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# Catalytic properties of $\text{Co}_3\text{O}_4$ nanoparticles for rechargeable Li/air batteries

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## Abstract

Three types of  $\text{Co}_3\text{O}_4$  nanoparticles are synthesized and characterized as a catalyst for the air electrode of a Li/air battery. The shape and size of the nanoparticles are observed using scanning electron microscopy and transmission electron microscopy analyses. The formation of the  $\text{Co}_3\text{O}_4$  phase is confirmed by X-ray diffraction. The electrochemical property of the air electrodes containing  $\text{Co}_3\text{O}_4$  nanoparticles is significantly associated with the shape and size of the nanoparticles. It appears that the capacity of electrodes containing villiform-type  $\text{Co}_3\text{O}_4$  nanoparticles is superior to that of electrodes containing cube- and flower-type  $\text{Co}_3\text{O}_4$  nanoparticles. This is probably due to the sufficient pore spaces of the villiform-type  $\text{Co}_3\text{O}_4$  nanoparticles.

**Keywords:** composites, nanostructures, chemical synthesis, electrochemical properties.

## Introduction

A significant increase in the energy density of rechargeable batteries is required to satisfy the demands of vehicular applications and energy storage systems. One approach to solving this problem is the introduction of a new battery system having a higher energy density. Li/air batteries are potential candidates for advanced energy storage systems because of their high storage capability [1-3]. They do not store a 'cathode' in the system, which allows for a higher energy density than any other commercial rechargeable batteries. Instead, oxygen from the environment is reduced by a catalytic surface inside the air electrode. Thus, catalysts are key materials that affect the capacity, cycle life, and rate capability of such batteries.

In this study, the  $\text{Co}_3\text{O}_4$  nanoparticles of various shapes and structures were tested as catalysts of air electrodes for rechargeable Li/air batteries.  $\text{Co}_3\text{O}_4$  with a spinel structure has attracted a considerable interest as a potential catalyst in various application fields [4-7]. In particular, this study was motivated by the notion that the catalytic efficiency of oxides is highly dependent on their morphology, size, and crystal structure [8,9]. Herein, three types of  $\text{Co}_3\text{O}_4$  of various shapes and

morphologies were synthesized, and the electrochemical properties of the air electrodes containing  $\text{Co}_3\text{O}_4$  nanoparticles were characterized.

## Experimental details

Three types of  $\text{Co}_3\text{O}_4$  nanoparticles were prepared by a hydrothermal reaction using cobalt nitrate (cube type, flower type) and cobalt chloride (villiform type), considering previous reports [10,11]. Surfactants such as urea were also added to obtain nanosized particles. X-ray diffraction [XRD] patterns of powders were measured using a Rigaku X-ray diffractometer (Rigaku Corporation, Tokyo, Japan). The microstructure of the powder was observed by field-emission scanning electron microscopy [FE-SEM] (JEOL-JSM 6500F, JEOL Ltd., Akishima, Tokyo, Japan) and field-emission transmission electron microscopy [FE-TEM] (JEOL-JEM 2100F JEOL Ltd., Akishima, Tokyo, Japan). The electrochemical performance of the air electrode containing  $\text{Co}_3\text{O}_4$  nanoparticles was examined using a modified Swagelok cell, consisting of a cathode, a metallic lithium anode, a glass fiber separator, and an electrolyte of 1 M LiTFSI in EC/PC (1:1 vol.%). The cathode contained carbon (Ketjen black EC600JD, Akzo Nobel, Amsterdam, The Netherlands; approximately  $1420 \text{ m}^2\cdot\text{g}^{-1}$ ), catalysts ( $\text{Co}_3\text{O}_4$  nanoparticles), and a binder (PVDF; Sigma-Aldrich, St. Louis, MO, USA). The molar ratio of carbon to catalysts was adjusted to 95:5. The binder accounted for 20 wt.%

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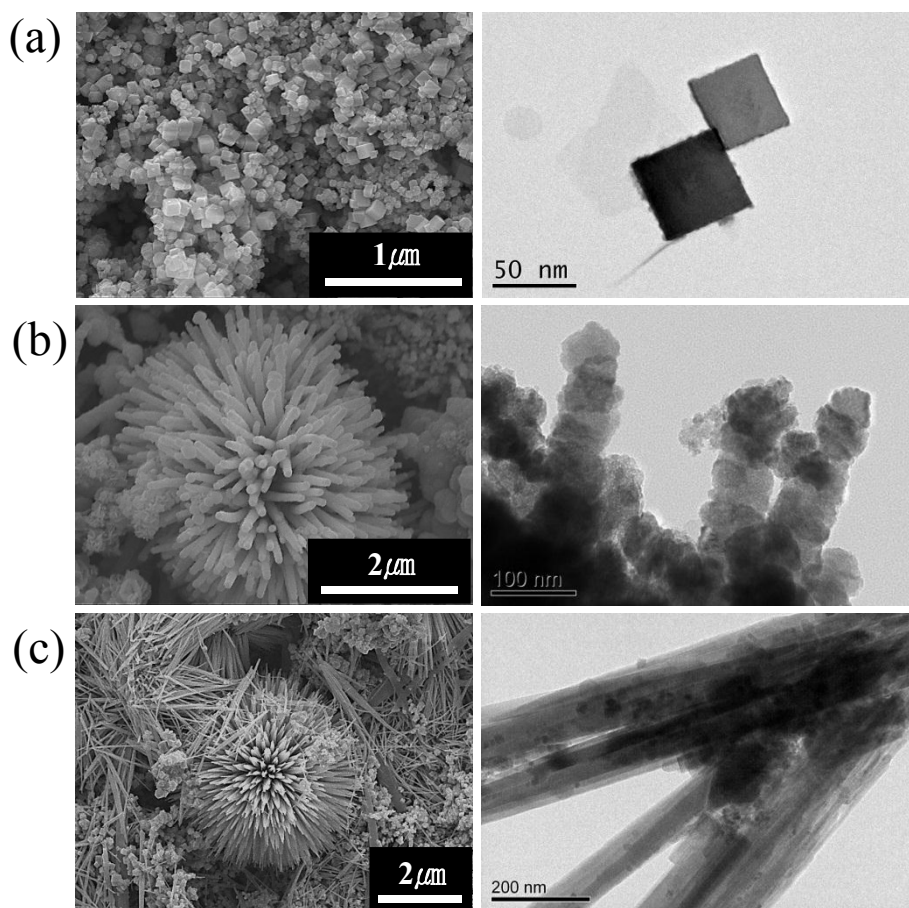
of the total electrode. The cells were assembled in an Ar-filled glove box and subjected to galvanostatic cycling using a WonATech (WBCS 3000, Seocho-gu, Seoul, Korea) charge-discharge system. Experiments were carried out in 1 atm of O<sub>2</sub> using an air chamber.

## Results and discussion

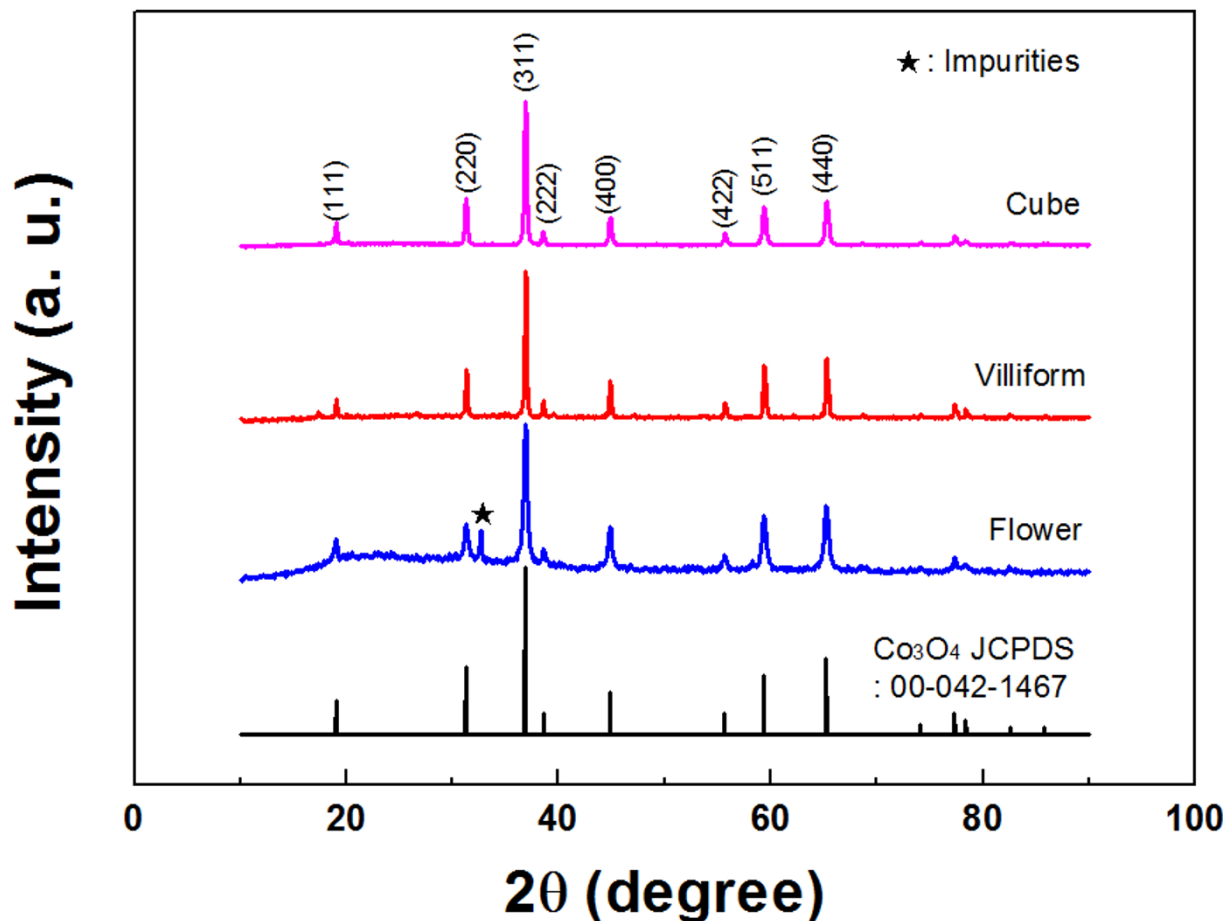
Scanning electron microscopy [SEM] and transmission electron microscopy [TEM] were employed to investigate the shapes of the samples (Figure 1). Cube-type Co<sub>3</sub>O<sub>4</sub> nanoparticles have a homogeneous cubic morphology (Figure 1a). The length of the nanocube was around 200 nm, and the dominant exposed plane of the cube-type Co<sub>3</sub>O<sub>4</sub> seemed to be {001}. The villiform-type Co<sub>3</sub>O<sub>4</sub> particles were formed by a nucleus covered with numerous micrometer-sized nanorods. In comparison with the length, the diameter of the nanorod was very small (less than 100 nm). It is interesting that the villiform-type Co<sub>3</sub>O<sub>4</sub> has a rough surface. As shown in the TEM image (Figure 1b), the nanorods seemed to be stacked with smaller nanoparticles with a diameter of approximately 80 nm. The flower-type Co<sub>3</sub>O<sub>4</sub> seemed to

have a similar shape and size to those of the villiform-type Co<sub>3</sub>O<sub>4</sub>. However, the nanorods of the flower-type Co<sub>3</sub>O<sub>4</sub> had a sharper end, smoother surface, and smaller diameter than those of the villiform-type Co<sub>3</sub>O<sub>4</sub>. Moreover, in contrast with the villiform-type Co<sub>3</sub>O<sub>4</sub>, the nanorods of the flower-type Co<sub>3</sub>O<sub>4</sub> particles were almost separated during the preparation process for the TEM experiments (Figure 1c). This implies that the flower-type Co<sub>3</sub>O<sub>4</sub> particles may turn to the nanorod type during the electrode fabrication process because of vigorous mixing in making a slurry. The crystallinity of the three types of Co<sub>3</sub>O<sub>4</sub> nanoparticles was investigated by XRD. As shown in Figure 2, all XRD peaks of the cube-type Co<sub>3</sub>O<sub>4</sub> nanoparticles can be indexed to the Co<sub>3</sub>O<sub>4</sub> spinel phase, indicating a single-phase sample. Most diffraction peaks for villiform- and flower-type Co<sub>3</sub>O<sub>4</sub> particles were also identical to those of the typical Co<sub>3</sub>O<sub>4</sub> phase; however, small impurities could be detected in the diffraction patterns.

The electrochemical properties of the air electrodes containing Co<sub>3</sub>O<sub>4</sub> nanoparticles were characterized at a constant current density of 0.4 mA·cm<sup>-2</sup> at 30°C. Figure 3a



**Figure 1** SEM (left side) and TEM (right side) images of the Co<sub>3</sub>O<sub>4</sub> nanoparticles. (a) Cube type, (b) villiform type, and (c) flower type.

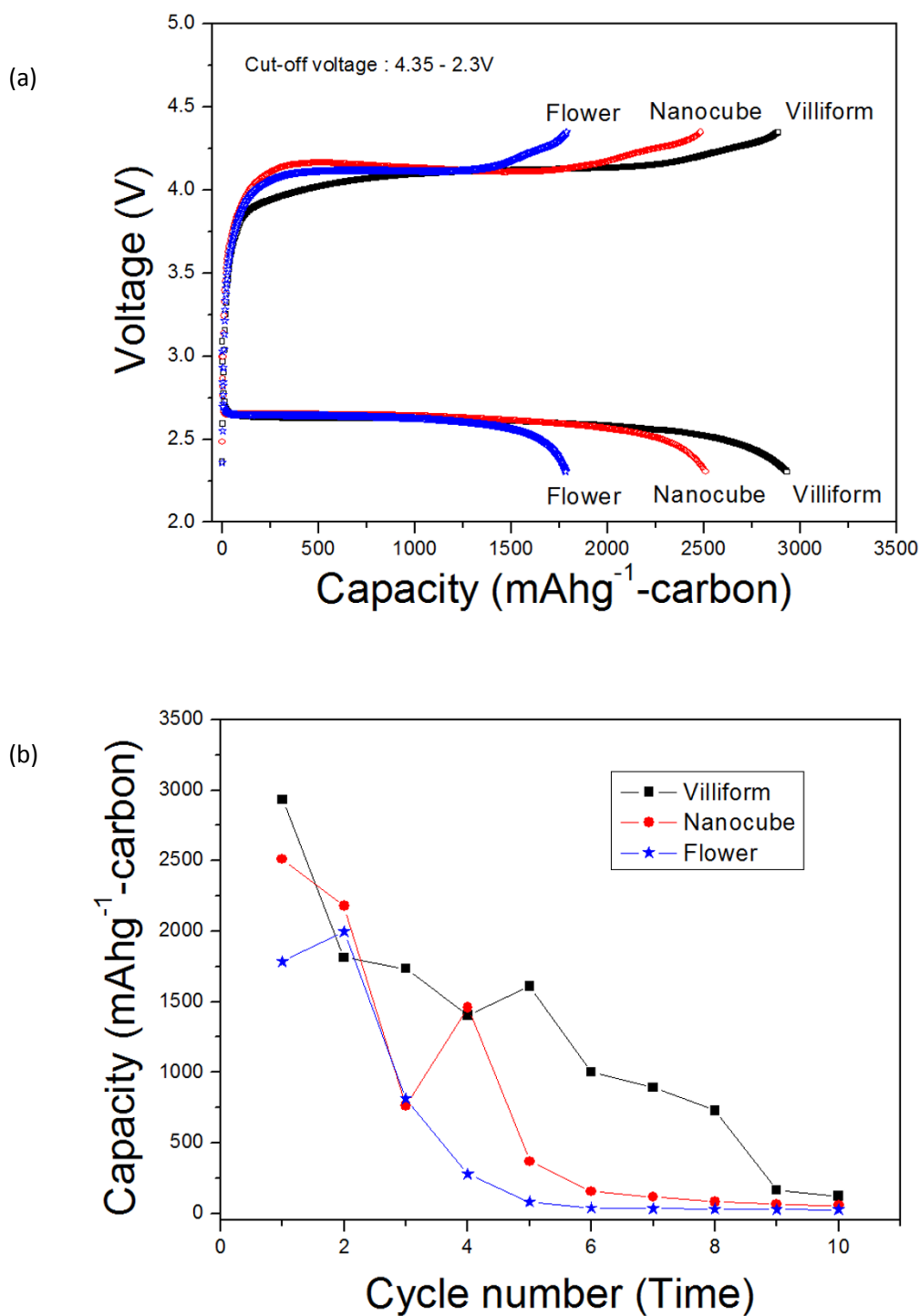


**Figure 2** XRD patterns of the  $\text{Co}_3\text{O}_4$  nanoparticles and reference  $\text{Co}_3\text{O}_4$ .

shows the initial voltage profile of the electrodes containing the  $\text{Co}_3\text{O}_4$  nanoparticles in the voltage range of 4.35 to 2.3 V. The discharge capacity shown in Figure 3 is based on the weight of carbon (Ketjen black) in the air electrode, which has generally been used for expressing the capacity of an air electrode [1,8,9,12]. The average charge and discharge voltages of the air electrode containing the  $\text{Co}_3\text{O}_4$  nanoparticles were approximately 4.2 and 2.6 V, respectively. The initial discharge capacity of the electrode was highly dependent upon the type of  $\text{Co}_3\text{O}_4$  nanoparticles. The electrode containing villiform-type  $\text{Co}_3\text{O}_4$  nanoparticles showed a relatively higher initial discharge capacity (approximately  $2,900 \text{ mA h g}^{-1}$ ) than with the other electrodes. In contrast, the initial discharge capacities of the electrodes containing flower-type  $\text{Co}_3\text{O}_4$  nanoparticles were just about  $1,800 \text{ mA h g}^{-1}$  although they have a shape very similar to the villiform-type  $\text{Co}_3\text{O}_4$  nanoparticles. As shown in Figure 3b, the cyclic performance of the air electrodes was not satisfactory. Actually, capacity fading has been a typical feature of all previous results about

air electrodes [8,12,13]. It has been known that cycle degradation is associated with irreversible reaction products, which accumulate in the pores of the electrode at a discharged state [13,14]. It seems that the practical rechargeability of air electrodes has yet to be achieved before these can be put to practical use.

After 10 cycles, the electrode was discharged to 2.3 V, and the surface was observed by SEM to investigate the morphology change during cycling. In the SEM images of the air electrodes before testing, the  $\text{Co}_3\text{O}_4$  nanoparticles and carbon (Ketjen black) could be clearly identified (Figure 4). It was noticeable that the villiform-type  $\text{Co}_3\text{O}_4$  nanoparticles maintained their shape during the electrode-fabrication process. However, the flower-type  $\text{Co}_3\text{O}_4$  nanoparticles were almost separated to become the nanorod type. When they discharged to 2.3 V, it was observed that the surface of the electrode was homogeneously covered with precipitates, which appeared to be reaction products such as lithium oxides, and lithium carbonates formed due to electrolyte decomposition [15,16].

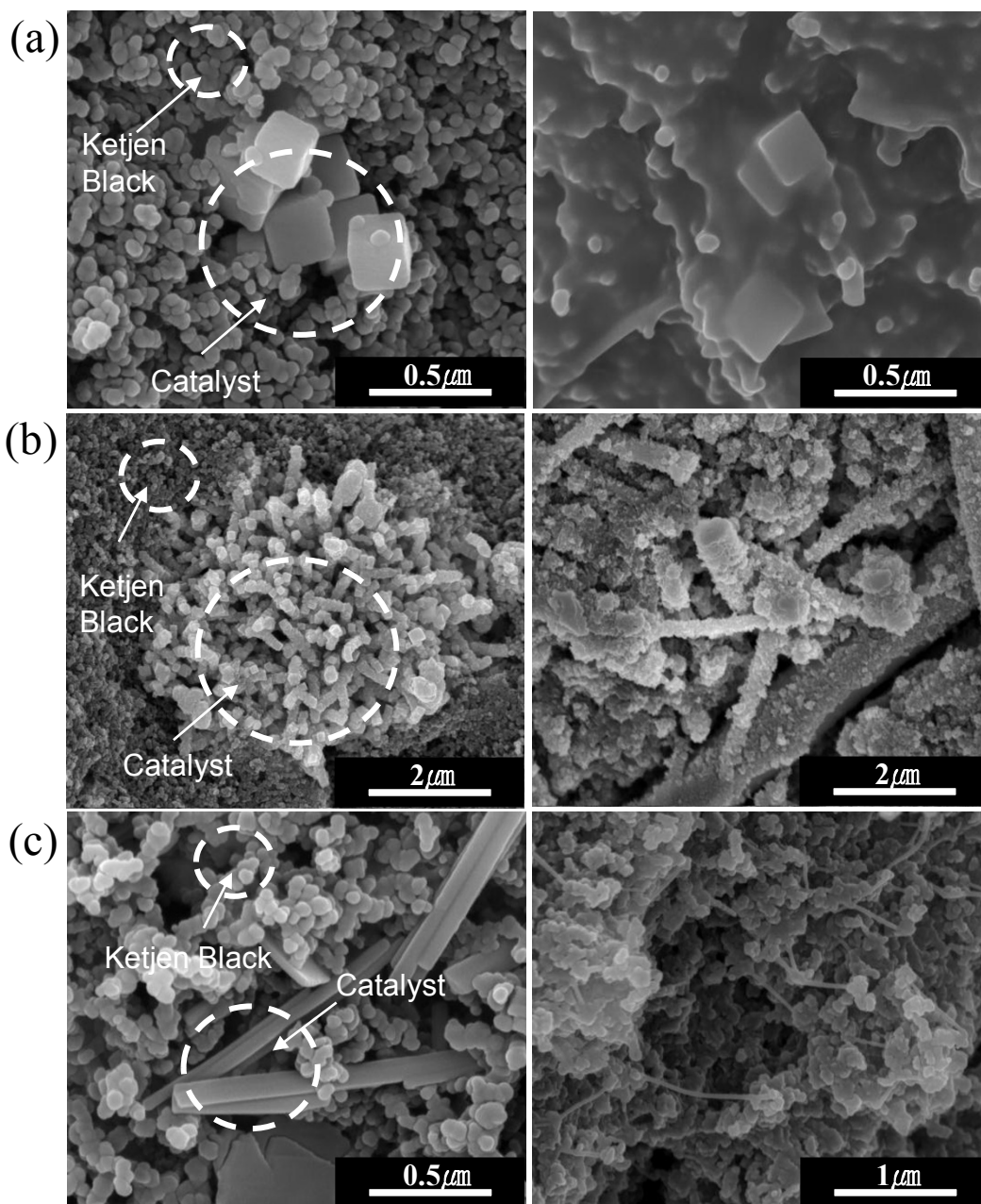


**Figure 3** Electrochemical properties of the air electrode containing  $\text{Co}_3\text{O}_4$  nanoparticles. Air electrode containing  $\text{Co}_3\text{O}_4$  nanoparticles at a constant current density of  $0.4 \text{ mA}\cdot\text{cm}^{-2}$  (voltage range of 4.35 to 2.3 V). (a) Initial voltage profile and (b) cyclic performance.

These reaction precipitates could block the catalyst/carbon contact area, thereby preventing  $\text{O}_2$  intake and  $\text{Li}^+$  delivery to the active reaction site and terminating the discharge process. According to previous reports [13,14], there was a

strong correlation between average pore diameter and discharge capacity. Reaction precipitates are likely to be formed near active sites so that the micropore of a porous electrode would be easily sealed with precipitates of





**Figure 4 SEM images of the air electrodes.** Air electrodes composed of  $\text{Co}_3\text{O}_4$  nanoparticles, carbon (Ketjen black), and binder before the test and after discharge at 2.3 V. (a) Cube type, (b) villiform type, and (c) flower type.

lithium oxides during discharge. Thus, securing enough space between catalytic active sites might increase the discharge capacity of the air electrode. The cube- and flower- (nanorod- in the electrode) type  $\text{Co}_3\text{O}_4$  nanoparticles may be well covered with small carbon particles (Ketjen black) in the air electrode so that a sufficiently small pore space could be obtained. On the other hand, the villiform-type  $\text{Co}_3\text{O}_4$  nanoparticles were composed of a nucleus covered

with many nanorods of approximately 100 nm in size, which could offer enough space between active catalytic sites. Thus, a greater amount of lithium oxide precipitation may be needed to block the pore orifices and terminate the discharge process; this could be an explanation for the higher discharge capacity of the air electrode containing villiform-type  $\text{Co}_3\text{O}_4$  nanoparticles in comparison with the air electrode containing other types  $\text{Co}_3\text{O}_4$  nanoparticles.

## Conclusions

Cube-, flower-, and villiform-type  $\text{Co}_3\text{O}_4$  nanoparticles were synthesized and introduced as catalysts for Li/air batteries. The electrochemical properties of the air electrodes containing  $\text{Co}_3\text{O}_4$  nanoparticles were found to be highly dependent on the type of  $\text{Co}_3\text{O}_4$  nanoparticles. The electrode containing villiform-type  $\text{Co}_3\text{O}_4$  nanoparticles showed a higher discharge capacity than the electrodes containing other types of  $\text{Co}_3\text{O}_4$  nanoparticles. This is likely due to the relatively sufficient pore space between active catalytic sites, which stores a large amount of reaction products.

## Abbreviations

EC: ethylene carbonate; FE-SEM: field-emission scanning electron microscopy; FE-TEM: field-emission transmission electron microscopy; LITFSI: lithium bis (trifluoromethanesulfonyl)imide; PC: propylene carbonate; PVDF: polyvinylidene fluoride; XRD: X-ray diffraction.

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## Authors' contributions

KS did the synthetic and characteristic works in this journal. YJ gave the advice and guided the experiment. All authors read and approved the final manuscript.

## Competing interests

The authors declare that they have no competing interests.

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## References

1. Ogasawara T, Débart A, Holzapfel M, Novák P, Bruce PG: **Rechargeable  $\text{Li}_2\text{O}_2$  electrode for lithium batteries.** *J Am Chem Soc* 2006, **128**:1390-1393.
2. Zhang SS, Foster D, Read J: **Discharge characteristic of a non-aqueous electrolyte  $\text{Li}/\text{O}_2$  battery.** *J Power Sources* 2010, **195**:1235-1240.
3. Zhang JG, Wang DY, Xu W, Xiao J, Williford RE: **Ambient operation of Li/Air batteries.** *J Power Sources* 2010, **195**:4332-4337.
4. Wang X, Yu L, Wu XL, Yuan F, Guo YG, Ma Y, Yao J: **Synthesis of single-crystalline  $\text{Co}_3\text{O}_4$  octahedral cages with tunable surface aperture and their lithium storage properties.** *J Phys Chem C* 2009, **113**:15553-15558.
5. Teng F, Yao W, Zheng Y, Ma Y, Xu T, Gao G, Liang S, Teng Y, Zhu Y: **Facile synthesis of hollow  $\text{Co}_3\text{O}_4$  microspheres and its use as a rapid responsive CL sensor of combustible gases.** *Talanta* 2008, **76**:1058-1064.
6. Yang Y, Huang K, Liu R, Wang L, Zeng W, Zhang P: **Shape-controlled synthesis of nanocubic  $\text{Co}_3\text{O}_4$  by hydrothermal oxidation method.** *Trans Nonferrous Met Soc* 2007, **17**:1082-1086.
7. Zhang Y, Liu Y, Fu S, Guo F, Qian Y: **Morphology-controlled synthesis of  $\text{Co}_3\text{O}_4$  crystals by soft chemical method.** *Mater Chem Phys* 2007, **104**:166-171.
8. Jiao BF, Bruce PG: **Mesoporous crystalline  $\beta\text{-MnO}_2$ -a reversible positive electrode for rechargeable lithium batteries.** *Adv Matter* 2007, **19**:657-660.
9. Débart A, Paterson AJ, Bao J, Bruce PG: **a- $\text{MnO}_2$  nanowires: a catalyst for the  $\text{O}_2$  electrode in rechargeable lithium batteries.** *Angew Chem* 2008, **47**:4521-4524.
10. Jiang A, Wu Yue, Xie B, Xie Y, Qian Y: **Moderate temperature synthesis of nanocrystalline  $\text{Co}_3\text{O}_4$  via gel hydrothermal oxidation.** *Mater Chem Phys* 2002, **74**:234-237.
11. Zhang Y, Liu Y, Fu S, Guo F, Qian Y: **Morphology-controlled synthesis of  $\text{Co}_3\text{O}_4$  crystals by soft chemical method.** *Mater Chem Phys* 2007, **104**:166-171.

12. Débart A, Bao J, Armstrong G, Bruce PG: **An  $\text{O}_2$  cathode for rechargeable lithium batteries: the effect of a catalyst.** *J Power Sources* 2007, **174**:1177-1182.
13. Kraytsberg A, Ein-Eli Y: **Review on Li-air batteries-opportunities, limitations and perspective.** *J Power Sources* 2011, **196**:886-893.
14. Tran C, Yang XQ, Qu D: **Investigation of the gas-diffusion-electrode used as lithium/air cathode in non-aqueous electrolyte and the importance of carbon material porosity.** *J Power Sources* 2010, **195**:2057-2063.
15. Xu W, Viswanathan V, Wang D, Towne S, Xiao J, Nie Z, Hu D, Zhang J: **Investigation on the charging process of  $\text{Li}_2\text{O}_2$ -based air electrodes in  $\text{Li}-\text{O}_2$  batteries with organic carbonate electrolytes.** *J Power Sources* 2011, **196**:3894-3899.
16. Freunberger SA, Chen Y, Peng Z, Griffin JM, Hardwick LJ, Bard F, Novak P, Bruce PG: **Reactions in the rechargeable lithium- $\text{O}_2$  battery with alkyl carbonate electrolytes.** *J Am Chem Soc* 2011, **133**:8040-8047.

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