7.1 Conclusions

In conclusion, thesis work has mainly focused on the simple technique to grow metal or metal sulfide nanoparticle within TiO_2 thin film by a cost effective solution-processed *in-situ* growth technique. These metal/TiO_2 or metal sulfide/TiO_2 heterojunction nanocomposite thin films have been utilized for photo-electrochemical hydrogen generation and broad band photodetector fabrication. For this synthesis, initially $Li_4Ti_5O_{12}$, a popular ion-conducting metal has been synthesis in a sol-gel technique. Due to the ion-conducting nature of this ceramic thin film, Li-ion can move through the crystal channel freely. Taking the advantage of this feature, Li^+ of this ceramic film has been exchanged with Ag^+(or Cu^+) by an ion-exchange process toform $Ag_4Ti_5O_{12}$(or $Cu_4Ti_5O_{12}$). For metal/TiO_2 junctions, these ion-exchange thin films have been reduced by $NaBH_4$ solution. On the other hand, for metal sulfide/TiO_2 heterojunctions formation, those ion-exchanged thin films have been dipped inside Na_2S solution to grow the metal sulfide nanoparticle inside TiO_2. This typical growth technique of nanoparticle allows us to fabricated metal/TiO_2 or metal sulfide/TiO_2 heterojunction with a very low trap state that enables us to utilize this thin film for efficient photo-electrochemical H_2 generation and efficient Vis-NIR photo-detector fabrication.

To date, the performance ofphotoelectrocatalytic H_2 generation by metal/TiO_2 or metal sulfide/ TiO_2 heterojunctions photoanode is very poor. Because, the charge transfer efficiency from metal or metal sulphideto TiO_2strongly depends on the nature of metal or metal chalcogenide/TiO_2 interfaces. In most of those studies, metal or metal chalcogenide NPs are deposited on top of TiO_2 surfaces that make poor interfaces exhibiting significant interface trap states. An ideal metal/metal oxide or metal chalcogenide/metal oxide heterogeneous photocatalysis requires a large interface with very low trap states to reach efficient charge transfer without significant recombination at the interfacial. To resolve those issues, in this thesis work has demonstrated *in situ* grown thechnique thatprovides the formation of metal/metal oxide or metal chalcogenide/metal oxide heterojunctions with less interfacial trap states.The photoelectrochemical H_2 generation performancs of these in situ grown heterostructures based photoanodes have been studied in a various device structure. From those studies it was realized that photoanodecoated withmetal/TiO_2 or metal sulphide/TiO_2 heterojunction in combination withunderlaying TiO_2 NP coated FTO gives the best perfornce. In addition, the advantage of batter charge transfer has been realized in a broadband photodetector fabrication.

The summary of those finding are

The photo-electrochemical measurements reveal that photoanodes with Ag-TiO_2, Ag_2S-TiO_2 and Cu_2S-TiO_2 show the excellent photo-electrochmical properties. The comparative studies of three photoanodes show that photoanode with Ag-TiO2, Ag2S-TiO2 and Cu2S-TiO_2 gives the maximum photocurrent density of 42, 39 and 50 $mAcm^{-2}$ respectively in 1M KOH solution under 0.45 V external bias which is more than three order (10^3) higher than pure TiO_2 photoanode.

- All photo-anodes show the good photo stability under one and half hour steady operation.and have sufficiently fast photo response.
- In addition, we have utilized *in situ* grown Cu_2S-TiO_2 heterojunction thin film to fabricatevisible light photo-detector with the device structure ofAl/Cu_2S-

TiO_2/ZnO/Glass. The responsivity and detectivity of this optimized photodetector 0.22 A/W and 1.7×10^{11} jones respectively at 830 nm.

7.2 The scope of future work

- In future, this *in situ* grown metal/TiO_2 and metal sulphide/TiO_2 synthesis route can be explored in various ways with different combination of metal/metal oxide junction and metal sulphide/metal oxide heterojunction. For example, ZnO and SnO_2 are very well known metal oxide with higher electron mobility. Due to their higher carrier mobility, charge transfer rate is expected to be higher. Therefore, metal/ZnO(or SnO_2) and metal sulphide/ZnO(or SnO_2) can be synthesize in future. Those in situ grown structures can be studied for various application including photoelectrochemical H_2 generation, photodetector and solar cell application.
- These *in-situ* grown Cu_2S NPs and Ag_2S NP inside TiO_2thin film can be utilized for solar cell application.
- Much lower size Ag NP, Cu_2S NPs and Ag_2S NP can be grown by changing the reaction condition and their different physical behavior can be studied.
- Since these *in situ* grown metal/TiO_2 and metal sulphide/TiO_2heterojunction thin films have been deposited by low cost dip coating method, therefore larger area photoanode or other device can be fabricated and tested in future.
- In place of FTO glass, some metal substrate, like Cu, Ni can be used as anode for these *in situ* grown metal/TiO_2 and metal sulphide/TiO_2heterojunction thin film fabrication that can lower the overall fabrication cost.