

# Hydrothermally Processed Oxide Nanostructures and Their Lithium–ion Storage Properties

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**Abstract** Y- and Si-based oxide nanopowders were synthesized by a hydrothermal reaction of Y or Si powders with NaOH or LiOH aqueous solution. Nanoparticles with different morphology such as elongated nanospheres, flower-like nanoparticles and nanowires were produced by a control of processing parameters, in particular, the starting composition of solution. The preliminary result of electrochemical examination showed that the hydrothermally processed nanowires exhibit high initial capacities of Li-ion storage: 653 mAh/g for  $Y_2O_3$  nanowires as anode materials and 186 mAh/g for  $Li_2Si_2O_5$  nanowires as cathode materials in a Li secondary cell. Compared to the powder with elongated sphere or flower-like shapes, the nanowires showed a higher Li-ion capacity and a better cycle property.

**Keywords** Hydrothermal reaction · Nanowires · Li-ion cell · Nanopowders · Crystal growth

## Introduction

Nano-sized metal oxides have interesting properties, which cannot be expected in conventional microcrystalline materials [1–5]. Due to high specific surface area and unique structures, they have attracted much attention among scientists for potential applications in electronic devices, chemical and physical sensors, photocatalysts, materials for energy conversion and energy storage, etc. In particular, one-dimensional (1-D) nanomaterials such as nanotubes and nanowires are expected to have novel properties due to higher specific surface area than 2-D or 3-D materials. In the field of energy storage, for instance, there is a strong demand to replace conventional carbonaceous and Li–M–O-based electrode materials to high-performance nanostructured electrodes in Li-ion rechargeable batteries. Recently, a very high Li-ion storage capacity combined with good cyclability was reported in nanowires such as Na–Ti–O [6]. A variety of methods has been employed to synthesize 1-D nanomaterial [7–10]. The chemical methods, such as a hydrazine reduction route in aqueous ethanol solutions assisted by external magnetic fields, are very effective to synthesize nanowires [11]. As well, hydrothermal process is considered as one of the most effective methods for the scaled-up to produce high-quality nanopowders. By a proper control of processing parameters such as the composition of starting solution, the morphology of nanopowders can be effectively controlled in this method [12–14].

In the present work, we synthesized Y- and Si-based oxide nanopowders with different morphology by a hydrothermal method using metallic Y and Si powders as starting materials. We also examined Li-ion storage property of the synthesized nanopowders to be potentially used as anode or cathode materials for Li-ion cells.

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## Experimental Procedure

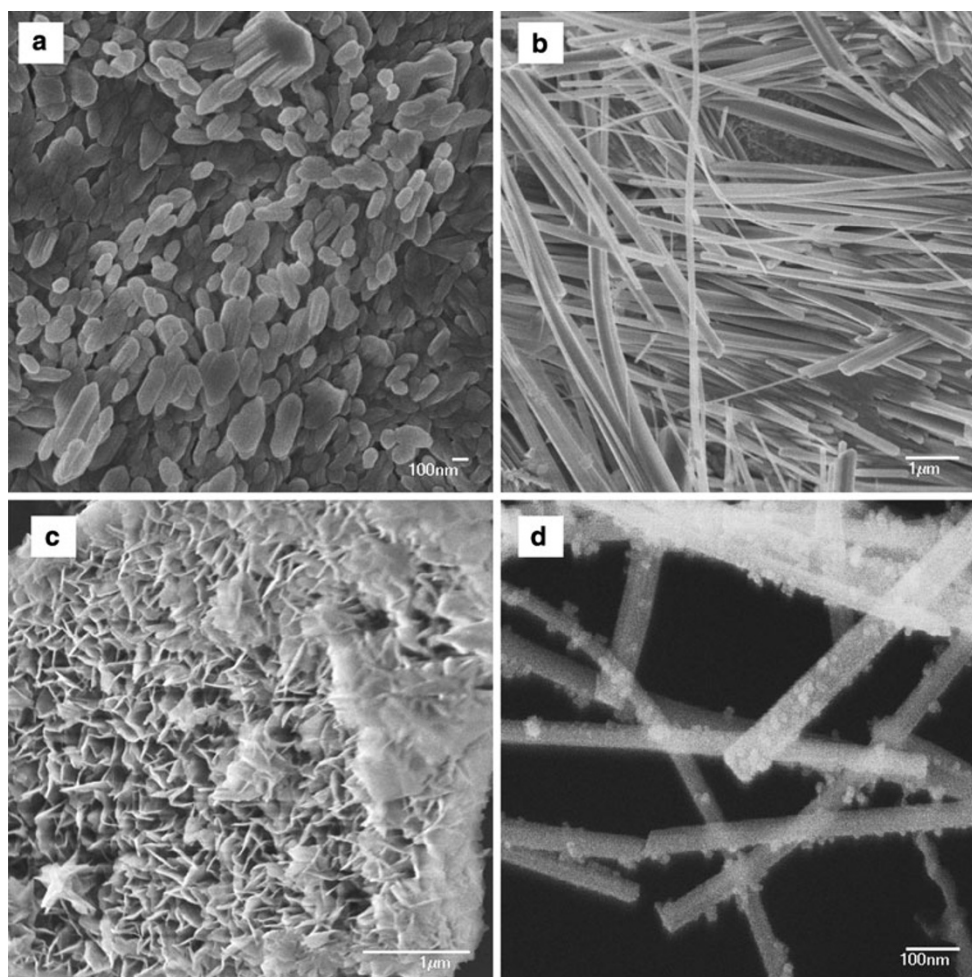
Pure Y (>99.5%, 10  $\mu\text{m}$ ), Si (>99.8%, 20  $\mu\text{m}$ ), NaOH and LiOH were used as starting materials. Y or Si powders were put into an aqueous solution of NaOH(1–5 M) or LiOH(1–5 M). The powder containing solution was then put into a Teflon-sealed mini-autoclave (80 $\phi$   $\times$  120 mm).

**Table 1** The synthesis condition for the nanopowders in this work

Specimen	Starting composition	Hydrothermal reaction	Resulting material
1	Y 1 g + 3 M LiOH	200°C, 24 h	Y(OH) <sub>5</sub> (elongated sphere)
2	Y 1 g + 1 M LiOH	200°C, 24 h	Y(OH) <sub>5</sub> (nanowire)
3	Si 1 g + 3 M NaOH	180°C, 24 h	Na <sub>2</sub> SiO <sub>3</sub> ·H <sub>2</sub> O (flower-like)
4	Si 1 g + 1 M LiOH	180°C, 24 h	Li <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> ·H <sub>2</sub> O (nanowire)

The sealed mini-autoclave was put in a heated furnace for hydrothermal reaction. The reaction took place in the autoclave at 220–250°C for several hours. After the hydrothermal reaction, the solid products remaining in the solution were isolated by centrifugal separation, followed by washing with de-ionized water and ethanol for three times. The products were then dried at 100°C for 3 h. A portion of the synthesized products was further heat-treated at 500°C in air for an hour. Phase identification and structural examination were performed by a XRD and a field-emission SEM.

The Li-ion storage property was evaluated by an electrochemical test using the synthesized nanopowders as anode or cathode electrodes in Li-ion cell. The electrodes were made by dispersing 80 wt% nanopowders, 15 wt% carbon black and 7 wt% polyvinylidene fluoride (PVDF) binder in *n*-methyl pyrrolidone (NMP) solvent to form the slurry. The slurry was then spread onto a Cu foil, followed by drying in an oven under a vacuum pressure of 30 torr at 120°C for 12 h. The dried electrodes were then pressed at a



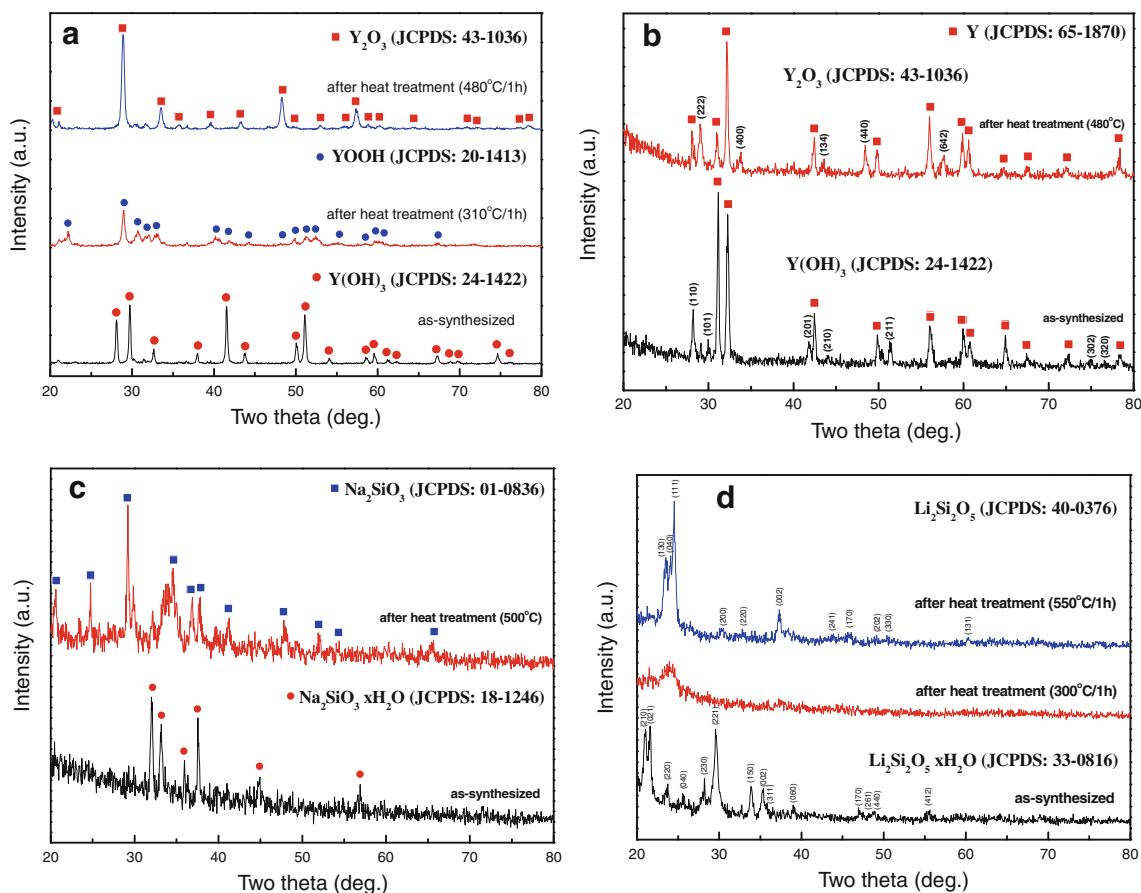
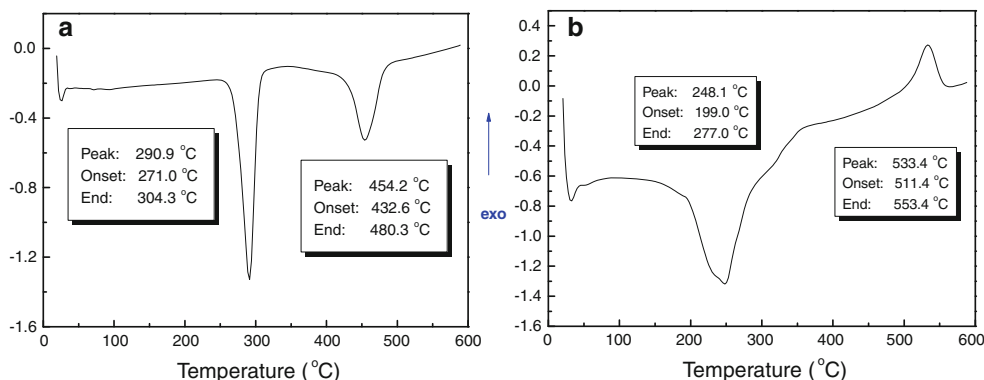
**Fig. 1** FF-SEM images of nanopowder with different morphologies after hydrothermal process described in Table 1. **a** specimen No. 1, **b** specimen No. 2, **c** specimen No. 3 and **d** specimen No. 4, respectively

pressure of  $12 \text{ kg/mm}^2$ . The nanopowder electrodes were finally assembled to CR2032 coin cells in an argon-filled glove-box using lithium metal foil as the counter electrode. The electrolyte was  $1 \text{ M LiPF}_6$  in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume, provided by MERCK, Germany). The cells were galvanostatically charged and discharged over a voltage range of 0–3.0 and 2.5–4.5 V for anode and cathode materials, respectively.

## Results and Discussions

After a series of hydrothermal experiments determining optimum working conditions in Y- and Si-oxide based systems, we could obtain nanopowders with three different morphologies: elongated nanospheres, flower-like nanoparticles and nanowires. The result of synthesis conditions is summarized in the Table 1. First, the hydrothermal reaction of Y with 1–5 M LiOH at  $200^\circ\text{C}$  for 24 h resulted

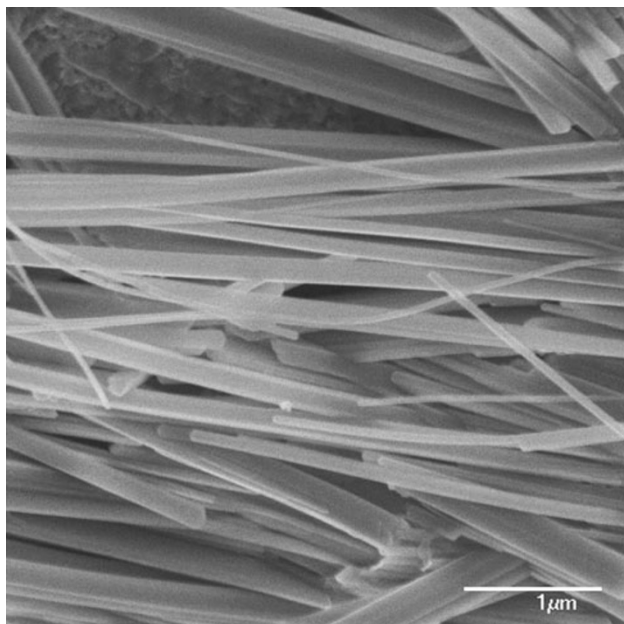
**Fig. 2** DSC curves of as-hydrothermally synthesized nanowires: **a** specimen No. 2 and **b** specimen No. 4



**Fig. 3** XRD patterns of nanopowder before and after heat treatment. **a** specimen No. 1, **b** specimen No. 2, **c** specimen No. 3 and **d** specimen No. 4, respectively

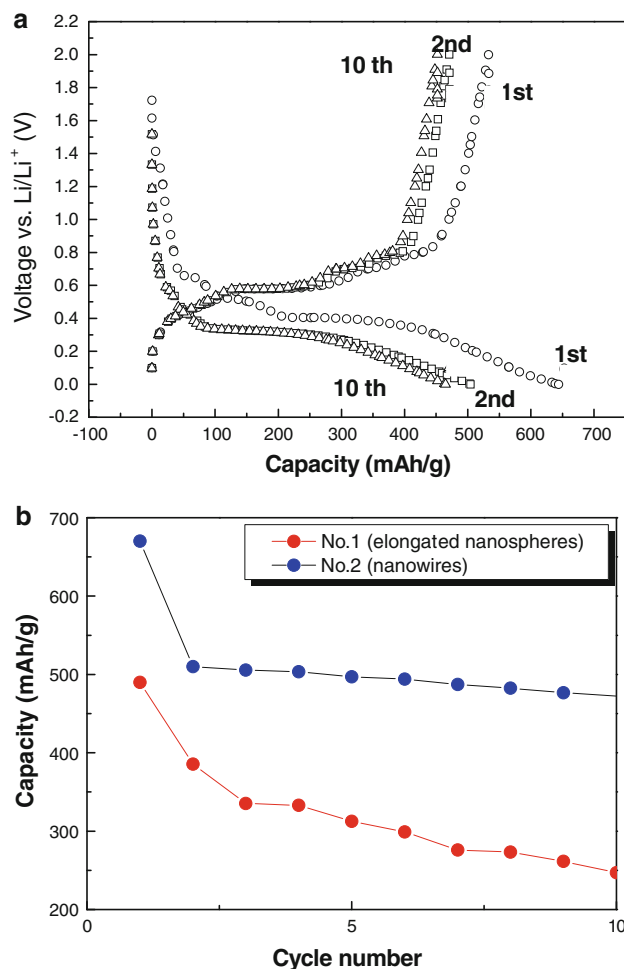
in the formation of  $Y(OH)_3$  particles. As the concentration of LiOH in aqueous solution decreased from 5 to 1 M, the powder morphology changed gradually from spherical shape to wire form. As shown in Fig. 1a, b, an elongated spherical particles formed when using 3 M LiOH solution, whereas the shape of particles transformed completely to nanowires when the concentration of LiOH further decreased to 1 M. Decreasing slightly the concentration resulted in a better formation of nanowires but reduced the yield of products. A similar tendency was observed in the case of Si-based system where Y powders were hydrothermally reacted with LiOH or NaOH. The formation of nanowires was generally facilitated when the concentration of hydroxide was drop to 1 M. In this case, however, higher hydroxide concentration resulted in the formation of flower-like particles (Fig. 1c), instead of spherical powders seen in the Y-based system. The individual flower-like particles have the size of about 5–10  $\mu\text{m}$ , but each particle consists of tiny plates of about 10 nm in thickness. The resulting materials were  $\text{Na}_2\text{SiO}_3 \cdot \text{H}_2\text{O}$  and  $\text{Li}_2\text{Si}_2\text{O}_5 \cdot \text{H}_2\text{O}$  for the use of NaOH and LiOH solution, respectively. The diameter of nanowires in both systems was 10–40 nm with the length of several hundred micrometers.

The behavior of as-synthesized nanopowders during heat-up was examined by a differential thermal analysis (Fig. 2). In Y-based system, two endothermic peaks appeared at 290.0 and 454.2 $^\circ\text{C}$ , corresponding to the reactions  $Y(OH)_3 \rightarrow YOOH$  and  $YOOH \rightarrow Y_2O_3$ , respectively. In Si-based system, on the other hand, both endothermic and exothermic peaks appeared at 248.1 and 533.4 $^\circ\text{C}$ , respectively.



**Fig. 4** The morphology of the specimen No. 2 after a post-heat treatment at 550 $^\circ\text{C}$  for 1 h in air

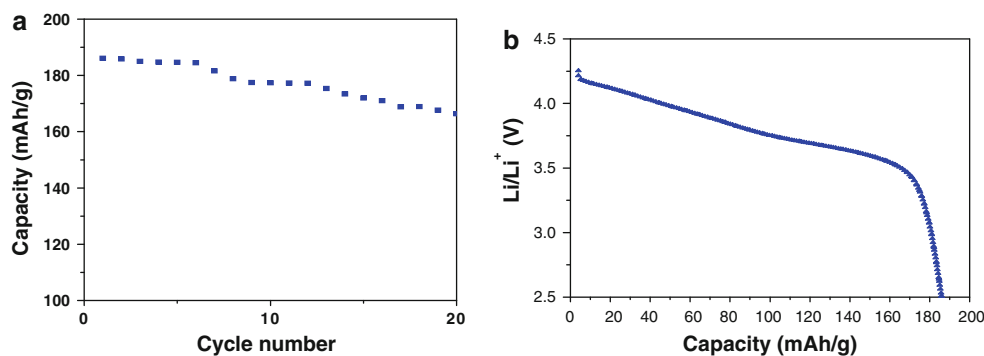
The result of XRD indicated that the hydrothermally synthesized  $Y(OH)_3$  nanopowders were successively transformed to  $YOOH$  and  $Y_2O_3$  after the heat treatment at 310 and 550 $^\circ\text{C}$  for an hour in air (Fig. 3a, b). In specimen No. 3 where Si powder had hydrothermally reacted with 3 M NaOH, the  $\text{Na}_2\text{SiO}_3 \cdot \text{H}_2\text{O}$  phase was transformed to  $\text{Na}_2\text{SiO}_3$  after the heat treatment at 248.1 at 550 $^\circ\text{C}$  for an hour in air (Fig. 3c). Slightly different XRD peaks were reported in specimen No. 4 where Si powder hydrothermally reacted with 1 M LiOH: the as-synthesized  $\text{Li}_2\text{Si}_2\text{O}_5 \cdot \text{H}_2\text{O}$  became an amorphous-like phase at temperature near 300 $^\circ\text{C}$  and then transformed to  $\text{Li}_2\text{Si}_2\text{O}_5$  at temperature above 550 $^\circ\text{C}$ . This might be related to the melting of residual lithium or lithium-rich phase from LiOH solution near 300 $^\circ\text{C}$ , as seen by Fe-SEM image of Fig. 1d where tiny droplets are present at the surface of nanowires. The most intense peak was (221) for  $\text{Li}_2\text{Si}_2\text{O}_5 \cdot \text{H}_2\text{O}$ , whereas (110) for  $\text{Li}_2\text{Si}_2\text{O}_5 \cdot \text{H}_2\text{O}$ .



**Fig. 5** Li-ion storage property of the Y-based specimens as anode materials in Li rechargeable cell: **a** the discharge-charge profiles of the specimen No. 2 and **b** comparison of the discharge capacity versus cycle number between the specimen No. 1 and 2



**Fig. 6** Li-ion storage property of the Si-based specimen (No. 4) as cathode materials in Li rechargeable cell: charge capacity versus cycle number and its first charge profile



An interesting feature was observed after subsequent heat treatments of the as-hydrothermally synthesized nanostructures. Although the phases identified by XDR were altered by the subsequent heat treatment, the initial morphology remained unchanged in all examined systems. An example is shown in Fig. 4, which was produced after the heat treatment of the specimen No. 2 shown in Fig. 1b.

The synthesized nanopowders were electrochemically tested as anode materials for Y-based system (specimen No. 1 and 2) and as cathode materials for Si-based system (specimen 4) in Li-ion cells. The testing for anode materials was conducted over the voltage range of 0.01–3.0 V versus a Li/Li<sup>+</sup> counter electrode. The discharge capacity of Y-based nanowire (specimen No. 2) was 653 mAh/g at first cycle but reduced to 533 mAh/g during charge (Fig. 5a). The difference might stem from the formation of a SEI film (solid electrolyte interface) on the surface of the nanowires, consuming irreversibly a certain amount of Li-ions. The Li-ion intercalation capacity was relatively well stabilized upon cycling: 513 and 472 mAh/g after second and tenth cycle, respectively. The values are higher than that of conventional carbon-based anode materials (372 mAh/g) in Li-ion batteries. Compared to the nanowires, the anode made from the slightly spherical nanopowders exhibited a lower discharge capacity with a poor retention upon repeated cycles (Fig. 5b). The higher discharge capacity of nanowires might be related to their higher surface area compared with spherical particles. For cathode materials, hydrothermally Si-based nanowires were examined by charge–discharge test over the voltage range of 2.5–3.5 V versus a Li/Li<sup>+</sup> counter electrode (Fig. 6). The charge capacity of the Si-based nanowire after the first cycle was 186 mAh/g, showing higher value than that of conventional Li–Mn–O or Li–Co–O cathode materials with relatively good cycle property.

## Conclusions

Y- and Si-oxide based nanoparticles with variable morphology were easily produced by a hydrothermal method

using metallic Y or Si powders. The difference in resulting morphology might be related to the supercritical condition of metal hydroxide solution at high pressure, influencing the crystal growth, but the knowledge of detailed mechanism is required to clarify the formation of nanowires. The preliminary result of the Li-ion storage property of the hydrothermally nanopowders showed clearly that the nanowires exhibit much higher capacity of Li-insertion than 2-D (flower-shaped) or 3-D (spherical) nanostructures. Further study is needed to optimize further electrochemical characteristics to be practically applicable to Li-ion cell.

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