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A Review on Mn_3O_4 and Its Composite Nano materials of Different Morphologies as an Electrode Material in Super capacitors

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ABSTRACT

Mn3O4 and its composite nanomaterials have become promising candidate as an electrode for supercapacitor devices, because of its low cost, non-toxicity, large abundance, high porosity and high capacitance values in aqueous electrolyte. Here, we systematically summarized the impact of different morphologies of Mn3O4 and its composite nanomaterials on supercapacitive performance. Different researchers synthesized various Mn3O4 and its composite nanomaterials of exceptional properties and different morphologies for energy storage. This article reviews recent efforts and developments in synthesis methods Mn3O4 and its composite nanomaterials as an electrode material in supercapacitors.

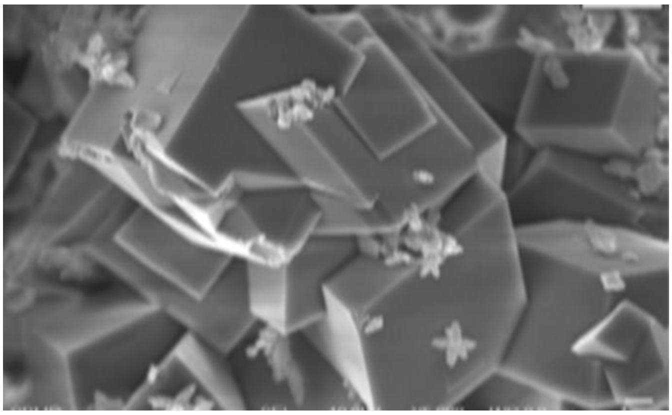
I. INTRODUCTION

Due to vital scientific significance and wide applications arises because of their tunable properties, nanomaterials having at least one dimension is less than 100 nm, have attracted great attention of many researchers. In addition, nanomaterials have phase, size and morphology dependent physical and chemical properties and applications; therefore, many efforts made to govern the phase, shape, size and morphologies of nanomaterials. The nanomaterials can be synthesized using variety of reagents and tactics with extensive range of reaction circumstances [1]. The electrodes of nanomaterials Manganese oxide have enormous applications in electrochemistry, due to their exceptional electrochemical properties such as high capacitance, huge surface area, and small current densities [2]. Water purification, catalysis, sensors, supercapacitors, and alkaline and rechargeable batteries were some fascinating applications of Manganese oxide having different phases such as MnO, MnO_2, and Mn_3O_4, and their composite materials. Particularly, the Mn_3O_4 electrode replaced the toxic RuO_2 electrode in electrochemical charge storage devices due to the its parameters like low cost, non-toxicity, large abundance, high porosity and high capacitance values in aqueous electrolyte [3]. The proper dopant can perturb the growth process of the Mn_3O_4 electrode, during chemical reaction and it can modify the morphology of nanostructure. So selecting proper dopant, there is possibility to change morphology of Mn_3O_4 nanostructured electrode. [4]. There are numerous synthesis techniques have been reported by various researchers to prepare Manganese oxide nanomaterials of several morphologies and distinct properties, such as Electrodeposition, Sol-gel, Hydrothermal, Chemical bath deposition, SILAR, Spray pyrolysis etc. [5]. In last decade, many efforts executed to inspect the different properties and applications of Mn_3O_4 nanostructured electrode, for example, Y. Kong et al. reported the synthesis of octahedron-like Mn_3O_4 nanocrystals by single-step hydrothermal reduction method and reported that it is the most promising element in assemble lithium-ion batteries [6]. X. Zhang et al successfully synthesized Mn_3O_4 nanowires of diameter 15 nm and a length of the order of several micrometers hydrothermally, without any use of surfactants [7]. H. Shah and coworkers prepared square-shaped nanostructures by hydrothermal-growth method and reported that it has potential applications in supercapacitors and Li ion batteries [8]. Thus, to keep the readers up-to-date of the rapid development, it is essential to review the advancement of Mn_3O_4 nanomaterials. In this article, we review the different Mn_3O_4 nanomaterials of various morphologies and their supercapacitive application.

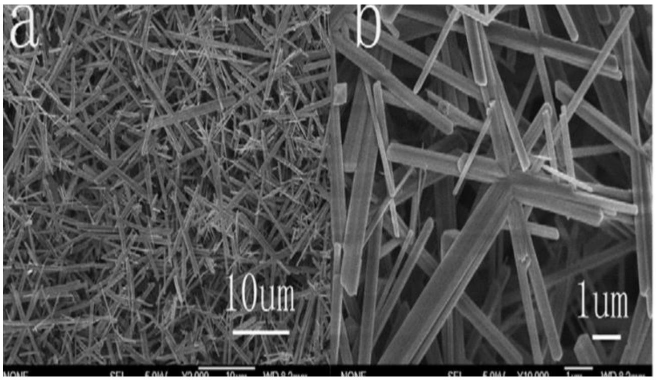
II. SYNTHESIS OF MN_3O_4 NANOMATERIALS

At room temperature, Mn_3O_4 has a tetragonal structure and due to Jahn–Teller distortion along c axis at the Mn^{3+} sites, it has a distorted spinel structure. Manganese ions lodge the octahedral site ($Mn^{3+)}$ and tetrahedral site ($Mn^{2+)}$ corresponds to a normal spinel structure. There are 32 oxygens and 24 cations in the unit cell. Generally, the ionic formula of Mn_3O_4 is Mn^{2+} [$Mn_2{}^{3+}$] O_4. At 33 K, the chemical and magnetic unit cells become identical with rearrangement of moments and it is ferromagnetic up to 43 K. Therefore, its study gains importance as it has wide applications [9].

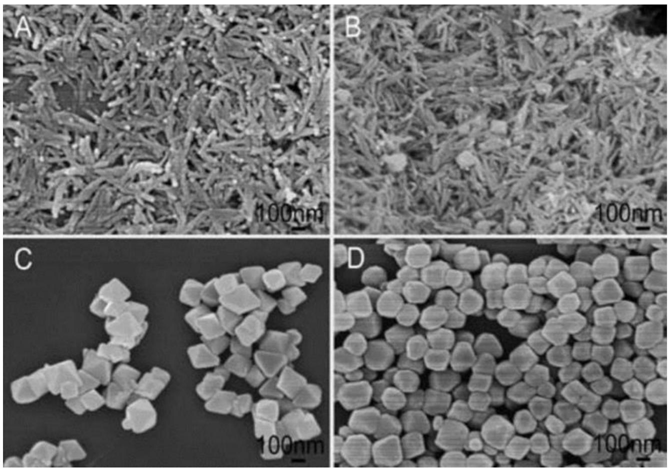
A. Ullah et al. via a gel formation route reduced the $KMnO_4$ with glycerol at 80 °C in aqueous media to synthesize Mn_3O_4 nanoparticles. They observed temperature dependent phase transformation of Mn_3O_4 into Mn_5O_8 and Mn_2O_3 with distinct surface morphologies viz., spherical, rod and cube shape respectively through heat treatment [10]. Using the precipitation method, in presence of CTAB, H. Dhaouadi et al. synthesized Mn_3O_4 nanoparticles of tetragonal structure with crystallite size ranges from 20 nm to 80 nm. They observed that temperature dependence of dielectric properties of Mn_3O_4 nanoparticles at higher frequency [11]. Y. Tan successfully fabricated 1D single-crystalline Mn_3O_4 nanostructures under solvothermal conditions. They easily tuned the diameter and length of nanostructures by altering the concentration of the precursor [12]. W. Wang did decomposition the precursor $MnCO_3$ nanoparticles in NaCl flux to synthesize nanowires of Mn_3O_4 with diameters 30 -60 nm [13]. Using co-precipitation, sol-gel and hydrothermal methods, B. Jhansi Rani et al synthesized different nanostructures of Hausmannite (Mn3O4) plate like nano-grains, coin like nano-sphere and nano-petals and they studied the structural, morphological, optical, electrochemical and magnetic properties of nanostructured materials [14]. A. U. Ubale et al employed simple and economic SILAR method for deposit nanostructured thin films on glass surface at room temperature [15]. Using $MnCl_2 \cdot 4H_2O$ and KOH precursors, A.M. Toufiq and coworkers grown self-assembled 3D coins-like nanostructures having single-crystalline tetragonal Mn_3O_4 nanoparticles of average diameter 95 nm and thickness 35 nm [16]. H. K. Yang et al. to fabricated homogeneous micro-spherical particles having porous structure of Mn_3O_4 carbon composite material using ultrasonic spray pyrolysis technique with the help of surfactants TX 114, P123, F127. They elaborated particles of smaller size and high surface area using TX 114 surfactant with active bi-functional catalyst [17]. H. L. Fei and coworkers explained the synthesis of microflowers of Mn_3O_4 made up of super thin nano sheets by solvothermal method using CTABr surfactant. They reported the morphology dependence of Mn_3O_4 on solvent [18]. Low temperature chemical bath deposition technique was used to prepare Mn_3O_4 thin films of smooth surface made up of the crystalline nanograins by H. Y. Xu.et al [19]. J. K. Sharma et al. reported the low budget green synthesis, using the reducing agent, a leaf extract of A. Indica (Neem) plant, synthesize uniform Mn_3O_4 nanoparticles for chemical sensor application [20].



The SEM images of Mn_3O_4 thin film at (a) ×2000 and (b) ×5000 magnifications (interlocked cubes) [21]



Low (a) and (b) high magnification FESEM images of Mn3O4 nanorods [22].



FESEM images of the Mn_3O_4 nano-octahedrons for various reaction times: (A) 1.5 h; (B) 2 h; (C) 3 h; (D) 8 h [33].

III. THE MN_3O_4 NANOMATERIALS FOR SUPER CAPACITOR APPLICATION

Super capacitors have the ability to charge and discharge quickly, high power density and outstanding cyclic stability, but their small energy density dragged them back in several such applications. Depending on mechanisms, that governing capacitance the super capacitors are classified into two types. First type is electrical double layer capacitor (EDLC) in which double layer of charges at the interface of electrode and electrolyte is responsible for capacitance and in second type pseudo or redox capacitor where capacitance arises due to oxidation-reduction reactions. Researchers are trying to search many novel materials and processes to improve energy density values by manufacturing new electrode materials, electrolytes and device designing [23]. Among many metal oxides, Mn_3O_4 and its composites have attracted more attentions due its large advantageous parameters and special properties.

Y. Luo and coworkers synthesized interlocked Mn_3O_4 cubes by mixing 1.9791g $MnCl_2 .4H_2O$ and ethyl alcohol with constant stirring for 30 min. at room temperature. Then they dried the solution in an oven at 100 °C for eight hours with final calcination at 500 °C for two hours. They observed that it could be a promising candidate as electrode material for super capacitors showing excellent specific capacitance in terms of fast charge–discharge rate, high specific power and long life span [24]. Microwave-assisted reflux synthesis method used by K. V. Sankar Mn_3O_4 nanoparticles of size 50 nm having tetragonal structure. Low internal resistance, high capacitance (94 F g^{-1}) in 6M KOH with long stability reveals Mn_3O_4 electrode is suitable for supercapacitor application [25]. J.W. Lee Mn_3O_4 nanorods of 100 nm to one μm length dispersed on graphene sheets using ethylene glycol as a reducing agent by simple template-free hydrothermal reaction of $KMnO_4$. The composite of Graphene/Mn_3O_4 showed better supercapacitive performance than free Mn_3O_4 nanorods [26]. D. Li et al. employed one-step hydrothermal method for synthesize Mn_3O_4 nanorods on Ni foam using aqueous solutions of Mn $(NO_3)_2$ and $C_6H_{12}N_4$. Due to porous Ni foam fast charge transfer takes place, high surface area and conductivity, this composite has shown better supercapacitor performance [27]. R. Aswathy anchored the surface of oxidized graphite paper by Mn3O4 nanoparticles using hydrothermal method. They calculated the high specific capacitance value 471Fg^{-1} at 1 mA cm^{-2} current density in 1 M Na_2SO_4 solution [28]. By heavily distributing, the Mn_3O_4 particles of size 10 nm graphene nanosheets, B. Wang et al. observed that the functional groups of Mn_3O_4 attached to the nanosheet and increased surface area plays a key role in improving the electrochemical performance. A specific capacitance value for these Mn_3O_4/graphene nanocomposites was 256 F g^{-1} that was almost double that of the pure graphene nanosheets [29].

H. U. Shah and coworkers have successfully synthesized exceptional spongy Mn3O4 nanoparticles, through hydrothermal method. They observed high specific capacitance value 380 Fg^{-1}, which is quite larger than previously synthesized Mn_3O_4 nanoparticles. [30]. H. Jiang fabricated octahedron of Mn_3O_4 of base length 160 nm with smooth surface by a simple EDTA-2Na assisted hydrothermal method, and he reported that it shows excellent electrochemical performance [31]. Doping with different transition-metal ions, size controlled synthesis of Mn_3O_4 octahedrons were synthesized by R. Dong et al. and reported improvement in the capacitive properties Mn_3O_4 by doping transition metals signifying a doping effect for the growth and electrochemical performance [32].

List of pure and composite materials based on Mn3O4 reported recently.

Sr. No.	Compound	Method	Morphology	Electrolyte	Specific Capacitance Fg^{-1}	Ref.
1.	Pure	Hydrothermal	Nanoparticles	0.5 M Li_2SO_4	198	33
2.	Graphene/Mn_3O_4	CBD	Nanoparticles	1 M Na_2SO_4	193	34
3.	Graphene/Mn_3O_4	Hydrothermal	Nano rods	1 M Na_2SO_4	121	26
4.	Pure	chemical precipitation	Nanoparticles	1 M Na_2SO_4	322	35
5.	Pure	CBD	Thin film	1 M Na_2SO_4	321	36
6.	Pure	Hydrothermal	Nano octahedron	1 M Na_2SO_4	153	37
7.	Ni-Mn_3O_4	Chemical oxidation	Nano composite	0.5 M Na_2SO_4	230	38
8.	Mn_3O_4/multi-walled carbon nanotube	CBD	Nano composite	1 M Na_2SO_4	257	39
9.	Graphene/Mn_3O_4	Arc discharge	Nano composite	1 M Na_2SO_4	38	40
10.	rGO–Mn_3O_4	microwave hydrothermal	Nano composite	1 M Na_2SO_4	153	41
11	rGO-Mn3O4	Electrodeposition	Nano composite	1 M Na_2SO_4	364	42
12	Pure	Electrodeposition	Nanostructure	3 M Na_2SO_4	210	43

13	Pure	Hydrothermal	Square-shaped nanostructures	1 M KOH	355.5	8
14	Mn3O4-Activated Carbon	Sonication-assisted mechanical-stirring method	Nano composite	1 M Li_2SO_4	106	44
15	Cr- Mn_3O_4	Hydrothermal	Nanocrystal	1 M Na_2SO_4	272	32
16	Pure	SILAR	Thin film	1 M Na_2SO_4	314	45
17	Pure	Hydrothermal	Nano sheet	1 M Na_2SO_4	1014	46
18	Pure	Hydrothermal	Nano octahedron	1 M Na_2SO_4	322	31
19	Mn3O4/rGO	Solution thermal decomposition	Nano sheet	0.1 M Na_2SO_4	342	47
20	Ni-Mn3O4	Spray pyrolysis	Thin film	1 M Na_2SO_4	705	48
21	Co - Mn3O4	Co-precipitation	Nano granules	6 M KOH	2701	49
22	Pure	Spray pyrolysis	Nanoparticles	1 M Na_2SO_4	187	50
23	RuO2-Mn3O4	Electrospinning	nanofiber	1 M Na_2SO_4	293	51
24	Pure	spray pyrolysis	Thin film	1M Na2SO4	394	52
25	Pure	Ultrasonic irradiation assisted co precipitation	Nanoparticles	1M Na2SO4	296	53
26	Pure	Hydrothermal	Nanoparticles	1M Na2SO4	435	54
27	Mn_2O_3 and Mn_3O_4	co precipitation	Nanoparticles	1M H_2SO_4	305	55
28	Mn_3O_4- CNT	chemical reflux method	Nanoparticles	PVP: Na_2SO_4	499	56
29	Mn_3O_4-$Li_4Mn_5O_{12}$	Electrochemical deposition	Nanofibers	Li_2SO_4	527	57
30	Mn_3O_4@carbon Foam	Hydrothermal	Nanoparticles	1M Na2SO4	212.8	58

IV. CONCLUSION

In summary, we have reviewed recent development of Mn3O4 nanomaterials. We discussed about simple and effective methods to synthesize Mn3O4 nanomaterials of high surface area, unique morphologies and showing outstanding supercapacitive performance. In short, we expect that this paper will not only show the recent advances in Mn3O4 nanomaterials but also give the readers some motivation to discover novel techniques for the synthesis of Mn3O4 nanomaterials of excellent supercapacitive properties.

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