Synthesis, phase transformation, and morphology of hausmannite Mn₃O₄ nanoparticles: photocatalytic and antibacterial investigations

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Nano structured Hausmannite (Mn₃O₄) has efficacious applications in numerous fields, such as catalytic, medical, biosensors, waste water remediation, energy storage devices etc. The potential application in wastewater treatment is due to its distinct structural features combined with fascinating physicochemical properties. Another area of interest is the oxidative properties imparted due to its reduction potential. Larger surface to volume ratio and high reactivity than the bulk form shows great progress as antimicrobial agent to control drug resistant microbial population. The distinct surface morphologies, crystalline forms, reaction conditions and synthetic methods exerts significant impact on the photo catalytic and bactericidal efficiency. Hence, the present paper focuses on a concise review of the multifarious study on synthetic methods of Mn₃O₄, growth mechanisms, structural forms, phase transformation and phase control, shape and dimensionality. The review also confers its applications towards photo catalytic and bactericidal studies.

1. Introduction

Numerous morphology of Mn₃O₄ have gathered benefits for their applications in sensing, ion exchange, batteries and as catalysts in its different oxidation states [1, 2, 3, 4, 5].

Unit cell of spinel structure Mn₃O₄ contains 32 oxygen and 24 cations of both di and trivalent of Mn. The fascinating physicochemical property is due to the following structural attributes: (i) oxide ions are cubic close packed (ii) Mn²⁺ occupies the tetrahedral site (iii) Mn³⁺ occupies the octahedral site (iv) d⁴ state of the Mn(III) atoms in high spin configuration brings about John-Teller distortion in it. The removal efficacies of the dye pollutants in waste water by Mn (III/IV) oxides are reliant on their crystallographic systems [6, 7, 8, 9, 10]. Highest eg orbital filling due to dual valency state of Mn plays crucial role in the catalytic degradation of dyes [11].

The spawned rising interest of Mn₃O₄ as heterogeneous photocatalyst, is a prospective technology, to cut down chemical constituents and unplug pathogen cells in water [12]. The photo catalyst has to be dynamically stable as the photo catalytic reaction proceeds in an air-saturated and water-rich environment. Mn₃O₄ has fairly good thermodynamic stability in comparison with other oxidation states. The portentous strategy to enhance the photo catalytic activity is to alter or modify morphology of nano material in different forms viz. nanotubes, nanorods, nanosheets, nanowires, nano belts, nano flower, nano coin etc.

It has also received prodigious attention as bactericidal agents and opened a new approach in encountering antibiotic resistant pathogens. This is because, materials in nano size can penetrate through nano pores of mill meter range of cell membrane and produce toxic O₂* radical to mutilate cell membranes of microbes which in turn results in an efficient restraint of microbial growth [13, 14].

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Chemical composition and synthesis methods influence the morphology and particle size distribution which are key parameters in surface area and reaction activity. Enormous synthetic methods like solvothermal, vapor phase growth, vacuum calcining precursors, thermal decomposition etc. assist to tailor morphology and particle size of nano compound [15, 16].

Several researchers have reported one-dimensional Mn₃O₄ nano-materials with different morphology. As per our literature survey, various synthetic routes to achieve different morphological forms of Mn₃O₄ have been reported. There were recent reports on the exploration of micro emulsion route for the synthesis of Mn₃O₄ nano crystals to achieve belt-like morphology phase [17, 18, 19, 20, 21]. Many research groups have worked on hausmannite nano structured composites for foreseeable applications.

Deepak Dubai and Rudolf Holze construed Mn₃O₄ nano-octahedra with anomalous magnetic template and enhanced photodecomposition properties, copyright (2011), with permission from The Wiley-VCH images.

Yu Li [20] employed preparation of octahedron Mn₃O₄ nano compound using 0.105 g containing aqueous potassium permanganate as a precursor for manganese ions and 30 ml of polyethylene glycol (PEG200), as reducing agent which contained hydroxyl group, reduced Mn⁷⁺ to Mn⁴⁺ state. Besides, PEG 200 at low concentration behaved as a structure guiding agent to control morphology of nano compound at 100 °C, which resulted in the formation of one dimensional MnO(OH) nano rods. However, PEG at high concentration and temperature produced pseudo spherical shape nano compound. With an increase in temperature from 100 °C to 180 °C, noticeable change in the shape was observed. The influence of time on evolution of size and shape of nano Mn₃O₄ is shown in Table 1.

The anisotropic crystal growth of nano compound was obtained due to self assembly followed by ostwald ripening mechanism [20] is shown in Figure 1. Morphology and formation of the nano particle is controlled by the polymers such as PEG, (Polyethylene glycol) PAA (Poly acrylamide), PVA (Polyvinyl alcohol) etc. The polymer will function as reducing agent and shape-directing agent. In the present reaction system, concentration of the polymer and temperature, regulated morphology of nano compound. Khalid Ahmed and co-workers [30] have found that phase transformation of manganese oxide has been occurred with variation of temperature. 0.5 mmol KMnO₄ was reduced by 0.2 ml formaldehyde (CH₂O) in the reaction mixture, was taken in a hydrothermal reactor and heated for 10 h at different temperatures viz. 120 °C and 300 °C. At low temperature 120 °C, the precursor solution was gradually reduced to MnOOH nanorods (JCPDS:88-649) which was latter transformed to β-MnO₂ (JCPDS-24-735) at 300 °C because of dehydration of MnOOH in the existence of air. When temperature of the reaction mixture was increased at intervals of 40 °C, the morphology was changed in sequence as irregular short nano rods to mixture of nano rods and octahedron and eventually, converted to Mn₃O₄ octahedron shape by means of the accelerated reduction, nucleation growth in the reaction mixture which is shown in SEM images (Figure 2). Figure 2a and b characterizes synthesized MnO(OH) nanorods with a cross-section of 50–60 nm and length of 2–3 micro meter at 120 °C. Figure 2c represents short rod like shape at

| Reaction time | Morphology                           |
|---------------|--------------------------------------|
| 0 min         | 10–15 mm, brown colored small particles are obtained |
| 30 min        | Agglomeration of small particles     |
| 60 min        | Pre octahedral shape                 |
| 120 min       | Octahedral shape                     |

2. Synthesis of hausmannite

2.1. Hydrothermal method

Hydrothermal method is a simple procedure wherein controllability of size and shape of nano particles are being achieved by means of controlling the temperature and pressure of a homogenous solution taken in teflon lined stainless-steel hydrothermal reactor.

Figure 1. SEM images of the evolution process (a–e), (f) a schematic illustration of the formation of octahedral shape Mn₃O₄ nanoparticles corresponding to the SEM images. Reprinted from Small, 7(4), Li, Y., Haiyan, T., Yang, X., Goris, B., Verbeeck,J., Bals, S., Colson, F., Cloots, R., Tendeloo, G., Su, B., 475–483., Well shaped Mn₃O₄ nano-octahedra with anomalous magnetic template and enhanced photodecomposition properties, copyright (2011), with permission from The Wiley-VCH Verlag GmbH & Co. KGaA.
160 °C. Figure 2d represents mixture of rod and octahedron at 180 °C. At 200 °C, the as-synthesized products are octahedron-like (some have 16 faces) with edge size of 300–400 nm (Figure 2f). The transformation from precursor nanorods to octahedron is explicated in terms of Ostwald ripening process. It is alike of BiPO₄ and alpha Fe₂O₃ nanostructures [31, 32].

Aslam Jamal and other co-workers prepared tetragonal Mn₃O₄ (JCPDS # 024-0734), by using manganese chloride (MnCl₂.H₂O) as precursor for manganese ions and urea as the reducing agent with pH of 10.5 [33].

\[
\begin{align*}
3\text{MnCl}_2 (s) &\rightarrow 3\text{Mn}^{2+}(aq) + 6\text{Cl}^-(aq) \\
\text{NH}_4\text{OH}(aq) &\rightarrow \text{NH}_4^+(aq) + \text{OH}^- (aq) \\
3\text{Mn}^{2+} + 10\text{OH}^- &\rightarrow 2\text{Mn}_3\text{O}_4(s) + 5\text{H}_2\text{O} + 1/2\text{O}_2
\end{align*}
\]

2.2. Solvothermal method

Solvothermal synthesis allows the precise control over the size, shape distribution, and crystallinity of metal oxide nanoparticles or nanostructures.

Khaled and group [34] have adopted solvothermal method in which tetragonal Mn₃O₄ nano belts were synthesized using coordination compound of manganese melamine solution. The obtained nano belts matched to JCPDS # 024-0734. Diffraction peaks in XRD spectrum of sheet- like Mn₃O₄ indexing the same card number of Mn₃O₄ nanobelts and nanoparticles. The reported tetragonal phase structured Mn₃O₄ with a lattice constant of \(a = 5.76\) Å and \(c = 9.47\) Å and space group of I41/amd; is in good agreement with the standard data JCPDS card No. 24-0734. The characteristic diffractogram of formed sheet like Mn₃O₄ nano crystals and nano particle synthesized by solvothermal approach without melamine are corroborated [34].

\[
\begin{align*}
\text{Mn(CH}_3\text{COO)}_2 &+ 2\text{KOH} \rightarrow \text{Mn(OH)}_2 + 2\text{CH}_3\text{COOK} \\
\text{Mn}^{2+} + n\text{C}_3\text{N}_6\text{H}_6 &\rightarrow \text{Mn}(\text{C}_3\text{N}_6\text{H}_6)_n \quad (n = 1 - 4) \\
6\text{Mn}^{2+} + \text{O}_2 + 12\text{OH}^- &\rightarrow 2\text{Mn}_3\text{O}_4 + \text{H}_2\text{O}
\end{align*}
\]

The concentration of melamine in the reaction mixture and reaction time had boundless impact on controlling the morphology of nano particles and its size. It functions as capping ligand. It also controls the discharge speed of Mn²⁺ ions and panels the growth direction of Mn₃O₄ nano belts [34]. It is well evidenced that the establishment of single crystalline 1D-nanobelts is through well-aligned lattice lines. The inter planar distance calculated from the lattice fringes of sample is 0.493 nm, matches to the (101) plane of tetragonal Mn₃O₄. Similar reports were cited in other works [35, 36].
In solvo thermal method, Jing Xu and co-workers [37] have found that there was no time effect on morphology of Mn$_3$O$_4$ nano particles. This was synthesized by using similar precursor for Mn and oleic acid as a reducing agent, dissolved in 100ml methanol and heated at 180 °C in different time intervals. The obtained compound was further dissolved in hexane and extracted using ethanol before subjecting it for calcination at 500 °C for 10 h while supplying air 50 ml/min in tubular furnace as to get α- Mn$_2$O$_3$ compound.

Lin Heteam [38] has deployed this method to get monodispersed spherical or cubic/octahedral Mn$_3$O$_4$ nano compound. The precursor of Mn underwent to hydrolysis and condensation in presence of template pebax 2533 (polyether amide block polymers) dissolved in isopropanol. The morphology of nano compound was being influenced with variation of pebax by % of weight in the reaction mixture. High % of weight of pebax enhanced the viscosity of reaction mixture resulted in formation of spherical Mn$_3$O$_4$ nano compound. However, cubic/octahedral shaped Mn$_3$O$_4$ was obtained at low % of weight of pebax. The surface area of this Mn$_3$O$_4$ nano crystals exhibited 38.6 m$^2$/g larger than purchased bulk Mn$_3$O$_4$ with 3.8 m$^2$/g in BET test.

Developing a simple synthetic method for shape or controlling size in nano crystals is of great importance. Song Rui group [39] have used one step solvo thermal route to prepare Mn$_3$O$_4$ nanoparticles. Apparently, experiments were carried out to investigate the consequence of reaction temperature on the particle size of Mn$_3$O$_4$ NP. The difference in temperature influences the nucleation rate and thus the size of nuclei formed.

### 2.3. Reflux method

This is an unsophisticated, low cost approach to get abundant produce with accurate regulator over reaction factors. The control of size, morphology and crystallinity of the materials depends on the reaction time, concentration of precursors and the type of solvent employed [40]. In reflux method, Yuli Wang and group [41] have prepared Mn$_3$O$_4$, 3D-flower like structure from the refluxed homogenous solution of manganese(II)sulphate (MnSO$_4$·H$_2$O), urea and cetyl trimethylammonium bromide (CTAB) as surfactant which was kept under stirring at 85 °C for 24 h. It was then treated with aqueous sodium hydroxide (NaOH) solution and 30% H$_2$O$_2$ at room temperature. Further, it was washed with aqueous alcohol and dried at 400 °C for 4 h. SEM and TEM images of flower like Mn$_3$O$_4$ materials is shown in Figure 3. The morphology of 3D-flower structure of nano Mn$_3$O$_4$ was dependant on certain reaction conditions such as time, temperature and rate of addition of aq. NaOH solution. It was noticed that with altering of temperature from 50 °C to 70 °C, the morphology of nano particle changed from nano sheets to 3D hierarchical structure and with increase in reaction time, from 12h to 24 h at 85 °C produced 2D nano sheets which were eventually changed to a well shaped 3D-flower structure respectively. Apart from this, the rate of addition of aqueous NaOH solution has brought some changes in the morphology of nano compound when the solution rate was 30 drops/min, gave nano particles size of 15 nm. The flower like spherical morphology and nano rods with smooth surface having 300–500 nm length were being obtained when the addition of NaOH solution rate was 60 drops/min and 120 drops/min respectively. This modification in morphology during synthesis of nano Mn$_3$O$_4$ were due to arrangement of capping agent like shell which surrounds the precursor particles in nucleation growth, that was not disturbed by the addition of alkaline solution in slow addition whereas fast increment rate of addition of aqueous NaOH solution disturbed shell around precursor particles, which leads to form nano rods [42].

Tetragonal hausmanite was prepared by Abdulhadi Baykal et al [43] and Anil Kumar et.al from the same precursor MnCl$_2$·H$_2$O mixed with aqueous NH$_4$OH solution adopting reflux synthetic route [44].
Srinivas Godavarty and group adopted this method in which aqueous 1% tannic acid was added to 0.05 M aqueous KMnO4 solution under stirring to get tetragonal Mn3O4 nano particle [45]. The XRD peaks of Mn3O4 brown precipitate coordinated to JCPDS card # 024-0734.

4K MnO4 + 2H2O → 4MnO2 + 4KOH + 3O2 

C7 H6 O5 + Mn2O4 → Mn(OH)2 + C7 H4 O5

Mn(OH)2 + O2 → Mn3O4 + H2O

2.4. Precipitation method

The precipitation method is more economical and efficient route for mass production. The particle size depends on nucleation and growth steps which in turn depends on solution chemistry and precipitation conditions.

Hassouna Dhaouadi and co-researchers [46] have prepared Mn3O4 octahedron nano crystals from the homogenous mixture of MnCl2-6H2O, aqueous NaOH solution in presence of cetyltrimethylammonium bromide (CTAB) which was put under stirring for 24 h, washed, dried in the oven at 80°C for 24 h [47].

Mn3+ + 2OH− → Mn(OH)2

Mn(OH)2 → MnO + H2O

3MnO + 2O2 → Mn3O4

In another synthesis through precipitation method, America Vaazquez-Olmos [48] prepared tetragonal Mn3O4 nano rods from the immobilized colloidal solution of Mn2+ ions left over a period of three months. This colloidal solution was prepared using the precursor for [Mn(CH3COO)2.4H2O], DMF and distilled water which was sent under vigorous mixing for half an hour at room temperature. Under the present reaction conditions, the morphology of Mn3O4 was obtained from the crystal growth towards (001) axis devolve on the availability of Mn2+ ions, and crystal growth towards (101) plan, depends upon the accessibility of Mn3+ UV spectrum of it showed that the peaks at 250–410 nm, 410–585 nm and 810 nm indicated transfer of charges in between O2− → Mn2+, O2 → Mn3+ respectively and the remaining peak at visible region of spectrum was due to d-d transitions in Mn3O4 nano rods.

Mn3+ + 2(OH−) → Mn(OH)2

(Initiation)

3Mn(OH)2 + (1/2)O2 → Mn3O4 + 3H2O

(13)

(14)

Sonochemical method is a simple, low cost eco-friendly, less time consumption method. In this method, there is an interfacial region around the bubble that faced large gradients of pressure, temperature, and the rapid motion of molecules which results in the formation of excited states, bond breakage, formation of free radicals, mechanical shocks, and high shear gradients which leads to homogeneous nucleation [55, 56, 57, 58, 59]. Vahid Safarifard group have synthesized Mn3O4 octahedral through sono chemical method is represented in Scheme 1 [60].

Another group Shujin Lei and co-workers [61] have developed colloidal Mn3O4 NP using ultra sonication in the absence of surfactant or additional nucleating factors under normal temperature and pressure. NP can also be formed without any stirring or oscillation. However, the ultrasonic pre-treatment was essential to attribute the acoustic cavitation that supports Mn3O4 nano crystal formation. The ultrasonic waves may quicken the dispersion of Mn ions from MnCl2 in ethanol amine (EA), which apparently is beneficial for the nucleation and growth of Mn3O4 nanocrystals.

In another simple and novel method, I.K. Gopalakrishnan group [62] has used ultrasonic irradiation method in which consequence of oxidation, reduction, dissolution and hydrolysis reactions of aqueous precipitation methods [49]. The growth mechanism of hausmannite depends on hydrolysis and decomposition of metallic salts. Different protocols have an effect on physical characteristics like shape, configuration, optical, magnetic and electrochemical performance of hausmannite (Mn3O4). The sample Mn3O4 synthesized by hydrothermal route retain crystalline and fine nano-petal morphology gave less resistance which displayed the intense mark on the electrochemical properties of hausmannite nanostructures [50]. The magnetic investigation revealed that the spin canting (canted movement of spin on nanoparticles) and spin slanting effect of the nano-sized particles have reduced its magnetization which is measured as coercivity (19650e) [51]. Therefore, the hydrothermal route could be a better method to synthesize Mn3O4 for super capacitor and electromagnetic applications.

There are reports that Mn3O4 was widely produced through several synthetic methods in which morphology and growth of Mn3O4 nano compounds was being controlled with the assistance of surfactant or templates [46, 52, 53]. Xinli Hao et al [54] have evaluated the effect of surfactants (CTAB, sodium oleate) and alkalies (NH3, NaOH) in the synthesis of spherical Mn3O4 nano compound using simple precipitation method. In the absence of surfactants, Mn3O4 samples were found to be mixture of nanoparticles and particle-assembled nanosheets. This is because, the arrangement of nuclei is fast in one dimension leads to formation of nano sheets along with nano particles. On the other hand, Mn3O4 samples were only nanoparticles in the presence of surfactants. The formation of nano particles points the assimilation of surfactants on clusters. The concentration of OH− ion plays a key factor in morphological changes from spherical to octahedral form.

In another synthesis through precipitation method, America Vaazquez-Olmos [48] prepared tetragonal Mn3O4 nano rods from the immobilized colloidal solution of Mn2+ ions left over a period of three months. This colloidal solution was prepared using the precursor for [Mn(CH3COO)2.4H2O], DMF and distilled water which was sent under vigorous mixing for half an hour at room temperature. Under the present reaction conditions, the morphology of Mn3O4 was obtained from the crystal growth towards (001) axis devolve on the availability of Mn2+ ions, and crystal growth towards (101) plan, depends upon the accessibility of Mn3+ UV spectrum of it showed that the peaks at 250–410 nm, 410–585 nm and 810 nm indicated transfer of charges in between O2− → Mn2+, O2 → Mn3+ respectively and the remaining peak at visible region of spectrum was due to d-d transitions in Mn3O4 nano rods.

Mn3+ + 2(OH−) → Mn(OH)2

(Initiation)

3Mn(OH)2 + (1/2)O2 → Mn3O4 + 3H2O

(13)

(14)

Spherical (coin shaped), grains and petal morphology of Mn3O4 was achieved through co-precipitation assisted hydro thermal, sol-gel and co-
Mn(CH₃COO)₂.4H₂O (1g) solution produced, body centered tetragonal Mn304 nano crystallite.

\[ \text{H₂O} \rightarrow \text{H} + \text{OH} \]  \hspace{1cm} (15)

\[ \text{H}^+ + \text{H}^+ \rightarrow \text{H₂} \]  \hspace{1cm} (16)

\[ \text{OH}^- + \text{OH}^- \rightarrow \text{H₂O₂} \]  \hspace{1cm} (17)

\[ \text{Mn(CH₃COO)₂} + \text{Mn}^{2+} + 2(\text{CH₃COO})₂ \]  \hspace{1cm} (18)

\[ \text{Mn}^{2+} + \text{H₂O₂} \rightarrow \text{Mn}^{3+} \]  \hspace{1cm} (19)

2.6. Surfactant free Mn₃O₄

Although high yields and a high crystallinity can be obtained in presence of surfactant, surfactant-free synthesis are highly desirable and appreciated as owing to absence of residual impurities on the surface of synthesized nano particles. Hence, surfactant-free synthetic routes are highly desirable [63, 64].

Zhengzhang Weng et al [65] have reported surfactant free Mn₃O₄ to oxidize toxins. Annealing Mn₃O₄ generated a porous nano-Mn₂O₃ from [BMIM]BF₄ at room temperature which was followed by drop-wise prepared similar tetragonal Mn₃O₄ in controlled manner using manganese action medium and electron transmission accelerator.

The temperature plays a critical role in this method. It acted both as the reaction medium and electron transmission accelerator.

2.7. Ionic liquid assisted Mn₃O₄

In thermal decomposition method, Ahmad Morsali and co-workers [66] used a coordination compound, Mn (pyterpy) (H₂O) (NO₃) as a precursor dissolved in oleic acid, subjected to thermal decomposition at 320 °C for 2h under nitrogen atmosphere to fabricate Mn₃O₄ nano particles. Additionally, Robert Bussamara and his group [67] have prepared similar tetragonal Mn₃O₄ in controlled manner using manganese precursor and one of the ionic liquids such as 1-n-butyl-3-methylimidazoliumhexa fluoro phosphate (BMI PF₆), 1-n-butyl-3-methylimidazolium tetrafluoroborate (BMI-BF₄), and 1-n-butyl-3- methylimidazoli um bis(- trifluoromethanesulfonyl) imide (BMI-NTF2) dissolved in oleylamine solvent. It was noticed that Mn₃O₄ was formed only in the combination of oleylamine and BMI NTF2 solution but failed to get Mn₃O₄ nano in other two ionic solutions due to the decomposition of ionic liquid (IL). In presence of oleylamine solvent alone, the obtained Mn₃O₄ had impurity of Mn₂O₃ which indicated that ionic liquids provided a suitable medium to stabilize manganese ions in nucleation growth of nano Mn₃O₄. The study of time effect on evolution of Mn₃O₄ showed that when sample mixture of precursor, BMI-NTF2 in oleylamine was kept in the reaction at 180 °C for 96 h, produced the pure compound that had no additional peaks in XRD related to MnOOH and Mn(CH₃COO)₂ but it gave tetragonal Mn₃O₄ with impurities of MnOOH and Mn(CH₃COO)₂ when the same reaction mixture heated at180 °C for 9 h indicated that the reaction was incomplete.

Mervan Gunay et al. [26] have reported the spinel-type Mn₃O₄ in the influence of ionic liquids at room temperature. Many important reactions were successfully employed using room temperature ionic liquids. The synthetic method involves addition of 0.86 g Mn(NO₃)₂.4H₂O into 2.0 g [BMIM]BF₄ at room temperature which was followed by drop-wise addition of 3ml of NaOH under continuous stirring. 5 mL of H₂O₂ was very slowly dropped in the mixture after about 30 min. The obtained brown precipitate was centrifuged, washed, and dried. The processing temperature plays a critical role in this method. It acted both as the reaction medium and electron transmission accelerator.

2.8. Solution combustion method

Synthesis of nano size materials by solution combustion method is adaptable, modest, low-cost and fast technique among other synthesis methods. This method comprises a self-sustained reaction in homogeneous solution of different oxidizers (e.g., metal nitrates) and fuels (e.g., urea, glycine, hydrazides). Chengjun Dong and research group [68] has adopted this route in which equimolar ratio of aqueous Mn (NO₃)₂.4H₂O and ethylene glycol are subjected to combustion at 300 °C for 30 min, to produce a fluffy Mn₃O₄.

\[ \text{Mn(NO₃)₂H₂O} + 6 \text{C₂H₄O₂} + \text{O}_2 \rightarrow 2\text{MnO₄} + 6\text{N₂}+12\text{CO₂}+4\text{H}_2\text{O} \]  \hspace{1cm} (20)

Jagadeesh and group [69] have reported the synthesis of Mn₃O₄ nano crystallites by solution combustion method using a combination of urea and glucose fuel mixture. Increase in temperature induces phase transformation from Mn₂O₃ to Mn₃O₄. Change in temperature (Figure 4) has an effect on structural transformation and morphology. The morphological changes from spherical to rod shape suggests the anisotropic growth in samples in one direction.

2.9. Solid state method

A solid state method was employed to prepare 1D nanowire was reported by Wenzhong Wang group. They used a mixture of MnCl₂·4H₂O, sodium carbonate, flux NaCl and nonyl phenylether (NP-9) as a capping agent which was thermally decomposed at 850 °C for 2h. Eventually, the product was cooled to room temperature by either gradual decrease of temperature 5 °C/min or rapid decrease of temperature 40 °C/min that produced 1D nanowires of Mn₃O₄ and washed it multiple times to wipe out flux and dried it at 80 °C for 5 h. The reaction was repeated with flux and surfactant distinctly and also in absence of both under the same synthetic conditions, produced Mn₃O₄ nano particles instead of nano wires. The growth of nano wires was explained by Ostwald ripening.

Figure 4. XRD patterns of Mn₃O₄ (350–850 °C) thermal stability of Mn₃O₄ and transition from Mn₂O₃ to Mn₃O₄. Reprinted from Journal of Magnetism and Magnetic Materials, Volume 476 (15), Lakshmi Narayani, V., Jagadeesha Angadi, Anu Sukhdev, Malathi Challa, Shidaling Mattepanavar, Deepthi, P.R., Mohan Kumar, P., Mehaboob Pasha, Mechanism of high temperature induced phase transformation and magnetic properties of Mn₃O₄ crystallites 268-273, copyright (2019), with permission from Elsevier.
mechanism was reliant on the characteristics of starting material size, chemical activity and solubility. The change in the morphology is also due to the alteration in the fluidity of the reaction mixture, mobility of the components and decrease in the eutectic temperature [70].

2.10. Green synthesis

Samaneh Ramezanpour group [71] have adopted a facile and green sol-gel method to synthesis undoped and vanadium doped Mn3O4 product. The characterized sample was crystallized in tetragonal Mn3O4 phase. It has been noticed that nano rod morphology are extended with an enhance in the vanadium doping content (upto 4%). However beyond 4% addition of dopant, the particle size decrease due to accumulation. This observation proved that the doping limitation for vanadium dopant in Mn3O4 is less than 10%. Also, highest percentage of decolorization is also shown in this range.

Zehra Durmus and co-workers [72] used a green synthesis route for preparation of Mn3O4 nano crystals where in Mn(NO3)2.4 H2O and an ionic liquid 1-n-butyl-3- methylimidazolium hydroxide (BMIM)OH (reaction medium and an electrical conductor for electron transfer) in aq. NaOH solution and then being treated drop wise by H2O2 (30w/w%, 5 ml) for 30 min. The XRD diffractogram of tetragonal Mn3O4 coincided with ICDD 24-0734.

\[
\text{Mn}_2^{2+} + 2\text{OH}^- \rightarrow \text{Mn(OH)}_2 \\
3\text{Mn(OH)}_2 + \text{H}_2\text{O}_2 \rightarrow \text{Mn}_3\text{O}_4 + 4\text{H}_2\text{O}
\]

(21) (22)

2.11. Other methods

Hasimur Rahaman et al. [73] reported a facile wet chemical approach for the soft-templated synthesis of Mn3O4 microcrystals. The superstructures of manganese oxide was synthesized using dye-surfactant in association with manganese acetate in a specific molar ratio. One of the key findings is that it has a higher BET surface area than the commercial Mn2O3.

Al-Nakib Chowdhary group [74] has employed forced hydrolysis method to get Mn3O4 nano particles by heating the precursor aq. Mn(acetate)2 and further quenched in cool water. The size of Mn3O4 nano particles was controlled by maintaining the heating time of reaction mixture and concentration of precursor [75, 76].

E. Ashir et.al. [77] employed a simple stirring method based on redox reaction between KMN04 and sodium dodecyl sulphate dissolved in aq.\text{N}_2\text{H}_4. \text{H}_2\text{O} solution leads to change the solution colour from purple to brown/black then to orange/brown which indicated the formation of nano Mn3O4. Finally, the product was cooled to room temperature, washed with water, ethanol and dried in vacuum. Conversely, A.K.M. Atique Ullah etal [78] and his group used Sol-Gel method to get tetragonal Mn3O4 crystallites. In this method, redox reaction took place between KMN04 solution and glycerol in the gel which was left, without disturbing for 24 h and subsequently heated at 80 °C. The XRD pattern of obtained product matched with JCPDS NO. 00-001-1127 (see Tables 2 and 3).

3. Phase transformations of manganese oxides

Manganese forms stable oxides viz. MnO, Mn3O4, Mn2O3, Mn3O4, MnO(OH) as well as the metastable Mn2O3 can coexist or progressively change one into the other during the oxidation process. The oxidation process in the existence of manganese oxides is usually monitored by rate of oxygen diffusion. Studies have shown that formation of Mn–O phases depends on temperature, stoichiometry and composition. Phase transformation is dependent on the calcination temperature, precursors, different atmospheric gases and oxygen partial pressures [79].

Leilei Lan et al [80] have prepared a selective preparation of MnOx nanostructures with crystalline phases of \(\gamma\)- MnOOH, \(\beta\)-MnO2, \(\alpha\)-Mn2O3, Mn3O4 in different phases by a facile and low-temperature route. The amount of Mn2O3 or reactant concentration governs the oxidation state of manganese, crystal phases, and morphologies of MnOx nanocrystals. Bundle-like \(\gamma\)-MnOOH nano rods was synthesized using addition of manganese acetate, H2O2 and NaOH. Different phases was obtained by calcining the \(\gamma\)-MnOOH precursors underneath varied temperature and atmospheric environments. Further, at small reactant concentration of Manganese acetate [\(\text{Mn(CH}_3\text{COO)}_2.4\text{H}_2\text{O}\)] and NaOH, the \(\gamma\)-MnOOH is altered to \(\alpha\)-Mn2O3 nano cubes whereas \(\beta\)-Mn2O3 nanosheets were obtained by concentrating NaOH. The growth mechanism of nano wires, rods and bundle form may be in line with hydrogen bonding interface and vanderwaals forces.

G.D. Mukherjee and group [81] have reported phase changes of Mn2O3, Mn3O4 and manganese oxide procured in sol-gel process under high pressure and temperature. Above 700 °C the sol gel Mn2O3 transforms to \(\gamma\)-Mn2O3. On quenching pressure from 5 GPa with a variance of 800–1200 °C temperature transmogrified [induce to a phase] to a combination of hausmannite and maronite-type structure (a mixture of Mn3O4 and CaMn2O4). Partial loss of crystallinity is notified in \(\alpha\)-Mn2O3 when pressure-quenched from 8 GPa at room temperature and further decomposition of \(\alpha\)-Mn2O3 increases with increase in pressure in quenching experiment.

Matthias Augustin and co-workers [82] have synthesized the time and temperature dependent phase transformations of MnOx species in oxygen and argon atmosphere. Noteworthy in this synthesis is that it is a tranquil entree to three different nanostructured MnOx species via one calcination process which rules out synthesis caused effects. Structural and morphological studies discloses that the lattice constants and particle sizes of the MnOx species reliant on calcination temperature (see Table 4).

K.M. Atique Ullah et al [78] have reported stability of crystallites and metamorphism of Mn3O4 in a temperature range from 80 °C to 700 °C. Mn3O4 nano rods and Mn2O3 nano cubes were prepared by soft synthesis route by heat treatment of Mn2O3. The spherical Mn3O4 NP was converted to Mn2O3 rod upon heat treatment at 350 °C. This may be due to anisotropic growth mechanism. Further, double fold increase in temperature, it was observed in XRD analysis that additional peaks appeared at 750 °C, nano rods were changed to cubic Mn2O3 NP. In this report, morphological changes as a function of temperature shows different properties whereas the results reported by Lee et al [83] are in contrast where transmogrification of manganese oxides viz. MnO, Mn3O4 and Mn3O4 with almost identical textural properties (morphologies, surface areas, pore volumes, and the size). The structural variations and alterations of ratio of Mn and O among the various oxidation states of Mn strongly affects the properties and the strategic reason to regulate its preparation technique.

Temperature dependant phase transition [79]:

\[
\text{MnO}_{100^\circ C} \rightarrow \text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4 \rightarrow \text{MnO}_{350^\circ C} \rightarrow \text{Mn}_3\text{O}_4
\]

(23)

Phase transition using different precursors/atmospheric gases/ temperature [79]:

\[
\text{Mn}_2\text{O}_3 \rightarrow \frac{4}{3}\text{Mn}_2\text{O}_3 + \frac{2}{3}\text{O}_2 \rightarrow \frac{5}{3}\text{Mn}_2\text{O}_3 + \text{(C}_3\text{H}_5\text{N)}_2 + 2\text{CO}_2
\]

(24)

\[
\text{Mn}_2\text{O}_3 + \frac{2}{3}\text{O}_2 \rightarrow \frac{1}{3}\text{Mn}_3\text{O}_4 + \text{(C}_3\text{H}_5\text{N)}_2 + 2\text{CO}_2
\]

(25)

\[
\text{Mn}_2\text{O}_3 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow \text{Mn}_3\text{O}_4
\]

(26)

\[
\text{Mn}_2\text{O}_3 + \frac{2}{3}\text{O}_2 \rightarrow \frac{1}{3}\text{Mn}_3\text{O}_4 + 2\text{CO}_2
\]

(27)
| Synthetic method          | Reactants                                      | Synthetic condition                                    | Morphology/ Applications                                      | Particle Size | Author                        |
|---------------------------|-----------------------------------------------|--------------------------------------------------------|----------------------------------------------------------------|---------------|-------------------------------|
| Hydro thermal method      | 0.5mmol KMnO₄, 0.2mol formaldehyde             | 120 °C for 12 h at 200 °C for 12hr                   | MnO₂ hydrate formed at 300 °C for 10 h                          | 50–60 nm      | Khalid Abdelazeez             |
|                           | KMnO₄ and 30 mL PEG                            |                                                       |                                                                  |               | Mohamed Ahmed et al.          |
|                           |                                              |                                                       |                                                                  |               |                               |
| Hydro thermal method      |                                              |                                                       |                                                                  |               |                               |
|                           |                                              |                                                       |                                                                  |               |                               |
| Hydro thermal method      | MnCl₂ [0.1M; 50 mL]                           | 160 °C for 12 h dried at 40 °C for 12 h              | Octahedral shaped Mn₃O₄ nanofibers                              | 10 nm         | Yu Li et al.                  |
|                           | Urea [0.1 M, 50 mL]                            |                                                       |                                                                  |               |                               |
|                           | pH -10.55 by NH₄OH                            |                                                       |                                                                  |               |                               |
| Hydro thermal method      | MnCl₂ [0.1M; 50 mL]                           | 150 °C for 16 h Drying at RT                          | Degradation of Acridine orange                                 | 99nm          | Aslam Jamala et al.           |
|                           |                                              |                                                       |                                                                  |               |                               |
| Hydrothermal method       | 0.7 mmol Mn(CH₃COO)₂.4H₂O Melamine [1 mmol]   | Refluxed at 80 °C for 2 h                             | Mn₃O₄ nano belts                                               | 40–70 nm      | Khalid Abdelazeez             |
|                           | Ethanol: water [70:30]: KOH [0.08mmol]         |                                                       |                                                                  |               | Mohamed Ahmed et al.          |
|                           |                                              |                                                       |                                                                  |               |                               |
| Reflux method             | MnSO₄. H₂O [0.19g]                            | At 180 °C for 4 h                                    | Mn₃O₄ 3D flower like structure.                                 | 1-5 micro metre| Yuli Wang et al.             |
|                           | Urea [1.35 g]                                 |                                                       |                                                                  |               |                               |
|                           | NaOH [2g]                                     |                                                       |                                                                  |               |                               |
|                           | 30% H₂O [15ml]                                |                                                       |                                                                  |               |                               |
|                           |                                              |                                                       |                                                                  |               |                               |
| Reflush method            |                                              |                                                       |                                                                  |               |                               |
|                           |                                              |                                                       |                                                                  |               |                               |
| Reflux method             | MnCl₂. H₂O [0.2M]                             | At 80-100 °C for 4 h                                 | Mn₃O₄ nano powder                                             | 50nm          | M. Anilkumar et al.           |
|                           | pH – 12 (NH₄OH)                               |                                                       |                                                                  |               |                               |
| Reflux method             | MnCl₂.H₂O [0.2M]                              | At 85 °C for 12 h                                    | Mn₃O₄ nano particle                                           | 32 nm         | A. Baykal et al.              |
| Thermal decomposition method | MnNO₃ [0.090g; 0.5 mmol]                      | Oil bath at 60 °C                                    | Mn₃O₄ nano particles                                          | 85 nm         | Ahmad Morsali et al.          |
|                           | NaN₂ [0.065 g, 1mmol]                         | Dried at 186 °C                                     |                                                                  |               |                               |
|                           | 4’-[4-pyridyl]-1,2,4,6,2’-tetrapyridine        | Thermal decomposition of coordination compound at 320 °C |                                                                  |               |                               |
|                           | Oleic acid                                    |                                                       |                                                                  |               |                               |
|                           | Methanol [100ml]                              |                                                       |                                                                  |               |                               |
| Precipitation method      |                                              |                                                       |                                                                  |               |                               |
|                           |                                              |                                                       |                                                                  |               |                               |
| Precipitation method      | MnCl₂.H₂O [0.22 mol]                          | Stirring for 24 h                                    | Mn₃O₄ nano dielectric properties                              | 20–30 nm      | Hassouna Dhaouadil et al.     |
|                           | NH₄OH                                        | Dried in the oven at 80 °C for 24 h                  |                                                                  |               |                               |
| Precipitation method      | MnCl₂. H₂O [0.2M]                             | Stirling 30 min                                       | Mn₃O₄ nano rods                                               | 20nm          | American Ramirez-Olmos et al.|
|                           |                                              | And left for months                                  | Magnetic properties                                           |               |                               |
| Controlled synthesis      | Mn(CH₃COO)₂.4H₂O [0.3g]                       | 180 °C for 9hr in an Ar atmosphere                    | Mn₃O₄ nano particles                                          | 15nm          | Robert Bussamana et al.       |
|                           | 1:24 oleylamine [7.6g]                        | Cooled to room temperature at 850 °C for 2hr         | Magnetic properties                                           |               |                               |
|                           | BMI-PPF [8.18g], BMI-PF [6.51g] BMI-NTF [22.28g] |                                                       |                                                                  |               |                               |
| Solid state reaction      |                                              |                                                       |                                                                  |               |                               |
|                           |                                              |                                                       |                                                                  |               |                               |
| Solid state reaction      | MnCl₂ [0.2g]                                  | Dried at 80 °C for 5hr                               | Mn₃O₄ nano wire                                               | 40–80nm       | Wenzhong Wang et al.          |
|                           | Na₂CO₃                                        |                                                       | Oxidation of methane and carbon monoxide                     |               |                               |
|                           | NaCl flux [1g]                                |                                                       | Reduction of benzyl nitrile                                  |               |                               |
|                           | NP-9 surfactant [3ml]                         |                                                       |                                                                  |               |                               |
|                           | nonylphenylether-9                            |                                                       |                                                                  |               |                               |
| Ultrasoundication method   | Mn(CH₃COO)₂.4H₂O [1g]                         | Sonicated for 3 h                                    | Mn₃O₄ nano crystalline                                         | 15nm          | I.K. Gopalakrishnan et al.    |
|                           | in 100ml distilled water                      |                                                       | Magnetic property                                             |               |                               |
|                           |                                              |                                                       |                                                                  |               |                               |
| Reflush method            |                                              |                                                       |                                                                  |               |                               |
|                           |                                              |                                                       |                                                                  |               |                               |
| Reflush method            |                                              |                                                       |                                                                  |               |                               |
|                           |                                              |                                                       |                                                                  |               |                               |
| Reflush method            |                                              |                                                       |                                                                  |               |                               |
|                           |                                              |                                                       |                                                                  |               |                               |
| Combustion method         |                                              |                                                       |                                                                  |               |                               |
|                           |                                              |                                                       |                                                                  |               |                               |
| Sono chemical method      |                                              |                                                       |                                                                  |               |                               |
|                           |                                              |                                                       |                                                                  |               |                               |

(continued on next page)
\[ \text{Mn}^{2+} + 2\text{OH}^- \rightarrow \text{Mn(OH)}_2 \]  
\[ 3\text{Mn(OH)}_2 + \text{H}_2\text{O}_2 \rightarrow \text{Mn}_3\text{O}_4 + \text{H}_2\text{O} \]  

\[ \text{Mn}_3\text{O}_4 \rightarrow \text{Mn}_2\text{O}_3 + \text{O}_2 \]  
\[ \text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4 + \text{H}_2\text{O} \]  

\[ 3\text{Mn}_3\text{O}_4 + 2\text{CO}_2 \rightarrow 3\text{Mn}_2\text{O}_3 + 2\text{CO}_2 \]  

\[ 3\text{Mn}_3\text{O}_4 + 2\text{H}_2\text{O}_2 \rightarrow 3\text{Mn}_2\text{O}_3 + 2\text{H}_2\text{O} \]  

4. Photo catalyst

Photo catalysis courtesy of advances in nano science is one of the most effective approaches for pollution abatement and recovery of wastewater. The photo degradation of pollutants in waste water using semiconductor nano metal oxides has been widely reported in various literature [84, 85, 86, 87]. The photo catalytic properties of metal oxide nano materials is dependent upon the following factors, namely electronic structure, desired band gap, suitable morphology, high surface area, reusability, light absorption properties and charge transport.

The general mechanism to degrade the pollutants in waste water is the generation of electrons and hole pairs from the photocatalytic semiconductor. The photo generated pair (e-/h+) can reduce or oxidize adsorbates on the surface of the catalyst, that is shown in Figure 5 [88, 89, 90, 91, 92,100].
| Synthetic method                           | Reactants                                      | Synthetic condition                                                                 | Morphology   | Applications                                      | Particle Size | Author                        |
|--------------------------------------------|------------------------------------------------|--------------------------------------------------------------------------------------|--------------|--------------------------------------------------|---------------|-------------------------------|
| MnO<sub>3</sub> thin films by CBD method    | Manganese sulphate, hexamethylenetetramine (HMT), Polyvinyl alcohol (PVA) | Well cleaned stainless steel mesh-like substrate was immersed into an aqueous solution of manganese sulfate complexed with HMT at temperature of 343 K. Brownish precipitate of MnO<sub>3</sub> appeared in the bath. Deposition of MnO<sub>3</sub> on substrate for 3 h Thin films were annealed at 473 K for 2 h, improve the crystallinity of deposited films. | Nano sheets  | Solid state super capacitor                      | -             | Deepak P. Dubal               |
| MnO<sub>3</sub>/MgO nanocomposites by Sol gel | Manganese acetate and Magnesium acetate tetra hydrate 0.5 M acetic acid | mixing Mn acetate and Mg acetate solutions to get homogeneous mixture. 0.5 M of acetic acid was added drop wise with stirring maintaining temperature range 50-60 °C for 4 h. The white product obtained was dried at 90 °C for 6 h in hot air oven. | spherical    | Transformer and electromagnets                   | -             | K. Tamizh Selvi               |
| Polyaniline-MnO<sub>3</sub> Nanocomposite by precipitation-oxidation method | Dodecyl benzenesulfonic acid sodium salt (SDBS, 25 %), Ammonium per sulphate (NH4) 2SO<sub>8</sub> (APS), Manganese acetate, urea (NH2)2CO and ethylene glycol (OHCH2–CH2OH) | Aniline-SDBS (0.4 M), MnO<sub>3</sub> NPs (3.72 g), (NH4)2S2O8 (0.46 M) was Ultrasonicated 2 h; 5 °C; N2 atmosphere. The obtained blackish green precipitate was filtered, washed and dried. | spherical    | Magnetic                                         | 37-40nm       | B.H. Shambharkar             |
| Solvothermal method                        | 0.490 g of Mn(CH<sub>3</sub>COO)2 and 15 mL of aceton | 2 mmol(0.490 g) of Mn(CH3COO)2 solution and 15 mL of aceton was added in the above solution and stirred for 10 min. Then the mixture was transferred into a 25 mL stainless steel autoclave and heated at different temperatures for 12 h. The resulting product is filtered, washed and dried | spherical    | Supercapacitors                                  | 9–15 nm       | Song Rui etal                 |
| Combustion method without fuel             | MnO<sub>3</sub> KMnO<sub>4</sub> Sodium acetate | In this method precursor MnCl<sub>2</sub> is converted to Mn<sup>III</sup>(acac)<sub>3</sub> followed by calcination at 600 °C and 1000 °C to obtain MnO<sub>3</sub>NP | spherical    | Super capacitors                                 | 20–40nm       | Mehdi Salehi                 |
| PEG-MnO<sub>3</sub> nanocomposites by hydrothermal route | Mn(acac)<sub>3</sub>, NH<sub>3</sub>, PEG-400, absolute ethanol | 1 g of Mn(acac)<sub>3</sub> was added dropwise into three-neck round-bottom flask. Then 16.7ml PEG-400, heated and melted, was injected to the flask under NH3 gas (pH – 11) with continuous stirring mixture was put in the autoclave and was kept at 160 °C for 12 h. The obtained precipitate was filtered, washed with ethanol and dried | spherical    | Magnetic                                         | 12nm          | Karaoglu                      |
| MnO<sub>3</sub>/graphene nanocomposites: solvothermal process | 20 mg RGO 200 mL DMF 20 mL of 0.2 M Mn(acac)<sub>3</sub>3H2O | dispersing 20 mg RGO in 200 mL DMF to 20 mL of 0.2 M Mn(acac)<sub>3</sub> followed by calcination at 600 °C and 1000 °C to obtain MnO<sub>3</sub>NP | Spherical    | Photocatalytic degradation of the MB dye         | 12nm          | Ahmed A. Amer [72]            |
| MnO<sub>3</sub>/Chitosan nano composites by solution casting method | 1.3 g of MnCl<sub>2</sub>3H2O 1.13 mL of hydrazine hydrate Chitosan | Chitosan and MnO<sub>3</sub> nano particles were dispersed through ultrasonication. The blend was solution casted in petri dish at 333K for 24 h which resulted in thin films | Thin film    | Energy storage                                   | -             | B. A. Harshita,               |
| MnO<sub>3</sub>/RGO by Sol gel method       | 0.6 g of graphite oxide 1.928 g of manganese acetate Tetrahydrate 10ml of hydrazine | Manganese acetate solution and GO were dispersed under vigorous magnetic stirring for 1 h. NaOH aqueous solution (50%) was added dropwise 10 mL of hydrazine hydrate was added with constant stirring at temp 80 °C for 5h Precipitate was filtered, washed and dried. hybrid consists of disorderedly stacked graphene and crystalline MnO3 NPs | hybrid       | Dye degradation, lithium-ion batteries and supercapacitors | 29 nm         | Yunjin Yao [73]               |
| Ultrasoundication                          | 0.6 g MnCl<sub>2</sub> 30 ml of ethanolamine | 0.6 g MnCl<sub>2</sub> solution and 30 ml of ethanolamine were ultrasonicated for 5 h. The obtained brown precipitate was centrifuged, filtered, washed and dried. | Tetragonal   | magnetic                                         | 5–10 nm       | Shijin Lei                    |
Table 3 (continued)

| Reactants | Synthetic method | Metalorganic | Thin film | Glass and Si wafer | morphology | Applications | Particle Size | Author |
|-----------|------------------|--------------|-----------|-------------------|------------|--------------|---------------|--------|
| MnO3O4/Au (HAuCl4) | Spray Pyrolysis technique | Manganese nitrate tetrahydrate and Chloroauric acid (HAuCl4) was stirred for one night at 70°C | nanosheets | The substrates were put on a hot plate which has 200°C surface temperature, and solutions were sprayed onto the substrates. The coated substrates were annealed at 400°C for 1 h in the air. | Glass and Si wafer | 28 nm | Antimicrobial agent | Bama Krishnan |

4.1. Role of manganese in improving the photo catalytic performance

Theoretical modelling demonstrated that among transition elements, manganese has intrinsic character of high optical absorption in visible and infra-red solar light. Enhancement of activity in visible region is due to the band gap of Mn3O4 which is 2.34 eV, whereas band gap of TiO2 ranges from 3.2 eV to 3.8 eV [94].

4.2. Comparative photocatalytic study

Manganese oxides were among the ancient observed metal oxide catalyst and originate to retain an impending action in redox reactions. The discussed photo catalytic reactions in the removal of most of the dyes have shown excellent photo catalytic activity under visible light (see Table 5).

The photocatalytic degradation of diphenyl thio carbazole (DPTC) by Mn3O4 was reported by Ahmed et al. [30, 34]. Catalytic performance was interpreted using UV studies. The absorbance peaks were observed at 600 and 259 nm respectively. The peak at 600 nm might be due to n→π* transitions of C=C=N=N bond and the latter at 259 nm corresponds to π→π* transition of aromatic ring in DPTC. The decrease in absorbance peaks indicate the degradation of dye into smaller fragments. Under the same reaction conditions, the photocatalytic efficiency has shown a remarkable improvement in the presence of oxygen and catalyst Mn3O4 as mixture than the individual constituents. Moreover, the morphology of Mn3O4 as nanobelt (NB), nanosheets (NS) and nano particles (NP) also played a role in efficiency of decomposition of dye. Mn3O4 nanobelt showed 99% of degradation of the dye. The improved photocatalytic activity is due to its band gap, non-toxicity, stability, strong oxidizing power and durability characteristics of titanium oxide have been promoted it as a hegemony among catalytic materials. The default of TiO2 as a photo catalyst is its restricted activation under UV region and easy recombination of its electron - hole pair in visible region that impedes its photo catalytic application under visible region. Most of the semiconductor catalysts only serve under UV light which reckon for ca.4% of the total solar energy. Therefore, there is a necessity to enhance or find photo catalyst that will be activated by light of visible spectral region i.e utilizing wave length between 380 and 500 nm as to profit a maximum amount of energy available from solar radiation. In this frame work, significant efforts put together in order to improve catalytic behaviour of semiconductor oxides by modifying specific surface area and energy bad gap via anchoring of noble metals, surface defect engineering textural designing, metal and non-metal doping etc [93]. The quantum confinement in nano size compounds gives shift in optical band gap as for TiO2 (anatase) is 3.2 eV and rutile is 3.0 eV whereas band gap of Mn3O4 ranges from 3.65 eV to 2.34 eV [94].
anisotropic and cubic spinel structure [10, 101]. Reactive oxygen species such as h\(^+\), O\(_2\)\(^{-}\) and OH\(^-\) are responsible for the photocatalytic degradation of the dye [101]. The reusability and catalytic efficiency was decreased slightly because of inescapable loss while recovery and ceasing of active centers on its surface in every cycle [30].

The kinetic and spectroscopic tools are important in understanding the catalytic behavior of the reaction. DPTC is a cationic dye which is an electron acceptor hence h\(^+\) did not take part in its degradation. Hence, super oxide radicals (O\(^-\)\(^2\)) initially took part and attacked C=S, N=N functional groups and further OH radical also involved for degradation of intermediates. The intermediates which were not stable and competing for their degradation on the same photocatalyst surface. Therefore, the equation for O\(^-\)\(^2\) attacked initially on DPTC degradation under visible light is [100].

\[
rx = - k_d [Xads] [O^-]
\]

(30)

\[
C_{13}H_{24}N_4S + O^- \rightarrow C_{13}H_{23}NO + SO + NH_4 + 2NO_3
\]

(31)

\[
C_{13} H_2NO + O^- + OH \rightarrow C_{13}H_2O_2 + NO_3 + H_2O
\]

(32)

\[
C_{13}H_2O_2 + O^- \rightarrow OH + CO_2 + H_2O
\]

(33)

The comparative research on photocatalytic efficiency of MnO such as \(\beta\)-MnO\(_2\), MnOOH nano rod and Mn\(_3\)O\(_4\) octahedron shape on degradation of Alizarin Yellow R (AYR) [27] was carried out at different temperature, pH and time. The band gap energy of \(\beta\)-MnO\(_2\), MnOOH nano rod, Mn\(_3\)O\(_4\) were 2.14, 1.81 and 1.72 ev respectively. In accordance with L.C. Zhang et al [102] an increase in band gap would efficiently improve charge separation of hole and e\(^-\), results in enhanced transfer of electron at the interface of solid catalyst and dye in liquid phase, large surface area, specific capacitance and the reduction peak potential shift towards more positive which in turn leads to improved photo catalytic behavior of \(\beta\)-MnO\(_2\) in degradation of AYR upto 98% compared to MnOOH nano rod and Mn\(_3\)O\(_4\) octahedron shape [103]. The degradation mechanism of dyes was given below.

\[
\text{MnO}_2 + h\nu \rightarrow \text{nano compound (e}^- + h^+)\]

(34)

\[
e^- + O_2 \rightarrow O_2^-\]

(35)

\[
O_2^- + H_2O \rightarrow O_2 + OH + \text{OH}^-
\]

(36)

\[
\text{OH}^- + AYR \rightarrow \text{degradation products}
\]

(37)

Degradation of AZY was carried out by OH radical attack at initial stage under visible light. This was confirmed by the PL studies with terephthalic acid and gradually increased peak at 427 nm with an increase in irradiation time opened that predominant oxidation reaction was of OH attack on AZY. Then,

\[
r_x = - k_d [Xads] [OH]
\]

(38)

The intermediates formed in AZY degradation were competing their degradation on the same catalytic surface and degraded within 3 h. These intermediates were stable up to a certain period and consuming OH for their degradation.

Table 4. Structure of Manganese oxides.

| Oxide        | MnO   | Mn\(_3\)O\(_4\) | Mn\(_5\)O\(_8\) | \(\alpha\)-MnO\(_2\) | MnO\(_2\) | \(\gamma\)-MnOOH |
|--------------|-------|-----------------|-----------------|--------------------|----------|-----------------|
| Mineral name | Manganosite | Hausmannite | Bixbyite | Pyrolusite | Manganite |
| Valence      | +2    | +2, +3          | +2, +4         | 3                  | 4        | 3               |
| Lattice parameters Å | a = 4.422 | a = 5.765 | b = 4.852 | a = 9.416 | a = 4.388 | a = 5.304 |
|             | c = 9.412 | c = 9.724 | c = 4.852 | a = 9.416 | a = 2.865 | c = 5.304(1) |
|              |       |                |                | b = 109.41°       | b = 5.277(1) | \(\beta\) = 114.38(2) |
| Crystal structure | Cubic | Tetragonal | Monoclinic | Cubic | Tetragonal | Monoclinic, pseudo orthorombic |

Figure 5. General mechanistic steps for the photocatalytic degradation. “Reprinted from Photochem. Photobiol. Rev, 18, Xu Zong, Lianzhou Wang, Ion-exchangeable semiconductor materials for visible light induced photocatalysis, 32-49, copyright (2014), with permission from Elsevier”.

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Table 5. Dye degradation by haumunite under different light regions.

| Dye                        | Morphology/Band gap     | Light region | Degradation % | Irradiation time | References          |
|----------------------------|-------------------------|--------------|---------------|------------------|---------------------|
| Acridine Orange, (AO)      | Mn3O4 nano structures   | UV-visible   | 47.38         | 170 min          | Adam Jamal et al.   |
| Alizarin yellow            | β-MnO2, Mn(OH) nano rod and Mn3O4 octahedron (2.14, 1.81 and 1.72 ev respectively) | UV-visible | Beta Mn3O4 nanowire -98% Mn3O4 octahedron -62% MnO(OH) nanorods -54% | 80 min | Khalid Abdelazeez Mohamed Ahmed et al. |
| diphenylthiocarbazone      | Mn3O4 nanobelts, Mn3O4 nano sheet, Mn3O4 nanoparticles (2.22, 1.98, 1.91 ev respectively) | Visible     | 99% Mn3O4 nanobelts shows higher catalytic activity than sheets and NP | 150 min | Khalid Abdelazeez Mohamed Ahmed |
| Methylene blue             | Mn3O4 NP                | visible      | 80%           | 60 min           | Atique Ullah       |
| Methylene blue             | Mn3O4 flower structure  | UV light     | 73%           | 180 min          | Yuli Wang          |
| Methylene blue             | Mn3O4 nano particles    | UV light     | 49%           |                  |                    |
| Brilliant cresyl blue      | Mn3O4 nano rods         | UV light     | 62%           |                  |                    |
| Alizarin Red               | Mn3O4/dandelion structure | Visible      | 97%           | 120 min          | Hasimir Rahman et al. |
| Methylene blue and procion red | Mn3O4 NP              | Visible      | 75%           | 1 min            | Al nakhb choudhury  |
| Malachite green            | Al doped Mn3O4 NP       | UV light     | 90%           | 60 min           | Dhanasekar et al.   |
| Methylene blue             | V doped Mn3O4 NP        | Visible      | 82.5%         | 40 min           | Samanbeh Ramezanpour |
| Methyl orange              | Mn3O4, hierarchical porous network | Visible light | 90%           | 10 min           | Chengjun Dong       |

Applying micro steady state approximation [100], it follows as:

\[
[\text{OH}^-] = \frac{k_2[H_2Oads][h^+]}{k_5[Mads] + k_{10}[\text{Hads}^+] + k_{10}[M]} \quad (39)
\]

A comparative study on the degradation capacity of synthesized Mn3O4 octahedral at 120 °C and Mn3O4 nanoparticles at 180 °C with commercial Mn3O4 was carried out using model pollutant Rhodamine-B (RhB) under UV light for 12h. Despite of two catalysts (Mn3O4 octahedral (9 μm/g); Mn3O4 na no particles (7 μm/g)), having almost the same surface area than commercial, Mn3O4 (1 μm/g), Mn3O4 octahedral (9 μm/g) exhibited higher degradation capacity as 76% than the other two catalysts (45 and 23 % respectively). This enhancement of degradation capacity was due to reduction of its particle size which suppressed recombination of hole and electron resulted in transfer of electrons and holes to RhB molecules for photo decomposition. The reason being high chemical activity by Mn3O4 octahedral was due to larger surface energy facets than Mn3O4 nanoparticles at 180 °C and also free double bonds of Mn- or O- on the surface [104]. Commercial TiO2 nanoparticles with < 25 nm size had shown greater effect on degradation of RhB than synthesized Mn3O4.

The degradation efficiency of nano particle was related to its morphology and it was noticed in degradation of methylene blue (MB) in waste water treatment. Three dimensional flower like nano structure showed 73% degradation efficiency than nano particles and nano rods (49% and 62% respectively) under the given reaction conditions as UV/ H2O2 for 3 h. The combination of nano compound and oxidizing agent without UV light showed 40% degradation of MB in waste water. The high catalytic activity of flower like structure nano compound had high surface area of 156 μm²/g, which was needed to interact with surrounding molecules of MB in degradation or adsorption process [30].

Al-Nakhb Chowdhary [74] reported methylene blue, MB(30 μM) solution colour was sharply bleached out around 75% within a minute after charging 0.25 g/L of Mn3O4 nanoparticles suspension. Further, the colour of MB gradually disappeared at 664 nm at pH 3 and 5, respectively, with shifting of wave length towards lower side. This decolorization of MB was confirmed with cyclic voltamgram (CV) in presence of sulphuric acid. The CV exhibited a well-defined redox process like anodic at 0.26 V and cathodic process at 0.21V recommended that the oxidation and reduction of MB respectively. Apart from it, the strong band at 310 nm of the procion red (200microB) reduced almost completely by Mn₃O₄NP (0.25 g/L) suspension at pH 3 for 24 h. All these decolorisation of dyes were occurred through surface mechanism as do many other pollutants [101, 102].

In the similar manner, degradation of MB was observed by A.K.M. Atique Ullah et al. [78], when 100 mg/mL of Mn3O4 NP added to 100 mL of 30μM of MB in acidic medium at pH-3. Further, the spectroscopic investigation of degradation of MB showed that the degradation efficiency was 80–85% at different time intervals (from 0 min to 240 min). As time passes, the λ max shifted towards shorter wavelength at 628, 638, 618 and 601 nm which revealed that MB was degraded to intermediate products such as azure A, azure B, azure C and thionine respectively. The rate constant of MB degradation was 0.0045 min⁻¹. The rate constant of MB degradation was compared with akhtenskite (0.0006 min⁻¹) and birnessite (0.0007 min⁻¹). The point of zero net electrical charge (pzc) on the surface of solid phase was also determined by partially immersing it in electrolyte solution. Variation of pH plays a major role in the degradation mechanism. The pHpzc of synthesized Mn3O4 was 4.5. Theoretically, pH of the solution influenced catalytic performance of NP because of charge developed on catalyst surface through protonation (+ve charge on NP with lowering of pH < 4.5) and deprotonation (-ve charge on NP with increasing of pH > 4.5). However, it was observed that heterogeneous surface oxidation assisted to occur high degradation of MB while lowering pH of medium [33, 104]. This results suggested that NP was suitable for MB degradation.

Mn₃O₄ whose morphology is 3d flower like structure exhibited greater degradation of MB than TiO₂ NP [1 g/L Mn3O4 NP and 300 ppm dye conc,1g/L TiO₂ NP with 20ppm dye Conc] with increase of surface area on morphological changes [105].

The degradation percentage of aq. acridine orange (AO) was improved in presence of Mn3O4 NP and excess oxygen rather than individually along with irradiation time [33]. There was 47% decolorization of AO achieved in presence of NP with 170 min irradiation time than simple manganese salts because of larger active and specific area of synthesized Mn3O4. The decolorization of methyl orange (MO) was achieved 96% within 10 min, in presence of NP, 2 mL of HNO3 and air when it was compared to only NP catalyst (2.5%) and NP with 2 mL of HNO3 (68%). The degradation of MO was assumed due to non-stoichiometric nature with both valencies (+3 and +2) of porous Mn₃O₄ NP lead to oxygen vacancies. This was the key issue in oxidative degradation of MO.

MO in high concentration showed 92% degradation under UV/TiO₂ NP which is due to prime factors such as particle size and band gap.
energy which influenced degradation capacity of nano sized compound [106].

The degradation of methylene blue by V doped MnOx [107] under visible light, follows the general photo catalytic mechanism. The degradation efficiency is shown better in doped MnOx than undoped MnOx. Nano rod structure, the dopant concentration, optimum temperature and pH plays a role in the better photo catalytic activity of the semiconductor [107].

During the dye degradation of alizarin by MnOx dandelions [73] under visible light, despite MnOx, energized dye molecule by visible light are jumped into fitted singlets and triplet states, subsequently, shifting of electron occurs from the excited dye on to conduction band CB of metal oxide forming cationic dye radicals [108]. The injected electron of MnOx (e- ) reacts with pre-adsorbed O2 to form oxidising species (O2•-, HOO• followed by OH radicals) results in photo oxidations. Even though nano metal oxide itself is not excited, it plays a chief role in electron transfer mediation.

Developing photo catalysts that are dynamic in visible light (λ ≥ 420 nm) is challenging and many alterations have been done to utilize the maximum energy from solar spectrum. One such route reported was loading nano MnOx and CuO in ZnS photo catalyst which shifted photo absorption properties from the ultraviolet region to visible light [28]. Loading the metals onto the photo catalyst can separate photo generated electrons and holes more effectively. The photo catalytic activity was enhanced due to the effective inter particle charge transfer which prevented electron–hole recombination [73].

It has been reported that MnOx shows greater oxidative capacity due its higher oxidation potential when compared to graphene material (rGO). Synergistic result is achieved when it is anchored [109]. Lin Duan et al have reported the significant enhancement in the oxidation of 1-naphtylamine by MnOx when it is anchored with graphene oxide. MnOx-rGO composites have shown superior degradation than the bare MnOx. The redox active surface functionalities in GO will re-oxidize the Mn(II) moiety and facilitates the oxidation mechanism of 1-naphthylamine by bare MnOx species, involves one electron transfer.

Recent studies [110] have shown that Graphite like carbon nitride is potential material for sunlight-driven photo catalyst. Several modifications are carried out on bare g-C3N4 material to improve the catalytic properties for target specific applications. One of the modification to improve is exfoliation to increase the surface area of the material.

Mario J. Muñoz-Batista and group have reported the exfoliation and deposition of Mn species in g-C3N4 material. Photoactivity analysis of the materials were tested under UV, visible and sunlight-type illumination for gas phase degradation of toluene. The performance is assessed by means of the quantum efficiency parameter and procedure for analysis is outlined. The simplest technique adopted for exfoliation is ultrasonication followed by surface modification using Mn species. Mn species supported in the carbon nitride materials do not show noteworthy changes in terms of the oxidation state and dispersion between the exfoliated and bulk carbon nitride samples. All structural studies carried out on the bulk, exfoliated, surface deposited samples showed physicochemical differences like in band gap energies which associated with light absorption, charge transfer and thus in photocatalytic properties. The authors have outlined the procedure for the analysis of the true quantum efficiency parameter provides a simple route to quantitative estimate and interpret the catalytic effects originated by physical modification of carbon nitride materials. The same can be extended to other photocatalytic materials. The highest quantum efficiency is observed in exfoliated g-C3N4/MnOx species under sunlight type illumination.

Yongjin Ma et al [111] have constructed a photo catalytic hetero-structure material to improve the catalytic efficiency in the visible region. Two types of hetero-junctions commonly known are: (i) Z-scheme and type-II semiconductor. They improve the separation and transportation of carriers (transferring the electrons from semiconductor A and semiconductor B) and optimal transportation path. Ma group have constructed the Mn3O4/CoO hetero-junction by depositing Mn3O4 nano particle on CoO nano rod surface via hydrothermal route. Mn3O4 is a p-type semiconductor whereas CoO is a n-type. The formed n-p junction allows the fast transfer of photo-generated carriers. The photo catalytic activity is studied on the degradation of Rhodamine (RhB) in the visible region. DMPO spin-trapping ESR on Mn3O4/CoO hetero-junction measurements explore the photo catalytic mechanism. The signals which were detected predicted the generation of O2 and .OH. Species. Trapping experiments were carried out to explore the existence of holes and free radical in the photo catalytic reaction. The O2 and h+ are main contributors for photo degradation and the latter one was the key contributor. Hence it can be concluded the degradation can be explained by dual mechanism. The enhanced activity might be attributed to uniformly deposited Mn3O4 can enlarge the visible light response range of CoO2, which in turn improve the transfer rates of photo-excited carriers and lower their recombination rate.

5. Bactericidal agent

As bacteria have become resistant against antibiotics, treatment using metallic nano particle is the new way to fight against dangerous pathogens. The size and morphology have strong influence on the bactericidal effect. The micro meter range bacterial cell contains nano size pores in its epi-cellular membranes which let to penetrate nano scale materials into bacterial cell. These nano scale materials entered into bacterial cell produces toxic oxygen radicals to mutilate cell membranes of microbes which results in an efficient control of bacterial growth [112]. Studies have shown that binding of positive charge of the metal nano particles binds with the negatively charged surface of the bacteria results in bactericidal enhancement. The bactericidal potency depends on the various factors such as the nature of the microorganisms, size of the particle, concentration, pH and morphology.

5.1. Nature of bacterial species

The sustainability or sensitivity of the bacteria against the antibacterial agents depends on the cell wall structure. Difference in cell wall structure of Gram positive and Gram negative brings some variance in their sensitivity to anti-bacterial agent. Gram positive bacteria, a denser peptidoglycan, possess a negative charge that allow to attach positive metal ions to it. On the other hand, Gram negative bacteria possess a thin negative peptidoglycan layer. This layer contains an epi membrane consisted of lipo-polysaccharide that brought structural integrity of the bacteria resulted in high immunity to antibacterial agents [112, 113, 117].

5.2. Size and shape of the particle

The size and shape of nano particles influences antibacterial activity. Decrease in particle size increases the antibacterial activity which is due to larger surface to volume ratio. Interaction of nanoparticles of various shapes with periplasmic enzymes causes different degrees of bacterial cell damage [117].

5.3. Concentration dosage

Various reports indicates that antibacterial activity increases with an increase in the dosage, but it also depends on the nature of microorganisms (gram positive and negative) [13, 117].

5.4. Effect of pH

AI Nakib etal [74] have reported the antibacterial activity carried out at pH 3.3 and 6.2. against the bacteria V. cholerae, Shigella sp., Salmonella sp., and E. coli at pH 3 and 6. Antibacterial activity of the Mn3O4 nanoparticle is nearly half to that of the standard ciprofloxacin antibiotic.
Moderate antibacterial activity was shown at pH 3.3 when compared to 6.2.

5.5. Procedures of assessment

Numerous bioassays like agar plug diffusion, agar well diffusion, dilution methods such as agar dilution, broth dilution are widely used to evaluate antibacterial activity in vitro. Agar disk diffusion is clinically and commonly used method to screen larger number of micro-organisms and antimicrobial agents. Since it is not possible to measure the antimicrobial agent diffused into the agar, this method is not suitable to determine the minimum inhibitory concentration (MIC) However, it offers other benefits such as plainness, inexpensive etc. Dilution methods such as agar and broth methods are more appropriate to determine MIC [13, 112, 113, 114, 115, 116, 117].

5.6. Mechanistic action of nano particles

The frequently proposed mechanistic action of metallic nano particles are (a) free metal ion toxicity arising from dissolution of the metals from surface of the nanoparticles (b) oxidative stress via the generation of reactive oxygen species (ROS) on surfaces of the nanoparticles, (c) non-oxidative mechanisms [113, 114, 115, 118, 119] which is shown in Figure 6.

Release of metal ions (NP) or generation of ROS species on the surface of the nano particles disrupts the cell wall, penetrates into the cell, damage or membrane potential modification or inhibition of t-RNA binding to ribosomes, decrease of ATP level, leakage of intracellular contents, cell differentiation, damaging vital enzymes which in turn lead to the death of bacterial cells.

5.7. Mn3O4 NP as antibacterial agent

The antibacterial activity of the Mn3O4-NPs tested against E. coli and S. aureus was reported by Azhir et al. [77]. Different concentrations of Mn3O4-NPs using Muller Hinton Broth (MHB) medium was prepared to evaluate the minimum inhibitory concentration (MIC) and minimal bactericidal concentration (MBC). S. aureus bacterial growth was impeded around 43, 93 and 100% while for E. coli were 66, 68 and 78%, respectively. This is because S aureus is a Gram- Positive while Escherichia coli is Gram-negative and due to alteration in their structure. The antibacterial mechanism is not well documented for Mn3O4 NP but expected to be similar that of ZnO NP where ROS (reactive oxygen species) produced from the nano particle disrupts the cell membrane inhibiting or destroying the bacteria.

The disk diffusion method was adopted to screen the vitro antibacterial activity against (Bacillus subtilis 168) and (Escherichia coli K12) using antibiotics ampicillin (1 microgram/disk), kanamycin (1 microgram/disk), tetracycline (0.5 microgram/disk), and ciprofloxacin (1 microgram/disk) along with Mn3O4 NP (10 microgram/disk). Later it was incubated at 37°C for 24 h. The authors [45] noted that bacterial species showed similar growth inhibition towards NP and antibiotic samples. However, it is to be noted that E. coli growth is limited by the NPs than B. subtilis. Jayandran and group [116] have observed higher antimicrobial activity of manganese NP than the standard drug Chloramphenicol. The disc diffusion method was deployed to check bacterial activity of manganese nano particle against gram-positive bacteria (Staphylococcus aureus and Bacillus subtilis) and gram negative bacteria (Escherichia coli and Staphylococcus bacillus), respectively and the antifungal activity against Candida albicans, Curvularia lunata, Aspergillus niger and Trichophyton simii fungi. In this comparative study, the results of inhibition diameter clearly revealed that restrained capacity of synthesized manganese nano particles against S. aureus was extremely superior to drug.

Another group of researchers Bama Krishnan [107] et al. have established a composite material Mn2O4/bentonite clay (BC) and tested for bacterial strains, viz. S. aureus 25923 and P. aeruginosa 27853, and C. albicans 26790 fungus. The antimicrobial activity was tested using the well diffusion and potato dextrose agar methods. The antimicrobial activity of bentonite clay was compared with Mn2O4/bentonite-clay composite through inhibition diameters. The bentonite clay slowed slight activity when compared to composite. This is because ions of Mn2O4 are unfettered, penetration through epi and endo cytoplasmic membranes of cell wall. M. Muhamed Haneefa group [117] have synthesized a bio functional manganese oxide nanoparticles for antimicrobial activity evaluation. The synthesized nano material were bio functionalized with salicylalchitosan (SC) to enhance the antimicrobial activity. The antibacterial and the antifungal activity was evaluated by disc diffusion method and agar well diffusion method. The outcomes were matched with standard drugs namely chloramphenicol and fluconazole. Zone of inhibition data indicated the higher antimicrobial activity of bio functionalized SC/Mn2O4 composite than the non-functionalized NP. The reactive functional groups present in chitosan played a vital role in the boost of inhibition activity of bio functionalized nano form. Manipulation of mechanical and solubility properties enhances its antimicrobial activity.

Figure 6. Various mechanisms of antimicrobial activity of the metal nanoparticles. “Reprinted from Materials Science and Engineering: C, Volume 44 Solmaz Maleki Dirzaj, Farzaneh LotfiPour, Mohammad Barzegar-Jalali, Mohammad Hossein Zarrintan, Khosro Adlibkia, Anti-microbial activity of the metals and metal oxide nano particles. 278-284, copyright (2014), with permission from Elsevier”.
6. Outlook and conclusion

MnO$_2$ is an important oxide of manganese. As can be gleaned from the review, various synthetic protocols were discussed to prepare highly crystalline and different shapes of MnO$_2$ nano material. Reaction time, pH, precursors and temperature has an effect on the morphology. The role of capping agent in controlling the growth and shape of NP was covered. This review compreheeds the achievements of MnO$_2$ NP on phase control, shape, morphology, and fabrication and growth mechanism. Dynamics that promotes the phase transition and different oxides of manganese by a single synthetic procedure was exemplified. The research on photo catalytic efficiency of manganese oxide in different structural forms on dye degradation was evidenced by various research articles which makes capable and synergic photo catalyst under UV and visible light radiations. On the large scale, industries should emphasize on design and strategies for the development of active material when addressing organic contaminants in water. Strategies such as constructing heterojunctions, anchoring with graphene like materials, metal sulfide, loading noble metals, doping metal ions can be adopted to improve the photo catalytic efficiency. There is a lot of scope to make MnO$_2$ as an effective photo catalyst by adopting different strategies in order to overcome the challenges by improving the separation efficiency of photo generated carriers, enlarge the range of photo response, and reducing the reorganization of photo generated carriers. It is an effective antimicrobial agent against various bacteria and fungus in comparison with standard antibiotic drugs. Apparently, limited work is focused on antimicrobial activity, hence adequate studies towards screening more pathogens will make MnO$_2$ nano material as a suitable material for drug resistant pathogens and in epidermal ointments used for eczema etc.

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Author contribution statement

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