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A green synthesis of a layered titanate, potassium lithium titanate; lower temperature solid-state reaction and improved materials performance

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ABSTRACT

A layered titanate, potassium lithium titanate, with the size range from 0.1 to 30 μm was prepared to show the effects of the particle size on the materials performance. The potassium lithium titanate was prepared by solid-state reaction as reported previously, where the reaction temperature was varied. The reported temperature for the titanate preparation was higher than 800 °C, though 600 °C is good enough to obtain single-phase potassium lithium titanate. The lower temperature synthesis is cost effective and the product exhibit better performance as photocatalysts due to surface reactivity.

1. Introduction

Layered materials and their intercalation compounds have extensively been investigated from both basic scientific viewpoints on the synthesis, structure, composition and characterization as well as from the viewpoints of their practical applications in the fields of environment, energy, electronic, photonics, and health and life problems [1]. Layered materials with a wide variety of composition and structures are available and some of them have been used practically. In addition, by means of host–guest interactions, intercalation compounds have been prepared for possible materials applications. In order to meet the requirements for the specific uses, one can select and use host and guest, composition of them, synthetic methods for the desired production scale and morphology. Thus, the materials chemistry of layered materials is rich and promising for the wide range of applications. We have been interested in the particle morphology of layered materials as a key issue to optimize the performance, and reported morphosynthesis of a layered material, layered double hydroxides [2]. In the present study, we synthesized a layered titanate with different particle size by simply changing the reaction temperature in the solid-state reactions in order to examine the effects of the particle size on the properties.

Layered titanates are forms of nanostructured titania with ion exchange, adsorption and (photo)catalytic properties [3–5]. Among layered titanates, lepidocrocite type titanates with the general formula of $A_xTi_{2-x/3}B_{x/3}O_4$ (where A=K, Rb, Cs and B=Mg, Co, Ni, Cu, Zn and so on) have been investigated so far [6–12]. The protonation and subsequent ion exchange with quaternary ammonium ions have been done to exfoliate the titanate sheets to give stable suspension. From the suspension of exfoliated nanosheet, thin films of alternating single layered negatively charged titanate nanosheet and ultrathin layer of cationic polymers were prepared by layer-by-layer assembly technique [6,13]. Potassium lithium titanates ($K_xTi_{2-x/3}Li_{x/3}O_4$, abbreviated as KTLO) is a family of the $A_xTi_{2-x/3}B_{x/3}O_4$ type material and their preparation and applications have been reported so far for such applications as electronic and optical materials [14,15]. We have reported the photocatalytic applications of KTLO powder modified with gold nanoparticle [16] as well as by the interlayer cation exchange [17]. After the modification, they exhibit unique and useful photocatalytic properties such as molecular recognitive decomposition of aqueous aromatic compounds as well as efficient phenol production from benzene. The organically modified KTLO showed unique molecular recognitive adsorption of a toxic compound from water [18]. The organically modified $A_xTi_{2-x/3}B_{x/3}O_4$ type titanates as well as

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pristine titanate has also been used as a filler to construct polymer based nanocomposites, where the properties have been modified or new functions arose from the incorporated titanate sheet has been added [18,19]. Thus, the application of $A_xTi_{2-x/3}B_{x/3}O_4$ type titanates is versatile especially in current materials science for environment and energy. In order to optimize the performances, we have been interested in preparing KTLO with varied chemical composition and surface modifications [18,21]. Here, we examined another key parameter, particle size in micrometer range, to improve the abilities of KTLO. The particle size is thought to affect the stability and transparency of aqueous dispersion, the surface area and so on, which are related to such useful properties of KTLO as photocatalysts, film and filler. The strategy employed here to obtain smaller particles is very simple, ecological and versatile that the solid-state synthesis at the temperature lower than reported value to avoid the crystal growth.

2. Material and methods

2.1. Materials

Potassium carbonate (K_2CO_3), lithium carbonate (Li_2CO_3) and methyl orange were purchased from Kanto Chemical Co., Ltd. AEROXIDE® TiO_2 P25 was purchased from Nippon Aerosil Co., Ltd. All the reagents were used without further purification.

2.2. Sample preparation

A break-down approach by ball milling the pre-synthesized KTLO was conducted to decrease the particle size. For this, KLTO was synthesized according to the previous report [22] buy the solid-state reaction from K_2CO_3, Li_2CO_3 and TiO_2 (at the molar ratio of 2.4:0.8:10.4). The starting materials were mixed manually with an agate mortar and a pestle for 2 h and the mixture was calcined in air at 800 °C for 20 h. After cooling to room temperature, the sample was mixed again with an agate mortar and a pestle for another 2 h and the mixture was heated again at 800 °C for 20 h. The product was designated as $K_{0.8}$TLO(T), where T indicate the temperature for the solid-state reactions in the second step. $K_{0.8}$TLO(800) was ball-milled using planetary ball mill (Planet M2-3, Gokin Planetaring, Japan), which has two mill pots (80 cm^3 inner volume each). $K_{0.8}$TLO(800) (1 g) and 5 g of zirconia balls with the diameter of 2 mm were added in 5 mL of isopropyl alcohol and the suspension was milled under the speed of 700 rpm (revolution) and 1750 rpm (rotation). After the drying at 80 °C, the product was calcined in air at 600 °C for 3 h.

$K_{0.8}$TLO(600) and $K_{0.8}$TLO(1000) were prepared as follows; The starting materials (K_2CO_3, Li_2CO_3 and TiO_2 at the molar ratio of 2.4:0.8:10.4) were mixed manually with an agate mortar and a pestle for 2 h and the mixture was calcined in air at desired temperatures (600 and 1000 °C for $K_{0.8}$TLO(600) and $K_{0.8}$TLO (1000), respectively) for 20 h. P25 was used as titania source because we thought that the finite size particle is better to obtain homogeneous products at lower temperature synthesis. After cooling to room temperature, the sample was mixed again with an agate mortar and a pestle for another 2 h and the mixture was heated again at the same temperature for 20 h.

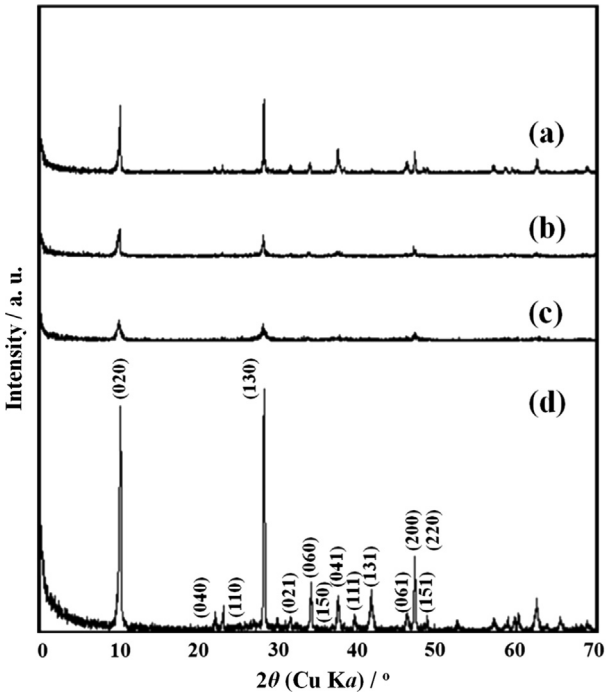

Fig. 2. The XRD pattern of ((a) and (b)) $K_{0.8}$TLO(800) (a) before and (b) after the ball-milling for a hour, (c) $K_{0.8}$TLO(600) and (d) $K_{0.8}$TLO(1000).

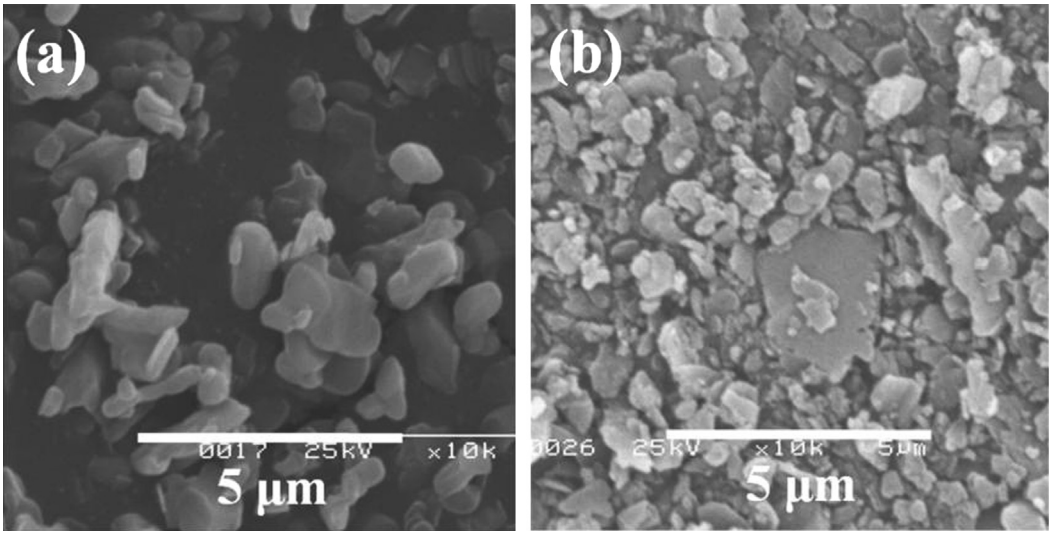

Fig. 1. SEM images of $K_{0.8}$TLO(800) (a) before and (b) after the ball-milling.