Diversity in the Family of Manganese Oxides at the Nanoscale: From Fundamentals to Applications

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ABSTRACT: The interesting chemistry of manganese is due to its various oxidation states. The possibility of several oxidation states has offered the element a special position among the transition metal elements in the periodic table. Amidst the possible oxidation states of manganese (in the range of −3 to +7), the +2, +3, and +4 oxidation states are the most prevalent in nature. Manganese possesses the ability to form multiple bonds with oxygen through spontaneous oxidation to a variety of stoichiometric oxides/hydroxides/oxyhydroxides that are collectively coined as "manganese oxides". However, using the recent advances in the synthetic strategies and characterization techniques over the past couple of decades, the investigation of the physicochemical properties of manganese oxides has been extended up to the nanoscale dimensions beyond the molecular. Moreover, the family of the manganese oxides also includes a series of porous architectures that are, often, stabilized at the nanoscale dimensions. Exquisite synthetic control over the size, shape, organization, and mass production of a variety of oxides at the nanoscale dimensions renders outstanding structural, optical, catalytic, magnetic, and transport properties. The tunable properties along with the chemical and biological accessibility open up new opportunities in a diverse range of niche applications critical to global society. Therefore, beyond the multivariance, polymorphism, thermodynamics, phase transition, crystallinity, magnetism, semiconducting behavior, and biogenericity may serve as the key factors to describe the compelling applications in health and other fields and to further understand the manganese oxides at the nanoscale.

1. INTRODUCTION

Manganese oxides minerals are ubiquitous in nature and have been exploited since antiquity—the palaeoanthropological evidence of clarification of minerals to cosmetic pigments in female reproductive strategies.¹ Since the middle of 19th century, manganese (Mn) is an essential element for the production of steel, nonferrous alloys, glassmaking, water purifying agents, plant fertilizers, as a deoxidizer and desulfurizer, circuit boards, additives to livestock feed, and as a colorant for bricks. Manganese is the second most abundant desulfurizer, circuit boards, additives to livestock feed, and as a purifying agents, plant fertilizers, as a deoxidizer and production of steel, nonferrous alloys, glassmaking, water environmental.² The Earth’s crust contains about 1000 ppm Mn in comparison with iron (53 000 ppm); the atomic weight (54.94) is similar to iron (55.85), and some resemblance of chemical behavior has signified its importance as an industrial metal, after iron, aluminium, and copper. Manganese, because of its special electronic configuration ([(Ar)3d⁵4s²], where manganese is a transition metal with five unpaired electrons),³ possesses several unique attributes, such as the occurrence of multiple valence states, the ability to form oxide with highest oxidation state (VII) in the entire periodic table, rich redox chemistry compared with other d-block elements, and the ability to form species with a high oxidizing potential. Moreover, among the common metals, manganese renders unusual behavior to exhibit similar sulphidation and oxidation processes from both kinetic (similar rates) and thermodynamic perspectives (similar activation energies as 88 kJ mol⁻¹ for sulphidation and 81 kJ mol⁻¹ for oxidation). Because of these distinctive physicochemical features, manganese is an essential element in photosynthetic systems, water-splitting reactions, catalysis, pollution abatement, and biological processes.³

The family of the manganese oxides (MnOₓ) is a class of materials depending on the variation of Mn−O linked together in their structure. Amidst the transition metal oxides that are capable of developing newer functional materials, manganese oxides have received special attention due to their inherent divergence in redox properties, morphology, crystalline structure, and surface nanoarchitectures. Due to the ease of synthetic strategies, a multitude of different synthetic strategies are possible toward the preparation of manganese oxides with specific stoichiometry, morphology, crystalline structures, size, or surface properties. Among most of the transition metal oxides, manganese oxides have been of significant interest as these oxides can exist in several easily exchangeable transition states with various structural forms over a wide range of temperatures (up to 1200 °C). Manganese oxides have great potential as selective heterogeneous catalysts toward a diverse range of industrial catalytic applications (e.g., ozone decomposition,
aerobic oxidation of amines, nitric oxide reduction, selective oxidations of volatile organic compounds, decomposition of hydrogen peroxide, hydrogenolysis of cyclopropane, oligomerization of methane, photocatalytic oxidation of organic pollutants, and electrocatalytic water-splitting reaction). Manganese oxides possess typical bertholitite structures containing labile lattice oxygen that make these oxides very promising, particularly, in the field of selective oxidations. The catalytic properties of manganese oxides can be ascribed to the capacity of manganese to form oxides with variable oxidation states and to the oxygen storage capacity in the crystalline lattice. Thus, the best catalytic performance can be attributed to the highest valence state of manganese species and can be correlated to the $\text{Mn}^{x}/\text{Mn}^{y−1}$ content. Manganese oxides have significant advantages over other oxidants as the reduced oxide can be readily oxidized by dioxygen and thus can play as electron transfer mediator during oxidation reactions. Therefore, the catalytic performance and reaction mechanism with manganese oxides are influenced by their crystalline structure, surface morphology and microstructure, surface active oxygen species, and reducibility under the microenvironmental conditions. Thus, manganese oxides, because of simple ease of preparation, low cost, environmental friendliness and relatively high activity, seem to be promising for solving many problems, including, energy sustainability, health issues, and environmental remedies critical to human civilization.

Manganese oxides are materials of significant interest due to their remarkable structural, optical, magnetic, catalytic and transport properties. More than 30 different crystalline forms of manganese oxides are found in nature that are spontaneously depleted through water and surface groundwater during the weathering of igneous and metamorphic rocks. These naturally occurring manganese oxides participate in diverse natural chemical reactions and thus determines the arability of soils and sediments, the composition of natural waters, and the potability of both surface and subsurface waters. Complex manganese oxides are very reactive and fine grained materials and govern significant roles that are important to life on Earth, such as transport of minerals, oxygen cycling in the water column, and biominalerization. Manganese oxides have great potential toward a wide range of technological applications, such as, ores of metallic manganese, components in ferrite production, selective heterogeneous catalysts, cross-linking agent in rubber, sorbents, corrosion-inhibiting pigments, pollutant monitoring, chemical and biological sensors, and black inners for dry cell batteries. Manganese oxide materials have also been utilized in designing chemically powered artificial micromotors capable of interconverting chemical energy into mechanical energy that can be exploited for cargo delivery, detoxification, or motion-based sensing. Nanostructures of manganese oxides have been more promising toward a variety of applications arising because of the unique characteristics triggered at small particle sizes. Moreover, manganese oxides with “layer” and “tunnel” structures, consisting of stacks of sheets sharing MnO₆ octahedra, are often stabilized at the nanoscale dimensions. These nanostructured manganese oxides could be utilized as promising cathodes for sodium ion capacitors, as cathode materials in rechargeable batteries, energy storage devices, and as water oxidation and oxygen evolution catalysts in fuel cells. Recent advent in the nanoscale synthetic strategies has offered the opportunity to realize the emergence of unique characteristics when the size of the materials shrinks to the nanometer length scale. The versatility of the synthetic approaches offering a high degree of control over the particle size, composition, and morphology has become an effective strategy to establish the structure–activity relationship of these materials. In the past couple of decades, there have been several Accounts, Feature Articles, and Reviews concerning many aspects of manganese oxides; however, these articles focus on specific aspects in the wide arena of the chemistry of manganese oxides. Therefore, the present Review aims to provide a critical and concise condensation of the incipient physicochemical attributes as a function of their oxidation state that encourage their applications in a diverse range of niche applications to offer a complete description of the manganese oxides at the nanoscale.

2. MULTIVARIANCE

Manganese is the tenth most abundant element in the Earth’s crust and can be easily oxidized, forming more than 30 different naturally occurring crystalline forms of oxides/hydroxides/ oxohydroxides (in general, coined as manganese oxides, $\text{MnO}_x$, where $x$ ranges from 1.0 to 2.0) that can adopt a vast number of structural geometries. There are several reasons for this diversity: (i) multivariance (II, III, IV) to different crystalline phases, (ii) remarkable structural varieties of the atomic architectures, (iii) abundance in the most geological settings, and (iv) ability to form minerals under a wide range of chemical, geochemical and biological conditions. Manganese possesses the ability to form numerous stable stoichiometric oxides, $\text{MnO}$, $\text{Mn}_2\text{O}_3$, $\text{Mn}_3\text{O}_4$, $\text{MnO}_2$ as well as metastable $\text{MnO}_x$ that could either coexist or gradually become interconvertible from one form to another during the oxidation process controlled by the diffusion of oxygen. Manganese monoxide, $\text{MnO}$ (manganosite), may take the form of minerals and provides a model system for the theoretical and experimental studies of rock salt oxides. Bulk MnO is a green crystalline solid that becomes converted to dark brown in the presence of air. It acts as highly reactive oxidizing species but becomes dangerous and explosive above a temperature of 55 °C. When the dimension of the particles shrinks to the nanometer size regime, MnO becomes blue in color and exhibits excellent magnetic, conductance, and electrochemical properties. Trivalent oxide, $\text{Mn}_2\text{O}_3$ (bixbyite), occurs in two structural forms: $\alpha$-$\text{Mn}_2\text{O}_3$ as the mineral bixbyite, and the other thermally less stable, $\gamma$-$\text{Mn}_2\text{O}_3$, which does not occur in nature. Bulk $\alpha$-$\text{Mn}_2\text{O}_3$ is blackish brown but turns yellow when the size of the particles is reduced to nanometer length scale. In the past few decades, the oxide has been of significant scientific interest because of its outstanding structural architecture. The spinel, $\text{Mn}_3\text{O}_4$ (hausmannite), is the stable phase of manganese oxides with the highest average oxidation state of Mn as +2.66 and occurs as a black mineral. Hausmannite possesses a normal spinel structure presented by the formula, $\text{Mn}^{x+}(\text{Mn}^{x−})_2\text{O}_4$, in which the $\text{Mn}^{x+}$ and $\text{Mn}^{x−}$ ions occupy the tetrahedral and octahedral sites, respectively, with tetragonal distortion of $\text{Mn}^{x−}$ ions due to Jahn–Teller effect. Bulk Mn$_3$O$_4$ is brown in color but becomes brownish yellow when the dimension falls in the nanometer range. The spinel structure has attracted great interest because of its potential technological applications, such as catalysis, ion exchange, molecular adsorption, and water treatment.

Manganese dioxide ($\text{MnO}_2$) (pyrolusite) can be found in the Earth’s crust as coatings, in massive deposits, and as important deep-sea minerals. The oxide can be used ranging from promising electrode materials for the design of high-performance supercapacitors to heterogeneous catalysis to cancer...
theranostic applications. The color of bulk MnO₂ is blackish brown, whereas it changes to yellowish brown at the nanoscale. Metastable Mn₃O₈ contains coexisting divalent and tetravalent manganese as Mn²⁺Mn⁴⁺O₈ and exhibits unique physicochemical attributes important for various applications. The oxide, MnO₉, does not appear to exist; numerous manganese(II) salts are known and presently have been exploited in the synthesis of a series of perovskites. Dimanganese heptoxide (Mn₂O₇) is a green explosive oil, and because of its unusual formal oxidation state and oxygen-bridged structure (O₃Mn), represents among the few known binary oxides in chemistry.

Manganese oxyhydroxide occurs in three natural polymorphic forms: manganeite (γ-MnOOH) is an abundant mineral, and the other two are feitknechtite (β-MnOOH) and groutite (α-MnOOH). Manganese possesses the most stable structure, where one-half of the O atoms are replaced by hydroxyl anions in comparison with that of pyrolusite and Mn(III) octahedrals are quite distorted because of the Jahn–Teller effect. The abundant mineral, γ-MnOOH can be exploited as an effective precursor for the synthesis of numerous intercalation compounds. Pyrochroite, (Mn(OH)₂), is an abundant mineral in aquatic and terrestrial environments and readily transforms to higher oxidation states, Mn(III/IV) hydroxides. The hydroxide governs the transport of redox active species and heavy metals in the environment and therefore plays crucial roles in elemental biogeochemical cycles. Structural representations of some common manganese oxides with different oxidation states of manganese are shown in Figure 1.

![Figure 1. Structural representations of common manganese oxides with different oxidation states of manganese. The yellow and orange polyhedrals denote the position of manganese atoms possessing up and down magnetic moments, respectively. Reprinted with permission from ref 8. Copyright (2018) American Physical Society.](https://pubs.acs.org/doi/10.1021/acsomega.0c03455)

3. POLYMORPHISM

The diverse polymorphism exhibited by manganese oxides makes the hydrothermal synthesis, often, challenging because the reaction products are sensitive to the mere variations in the experimental conditions. Among the series of oxides, manganese dioxides encompass the entire family of polymorphic structures; the structural diversity, morphology, composition and porosity of these materials enable to possess a rich chemistry within the defined framework. MnO₂ may exist in different crystalline modifications (α, β, γ, δ, ε) in nature and naturally stabilized at the nanoscale dimensions. These polymorphic crystallographic modifications occur as a consequence of divergence in the connectivity of corner- and/or edge-shared octahedral [MnO₆] building blocks, leading to the construction of “layer” and “chain/tunnel” structures with enough space to accommodate the foreign cations. The group of compounds, viz., Mn(IV) oxides and the mixed Mn(III,IV) (hydroxy)oxides are termed as manganates to highlight their oxyanion properties. Manganates typically possess open crystal structures, high surface areas with appreciable negative charges, and exchangeable cations to maintain the charge neutrality (viz., Na⁺, K⁺, Mg²⁺, Ca²⁺, Cu²⁺, Ni²⁺, and Mn²⁺). These porous manganates are either amorphous or crystalline as tunnel-structured (octahedral molecular sieves, OMSs) or layer-structured (octahedral layered phases, OLs) and consist of a large family of materials with pore dimensions varying in the range of ultramicropores to mesopores. In these architectures, manganese oxides exhibit variable valences depending upon their immediate chemical surroundings; typically, manganese as the central atom possesses octahedral coordination with subsequent decrease in the average oxidation state decreasing from 4.0 to the range of 3.5 and 3.9 because of the presence of mixed trivalent and tetravalent oxidation states within the same building block.

The precise characterization of the nanostructural features in these complex manganese oxides is a prerequisite to understand the emerging behavior of these materials. Among these dioxides, α-, β-, γ-MnO₂ all have tunnel structures, while δ-MnO₂ (birnessite) has a layered structure composed of two-dimensional sheets of edge-shared [MnO₆] octahedra. Manganese oxides with layered topologies are ubiquitous in the natural setting and also can be manufactured in the industries. The variations in the key structural aspects that govern their physicochemical properties make them indispensable in natural environment and industrial applications. Because the cations are mobile in nature, they can be displaced by other species in the interlayer region. Because electrostatic attraction or van der Waals forces are operative between the interlayers, the layered materials can be delaminated into unilamellar nanosheet units with thickness of the order of ~1 nm and the lateral size in the range of submicrometer to several tens of micrometers. The specific materials properties are determined by the average manganese oxidation state, degree of interlayer hydration, porosity, and presence/quantity of cation vacancies in the interlayers. The relatively open layered structure, δ-MnO₂, with an interlayer distance of ca. 7 Å (referred to as birnessite/synthetic 7 Å sodium manganese/chalcophanite) could be regarded as a promising electrode material for supercapacitors because of the presence of suitable channels for fast electrolyte ion transfer. Another layered manganese oxide mineral, phyllosilicates consist of layered sheets of [MnO₄] octaheda with an interlayer distance of 10 Å (referred to as lithiophorite/10 Å manganese/buserite) and contain an extra layer of water molecules as compared with that of birnessite. Phyllosilicates are not official minerals, but their structures closely resemble that of birnessites. High surface areas arising from porosity and small particle sizes encourage their application as cathodes in lithium ion batteries, while the cation vacancies in the interlayers, because of the creation of negative charge, provide a driving force for cation sorption and cation intercalation. The access of reacting species to the active reaction sites and the absorption of small molecules are...
facilitated within the tunnel structures that encourage their applications as molecular filters and adsorbents for the elimination of toxic waste gases. The electronic and structural properties of these layered structures play a deterministic role in the transport, speciation, and environmental remediation of metals and natural organic matters in the environment.

Octahedral molecular sieve (OMS) materials are a special class of synthetic manganese oxides with tunnel structures analogous to several naturally occurring minerals. The tunnel structures consist of single, double, or triple chains of edge-sharing \([\text{MnO}_6]\) octahedra, where the corners of the chains are shared to form tunnels having square or rectangular cross-section.

Thus, an infinite number of OMS structures can be formed by manganese dioxides with alternating \((1 \times 1)\) and \((m \times n)\) tunnels. When, \(m = 1\) and \(n = 1\), the structure is \(\beta\)-\(\text{MnO}_2\) and when, \(m = 2\) and \(n = 2\), the well-known \(\alpha\)-\(\text{MnO}_2\) phase is formed. The most familiar \(\alpha\)-\(\text{MnO}_2\) possessing one-dimensional \((2 \times 2)\) tunnels (4.6 x 4.6 Å) in the crystal structure enables sufficient storage and fast diffusion of foreign cations along the z-axis. Depending on the presence of these additional species, \(\alpha\)-\(\text{MnO}_2\) is named as hollandite or cryptomelane. Thus, the minerals, viz., hollandite, cryptomelane, and coronadite form an isostructural series (where some of the Mn\(^{4+}\) is replaced by Mn\(^{3+}\) and when, Mn\(^{2+}\)) to maintain electroneutrality with the general formula \(\text{A}_x\text{B}_y\text{O}_{16}\), where \(\text{A}\) represents large cations (Ba\(^{2+}\), K\(^{+}\), Pb\(^{2+}\)) and \(\text{B}\) represents Mn or other octahedral cations.

Pyrolusite (\(\beta\)-\(\text{MnO}_2\)) is one of the most stable manganese oxides with narrow \((1 \times 1)\) tunnel (2.3 x 2.3 Å) structure. The ramsdellite (R-\(\text{MnO}_2\)) structure consists of \([\text{MnO}_6]\) double chains that link corners with each other to form a framework of \((2 \times 1)\) tunnel (4.6 x 2.3 Å) structure with rectangular cross sections. The low-temperature nsutite (\(\gamma\)-\(\text{MnO}_2\)) phase possesses an intergrowth tunnel structure composed of stochastically distributed pyrolusite (1 x 1) tunnel (2.3 x 2.3 Å) and ramsdellite (2 x 1) tunnel (4.6 x 2.3 Å) domains. Akhtenskite (\(\varepsilon\)-\(\text{MnO}_2\)) is a metastable phase comprising face-shared \([\text{MnO}_6]\) and \([\text{YO}_6]\) domains (where \(\text{Y}\) denotes the vacancy) octahedra, where Mn\(^{2+}\) cations randomly occupy half of the octahedral positions of the hexagonal-close packed oxygen sublattice.

Among these porous structures, \(\alpha\)-\(\text{MnO}_2\) is of paramount importance because of its unique adsorption, oxidative, and catalytic properties, while both \(\alpha\) and \(\gamma\)-\(\text{MnO}_2\) can be used for lithium ion batteries.

Structural representations of some common polymorphs of \(\text{MnO}_2\) are displayed in Figure 2.

In addition, the synthesis of thermally stable molecular sieve material corresponding to natural todorokite is of immense interest because of the large (3 x 3) tunnel (7.0 x 7.0 Å) as well as cation-exchange behavior, like, zeolites.

The single chain structure (i.e., pyrolusite) differs from the double or triple chains (e.g., hollandite or todorokite) in the diameter of the tunnels that makes these structures obviously specific in terms of surface area, hydration, and accessibility to exchangeable cations. Moreover, manganese oxides with different tunnel sizes, such as romanéchtite (2 x 3), RUB-7 (2 x 4), \(\tau\) (3 x 4), and \(\tau\) (3 x 5), where \(\tau\) refers to the family of todorokite-type (3 x \(p\)) tunnel structures, are also possible. However, the presence of larger cations in the tunnels is indispensable so as to prevent from the collapsing of framework architectures. Polytypism, or stacking disorder, in certain manganese crystals also becomes significant to influence the materials’ properties. However, natural minerals, sometimes, cannot be directly employed for applications because of various impurities typically present in these porous crystallites, which have motivated the syntheses of these large varieties of complex morphologies with well-defined architectures.

The increasing demand for large-scale energy storage, consumer electronics, and electric vehicles requires rechargeable batteries featuring environmental friendliness, safety, high energy density, low manufacturing cost, and cost-effectiveness. Lithium ion batteries have been widely utilized as the principal energy storage systems over the past decades to empower modern portable electronics because of their high energy density; however, the intrinsic limitations of using volatile organic electrolytes and the related safety issues of these battery materials are driving the quest for alternative energy storage devices. Recently, the utilization of sodium ion batteries has been considered as possible alternatives because of the low cost and high abundance of the sodium element. The manganese oxide tunnel structures can act as hosts to various kinds of metal ions, such as, Ni\(^{2+}\), Co\(^{2+}\), Zn\(^{2+}\), Cu\(^{+}\), Mg\(^{2+}\), and Al\(^{3+}\), and those are alternatives to Li\(^+\) toward the fabrication of next generation battery electrodes. The increasing energy demand and environmental pollution warrant the necessity of efficient and greener energy conversion and storage devices. In comparison with conventional batteries and fuel cells, supercapacitors seem to be appropriate alternative energy storage devices because of the high power density, long lifetime, faster charge/discharge, low manufacturing cost, and environmentally benign processes. Manganese oxides have attracted immense interest toward the energy storage applications as supercapacitors. The high theoretical capacitance resulting from a greater number of accessible oxidation states and wide potential window make the manganese oxides as promising electrode materials for energy storage applications. The conversion and utilization of solar energy is a viable alternative to meet the clean energy demand toward the sustainable development of the global society. It is now established that the photocatalytic splitting of water could directly convert the solar energy into carbon-free hydrogen fuel. Manganese oxides have been promising toward the design of efficient water oxidation catalysts for the fabrication of artificial photocatalytic systems. The tunnel structures are also

![Figure 2. Structural representations of some common polymorphs of MnO2.](https://dx.doi.org/10.1021/acsomega.do.0c03465)
4. CRYSTALLINITY

Bulk manganese oxides are typically strong with precise crystallographic orientations; however, while the dimension of the materials shrinks into the nanometer size regime, different atomic arrangements are observed because of alteration in atomic positions and presence of vacancies in the nanostructures. The presence of oxygen vacancies in the manganese oxide structures renders active sites for redox reaction intermediates. The dimension of manganese oxides at the nanoscale impacts the properties mainly in two aspects: (i) a change in structural features (viz., the lattice symmetry and cell parameters) and (ii) the presence of low coordinated atoms (viz., corners or edges or oxygen vacancies). The structural properties of manganese oxides that adopt versatile geometries with variable crystal structures possess different chemical composition and surface microstructure that lead to different properties. Among the series of manganese oxides, Mn5O8 adopts a base-centered tetragonal lattice (I4/mc, a = 9.750 Å, c = 2.861 Å), while Laox2 crystallizes as the pure tetragonal/rutile structure (P4/2/mmm, a = 4.399 Å, c = 2.874 Å). γ-MnO2 is poorly crystalline as it is the product of intergrowth of the elements of pyrolusite and ramsdellite and as a result, complete single crystal does not emerge in this structure. The reflection peaks can be indexed to pure orthorhombic phase (Pnma (62), a = 6.36 Å, b = 10.15 Å, c = 4.09 Å). The δ-MnO2 crystal has the space group symmetry (P63/mmm, a = 6.36 Å, b = 10.15 Å, c = 4.09 Å) corresponding to birnessite and the interlayer spacing of 7 Å which suggests that the single crystalline water sheet are formed inside the layered structure of sodium manganese oxides. The presence of water molecules in the interlayer space is strongly dependent upon experimental conditions. Mn2O3 adopts a base-centered monoclinic structure (C2/m, a = 10.325 Å, b = 5.7181 Å, c = 4.8594 Å, β = 109.36°) possessing an infinite elemental sheets of Mn2+[O2]4− where the Mn2+ ions are held together by Mn4+ ions. The structure of groutite, α-MnO(OH) (Pnma, a = 10.667 Å, b = 2.871 Å, c = 4.554 Å, Z = 4), and manganite, γ-MnO(OH) (P2₁/c, a = 5.304 Å, b = 5.277 Å, c = 5.304 Å, Z = 4), are isostructural to the MnO2 polymorphs, ramsdellite and pyrolusite, respectively. The crystal structure of pyrochroite (Mn(OH)2), a mineral of the brucite group, consists of sheets of hexagonally close packed oxygen octahedra with space group, P3m1 and lattice parameters, a = 3.323 Å, c = 4.68 Å, Z = 1.2. Todorkite [(NaCa,K,Ba,Sr), (Mn,Mg,Al)6O12·3H2O], a tunnel-structured manganese oxide, popularly known as, octahedral molecular sieve (OMS-1) possesses space group symmetry (P2₁/m, a = 9.76 Å, b = 2.84 Å, c = 9.56 Å, β = 94.16°). Romanchite [(Ba, H2O),2(Mn4+,Mn3+),O4] adopts a monoclinic structure, with space group C2/m, and lattice parameters, a = 13.929 Å, b = 2.8459 Å, c = 9.678 Å, β = 92.39°. Another tunnel-structured manganese oxide, RUB-7 (2 × 2 × 2), exhibit a monoclinic structure with unit cell parameters, (C2/m, a = 14.22 Å, b = 2.853 Å, c = 24.28 Å, β = 91.32°). Chalcophanite (ZnMn2O4·3H2O) exists as triclinic system with space group, P1, having lattice parameters, a = 14.22 Å, b = 2.853 Å, c = 24.28 Å and α = 90°, β = 117.2°, γ = 120°. X-ray diffraction study of lithiophorite ([AlLi]MnO2(OH)2) reveals that the structure consists of alternating stacked layers of Mn−O and (Al,Li)−OH octahedra is trigonal (R3m) with unit cell parameters, a = 2.9247 Å, c = 28.169 Å.3 Vernadite (Mn2Fe3Ca2Na2(OH)6·nH2O) is stabilized as the fine-grained attractive candidates to the mineralogists as polymetallic sources. Therefore, the miniature tunnel size in these porous structures enables separation of different types of molecules on the basis of their size and shape, which renders these materials appropriate toward the applications as sorbents, heterogeneous catalysts, oxygen storage component and energy storage materials.9−12
Table 1. Structural Parameters for Some Representative Manganese Oxide Systems

| System                  | Crystal Structure | Space Group | Lattice Parameters |
|-------------------------|-------------------|-------------|-------------------|
| Manganosite (MnO)       | Cubic             | Fm3m        | a = 4.442 Å       |
| Bixbyite (α-Mn3O4)      | Cubic             | Ia3         | a = 9.904 Å       |
| Hausmannite (MnO4)      | Tetragonal        | I4 /amd     | a = b = 5.762 Å, c = 9.470 Å |
| Hollandite (α-MnO2)     | Tetragonal        | I4 /m       | a = 9.750 Å, b = 2.861 Å |
| Pyrolusite (β-MnO2)     | Tetragonal        | P4_2 /nnmm  | a = 4.37 Å, b = 2.874 Å |
| Todorokite              | Monoclinic        | P2/m        | a = 9.76 Å, b = 2.84 Å, c = 9.56 Å |
| (Na, Ca, K, Ba, Sr)3(Mn, Mg, Al)O12-3H2O | Monoclinic        | C2/m        | a = 13.93 Å, b = 2.85 Å, c = 9.68 Å |
| Romanècheite            | Monoclinic        | C2/m        | a = 92.3° |
| ([Ba(H2O)3]2[MnO4]3O16 | Trigonal          | P31       | a = 14.22 Å, b = 2.853 Å, c = 24.28 Å |
| Chloropanite            | Hexagonal         | R3m         | a = 2.9247 Å, c = 28.169 Å |
| Lithiophorite           | Hexagonal         | n. d.       | a = 2.84 - 2.86 Å, c = 4.7 Å |
| (Mn, Fe, Ca, Na)2(OOH)4-nH2O | Hexagonal         | n. d.       | a = 2.84 - 2.86 Å, c = 4.7 Å |

Microcrystalline hexagonal phase (n. d., a = 2.84–2.86 Å, c = 4.7 Å) and can be considered a nanosized phyllosilicate consisting of turbostratic stacking layers made up of [MnO6] octahedra linked by sharing edges resembling to fibers. Hollandite [Ba(Mn4+3Mn3+)2O16], cryptomelane [K-(Mn4+3Mn3+)O16] and coronadite [Pb(Mn4+4Mn3+)O16] form an isostructural series, where the unit cell is tetragonal or pseudotetragonal with space group, Cs4h - 14 /m and lattice dimensions, a = 9.8 Å, c = 2.86 Å, β = 91.52°.[14]

A lexicon of the structural parameters for some representative manganese oxide systems is summarized in Table 1. It is, therefore, possible to define the crystallinity of manganese oxide materials that depend on the composition as well as chemical substitutions.2,10,11 The structure-function relationship in these transition metal oxides is governed by the crystal structures. Thus, the well-crystalline structure of these structures associated with different oxidation states of manganese oxides provide unique opportunities to improve their functions.2,10,11 The crystalline modifications, thus, provide ample opportunities to tune their various synthetic routes and/or chemical compositions of the manganese oxide minerals and correlate the activities under various microenvironmental conditions.

5. THERMODYNAMICS

Natural manganese oxides are ubiquitous on the vicinal surface in the environment and play valuable roles in the life processes on the Earth.15,16 These intrinsic processes are directed by the critical interplay between kinetics and thermodynamics that deserve to be crucial to understand the energetics of different manganese oxide phases. The thermodynamics explores the role of oxidation state, composition, crystalline structure, and surface energy in the thermodynamic stability of the family of manganese oxides.13 The corresponding surface enthalpy (the water-corrected drop solution enthalpy normalized with respect to nanophase surface area becomes essentially equivalent to surface energy) values of the hydroxysurfaces of Mn3O4, Mn2O3, and MnO2 are 0.96 ± 0.08, 1.29 ± 0.10, and 1.64 ± 0.10 J m⁻², respectively, while that of the anhydrous surfaces are 1.62 ± 0.08, 1.77 ± 0.10, and 2.05 ± 0.10 J m⁻², respectively.10 It is, therefore, evident that Mn3O4 has a lower surface energy than Mn2O3, while the latter has a smaller surface energy than MnO2, which means hausmannite is more stable than bixbyite followed by pyrolusite. These differences in the corresponding surface energy values significantly alter the positions in the oxygen fugacity-temperature space of the redox couples, Mn3O4 – Mn2O3 and Mn2O3 – MnO2. Therefore, the surface energies, generally, decrease with decreasing average oxidation state of manganese. It could also be anticipated that the stability of the spinel, Mn3O4 should be the most favored due to lower surface enthalpy phase corresponding to the smaller particle sizes. The enthalpy of water adsorption scales with the surface enthalpy for several manganese oxides. The water molecules prefer to be adsorbed at the Mn2⁺ sites of hausmannite with an energy of 19.7 kJ mol⁻¹, while the dissociative energy is estimated to be 21.8 kJ mol⁻¹ higher. Under the limit of monolayer formation, the adsorption energy is negative, and the dissociative mechanism involves 19.7 kJ mol⁻¹ higher in energy. This is another important aspect to understand the chemical reactivity at the hausmannite/water interface.15,16

Again, the crystalline structure, the manganese average oxidation state, the cation content, and the degree of hydration also differ significantly in the family of manganese dioxides as has been discussed in the previous section.2,10,11 The surface enthalpies (expressed as surface energies) for hydrous surfaces are 0.77 ± 0.10, 0.69 ± 0.13, 0.75 ± 0.11, and 0.51 ± 0.11 J m⁻² corresponding to cryptomelane, sodium birnessite, potassium birnessite, and calcium birnessite, respectively. In addition, the surface enthalpies (expressed as surface energies) of the hydrous surfaces of the calcium manganese oxide nanosheets are 0.75 ± 0.10 and 0.57 ± 0.12 J m⁻² corresponding to δCa0.43MnO2.3nH2O and δCa0.39MnO2.2nH2O, respectively. The profile showing the variation of surface enthalpy (hydrous surface) as a function manganese average oxidation state corresponding to these complex manganese oxides is shown in Figure 4. It is, therefore, evident that the surface enthalpies of binary phases are significantly higher than those of the layer- and tunnel-structured complex manganese oxides. The overall manganese average oxidation states are 3.78, 3.56, 3.52, and 3.50 for cryptomelane, sodium birnessite, potassium birnessite, and calcium birnessite, respectively.10 Studies have shown that the surface enthalpy of the complex manganese oxides decreases with decreases in manganese average oxidation state.10 The lower surface energy values corresponding to the complex manganese oxides suggests loose binding of the water molecules on the internal and external surfaces that may be crucial to both natural and technological catalytic applications. The degree of hydration of the layer structures, such as vermicidite...
The design of phase diagrams and as a result, multivalence mixtures of manganese oxides are usually obtained. Therefore, the formation of cryptomelane is favored by more oxidizing conditions. It has also been noted that manganese oxide with a (3 × 3) tunnel (todorokite) structure is stable at 250 and 450 °C in nitrogen atmosphere and under ambient conditions, respectively. Upon heating to a temperature above 600 °C, the material is transformed to MgMn2O4 in both the conditions. Thus, it is evident that phase formation and transformation have been obvious with manganese oxide

$$[\text{Mn,Fe,Na}_x\text{O}_y(\text{OH})_z\cdot n\text{H}_2\text{O}], \text{ chalcohanite } ([\text{Zn, Mn, Fe}]+\text{MnO}_2\cdot n\text{H}_2\text{O}], \text{ and lithiophorite } ([\text{Al, Li})\text{MnO}_2\cdot (\text{OH})_z]), \text{ also varies because the layers of } [\text{MnO}_6] \text{ octahedra are stacked together by O–H–O bonds as integral part of the structures}.\text{15,16}$

6. PHASE TRANSITION

During the synthesis of MnOx nanostructures, the non-equilibrium nature of crystallization at ambient temperatures initiates the competition between different metastable phases, and as a result, multivalence mixtures of manganese oxides are usually obtained.3,4,17 Therefore, the design of phase diagrams that offer guiding insights on the complexity of the energy landscape is indispensable to determine the experimental conditions required to synthesize a particular stable or metastable phase.3,4,17 A plethora of experimental evidence can be enunciated to correlate the functional changes with structural transformations in the family of manganese oxides. The stability relations based on the energetics of hydration of the common manganese oxides at the nanoscale are of paramount significance.12 The enthalpy of chemisorption of water corresponding to manganese oxide phases is −166.0, −106.7, and −71.3 kJ mol$^{-1}$ for Mn$_3$O$_4$, Mn$_2$O$_3$, and MnO$_2$, respectively, which indicates that water molecules are chemisorbed more strongly on the Mn$_3$O$_4$ surface than those of the other two oxides. Calculation of water coverage shows 3.3, 4.8, and 9.3 molecules nm$^{-2}$, corresponding to the nanophases of Mn$_3$O$_4$, Mn$_2$O$_3$, and MnO$_2$, respectively, which indicates that the water coverage is, surprisingly, high on the MnO$_2$ surface. Therefore, the pattern of better coverage but weaker overall bonding energetics associated with higher surface enthalpy occurs in the sequence of hausmannite, bixbyite, and pyrolusite.2−4 The thermodynamics of water adsorption/desorption on the surface of manganese oxides with nanoscale dimension governs rapid and reversible structural and phase changes. The formulation of the Mn−O binary phase diagram demonstrates that the redox equilibria at the nanoscale are shifted to favor the formation of lower surface energy phases: Mn$_3$O$_4$ < Mn$_2$O$_3$ < MnO$_2$.2−4 It is known that MnO$_x$ is a binary manganese oxide that contains coexisting divalent and tetravalent manganese. The small energetic metastability (endothermic enthalpy < 6 kJ mol$^{-1}$) of MnO$_x$ does not allow the presence of MnO$_x$ on the equilibrium phase diagram of Mn−O systems and allows the synthesis of this oxide under low-temperature conditions. However, the observation of slightly higher enthalpy than an isochemical mixture of Mn$_3$O$_4$ and MnO$_2$ reveals the production of a small amount of MnO$_x$ as the secondary phase during the synthesis of this metastable oxide. The structural phase transition can also occur from the cubic to orthorhombic through the modification of lattice parameters at various pressures during compression as presented in Figure 5. Moreover, thermodynamic considerations have revealed that among the four important MnO$_2$ phases: α-MnO$_2$ (hollandite), β-MnO$_2$ (pyrolusite), R-MnO$_2$ (ramsdellite), and δ-MnO$_2$ (birnessite, be classified as δ′ and δ′′), δ′ phase is metastable with respect to the α-phase; however, an increase in [K$^+$], further, increases the stability of the α-phase.18 A comparative study on the structural stabilities of two tunnel structures has shown that the surface enthalpy of cryptomelane is relatively low but higher than that of the corresponding potassium birnessite. Therefore, the formation of cryptomelane is favored by more oxidizing conditions. It has also been noted that manganese oxide with a (3 × 3) tunnel (todorokite) structure is stable at 250 and 450 °C in nitrogen atmosphere and under ambient conditions, respectively. Upon heating to a temperature above 600 °C, the material is transformed to MgMn$_2$O$_4$ in both the conditions. Thus, it is evident that phase formation and transformation have been obvious with manganese oxide

![Figure 4](https://dx.doi.org/10.1021/acsomega.0c03455)
Figure 4. Profile showing the variation of surface enthalpy (hydrous surface) as a function manganese average oxidation state corresponding to (■) sodium birnessite (Na$_0.09$MnO$_{1.22}$·0.52H$_2$O), (●) potassium birnessite (K$_{0.31}$MnO$_{1.26}$·0.33H$_2$O), (▲) calcium birnessite (Ca$_{0.12}$MnO$_{1.74}$·0.72H$_2$O), (▼) cryptomelane (K$_{0.11}$MnO$_{1.46}$·0.37H$_2$O), (♦) Ca−Mn−oxide nanosheets [Ca$_{0.39}$MnO$_{1.33}$·0.42H$_2$O], and (●) [Ca$_{0.13}$MnO$_{1.27}$·0.31H$_2$O]. Reprinted with permission from ref 15. Copyright (2017) National Academy of Sciences.

![Figure 5](https://dx.doi.org/10.1021/acsomega.0c03455)
Figure 5. Structural modification of Mn$_3$O$_4$ during compression: (a) the pressure-dependent lattice parameters and (b) volume evolution under high pressure. Insets in panel b represent the atomic structures of cubic and orthorhombic phases. It is observed that there is a huge collapse in volume at the phase transition pressure. Reprinted with permission from ref 17. Copyright (2017) Nature Publishing Group.
systems both under ambient and laboratory conditions.\textsuperscript{17–19} Therefore, a clear depiction of the phase diagrams predicting dramatic thermodynamic crossovers in polymorph stability can act as a practical guide toward the synthesis of target manganese oxides.

7. MAGNETISM

The family of manganese oxides provides an eminent platform to alter the intrinsic magnetic ordering by manipulation of size, shape and internal strain of the colloidal particles.\textsuperscript{20} Some aspects of the magnetic properties of these materials, like the spontaneous magnetization, the Curie temperature, and the anisotropic energy, are strongly affected by the particle size. The magnetic properties of manganese oxide nanostructures have attracted considerable interest during the past three decades as manganese is expected to adopt different local configurations, including room-temperature ferromagnetism that is hard to achieve. The magnetic properties of these oxides with dimension at the nanometer regime are of significance in diverse arenas of technological applications in high-density magnetic storage media, which have extensive applications in audio and video devices, electrical energy storage, electronics and information technologies, supercapacitors, computer data storage, and as precursors for synthesizing soft magnetic materials.\textsuperscript{21} Magnetism of these oxides are also envisaged because of their promising applications in magnetic resonance imaging, ferrofluid technology, spin valves, magnetocaloric refrigeration, catalysis, and so on.\textsuperscript{17} The oxide, MnO, can provide useful information regarding the nature of magnetic interactions of rock salt oxides. MnO nanoclusters show a phase transition from ferromagnetic to paramagnetic behavior below 50 K which is quite different from the bulk α-MnO\textsubscript{2}. This transition temperature, \(T_\text{f} \sim 47\) K is higher in comparison with the Neel temperature, \(T_\text{N} \sim 24.5\) K of bulk α-MnO\textsubscript{2}, and seems to exhibit an obvious ferrimagnetic transition at \(T = 52\) K. This could be explained based on the fact that all the [MnO\textsubscript{3}] octahedra connected to one another by point or ridge sharing that leads to the reduction in oxidation state of Mn\textsuperscript{3+}. Therefore, Mn\textsuperscript{3+} ions exist in the lattice to compensate for the charge and the distribution of Mn\textsuperscript{3+} and Mn\textsuperscript{4+} that causes a change in magnetic ground state and as a consequence, an antiferromagnetic ordering in MnO\textsubscript{2}. This transition temperature, \(T_\text{N} \sim 92\) K and \(T_\text{N} \sim 20\) K, respectively, while \(\gamma\)-MnO\textsubscript{2} preserves the paramagnetism over a wide temperature range. Moreover, \(\delta\)-MnO\textsubscript{2} has the highest magnetization value while \(\beta\)-MnO\textsubscript{2} the lowest. It can be anticipated that the presence of impurity ions/molecules and vacancies are the main contributing factors to the magnetism of \(\delta\)-MnO\textsubscript{2}, although the layer structure could also be the origin of ferromagnetic interaction.\textsuperscript{3,4} The local magnetic moment is enhanced in smaller dimensions because of the reduction in the number of neighboring atoms compared to their bulk counterparts. From the above observations, it can be concluded that manganese oxide nanostructures exhibit diverse and tunable magnetic properties that have made these materials of interest to the researchers.\textsuperscript{4,20,21} The local magnetic moment is enhanced in smaller dimensions because of the reduction in the number of neighboring atoms compared to their bulk counterparts. Moreover, magnetic coupling among the adjacent nanostructures becomes important when the particles are close packed in the colloidal dispersion. The exchange bias becomes enhanced when the interparticle interactions are strong; the large exchange bias implies strong interfacial coupling between the adjacent nanostructures.\textsuperscript{4,26}

8. SEMICONDUCTING PROPERTIES

When the size of the materials shrinks into the nanoscale dimension, the occupied electronic states located above the valence band of the corresponding bulk materials augments the physical and chemical activities of the systems.\textsuperscript{22,23} It has been

Figure 6. Temperature-dependent magnetization curves of (a) Mn\textsubscript{3}O\textsubscript{4}, (b) MnO and (c) Mn\textsubscript{2}O\textsubscript{3} nanoparticles at a magnetic field of 5 kOe. Reprinted with permission from ref 21. Copyright (2004) Royal Society of Chemistry.
noted that the bandgap increases with decrease in size of the nanostructures. This is because as a result of the spatial confinement of the electrons in the conduction band and holes in the valence band, the lowest energy corresponding to the optical transition from the valence to conduction band increases, resulting in an increase of the effective bandgap of the semiconductors. Manganese oxides at the nanometer size regime exhibit numerous intriguing physical aspects, including high-temperature superconductivity, metal-to-insulator transitions, colossal magnetoresistance, and colossal dielectric constants that are strongly correlated to the nature of the localized d-orbital electrons.\textsuperscript{3,22,23} MnO is a wide band gap material with energy gap (\(E_g\)) of 3.6–3.8 eV that results from the localized band structure corresponding to the monoxides of the 3d transition metal elements.\textsuperscript{3} These highly stable p-type semiconductors are of enormous importance for cost-effective and upscaled industrial production of optoelectronic nanodevices. Mn\textsubscript{2}O\textsubscript{3} is an important p-type semiconductor because of acceptor-type native defects (Mn\textsuperscript{3+} in Mn\textsubscript{2}O\textsubscript{3}) in the lattice with band gap of 5.12 eV and can be utilized as high-performance anode material in lithium ion batteries. Furthermore, the transfer of one electron originated from the electrochemical redox activity through Mn\textsuperscript{3+} to Mn\textsuperscript{4+} transition can be exploited for electrode reactions in electrochemical capacitors. The energy band gap value of \(\alpha\)-Mn\textsubscript{2}O\textsubscript{3} is 4.1 eV, which can be utilized for the remarkable applications in the fields of electronics, optics, magnetics and other industries.\textsuperscript{3,4} The spinel, Mn\textsubscript{3}O\textsubscript{4}, is a p-type semiconductor material with a wide direct band gap of 2.3 eV. The hausmannite-like structure produces an attenuated gap composed of states with HOMO having predominantly O\textsuperscript{2−} 2p character and LUMO with antibonding states of tetrahedral Mn\textsuperscript{3+}(\(T_d\)).\textsuperscript{22} MnO\textsubscript{2} is a n-type semiconductor with the energy band gap value as 3.26 eV. Because of the ligand field of \([\text{MnO}_6]\) octahedra, the Mn 3d energy level is split, and the band gap energy corresponds to the energy difference between lower (\(t_{2g}\)) and higher (\(e_g\)) levels that serve as valence (O\textsuperscript{2−}–like) and conduction bands (Mn(IV) d–like) of the semiconductor, respectively. Pure \(\alpha\)-MnO\textsubscript{2} behaves as a semiconductor with an indirect band gap of 1.3 eV, while \(\beta\)-MnO\textsubscript{2} has an energy band gap of 1.5 eV. It has been observed that the water content inside the tunnel structure impacts the electronic band structure through successive deformation of the rutile structure of \(\beta\)-MnO\textsubscript{2} and the interatomic Mn–Mn distances within the lattice. Birnessite (\(\delta\)-MnO\textsubscript{2}) is a semiconductor with a direct band gap of 2.23 eV\textsuperscript{2}; imposing tensile strain enhances the oxygen evolution reaction activity with the HOMO oxygen band extending up to 0.6 eV above the Fermi level as has been presented through the electronic structure\textsuperscript{21} of the \(\delta\)-MnO\textsubscript{2}/\(\delta\)-MnO\textsubscript{2}\textsuperscript{act} in Figure 7. Under the normal octahedral environment of Mn\textsuperscript{3+}(\(O_6\)), the unoccupied antibonding state becomes higher in energy above the LUMO of tetrahedral Mn\textsuperscript{3+}(\(T_d\)). The presence of local strain imposes more ionic character to the tetrahedral Mn–O interaction and as a consequence lowers the energy of the antibonding LUMO, which further decreases the energy gap between the occupied O 2p states and unoccupied Mn states. Thus, Mn\textsuperscript{3+} becomes more stabilized kinetically in the tetrahedral sites and confers higher strain to the oxide lattice, leading to lower absolute energy of the oxygen band that favors enhanced oxygen evolution activity.

The semiconducting behavior of manganese oxides has been attributed because it can be used to design smart functional materials, such as interspace communications, missile detection, military surveillance, target detection and acquisition, solar cells, thin film transistors, white lighting emitting diodes, and display devices.\textsuperscript{3,22,23} Manganese oxide materials have been recognized as promising electrode materials because of their performance toward charge transfer reactions. Since these materials possess higher capacitance in comparison with double layer capacitance, they can be employed as electrochemical capacitors. In addition, as the electrode surface can adsorb electrolyte ions, these materials can also be employed for charge storage. Moreover, the conduction/valence band energy levels can be correlated to the redox potentials of the couples in solution, and the energy barrier concept can predict the fate of oxidative or reductive dissolution processes that are of prolific importance in the field of hydrometallurgy and semiconductor etching processes.\textsuperscript{3,22} Furthermore, the semiconducting manganese oxide materials can be utilized in the arena of catalysis, sensors, battery materials, separation, and selective adsorption toward pollution abatement because of their specific mixed valence character, tunable pore size distribution, and versatility in the nanostructures.\textsuperscript{22,23}

9. BIOGENICITY

Manganese oxides are highly reactive minerals that can perform significant roles in maintaining the elemental cycles in the biogeochemical environment.\textsuperscript{2,24} These materials have, at times, been recognized through specific terminologies, like “scavengers of the sea” or “catalytic Swiss army knife”, to emphasize their significance to the environment and technology.\textsuperscript{24} Both the layered and tunnel structures of manganese oxides are also found in natural environments. Most of the manganese oxides available on Earth are biogenic as oxidation of these minerals by microorganisms is kinetically more favorable than the corresponding abiotic processes. The manganese cycle consists of reduced soluble form, Mn(II), and oxidized insoluble forms, Mn(III,IV). It has been established that microorganisms, especially, bacteria, fungi, algae, and/or eukaryotes, referred to as manganese oxidizers, can catalyze the oxidation of Mn(II) to Mn(III,IV) oxide minerals.\textsuperscript{24} This relative chemical inertness and the remarkable morphological tunability of biogenic MnO\textsubscript{x} makes these materials attractive candidates as conductive supports or high-surface-area electrodes.\textsuperscript{24} Bacteria and fungi that produce manganese oxides are extraordinarily skilled engineers of nanomaterials that contribute significantly to global biogeochemical cycles. The bacterial enzyme complex is
imaging, therapeutics, and other enzymatic applications. Because of their diverse potential applications in diagnosis, referred to as nanozymes, have attracted enormous interest. Manganese oxide nanostructures exhibiting enzyme-like activities, often coined as biogenic manganese oxides or manganese biooxides, can mediate a variety of redox reactions with organic and inorganic compounds in the environment. The vacant sites at the octahedral layers of these biogenic manganese oxides can lead to sequestration of several metallic elements. The multi-copper oxidase enzymes include a family of proteins that are found in plants, animals, bacteria, and fungi and are associated with the four stepwise single electron oxidations of O₂ to H₂O. The cycle of different oxidation states of manganese found in nature and plausible mechanism of the MnO₂ mineralization catalyzed by multicooper oxidase, Mn₅G are enunciated in Figure 8.

Biologically catalyzed oxidation of Mn(II) serves as one of the major avenues toward the formation of layered manganese oxides in soils and sediments. The octahedral geometry of these layered structures governs the metal sequestration properties, oxidizing ability, photochemistry, and topotactic transformation to various tunnelled structures. Birnessite-like manganese oxides formed through microbial oxidation are utilized as adsorbents and ion exchangers, filtration media, as materials for remineralization and deacidification, to prevent coagulation toward water purification technology. These oxides can also be used as substrates to produce inorganic membranes or adsorbents for the abatement of petroleum substances. Todorokite and buserite produced through microbial activities exhibit interesting redox capacities to the environmental chemistry of soil and aquatic ecosystems. High sorptive capacities enable the applications of these oxides for the effective removal of organic dyes and adsorption of a wide range of heavy metal ions in contaminated water and cycling and mobility of various elements in the environment. Manganese oxide nanostructures exhibiting enzyme-like activities, often referred to as nanozymes, have attracted enormous interest because of their diverse potential applications in diagnosis, imaging, therapeutics, and other enzymatic applications. Because of their inherent capability to mimic the cellular antioxidant enzymes, such biocompatible nanomaterials can be exploited as possible therapeutics toward various oxidative-stress-related disorders. The enzymatic activities can also be exploited toward pollutant oxidation in wastewater treatment. The naturally occurring MnO₂ minerals can find potential biomedical applications in genotoxicity, oral toxicity, histopathological changes, biochemical alterations, and tissue distribution around the nanostructures.

10. CONCLUSIONS AND OUTLOOK

In conclusion, we have elucidated that at the nanoscale dimension, manganese oxides, beyond the chemistry arising due to the multivariance, also exhibit fascinating polymorphism, crystalline structures, thermodynamic stability and phase transition, magnetic and semiconducting behavior and excellent geochemistry associated with biogenecity. These physiochemical features have enabled interdisciplinary perspectives of chemistry, physics, materials sciences and biology of manganese oxides at the nanoscale. The rich inorganic chemistry of manganese oxides at the molecular level has been a subject of immense interest due to intriguing aspects emerging from the individual oxidation states. We have enunciated a critical and concise account of the health and prospects of the compelling story of manganese oxides at the nanometer regime that has attracted immense interest in the state-of-the-art scientific and technological parable. Precise correlation to build up the interdisciplinarity among the various physicochemical aspects will provide the impetus to explore the synthesis of nanomaterials of manganese oxides and deeper understanding of these attributes from both the theoretical and experimental perspectives, as well as to pioneer their plausible applications apart from the conventional usages. A critical condensation of the physical, chemical, materials, and geochemical aspects in view of the conventional manganese chemistry will be helpful to elucidate the enhanced properties that will pave the way to exploring the substantive challenges in materials sciences and technology. Incidentally, manganese oxides with “layer” and “tunnel” structures are a large family of phase structure oxides, the dimensions of which belong to the nanoscale and the pore dimensions in the range of ultramicropores to mesopores. Possible statistical variations of complex manganese oxides with tunnel size, the nature and the amount of the intra- and extraframework cation content, the degree of hydration, and the average manganese oxidation state will foster the design and synthesis of newer polymorphs apart from the synthetic analogues and to find their plausible applications in ion/electron transport kinetics, sodium storage technologies as potential substitutes to lithium ion batteries, supercapacitance, advanced energy storage, and other technologies relevant to enhanced electrochemical performance. Specific knowledge about the energetics and phase transformation under a variety of microenvironmental conditions will help to overcome the challenges of obtaining mixed phases of manganese oxides during the syntheses. The structural diversity along with requisite stability will direct the synthesis of a series of perovskites as prospective materials for the fabrication of cost-effective solar cells and different photonic applications.
Polytypism, which means stacking disorder, observed in certain manganese oxide phases complicates the structure–function correlation during practical applications, and suitable theoretical protocol should be devised to normalize their activities. The diverse magnetism in nanostructured manganese oxides can be utilized in the interdisciplinary areas of nanotechnology and molecular biology from diagnosis to treatment and even, theranostics, especially, in the field of biomedicine, magnetic resonance imaging, biosensing, and cargo loading functionality. It appears that catalysis and magnetism are different manifestations of the manganese oxide materials, but efforts to bridging these two dimensions will enrich the scientific perspectives of this arena of research and technological applications of these materials in a wide variety of heterogeneous catalysis and magnetic device applications. The calculation of electronic structures that are strongly related to the inherent geometrical features in this variety of manganese oxide materials can be performed to establish the relationship between their magnetic and catalytic properties. The interplay of magnetic and semiconducting properties provides an excellent platform in which both charged electrons and spin are coupled into the same substance, which are of utmost importance to understand the fundamental physical problems and novel functionalities in spintronic devices. Owing to the advantages of being earth abundant, nontoxic, and cost-effective, manganese oxide nanomaterials can be employed in next-generation clean energy production and storage and environmental remedies that are the two most important challenges of the modern world. Chemically powered micromotors, typically driven through bubble formation at the solid–liquid interface, using manganese oxides as catalysts could represent an exciting area of research in nanotechnology. Knowledge about the biogenecity will be advantageous to explore the green synthetic approaches of manganese oxides at the nanoscale and will add new options to investigate their aspects in geochemistry, biology, and mineralogy. Manganese oxide clusters perform a vital role in numerous biological processes ranging from photosynthesis to bacterial decomposition of diverse organic matters. The enzyme-like activities of nanostructured manganese oxides can be employed to upscale the productivities in fertilizers, pesticides, and pharmaceutical industries and to explore their possibilities in several health and safety issues, bioenergy production, wastewater treatment, pollution abatement, and environmental remedies. Nanotechnology is envisaged to have widespread applications to provide the materials critical to human society; manganese oxides at the nanoscale dimensions with their diversities in physical, chemical, materials, and geochemical aspects can play a major role in the rapid growth in worldwide development and commercialization of products and technologies to meet the future challenges of the global society.

Notes
The author declares no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from DST-SERB, New Delhi (Project No.: EMR/2016/006842) is gratefully acknowledged. I am grateful to Prof. Naoki Toshima, Sanyo-Onoda City University, Japan, and Prof. Tarasankar Pal, Indian Institute of Technology, Kharagpur, for valuable advice and suggestions. I am thankful to Dr. Hasimur Rahman, Diamond Harbour Government Polytechnic, West Bengal, for helpful discussions.

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