Supplementary information

Reconstruction of (001) surface on TiO_2 nanosheets induced by the fluorine-surfactant removal process under UV-irradiation for dye-sensitized solar cells

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1. TG-DSC Spectra. In order to investigate the thermal degradation temperature of the organic template,

Thermogravimetric-differential scanning calorimeter (TG-DSC) analysis was conducted, as shown in Fig. S1.

The paste for TG-DSC was dried in an oven for 12 h to remove terpineol.



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Fig. S1 TG-DSC spectra of the dried paste.

It can be seen that the ethanol cellulose began to degrade at 220 $^{\circ}$ C. When the temperature reached 450 $^{\circ}$ C, the mass didn't change, which illustrated that the ethanol cellulose was completely decomposed.

2. X-ray Photoelectric Spectra of Ti. In order to exclude the effect of oxygen vacancies on the increased signal ascribed to electrons trapped on TiO₂ surface, XPS for Ti was conducted, as shown in Fig. S2. 10 It can be seen that all the spectra show two main peaks distributing at 458.9 and 464.7 eV, which are ascribed to Ti⁴⁺ 2p_{3/2} and Ti⁴⁺ 2p_{1/2}, respectively. All the samples appear good Gaussian peak lines and no signal of Ti³⁺ is observed, which illustrates that almost all the titanium shows +4 valence either before or after the UV irradiation treatment. Thus, the oxygen vacancies are little. The increased amount of dye adsorption does not origin from the dye anchoring to oxygen vacancies.



Fig. S2 Ti 2p XPS spectra of UV 0 (a), UV 20 (b) and UV 80 (c). The black curves are the measured and the green curves are baselines. All the titanium shows Ti⁴⁺.

3. Photocatalytic Degradation Performance. In order to test and verify the removal of fluorine-surfactant and the theoretical calculation further, photocatalytic degradation experiment for Rhodamine B (Rh B) was conducted. 0.1 g white precipitate, obtained in the section of *preparation of TiO*₂ *nanoparticle*, was dispersed into 4.0 g H₂O with an ultrasonic horn to make a colloid. Then the colloid was dropped onto a piece of glass and dried in an air flow. The glass was then exposed to UV irradiation. TiO₂ 10 was then scrapped off the glass and the sample for photocatalytic degradation was obtained. The result was present in Fig. S3. It can be seen that the samples without catalyst shows a slow self degradation. All the samples show a decrease C/C₀ overall. The slight increase and nearly unchanged C/C₀ at 15 min were caused by desorption of Rh B from surface of catalyst induced by the UV-visible irradiation. Moreover, the TiO₂ irradiated by UV-light shows an enhanced absorption for Rh B. Compared with the TiO₂ without UV irradiation, the degradation time of the UV irradiated TiO_2 was shortened from 120 to 75 min. Thus, the UV irradiation enhanced the photocatalytic degradation activity of the TiO_2 nanosheets. The enhanced performance can be ascribed to the more adsorption of RhB on the increased titanium atoms exposed, yielding from the removal of fluorine-surfactant and the reconstruction, as well as the active sites generated 5 from reconstruction. The removal of fluorine-surfactant and the theoretical calculation was thus testified.



Fig. S3. Photocatalytic degradation performance for Rhodamine B. The experiment was carried out with 0.05 g catalyst and 10 mg/L Rhodamine B in 200 mL water, illuminated by the full arc of xenon lamp. The black (with out catalyst), red (TF) and blue line (TUV) denote the samples without catalyst, TiO₂ without moving F and TiO₂
10 irradiated by UV-light for 80 min, respectively. The UV irradiated TiO₂ shows an enhanced photocatalytic activity.

4. UV-vis Transmittance Spectra. It is well known that TiO₂ absorbs UV-light intensely. In order to clarify the penetration depth of 254 nm UV-light into the porous TiO₂ film, UV-vis transmittance measurements were conducted on porous film fabricated onto quartz, using a Varian Cary 50 UV-vis transmittance spectrophotometer. The film thickness was measured on a Dektak 6M stylus profiler. The 15 results were shown in Fig. S4.

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Fig. S4 UV-vis transmittance spectra of the porous film. a, b, c and d possesses thicknesses of 0.6, 1.7, 2.8 and 4.1 μ m, respectively. The transmittance of a, b, c and d are about 40%, 9%, 1% and 0 at the wavelength of 254 nm, respectively.

5 It can be seen from Fig. S4 that the transmittance of the porous TiO_2 film with thicknesses of 0.6 µm (a), 1.7 µm (b), 2.8 µm (c) and 4.1 µm (d) are about 40%, 9%, 1% and 0 at 254 nm. That is to say that the 254 nm UV-light can penetrate a depth of about 3µm of the porous TiO_2 film, which is similar to the report of Jan Augustynski.¹ This penetration depth ensures an effective depth of the UV-light for the 12 µm porous TiO_2 film of the DSSCs.

10 **5. Layer thickness**



Fig. S5 Layer thickness of the photoanodes measured on a Dektak 6M profilometer.

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Reference:

1. A. Wahl and J. Augustynski, J. Phys. Chem. B, 1998, 102, 7820-7828.