

Effects of dopant materials on the characteristics of the nano-sized Co_3O_4 powders prepared by spray pyrolysis

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Pure and M-doped Co_3O_4 (M = Cr, Fe, Mg, Zr) powders with a nanometre size and a narrow size distribution were prepared by spray pyrolysis from a spray solution with citric acid and ethylene glycol. The precursor powders with a hollow and thin walled structure were turned to nano-sized Co_3O_4 powders after post-treatment. The mean size of the pure Co_3O_4 powders post-treated at a temperature of 600 °C was 77 nm. On the other hand, the mean sizes of the doped Co_3O_4 powders with a doping concentration of 3 mol.% were changed from 24 to 63 nm. The Mg-doped Co_3O_4 powders had the minimum mean size. The mean sizes of the Mg-doped Co_3O_4 powders with doping concentrations of 1 and 5 mol.% were 60 and 61 nm. The mean sizes of the Mg-doped Co_3O_4 powders with a doping concentration of 3 mol.% post-treated at temperatures of 700 and 800 °C were 63 to 102 nm.

Key words: Spray pyrolysis, Cobalt oxide, Nano powders, Gas phase reaction, Black matrix, Display material.

Introduction

Cobalt oxide (Co_3O_4) powders has been extensively used as the material for solid sensors, ceramic pigments, intercalation compounds for energy storage, rotatable magnets, heterogeneous catalysts, and electrochromic devices [1-3]. The performance of Co_3O_4 powders in their applications is influenced by the morphology, mean powder size, size distribution, and crystallinity. In particular, the properties of Co_3O_4 powders are strongly related to the mean powder size. Nano-sized Co_3O_4 powders are mainly used as a material of the black matrix for flat panel displays. The black matrix is a black coating layer surrounding pixels of a display device. The black matrix is used to improve the contrast of flat panel displays such as plasma display panels (PDP). When applied to the substrate of the display device, the black matrix exhibits an excellent external light absorbing effect. Therefore, a display device having improved luminance and contrast characteristics can be attained.

A black matrix pattern was formed on a glass substrate by a lithography process. The characteristics of the black matrix pattern are strongly affected by the properties of the black paste. Therefore, nano-sized Co_3O_4 powders prepared by various liquid-solution and gas phase reaction methods were tried as the black matrix material [4-9]. Spray pyrolysis, which is one of the gas-phase reaction methods, has been widely used to synthesize the ceramic powders because it is a simple and continuous process. The powders prepared by conventional spray pyrolysis have submicro-

metre or micrometre sizes because of a droplet-to-powder conversion process. Nano-sized oxide powders have also been prepared by spray pyrolysis applying the polymeric precursors [9, 10]. The precursor powders formed by spray pyrolysis from the polymeric precursors were turned into nano-sized oxide powders with a narrow size distributions after post-treatment at high temperatures. Therefore, nano-sized oxide powders prepared by spray pyrolysis had a high crystallinity and a high purity without organic contamination. A small amount of dopants could be expected to aid control of the grain-growth rate during the post-treatment process at high temperatures. Therefore, dopants could be applied to control the growth of the nano-sized powders.

In this study, nano-sized Co_3O_4 powders with a uniform morphology and a narrow size distribution were prepared by spray pyrolysis from a spray solution containing citric acid and ethylene glycol. The effects of dopant materials on the morphology, mean powder size and crystallinity of the M-doped Co_3O_4 (M = Cr, Fe, Mg, Zr) powders prepared by spray pyrolysis were investigated.

Experimental Procedure

The spray pyrolysis system consists of a droplet generator, a quartz reactor, and a powder collector. A 1.7-MHz ultrasonic spray generator with six vibrators was used to generate a large amount of droplets, which were carried into the high-temperature tubular reactor by a carrier gas. The droplets and powders evaporated, decomposed, and/or crystallized in the quartz reactor. The length and diameter of the quartz reactor are 1,200 and 50 mm, respectively. The precursor solutions were prepared by dissolving stoichiometric ratios of cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$,

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Aldrich), chromium (III) nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Aldrich), iron (III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Aldrich), magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Aldrich) and zirconyl nitrate hydrate ($\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, Aldrich) in distilled water. The total concentration of cobalt and dopant precursors was fixed at 0.3 M. The doping concentrations of Cr, Fe, Mg and Zr component were changed from 1 to 5 mol.% of the cobalt component. The concentrations of citric acid and ethylene glycol used as organic additives were each 0.3 M. The flow rate of air used as carrier gas was 40 Lmin^{-1} . The precursor powders prepared by spray pyrolysis at 700°C were post-treated in a box furnace at temperatures between 600°C and 800°C .

The crystal structures of pure and doped Co_3O_4 powders

were investigated using X-ray diffractometry (XRD, RIGAKU, DMAX-33). The mean crystallite sizes of the Co_3O_4 powders were estimated from Scherrer's equation. The morphological characteristics of the powders were investigated using scanning electron microscopy (SEM, JEOL, JSM 6060) and TEM (TEM, FEI, TECHNAI 300 K). Surface area measurements were done by the Brunauer-Emmett-Teller (BET, PROTECH, TRISTAR 3000) method using N_2 as the adsorbate gas.

Results and Discussions

Fig. 1 shows the SEM images of the pure and doped Co_3O_4 powders prepared by spray pyrolysis. The doping

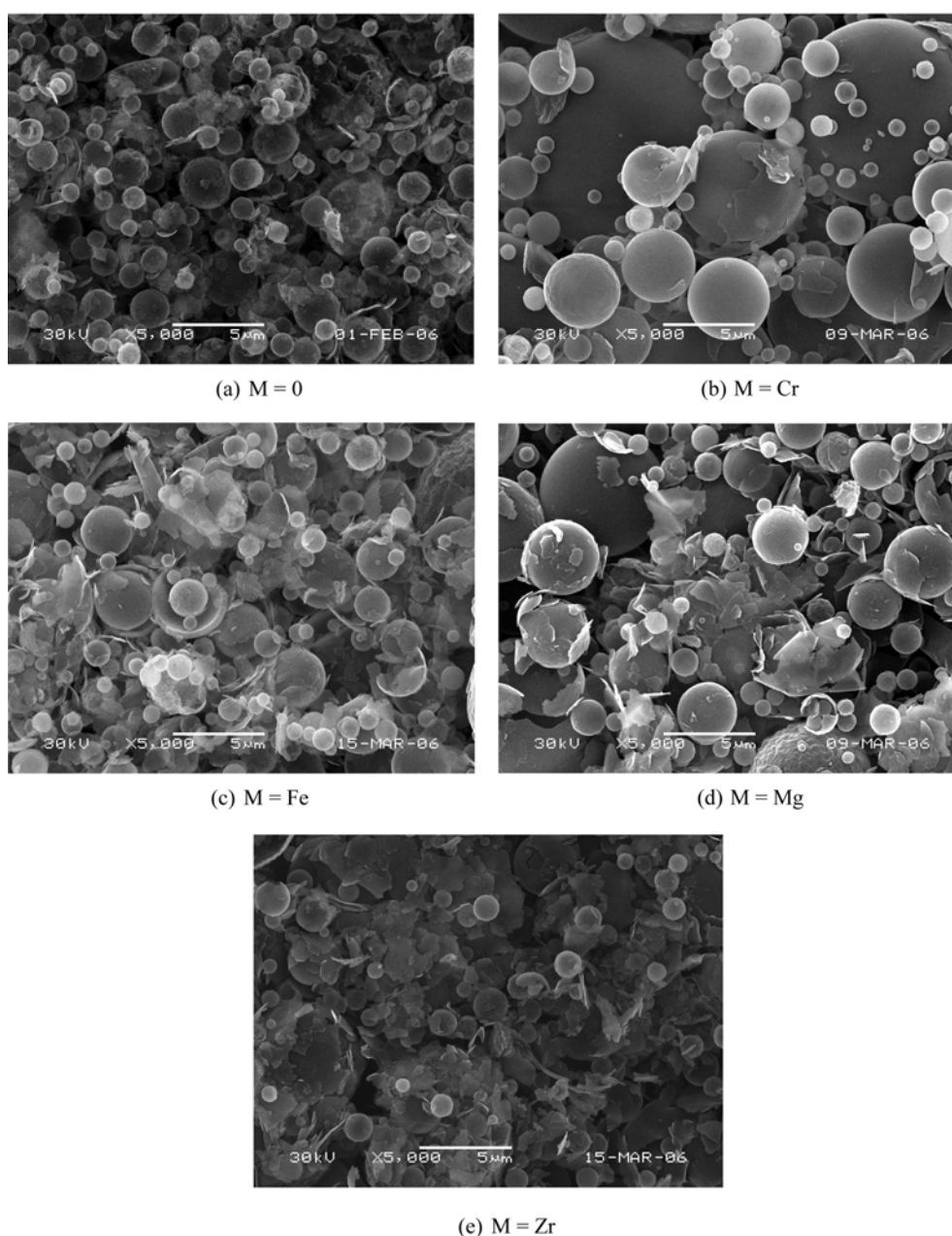


Fig. 1. SEM images of the precursor $\text{Co}_3\text{O}_4/\text{MO}_x$ ($\text{M} = \text{Cr}, \text{Fe}, \text{Mn}, \text{Zr}$) powders prepared by spray pyrolysis.

concentration of Cr, Fe, Mg, and Zr components was fixed at 3 mol.% of cobalt component. The powders were several micrometres in size, hollow and thin wall structures irrespective of the doping material. The severe preparation conditions of high flow rate of the carrier gas and short residence time of the powders produced the powders with hollow and thin wall structures. Addition of citric acid and ethylene glycol into the spray solution improved the hollowness of the precursor powders by gas evolution from the decomposition of the organic materials.

The effects of the type of doping material on the morphologies of the post-treated M-doped Co_3O_4 (M = Cr, Fe,

Mg, Zr) powders are shown in Fig. 2. The precursor powders obtained by spray pyrolysis were post-treated at a temperature of 600 °C for 3 h. The concentration of doping materials was 3 mol.% of the cobalt component. The post-treated powders had different morphologies to those of the precursor powders obtained by spray pyrolysis. The spherical shape of the precursor powders with micrometre sizes disappeared after post-treatment. The post-treated pure and doped Co_3O_4 powders had a fine size and regular morphology. The precursor powders with hollow and thin wall structures were turned into the fine size Co_3O_4 powders during the post-treatment process irrespective of

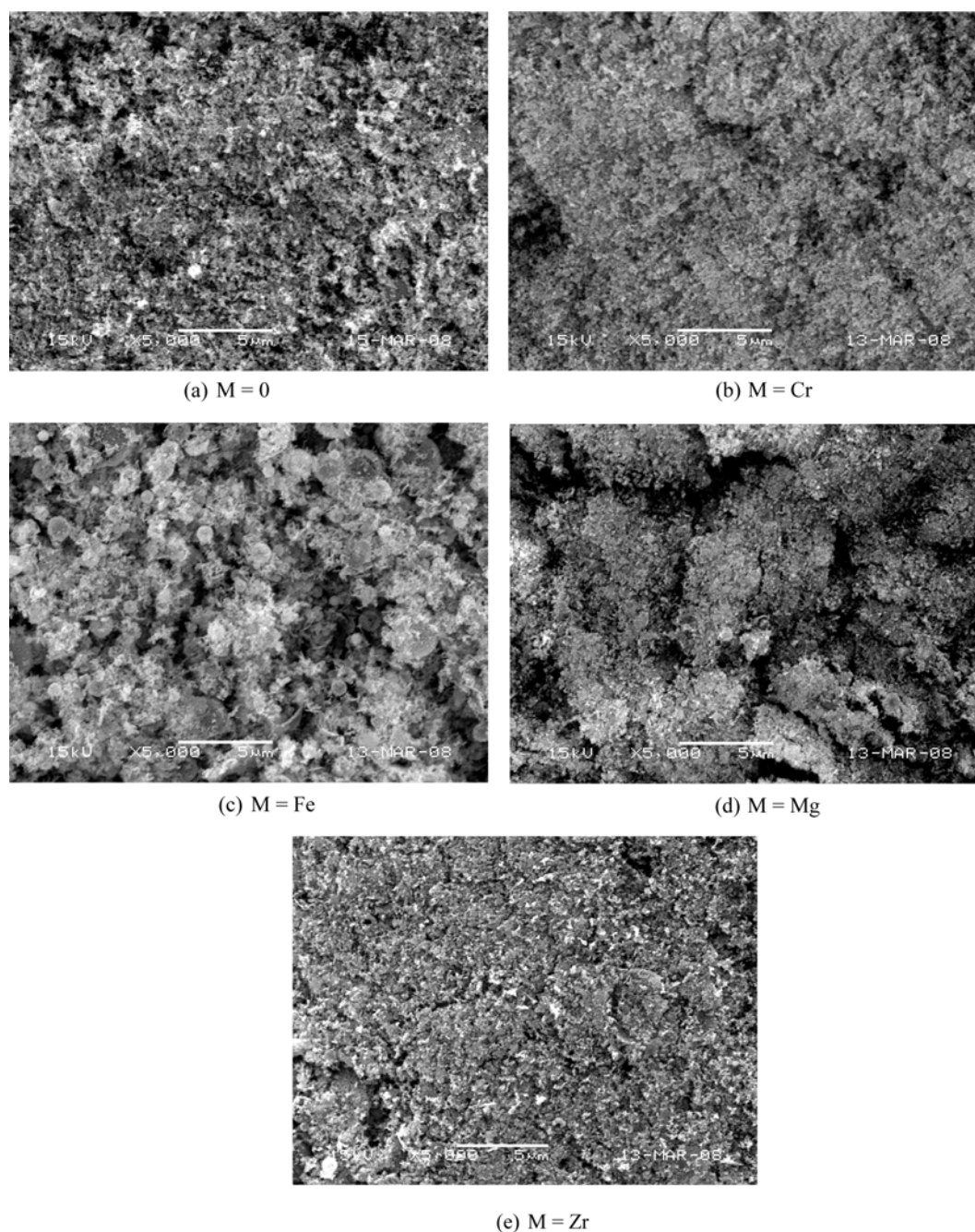


Fig. 2. SEM images of the pure and M-doped Co_3O_4 powders post-treated at a temperature of 600 °C.

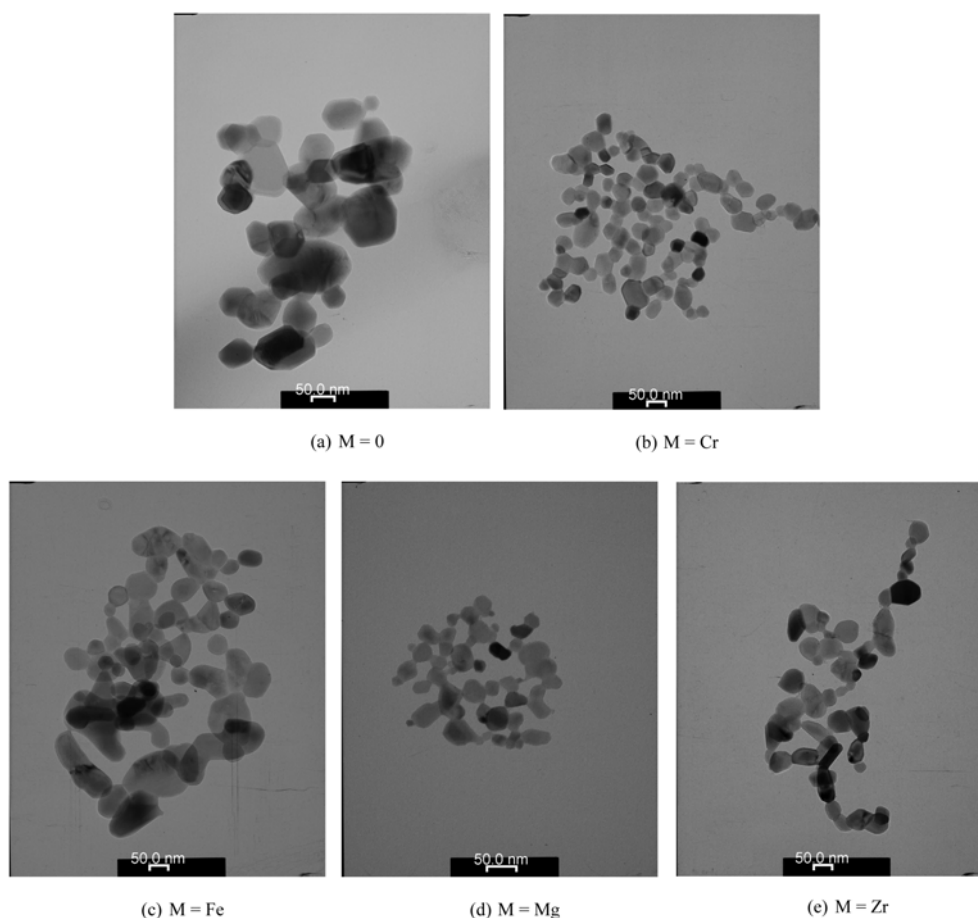


Fig. 3. TEM images of the pure and M-doped Co_3O_4 powders post-treated at a temperature of 600 °C.

the doping material. However, the doping material affected the mean sizes of the post-treated Co_3O_4 powders. Fig. 3 shows the TEM images of the post-treated pure and doped Co_3O_4 powders. The TEM samples were prepared by dispersing the powders milled by hand using an agate mortar in ethyl alcohol. The nano-sized powders had slightly aggregated structures between the powders. The mean sizes of the powders were affected by the type of the doping material. The mean size of the pure Co_3O_4 powder measured from a TEM image was 77 nm. On the other hand, the mean sizes of the doped Co_3O_4 powders doped with Cr, Fe, Mg, and Zr were 40, 63, 24, and 50 nm, respectively. The Mg-doped Co_3O_4 powder had a finer size than those of the Cr, Fe and Zr-doped Co_3O_4 powders. The BET surface areas of the powders are shown in Table 1. The doped Co_3O_4 powders had larger surface areas than that of the pure Co_3O_4 powder. The Mg-doped Co_3O_4

powders had the largest BET surface area of 36 m^2/g .

The XRD patterns of the pure and doped Co_3O_4 powders post-treated at a temperature of 600 °C are shown in Fig. 4. All the diffraction peaks can be perfectly indexed to a cubic phase of Co_3O_4 . The post-treated powders had a pure cubic phase of Co_3O_4 irrespective of the type of doping material.

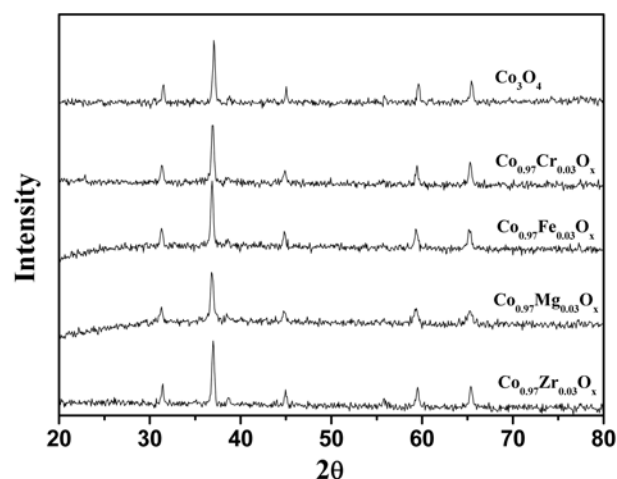


Fig. 4. XRD patterns of the pure and M-doped Co_3O_4 powders post-treated at a temperature of 600 °C.

Table 1. Characteristics of pure and doped Co_3O_4 powders

Doping material	No	Cr	Fe	Mg	Zr
BET surface area (m^2/g)	11	12	18	36	15
Mean powder size (nm)	77	40	63	24	50
Mean crystallite size (nm)	29	25	29	24	29

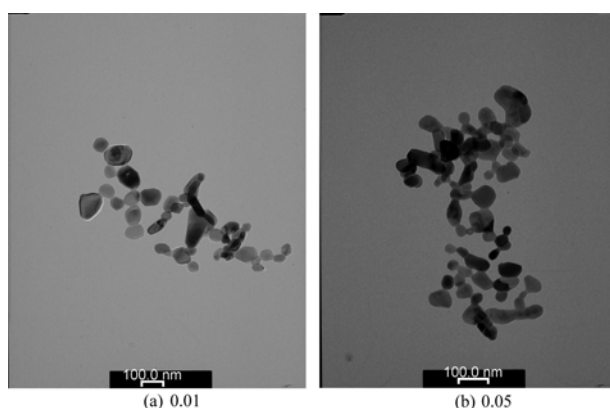


Fig. 5. TEM images of the Mg-doped Co_3O_4 powders with different doping concentrations.

The mean crystallite sizes of the pure and doped Co_3O_4 powders are shown in Table 1. The mean crystallite sizes of the Co_3O_4 powders were changed from 24 to 29 nm according to the type of doping material. The mean size of the Mg-doped Co_3O_4 powder measured on a TEM image and the mean crystallite size measured from the XRD pattern were the same at 24 nm. Therefore, the Mg-doped Co_3O_4 powder particles as shown in Fig. 3(d) were single crystals.

The effects of the doping concentrations of the Mg component on the mean sizes, BET surface areas and mean crystallite sizes were investigated. Fig. 5 shows the TEM images of the Mg-doped Co_3O_4 powders with different doping concentrations. The doping concentrations of the magnesium component were 1 and 5 mol.% of the cobalt component. The precursor powders obtained by spray pyrolysis were post-treated at temperature of 600 °C for 3 h. The doping concentrations of the magnesium component affected the mean sizes of the Mg-doped Co_3O_4 powders. The mean sizes of the Mg-doped Co_3O_4 powders with doping concentrations of 1 and 5 mol.% were 60 and 61 nm. However, the mean size of the Mg-doped Co_3O_4 powders with a doping concentration of 3 mol.% was 24 nm. The mean sizes of the Mg-doped Co_3O_4 powders decreased with an increase in the doping concentrations of the magnesium component below 3 mol.%. However, the doping with the magnesium component at a high concentration of 5 mol.% increased the mean size of the Mg-doped powders. The BET surface areas of the Mg-doped Co_3O_4 powders with doping concentrations of 1 and 5 mol.% were 18 and 17 m^2/g . Fig. 6 shows the XRD patterns of the Mg-doped Co_3O_4 powders. The mean crystallite sizes of the Mg-doped Co_3O_4 powders with doping concentrations of 1 and 5 mol.% were 31 and 27 nm, respectively. The Mg-doped Co_3O_4 powders with a doping concentration of 3 mol.% had the lowest mean crystallite size of 24 nm.

The morphologies and mean sizes of the Mg-doped Co_3O_4 powders with a doping concentration of 3 mol.% post-treated at different temperatures were investigated by TEM images as shown in Fig. 7. In Figs. 3 and 7, the mean sizes of the Mg-doped Co_3O_4 powders increased

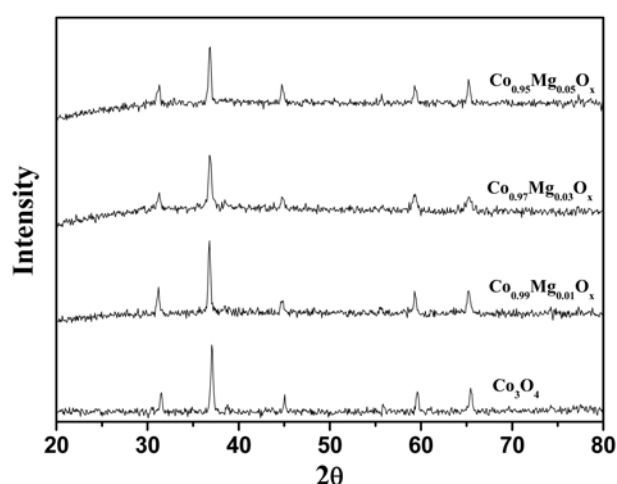


Fig. 6. XRD patterns of the Mg-doped Co_3O_4 powders with different doping concentrations.

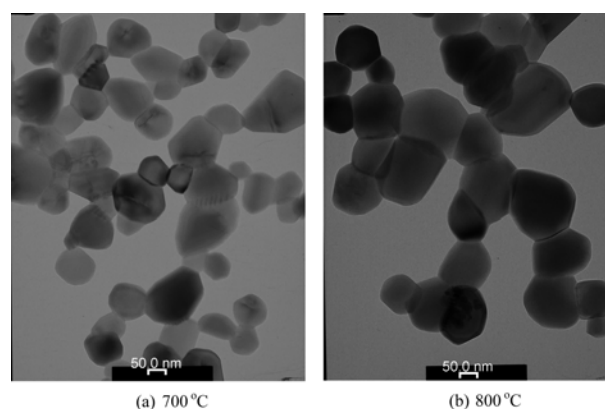


Fig. 7. TEM images of the Mg-doped Co_3O_4 powders post-treated at different temperatures.

with an increase in the post-treatment temperature. The mean sizes of the Mg-doped Co_3O_4 powders post-treated at temperatures of 700 and 800 °C were 63 to 102 nm. The Mg-doped Co_3O_4 powders had slightly aggregated structures even at a high post-treatment temperature of 800 °C. Therefore, post-treatment temperature was a powerful variable to control the mean sizes of the Mg-doped Co_3O_4 powders.

Conclusions

Pure and doped Co_3O_4 powders with a nanometre size were prepared by spray pyrolysis. The type of doping material, doping concentration and post-treatment temperature changed the mean size of the Co_3O_4 powders. Magnesium was an efficient doping material to prepare Co_3O_4 powders with a nanometre size under 30 nm. The optimum doping concentration of the Mg component was 3 mol.% of the cobalt component. Post-treatment temperature was a powerful variable to control the mean size of the Mg-doped Co_3O_4 powders. Therefore, the mean sizes of the Mg-doped Co_3O_4 powders could be controlled from 24 to

102 nm by changing the post-treatment temperatures between 600 and 800 °C.

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References

1. W.Y. Li, L.N. Xu and J. Chen, *Adv. Funct. Mater.* 15 (2005) 851-857.
2. Y. Yamaura, J. Tamaki, K. Moriya, N. Miura and N. Yamazoe, *J. Electrochem. Soc.* 144 (1997) 158-160.
3. P. Nkeng, J.F. Koenig, J.L. Gautier, P. Chartier and G. Poillerat, *J. Electroana. Chem.* 402 (1996) 81-89.
4. J. Jiu, Y. Ge, X. Li and L. Nie, *Mater. Lett.* 54 (2002) 260-263.
5. Y. Ni, X. Ge, Z. Zhang, H. Liu, W. Whu and Q. Ye, *Mater. Res. Bull.* 36 (2001) 2383-2387.
6. H. Yang, Y. Hu, X. Zhang and G. Qiu, *Mater. Lett.* 58 (2004) 387-389.
7. Y. Jiang, Y. Wu, B. Xie, Y. Xie and Y. Qian, *Mater. Chem. Phys.* 74 (2002) 234-237.
8. N. Koshiaki, A. Narazaki and T. Sasaki, *Scripta Mater.* 44 (2001) 1925-1928.
9. D.Y. Kim, S.H. Ju, H.Y. Koo, S.K. Hong and Y.C. Kang, *J. Alloy. Comp.* 417 (2006) 254-258.
10. S.H. Ju, D.Y. Kim, H.Y. Koo, S.K. Hong, E.B. Jo and Y.C. Kang, *J. Alloy. Comp.* 425 (2006) 411-415.