationic and thus adsorb molecular hydrogen with desired adsorption energies.

Metal organic frameworks (MOFs) are found to be promising materials for hydrogen storage because of their porous and robust nature and also exceptionally high specific surface areas and pore volumes.²⁷

However, the main driving force for binding is through van der Waals interaction and requires low temperatures for achieving a significant hydrogen storage capacity. One of the important strategies to improve the hydrogen adsorption enthalpies is through metal decoration. In most of the metal-doped framework materials studied, the metal atom is found to be positioned on top of the aromatic six-membered carbon rings with poor metal binding energies leading to aggregation of adsorbed metal atoms to form clusters, and is therefore not suitable for reversible hydrogen adsorption. We have proposed that the substitutional doping with boron to improve the metal binding energies. From our calculated results, it is observed that the binding energy of metal with MOF-5 can be improved by disturbing the aromatic nature of the linker group through the substitution of its two carbon atoms with two boron atoms, thus making it electron-deficient. The calculated metal binding energy with the modified linker is found to be extremely high. These adsorbed metal sites are shown to possess partial positive charges and thus can adsorb molecular hydrogen. We have also modelled different three-dimensional supercubane based porous carbon materials with varying number of carbon atoms starting from C₈ cubane unit to an expanded C₅₆ cubic unit and also with different inter-cubane C-C linking units.²⁸ The expanded supercubane, C₃₂ is found to adsorb hydrogen with a gravimetric density of 2 wt% and adsorption energy of -2.5 kcal/mol. However, at higher hydrogen densities and in the case of highly porous systems like C₁₄₄, the hydrogen adsorption energies are very low indicating that porous materials with medium size pores are preferred for better hydrogen storage.

Concluding Remarks

Using first principle calculations, we have investigated different molecular systems and materials for their possible applications in hydrogen energy. We have explored the g-CN based materials as an important class of materials for use in photocatalytic water splitting to generate hydrogen. These kinds of polymeric materials are shown to have more advantages over the conventional metal oxide based semiconductors. The modelled g-CN materials are found to be wide band gap semiconductor materials and we have tried to engineer the band gap through doping of different metals as well as non-metals. The importance of the presence of an ionic site on the hydrogen adsorption energies in carbon and boron based materials has been explained. Light metal decorated carbon fullerenes and its hetero atom substituted fullerenes were explored for hydrogen adsorption. Varieties of two-dimensional and three-dimensional porous materials were designed for efficient hydrogen storage. These computational studies can provide valuable insights for exploring new functional materials for hydrogen energy applications.

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References

- Hoffert, M. I.; Caldeira, K.; Jain, A. K.; Haites, E. F.; Harvey, L. D. D.; Potter, S. D.; Schlesinger, M. E.; Schneider, S. H.; Watts, R. G.; Wigley, T. M. L. Wuebbles, D. J. *Nature*, 395 (1998) 891.
- Züttel, A.; Remhof, A.; Borgschulte, A.; Friedrichs, O. *Phil. Trans. R. Soc. A* 368 (2010) 3329.
- Lewis, N. S.; Nocera, D. G. *Proc. Natl. Acad. Sci. U.S.A.*, 103 (2006) 15729.
- Lubitz, W.; Tumas, W. *Chem. Rev.* 107 (2007) 3900.
- <http://www.cleanenergystates.org/>
- Fujishima, A.; Honda, K. *Nature* 238 (1972) 37.
- Yerga, R. M. N.; Galván, M. C. A.; del Valle, F.; de la Mano, J. A. V.; Fierro, J. L. G. *ChemSusChem* 2 (2009) 471.
- Wang, X.; Maeda, K.; Thomas, A.; Takanabe, K.; Xin, G.; Carlsson, J. M.; Domen, K.; Antonietti, M. *Nat. Mater.* 8 (2008)76.
- Wang, X.; Maeda, K.; Chen, X.; Takanabe, K.; Domen, K.; Hou, Y.; Fu, X.; Antonietti, M. *J. Am. Chem. Soc.* 131 (2009) 1680.
- Shalom, M.; Inal, S.; Fettkenhauer, C.; Neher, D.; Antonietti, M. *J. Am. Chem. Soc.* 135 (2013) 7118.
- Lin, Z.; Wang, X. *Angew. Chem. Int. Ed.* 52 (2013) 1735.
- Pan, H.; Zhang, Y.; Shenoy, V. B.; Gao, H. *ACS Catal.* 1 (2011) 99.
- Grochala, W.; Edward, P. P. *Chem. Rev.* 104 (2004) 1283.
- Schmidt, M. W.; Baldrige, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunga, N.; Nguyen, K. A.; Su, S. J.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* 14 (1993) 1347.
- Kresse, G.; Furthmüller, J. *Comput. Mat. Sci.* 6 (1996) 15.
- Kresse, G.; Furthmüller, J. *Phys. Rev. B.* 54 (1996) 11169.
- Srinivasu, K.; Modak, B.; Ghosh, S. K. *J. Phys. Chem. C* 118 (2014) 26479–26484.
- Srinivasu, K.; Ghosh, S. K. *J. Mater. Chem. A* 3 (2015) 23011-23016.
- Srinivasu, K.; Chandrakumar, K. R. S.; Ghosh, S. K. *Phys. Chem. Chem. Phys.*, 10 (2008) 5832-5839.
- Srinivasu, K.; Chandrakumar, K. R. S.; Ghosh, S. K. *ChemPhysChem* 10 (2009) 427-435.

21. Srinivasu, K.; Ghosh, S. K. *Int. J. Hydrogen Energy* 36 (2011) 15681–15688.
22. Srinivasu, K.; Ghosh, S. K. *J. Phys. Chem. C* 115 (2011) 1450–1456.
23. Chandrakumar, K. R. S.; Srinivasu, K.; Ghosh, S. K. *J. Phys. Chem. C* 112 (2008) 15670–15679.
24. Srinivasu, K.; Ghosh, S. K. *J. Phys. Chem. C* 116 (2012) 25184–25189.
25. Srinivasu, K.; Ghosh, S. K. *J. Phys. Chem. C* 116 (2012) 5951–5956.
26. Srinivasu, K.; Ghosh, S. K. *RSC Adv.*, 2 (2012) 2914–2922.
27. Srinivasu, K.; Ghosh, S. K. *J. Phys. Chem. C* 115 (2011) 16984–16991.
28. Srinivasu, K.; Ghosh, S. K. *J. Phys. Chem. C* 116 (2012) 25015–25021.