Chapter 7 *Conclusions and Future Work*

The important findings of the thesis are outlined below

The basic objective of the present thesis is to synthesise various polymorphs of MnO_2 and study their structure, microstructure, magnetic and electrochemical properties. We use simple and facile hydrothermal technique to synthesise α-, β, and δ-MnO_2. Further, the effect of doping of rare earth dopant Dy in α-MnO_2 on magnetic and electrochemical performance is discussed in detail for the application of supercapacitor.

The summary of the findings are

➢ Polymorphs of MnO_2 such as α, β and mixed phase of α and β phase of MnO_2 were synthesised via hydrothermal technique by varying the concentration of $KMnO_4$. The structure, optical, magnetic aling with electrochemical performance were discused. Though XRD and FTIR spectroscopy confirmed the pure phase formation of MnO_2, from Rietveld refinement fitting, the phase fraction of α and β phase were found to be ~73% and ~27%, respectively in αβ-MnO_2. Field emission scanning electron micrographs showed the formation of nanorods irrespective of the phase. While α, and β-MnO_2 nanorods were grown with an average diameter of 28 and 116 nm in αβ-MnO_2, two different aspect ratio of nanorods were attributed to the presence of α and β-MnO_2 phase. Small size of nanorods in β-MnO_2 resulted high specific capacitance in comparison to α- and αβ-MnO_2 nanorods. The optical bang gap estimated through UV-visible spectra for α-, β- and αβ-MnO_2 nanorod was found to be 1.53, 1.30 and 1.45 eV, respectively. We studied the magnetic

properties of α-MnO$_2$, β-MnO$_2$ and $\alpha\beta$-MnO$_2$ nanorods by performing DC magnetization, frequency dependent ac susceptibility and relaxation remanant magnetization. The negative Curie-Weiss temperature (θ_{cw}) while confirmed the antiferromagnetic ordering in α-MnO$_2$ and $\alpha\beta$-MnO$_2$, positive θ_{cw} in β-MnO$_2$ showed strong ferromagnetic interaction due to dominating intra sublattice interaction. No shifting of the peak in $\chi'(T)$ ruled out the presence of spin-glass behaviour in α-MnO$_2$ nanorods. However, in β-MnO$_2$ and $\alpha\beta$-MnO$_2$ T$_f$ was observed at 22 K and 19 K.. The spin-glass and/or cluster-glass feature was further confirmed from the fitting of susceptibility with Vogel-Fulcher, Power law and remanant magnetization measurement observed in β- and $\alpha\beta$-MnO$_2$ nanorods. It was important to mention here that, such SG behaviour was found to be critical depending on the presence of Mn^{3+} in MnO$_2$ compound.

➢ Bernessite structure of δ-MnO$_2$ has been synthesised through facile hydrothermal technique without using any template. XRD, FT-IR and Raman spectroscopy confirmed the formation of the δ phase of MnO$_2$. We studied the magnetic properties of δ-MnO$_2$ by carrying out dc magnetization, frequency-dependent ac susceptibility, and magnetic relaxation measurements. While dc magnetization showed the existence of AT type phase boundary with freezing of spin clusters at 11.2 K, frequency-dependent ac susceptibility predicted the freezing of interacting spin clusters. Frequency-dependent ac susceptibility analyzed using both Vogel-Fulcher law as well as power law, demonstrated the relaxation time constant, τ_o and interaction parameter, T$_o$ as 4.7 x 10^{-9} s, 10.43 $\pm$ 0.2 K and 1.62 x 10^{-9} s, 11.32 $\pm$ 0.03 K, respectively. Higher τ_o compared to that of conventional spin-glass clearly recommended the presence of clusters in this system. Below freezing temperature,

remanent magnetization measurement confirmed the spin-glass behavior. The occurrence of the low temperature freezing of spin clusters was attributed to the complexity of the mixture of Mn^{3+}/Mn^{4+} with strong magnetic frustration in δ-MnO_2.

➢   Tetragonal, I4/m structure of α-MnO_2 nanorods with different concentration of Dy were synthesised via simple one step hydrothermal method followed by heat treatment by optimizing synthesis conditions. Incorporation of Dy ion not only influenced the crystalline nature but also inhibited the growth of nanorods. With increasing Dy concentration in α-MnO_2 although, the structure of MnO_2 remained tetragonal, the crystallinity was reduced and inhibited the growth rate of nanorods. We observed that when the concentration of Dy reached to 15 mol%, the diameter and length of α-MnO_2 nanorods significantly reduced from 40 nm and 4-5 µm to 20 nm and 70 nm, respectively. Being MnO_2 as a good electroactive material, a significant enhancement in specific capacitance accompanied with a decrease in charge transfer resistance after incorporating 15 mol% Dy was observed. Such enhancement in specific capacitance attributed to the poor crystallinity along with large surface area and pore size distribution. Here we concluded that rare earth doped α-MnO_2 can be explored as an eminent electrode material for an application of supercapacitor.

➢   The magnetic properties of hydrothermally synthesised α-MnO_2 and α-MnO_2:Dy nanorods were explored in this chapter. Neel temperature of α-MnO_2 was found to be 18 K less than that of bulk α-MnO_2 ($T_N = 24.5$ K) and further decreased to 11 K after doping Dy with an increasing antiferromagnetic interaction. The existence of exchange bias was found

in both samples by observing a clear shift in field cooled M-H loops. For α-MnO$_2$, large H$_{EB}$ of 565 Oe was obtained which decreased to 140 Oe after doping Dy at the cooling field of 30 kOe. Such variation of exchange bias field was understood on the basis of core shell structure which consists of frozen and rotatable spins in the core and surface of nanorods respectively. The competition between them resulted in spin-glass behaviour and high exchange bias in α-MnO$_2$ than in Dy doped MnO$_2$. We proposed a mechanism for the variation in exchange bias with number of cycles of hysteris loops using power law and double exponential equation.

The scope of future work

The effect of the variation in synthesis parameters in hydrothermal technique results in the formation of different polymorphs of MnO$_2$. Although the structure based electrochemical and magnetic properties have shown few important findings, there are still several issues which needs to be clarified with proper experimentations in future. Here are couple of suggestions

➢ The composite of Dy doped MnO$_2$ with graphene oxide/reduced graphene oxide or with other metal oxide to achieve high specific capacitance.

➢ Phase transformation from β to α-MnO$_2$ after doping rare-earth element be undertaken in order to achieve high capacitance.

➢ Effect of SHI irradiation on phase transformation and supercapacitive performance of MnO$_2$ has not been done as per the reports. To achieve phase transformation one can probe this technique which ultimately affect the specific capacitance.