

Synthesis and characterization of cobalt oxide nanoparticles by using industrial pulp as impregnated precursor

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Cobalt oxide (Co_3O_4) nanoparticles were prepared using impregnation method associated with the liquid phase synthesis. Cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was used as a starting material, and industrial pulp was used as impregnated matrix. As a result of heat treatment of cobalt oxide precursors impregnated with pulp for one hour at a temperature range of 380-800 °C, cobalt oxide nanoparticles with a particle size of 100-500 nm were obtained. The crystallization process, morphology, and thermal decomposition were studied as a function of firing temperatures. The synthesized powders were evaluated by Scanning Electron Microscope (SEM), X-ray diffractometer (XRD), Thermo gravimetric analysis (TG) and Differential scanning calorimetry (DSC). It is found that the formation of Co_3O_4 crystal phase is generated at about 380 °C. The crystal phase of Co_3O_4 is maintained to a temperature of about 800 °C, and the size of the crystals has increased as the temperature increases. This Co_3O_4 crystal phase was changed to a CoO crystal phase at 900 °C.

Keywords: Nanoparticle, Cobalt oxide, Liquid phase synthesis.

Introduction

Cobalt oxides have been studied extensively due to a variety of applications in sensor, electromagnetic materials, photocatalyst, electrochromic device, and lithium ion battery. In addition Cobalt oxides have been used for R, G, B pixel barrier rib of flat panel display [1-5]. Cobalt oxide is a p-type semiconductor with direct optical band gaps at 1.48 and 2.19 eV. Co_3O_4 has a stable normal spinel structure. As a mixed valence compound, its formula is written as $\text{CoO} \cdot \text{Co}_2\text{O}_3$. Where Co^{2+} ions occupy the tetrahedral 8a sites and Co^{3+} occupy the octahedral 16d sites [6-9]. An industrial method of producing Co_3O_4 is to heat $\text{Co}(\text{OH})_2$ in air to a high temperature. In addition, it is synthesized by coprecipitation by adding carbonate, ammonia, sodium hydroxide, etc. to a salt of cobalt. Also, a method of manufacturing by hydrothermal synthesis has been reported [10-12]. Fig. 1 shows the steps of manufacturing the cobalt oxide (Co_3O_4) obtained industrially. In this process, CoSO_4 obtained by solvent extraction of cobalt ore was precipitated with sodium hydroxide to prepare cobalt hydroxide. After drying the cobalt hydroxide, and heated to a high temperature in air to produce a cobalt oxide (CoO , Co_3O_4). This method has the disadvantage of using a large amount of solvent in the step for obtaining the cobalt hydroxide. It can also be seen that the shape and size of the cobalt oxide particles synthesized by

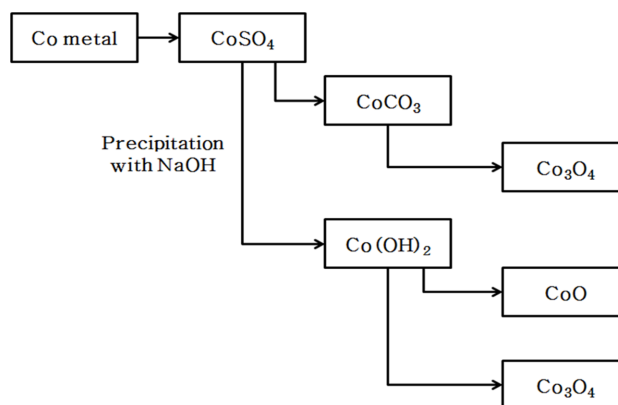


Fig. 1. Industrial manufacturing process of Co_3O_4 .

this method are uneven as shown in Fig. 2. Various liquid-phase syntheses of CoO and Co_3O_4 nanoparticles have been reported [13-17]. The precipitation operation common to these methods, since by using a large amount of solvent includes a step for obtaining a cobalt hydroxide precipitate is recovered and the processing cost of the solvent is a problem. By synthesis method used in this study is heat treated by impregnating a hydrate of a metal salt or metal salt in a polymer matrix to produce the ceramic fine particles, it is possible to easily manufacture the ceramic multi-component particles [18, 19]. The pulp used as a cellulose source in the impregnation operation and there is a microfibrillar structure of a size below 1 μm . Therefore, the shape of the particles produced after the heat treatment is a powder which particle size is uniform, depending on the microstructure of the pulp. This synthesis method

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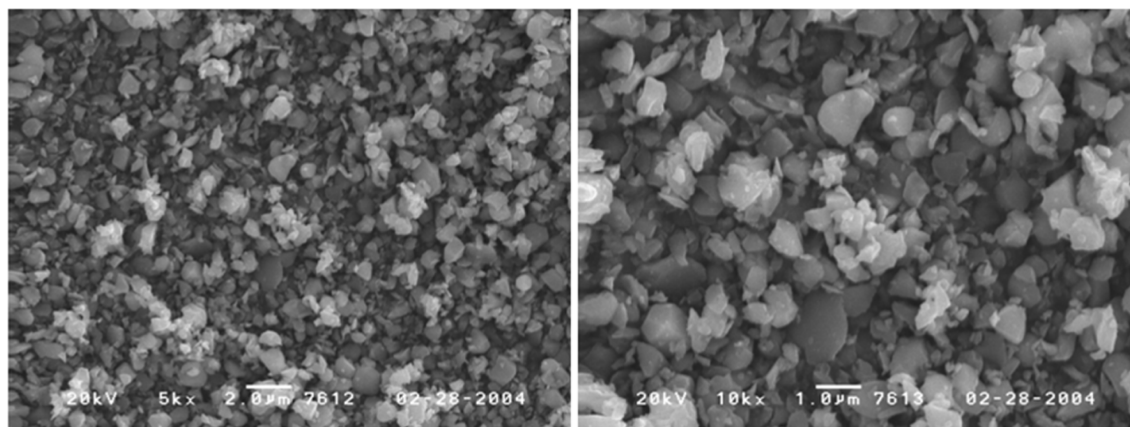


Fig. 2. SEM micrographs of commercial Co_3O_4 powders fabricated by solid reaction.

can easily control the particle size different from the type of the matrix or by changing the firing conditions [20]. And it has the advantage that you do not use strong alkaline organic solvents used in other synthesis methods, such as co-precipitation method. In this study by using a water-soluble cobalt compounds $\text{Co}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as the starting material was dissolved in water to prepare a cobalt salt solution. After the cobalt salt solution is impregnated to a pulp used in the polymer matrix, the cobalt oxide was prepared by heating at a lower temperature range; it was investigated by the difference between the particle formation processes according to the change in the heat treatment temperature.

Experimental

Preparation of cobalt oxide powder

Nano-sized Co_3O_4 particle have been synthesized by a liquid phase precursor technique using Cobalt nitrate hexahydrate as a source of Cobalt oxide. Pulp was used as a cellulose source. Fig. 3 shows a schematic flow diagram of a cobalt oxide nanoparticles prepared by the liquid phase precursor method used in this study. Dissolving a certain amount of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in distilled water to remove the ions, and then the saturated aqueous solution was prepared by stirring for 2 h at 25°C . The weight ratio of the saturated metal salt solution and the pulp used for the impregnation is 1:1. This impregnated mixture was dried at 80°C for 12 h, and heat treated in the temperature range of $380\text{--}900^\circ\text{C}$ for 1 hr in air with a heating rate of 5°Cmin^{-1} .

Characterization

The X-ray Diffraction (XRD) measurements of the calcined powder samples were carried out by using a Rigaku (RINT-2000) X-ray diffractometer with monochromated Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$). XRD patterns were recorded in the 2θ range from 10° to 80° at a resolution of 0.05° . Identification of phases was carried out by comparing the diffraction patterns with the standard PDF cards. In order to measure the size, shape

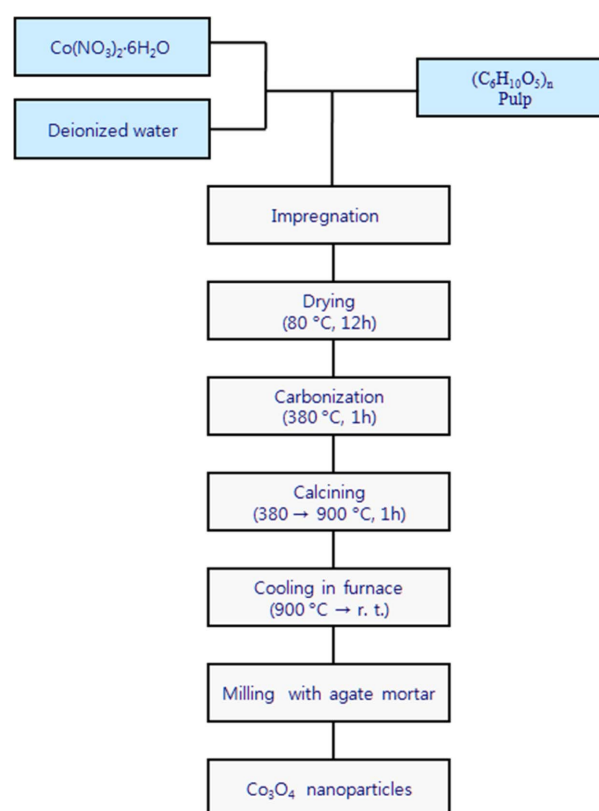


Fig. 3. Experimental procedure of preparing Co_3O_4 .

and distribution of Co_3O_4 powder particles, measurements were conducted using a field emission scanning electron microscope (FE-SEM, model JSM-6700, JEOL). For a more accurate comparative analysis of particle size and particle size distribution, the magnification of all samples was uniformly set to $30,000\times$, $50,000\times$, and $100,000\times$. All samples were covered with a thin gold layer. The thermal analysis of the impregnated precursor was determined by differential scanning calorimeter (Scinco DSC N-650) and thermogravimetric analysis (Scinco TGA N-1000). The heating rate of the sample was $10^\circ\text{C min}^{-1}$, with a flowing N_2 atmosphere.

Results and Discussion

In this study, liquid phase precursor method was used to prepare Co_3O_4 nanoparticles. Pulp, a cellulose polymer having a microfibril structure, was used as an impregnation medium. Dissolving the cobalt nitrate in deionized water, it was impregnated in pulp with a micro fibril structure of microscopic size less than $1\ \mu\text{m}$. The dissolved cobalt nitrate aqueous solution is stirred sufficiently to uniformly disperse the pulp. The particle size of the Co_3O_4 fine particles obtained by heat treatment was uniform, and this Co_3O_4 particle was excellent crystallinity. Fig. 4 shows the micro structure change of pulp before and after impregnation. Fig. 4(a) shows the pure pulp prior to impregnation, Fig. 4(b) shows the microstructure of the pulp that was dried by impregnating it with an cobalt nitrate aqueous solution. Raw material solution of the cobalt nitrate solution, as shown in Fig. 4(b) it can be seen that it is uniformly impregnated in the fine structure of the polymer micro fibrils. Fig. 5 shows a process to perform

the impregnation operation. It was impregnated by changing the weight ratio of the cobalt nitrate solution and the pulp to 0.5-1.5. A cobalt salt aqueous solution with a weight ratio of pulp 1:1 or less, the amount of pulp than the cobalt salt solution is the cause of degradation of purity after firing because of the presence in excess. On the other hand, when the weight ratio of the cobalt salt solution and the pulp is 1:1 or more, an excessive amount of unimpregnated aqueous solution is present. Therefore, even after the impregnated pulp is dried, cobalt nitrate crystals remain on the surface of the pulp. They are the cause of action of the non-uniform distribution of particles because it failed to enter the micro fibril structure of the pulp. Therefore, In this study, the weight ratio of the aqueous solution of cobalt nitrate and pulp 1:1 was carried out to determine the impregnation operation. In order to examine the thermal weight decrease properties of the impregnated mixture, Thermogravimetric analysis (TGA) results is shown in Fig. 6. Between $120\ ^\circ\text{C}$ and $200\ ^\circ\text{C}$ showed a weight loss due to evaporation of the crystal water in

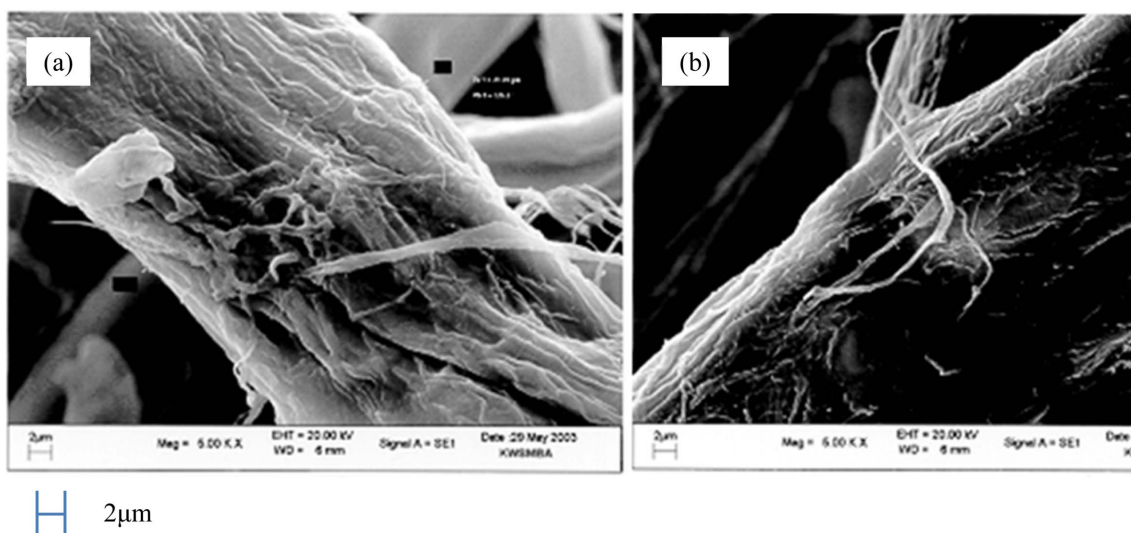


Fig. 4. SEM photographs of (a) pure pulp and (b) pulp impregnated with solution of cobalt nitrate.

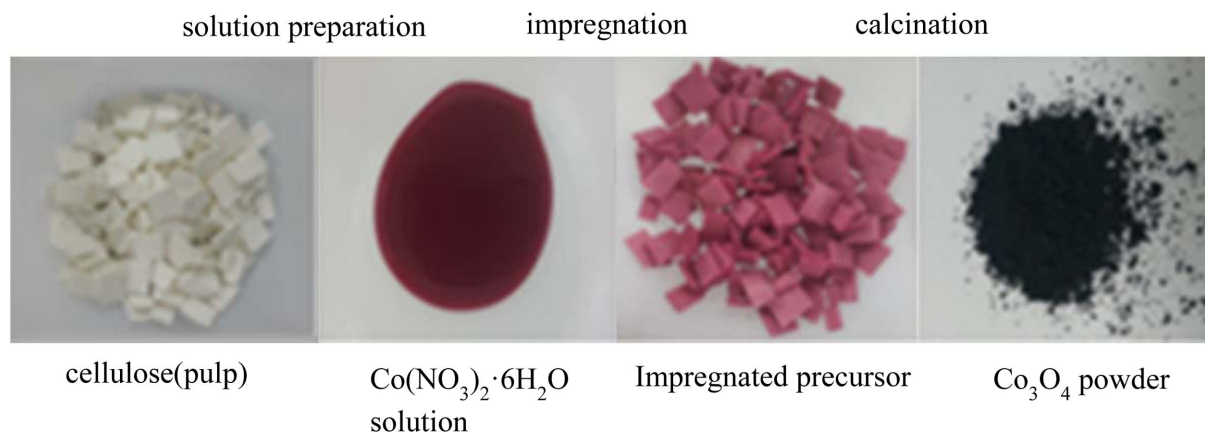


Fig. 5. Impregnation and calcination procedure of Co_3O_4 nanoparticle.

the precursor. At temperatures between 340 °C and 380 °C after showing a remarkable weight decrease due to thermal decomposition of the organic matter in the precursor, gradually modest weight loss is continued until 520 °C. A moderate weight loss appeared between 380 °C and 520 °C has shown that the organic components contained in the starting material and fibrous components of the pulp to be completely thermally decomposed, in the above 520 °C did not show a weight decrease. Fig. 7 shows the DSC curve of the impregnated mixture. As shown in Fig. 7, between 327-354 °C showed an endothermic peak due to thermal decomposition of the organic material. Therefore, the heat treatment temperature of the impregnated mixture was set to above 354 °C. A thermal decomposition of the organic material and the creation of cobalt oxide during the heat treatment is can be estimated that proceeds as shown in the following expression.

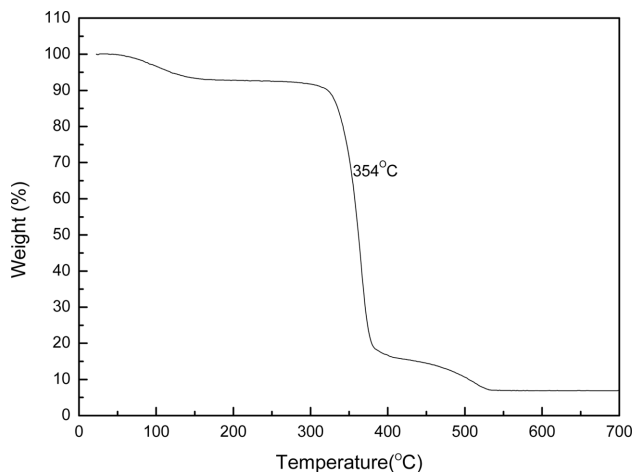
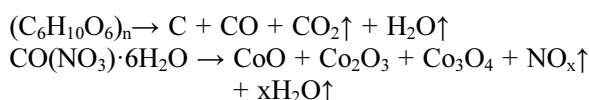


Fig. 6. TG analysis of impregnated precursor.

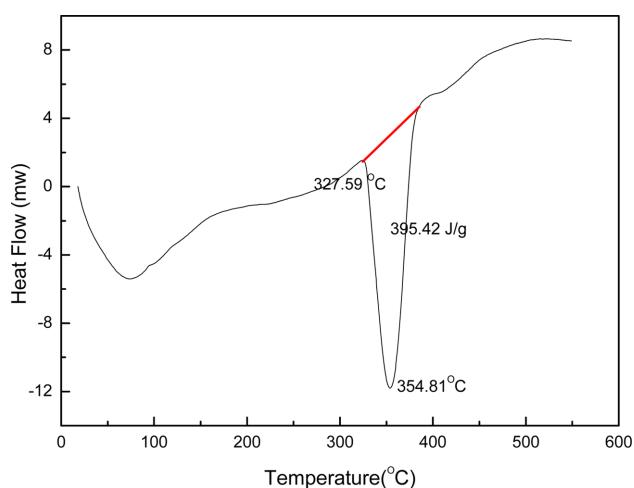


Fig. 7. DSC analysis of impregnated precursor.

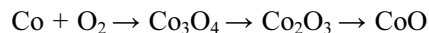


Fig. 8 shows the XRD patterns of Co_3O_4 powders calcined at 380 °C, 500 °C, 700 °C and 800 °C, respectively. As shown in the figure, the diffraction peaks ($2\theta = 31^\circ, 37^\circ, 44^\circ, 56^\circ, 59^\circ, 65^\circ$) of Co_3O_4 were distinctly observed. As the primary peaks exhibiting high diffraction intensity were in good agreement with the standard JCPDS card No. 43-1003, the crystalline phase of the synthesized Co_3O_4 is confirmed. The heating rate and the calcination time for all experiments were fixed at 5 °C/min and 1 h, respectively. At 380 °C, the crystalline phase of Co_3O_4 started to form, and with increase in the calcination temperature from 500-800 °C, the intensity of the peaks also increased, indicating progress in crystallization. Fig. 9 shows SEM images of the Co_3O_4 powder prepared by calcination of the impregnated precursor, which measures the surface structure of the prepared Co_3O_4 particles at a fixed calcination time of 1 h and by the variation of temperature from 500-800 °C. As can be observed in the XRD pattern in Fig. 8, at 500 °C, Co_3O_4 crystals had already formed. We can see that most of the particles exhibit a granular morphology. Fig. 9(a) the sample was calcined to 500 °C was the start of Co_3O_4 crystal phase are generated, Fig. 9(b) in the sample calcined at 600 °C, the size of the growing up of the particle was grown to the 100-200 nm, Fig. 9(c) calcined at 700 °C, the growth of the particles were further expanded. In Fig. 9(d), with the increase in the calcination temperature to 800 °C, crystallinity increased, with growth in the particle size (100-500 nm). From the above results, such as Co_3O_4 crystal phase is being formed from a relatively low temperature in about 350 °C, and was available a uniform fine powder prepared in the nanometer order was confirmed that single-phase Co_3O_4 is generated in a temperature range of 380-800 °C.

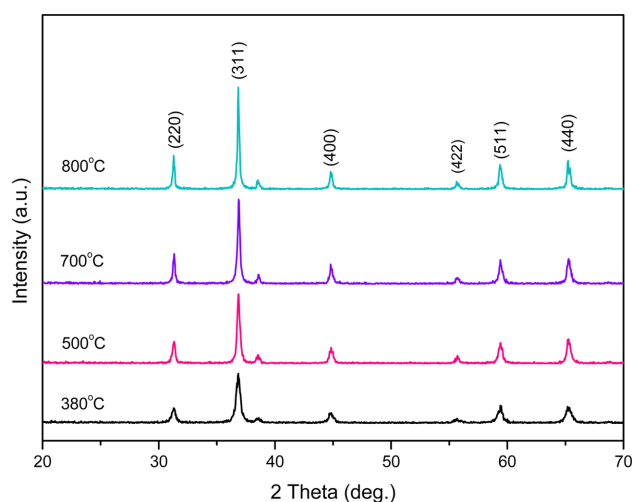


Fig. 8. XRD patterns of Co_3O_4 powders with various calcining temperature.

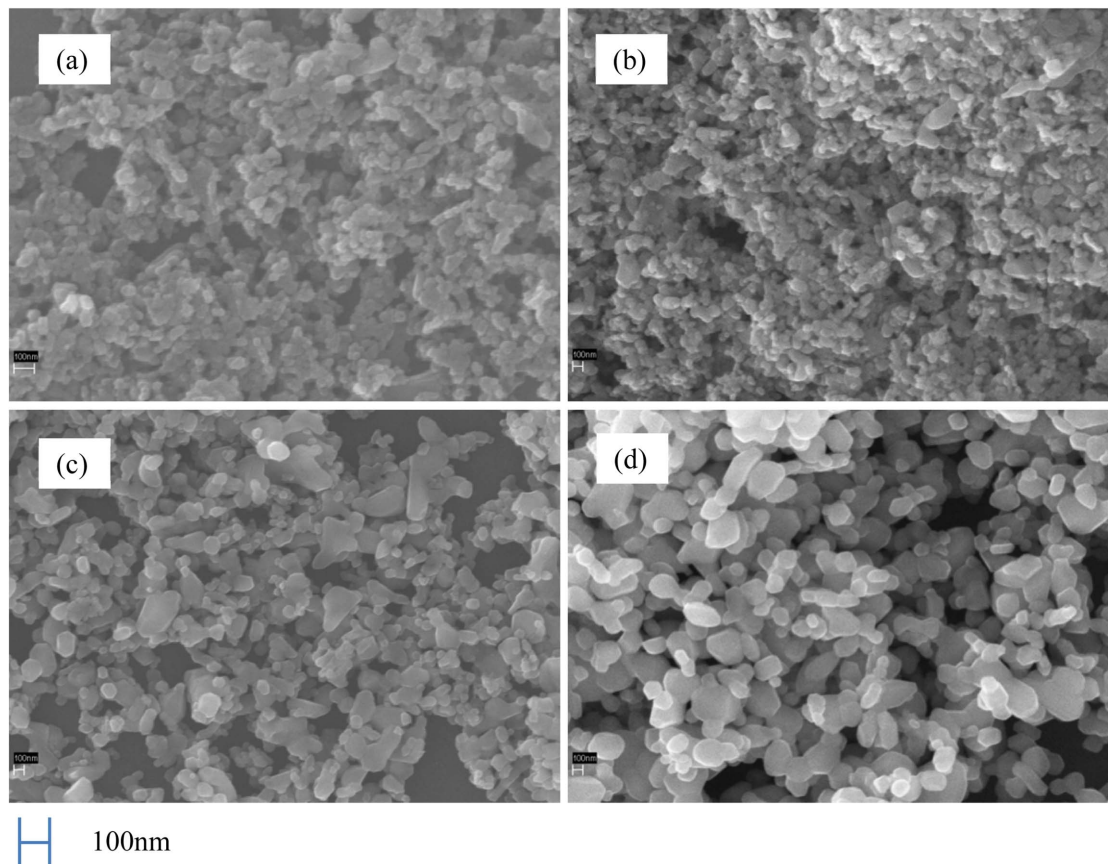


Fig. 9. SEM micrographs of calcined powders, (a) 500 °C, (b) 600 °C, (c) 700 °C and (d) 800 °C.

Conclusions

In this study, Co_3O_4 nanoparticles were synthesized by the simple impregnation method. Cobalt nitrate was impregnated with pulp, a polymer matrix, and calcined to prepare Co_3O_4 nanoparticles. The method of synthesizing these Co_3O_4 nanoparticles is simple and inexpensive. Also, as in the case of the synthesis method by the precipitation method, there is an advantage that the wastewater treatment of the precipitation solution is not necessary. The XRD result indicates the formation of the single phase of Co_3O_4 . At a temperature ranging from 380 °C to 800 °C, with increasing calcinations temperature, crystallization was accelerated, and particle growth (100-500 nm) was observed.

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