Preparation of $H_2Ti_4O_9$ with High Specific Surface Area

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$H_2Ti_4O_9$ nanocrystals with high specific surface areas were prepared by exfoliation and reassembly process through a novel way of ball milling and ion-exchange reaction. The specific surface area of $H_2Ti_4O_9$ nanocrystals depends on solution pH value and ball milling time. $H_2Ti_4O_9$ nanocrystals precipitated by milling $K_2Ti_4O_9$ for 2 h and exfoliating in 1 M HCl followed by adjusting solution pH at 8 has the specific surface area of 328.2 m^2/g.

Nanosized materials have novel physicochemical properties compared with bulk materials. The layered compounds have been reported to delaminate into their elementary host layers through soft-chemical methods. These crystallites, which are usually described as nanosheets, have a thickness from one to several tens of nanometer and the lateral size is in the range of one to several micrometers. Since catalytic activities are highly surface-dependent, it is expected that the decrease of the crystallite size could improve the photocatalytic activities.

In the past, all of the layered-structure compounds were delaminated by using organic substance, such as tetramethylammonium hydroxide (TBAOH),[1,2] *n*-alkylamine,[3] and organoammonium chlorides.[4] In addition, it required long time, low solid content and high organic compound concentration; therefore, the production of low cost materials in large scale is impossible. In this paper, we prepared $H_2Ti_4O_9$ with high specific surface area through exfoliation and reassembly process using a unique method, mechanochemical reaction combined with ion-exchange reaction. To the best of our knowledge, this is the first report on the delamination of layered titanates without using organic compound and preparation of protonic tetratitanates possessing very high specific surface area.

Potassium tetratitanate, $K_2Ti_4O_9$ (Otsuka Chemical Co. Ltd., Tokyo, Japan) was used as a starting material. Four grams of the powder was put into a zirconia pot of 45 cm^3 of internal volume together with seven zirconia balls, 15 mm in diameter, and dry milled for a certain time using a high energy planetary mill (Pulverisette-7, Fritsch, Germany) at 700 rpm rotation speed and room temperature. Thus obtained 10 g of the powder was suspended in a 1000 cm^3 vigorously stirred 1 M HCl at room temperature for 2 h. After that the pH of the solution was adjusted to different value with 0.5 M aqueous ammonia solution to precipitate the sample. The products were collected by centrifugation, washed with distilled water, and then dried overnight in vacuum at 60 °C. The content of K in the sample was determined by atomic absorption spectroscopy (Shimadzu, AA-6500S) after dissolving the sample in HCl solution by boiling for 4 h in a glass covered flask.

The exfoliation behavior of $K_2Ti_4O_9$ was examined through ion-exchange treatment with 1 M HCl. When the milled $K_2Ti_4O_9$ (milling time 1 and 2 h) was dispersed in 1 M HCl solution, a stable colloidal suspension with an opalescent appearance was formed. Sasaki et al. claimed that this kind of colloidal suspension contains unilamellar crystallites in the form of titania nanosheets in delaminated $H_{0.7}Ti_{1.825}\square_{0.175}O_4 \cdot H_2O$ system.[5] We found the colloidal state was stable for several 10 h, after stopping stirring. On the other hand, when $K_2Ti_4O_9$ without ball milling was used, precipitation generated promptly after stopping stirring. Ammonia solution was added into the colloidal suspension to get the sediment. The pH value was adjusted to 2, 4, 6, and 8. The sedimentation time changed depending on pH value. When the solution pH was adjusted to 8, precipitation generated within several minutes, while it took several tens of minutes to sediment the sample at pH 2. The samples were then centrifuged at 15000 rpm for 10 min, and the recovered solid were examined by XRD and chemical analysis. More than 99.9% of K^+ had been exchanged with H^+ under present reaction conditions. The diffraction patterns of the sediment obtained from the solution at pH 4 are shown in Figure 1. It exhibits typical $H_2Ti_4O_9 \cdot 1.9H_2O$ XRD pattern, indicating that this compound could be synthesized by delamination and reassembling process of ${Ti_4O_9}^{2-}$ and ion exchange of K^+ to H^+. However, compared with the XRD pattern of fibrous $H_2Ti_4O_9 \cdot 1.75H_2O$ prepared with $K_2Ti_4O_9$ without ball-milling, the samples prepared with $K_2Ti_4O_9$ ball-milled for 2 h, as shown in Figure 1c, showed broad diffraction peaks. Sasaki et al. also found the line broadening of (0*k*0) of $H_xTi_{2-x/4}\square_{x/4}O_4 \cdot H_2O$ (x–0.7; $\square$, vacancy) for the parallel sheets $N \geq 2$ with the spacing of 12 nm and they denied the effect of sheet bending and interstratification on the broad diffraction line.[1] However, in our case, the sheet bending might mainly lead to the broad diffraction lines. The sheet bending could be taken as nonuniform distortion of the lattice. During mechanical grinding, the powders are subjected to severe mechanical deformation from collisions with the milling tools. Consequently, plastic deformation at high strain rates occurs within particles. The average grain size can be reduced after extended mechanical grinding. The overall line width is a sum of

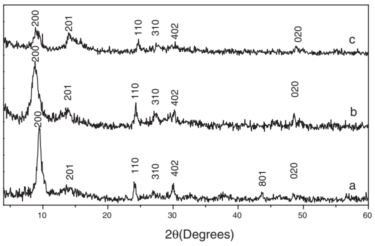

Figure 1. XRD patterns of $H_2Ti_4O_9$ (a) prepared by dispersing $K_2Ti_4O_9$ without grinding in 1 M HCl; (b) prepared by exfoliation in 1 M HCl and reassembling at pH 4 using $K_2Ti_4O_9$ ball-milled for 1 h, and (c) prepared by exfoliation in 1 M HCl and reassembling at pH 4 using $K_2Ti_4O_9$ ball-milled for 2 h.

those caused by random strain and crystallite size. During the milling, the incorporation of lattice defect into the crystal lattice is inevitable, which might also contribute to the peak broadening. The effect of grain size and strain on the line broadening can be clearly seen by comparing the broadening of the samples prepared using $K_2Ti_4O_9$ milled for 1 and 2 h. $H_2Ti_4O_9$ prepared by longer grinding time contains much more defects, strains and smaller grain size, as a result, this sample shows broader XRD peaks, see Figures 1b and 1c. Consequently, the broad profile could be regarded as evidence of exfoliation of the layered protonic tetratitanate. The degree of crystallization of materials calculated by the DP-D1 software was in the order: Fibrous $H_2Ti_4O_9$ prepared with $K_2Ti_4O_9$ without ball-milling (100%) > $H_2Ti_4O_9$ prepared with $K_2Ti_4O_9$ milled for 1 h (98.9%) > $H_2Ti_4O_9$ prepared with $K_2Ti_4O_9$ milled for 2 h (95.1%).

Figure 2 shows a typical TEM image of $H_2Ti_4O_9$. The sample made with $K_2Ti_4O_9$ milled for 2 h consisted of two types of particles, i.e., the most of them existed as nanosheets of lateral dimensions about 50 nm and the others were the aggregates of fibrous particles. In addition, there are some areas where two crystallites overlapped (such as spot A) and their contrast nearly double of that of other spots, indicating that the crystallites are very thin and likely to be unilammellar. In contrast, the ion-exchange product of $K_2Ti_4O_9$ without grinding was fibrous similar to $K_2Ti_4O_9$ used as the raw material.

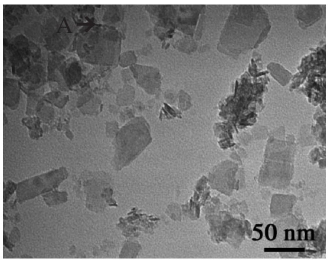

Figure 2. TEM photograph of sample prepared by exfoliation in 1 M HCl and reassembling at pH 4 with $K_2Ti_4O_9$ ball-milled for 2 h.

The nitrogen adsorption–desorption isotherms and pore size distribution (BJH) of $H_2Ti_4O_9$ nanocrystals are shown in Figure 3. In terms of shape, the adsorption isotherms may be classified as type IV with a hysteresis loop, which can be classified as H3 type. This kind of hysteresis loop is indicative of the presence of slit-like pores. The restacked $H_2Ti_4O_9$ showed a very narrow pore size distribution of mesopores of the diameter less than 10 nm. This disordered porous structure might be due to the voids between the lamellar crystallites consisted of random stacked 2-D nanosheetes. The total pore volume of restacked $H_2Ti_4O_9$ is 481.0 cm^3g^{-1}.

$H_2Ti_4O_9$ nanocrystals prepared by ball-milling, exfoliation and reassembling possessed very high specific surface area above 236 m^2g^{-1} (see Table 1), whereas the specific surface area of the sample prepared using $K_2Ti_4O_9$ without ball-milling was only 21.8 m^2g^{-1}. The specific surface area increased with ball-milling time and pH of reassembling solution. Consequently, the sample prepared using $K_2Ti_4O_9$ ball-milled for 2 h and reassembled at pH 8 showed quite high specific surface area such as 328.2 m^2g^{-1}. The reassembly process in the solution at high pH involves an increase in the population of the reassembly nuclei, as a result, much more smaller $H_2Ti_4O_9$ crystallites could be obtained which lead to the high specific surface area of the powder.

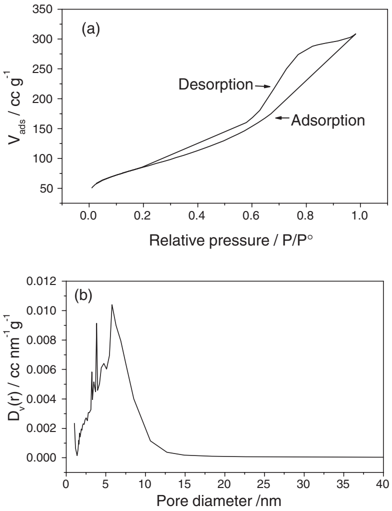

Figure 3. (a) Nitrogen adsorption–desorption isotherms and (b) pore volume distribution (BJH) of $H_2Ti_4O_9$ nanocrystals prepared by exfoliation in 1 M HCl and reassembling at pH 4 using $K_2Ti_4O_9$ ball-milled for 2 h.

Table 1. Specific surface area of $H_2Ti_4O_9$ prepared under different conditions

Sample	BET specific surface area (m^2g^{-1})			
	pH 2	pH 4	pH 6	pH 8
Prepared with $K_2Ti_4O_9$ grinded for 1h	236.4	241.3	244.9	272.1
Prepared with $K_2Ti_4O_9$ grinded for 2h		298.4		328.2
Prepared with $K_2Ti_4O_9$ without grinding[a]	21.8			

[a] Ion exchange at pH0

In summary, $H_2Ti_4O_9$ nanocrystals could be prepared by exfoliation and reassembly process combined with ball-milling and ion-exchange reaction. The specific surface area of $H_2Ti_4O_9$ nanocrystals attained 328.2 m^2g^{-1} which is ca. 16 times greater than that of fibrous $H_2Ti_4O_9$ prepared using $K_2Ti_4O_9$ without ball-milling.

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