Design and development of high performance photocatalysts using theoretical and experimental methods

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Abstract

Recently, we have synthesized Sn_3O_4 based photocatalyst by hydrothermal method and measured its photocatalytic activity in my M.Sc project. In this proposal, I propose to investigate photocatalytic activity of Sn based materials for photocatalytic activity by using ab initio density functional theory (DFT) and time-dependent density functional theory (TDFT). In the recent past, Sn_3O_4 has been shown to be a potential candidate for photoinitiated process in H_2 reduction reactions. The Sn_3O_4 has large band gap which can be tuned by doping. Several different Sn_3O_4 based complexes can be designed using density functional theory with different geometries, electronic structures, and optical characteristics. Experimentally, it is highly time consuming and need a lots of resources to test the photocatalytic activities of all possible Sn_3O_4 based complexes. In this situation, theoretical techniques such as DFT can easily guide experimental studies by screening materials and provide insights into the photoactivity of the complexes. The main aim of this proposal is to design and develop Sn_3O_4 complexes for hydrogen production applications and to provide a direction for chemical synthesize of these photocatalysts. After finding the potential materials for photocatalysts, with the supervisor's advice, I will do experimental synthesize and measure the catalytic activities.

Introduction

The need for the energy will never end and it is essential in the modern world. Hydrogen plays an important role in the energy sector. It is used in various industries including various chemical synthesizes, fossil fuel separation, ammonia synthesis, onboard applications as fuel, etc. One of the most important and environmental friendly applications is water splitting using the phenomena of photocatalysis.

Currently other photocatalysts based on metal oxides, metal sulfides and metal nitrides are also gaining attention for water splitting applications in large amounts. These heterogeneous catalysts are semiconductors and their band gap leads to better photocatalytic activities compared to metals (zero band gap) and insulators (high band gap). In heterogeneous photocatalysis the same process occurs on the surface of the heterogeneous photocatalysis. So we need a suitable band gap for the design a photocatalyst with good photocatalytic activity. One of the ways is to tune the band gap of potential materials so that we can tune their photocatalytic activities. In photocatalytic reactions, trapping and recombination center between photogenerated electrons and holes results in a decreased photocatalytic activity in active sites. Some of the co-catalysis Pt, NiO and RuO_2 are also used. These are unnecessary for oxide based photocatalysts.

For the past few decades, TiO_2 photocatalysts are widely studied. Honda and Fujishima synthesised TiO_2 photocatalysts for the first time early 1970s . When TiO_2 is irradiated with UV light, the electron and hole pairs are generated which are relevant in the production of hydrogen. However the efficient splitting of water into H_2 and O_2 under visible light irradiation is not observed. Frank and Bard examined the possibility of using

TiO_2 to decompose cyanide in water which is of great interest for environmental applications. Now, TiO_2 is one of the most important ecofriendly photocatalyst because of its availability, economical and high stablility.

Photocatalysts like TiO_2 has different forms Anatase and Rutile. Compared to Rutile for anatase has a high band gap. The crystallinity is increased by calcination. Some sacrificial agents also used to evaluvate photocatalytic activity such as alcohol and a sulfide ions. It enhance the electrons in a photocatalyst.

Photocatalytic production of hydrogen has been paying attention to solve the energy and environmental problems. Generally, the photocatalyzed hydrogen production inherently proceeds via two charge processes, such as (a) the trapping of photo-generated electrons and holes on surface active sites of semiconductors, and (b) the interfacial transfer of electrons and holes from active sites to reacting substrates. In recent times, the metal/semiconductor and semiconductor/semiconductor composite materials are used to modify band gap position, improve carrier separation and facilitate charge recombination for photocatalytic generation of hydrogen. For this reason, construction of photocatalysts with some metal sulfides, metal oxides, and noble metals were useful to enhance the hydrogen generation.

Moreover, it has been reported that the structure and morphology of the photoactive sites of semiconductor to improve the light harvesting and photocatalytic activity. However, the efficiency, expensive and toxic nature of materials would also be calculated for practical applications. Very recently, non-toxic tin oxide (Sn_3O_4) sheet like structure photocatalysts have been shown to enhance the activity for hydrogen evolution. There is a lot of scope in the area in developing and enhancing Sn based photocatalysts. In this research, we propose design and develop Sn_3O_4 based complexes for photocatalytic applications. We plan to use density functional methods to get useful insights in to the structural, electronic and photocatalytic activities followed by experimental synthesis and measurements.

What I have done so far

In my present M.Sc project, with the guidance of my supervisor, I have synthesized a visible light driven Sn_3O_4 supported bimetallic nanoparticles and have measured its photocatalytic activity using basic experimental techniques. I have been writing a paper and it is to be submitted soon. In the project titled “Facile Synthesis of Visible Light Driven Tin Oxide (Sn_3O_4) Supported Bimetallic Nanoparticles and its Photocatalytic Activity”, we have prepared Sn_3O_4 based photocatalyst through two-step hydrothermal process and the photocatlaytic activity has been examined by the generation of hydrogen. The synthesized Sn_3O_4 supported photocatalyst has been characterized by XRD, TEM, EDX and XPS.

Objectives of this Proposal

- To design Sn_3O_4 based photocatalyst with various compositions
- To calculate the structural properties of Sn_3O_4 with different compositions using DFT

- To calculate the electronic properties of Sn_3O_4 using DFT

- To calculate the photocatalytic activities of Sn_3O_4 with various compositions using DFT and time-dependent DFT.

- To design a novel Sn_3O_4 based photocatalyst in effective manner other than hydrothermal method (for reducing the cost).

- To develop Sn_3O_4 based semiconductors from changing several electronic characteristics like atomic configuration, bandgap energy,
band position, and lifetime of electrons and holes using DFT followed by synthesis and experiments

- Doping with metals and nonmetals to enhance the visible-light response of Sn_3O_4 photocatalysis (Au and Pd are currently used).

- To develop a Z-Scheme photocatalyst materials for production of hydrogen, environmental pollution and dye degradation.

Methodology

This project has two parts.

1) Theoretical calculations:

The theoretical calculations will be performed with the Kohn-Sham Density functional theory for the structural and electronic properties calculations of Sn_3O_4 based photocatalysts. The photocatalytic activities will be studied by time-dependent density functional theory. At present I have been using ASE computational package (site) to study the catalytic activity of different substrates. I will start with this ASE package which is a open source code. Then, the calculations may be performed using Quantum Espresso code and other open source codes. At present, I have been using my laptop (4 GB RAM) to compute my calculations. Based on the availability of the resources at the university, I will use it. With the support of my Professor, I will collaborate with other research institutions where computation facility is available to complete my calculations.

2) Expermental Methods:

After finding the potential Sn_3O4 based photocatalysts, with the help of the supervisor, I will synthesis selective photocatalysts and study their properties by various methods. Since in my MSc project, since I have synthesized a visible light driven Sn_3O_4 supported bimetallic nanoparticles and have measured its photocatalytic activity using basic experimental techniques, I can start with the same procedure. The newly synthesized photocatalysts will be characterized by various techniques such as XRD, TEM, EDX and XPS.

Research Outcome

- A complete understanding of Sn3O4 based photocatalysts by using DFT/TDFT

- A 3-6 papers in peer-reviewed international journals from the results obtained using DFT/TDFT calculations and experimental studies.

- There is a possibility to enhance the band gap of the photocatalyst with computational methods using some open source software like python.

- Currently we are using this Sn_3O_4 based photocatalyst is used for the production of hydrogen. In further research there is a possibility of some relevant photocatalytic applications such as removal of inorganic pollutants, water splitting, and organic synthesis.

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