Chapter 5

Conclusion

The goal of the research presented in this thesis was to evaluate whether the photoresponse of hematite can be improved by nanostructuring or and by the use of dopant or and by SHI irradiation, to combat with its poor performance due to short diffusion lengths of charge carriers and/or poor charge transfer. An extensive experimental work and analysis of the structural, morphological, electrical and optical properties of doped/undoped/SHI modified nanostructured hematite films prepared by electrodeposition and spray pyrolysis was undertaken in order to elucidate the role of the dopants/SHI irradiation in enhancing the photoelectrochemical response. The effect of Zr, Si, Al dopants and 100 MeV Si$^{1+}$ ion swift heavy ion irradiation on phase formation, particle size, bandgap, on-set potential, donor density, flatband potential, photocurrent density and photoconversion efficiency have been studied and discussed.

Below is the summary of the significant findings derived from the piece of research work presented in this thesis:

1. Zr doped electrodeposited hematite sample exhibited the maximum photocurrent density of $\sim 3.0 \text{ mA/cm}^2$ at 0.7 V/SCE for 2.0 at% Zr doped. The solar to hydrogen conversion efficiency for same sample was 1.84% at 0.7 V/SCE with 2.4 ml/h-cm$^2$ of hydrogen production rate. For spray deposition 1.0% Zr doped hematite was identified as best performing photoelectrode. This sample exhibited 1.6 mA/cm$^2$ photocurrent at external bias of 0.7 V/SCE, up to which a negligible photocurrent was shown by undoped sample. Same sample showed a photocurrent density of 132 $\mu$A/cm$^2$ at no bias condition. The STH conversion efficiency for 1.0% Zr doped hematite sample was 0.88% with 1.2 ml/h-cm$^2$ measured rate of hydrogen. The improved photoresponse of Zr doped sample has been attributed to its porous morphology, which provides maximum contact area between semiconductor and electrolyte. Increase in absorbance, maximum donor density, negative shift in flatband potential and reduction in depletion layer width also support the enhancement in photocurrent after Zr doping.
2. 0.005M Si doped electrodeposited hematite samples showed maximum photocurrent density of 1.9 mA/cm² at 0.7 V/SCE with 1.2% STH conversion efficiency. Factors, responsible for better PEC response exhibited by 0.005M Si doped hematite are its maximum value of donor density, flatband potential, minimum onset potential and peculiar morphology with optimum porosity. The measured rate of hydrogen production for same sample was 1.5 ml/h-cm². Highest photocurrent density of ~680 μA/cm² at 0.7 V/SCE exhibited by spray deposited 0.002M Si doped sample has been attributed to preferential orientation of thin films, increased donor density and flatband potential. The STH conversion efficiency for best performing Si doped samples was 0.35%. No hydrogen could be collected with this sample due to slow rate of evolution.

3. Electrodeposited 1.0 at% Al doped hematite sample exhibited the maximum photocurrent density of 2.81 mA/cm² at 0.7 V/SCE. The best photoresponse may be attributed due to improved crystallinity, higher absorbance and negative shift in onset potential. Same sample exhibited the 1.7 % solar to hydrogen conversion efficiency with 1.92 ml/h-cm² measured rate of hydrogen. In case of spray deposition, 2.0 at% Al doped samples showed the highest photocurrent density of 720 μA/cm² at 0.7 V/SCE. Improved photoresponse may be attributed to the change in surface morphology after Al doping. Negative shift in onset potential and more negative flat band potentials also favor the flow of photogenerated carrier at the photoelectrode/electrolyte junction. The STH conversion efficiency for best performing Al doped samples was 0.39%. The rate of hydrogen production was very slow and could not measure.

4. The electrodeposited undoped sample irradiated with Si⁺⁺⁺⁺ ion at 5×10¹² ions/cm² exhibited the maximum photocurrent density of 2.5 mA/cm² at 0.70 V/SCE. After irradiation better crystallinity, reduction in resistivity, maximum value of donor density and flatband potential favor the improvement in photoresponse. The STH conversion efficiency was 1.52% with measured rate of hydrogen of 1.8 ml/h-cm². In case of spray deposition undoped sample irradiated at fluence 2×10¹³ ions/cm² exhibited the maximum photocurrent density ~867 μA/cm² at 0.70 V/SCE. Similar to electrodeposited samples better crystallinity, reduction in resistivity played
major role to improve conductivity of the material as it reduces the total surface of the grain boundaries in the material, improves the carrier movement from one particle to other particles flow of photogenerated carrier within bulk of material and at the photoelectrode/electrolyte junction. The STH conversion efficiency for same sample was 0.49%. No hydrogen was produce.

5. Zr doped sample irradiated at fluence $1 \times 10^{12}$ ions/cm$^2$ with Si$^{8+}$ ions showed the photocurrent density of 3.32 mA/cm$^2$ at 0.70 V/SCE with 2.09 % STH conversion efficiency. Increase in crystallinity played a positive role in improving photoelectrochemical response. The measured rate of hydrogen for same sample was 3.0 ml/h-cm$^2$. Zr doped spray deposited irradiated sample showed a maximum photocurrent of 1.7 mA/cm$^2$ at 0.7V/SCE at same fluence $2 \times 10^{13}$ ions/cm$^2$. The STH conversion efficiency for same sample was 0.96% with 1.32 ml/h-cm$^2$ measured rate of hydrogen.

Based on the results presented above following conclusions can be drawn:

- Nanostructured $\alpha$-Fe$_2$O$_3$ thin films, with modified morphology of the photoelectrode, exhibited significantly good photocurrent due to efficient harvesting of visible light and by offering short distance required for the photogenerated holes to reach the electrolyte interface.
- Method of preparation of $\alpha$-Fe$_2$O$_3$ photoelectrode largely affects its performance. Electrodeposited nanostructured hematite has proven all the way to be better photoelectrode in PEC splitting of water, as compared to spray deposited films which may be due to its highly porous morphology.
- Research work carried out clearly indicates that doping is necessary to achieve significant photoelectrochemical response, even with nanostructured hematite.
- Zr has been identified as best dopant in hematite with respect to PEC splitting of water as compared to other dopants studied. The proposed mechanism for the enhanced photocurrent with Zr doping is an improvement of the transfer rate of photogenerated charge carriers at the surface and possibly also passivation of the grain boundaries by the dopants.
➤ The swift heavy ion irradiation, especially irradiation by $\text{Si}^{8+}$ ions appeared as a dominant strategy to enhance the photoelectrochemical response of nanostructured hematite thin films by modifying its morphological, optical and electrical properties.

➤ Although Si ion irradiation on undoped hematite thin film improved the PEC response significantly for many samples, but enhancement in photocurrent is of the same order as obtained by the doping. On the other hand, irradiation on doped sample exhibited small increase in photocurrent.

Thus, it may be concluded that nanostructured, nanoporous $\alpha$-$\text{Fe}_2\text{O}_3$ thin films, prepared by electrodeposition doped with Zr at optimum level of doping and irradiated with $\text{Si}^{8+}$ ion at optimum fluence offer significantly good photocurrent. However, photocurrent obtained in the study is not sufficient enough for efficient hydrogen production and could not achieve the value needed for commercial viability of the PEC system for production of hydrogen. This research work was an effort in the direction of improving PEC response of hematite thin film by using various modifications strategies. Results are encouraging and have definitely added few drops to water to the scientific knowledge of ocean. Research work can be extended in future with other dopants, surface modifications techniques and layered structure to realize efficient production of hydrogen.