Dedicated

To my beloved parents

CERTIFICATE

It is certified that the work contained in the thesis titled ***"STRUCTURAL, MAGNETIC AND ELECTROCHEMICAL PROPERTIES OF MULTIFUNCTIONAL NANOSTRUCTURED POLYMORPHS OF MnO_2 AND Dy DOPED MnO_2"*** by ***"DEEPTI GANGWAR"*** has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

It is further certified that the student has fulfilled all the requirements of Comprehensive, Candidacy and SOTA for the award of Ph.D. degree.

Date: 10th Nov 2021

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DECLARATION BY THE CANDIDATE

I, ***DEEPTI GANGWAR***, certify that the work embodied in this Ph.D. thesis is my own bonafide work carried out by me under the supervision of **Dr. (Mrs.) CHANDANA RATH** for a period from **July 2016** to **Nov 2021** at the **SCHOOL OF MATERIALS SCIENCE AND TECHNOLOGY**, Indian Institute of Technology (Banaras Hindu University), Varanasi, India. The matter embodied in this Ph.D. thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not willfully copied any other's work, paragraphs, text, data, results, *etc*., reported in journals, books, magazines, reports, dissertations, thesis, *etc*., or available at websites and have not included them in this thesis and have not cited as my own work.

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CERTIFICATE BY THE SUPERVISOR

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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Abbreviations

TMOs	Transition metal oxides
MnO_2	Manganese Dioxide
NPs	Nanoparticles
OMSs	Octahedral molecular seives
1D	One dimensional
2D	Two dimensional
3D	Three dimensional
FM	Ferromagnetic
T_C	Curie temperature
M_R	Remanant magnetization
H_C	Coercive field
AFM	Antiferromagnetism
T_N	Neel temperature
SG	Spin-glass
T_f	Freezing temperature
ZFC	Zero field cooling
FC	Field cooling
DE	Double exchange
EDLC	Electrical double layer capacitor
CV	Cyclic voltammogram
PVP	Polyvinyl pyrrolidone

CTAB	Cetyltrimethylammonium bromide
NaOH	Sodium hydroxide
MWI	Microwave Irradiation
H_{EB}	Exchange bias
RE	Rare earth
CNTs	Carbon nanotubes
CNFs	Carbon nanofibers
MCNT	Multiwall carbon nanotube
PCNF	Porus Carbon nanofibers
GCD	Galvanostatic charge discharge
EIS	Electrochemical impedance spectroscopy
XRD	X-ray diffraction
FTIR	Fourier Transform Infrared Spectroscopy
SEM	Scanning electron microscope
EDX	Energy Dispersive X-ray Spectroscopy
TEM	Transmission Electron Microscope
HRTEM	High Resolution Transmission Microscope
XPS	X-ray Photoelectron Spectroscopy
KE	Kinetic Energy
BE	Binding Energy
BET	Brunauer, Emmett, and Teller
BJH	Barrett-Joyner-Halenda
VSM	Vibrating Sample Magnetometer
SQUID	Superconducting Quantum Interface Device
SC	Specific capacitance

WE	Working electrode
RE	Reference electrode
CE	Counter electrode
GCE	Glassy Carbon Electrode
Θ_{CW}	Curie Weiss Temperature
MT	Temperature dependent magnetization
MH	Field dependent magnetization
T_{irr}	Irreversible temperature
μ_{eff}	Effective magnetic moment
CG	Cluster-glass
SPM	Superparamagnetic
AT	Almeida-Thouless
T_{SG}	Spin-glass transition temperature
C_p	Pseudocapacitance
C_{dl}	Double layer capacitance
R_s	Solution resistance
R_{ct}	Charge transfer resistance

PREFACE

Nanostructured transition metal oxides (TMOs) is probably one of the most interesting class of solids, exhibiting a wide range of crystal structures, great chemical stability and low-cost production. They are the compounds in which transition metal bound with oxygen atom forms a metal-oxygen bond whose nature varies from ionic to covalent or metallic. TMOs have an unusual number of accessible stable oxidation states per element with partially filled outer-d orbitals lead to characteristic properties such as magnetism due to the presence of unpaired electrons, which attract the interest of researchers. Among other inorganic TMOs, Manganese dioxide is an important functional metal oxide with half-filled outer d-orbital exhibits +4 oxidation state of Mn. Nanostructured MnO_2 has rich structural flexibility which adopts various crystallographic forms depending upon the size of the tunnel owing to their distinctive physical and chemical properties, as well as their wide applications in catalysts, component of the dry cell (Leclanché cell), inorganic pigment in ceramics, electrodes for electrochemical batteries (lithium, magnesium, sodium), and electrodes for supercapacitors. Such a great interest in MnO_2 is also due to its low price, toxicity, environmental friendliness and relative abundance in nature. The sharing of edges and vertices of basic MnO_6 octahedral unit with different linkage gives rise to α, β, δ and γ phase of MnO_2. In α-MnO_2, the size of (2 × 2) tunnel is ~4.6 Å, which is required to stabilize through insertion/extraction of alkali cations such as Li^+, Na^+, K^+, NH^{4+}, Ba^{2+}, or H_3O^+. 1D (1x1) tunnel structure pyrolusite, β-MnO_2 of size 1.89 Å is composed of a single strand of edge-sharing MnO_6 octahedra which can't accommodate cations because of its narrow size. 2D layers of edge shared MnO_6 octahedra form birnessite, δ-MnO_2 with an interlayer separation of ~7 Å. The sheets of MnO_6 octahedra can be stabilized by inserting

a significant amount of water molecules or cations such as Na^+ or K^+ between them. The morphology, porosity and surface area strongly affect the physical and chemical properties of MnO_2. Several authors have demonstrated the constructive modifications in the structure and morphology, making it a practical tool for studying their effects on magnetic and electrochemical properties as well. As a result, the synthesis and study of the properties of MnO_2 in different morphologies and structures for a wide range of applications are crucial.

Rich varieties in magnetic properties of MnO_2 come from differences in composition and structure which are provoked by distinct synthesis pathways and the presence of a large number of cations within the tunnels. Depending on the synthesis technique, sputtered grown α-MnO_2 nanorods possess an exchange bias of 1340 Oe for 30 kOe field cooled M-H plot [1] whereas α-MnO_2 nanoribbons synthesized through molten salt method possess a large zero-field cooling exchange bias of 1100 Oe [2]. *Luo et al*. have obtained that α-K_xMnO_2 ($x \leq 0.07$) show antiferromagnetic ordering below 24.5K, while α-$K_{0.166}MnO_2$ single crystals show an antiferromagnetic ordering below 18 K [3][4]. The magnetic properties of α-MnO_2 nanotubes have been tuned by intercalating Na, Li, and K cations within the tunnels. The doping concentration of K^+ affects the magnetic ordering in α-MnO_2 nanotubes. When the concentration of K^+ is ≤ 12 at%, it shows ferromagnetic behaviour and with doping concentration more than 12 at %, it shows antiferromagnetic behaviour [5]. The structure and magnetic properties of hydrothermaly synthesized β- and α-K_xMnO_2 (x = 0.15 and 0.18) nanorods are thoroughly investigated by *Barudzija et al*. β-MnO_2 exhibits AFM transition at 93 K, while both α-K_xMnO_2 (x = 0.15 and 0.18) nanorods possess reentrant spin-glass type behaviour at T_f = 21 K and 20 K, respectively [6].

On the other hand, morphology, porosity and surface area also affect the electrochemical properties of MnO_2. One can tune them by using different synthesis techniques and altering the synthesis parameters to improve pseudocapacitive performance. In this context, MnO_2 nanosphere, hollow urchin and smooth ball show quite high capacitance of 317, 204 and 276 Fg^{-1} at a scan rate of 5 mV/s, respectively [7]. γ-MnO_2 microspheres, α- and β-MnO_2 nanorods possess specific capacitance of 237.6 Fg^{-1}, 103.9 Fg^{-1} and 57.7 Fg^{-1} in 1M Na_2SO_4 electrolyte at 5 mV/s, respectively [8]. In addition, dopants in α-MnO_2 also may offer high specific capacitance as it possesses tunnel cavity of as large as 0.46 nm which is appropriate for the intercalation/de-intercalation of an external cation. *Tang et al.* achieve a significant improvement in specific capacitance (415 F g^{-1} at 0.2 A g^{-1}) for Co doped MnO_2 spheres, double than that of MnO_2 spheres (231 F g^{-1}) [9]. MnO_2 nanoflowers with specific capacitance of 160 Fg^{-1} transforms into MnO_2 orchids having high capacitance 202 Fg^{-1} after doping Cr [10]. Many efforts have been made by various researchers to increase the specific capacitance by synthesizing various doped MnO_2 nanostructured materials under different physical conditions.

Important findings of the present work

Our thorough investigations focus detailed study on the influence of the synthesis parameters on polymorphic structures and properties of MnO_2 nanostructures. These are the important factors for tailoring the features required for certain applications. The structural, magnetic and electrochemical properties of polymorphs of MnO_2 and the effect of Dy doping in MnO_2 have revealed several key findings which we have reported and published in peer reviewed journals. Some of the important results are listed below:

1. Detailed investigations on magnetic properties of α, β, and mixed phase of α and β-MnO_2 by understanding their magnetic transitions and spin-glass behaviour based on different concentration of Mn^{3+}/Mn^{4+} in each sample has been discussed using XRD, Raman, XPS, magnetization, ac susceptibility and remanant magnetization measurement. α, β, and mixed phase of α and β-MnO_2 have been successfully synthesised through hydrothermal technique by varying the concentration of potassium ion. XRD and FTIR spectroscopy confirmed the pure phase formation of MnO_2. Rietveld refinement reveals the phase fraction of α and β phase to be ~73% and ~27%, respectively in αβ-MnO_2. SEM micrograph shows that the polymorphic phases crystalize in the form of nanorods. Small size of nanorods in β-MnO_2 resulted high specific capacitance in comparison to α- and αβ-MnO_2 nanorods. XPS confirms the presence of large concentration of Mn^{3+} in α- and αβ-MnO_2 nanorods results high effective magnetic moment and high optical band gap. Negative Curie-Weiss temperature (θ_{cw}) while confirmed the antiferromagnetic ordering in α-MnO_2 and αβ-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 χ' (T) in ac susceptibility ruled out the presence of spin-glass behaviour in α-MnO_2 nanorods. However, in β-MnO_2 and αβ-MnO_2, T_f observed at 22 K and 19 K absent in M Vs. T curve showed frequency dispersion behaviour. SG behaviour was critical towards the presence of Mn^{3+} in MnO_2 compound which also affects the bandgap of the material.
2. Monoclinic, $P6_3/mnm$ structure of δ-MnO_2 has been synthesised through a facile hydrothermal technique. XRD, FT-IR and Raman spectroscopy confirmed the formation of the δ phase of MnO_2. Temperature-dependent susceptibility confirms the

strong antiferromagnetic ordering and high effective magnetic moment attributed to the presence of both Mn^{3+} and Mn^{4+}, as confirmed by XPS. The reduced valency of Mn from 4 to 3 is accompanied with oxygen vacancies, affording the exact composition of $MnO_{1.58.}$ DC magnetization showed the existence of an AT-type phase boundary with the freezing of spin clusters at 11.2 K. The dynamic magnetic properties of the δ-MnO_2 were investigated using the frequency-dependent ac susceptibility fitted with various phenomenological models like the Vogel–Fulcher law and power law, indicating the existence of interacting spin clusters, which could freeze at 11.2 K. The time dependence of thermoremanent magnetization fitted well with a stretched exponential function, supporting the existence of relaxing spin clusters. Thus, the spin glass relaxation in the δ-MnO_2 is attributed to the interaction between Mn^{4+} and Mn^{3+}, which results in intrinsic magnetic frustration.

3. Tetragonal, I4/m structure of α-MnO_2 nanorods with different concentration of Dy were synthesised via simple one step hydrothermal method. 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 deteriorated and inhibited the growth rate of nanorods. We observe that when the concentration of Dy reached to 15 mol%, the diameter and length of α-MnO_2 nanorods 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 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.

4. α-MnO_2 and α-MnO_2:Dy (15 mol%) nanorods of diameter 40 and 20 nm are further characterized to study the effect of Dy doping on their magnetic properties. 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 core and surface spins depending on the size of nanorods thus decides the spin-glass behaviour, EB field observed in these nanorods. Change in exchange bias field with consecutive cycles showing the training effect has been discussed after fitted with phenomenological models like Power law and multiple exponent function.

This thesis is organized into VII chapters:

Chapter I A brief introduction and literature survey on MnO_2 is presented.

Chapter II describes the synthesis technique for the preparation of the polymorphs of MnO_2 (α, β and δ-MnO_2) and Dy doped α-MnO_2. It also includes the synthesis method used for the preparation of electrode for electrochemical characterization. Working electrode was prepared by drop casting synthesised active material on tore paper of area 1 cm^2. A concise overview of the instruments is provided which are used for structural

characterization of MnO_2 through XRD, for particle morphology SEM and UV visible spectroscopy for optical bandgap. XPS is used for elemental analysis and magnetic properties are studied using MPMS. An electrochemical workstation (CHI 7044) was used to study the electrochemical performances of the samples by performing cyclic voltammetry (CV), Galvanostatic charge discharge (GCD) and electrochemical impedance spectroscopy (EIS) using electrochemical three electrode cell in 1M Na_2SO_4 electrolyte solution.

Chapter III deals with the structural, magnetic and electrochemical properties of α-, β- and mixed phase of α and β MnO_2 nanorods.

Chapter IV includes the study of structure and magnetic properties of δ-MnO_2.

Chapter V shows the influence of Dy doping on electrochemical properties of α-MnO_2 nanorods. For α-MnO_2: Dy (15 mol %), capacitance enhances by twice than that of bare α-MnO_2.

Chapter VII The effect of Dy incorporation on magnetic properties of α-MnO_2 nanorods. Change in exchange bias field with consecutive cycles showing the training effect has been discussed after fitting with phenomenological models.

Chapter VII summarizes the main findings of the present work. We present the future works to be done in this area.

List of publications, journals and books used to bind up the thesis has been given at the end of the thesis as references.