PREFACE

This thesis entitled **"*In-Situ* Growth of Metal and Metal Sulfide Nanoparticles within Solution Processed TiO_2 Thin Film for Photodetection and Energy Harvesting Applications"** is mainly focused on the new technique to grow metal or metal sulfide nanoparticle within TiO_2 thin film by a low-cost solution-processed technique. These *in-situ* grown metal/TiO_2 or metal sulfide/TiO_2 heterojunction nanocomposite thin films have been utilized for photoelectrochemical hydrogen generation and photodetector fabrication. For this synthesis, initially $Li_4Ti_5O_{12}$, a popular ion-conducting metal oxide (ICMO) 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. Taking advantage of this feature, Li^+ of this ceramic film has been exchanged with Ag^+ or Cu^+ by an ion-exchange process that forms $Ag_4Ti_5O_{12}$ and $Cu_4Ti_5O_{12}$ respectively, after ion-exchange. For metal/TiO_2 heterojunctions, 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 interface trap state that enables us to utilize this thin film for efficient photoelectrochemical H_2 generation and efficient Vis-NIR photodetector fabrication.

So far, photoelectrocatalytic H_2 generation by metal/TiO_2 or metal sulfide/TiO_2 heterojunctions photoanode is very poor. Because its efficiency strongly 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. Therefore, a better synthesis technique providing the formation of heterojunction with less interfacial trap states is needed to achieve, which can certainly improve the catalytic performance useful for different industrial applications.

Important Finding of the Present Work:

1) A noble synthesis method for metal/TiO_2 or metal sulfide/TiO_2 heterojunctions thin film

As mention earlier, in our present study, a unique approach has been adopted to develop an **in-situ** growth technique to form metal (Ag, Au, or Cu), and metal sulfide (M_2S, M = Ag, Cu), Cu_2S, and Ag_2S NPs within solution-processed TiO_2 thin film. This heterojunction thin-film fabrication has been performed in three simple consecutive steps. In the first step, sol-gel derived **$Li_4Ti_5O_{12}$** thin film has been fabricated by dip-coating method. In the second step, the ion-exchange process replaced the Li+ by either Ag+ or Cu+. Finally, reduction or sulfurization process converted Ag+ (or Cu+) to Ag-NP (Cu NP) or Ag_2S (or Cu_2S-NP). Utilizing this technique, the large area Ag-TiO_2, Ag_2S-TiO_2, and Cu_2S-TiO_2 thin film devices have been fabricated and characterized thoroughly for fundamental properties.

2) Metal/TiO_2 or metal sulfide/TiO_2 heterojunctions thin film for efficient photoelectrochemical H_2 generation.

Three different heterojunction thin films have been fabricated including Ag/TiO_2, Ag_2S-TiO_2, and Cu_2S/TiO_2 which have been grown on a transparent conducting substrate. Again each type of heterojunction thin film was grown on three different conducting substrates, including fluorine-doped tin oxide (FTO), FTO/TiO_2 (sol-gel), and FTO/TiO_2 (NPs) coated glass. A comparative photo-electrocatalytic measurement has been done for each heterojunction films that shows that photoanodes on FTO/TiO_2 (NPs) coated glass generate highest photocurrent density ~42, 50 and 36 mA cm^{-2} respectively at 0.5 V vs. NHE in 1M KOH solution which is three orders higher than pure TiO_2 and stable for more than 1.5 hours, indicating their excellent potential application for photoelectrochemical (PEC) water splitting.

3) Metal sulfide/ TiO_2 heterojunctions thin film for broadband photodetection

A Cu_2S/TiO_2 heterojunction thin film was fabricated on a glass substrate exactly in the same method as mention earlier. This process allows us to fabricate smooth and large area TiO_2 thin film containing Cu_2S NPs with an average particle size of 10.5 nm. A visible light lateral photodetector has been fabricated based on this Cu_2S-TiO_2 thin film that shows a very good photoresponsivity. For better sensitivity device has been fabricated with ZnO underlying layer with a device architecture Al/Cu_2S-TiO_2/ZnO/glass. This lateral heterojunction photodetector shows a detectivity of 1.7×10^{11} jones.

A list of journals and books used to bind up the thesis has been given at the end of the thesis as references.