Supporting Information

Anatase TiO_2 Films with Reactive {001} Facets on Transparent Conductive Substrate

Bin Liu and Eray S. Aydil*

Department of Chemical Engineering and Materials Science
University of Minnesota
421 Washington Avenue SE, Minneapolis, Minnesota 55455

Experimental Procedure

Materials Preparation. The synthesis of anatase TiO_2 films with large fraction of {001} surfaces is based on hydrolysis and condensation of titanium tetrafluoride (TiF_4). In a typical synthesis, 0–2.808 g of NaCl was mixed with 60 ml of 0.04 M TiF_4 aqueous solution, which was prepared by adding 0.297 g of TiF_4 into 60 ml of 0.01 M HCl, in a Teflon-lined stainless steel autoclave (125 ml volume, Parr Instrument Co.). The concentration of F in the reaction medium is 0.16 M. The mixture was stirred at ambient conditions for 10 minutes to ensure the complete dissolution of NaCl. Following, two FTO substrates (F:SnO_2, TEC 15, 10Ω/□, Hartford Glass Company), ultrasonically cleaned for 60 minutes in a mixed solution of deionized water, acetone, and 2-propanol with volume ratios of 1:1:1, were placed at an angle against the wall of the Teflon-liner with the conducting side facing down. The hydrothermal synthesis was conducted at 200 ^oC for 0–4 hours in an electric oven. After synthesis, the autoclave was cooled naturally to room temperature. The FTO substrates were taken out, rinsed extensively with deionized water and allowed to dry in ambient air. In some control experiments, ultrasonically cleaned silicon, indium tin oxide (ITO) or glass substrates were used instead of FTO to study the effect of the substrate.

Materials Characterization. The crystal structure of the TiO_2 films was studied using X-ray diffraction (XRD). The XRD patterns were recorded in a Bruker-AXS Microdiffractometer (model D5005) with Cu Kα radiation (λ = 1.5406 Å) from 20^o to 70^o at a scanning speed of 2.4^o min^{-1}. The X-ray tube voltage and current were set at 45 kV and 40 mA, respectively. Morphology and composition of the films were studied using field emission scanning electron microscopy and energy-dispersive X-ray spectroscopy (FESEM/EDX, JSM-6700F) respectively. Transmittance spectra were recorded with a UV-vis-NIR spectrophotometer, which includes a combination of deuterium and tungsten halogen lamps (Ocean Optics, DH-2000-Ball) and a spectrometer (Ocean Optics, HR 2000) equipped with a grating and a silicon detector, sensitive in the 200-1100 nm range. Chemical composition of the anatase TiO_2 film was also examined with X-ray photoelectron spectroscopy (XPS, Surface Science SSX-100). All binding energies were referenced to the C1s peak (284.6 eV) arising

from adventitious hydrocarbons. Adhesion of the TiO_2 film on the FTO substrate was checked by adhesive tape test wherein an adhesive tape is placed on the film and pulled with a steady force. In addition, substrates coated with TiO2 films were ultrasonicated vigorously for over 1 hour. In all tests the films were found to remain on the FTO substrate showing that the binding force of the TiO_2 films on the FTO substrate is larger than those created during the adhesive tape test and vigorous ultrasonication.

Estimation of the (001) surface percentage

We estimated the fraction of {001} surfaces by measuring the dimensions of the crystallites from SEM figures such as those shown in Figure SI-9 and calculating the respective areas of the {101} and {001} planes. The fraction of {001} facets was calculated by assuming that these two planes make up nearly 100% of all the surfaces and using

$$\text{The Fraction of } \{001\} \text{ facets} = \frac{\sum A_{(001)}}{\sum A_{(001)} + \sum A_{(101)}}$$

The results are as follows.

	TiO_2 film grown for 2 hours	TiO_2 film grown for 4 hours
Percentage of (001) facets	~ 80%	~ 70%

Photodegradation Reaction. Two pieces (1.7 cm × 2.5 cm) of TiO_2 film covered FTO substrates were added to 10 ml of 10 mg/l methyl orange (MO) solution, which had been bubbled with purified air for 1 hour, in a 100 ml beaker. This solution was kept in the dark for 30 minutes to achieve adsorption equilibrium and later illuminated with a UV lamp (Mineralight Lamp, Model UVGL-25) for 60 minutes. During the illumination, 5 ml of solution was drawn out every 10 minutes to determine the concentration of the remaining MO using UV-vis spectrophotometry. After UV-vis measurement, the solution was poured back to the reaction beaker to maintain a constant reaction volume. The decay of the initial MO concentration (C_o) is shown in Figure SI-11

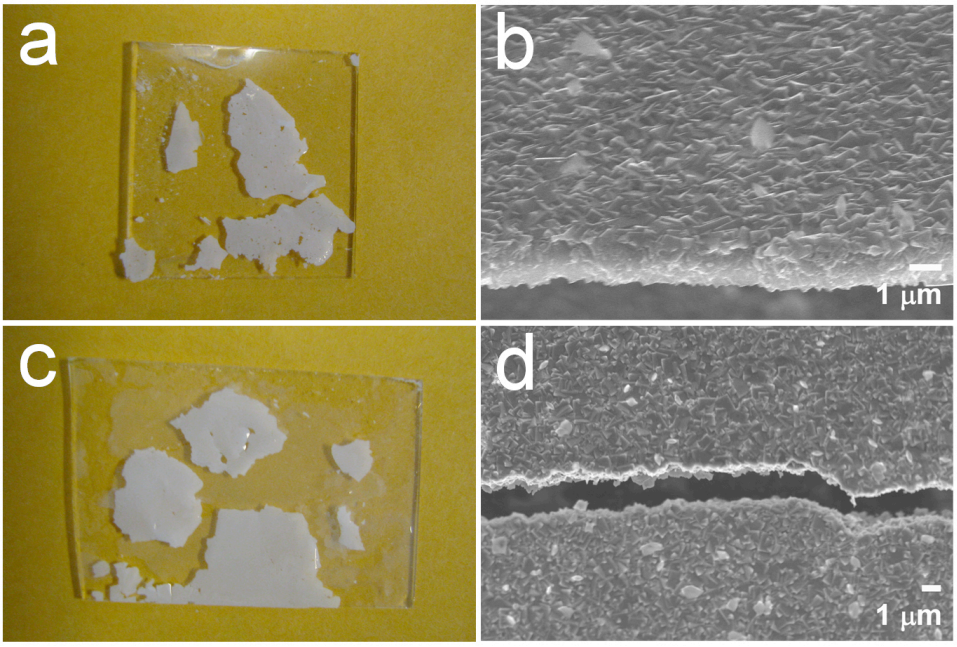

Figure SI-1. (a) & (b) Photograph and the corresponding FESEM image of anatase TiO_2 film grown on ITO. (c) & (d) Photograph and the corresponding FESEM image of anatase TiO_2 film grown on glass.

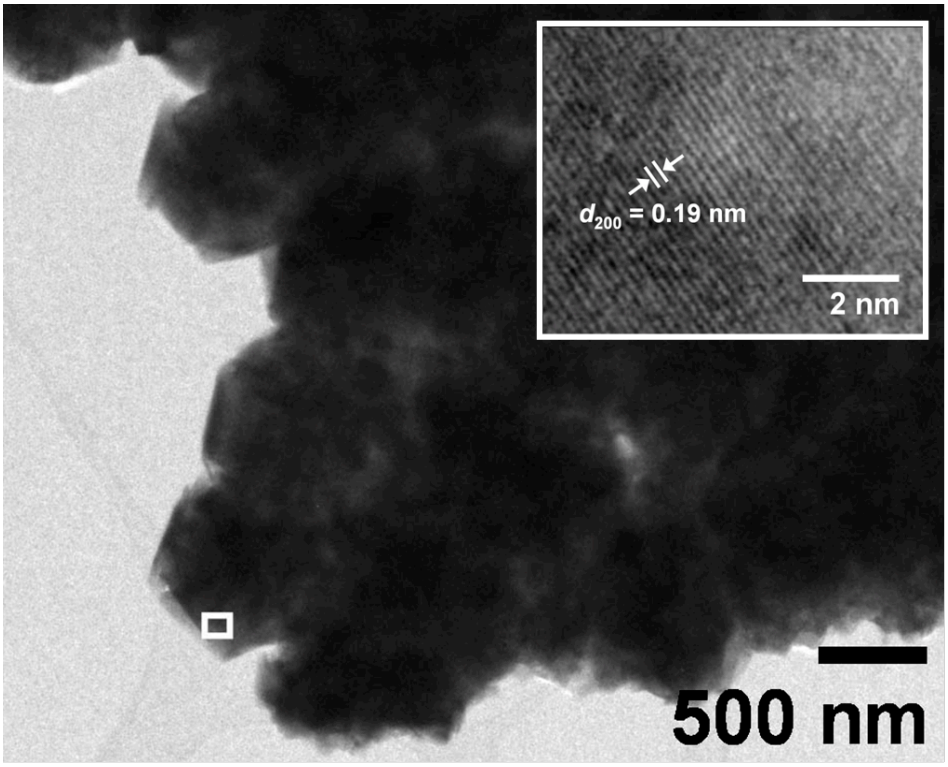

Figure SI-2. TEM image of a detached anatase TiO_2 film. Inset is the high-resolution TEM image recorded from the selected area.

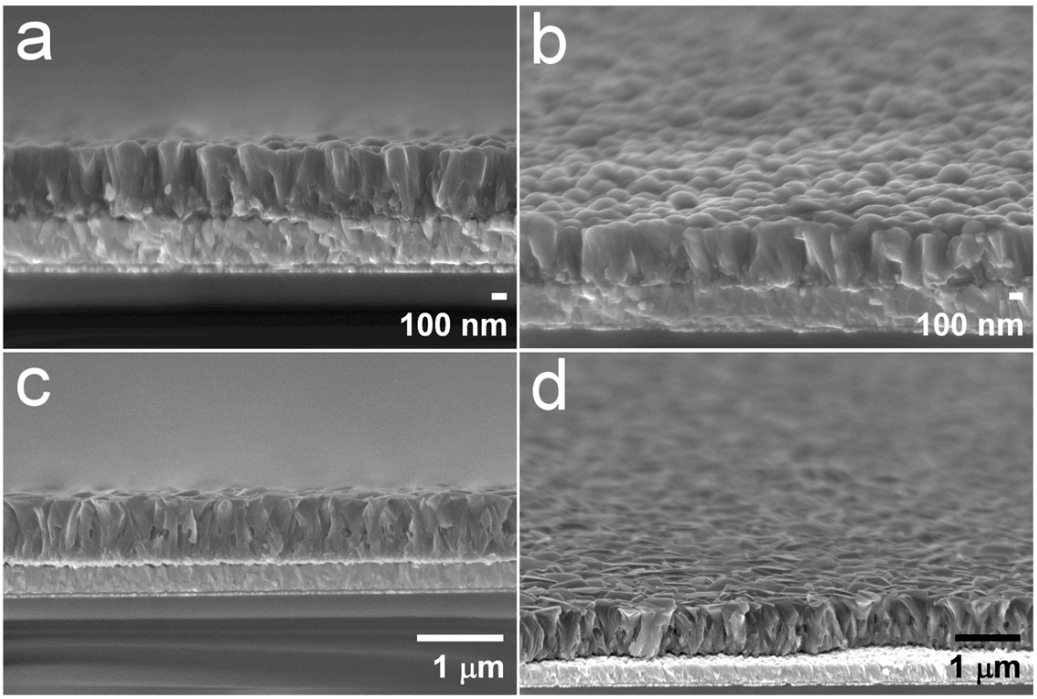

Figure SI-3. (a) & (b) Cross-sectional and tilted cross-sectional FESEM images of anatase TiO_2 film grown on FTO substrate through hydrothermal growth for 1 hour. (c) & (d) Cross-sectional and tilted cross-sectional FESEM images of anatase TiO_2 film grown on FTO substrate through hydrothermal growth for 2 hours.

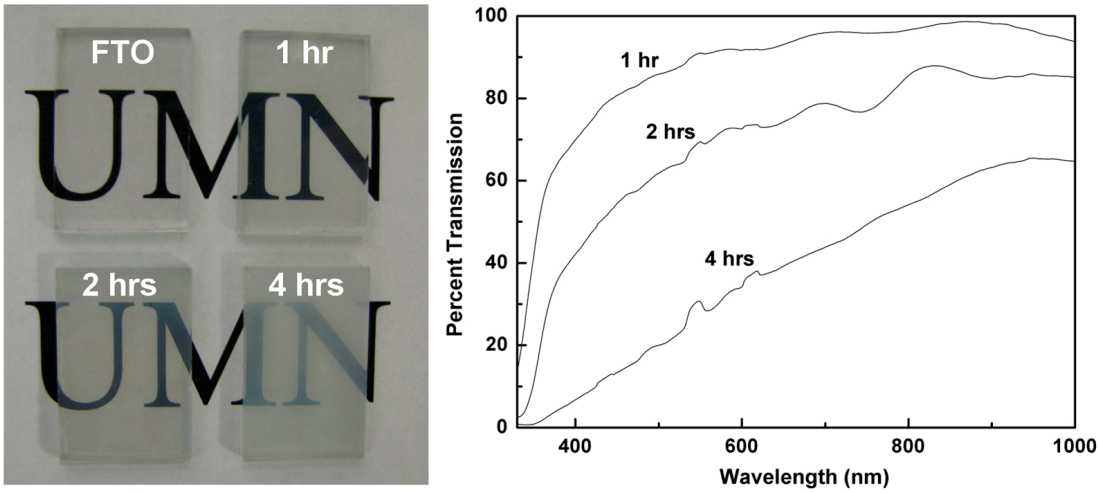

Figure SI-4. Digital photograph of anatase TiO_2 films grown on FTO substrate for different durations and the corresponding transmittance spectra. Thicker films scatter light in the visible due to faceted crystals.

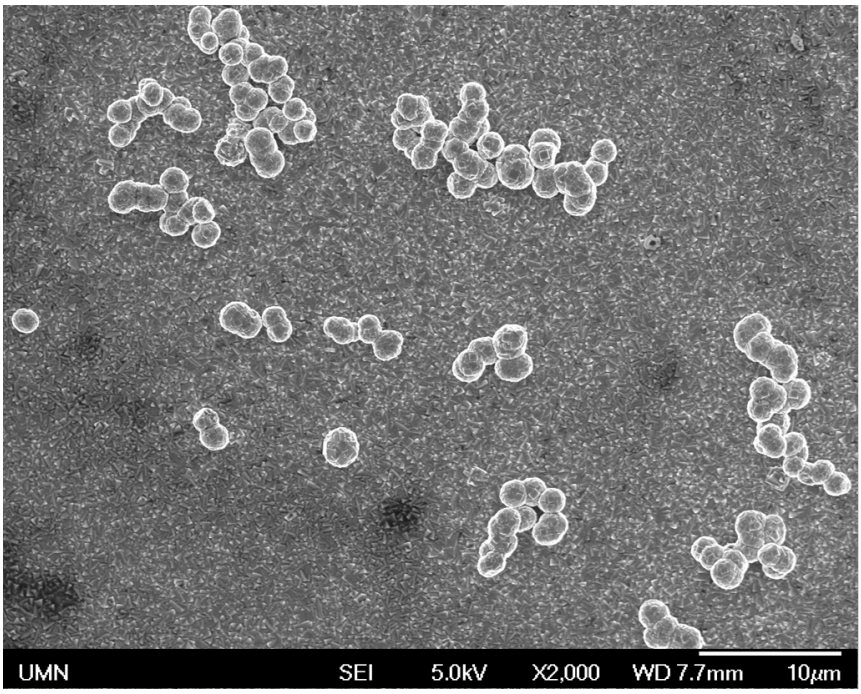

Figure SI-5. FESEM image of anatase TiO_2 film on FTO substrate prepared without adding NaCl.

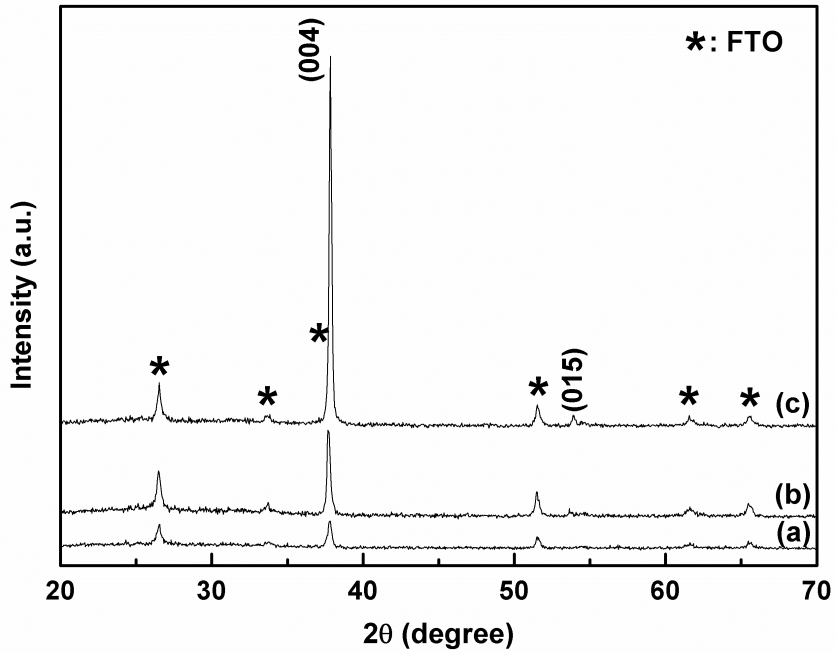

Figure SI-6. XRD patterns from (a) FTO substrate, (b) anatase-film-covered FTO substrate prepared by growing TiO_2 for 1 hour of hydrothermal reaction, and (c) anatase-film-covered FTO substrate prepared by growing TiO_2 for 2 hours of hydrothermal reaction.

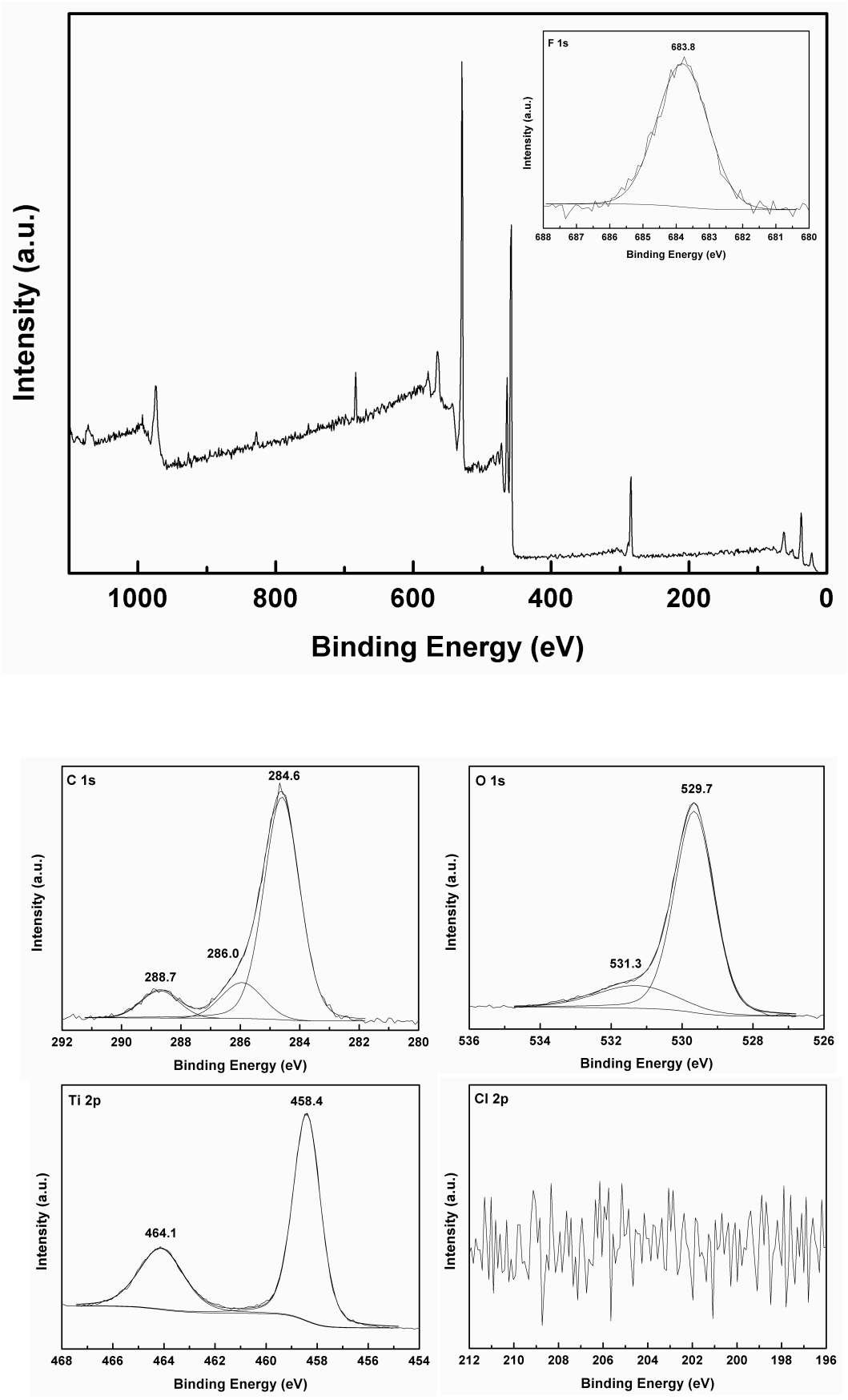

Figure SI-7. XPS spectra of the as-prepared anatase TiO_2 film on FTO substrate, showing five characteristic peaks from Ti, O, C, F and Cl.

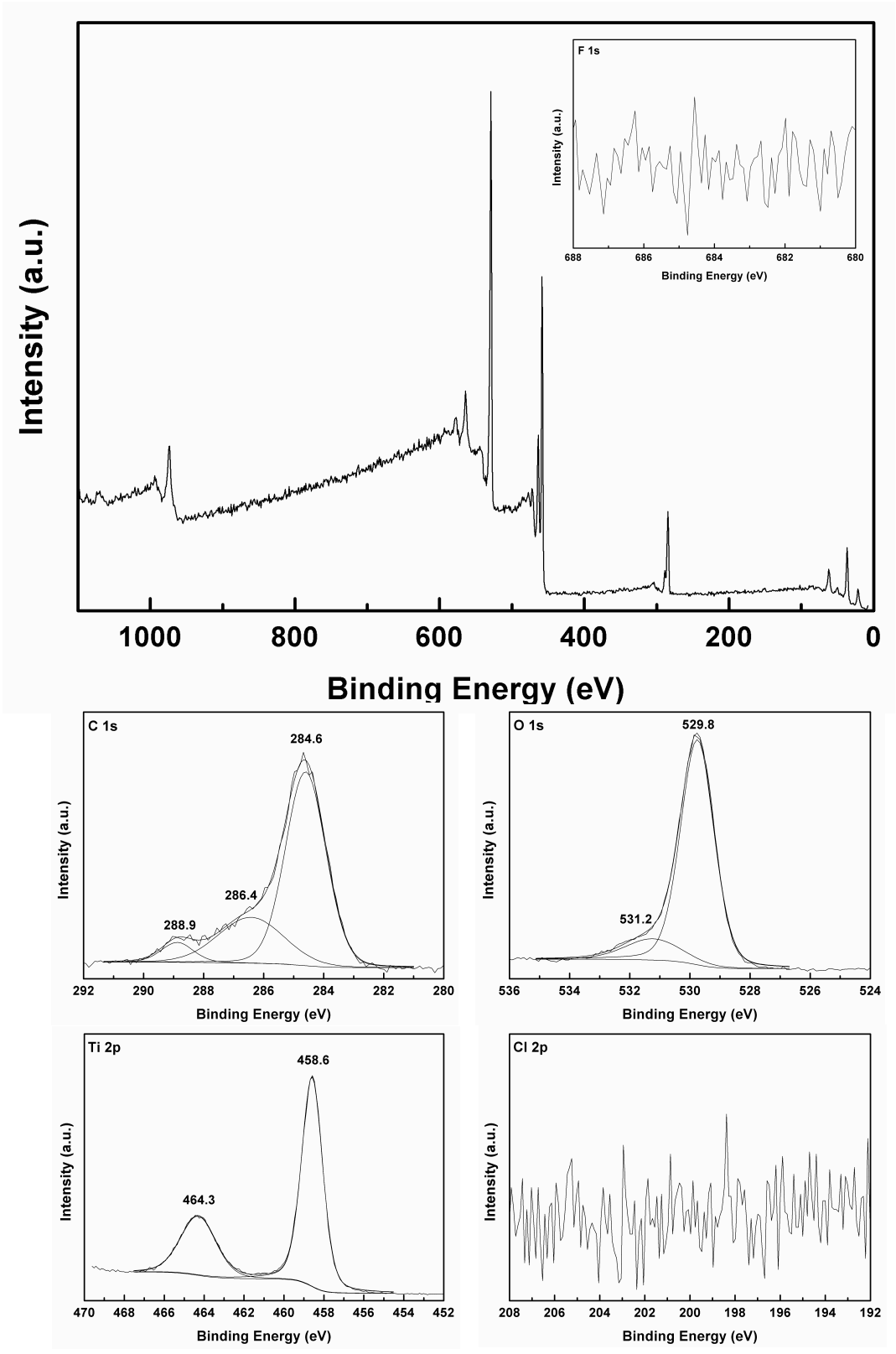

Figure SI-8. XPS spectra of the anatase TiO_2 film on FTO substrate after annealing at 600 ^{o}C for 60 minutes, showing five characteristic peaks from Ti, O, C, F and Cl. The adsorbed fluorine on the surface of TiO_2 can be completely removed through a post growth thermal treatment.

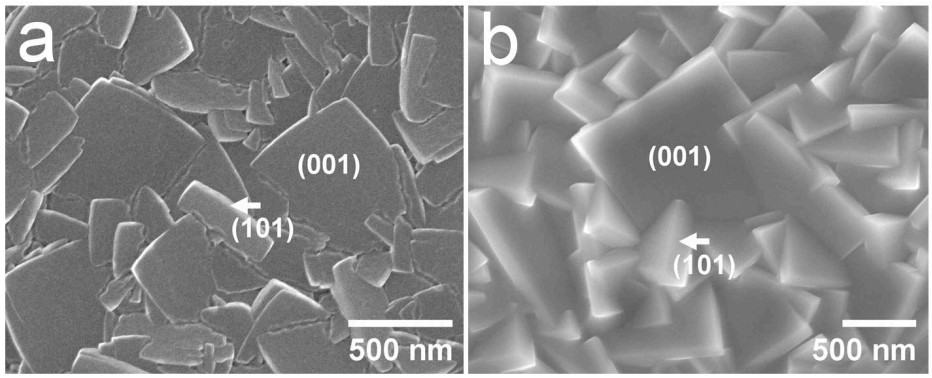

Figure SI-9. FESEM images of anatase TiO_2 film grown on FTO substrate for (a) 2 hours and (b) 4 hours.

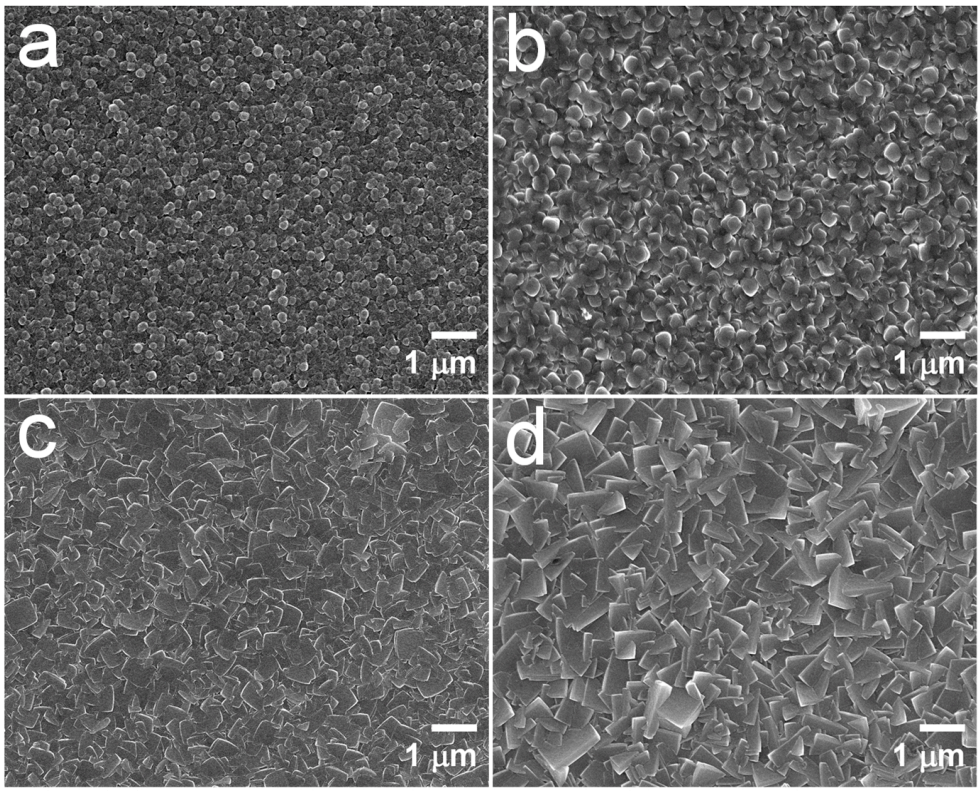

Figure SI-10. Enlarged view of Figure 3.

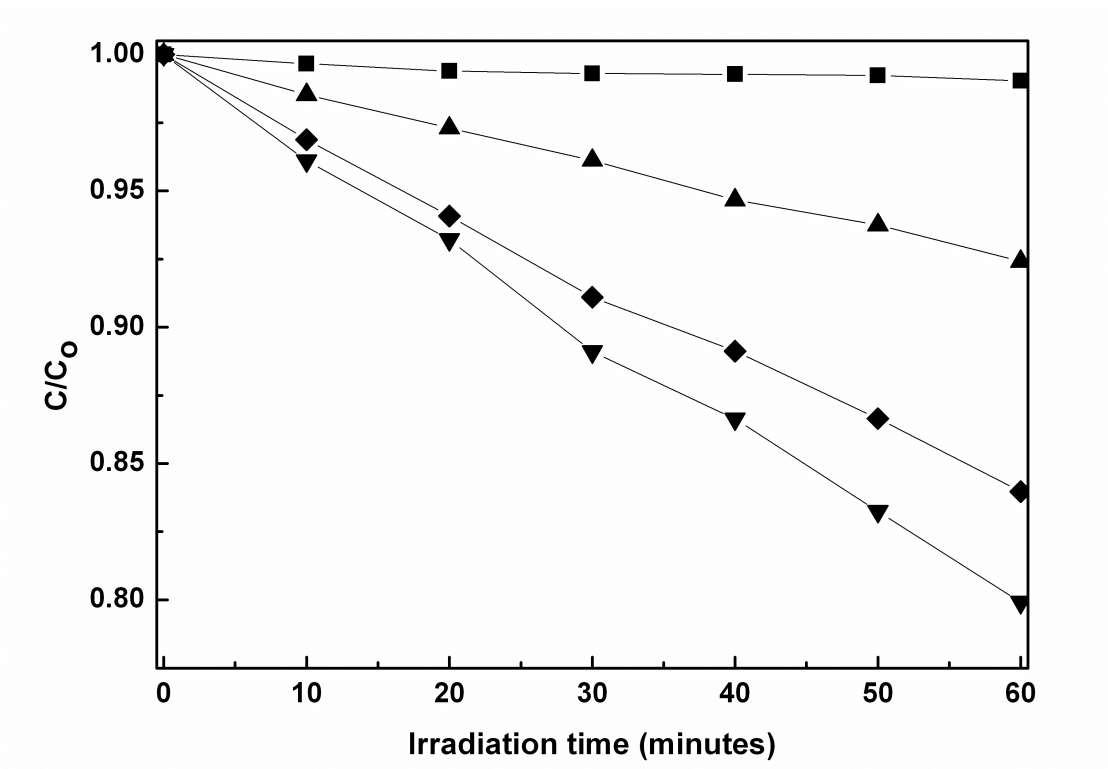

Figure SI-11. Photocatalytic degradation of methyl orange with anatase TiO_2 films prepared after different amount of hydrothermal growth time: (■) no photocatalyst, (▲) anatase TiO_2 film grown for 1 hour, (▼) anatase TiO_2 film grown for 2 hours, and (◆) anatase TiO_2 film grown for 4 hours. The anatase TiO_2 film grown for 2 hours under hydrothermal condition shows the highest photocatalytic activity. The improved photocatalytic activity is due to the high fraction of exposed (001) surfaces.