Overall Conclusion and Future Scope of the Work

7.1. Overall Conclusion

Four chapters of the thesis, i. e., chapter 3, 4, 5 and 6 describing the research work, mainly, focused on the physicochemical properties of various manganese oxides nanostructures and their nanocomposites with different noble metals and other metal oxide nanostructures.

In chapter 3.1, we have mentioned facile wet chemical approach for the soft-templated synthesis of self-assembled Mn_3O_4 microdandelions through effective dye/surfactant aggregates as soft templates for the formation of Mn_3O_4 microdandelions upon addition of a weak base, diethanolamine to manganese acetate as the precursor under mild refluxing conditions. The Mn_3O_4 microdandelions, bearing high surface area, exhibit potential photocatalytic activity towards the degradation of dye, *viz.*, alizarin red under visible light irradiation under ambient condition. It is, apparent, that the reaction follows first-order kinetics and corresponding rate constants were calculated to be 1.9×10^{-4} and 6.7×10^{-3} min^{-1} in the absence and presence of the catalysts, respectively, which indicate that the rate of reaction increases approximately 35 times in the presence of microdandelios.

Chapter 3.2 describes the wet chemical approach towards preparation of self-assembled high surface area nanostructured Mn_2O_3 through an effective polymer/surfactant interaction. The Mn_2O_3 nanorods were found as efficient and selective catalysts for synthesis of valuable aldehydes and ketones over undesirable acid byproduct using low catalyst loading. The precursor alcohols bearing activated and unactivated aromatic rings, double and triple bonds, and chiral sugar moiety were tolerated in this direct oxidative transformation strategy developed under benign reaction conditions. This unprecedented property of Mn_2O_3 nanorods under very low catalyst loading (0.01 mol%) provides new prospects and perspectives in catalysis by nanostructured materials.

In chapter 4.1, we have reported the controllable integration into gold-manganese oxide nanocomposites by seed-mediated epitaxial growth at water/*n*-heptane interface and investigated the electrocatalytic activity of these combinatorial catalysts towards water oxidation and oxygen reduction at low overpotential and the, most importantly,

under neutral pH condition. These synthesized catalyst successfully, overcome the key challenge of recent research of electrocatalytic water oxidation, surprisingly, at nearly neutral pH (pH~7.5) and low overpotential of 370 mV which is beyond the typical range of many homogeneous water oxidation catalysts (600 – 900 mV). As manganese oxides are available in various oxidation states and exhibit extensive biomimetic chemistry with oxygen, this result adds a new feather and illuminates ample opportunities in water oxidation electrocatalysis using wide varieties of inexpensive and earth-abundant materials. This facile and environmentally benign synthetic strategy for the nanocomposites could be upscaled at the industrial level and may offer a promising future for renewable energy technologies.

Chapter 4.2 illustrates the synthesis of trimanganesetetraoxides (Mn_3O_4)−silver (Ag) nanocomposites by seed-mediated epitaxial growth of manganese oxide by alkaline hydrolysis of manganese precursor on preformed silver nanoparticles at water/*n*-heptane interface. The morphology of the nanocomposites has been varied by individual addition of five size-selective silver nanoparticles for the epitaxial growth of the manganese components. A variety of techniques have been used to characterize these materials, such as, absorption spectroscopy, diffuse reflectance spectroscopy, transmission electron microscopy, high resolution transmission electron microscopy, Fourier transform infrared spectroscopy, Raman spectroscopy, X-ray diffraction pattern, cyclic voltammetry, selective area electron diffraction pattern, energy dispersive X-ray analysis, elemental mapping and thermogravimetric analysis. Now, the efficacy of these as-synthesized nanocomposites has been demonstrated towards the sensing of various hazardous volatile organic compounds, exhibiting high sensitivity and selectivity to ethanol. Moreover, the structure-function relationship of the Mn_3O_4−Ag nanocomposites upon variation of the size of silver particles towards the sensory activity of ethanol has been elucidated.

Chapter 5.1 contains the synthesis of magnetic iron oxide/manganese oxide nanocomposites by alkaline hydrolysis of manganese precursor in the presence of preformed polyethylene glycol (PEG)-stabilised magnetite (Fe_3O_4) nanoparticles. The as-synthesised nanocomposites have been characterised by several spectroscopic and

microscopic techniques. The as-prepared Fe_3O_4–Mn_3O_4 nanocomposites exhibit reduced magnetism compared to the superparamagnetic Fe_3O_4 nanoparticles. The moderate magnetism of the Fe_3O_4–Mn_3O_4 nanocomposites offers a viable platform for i*n-vitro* cytotoxicity studies on macrophages.

Chapter 5.2 demonstrates the synthesis of dual oxide nanocomposites consisting of manganese oxide (Mn_3O_4) and nickel oxide (NiO) for electrochemical water oxidation reaction in the presence of sunlight and ultraviolet light under neutral pH conditions. Kinetic parameters of the electrocatalytic oxygen evolution reaction have been extracted from Tafel plots and Faradic efficiency calculations. Our results show that these nanocomposites could catalyse water oxidation in neutral phosphate buffer saline with a current density of 2.2 mV cm^{-2} and turnover frequency of 4.3 s^{-1} and that of in presence of UV light are 4.5 mV cm^{-2} and 5.1 s^{-1} at an applied overpotential of just 280 mV. The significance of this approach, includes, the use of earth-abundant nickel and manganese precursors, facile preparation of the electrocatalysts, the low overpotential and extremely high turnover frequency for O_2 evolution in neutral aqueous media.

In chapter 6, we have described the synthesis of Mn_3O_4−ZnO−CdO triple semiconductor nanocomposites by facile wet chemical approach. The as-synthesized metal oxides (*viz.*, Mn_3O_4 and CdO), dual oxides (*viz.*, Mn_3O_4-ZnO, ZnO-CdO and CdO-Mn_3O_4) and triple semiconductor (*viz.*, Mn_3O_4−ZnO−CdO) nanocomposites have been characterized using several spectroscopic and microscopic techniques. It has been found that band gap of the semiconducting particles decreases with increase in hierarchy of the system. Then, the as-synthesized nanocomposites have been exploited for the photocatalytic degradation of Evans blue under ambient condition. Interestingly, it seen that, with increase in hierarchy, the catalytic activity of the semiconducting particles increases and therefore, the reduction in the band gap has been validated.

7.2. Future Scope of the Work

In the near future, it would be interesting to elucidate the crystal structures of the as-synthesized nanocomposites and derive structure-function relationship in the field of catalysis, photocatalysis, electrocatalysis and sensing. From materials perspectives, it is worthwhile to upscale the synthesis of the manganese oxide-based materials and to exploit the particles as industrial catalysts to meet the challenges of global energy crisis.