Supporting Information

Superior Electrochemical Properties of Co_3O_4 Yolk-Shell Powders with a Filled Core and Multishells Prepared by a One-Pot Spray Pyrolysis

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This file includes:

• Detailed experimental procedure.

• Schematic diagram of the ultrasonic spray pyrolysis process.

• HR-TEM images of the Co3O4 powders; (a) yolk-shell, 800°C, (b) yolk-shell, 900°C, (c) yolk-shell, 1000°C, (d) hollow, 900°C.

• SEM and TEM images of the hollow Co_3O_4 powders prepared by spray pyrolysis from the spray solution without sucrose at 900°C.

• XRD patterns of the yolk-shell and hollow Co_3O_4 powders prepared by spray pyrolysis from the spray solutions with and without sucrose.

• HR-TEM images of the Co3O4 powders; (a) yolk-shell, 800°C, (b) yolk-shell, 900°C, (c) yolk-shell, 1000°C, (d) hollow, 900°C.

• SEM images of the Co_3O_4 powdersprepared by spray pyrolysis at 900°C from the spray solutions with various concentrations of sucrose.

• Cyclic voltammograms (CVs) generated at a scan rate of 0.1 mV s^{-1} during the first five cycles in the voltage range 0–3.0V for the electrodes produced using the yolk-shell Co_3O_4 powders prepared at 900°C.

• TG curves of Co_3O_4 yolk-shell powders prepared by spray pyrolysis at various temperatures.

• SEM images with low magnification of electrode formed by yolk-shell and hollow Co_3O_4 powders after the 1st and 50th cycling; (a) yolk-shell, 1000°C; (b) hollow, 900°C; (c) yolk-shell, 900°C.

Detailed experimental procedure:

Synthesis of the Co_3O_4 yolk-shell powders: Multishelled Co_3O_4 yolk-shell-structured powders were directly prepared by spray pyrolysis from aqueous spray solutions containing Co nitrate and sucrose. Sucrose was used as the carbon source to form the yolk-shell-structured powders. A schematic diagram of the ultrasonic spray pyrolysis system used in this study is shown in Fig. S1. The spray pyrolysis system consisted of a droplet generator, a quartz reactor, and a powder collector. The length and diameter of the quartz reactor were 1000 and 55 mm, respectively. A 1.7-MHz ultrasonic spray generator with six vibrators was used to generate a large quantity of droplets, which were carried into the high-temperature tubular reactor by air, which was used as a carrier gas at a flow rate of 5 L min^{-1}. The reactor temperature was increased from 800 to 1000°C. An aqueous spray solution was prepared by dissolving cobalt nitrate [$Co(NO_3)_2 \cdot 6H_2O$, Junsei] in distilled water. The concentrations of the Co nitrate and sucrose were 0.2 and 0.7 M, respectively.

Materials Characterization: The crystal structures of the Co_3O_4 yolk-shell-structured powders were investigated using X-ray diffractometry (XRD, Rigaku DMAX-33) at the Korea Basic Science Institute (Daegu). The morphologies of the powders were characterized using scanning electron microscopy (SEM, JEOL JSM-6060) and high-resolution transmission electron microscopy (TEM, JEOL JEM-2010). The Brunauer-Emmett-Teller (BET) surface areas of the powders were measured using N_2 gas as adsorbate.

Electrochemical Measurements: The capacities and cycle properties of electrodes produced on the basis of the Co_3O_4 powders were measured using 2032-type coin cells. The electrodes were prepared by mixing 40 mg of the Co_3O_4 powders, 5 mg of carbon black (Super P) as conductive material, and 5.4 mg of sodium carboxymethyl cellulose (CMC) with a few mL of distilled water. The weight of active materials on the electrode film was 1.5 mg cm^{-2}. Lithium metal and a microporous polypropylene film were used as counter electrode and separator, respectively. $LiPF_6$ (1 M) in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) in a 1:1 volume ratio with 2 wt% vinylene carbonate (VC) was used as the electrolyte. The entire cell was assembled under an argon atmosphere in a glove box. The charge/discharge characteristics of the samples were measured at various current densities in the voltage range 0.01–3 V.

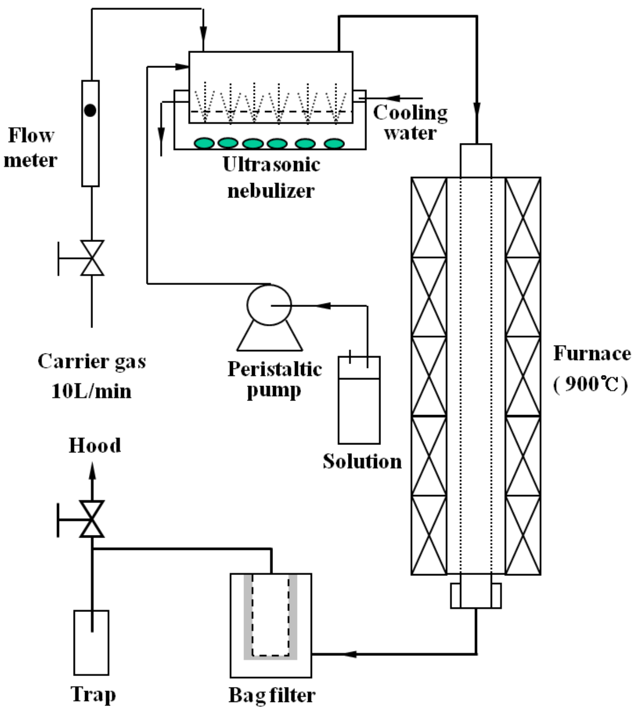


Fig. S1 Schematic diagram of the ultrasonic spray pyrolysis process.

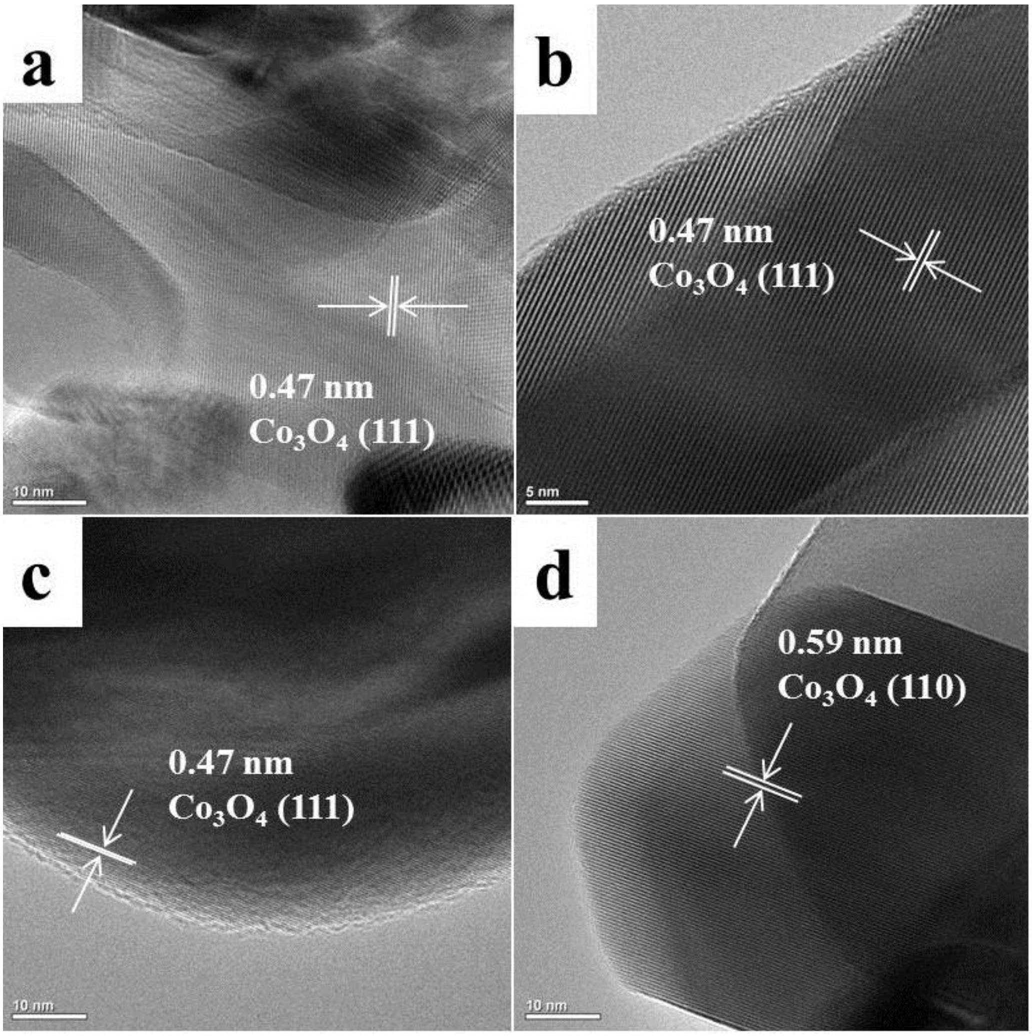


Fig. S2 HR-TEM images of the Co_3O_4 powders; (a) yolk-shell, 800^oC, (b) yolk-shell, 900^oC, (c) yolk-shell, 1000^oC, (d) hollow, 900^oC.

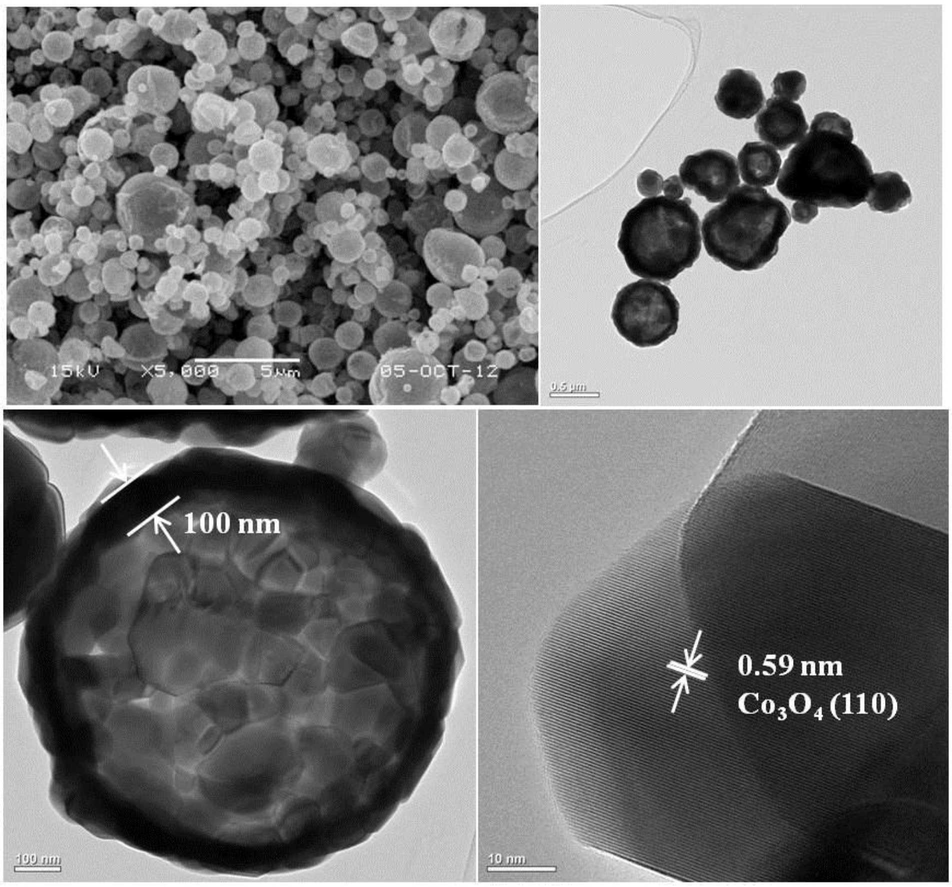


Fig. S3 SEM and TEM images of the hollow Co_3O_4 powders prepared by spray pyrolysis from the spray solution without sucrose at 900°C.

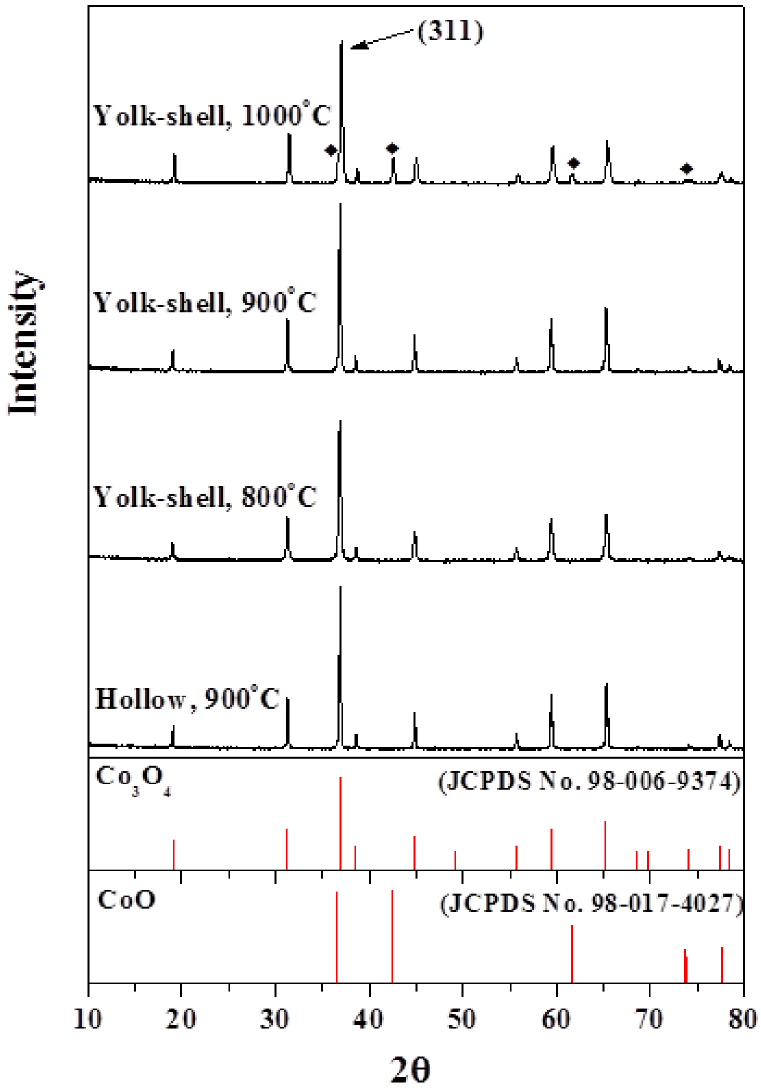


Fig. S4 XRD patterns of the yolk-shell and hollow Co_3O_4 powders prepared by spray pyrolysis from the spray solutions with and without sucrose.

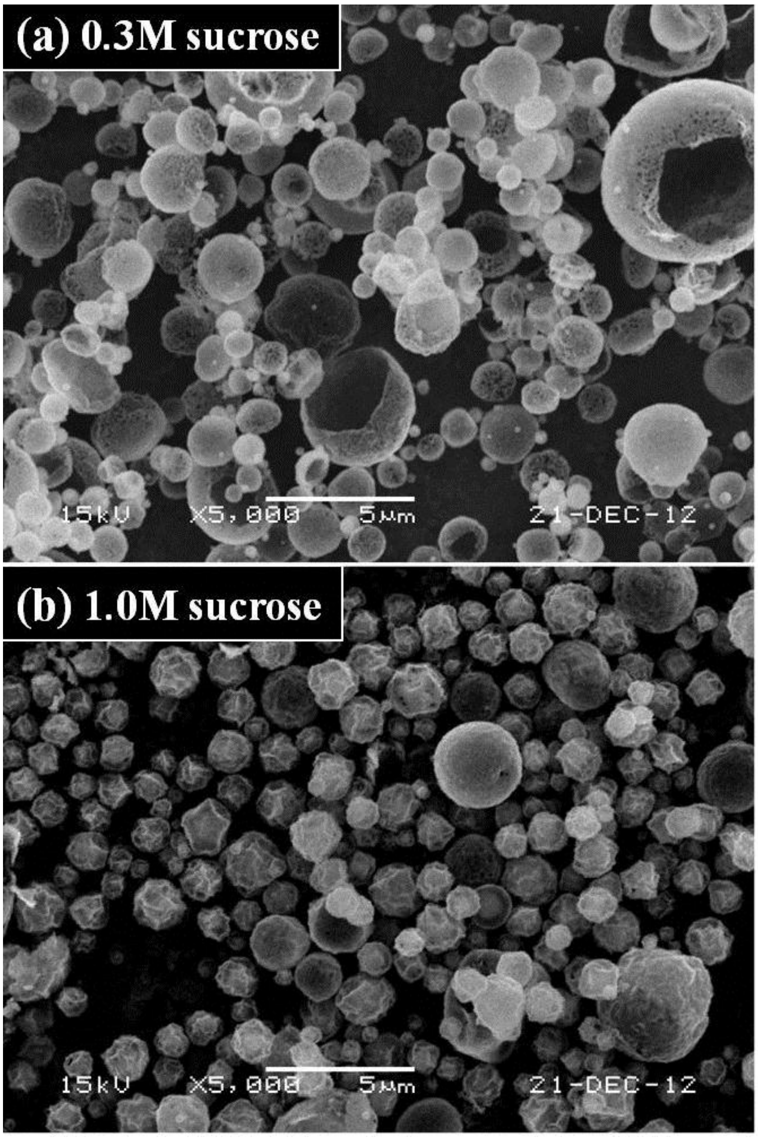


Fig. S5 SEM images of the Co_3O_4 powders prepared by spray pyrolysis at 900°C from the spray solutions with various concentrations of sucrose.

Fig. S5 shows the morphologies of the Co_3O_4 powders prepared from the spray solutions with various concentrations of sucrose used as the carbon source material. The powders prepared from the spray solution with 0.3 M sucrose had hollow structure. However, the Co_3O_4 powders prepared from the spray solution with 1 M sucrose had yolk-shell structure. In this study, the Co_3O_4 powders prepared from the spray solution with sucrose above 0.7 M had yolk-shell structure. The carbon amount formed by polymerization and carbonization of sucrose played a key role in formation of yolk-shell-structured Co_3O_4 powders.

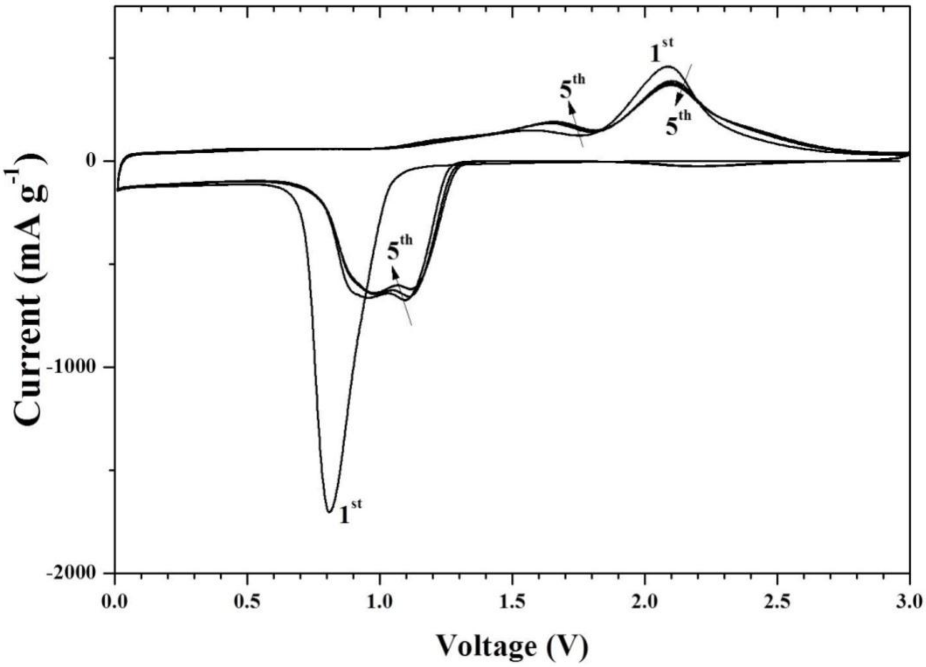


Fig. S6 Cyclic voltammograms (CVs) generated at a scan rate of 0.1 mV s^{-1} during the first five cycles in the voltage range 0–3.0 V for the electrodes produced using the yolk-shell Co_3O_4 powders prepared at 900°C.

Fig. S6 shows the CV curves of the yolk-shell Co_3O_4 powders prepared by spray pyrolysis. One cathodic peak was observed at 0.8 V in the first discharging process, corresponding to the reduction of Co_3O_4 to Co metal accompanying with the formation of amorphous Li_2O. Two anodic peaks were observed at 1.7 and 2.1 V in the first charging process, which can be ascribed to the oxidation of Co metal to Co_3O_4 and the decomposition of Li_2O [*CrystEngComm.*, 2013, **15**, 3568.; *ACS Appl. Mater. Interfaces*, 2013, **5**, 997]. The reduction peak shifted to about 1.0 V after the second cycle. From the second cycle onward, the reduction and oxidation peaks in the CV tests overlapped substantially, indicating that the electrode of the yolk–shell Co_3O_4 powder showed outstanding cycle ability for the insertion and extraction of lithium ions.

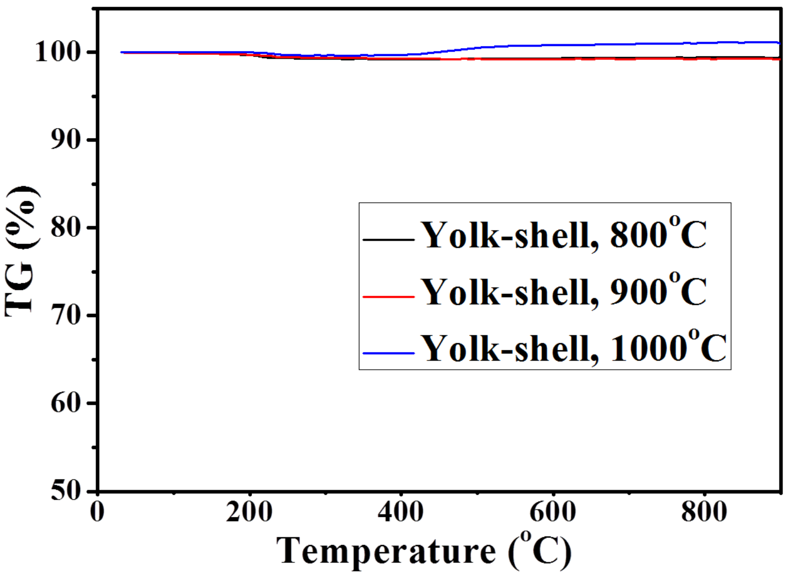
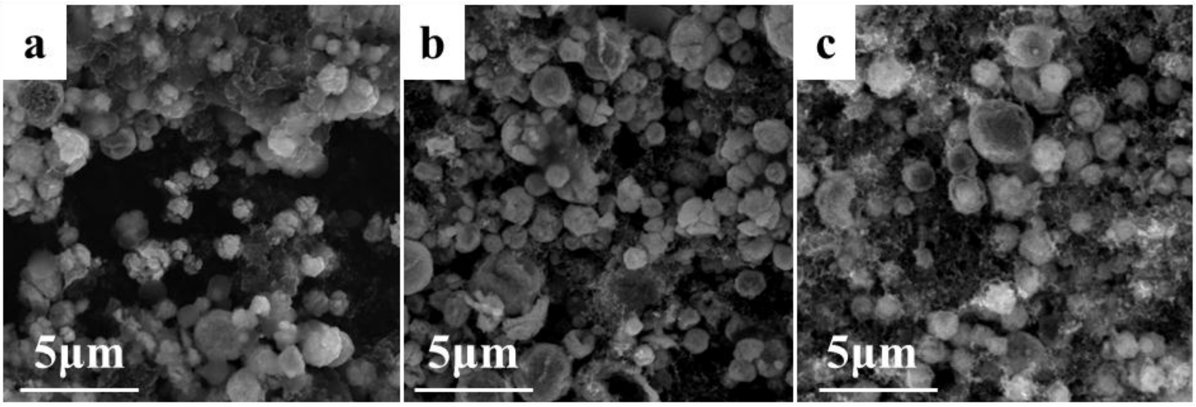
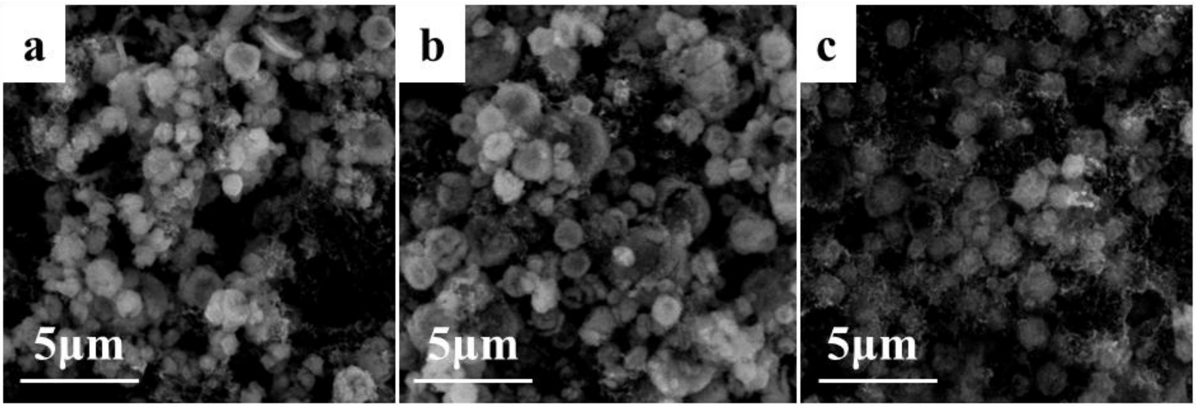


Fig. S7 TG curves of Co_3O_4 yolk-shell powders prepared by spray pyrolysis at various temperatures.

TG curves of the Co_3O_4 powders prepared at various temperatures were measured to show the carbon contents of the yolk-shell powders. The weight losses of the yolk-shell powders by carbon decomposition were not observed irrespective of the preparation temperatures of the yolk-shell powders.



(a) electrode after 1 cycling



(b) electrode after 50 cycling

Fig. S8 SEM images with low magnification of electrode formed by yolk-shell and hollow Co_3O_4 powders after the 1^{st} and 50^{th} cycling; (a) yolk-shell, 1000^oC; (b) hollow, 900^oC; (c) yolk-shell, 900^oC.