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Review Article

A review on Co_3O_4 nanostructures as the electrodes of supercapacitors

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Abstract: Usage of supercapacitors in energy storage applications has now become a new trend due to its high auspicious features. Introduction of pseudocapacitance has increased its weightage to be used in greater number of practical utilization. Electrodes are the major constituents of a supercapacitor based on which the electrochemical performance of the supercapacitor is decided. Among varieties of electrode materials available, transition metal oxides are the most suitable ones to fulfill the required its criteria. Due to the occurrence of faradic redox reactions on the surface of electrodes, selection of efficient and favorable electrode material plays major role. Co_3O_4 (Cobalt (III) oxide) is one among the most desiring electrode materials due to its various peculiar features. This paper reviews briefly on several factors of Co_3O_4 as electrode material in supercapacitor applications. It includes comparative discussions towards different synthesize methodologies, influence of its dimensional morphology on the electrochemical outputs like specific capacitance, energy density and the power density.

Keywords: cobalt oxide; morphological structure; specific capacitance; energy density; power density

1. Introduction

Supercapacitors are one of the topmost investigated materials which expand their applications further day by day. It has overwhelmed the constraints of fuel cells and the batteries for energy storage practices in assorted fields including regenerative breaks, submarines, backup power systems, and voltage stabilizers. Also, due to the high efficiency of supercapacitors and high oil cost, supercapacitors rapidly engage all automobile applications[1]. Multiple investigations are under progress to enhance the competence and explore its usage in more and more fields with major practical applications. Electrolyte, separator and the electrodes are the major components of the supercapacitor which highly impacts on the electrochemical output. Here in this paper, a brief review on several factors of Co_3O_4 which is one of the highly demanded electrode materials is discussed.

A number of materials are available which are applied as the electrode materials for these supercapacitors. But transition metal oxides own their importance due to their highly ambitious features with high stability and durability[2,3]. Prime transition metal oxides like ruthenium oxide, manganese oxide, vanadium pentoxide, nickel oxide and cobalt oxide come across this route. They assure less toxicity, more economic and environmental friendliness[4,5]. Kumar et al.[3] used nickel oxide to fabricate the electrodes with highly applicable upshots. Vast literature survey proves that Co_3O_4 based electrodes establish their eminence role with exclusively anticipating qualities[6–8]. Zhu et al.[9] synthesized Co_3O_4 microspheres via hydrothermal route and reached a specific capacitance of 879 Fg^{-1}. Tian et al.[10] synthesized Co_3O_4 thin films using chemical bath deposition method which demonstrated a high specific capacitance of 743 Fg^{-1}.

There are various convenient procedures to synthesize desired Co_3O_4 nanostructures including co-precipitation, solvothermal, hydrothermal, chemical bath deposition and so on. Nan et al.[11] synthesized Co_3O_4/In_2O_3 nanostructures utilizing hydrothermal strategy. Luo et al.[12] synthesized composite of MXene-Co_3O_4 via solvothermal approach. Xiao et al.[13] evidenced the synthesize of Pt@Co_3O_4 by in situ methods. Barbieri et al.[14] synthesized cobalt oxide nanostructures with chemical deposition manner with the gain of 130 Fg^{-1} of specific capacitance.

Since transition metal oxides execute the redox reactions, the charge storage mechanism behind these supercapacitors is pseudocapacitive in nature. Hence the outcome obviously depends on the availability of electrode surface area for the redox reactions, flexibility and agglomerations of nanoparticles of electrode material, presence of pores in the nanostructures, dimensionality of the nanostructures. Hence synthesize of nanostructures with tunable morphology is being developed by different researchers[15]. Utilizing a number of synthesis procedures, a variety of morphological features of nanomaterials can be obtained. Zero dimensional (0D) nanomaterials include nanospheres and nanoclusters, one dimensional (1D) nanomaterials include nanorods, nanowires, nanotubes, nanofibers and two dimensional (2D) nanomaterials includes thin films, nanodiscs and nanoplates. Similarly, wide varieties of three dimensional (3D) structures like nanoballs, nanocoils, nanocones, nanopillars and nanoflowers can be synthesized. Luo et al.[16] synthesized Co_3O_4 with the 3D enoki mushroom-like structures. Raman et al.[17] synthesized Co_3O_4 with block and sphere morphology. Morphological structure which donates for highest electrochemical outputs with practical applications are most desired.

In this paper, transition metal oxides to be implemented in developing electrodes for supercapacitors are examined and Co_3O_4 is found to be the most anticipating material for this. A brief overview on the different synthesize procedures is carried and hydrothermal route of synthesize is considered as the best one to serve for the electrochemical features like high specific capacitance. Finally, the impact of zero to three dimensional Co_3O_4 nanostructures on electrochemical outputs likes specific capacitance, energy and power density are scrutinized. A three dimensional structure with its high efficiency is found to be at the topmost than all other dimensional morphology[18].

2. Result and discussion

A simple combination of electrode-separator network is folded and impregnated with the electrolyte to get a basic structure of a supercapacitor. Here the nature of electrodes forms a major contributor to the consequences of the supercapacitor applications. Nanostructured transition metal oxides are well known materials with most aspiring features to be used in the manufacture of electrodes. Presence of several oxidation states bring their applications to the next level. Due to this, extremely large number of conducting paths can be formed which increase the number of electrochemical redox reactions. Moreover, these materials demonstrate high electrical and electrochemical stability, fast and reversible redox reactions together with elevated cycling stability.

Based on observations of several investigations[19–27], **Figure 1** shows the maximum specific capacitance reached when composites of several transition metal oxides is used. For example, in case of ruthenium oxide, rGO/RuO_2 is used as the electrode material. Similarly composites of nickel oxide (NiO nanocrystals as electrodes), molybdenum oxide (carbon/α-MnO_2 electrodes), indium oxide (In_2O_3), iron oxide (Fe_3O_4), manganese oxide (MnO_2), cobalt oxide (Co_3O_4), vanadium pentoxide (V_2O_5), bismuth oxide (copper bismuth oxide electrode) are used in fabricating the electrode materials of supercapacitors. Besides these, there are some lesser used oxides like perovskite bismuth iron oxide, ferrites, Ti-V-W-O/Ti oxide, Na_2SO_3. But due to their various limitations and considerably lesser electrochemical outputs, they are not mentioned.

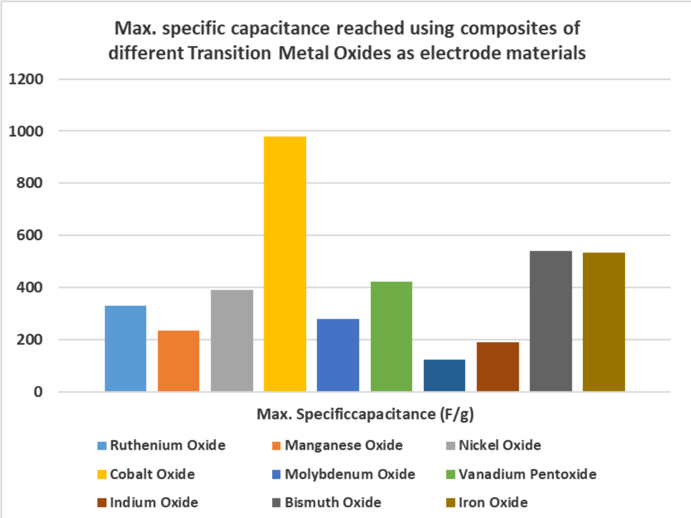

Figure 1. Maximum specific capacitance reached using composites of different transition metal oxides as electrode materials.

Among all the above transition metal oxides, cobalt oxide is found to demonstrate a highest specific capacitance value on account of its small band gap, structure of Co_3O_4 spinel, high crystallinity, high flexibility, exhibition of different morphological structures and utilization of maximum oxidation states. Pure Co_3O_4 and Co_3O_4-based composites submit maximum impression on the enhancement of electrochemical activity of the generated electrodes[28]. All the other transition metal oxides exhibited considerably lesser electrochemical performance compared with the electrodes developed by cobalt oxide spinels. Number of investigations is increased concentrating towards extracting several features of Co_3O_4 shows the efficiency of this spinel. Highly flexible Co_3O_4 nanostructures in various external features with high energy and power density values are employed in both pseudocapacitors and hybrid capacitors[29,30].

Synthesize strategy of these Co_3O_4 nanostructures in various appearance are large in counts applicable in accordance with convenience and availability of primary materials[31].

There are several which are time, cost and manpower saving approaches like hydrothermal, solvothermal, co-precipitation, in-situ, chemical bath deposition and solution combustion as mentioned in the **Figure 2**. This figure expresses the maximum specific capacitance exhibited by the differently prepared Co_3O_4 nanostructures used in the electrodes. Hydrothermal is a single step easy method where cobalt nitrate and urea solution is heated at 150 °C under high pressure followed by calcination for 24 h. Solvothermal includes dissolution of 0.1M of cobalt II acetylacetonate and 0.2 M of cobalt III acetylacetonate in dilute ethanol followed by heating at different temperatures under high pressure. Co-precipitation includes the drop-wise addition of cobalt nitrate solution to sodium hydroxide solution under constant temperature of 90 ℃ and a constant pH of 10. This is followed by the collection, filtration and calcination processes. In-situ synthesizes highly yields various metal-organic frameworks containing composites of Co_3O_4 nanostructures by various chemical reactions. Using precursor solution, a chemical bath method can be used by depositing thin films of required materials like Co_3O_4. A chemical bath was generated by using proper amount of solutions of 1 M $CoSO_4$, $NH_3 \cdot H_2O$, 0.25 M $K_2S_2O_8$ and demineralized water and it is deposited on a suitable substrate. Solution combustion method includes the distribution of ions from exothermic reactions in a sol gel medium. To synthesis Co_3O_4, various solvents like citric acid monohydrate, cobalt nitrate hexahydrate, and ammonium nitrate can be utilized in the form of fuel, oxidizer and combustion enhancer followed by calcination process[32–35]. When these techniques are electrochemically compared, Co_3O_4 nanostructure developed using hydrothermal technique submitted highest outputs.

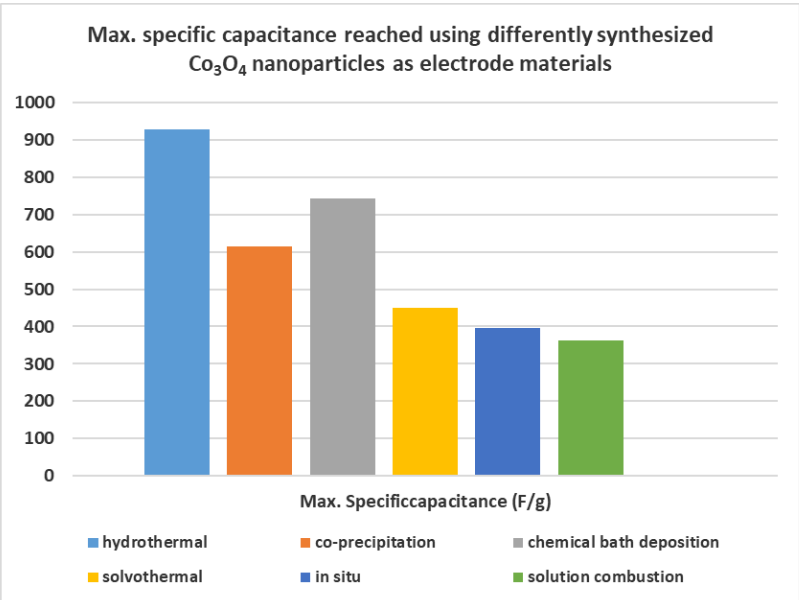

Figure 2. Maximum specific capacitance reached using differently synthesized Co_3O_4 nanoparticles as electrode materials.

The reason behind this can be justified as follows. Hydrothermal method is a soft chemical technique where an insoluble material at ambient temperatures is possible to make soluble at high temperatures and pressures. Hydrothermal technique shows maximum possibility to process the advanced materials from the bulk to nano range where toughest and the most complex compounds are synthesized[36]. A number of merits can be observed in hydrothermal method over other synthesize methods and it is used to bring out nanomaterials that are not stable at elevated temperatures[37,38]. Since the resultant nano powder is ultra pure, the high-temperature calcinations are not necessary. This fact eliminates the chance of re-clustering of nanoparticles and contamination. Nanoparticles with high vapor pressures can be prepared where stoichiometry of the reaction, the size, shape and composition of the resultant can be easily controlled. Purity of the prepared samples will be higher than the purity of the raw materials[39–41].

External morphology including shape, porosity, flexibility of the electrode material shows high impact on the electrochemical charge storage mechanism and hence on the efficiency of supercapacitor. Wang et al.[42] synthesized 3D nanonet hollow structure via heterogeneous precipitation method and obtained 820 F/g of specific capacitance. Hou et al.[43] developed microspherical structures of Co_3O_4 by co-precipitation technique and 614 F/g of specific capacitance was achieved. Piskin et al.[44] synthesized 1D zinc oxide/cobalt oxide composite with highest power density of 7500 Wg^{-1}. Co_3O_4 nanostructures which are used as the electrode materials exist in all 0, 1, 2 or 3D shapes synthesized via different routes[45–47]. **Figure 3** represents the relation between the maximum specific capacitance reached versus the dimensional morphology of Co_3O_4 nanostructures.

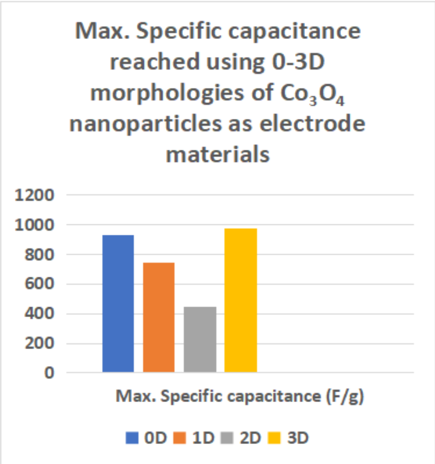

Figure 3. Relation between maximum specific capacitance and dimensional morphology of Co_3O_4 nanostructure.

0D nanomaterials exhibits high specific capacitance because of high conductance, chemical inertness, minimized agglomeration with high mechanical stability and high surface area available for the faradaic redox reactions when compared with to 1D or 2D nanomaterials. Yuan et al.[48] synthesized nanospheres for electrodes of supercapacitors with the specific capacitance of 928 Fg^{-1}. Deng et al.[49] showed that the high agglomeration of nanoparticles, the specific capacitance is decreased to 362 Fg^{-1}.

1D nanostructures of Co_3O_4 ensure external active area thereby facilitating the motion of charged particles due to the influence of nanoscopic scale. But only the longitudinal axis of the material is the major pathway for the electron transfer[50]. Gao et al.[51] developed nanowire arrays which could provide a specific capacitance of 746 Fg^{-1}. Different morphological types of 1D nanostructures can be formed by different folding of nanosheets with difference in their electrical conductivity.

In the 2D nanosized structures, even though surface area is available, it lacks depth and dimensions. Also due to the presence of point and line defects like vacancies, grain boundaries and pattern defects, crack, areal defects the conductivity will be reduced. Yuan et al.[52] fabricated 2D Co_3O_4 film with mesoporous walls with the 443 Fg^{-1} of specific capacitance. 3D nanomaterials are the most abundant materials on comparison with other dimensional materials.

3D nanoparticles can be arranged into layers on surfaces, availing a high surface area leading to the increased surface activities[53]. They provide high absorption sites in all dimensions to cover all the molecules present. In addition to this, a porous 3D nanostructures highly contribute to increased transportation of charged particles. 3D printing technology also favors the electrochemical results of the supercapacitors[54]. Zheng et al.[55] prepared 3D hierarchical structure of Co_3O_4 with the highest specific capacitance of 978 Fg^{-1}.

Nearly the similar result appears in the **Figures 4** and **5** which show the variation of energy and power density with respect to dimensional morphology of Co_3O_4 nanostructures[56,57]. The energy density (E, Wh kg^{-1}) and power density (P, W kg^{-1}) are calculated using the equations[58,59],

$$E = 0.5 \times C_S \times (\Delta V^2)/3.6$$

$$P = E \times 3600/\Delta t$$

where ΔV speaks for the potential window during discharging time Δt.

Variation in energy density can be observed when specific capacitance and potential window vary. Also, power density depends upon energy density and the discharge time[60–64]. In both the cases, as expected, 3D nanostructures provide huge amount of electrochemical outputs.

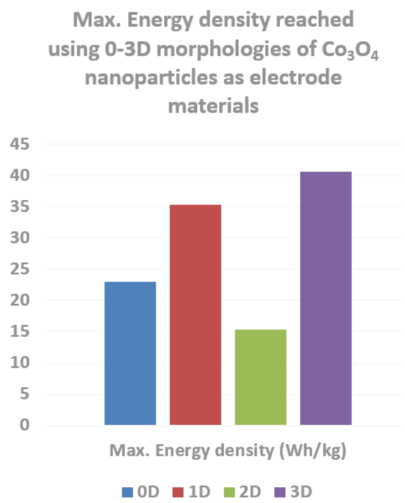

Figure 4. Relation between maximum energy density and dimensional morphology of Co_3O_4 nanostructure.

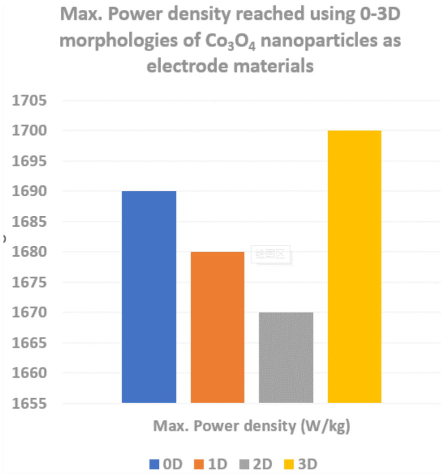

Figure 5. Relation between maximum power density and dimensional morphology of Co_3O_4 nanostructure.

3. Conclusion

Considering all transition metal oxides, Co_3O_4 is appraised as the efficient electrode material with innumerable practical merits. It can be synthesized by simple time saving, low cost procedures in various morphological structures. According to huge literature study, hydrothermal is found to be the most suitable methods which has provided high electrochemical outputs. Though all 0D to 3D nanostructured Co_3O_4 is widely used in the electrodes of supercapacitors, 3D structured have proven comparatively more efficient due to accessibility of large surface area, possibility of various shapes and porosity along with high conductance. Hence it leads to the enhanced electrochemical results like high specific capacitance, energy and the power density of a supercapacitor.

Conflict of interest: The authors declare no conflict of interest.

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