Electronic Supporting Information (ESI)

Pore shape-reflecting morphosynthesis of lithium niobium oxide via mixed chloride flux growth in the presence of mesoporous silica

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1. Experimental

Materials

Tetraethoxysilane (TEOS) and 1,3,5-trimethylbenzene (TMB) were purchased from Tokyo Chemical Industry Co., Ltd. Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (P123) was obtained from Sigma-Aldrich Co. LLC. LiCl was purchased from Wako Pure Chemicals Industries Co. NaCl, KCl, Nb$_2$O$_5$, Li$_2$CO$_3$, NaOH, and 35-37 wt% HCl, were obtained from Kanto Chemical Co., Inc. All the chemicals were used without further purification.

Sample preparation

Preparation of mesoporous silicas with various pore sizes (SBA-15)

Mesoporous silicas (SBA-15) with various pore sizes were synthesized by the method described in the previous report.$^1$ P123 (4.0 g), TMB (0.2 or 4.0 g), HCl (20 mL), and deionized water (104 g) were mixed in a polypropylene vessel and stirred at 50°C to make a homogeneous solution, and 8.56 g of TEOS was then added slowly to the mixture under stirring. The mixture was stirred for 24 hours, transferred into a Teflon*-lined autoclave, and aged at 100°C for 72 hours. The white precipitates were then centrifuged and washed with deionized water and dried at 60°C for 1 day. Finally, the as-synthesized samples were calcined in air at 550°C for 6 hours. The products were abbreviated as SBA-15(x), where x denotes the pore size diameter calculated by the BJH method.

Preparation of lithium niobium oxide via flux growth in the presence of mesoporous silica

The following procedure is representative of synthesis in the presence of SBA-15(33). The volumes of the solutes and the mixed flux were adjusted (based on the density of each material) to the pore volume of mesoporous silica, SBA-15(x).

NaCl, KCl and LiCl were ground with a mortar and pestle, in a molar ratio of Na : K : Li = 9: 36 : 55. Subsequently, 209 mg of Nb$_2$O$_5$, 175 mg of Li$_2$CO$_3$, and 1540 mg of the mixed flux (weight ratio of the solutes in the additives = 20%) were ground with a mortar and pestle, 0.500 g of mesoporous silica, SBA-15(33), was added, and the mixture was then beaten lightly (Nb : Li = 1 : 3 in mol). After beating, the mixture was poured into a platinum crucible with a capacity of 30 cm$^3$ and calcined at 550°C in air for 10 h (heating rate = 10°C min$^{-1}$), cooled down to 300°C at a cooling rate of 10°C min$^{-1}$, and then cooled to room temperature. The resulting sample was washed with deionized water repeatedly until a negative AgNO$_3$ test was obtained, and dried in air at 60°C. The obtained powder was immersed in ca. 100 mL of 1 M NaOH aqueous solution at 100°C to dissolve the silicate and dried in air at 60°C.
Characterization

The nitrogen adsorption/desorption isotherms of the mesoporous silica samples were measured at 77 K with a BELSORP mini instrument (BEL Japan, Inc.). Prior to measurement, the samples were heated at 120 °C for 2 h under a nitrogen flow. The differential scanning calorimetry (DSC) curve for the mixed chloride flux was obtained with a Rigaku Thermo Plus DSC 8230L. The morphologies of the products were observed with a Hitachi S-5500 field emission scanning electron microscope (FE-SEM) and a JEOL JEM-2100 field emission scanning transmission electron microscope (FE-TEM). The selected-area electron diffraction (SA-ED) patterns were also obtained with a JEOL JEM-2100. XRD patterns of the solid products were recorded on a Rigaku SmartLab powder diffractometer equipped with monochromatic CuKα radiation operated at 30 mA and 40 kV. Optical microscopic images were obtained with a Nikon Eclipse E600 equipped with a temperature-controlled stage TMS94 (Linkam Scientific Instrument).

2. Consideration on Phase diagram of the Li2O-Nb2O5 system

The phase diagram of the Li2O-Nb2O5 system proposed by Svaasand et al., which is a modified version of that presented by Reisman and Holtzberg, shows that both Li3NbO4 and LiNbO3 are obtained in the Li2CO3 molar ratio range from 51% to below 75% and that both LiNbO3 and LiNb2O8 are obtained in the range from above 25% to 47%. LiNbO3 can be synthesized via mixed flux growth at 25% of the Li2CO3 molar ratio (corresponding to Nb : Li = 3:1 in mol; Fig. S4b), but single-phase Li3NbO4 was not obtained at 75% of the Li2CO3 molar ratio (corresponding to Nb : Li = 1 : 3 in mol; Fig. S4a), as mentioned above. The reaction conditions of mixed chloride flux growth conducted in this paper must reflect a different phase diagram, but they may exhibit similar tendencies.
3. Supporting Figures (Fig. S1-S6)

**Fig. S1** Nitrogen adsorption/desorption isotherms of SBA-15 (33) (a), (21) (b), and (9) (c).

**Fig. S2** Pore size distributions of SBA-15 (33) (a), (21) (b), and (9) (c), evaluated by the BJH method.
**Fig. S3** FE-TEM image of the product synthesized in the presence of SBA-15(21).

**Fig. S4** XRD pattern of SBA-15 calcined with the mixed chloride flux.
Fig. S5 XRD patterns of the products synthesized without SBA-15; Nb$_2$O$_5$:Li$_2$CO$_3$ = 1 : 3 (a) and = 3 : 1 (b). The marks white and black correspond to LiNbO$_3$ and Li$_3$NbO$_4$, respectively.

Fig. S6 Optical micrographs of the mixed chloride flux and the solutes: (a) at 20 °C, (b) at 500 °C for 0 min., (c) at 500 °C for 5 min., and (d) at 500 °C for 10 min.

4. References

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