6
Summary and conclusion

6.1 SUMMARY

In summary, a facile and effective hydrothermal methods for in-situ preparation of surface fluorinated hematite have been developed. The new materials were studied for their effect on solar water splitting, magnetic properties, microwave absorption and uranium removal capacity from waste water. The fluorinated hematite samples were compared against pristine hematite.

Chapter 1 introduces about hematite, its various applications and fundamental process of photoelectrochemical water splitting. Also, an introduction survery about radar absorbing and related materials, uranium removal from drinking water in addition to their literature is presented. Further, motivation and scope of thesis described in chapter 1.

Chapter 2 describes the synthesis and characterization of fluorinated hematite. The fluorinated hematites were characterized by X-ray diffraction, SEM, TEM, Raman, FTIR, UV-Vis, XPS, ^{19}F-NMR, SQUID magnetometer, BET surface area analyzer and network analyzer. The fluorinated hematites were prepared at various scales from 400 mg to 5 g with high reproducibility. Chapter 3 to 5 explores the application of surface fluorinated hematite.

Chapter 3 described hydrothermal synthesis of nanostructured surface fluorinated hematite using Selectfluor (F-TEDA) as a fluorinating as well as growth directing agent. The addition of successive increasing amount of F-TEDA to Fe precursor under hydrothermal conditions resulted in preferential growth of α-Fe_2O_3 along (110) orientation and suppressing the commonly observed (104) direction by almost 35%. With increasing fluorination (using F-TEDA-20%), the hierarchical dendritic type α-Fe_2O_3 converts to a snow-flake type structure, indicating anisotropically growing along the six directions. However, above 30% F-TEDA, loosely held particulate aggregates get formed. The extent of fluorination was highest of 1.21 atomic % with 30% F-TEDA and it was demonstrated by X-Ray Photoelectron Spectroscopy. Due to fluorination, optical absorption exhibited a reduction in optical bandgap from 2.10 eV in case of pristine to 1.95 eV for F-Fe_2O_3. Screen-printed films of F-Fe_2O_3 on FTO in photo electrochemical cell showed an enhanced current density at illumination of ~100 W/m^2. This increase in photo electrochemical activity was ascribed to the improved charge transfer efficiency and reduced recombination losses due to surface fluorine and moreover fluorination induced preferred growth along the (110) direction. As a photo anode material, 20% F-Fe_2O_3 was taken in an optimized ratio of 10:90 with respect to Degussa TiO_2 showed enhanced performance in dye sensitized solar cells with an increment in efficiency by nearly 16%.

The Chapter 4 reveals that the fluorination of α-Fe_2O_3 changes the magnetic characteristics of α-Fe_2O_3. The saturation magnetization increased appreciably upon fluorinating with F-TEDA. 30 wt.% of F-TEDA was found to be optimum value for introducing 37 times more saturation magnetization value as compared to pristine α-Fe_2O_3. The same behavior was absent with other fluorinating agents such as $TBABF_4$, NaF, NH_4F and HF. The fluorinated α-Fe_2O_3 was explored for microwave absorption properties. The microwave absorption characteristics were studied by measuring real part and imaginary part of permittivity (ε) and permeability (μ) both for pristine α-Fe_2O_3 and surface fluorinated Fe_2O_3 in the frequency range of 5.85-18 GHz. The imaginary part of permeability (μ_r'') and magnetic loss tangent value ($tan\ \delta_\mu$) of surface fluorinated Fe_2O_3 were found to be superior to pristine α-Fe_2O_3. The maximum reflection loss in surface fluorinated Fe_2O_3 was observed at different frequencies as a function of sample's thickness; for example, RL -18 dB at 7.5 GHz (t = 3.5 mm), -12 dB at 9 GHz (t = 3 mm), respectively. These characteristics make this material a potential candidate, in fact better than pristine α-Fe_2O_3, as radar absorbing material (RAM) both in C-band and X-bands.

Chapter 5 discussed about application of surface fluorinated hematite (F-α-Fe_2O_3) for uranium removal from drinking water. The sorption of U(VI) from aqueous solution was investigated as a function of pH, contact time and concentration using batch technique. The results indicated that the adsorption capacity of F-α-Fe_2O_3 was affected by the pH, contact time and initial concentration of uranium. The optimal adsorption of uranium was achieved at pH 5. The Langmuir and Freundlich adsorption models were used for mathematical description of the adsorption equilibrium and Langmuir model fitted better in the studied concentration range and follow the pseudo-second-order kinetics. The adsorption capacity of F-α-Fe_2O_3 was found 79 mg/g. The maximum uranium removal was associated with presence of fluorine in F-α-Fe_2O_3. Therefore, fluorine assists for adsorbing uranium at F-α-Fe_2O_3 surface irrespective of changes in surface area. The adsorption equilibrium was achieved within 1h time. FTIR, EDX, and XPS analysis confirmed the presence of uranium onto F-α-Fe_2O_3.

6.2 CONCLUDING REMARKS

The fluorinated hematite have been synthesized and investigated for photoelectrochemical, magnetic, microwave absorption and uranium removal. F-α-Fe_2O_3 synthesized with F-TEDA-30% exhibited maximum, 1.21 atomic %, fluorine content in hematite. Incidentally the same sample showed maximum photoelectrochemical performance, highest saturation magnetization and maximum removal of uranium form contaminated drinking water.

As a result of surface fluorination, hematite showed an enhanced current density and improved DSSC performance at illumination of ~100 W/m^2.

The improvement in saturation magnetization properties upon fluorination opens new area of their application. F-α-Fe_2O_3 demonstrated improved microwave absorption properties. Though the quantum of microwave absorption may not be very high as compared to γ- Fe_2O_3 or spinal ferrite; but in its own right is first of its kind observation of microwave absorption over the broad frequency range (5.85 to 18 GHz) for any surface modified hematite. It also opens new research opportunities to explore the potential of surface modified readily available α-Fe_2O_3 as radar absorbing materials. Further, there is a scope of improvement by imparting permittivity loss part by using dielectric materials along with F-Fe_2O_3 as one of the ingredient.

The fluorinated hematite showed excellent uranium removal capacity. Therefore, there is good potential to use F-α-Fe_2O_3 for uranium removal for large scale applications.

6.3 CLOSING COMMENTS

Surface fluorinated hematites show improved properties for photoelectrochemical, magnetic, microwave absorption and uranium removal from waste water. The synthetic methods and concepts developed in this study could be extended for fluorination and application of other metal oxides. Further, F-α-Fe_2O_3 may also be used in combination with other active materials for tailoring their catalytic activity.

Appendix I

List of Published Papers

Janu,V.C., Bahuguna,G., Laishram,D., Shejale,K.P., and Kumar,N. (2018) Surface fluorination of α-Fe_2O_3 using selectfluor for enhancement in photoelectrochemical properties, *Solar Energy Materials and Solar Cells*, Vol. 174, pp. 240–247

Bahuguna,G., Janu,V.C., Uniyal,V., Kambhala,N., Angappane,S., Sharma,R.K., and Gupta,R. (2017) Electrophilic fluorination of α-Fe_2O_3 nanostructures and influence on magnetic properties, *Materials & Design*, Vol. 135, pp. 84–91