

Target of Net-Zero Emission

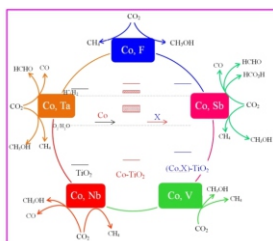
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Computational Modeling for Energy Conversion and Storage

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CO₂ conversion behavior of TiO₂ in the presence of different dopant

ABSTRACT

In this article, a brief account of the theoretical chemistry research activities related to green energy mission towards the net-zero targets has been presented. Specifically, the theoretical and computational studies related to the design of novel materials for solar energy conversion, including the solar hydrogen generation through photocatalytic water splitting, solar CO₂ conversion to usable fuels, and photovoltaic applications, development of efficient materials for reversible storage of hydrogen, and solid-state battery have been discussed. The whole spectrum of work discussed here includes design of novel materials with tunable properties and explaining complex phenomena using first principle quantum mechanical methods.

KEYWORDS: Green energy, Solar energy, Quantum mechanical, DFT

Introduction

Development of alternate energy sources have become one of the major areas of interests due to limitation of long term availability of fossil fuels as well as environmental issues. There has been a growing interest on hydrogen energy as a renewable source. During past few decades extensive research activities including both experimental and theoretical are going on to make hydrogen energy realizable [1]. However, there are few challenges for the so called hydrogen economy viz., designing efficient strategy for the generation of hydrogen, developing cost effective, durable, safe, and environment friendly storage system. In this article, we have focused on both the important aspects related the hydrogen economy as mentioned above. Using the density functional based electronic structure calculations, we have designed wide variety of photocatalyst for the generation of hydrogen via visible light driven water splitting. To develop efficient materials for hydrogen storage, we have investigated different light metal decorated carbon porous nanostructures which can adsorb molecular hydrogen. The other major renewable energy source that has been used extensively is the photovoltaic (PV) systems/solar systems. Unlike the other renewable energy generation, where it is required to have continuous monitoring, maintenance and geographical limitations, solar cells system can be left unattended and require very minimal maintenance. However, the major disadvantage of solar panel to date is its low efficiency, which is affected by different parameters, including, the panel temperature, cell type, panel orientation, irradiance level, etc. In this regard, computational modeling of novel materials has been found to be very popular. Finally, we will present a brief discussion related to energy storage technologies, using rechargeable lithium/sodium ion battery, which are superior to all other secondary batteries due to their high energy density.

Computational Details

Spin polarised DFT calculations for the material systems have been carried out using PAW based electronic structure code, viz. the Vienna ab initio simulation package (VASP) [2]. During geometry optimization, we use generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) functional for the exchange correlation contribution [3]. On the other hand, electronic structure calculations have been carried out using Heyd–Scuseria–Ernzerhof (HSE) hybrid density functional to overcome the limitations of standard density functional [4].

Results and Discussion

Computational Design of Novel Materials for Hydrogen Energy

This section focuses mainly on both the important aspects related to the hydrogen energy, viz., design of efficient photocatalyst for water splitting to generate hydrogen, and developing materials for efficient reversible storage of hydrogen.

H₂ Generation: One of the most promising ways to produce hydrogen is the photocatalytic water splitting using solar energy. However, finding a suitable catalyst which can split water and produce hydrogen under visible light is a major challenge in this field of research. Till now, a wide range of photocatalysts have been developed, most of which are oxide based semiconductors, and recently various perovskite type materials have also attracted immense interest due to their potential catalytic property to split water. Among them, NaTaO₃, KTaO₃, KNbO₃, NaNbO₃, SrTiO₃ have been shown to be an excellent photocatalyst for the generation of hydrogen. However, their large band gap limits the photoactivity only to the range of UV light, which covers ~5% of the solar spectrum. Hence one of the biggest challenges is to modify its band gap so that it can utilize the visible light of solar spectrum for the photocatalytic applications. The introduction of foreign

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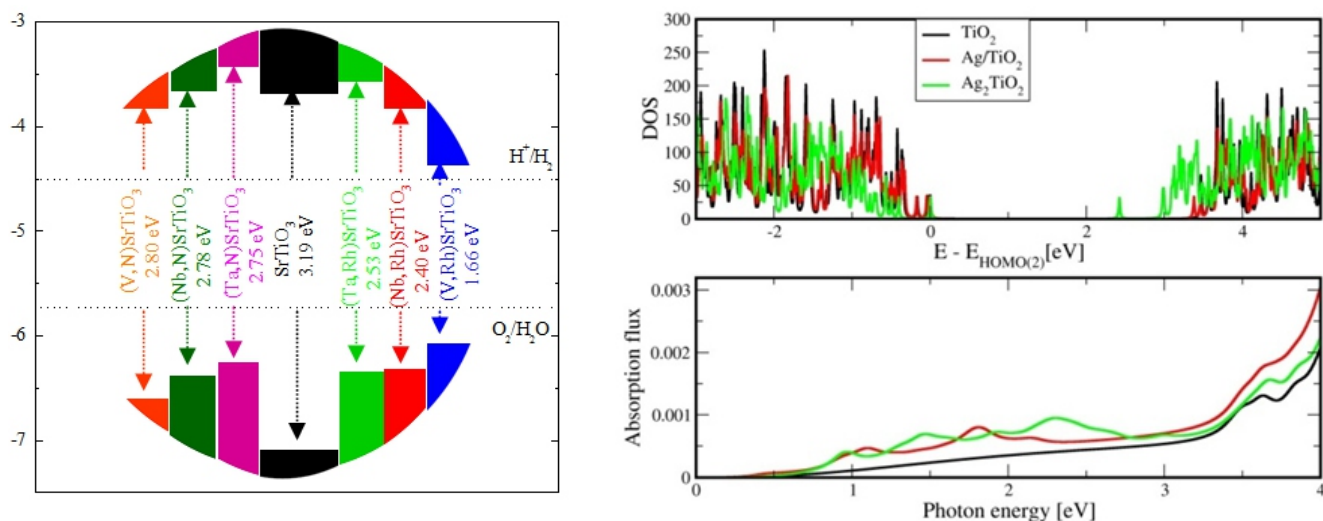


Fig.1: (a) Change of band gap and band edge of SrTiO_3 in the presence of different dopant. (b) Density of states and absorption spectra of TiO_2 and Ag/TiO_2

elements in the crystal lattice to change the band structure is observed to be one of the most promising ways to improve the visible light activity of the wide band gap semiconductor photocatalysts. Significant contribution has been made to enhance the photocatalytic activity of a wide range of perovskite based photocatalyst, viz. NaTaO_3 , KTaO_3 , KNbO_3 , NaNbO_3 , and SrTiO_3 [5,6]. An efficient strategy has been demonstrated to engineer the band structure of the photocatalyst in a controlled manner through doping with foreign element. It has been revealed that the choice of dopant atoms is highly material specific. Thus, it is shown that doping of (Mo, N) pair into NaTaO_3 is one of the most promising ways to improve the water splitting activity under solar light, while, (W, N) pair has been found to be most effective for enhancing visible light photocatalytic activity of KNbO_3 , and NaNbO_3 . However, in case of KTaO_3 , (N, F) pair is found to be the most preferred one because of significant band gap lowering and the unique advantages of F for accelerating photocatalytic water splitting activity. The (V, Rh) pair is shown to be very effective for SrTiO_3 due to remarkable reduction in band gap with capability of releasing both hydrogen and oxygen during water splitting reported to date. Interestingly, these dopant pairs are chosen so that they form charge compensated system, thus greatly reducing the unwanted vacancy formation. More importantly, these dopant pairs result into the formation of clean band structure without any localized defects states in the forbidden region, which is very much essential for achieving higher photo-conversion efficiency. It is interesting to note that the reported results are found to be of great interest and beneficial to the researchers involved in the synthesis of new photocatalyst with improved features.

Recently, polymeric materials like graphitic carbon nitrides were also reported as potential catalysts for solar water splitting reaction to generate molecular hydrogen. Through our first-principles calculations, we proposed two-dimensional graphitic carbon nitride (g-CN) composed of the s-triazine units as a potential candidate for photocatalytic water splitting reaction [7]. The measured electronic band gap of the single layer g-CN through the more efficient hybrid energy density functionals is found to be 2.89 eV, which was found to further decrease to ~ 2.75 eV in multilayered structure. To further improve the visible light activity of g-CN, doping with different non-metal elements like B, O, P and S was considered to fine tune its electronic structure. Among the various dopants considered, phosphorus doping was found to

be more effective in reducing the band gap to 2.31 eV. In a different study, effect of decorating with metal and metal cluster on the photocatalytic activity of graphitic carbon nitride has been investigated. Interestingly, Ag and Ag_4 cluster deposition on g-CN does not lead to any mid gap states which can be a better candidate. Calculated optical absorption spectra also indicate that the metal decoration leads to a clear shift in the absorption peak towards the visible region [8].

We also attempted to understand the overall photocatalytic water splitting reaction mechanism over the g-CN surface and calculate the associated overpotentials for both oxygen and hydrogen evolution reactions (OER and HER) [9]. OER over g-CN becomes completely downhill at and above the potential of 2.16 V and since the valence band of g-CN was located at a potential of 2.64 V, the photo-generated holes in the valence band of g-CN should be able drive OER without the aid of any co-catalyst. However, HER on g-CN was found to have an overpotential of around 1.1 V while the conduction band minimum of g-CN was at around 0.26 V above the hydrogen reduction potential and hence the HER needs a co-catalyst. Since the g-CN can be efficient for the OER and $\text{g-C}_3\text{N}_4$ was known to be a better candidate for HER, we also proposed a composite of these two materials as a better photocatalyst and was later experimentally realized.

The metal oxide surfaces with metal clusters play crucial role in photocatalytic applications. TiO_2 is extensively used in photocatalytic applications. Especially, the decoration of Ag clusters on the surface is a successful strategy to improve the efficiency. The Ag and Ag_2 adsorbates added new states near the bandgap region (Fig.1 (b)). The absorption flux is significantly increased in the 0.75 – 2.5 eV photon energy region for Ag/TiO_2 and Ag_2/TiO_2 which is important in photocatalytic and photovoltaic applications. The new states created by adsorption of Ag clusters are localized in nature, which prevents the hole carriers from recombination with electron carriers [10]. The relaxation lifetimes for electrons are comparable in the three structures. However, hole relaxation lifetimes are higher than electrons. The lifetimes of photo induced charge carriers such as electrons and holes amends the reduction and oxidation of molecular adsorbates, and reaction yields of their fragments and are very significant to photocatalysis.

H_2 Storage: Hydrogen has high chemical energy per mass (142 MJ kg^{-1}) and it is environmentally friendly, has infinite

reserve in the form of water. For the successful implementation of hydrogen as one of the alternative fuels, developments have been focused on a safe, efficient and reversible hydrogen storage medium which works at ambient conditions. In this regard, we have proposed few materials for hydrogen storage using the concepts such as electrostatics, curvature and aromaticity of the material [11,12]. The new predictions reported in our work demonstrate that the s-block metal cations can adsorb molecular hydrogen (without dissociation into atomic hydrogen) and form MH_{16} complexes. It may be noted that the number of hydrogen atoms ($nH=16$) interacting with s-block ions is more than that for any transition metal cations and is the highest ever reported in the literature. The interaction of this kind is shown to be mediated by the simple electrostatic interactions and these concepts of ion-molecule interactions have been explored in utilizing to design the suitable materials for hydrogen storage purpose by considering the alkali metal doped fullerenes. Accordingly, it has been demonstrated that achievement of forming a stable complex of sodium doped fullerene molecule along with 48 hydrogen molecules is possible, corresponding to 9.6 wt %. Since the important requirements for the hydrogen storage materials, namely, weak interaction between the ion and molecular hydrogen and larger number of hydrogen molecules surrounding the ions, are met with the s-block elements, it can have important implications in designing the alkali metal ions based hydrogen storage materials. Although the synthetic procedures and applications of these metal hydride complexes are still at the embryonic stage, the present theoretical predictions and other experimental studies are likely to pave the way to the hydride chemistry of s-block elements, leading to better hydrogen storage materials. Very recently, we have put forward the single-walled carbon nanohorns as one of the potential candidates for hydrogen storage on the basis of 'intra-curvature'. An attempt has also been made to investigate magnesium clusters for the purpose of hydrogen storage and our results have shown that a complete dehydrogenation from these Mg nanoclusters occurs at $\sim 100^\circ\text{C}$ which is a significant improvement over bulk MgH_2 ($\sim 300^\circ\text{C}$) through *ab-initio* molecular dynamic simulation. The understanding gained from the above works has led to the development as well as rational design of hydrogen storage materials especially on the basis of carbon based nanomaterials.

Efficient Materials for Photovoltaics Applications

We investigate the photovoltaic properties of two-dimensional (2D) cesium lead bromide (CsPbBr_3) perovskite nanoplatelets (NPL) with thickness of few monolayers (ML) [13]. The photovoltaic properties of CsPbBr_3 NPLs are changing with layer thickness and show variation from bulk CsPbBr_3

perovskite. The band gap values for Pb-Br surface terminated CsPbBr_3 NPLs are 2.17 eV, 2.12 eV, 2.10 eV and 2.04 eV for 1 ML, 2 ML, 3 ML, and 4 ML, respectively from our DFT calculations. The band gap is reduced with increasing thickness of the NPLs due to the quantum confinement effects. The band gap obtained for 1 ML thickness from HSE06 calculations is 3.29 eV. Similarly, the band gap for bulk perovskite structure is 3.08 eV. Thus, the confinement along z-axis for 2D NPL can also affect other photovoltaic properties such as light absorption, binding energy of excitons and charge transport.

Computational Design of Efficient Catalyst for CO_2 Conversion to Fuels

Solar energy conversion of carbon dioxide to hydrocarbon fuels (CH_4 , CH_3OH , CO , HCHO , and HCOOH) is considered as one of the promising approaches to reduce global warming and generation of sustainable energy. The mission for utilization of the sunlight to the maximum extent for these purposes has provided motivation to find efficient materials. Interestingly, codoping with (F/Nb/Ta) into Co-doped TiO_2 successfully reduce the band gap without forming any localized defect states, which is very much important for good charge carrier mobility and longer life time of the photogenerated charge carriers [14]. More interestingly, these materials show enhanced photoactivity for the CO_2 conversion processes under visible light irradiation (Fig.2). In a recent study, it has been predicted that the codoping of (Ni, La) or (Ni, W) pair into SrTiO_3 can lead to improved CO_2 conversion activity under sunlight.

Development of Materials for Next-generation Li-ion Batteries

During the past few decades, there has been an emerging trend in energy storage technologies. An excellent example of energy storage devices includes the rechargeable lithium battery, which is superior to all other secondary batteries due to their high energy density. With experimental group biomass-derived carbon has been explored as versatile anodes for high-performance sodium and lithium-ion batteries using $\text{Na}_2\text{Ti}_3\text{O}_7$ nanorods, layered oxide material, $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$. The structural changes in the Fe_3O_4 electrode due to Li intercalation and de-intercalation process in the electrodes during charging and discharging of the batteries have also been revealed. Sodium super ion conductors based structures are being explored as cathode materials for application in sodium ion battery technology. Doping with W has been found to enhance the structural integrity and enhanced Na-ion mobility significantly. Interestingly, Phosphorous/Fluorine-codoped carbon has been explored for enhanced both sodium ion and lithium ion storage [15].

Conclusion

Under the present global climate of having large demand for developing a sustainable energy supply and effective environmental solutions, the utilization of solar energy holds a bright future for simultaneously addressing the energy demand and environmental challenges. In addition to the experimental approach in photocatalyst development, theoretical prediction and high throughput material screening should provide very powerful tools to guide the experimental community for rationally designing better materials with enhanced light harvesting, improved charge separation, transfer, and appropriate redox potential to drive the redox reactions. The principal objectives of our theoretical studies are to play a predictive role in the development of promising new materials, to provide fundamental understanding of processes that are difficult to extract from experiment alone,

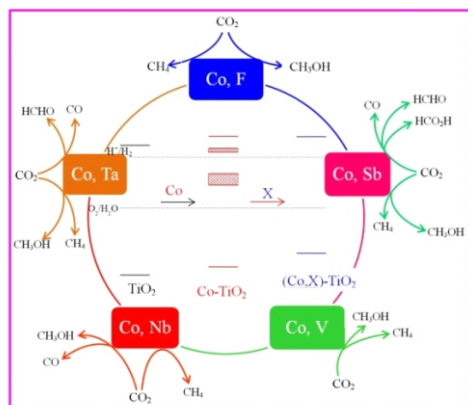


Fig.2: CO_2 conversion behavior of TiO_2 in the presence of different dopant.

and to assist in the analysis of experimental results, and to elucidate the key atomic-scale features.

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