Supporting Information

Particle size for photocatalytic activity of anatase TiO_2 nanosheets with highly exposed {001} facets

Zhenquan Tan[1,2,]*, Kazuyoshi Sato[3], Seiichi Takami[4], Chiya Numako[5], Mitsuo Umetsu[6], Kohei Soga[7], Masao Nakayama[8], Ryohei Sasaki[8], Tsutomu Tanaka[1], Chiaki Ogino[1], Akihiko Kondo[1], Kazuhiro Yamamoto[2], Takeshi Hashishin[2], and Satoshi Ohara[2].

[1]Department of Chemical Science and Engineering, Graduate School of Engineering, Kobe University, Kobe, Hyogo 657-8501, Japan. [2]Joining and Welding Research Institute, Osaka University, Ibaraki, Osaka 567-0047, Japan. [3]Graduate School of Engineering, Gunma University, Kiryu, Gunma, Japan. [4]Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Miyagi, Japan. [5]Graduate School of Science, Chiba University, Chiba, Japan. [6]Graduate School of Engineering, Tohoku University, Sendai, Miyagi, Japan. [7]Department of Materials Science and Technology, Faculty of Industrial Science and Technology, Tokyo University of Science, Noda, Chiba 278-8510, Japan. [8]Graduate School of Medicine, Kobe University, Kobe, Hyogo, Japan.

* E-mail: zq-tan@jwri.osaka-u.ac.jp

Experimental Methods

Synthesis of TiO_2 nanosheets. Ammonium hexafluorotitanate (1 g; 99.99% purity) was dissolved into 5 ml of hydrochloric acid (5 M). titanium(IV) butoxide (97% purity) was then added to the above solution under strong stirring in a controlled amount such that the total F/Ti molar ratio was 1.0, 1.2, 1.5, 1.8, or 2.0. White gels formed under continuous stirring. The gels were placed into a 50 ml Teflon tube for a 6-hour hydrothermal reaction at 180 ºC. The products of the hydrothermal reaction were washed with ultrapure water (resistance = 18.2 MΩ) three times and by methanol once, all with subsequent centrifugal separation (10,000 G, 10 min).

Photocatalytic activity characterisation. The obtained TiO_2 nanosheets were dried under air atmosphere at 80 ºC. For evaluation of the photocatalytic activity of the TiO_2 nanosheets, 200 mg of TiO_2 was mixed and dispersed in 200 ml of a solution containing organic dyes (5 mg/l). The mixture solutions were irradiated by a low-pressure mercury arc lamp (210 W) for 5 hours, and the samples were collected every 30 min. The concentrations of the dyes were determined by UV-Vis absorption measurements after two centrifugations for 30 min each. Four types of dye were used in this study: methylene blue, bromothymol blue, cresol red, and phenol red. Control experiments that used two types of commercial TiO_2 nanoparticles, ST-01 (Ishihara Sangyo, Japan) and P25 (Degussa AG, German), which are both well-known high-performance photocatalysts, were also performed to evaluate the photocatalytic activity.

Supplementary Figures

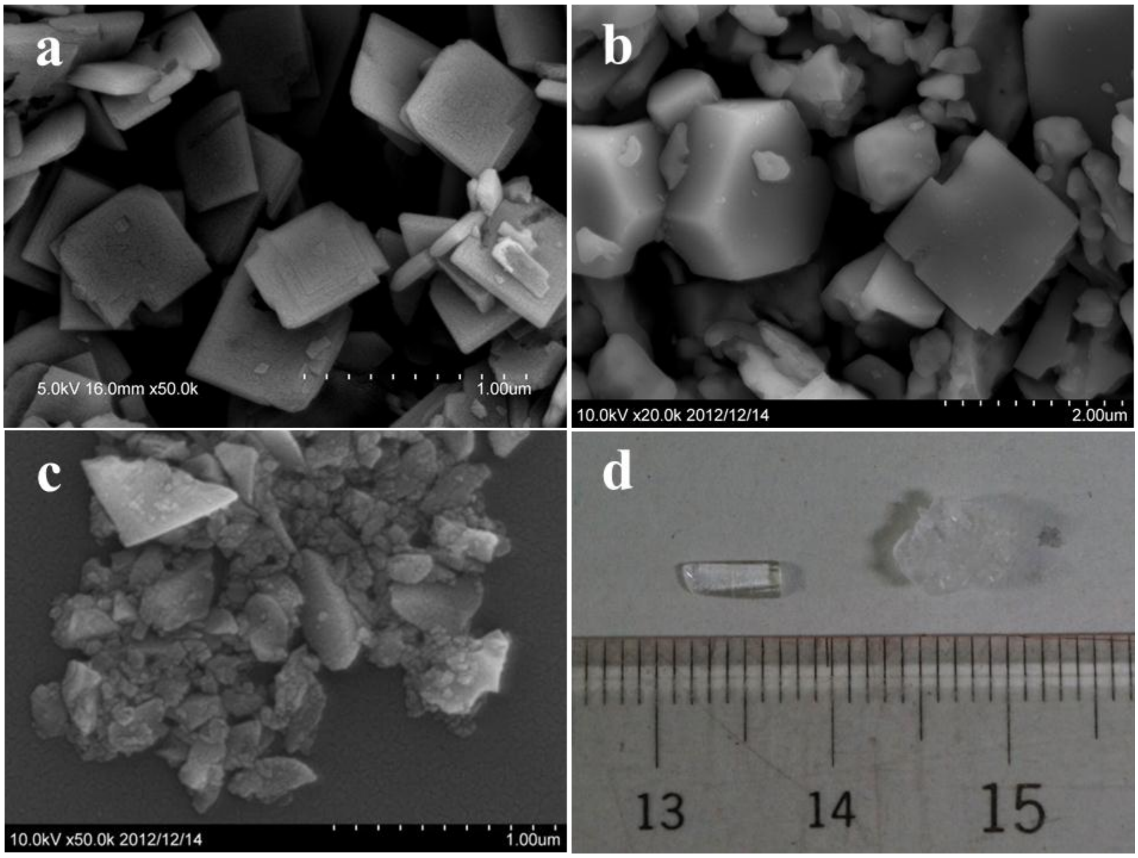

Fig. S1 SEM images of TiO_2 particles prepared with various F/Ti ratios. The F/Ti molar ratios are a) 2.0, b) 3.0, c) 4.0, and d) 6.0, respectively.

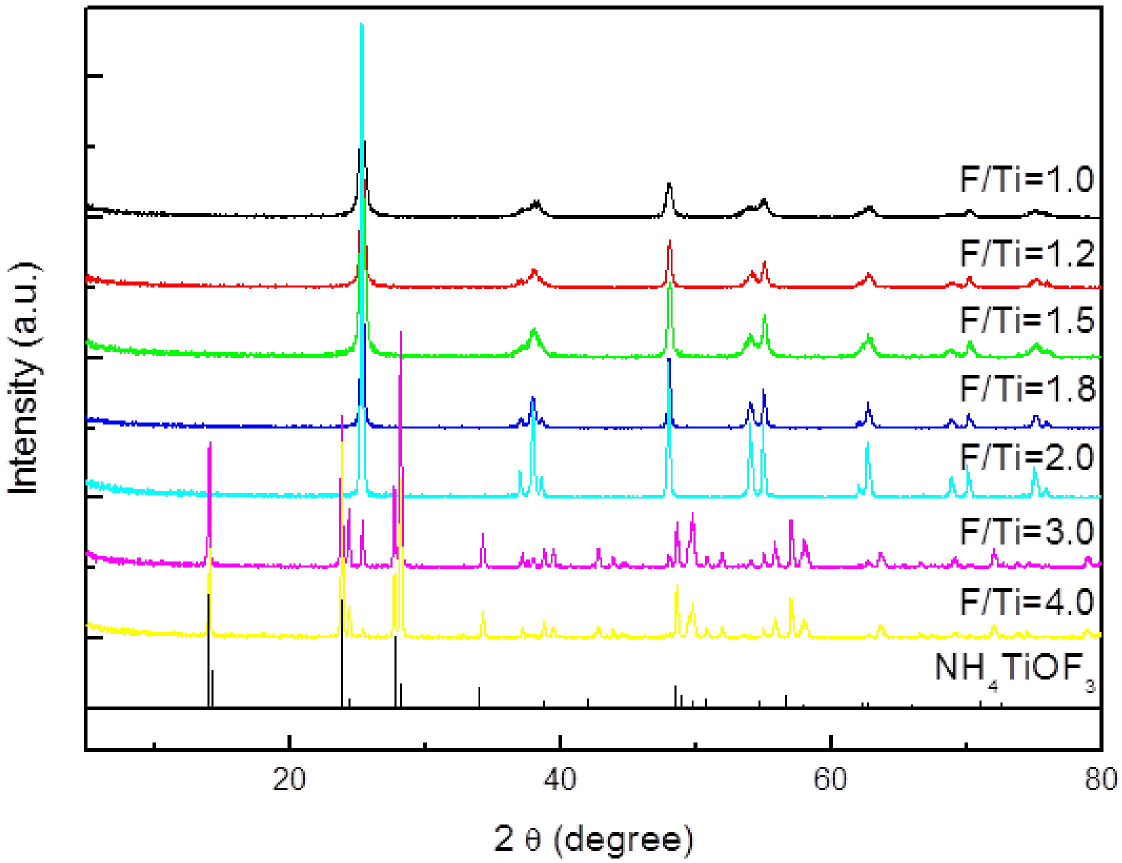

Fig. S2 XRD patterns of TiO_2 prepared with various F/Ti ratios. TiO_2 prepared with F/Ti molar ratios of 1.0, 1.2, 1.5, 1.8, and 2.0 are anatase crystals. The crystallinity was improved with increased particle size when the F/Ti molar ratio increased from 1.0 to 2.0. When the F/Ti molar ratio was 3.0 and 4.0, the XRD patterns were assigned to NH_4TiOF_3 but not to TiO_2. The standard XRD pattern of NH_4TiOF_3 is shown at the bottom of the graph.

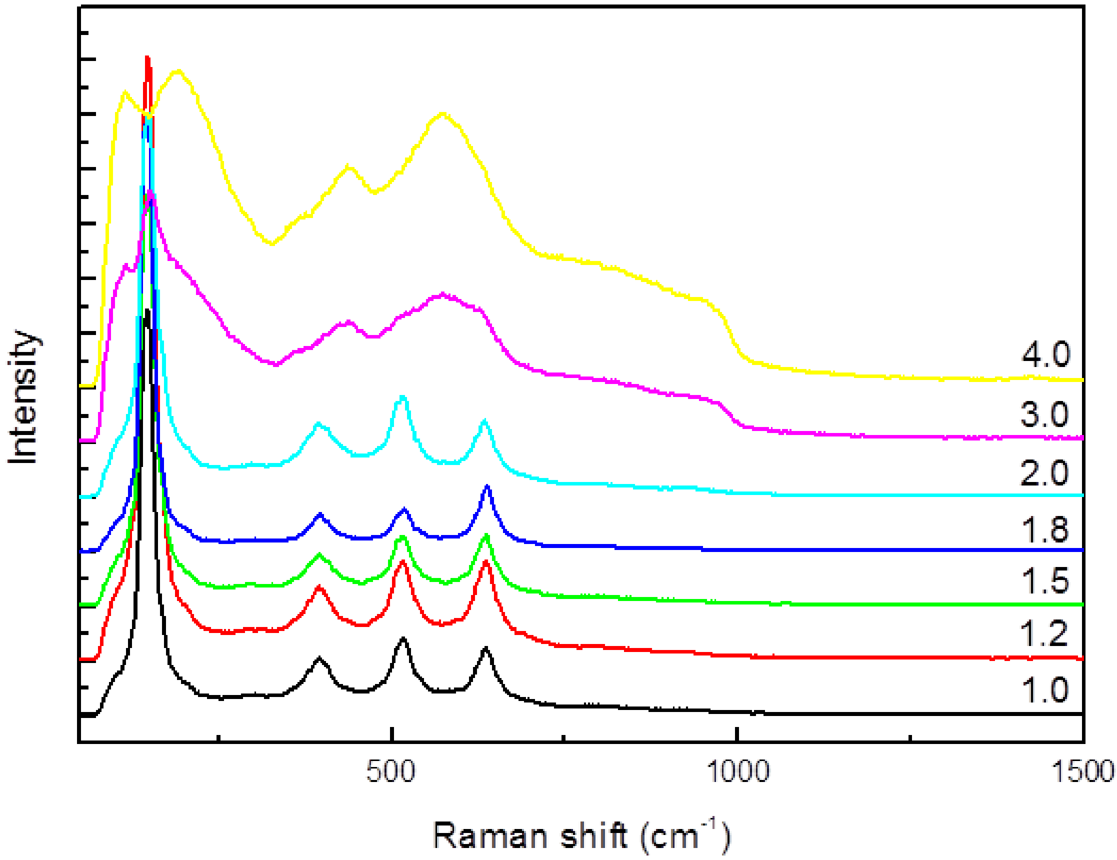

Fig. S3 Raman spectroscopy of TiO_2 prepared with varying F/Ti molar ratios. TiO_2 nanosheets prepared with F/Ti molar ratios of 1.0 ~ 2.0 clearly show the four main Raman vibration modes assigned to the anatase crystal. The samples prepared with F/Ti molar ratios of 3.0 and 4.0 show different Raman profiles comparing to the characteristic Raman peak from anatase TiO_2.

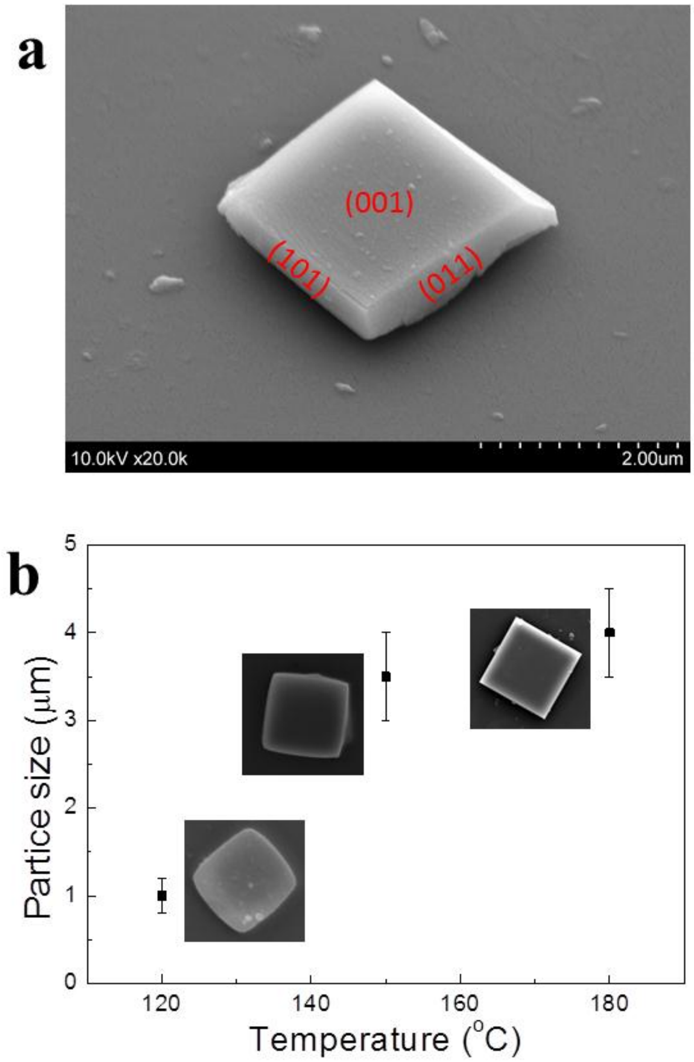

Fig. S4 Synthesis of micrometre-sized TiO_2 single crystals with exposed {001} facets. (a) SEM image of a micrometre-sized TiO_2 single crystal with a high percentage of exposed {001} facets from a 45° view. (b) Size distribution of micrometre-sized TiO_2 single crystals prepared at various hydrothermal temperatures.

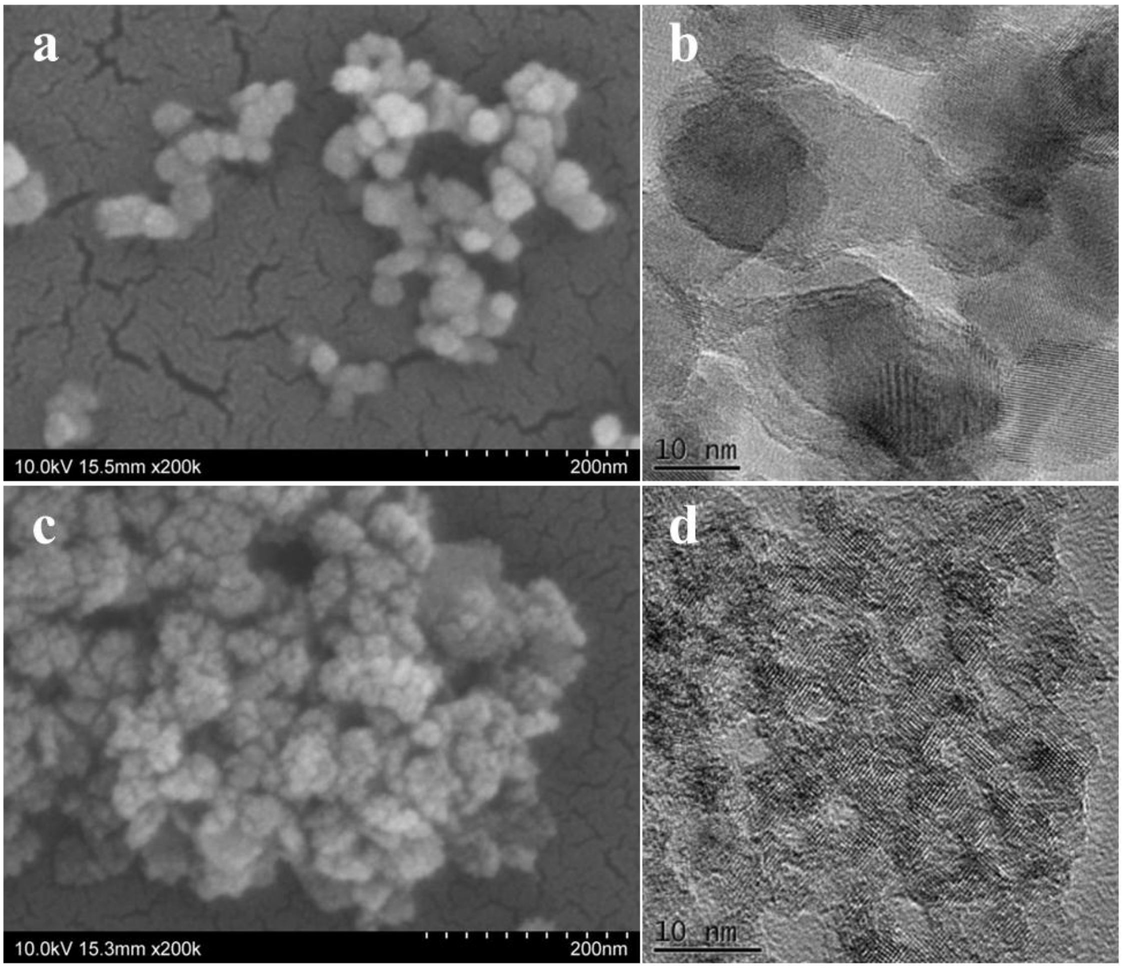

Fig. S5 SEM and TEM images of P25 and ST01 commercial TiO_2. (a, b) show P25 TiO_2, whereas (c, d) show ST01 TiO_2. TiO_2 P25 consists of highly dispersed nanoparticles with an average size of 30 nm. TiO_2 ST01 is much smaller than P25. The average size is approximately 5 nm, but aggregation of approximately 70-nm particles occurs.

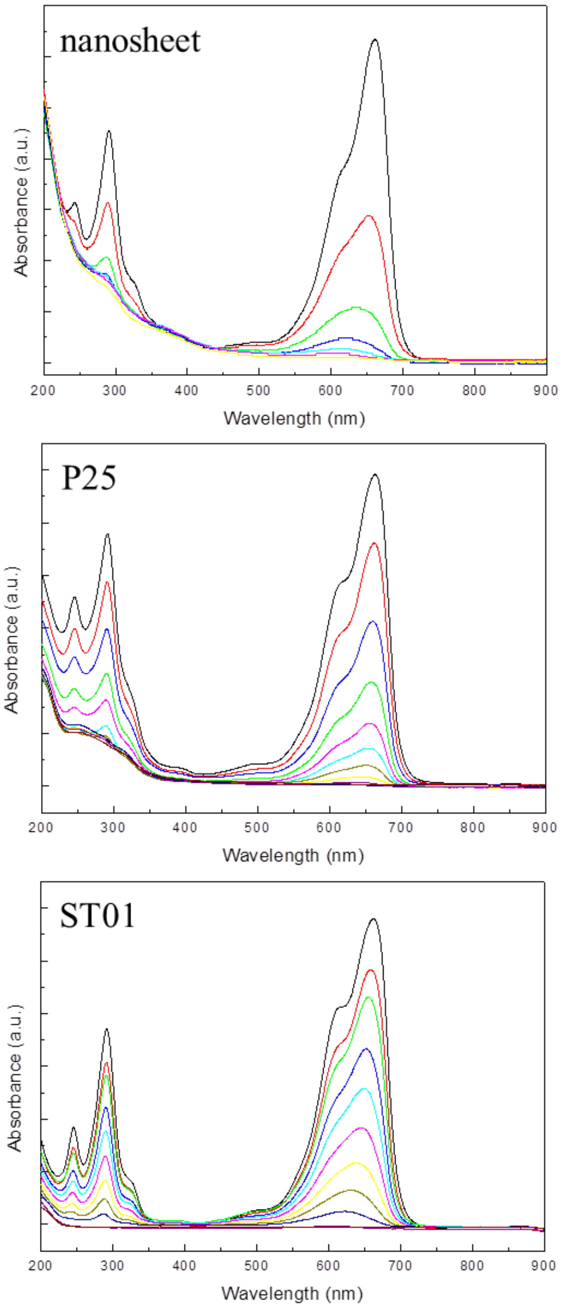

Fig. S6 Absorption spectroscopy of methylene blue in the TiO_2 photocatalytic degradation reaction. The strong characteristic absorption peak of methylene blue appears at 660 nm.

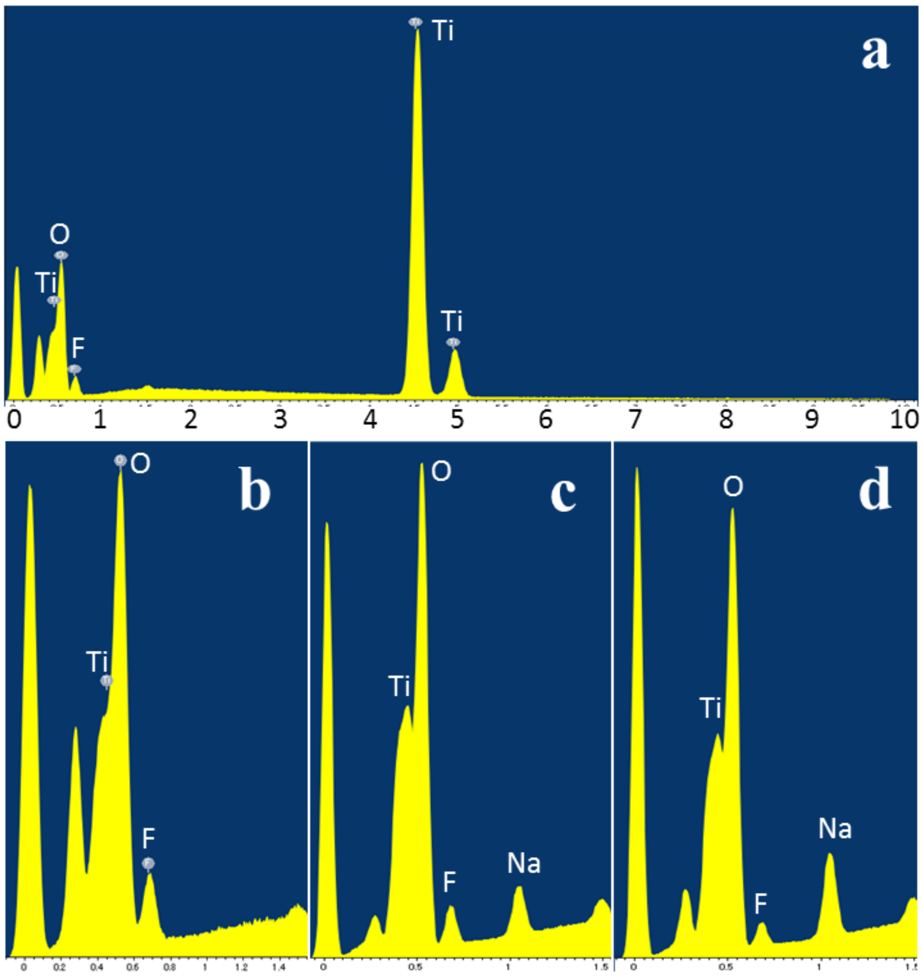

Fig. S7 Energy-dispersive X-ray spectroscopy (EDS) of TiO2 nanosheets. (a) EDS in the energy range from 0 to 10 ev. EDS of TiO2 nanosheets before (b) and after directly cleaning with NaOH solution in 0.1 M (c) and 1.0 M (d). F element was still detected by EDS even after cleaning with 1.0 M NaOH.

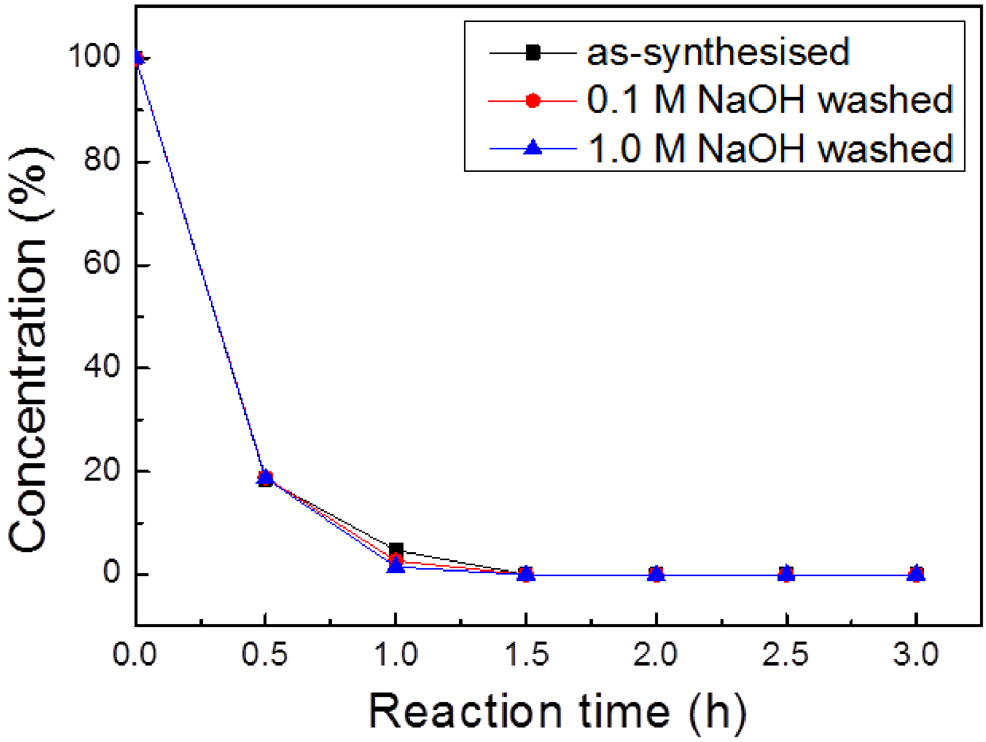

Fig. S8 Comparison of the photocatalytic activity of TiO2 nanosheets (25 nm size) before and after NaOH washed. There was not remarkable improvement in photocatalytic activity even after 1.0 M NaOH washed.

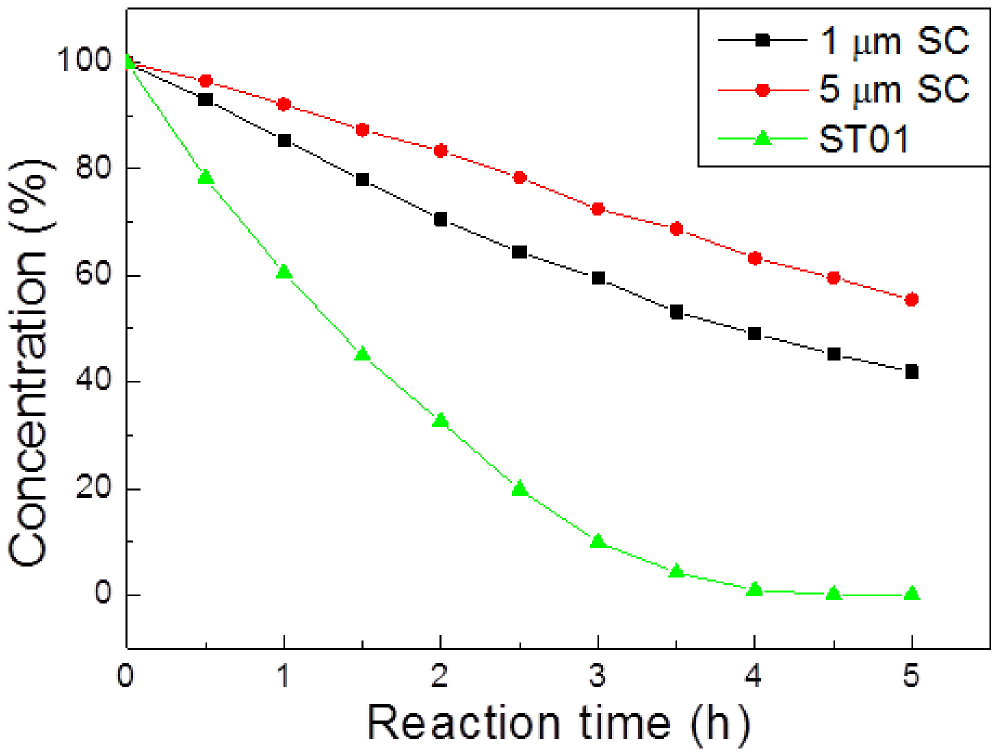

Fig. S9 Photocatalytic activity of micrometer-sized TiO_2 nanosheets. (a) Variation of concentration of methylene blue with reaction time when TiO_2 single crystals are used as photocatalysts. (b) Specific surface area and k_{app} of TiO_2 single crystals in the photocatalytic degradation of methylene blue.