Hydrothermal synthesis of crystalline rectangular titanoniobate particles†

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Potassium titanoniobate ($KTiNbO_5$) crystalline powders possessing rectangular particle shapes and large surface areas which are prerequisite for high photocatalytic performance have been successfully synthesized by a novel hydrothermal method.

With the rising demand for clean and efficient energy sources which exist abundantly in the earth, studies on the photodecomposition of water and hydrogen evolution have attracted more and more attention.[1] A group of ternary or multicomponent oxides based on alkali metal titanate and niobate, were expected to be a new group of photocatalysts having high catalytic activities.[2] On the other hand, it was found that the high photocatalytic efficiency of some novel layered oxide compounds was attributed to the utilization of their interlayer space as reaction sites.[3] Accordingly, as a potential mother compound for photocatalysts, potassium titanoniobate ($KTiNbO_5$) has been a focus in material science due to its unique layered structure and stable photochemical properties.[4] Furthermore, the layered structure of $KTiNbO_5$ enables the intercalation of organic molecules, which is expected to have use as nanodevices and nanoreactors.[5] Thus, studies on the titanoniobate compounds are pivotal subjects in both photochemistry and nanotechnology science. $KTiNbO_5$ is commonly prepared by a high temperature method, such as solid-state synthesis (around 1100 °C)[6] and the polymerizable complex method (around 700 °C).[4a] The high temperature heating treatments usually cause component loss and an increase in particle size, thus lowering its reaction activity. Therefore, it is a great challenge to explore an alternative method adopting mild reaction condition to synthesize $KTiNbO_5$.

The experimental conditions of the hydrothermal process are not severe and this method is effective for synthesizing inorganic photocatalysts such as titanium oxide, niobium oxide and their ternary oxides.[7] Supercritical water has proved to be an environmentally benign and ideal reaction medium in materials synthesis.[8] Reactions in supercritical water could happen easier than those under conventional hydrothermal conditions because of the drastic changes of water's properties in the region of supercritical state. Until now it has been reported that titania and potassium hexatitanate exhibiting high photocatalytic activities have been synthesized under supercritical or subcritical water conditions.[7a,9]

Here for the first time we report that $KTiNbO_5$ crystalline powders can be synthesized by a novel hydrothermal method. The one-step hydrothermal synthesis of a multicomponent oxide compound which is commonly synthesized by a high temperature solid-state method is successfully achieved in this work. The obtained $KTiNbO_5$ powders have very thin, regular, rectangular particle shapes and large surface areas, which should play an important role in its catalytic activity.

The starting reagents used in the hydrothermal preparation were titanium tetraisopropoxide (95%, Wako Pure Chemical Industries, Ltd), Nb_2O_5 fine powder (99.95%, Koso Chemical Co., Ltd) and potassium hydroxide (85%, Wako Pure Chemical Industries, Ltd) aqueous solution. Stoichiometric amounts of Nb_2O_5, titanium tetraisopropoxide and 250 ml KOH aqueous solution were mixed together and stirred for 4 h to become a white slurry. Then the slurry was put into a gold tube in the autoclave. The autoclave in this work is made of incorruptible nickel alloy (Inconel 625) with cylindrical shape (500 cm^3 capacity). The hydrothermal reaction was carried out at 300 °C or 400 °C with autogenous pressure inside the autoclave. The Teflon-lined autoclave which is commonly used in conventional hydrothermal synthesis is not suitable for the experimental conditions in this work. Accordingly, a gold tube is used here since its incorruptible and heat-stable properties. The pressure inside the autoclave is measured by using a pressure transducer connected with an electrical displaying system. The value was 3 MPa when the temperature was 300 °C, and 25 MPa when the temperature was 400 °C, respectively. Upon completion of the reaction, the gold tube with product in it was taken out. The white precipitates were filtrated and washed with distilled water, then dried at 60 °C.

Crystal structures of the resulting powders were determined by X-ray powder diffraction (XRD), performed on a Rigaku RINT 2200 diffractometer using Cu Kα radiation (40 kV and 20 mA). The morphology of the prepared $KTiNbO_5$ was observed by using a Hitachi S-800 scanning electron microscope (SEM) and JEOL JEM-2000EXII transmission electron microscope (TEM) operating at 200 kV. BET surface area was measured with a YUASA IONICS CHEMBET-3000. Thermal analysis was performed using a Rigaku Thermo Plus TG-8120 thermal analyzer with alumina as reference. Elementary analysis (atomic ratio) was performed by using a Hitachi S-800 scanning electron microscope equipped with a Horiba EMAX ENERGY energy disperse spectroscope (SEM-EDS).

Fig. 1 presents the XRD patterns of the hydrothermally synthesized $KTiNbO_5$ powders. According to Fig. 1, the hydrothermally synthesized $KTiNbO_5$ powders show broadened diffraction peaks in comparison with the sample prepared by the

† Electronic supplementary information (ESI) available: (a) XRD pattern of hydrothermally prepared sample 400-0.5-8. (b) SEM image of $KTiNbO_5$ particles prepared by the solid-state method. (c) SEM image of $KTiNbO_5$ particles of sample 400-0.5-2. See http://www.rsc.org/suppdata/cc/b4/b418002j/

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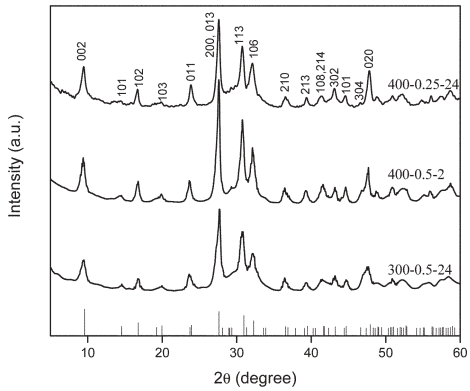

Fig. 1 XRD patterns of hydrothermally synthesized $KTiNbO_5$. The samples are named by reaction temperature (°C)-KOH concentration (M)-reaction time (h). Lines at the bottom indicate the peak position of $KTiNbO_5$ calculated from JCPDS 71-1747.

solid-state method due to the smaller crystallite size. It is seen that pure phase $KTiNbO_5$ is formed after 24 h reaction in 0.25 M KOH solution at 400 °C (sample 400-0.25-24). All the diffraction peaks can be indexed as $KTiNbO_5$ (JCPDS 71-1747). As 0.5 M KOH aqueous solution is employed in the reaction, the obtained powder has the pure structure of $KTiNbO_5$ after 2 h reaction (sample 400-0.5-2). Extending the reaction time would result in a trace of contaminant in the final product (see ESI (a)†). When the hydrothermal reaction is carried out at 300 °C in 0.5 M KOH solution with reaction time of 24 h, $KTiNbO_5$ powders displaying strong and sharp diffraction peaks in the XRD patterns could be still obtained (sample 300-0.25-24). Moreover according to Fig. 1, the intensities of the (200) peak in all the XRD patterns are relatively stronger in comparison with the JCPDS file data of $KTiNbO_5$, indicating that the preferred crystal growth direction of hydrothermally synthesized $KTiNbO_5$ is along (200). SEM-EDS characterizations confirm the atomic ratio of component elements is stoichiometric as the molecular formula $KTiNbO_5$.

Thermal analysis reveals that the dehydration of $KTiNbO_5$ in the hydrothermal process is complete, and no phase transition is observed in the DTA curve up to 1000 °C, suggesting that the $KTiNbO_5$ powders synthesized by the hydrothermal method are thermally stable. BET surface area measurements demonstrate that the hydrothermally synthesized $KTiNbO_5$ powders possess large surface areas. The $KTiNbO_5$ sample of 300-0.5-24 has the largest BET surface area of 97.4 $m^2\ g^{-1}$, which is 75 times the surface area of the $KTiNbO_5$ powder prepared by the solid-state method. Increasing the hydrothermal temperature results in better crystallinity but lowers the surface area. The BET surface area of $KTiNbO_5$ powders synthesized at 400 °C, such as 400-0.5-2 and 400-0.25-24, is 69.6 $m^2\ g^{-1}$ and 55.9 $m^2\ g^{-1}$, respectively.

Fig. 2a shows the TEM image of $KTiNbO_5$ particles synthesized by the hydrothermal method. The particles of $KTiNbO_5$ prepared by the solid-state method have neither regular shape nor uniform particle size (see ESI (b)†), while all the $KTiNbO_5$ particles synthesized by the hydrothermal method show a rectangular flake shape with sizes in the range 1–3 μm. Furthermore, the particle size of sample 400-0.25-24 is larger than that of sample 400-0.5-2 due to its extended reaction time (see ESI (c)†). All of the rectangle particles are very thin since the supporting carbon film under the particles can be observed as shown in Fig. 2a and Fig. 2b. The

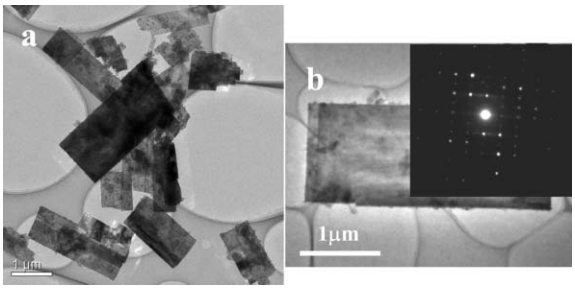

Fig. 2 (a) TEM image of rectangular $KTiNbO_5$ particles; (b) TEM image of an individual $KTiNbO_5$ particle (sample no. 400-0.25-24). The inset of (b) is the corresponding SAED pattern.

inset of Fig. 2b is the selected area electron diffraction (SAED) pattern for an individual particle, indicating that the hydrothermally synthesized $KTiNbO_5$ particle is a single crystal.

Fig. 3a is the lattice fringe image of a $KTiNbO_5$ particle observed by using high resolution transmission electron microscope (HRTEM). The distance between the lattice fringe is about 0.32 nm which coincides with the *d*-spacing of the (200) lattice plane of $KTiNbO_5$, suggesting that the crystals grow along the plane (200). Such a conclusion is also in agreement with the XRD results that the crystals grow along the (200) direction. Furthermore another thing we should mention is that in all cases the surface of the large rectangular particles of $KTiNbO_5$ is attached to small particles (around 30 nm in length and 10 nm in width). The shapes of the small particles are also rectangular as shown in Fig. 3b. The HRTEM image of the selected small particles shown in Fig. 3b is given in Fig. 3c, in which the lattice fringes with a distance of 0.32 nm is clearly observed, indicating that the small particles are not amorphous. By analyzing the XRD patterns, atomic ratios, DTA curve and the HRTEM images, the structure of such small particles should be identical with that of the big rectangular particles, *i.e.* $KTiNbO_5$. Generally say, the small particles of $KTiNbO_5$ might form at the start of crystal growth of $KTiNbO_5$, during the hydrothermal process. Moreover, it is found that the amount of small particles in the $KTiNbO_5$ samples prepared using short reaction times is larger than in the samples

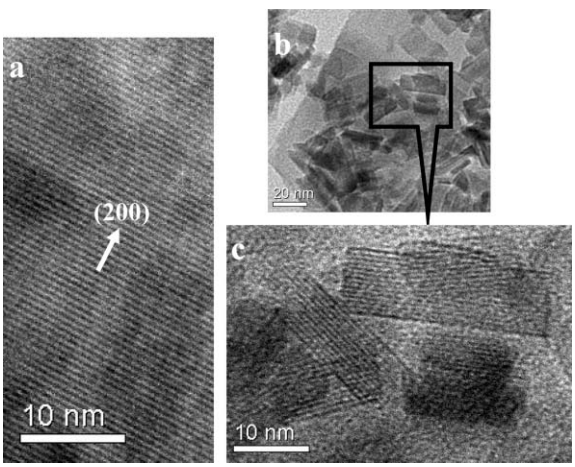

Fig. 3 (a) HRTEM image of a $KTiNbO_5$ particle (sample no. 400-0.5-2); (b) TEM image of small rectangular particles attached to a large and thin particle; (c) the HRTEM image of the selected area shown in (b).

prepared using relatively long reaction times, suggesting that this explanation is reasonable.

In conclusion, pure phase $KTiNbO_5$ powders having thin and rectangular particle shapes and large surface areas have been successfully synthesized by a novel hydrothermal method. This study develops an efficient and mild preparation process to synthesize $KTiNbO_5$ which is regarded as an ideal mother compound for photocatalysts and nanoscale devices.

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