Chapter 6: Summary, Conclusion and Scope for Future Work

The central objective of the thesis is to optimize the synthesis conditions for metal oxides viz. ZnO and $BiVO_4$ and their nanocomposites and photoanodes by varying different parameters with an aim to study their photoactivity for use in applications in the field of photocatalysis and photoelectrochemical cell for organic pollutant degradation and hydrogen generation respectively. Hydrothermal route was followed to synthesize nanocmposite materials. To study the photocatalytic and photoelectrochemical response of the semiconductor, composites/photoanodes with different weight ratios were prepared and results were compared with the pristine samples. Pristine samples showed very less photoactivity for both photocatalytic and photoelectrochemical property. In the following sections, summary, conclusions and future scope of this study are given:

6.1 Summary and conclusion of this study

6.1.1 Hydrothermal route for pure ZnO and $BiVO_4$ materials

ZnO was synthesized at 200ºC with SDBS as a surfactant through hydrothermal method. The process results in the formation of nanosheets with hexagonal morphology and the sheets exhibited pure hexagonal wurtzite phase which was confirmed by XRD. Surface of the sheets has zinc interstitial defects which were further enhanced by milling process. The zinc interstitial defects acts as an active sites to bond with BiVO4 at the interface.

Pure crystalline monoclinic phase of BiVO4 was synthesized by hydrothermal route at 200ºC. The phase of the BiVO4 was confirmed by XRD analysis. The particles exhibited the irregular morphology with dimensions ranging from 40-100nm. To prepare the nanocomposite, both the materials were mixed in different ratios and mechanically milled. This process resulted in the increased zinc interstitial defects which were confirmed by PL study. The defects acted as active chemical sites to form weak bond with BiVO4. The sample was then annealed at 400ºC. The process of annealing at high temperature resulted in strengthening the bond with BiVO4 and other defects which were not bonded to BiVO4 were also removed by the annealing process. This was also confirmed by the PL spectrum. The strong bond of interaction between ZnO and BiVO4 facilitated the charge exchange at the interface rather it allowed the transition of charge carriers from VB of BiVO4 to the CB of ZnO thus reducing the band gap of the nanocomposite.

6.1.2 ZnO/$BiVO_4$ nanocomposite for photocatalysis

- ZnO/$BiVO_4$ hetero-structured photo catalyst was prepared via physical route method of mechanical milling followed by its annealing treatment. Various samples with different weight ratios of ZnO-$BiVO_4$ (1:1), ZnO-$BiVO_4$ (1:2) and ZnO-$BiVO_4$ (2:1) were prepared.
- It was observed that ZnO-$BiVO_4$ (1:1) composite showed significant dye degradation efficiency with almost 86% of methylene blue degradation. Degradation response for MB was compared with the ZnO-$BiVO_4$ (1:2), ZnO-$BiVO_4$ (2:1), pristine ZnO and $BiVO_4$ samples. The degradation efficiency response was obtained in the order of: ZnO-$BiVO_4$ (1:1) > ZnO-$BiVO_4$ (1:2) > ZnO-$BiVO_4$ (2:1) > ZnO > $BiVO_4$. The as-prepared heterostructured photo catalysts showed 2.5 and 3.5 times better visible-light driven photocatalytic activity for degradation of MB than pure ZnO and $BiVO_4$ respectively.
- The XPS results indicated that ZnO and $BiVO_4$ were in close contact and formed an interface at heterojunction which was majorly responsible for the efficient charge transfer between the materials and increasing its photo response.
- The electronic structures of the ZnO- $BiVO_4$ nanocomposite were investigated through DFT calculations. Bi s orbital of $BiVO_4$ in ZnO- $BiVO_4$ forms the intermediate band in ZnO and reduces the band gap of the material which then requires less energy to become photoactive.
- The mechanism of action upon irradiation involves charge transfer process, which takes place from VB of $BiVO_4$ acting as intermediate band to the CB of ZnO. This makes the

material sensitive towards visible region of solar spectrum and thus shows high photocatalytic activity.

- Further, low recombination rate exhibited by ZnO-$BiVO_4$ (1:1) adds to its superior photo activity and remarkable results.
- Our results provide insight into the understanding the mechanism of heterojunction on photocatalytic activity, which will help in designing new heterojunctions for photocatalytic reactions for dye degradation and water splitting applications.

6.1.3 ZnO/$BiVO_4$ photo anode for PEC

- Dual layer $BiVO_4$/ZnO photo anode were prepared and instigated for photo-electrochemical water splitting applications. Three sets of $BiVO_4$/ZnO photo anode samples were prepared with varying $BiVO_4$ concentration designated as B1 (0.038M $BiVO_4$/ZnO), B2 (0.05M $BiVO_4$/ZnO) and B3 (0.1 M $BiVO_4$/ZnO). All measurements were compared with bare ZnO photo anode.
- The sample B1 showed maximum photocurrent density of 13.5 x 10^{-4}A/cm^2 upon illumination which was significantly higher than those from the bare ZnO (6.0 x 10^{-4} A/cm^2) electrode.
- The flat band potential mechanism is of significant importance to improve the solar to hydrogen efficiency (SHE). The V_{FB} was observed to increase from V_{FB} (B1) > V_{FB} (ZnO) > V_{FB} (B2) > V_{FB} (B3).
- The enhanced photo response of B1 photo anode was attributed to (i) extended photo response to the visible region as $BiVO_4$ is a visible light driven photo catalyst and (ii) suitable flat band positions involving electron transfer from $BiVO_4$ to ZnO, thus enhancing the charge separation. Two different photocatalytic layers ZnO and $BiVO_4$, reduces charge carrier recombination and charge transfer resistance at photo anode/electrolyte junction.

- The present study provides the proof of concept for developing photo anodes having concentration specific, tunable and without ‘spike and overshoot’ features, photocurrent density response with efficient utilization of solar spectrum and reduced electron-hole recombination by synergistically combining visible light driven photo catalyst $BiVO_4$ and wide band gap semiconductor ZnO.
- The varying $BiVO_4$ concentration provides us the handle to tune the photo response current density curve (by controlling two competitive mechanisms, water oxidation and surface recombination) in the dual layer $BiVO_4$/ZnO based photo anode.

6.2 Scope for future work

Synthesis, characterization and applications of metal oxide materials viz. ZnO, $BiVO_4$ and their nanocomposites is an active research area. Based on the conclusions of the present study, some suggestions for further research work are provided below:

(i) Synthesis of materials to alter their structural properties via methods like doping is an important research direction.

(ii) Doping of ZnO with materials like nitrogen, aluminium or gallium and coupling with $BiVO_4$.

(iii) Optimization of content of dopant material.

(iv) Study of photocatalysis for dye-degradation and photoelectrochemical for water splitting applications.

6.3 Future aspects of hydrogen energy

With the emergence of a broad based ‘advocacy coalition’ [219] comprising a diverse range of academic researchers, politicians, business and civil society organisations, the concept of ‘hydrogen economy’ has received considerable attention in recent years, promoting hydrogen as a means of delivering a sustainable and secure energy system [220]. Presently, there are three major technological barriers that must be overcome for a transition from a carbon-based (fossil fuel) energy system to a hydrogen-based economy. First, the cost of efficient and sustainable hydrogen production and delivery must be significantly reduced to bring it on par with other alternatives. Second, new generations of hydrogen storage systems for vehicular applications must be developed to provide adequate driving range. Finally, the cost of fuel-cell and other hydrogen-based systems must be reduced along with improvement in their useful life.

The major future markets for hydrogen transport and delivery depend primarily upon four factors: (a) the future cost of hydrogen, (b) the rate of advances of various technologies that use hydrogen, (c) potential long-term restrictions on greenhouse gases, and (d) the cost of competing energy systems [221,222]. Hydrogen holds the promise as a sustainable fuel of the future with many social, economic and environmental benefits to its credit. It has the long-term potential to reduce the dependence on fossil oil and lower the carbon and criteria emissions from the transportation sector [223].

With every new technological transition, understanding of social cultural factors holds significance to understand the concept of socio- technical systems. In our predominantly fossil fuel based energy system, issues in relation to transport and mobility as well as household and equipment are important features to discuss. In terms of speed and range of vehicles, existing practices and technologies cannot be easily surpassed by upcoming new ways of transportation in society and thus transition to hydrogen economy will be rather slow. However reduced CO_2 emissions associated with hydrogen economy based on renewable will have an advantage over other methods.

Socio-cultural barriers with technological developments may well be overcome through economic means. Other strategies such as prohibitions and campaigns– all of which can be part of policies to promote a certain technological development (such as the spread of hydrogen as energy carrier) can be adopted. The kinds of barriers that are embedded in everyday practices and routines, in social norms and values, and in aesthetic preferences etc. have to be recognised and understood.

The obstacles are serious but not unfeasible to achieve. Current architecture of the energy system and social practices need certain changes along with proper political-administrative support by way of public funding, investment and regulation.

6.4 Future aspects of water treatment via pollutant degradation

Waste water from textile dyeing and other related industries is one of the major sources of water pollution, currently. Such water is characterized by the presence of harmful chemicals such as higher value of colour, COD, BOD, large emission, complex composition and difficult degradation. This brings serious harm to the ecological environmental if directly discharged without being treated.

Minimization of waste is very vital step in order to decrease production cost and pollution load. Though there are many traditional technologies methods to treat textile waste water that includes various combinations of physical, biological, and chemical methods but these methods require high operating cost and high capital. Technologies based on photocatalysis systems are among the best alternative methods that can be adopted for large-scale ecologically friendly treatment processes. They are cost effective, and are eco-friendly simultaneously. For their many advantages, they hold a great deal of promise in this area of waste water treatment. Many materials already exhibit suitable properties to be a potential photo catalyst, while some require certain modifications to fall in range of appropriate photo catalyst.

Prevention and treatment of dyeing wastewater pollution are complementary. Focus should be shifted on clean production and conduct more in-depth research for production technology and process management. Moreover, the preventive, comprehensive, strategic measures and advanced production technology can be used to improve the energy and material utilization.

6.5 Conclusions

Hydrogen is considered as the second best energy carrier next to electricity. It can be produced from a variety of sources both renewable and non-renewable. Currently, non-renewable sources are mainly used for hydrogen production but for its future on sustainability, it is important that renewable energy sources like solar, wind or biomass are used primarily for its production. Hydrogen is an important feedstock/energy carrier in today's world and it has a variety of applications such as ammonia production, hydrogenation of hazardous wastes, synthesis of methanol and ethanol as rocket fuels. One of its most important potential uses can be in the transportation sector for both IC engines and fuel cell technologies as it has many potential advantages over conventional fuels like containing NO_X emission in the IC engine technology, and higher durability and lower cost of production in the case of fuel cells. It is also believed to be a safe fuel, which needs to be fully validated.

One of the major technical challenge in using hydrogen as a fuel is its on-board storage. Adequate quantities of hydrogen are required to provide a preferred driving range for any vehicle. Various storage routes have been investigated such as compressed gas, cryogenic tanks, metal hydrides, carbon nanotubes, etc. Research is still underway in determining the most economical and efficient storage mechanism. The second most important challenge is the transport and distribution of hydrogen. This is an imperative factor while deriving the hydrogen economy. Currently, compressed tube trailers, cryogenic liquid trucks and compressed gas are the three prospective hydrogen delivery pathways used for the various applications.

The infrastructure requirement and financial value allocated for the production and supply of oil and natural gas was enormous during the several decades of its findings. It was more of a politico-economic policy and funding which brought oil and natural gas to its present state. Hence, it will require a huge initiative for replicating the same for hydrogen in the near future and the Governments of various countries must align their requirement of energy for the future in terms of increasing the usage of hydrogen as a transport fuel. Research and commercial use of this niche area will be the pathway ahead for making the use of hydrogen in various applications. The potential of hydrogen to be used in the transport sector is vast provided the right measures and pathways are taken to make it safe, trustworthy and robust.