# Hydrothermal synthesis of photocatalyst potassium hexatitanate nanowires under supercritical conditions

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Potassium hexatitanate ($K_2O \cdot 6TiO_2$: KTO) is a material with high heat resistance and chemical stability. Fibrous KTO particles are used as insulator for polymers [1] and metal alloys [2]. KTO has a specific crystal structure with a rectangular tunnel structure, and is one of the photocatalysts for water decomposition [3]. KTO particles are synthesized by solid-state reaction of stoichiometric titanium dioxide and potassium carbonate at 900 °C for 18 h, conventionally. Particles obtained by the solid-state method were whickers with particle size of several micrometers. Since photocatalytic reactions occur on the surface of catalysts, fine particles having large surface area are desirable. KTO particles can be produced by hydrothermal synthesis [4, 5] and can also melt [7]. However, there is no fine particle proper to photocatalytic applications because the main purpose of these researches was to make long and fibrous materials for reinforcement materials.

The objective of this study was to synthesize potassium hexatitanate fine particles with high photocatalytic activity. Hydrothermal synthesis near the critical point of water using a flow reactor was well known as one of the methods of producing fine metal oxide particles [8, 9]. Near the critical point (374 °C, 22.1 MPa) of water, the rate of hydration (hydrothermal reaction) of metal salts increases with decreasing dielectric constant of water, while solubility of metal oxide decreases. Since nucleation is driven by a high level of supersaturation, fine particles can form [10] based on conventional nucleation theory in solution. When this method is applied to the synthesis of KTO particles, one expects to obtain finer KTO particles with better photocatalytic performances.

This paper reports the fabrication of KTO nanowires by hydrothermal synthesis under supercritical conditions using a flow reactor. We investigated suitable synthetic conditions for single phase and fine KTO particle by varying reaction temperatures and KOH concentrations. Photocatalytic performance of KTO particles obtained was evaluated by a methanol photodecomposition.

The starting materials were titanium hydroxide sols and potassium hydroxide (Wako Chemicals Co. Ltd.). The starting solutions were prepared by dissolving these materials into distilled water. Titanium ion concentration was set to 0.02 M and potassium hydroxide concentration was varied in the range of 0.02–0.4 M.

Fig. 1 illustrates a schematic diagram of an experimental apparatus used in this study. Titanium hydroxide sol solution and aqueous potassium hydroxide solution were fed separately by a high-pressure pump at a flow rate of 2.0 cm$^3$/min. These two solutions were mixed at the mixing tee (MP1) and then fed to a reactor. On the other hand, distilled and deionized water was fed by another pump at a flow rate of 11.0 cm$^3$/min and heated in an electric furnace. Titanium and potassium ion mixed solution was mixed with preheated water at a second mixing tee (MP2) and thus heated to reaction temperature rapidly. Reactants were resisted in the reactor (volume of 1.8 cm$^3$) and then cooled by a heat exchanger. Reactants were also depressurized through a back-pressure regulator and then recovered in a reservoir. Reaction temperatures were 350, 400 and 420 °C and the pressure was set to 30 MPa. Residence time was 2–3 s. The productivity of KTO was about 0.3 g/h.

The powder recovered was dried in an oven at 60 °C for 24 h. The crystal structure was determined by powder X-ray diffraction (RIGAKU, Lint 2000). Cu-K$_\alpha$ radiation was used as a source and scanning speed was set to 2 °/min. Particle sizes and morphologies were observed by transmission electron microscopy (TEM) (Carl Zeiss, LEO 120). Specific surface areas were measured by the BET one point method. The K/Ti ratio of the product was determined by the ICP (ion coupled plasma) technique.

Photocatalytic performance was evaluated by methanol photodecomposition. The light source was a high-pressure Hg lamp (400 W). The catalyst (300 mg) was placed in a glass reactor containing 500 cm$^3$ water–methanol mixture (10 vol%). The evaluated hydrogen concentration was measured by a gas chromatograph with auto-sampler every 30 min.

Table I summarizes experimental conditions and results. Fig. 2 shows XRD patterns of particles obtained at various KOH concentrations of 0.02, 0.2, and 0.4 M. The reaction temperature was 400 °C and pressure was 30 MPa. At 0.02 M KOH concentration, the main product was not an amorphous $TiO_2$ of starting materials but a crystalline titanium dioxide (anataze). With increasing KOH concentration, peaks of $TiO_2$ became small and several broad peaks appeared at around 10°, 14°, and 30°. At 0.4 M KOH concentration, peaks of $TiO_2$ disappeared. Since all peaks on the XRD pattern of (c) were assigned by $K_2Ti_6O_{13}$ (JPDPS 40-403), this implied that these particles were single-phase KTO. The BET surface area of these particles was about 220 m$^2$/g, which is three times greater than that of a crystalline $TiO_2$ (70 m$^2$/g) as shown in Table I.
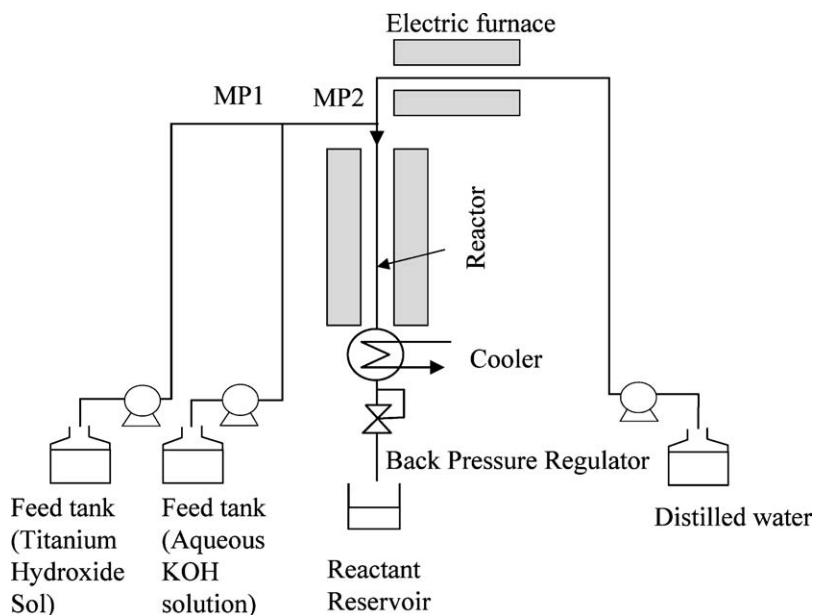
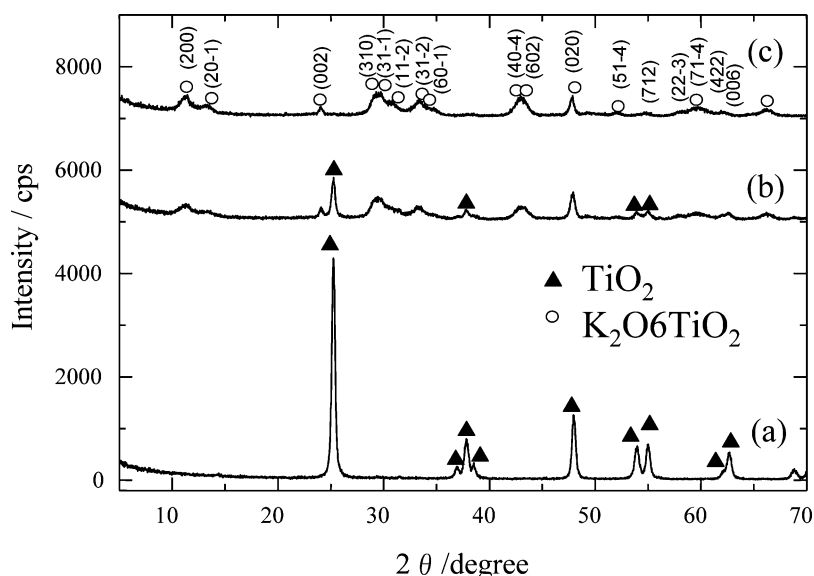*Figure 1* Flow apparatus for producing fine potassium hexa-titanate nanowires.



*Figure 2* XRD profiles of products obtained from various KOH concentrations of (a) 0.02 M, (b) 0.2 M and (c) 0.4 M. (Conditions: T: 400 °C, P: 30 MPa, Residence time: 1.8 s.)

Fig. 3 shows TEM images of products at various reaction temperatures of (a) 350 °C, (b) 400 °C, and (c) 420 °C. As shown in Fig. 3a, spherical particles of width 30 nm and fibrous particles of width 10 nm were observed. The product at 350 °C was a mixture of $TiO_2$ and KTO according to XRD analysis. Fibrous particles were KTO and probably spherical particles were crystalline $TiO_2$. On the other hand, at 400 and 420 °C spherical particles are not observed and only fibrous particles can be observed in the figures. These were single-phase KTO particles by XRD analysis. The width of KTO particles obtained at 400 °C was about 10 nm with the length ranging from 500 to 1000 nm as shown in Fig. 3d. The particle size at 420 °C was five times larger than that of particles obtained at 400 °C. The particle morphologies of potassium hexatitanate obtained by this flow method were fibrous independent of reaction temperature and particles became larger with increasing reaction temperatures.

The conventional hydrothermal method using a batch reactor produces micron-order KTO particles in supercritical water for a reaction lasting several hours [6]. But the flow method used in this study could produce nano-scaled KTO particles in several seconds, even at nearly the same temperature and pressure. In a batch system, since reactants are elevated to temperature very

TABLE I Experimental conditions and results

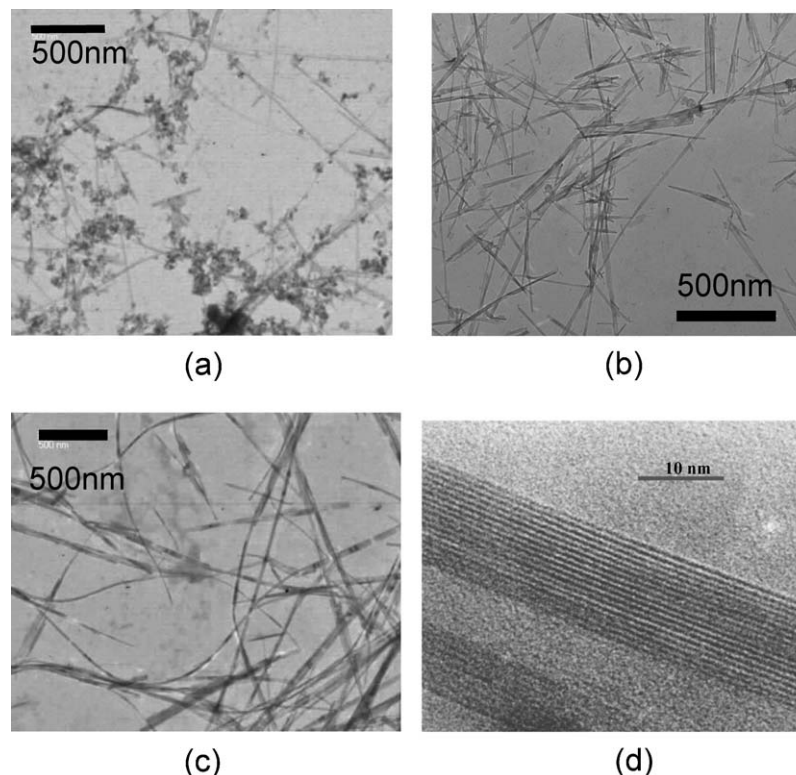| Temperature (°C) | Pressure (MPa) | K/Ti ratio | Molar product | BET surface area ($m^2$/g) |
|---|---|---|---|---|
| 350 | 30 | 20 | $TiO_2$, $K_2O6TiO_2$ | 91.0 |
| 420 | 30 | 20 | $K_2O6TiO_2$ | 79.0 |
| 400 | 30 | 1 | $TiO_2$ | 66.6 |
| 400 | 30 | 2 | $TiO_2$ | 70.1 |
| 400 | 30 | 10 | $TiO_2$, $K_2O6TiO_2$ | 71.1 |
| 400 | 30 | 20 | $K_2O6TiO_2$ | 219.8 |

*Figure 3* TEM photographs of the KTO nanowires obtained at various reaction temperatures of (a) 350 °C, (b) 400 °C and (c) 420 °C. (d) is a high resolution image of (b).

slowly (20 °C/min), low-temperature materials, i.e. a crystalline $TiO_2$, formed before the reactant reached the intended reaction temperature. The slow $TiO_2$ dissolving rate controlled KTO formation and thus KTO particles grew larger as reactions proceeded further. On the other hand, an extremely short heating time of the flow reactor could prevent the formation of a crystalline $TiO_2$ and thus KTO was synthesized only at suitable solution condition. Since hydrothermal crystallization of KTO

particle was completed in a short time, particles did not grow. This is the reason why KTO nanowires could be obtained with high efficiency by the flow method.

KTO particles obtained at 400 °C and 30 MPa were well dispersed into water–methanol mixture and not precipitated. This means crystalline KTO particles obtained were not aggregated strongly. Fig. 4 shows hydrogen evolution for photodecomposition of methanol with reaction times. The amount of hydrogen evolution
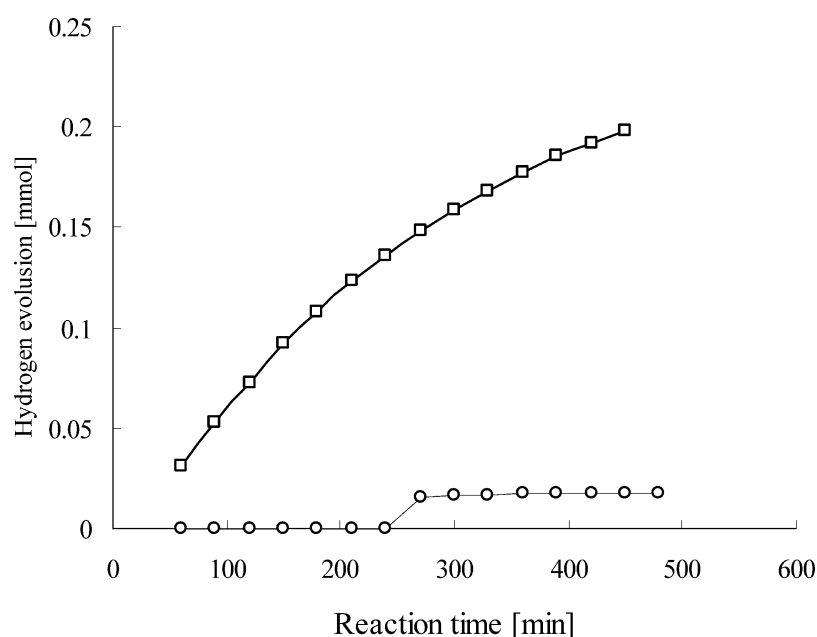


*Figure 4* Time course of hydrogen evolution from methanol decomposition over KTOs with various specific surface areas. □ : KTO particles obtained by the flow apparatus at 400 °C and 30 MPa for 1.8 s; ○: KTO particles obtained by conventional batch apparatus at 400 °C and 28 MPa for 24 hr. Reaction conditions: catalyst 0.3 g; 50 vol% methanol-$H_2O$, 500 cm$^3$, a high-pressure mercury lamp (400 W); an inner irradiation type Pyrex cell.

from KTO obtained in this study was 10 times greater than those of KTO particles with micron size, which were produced by a conventional hydrothermal reaction at 400 °C and 28 MPa for 24 hr.

Novel potassium hexatitanate nanowires could be synthesized from titanium hydroxide sols and potassium hydroxide via hydrothermal synthesis under supercritical conditions using a flow reactor. The KTO particles obtained at 400 °C and 30 MPa were crystalline particles, 10 nm in width and length ranging from 500 to 1000 nm. The photocatalytic activity of KTO nanowires was 10 times greater than that of micron-order particles.

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