Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

The details of synthesis, characterization and catalytic reactions, N_2 adsorption-desorption isotherms, the calculation of percentage of {001} facets and proposed mechanism of reaction are provided here.

Synthesis of TiO_2

5 ml of $Ti(OC_4H_9)_4$ was mixed with a certain amount of hydrofluoric acid (40~48 *wt.*%) (***Caution****: hydrofluoric acid is extremely corrosive and it should be handled with extreme care!*) in a Teflon-lined autoclave with a capacity of 40 ml and subsequently heated to 180 °C at a ramp rate of 2 $°C·min^{-1}$. The temperature was kept at 180 °C for 24 h. After hydrothermal reaction, the white precipitate was collected, washed with ethanol and distilled water three times, and then dried in an oven at 80 °C overnight. 0.6 ml and 0.2 ml of hydrofluoric acid was added for ST_{001} and $ST_{001/101}$, respectively, while, instead of hydrofluoric acid, 0.6 ml of H_2O was employed for ST_{101}.

The removal of fluorine on surface is described below: 1 g of as-prepared TiO_2 was treated in 50 ml of 0.1 M NaOH solution under magnetic stirring for 10 h. Then the solid sample was washed with distilled water several times until neutral. After centrifugation, the solid was dried at 80 °C overnight.

Sulfation of TiO_2

To obtain the sulfated catalyst, ammonium sulphate, $(NH_4)_2SO_4$, was utilized as an initial precursor of sulfate in the catalyst preparation. 1 g of fluorine-free TiO_2 was added into 10 ml of 1 $mol·L^{-1}$ $(NH_4)_2SO_4$ solution to stir for 8 h, and then collected and dried. Afterwards, the dried solid was calcinated at 450 °C for 4 h.

Characterization

XRD patterns were recorded on a Bruker D8 Advance diffractometer with Cu *Kα* radiation (λ = 0.15418 nm) operated at 40 mA and 40 kV. The scanning rate was 3 $°·min^{-1}$ from 20 to 80°. The FT-IR spectra were recorded in the range of 4000-400 cm^{-1} with a Nicolet Nexus 470 FTIR spectrometer using KBr pellets. TEM images of the catalysts were taken with a JEOL 2010 transmission electron microscope operating at 200 kV. Samples were dispersed in ethanol and deposited onto a carbon-coated copper grid. Elemental analysis was performed on a Thermo Elemental IRIS Intrepid ICP atomic emission spectrometer. N_2 adsorption-desorption isotherms were obtained at -196 °C using a Micromeritics Tristar 3000 apparatus.

Sample treatment for NMR measurements

A certain amount of catalyst was placed in a home-made glass tube, which was subsequently connected to a vacuum system. After pretreating the catalyst at 573 K for 1.5 h under vacuum (10^{-1} Pa), the tube was immersed in liquid nitrogen to introduce a certain amount of adsorbed molecules. Then the tube was carefully flame sealed. Prior to NMR experiment, the sample was transferred into a Bruker 4 mm zirconia rotor with a Kel-F endcap in a glove box under a dry nitrogen atmosphere.

Catalytic activity test

The catalytic activities of sulfated titania catalysts were studied for the synthesis of 5,7-dihydroxy-4-methyl coumarin from phloroglucinol and ethyl acetoacetate under solvent free condition. In a typical reaction, 5 mmol of phloroglucinol was reacted with 10 mmol of ethyl acetoacetate in the presence of 0.1 g of catalyst. The reaction mixture was kept at 130 °C under reflux for a desired time. On completion of the reaction, the mixture was allowed to cool down to the room temperature followed by the addition of ethanol. The reaction mixture was filtered to separate the catalyst and the filtrate was analysed by liquid chromatography (DIONEX U3000). The yield of 5,7-dihydroxy-4-methyl coumarin was calculated as follows:

Yield (%) = (Obtained weight of product)/ (Theoretical weight of product) × 100

The catalyst was recovered by washing with ethanol, centrifugation and drying.

Table S1 The physico-chemical properties of the sulfated titania samples

Sample	Volume of HF[a] (ml)	Crystallite size (nm)	Percentage of {001} facets	S_{BET}[b] ($m^2 \cdot g^{-1}$)	Content of SO_4^{2-} [c] (wt. %)
ST_{001}	0.6	50×6	80%	67.4	6.6%
$ST_{001/101}$	0.2	25×10	54%	77.3	5.5%
ST_{101}	0	10	< 10%	107	5.7%

[a] Volume of HF employed during the preparation of TiO_2 (with 5 ml of $Ti(OC_4H_9)_4$).

[b] BET surface area.

[c] Determined by ICP analysis.

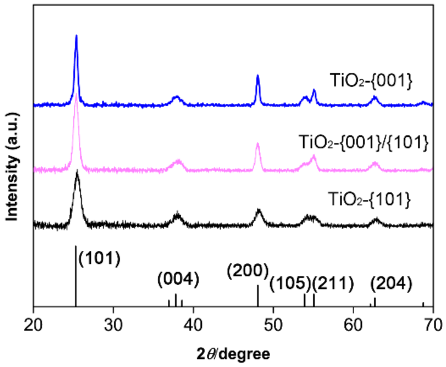

Fig. S1 XRD patterns of TiO_2 parent samples before sulfation treatment.

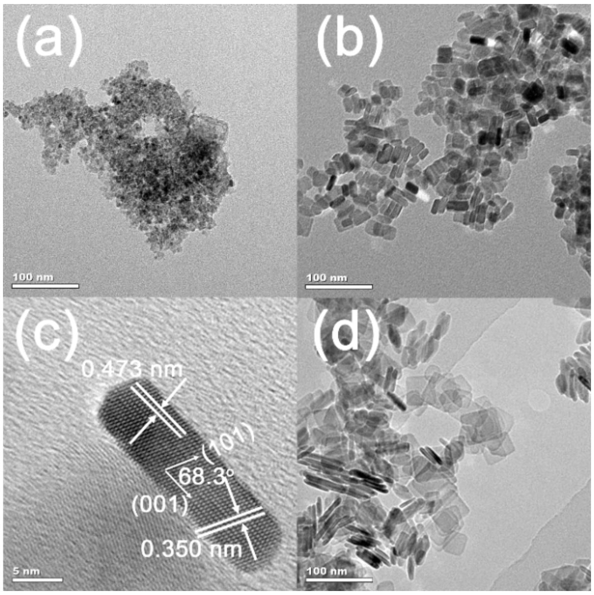

Fig. S2 TEM images of TiO_2 parent samples before sulfation treatment: (a) TiO_2-{101}, (b) TiO_2-{001}/{101}, (c) HRTEM image of TiO_2-{001}/{101}, (d) TEM image of TiO_2-{001}.

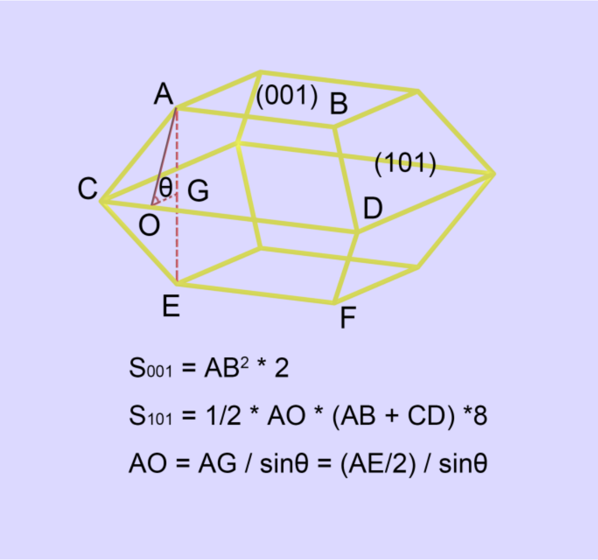

Fig. S3 Simulated shape of the TiO_2 anatase single crystal and the calculation process for percentage of {001} facets (AB and CD are considered of the same value approximately, equal to side length of truncated octahedral bipyramid in TEM images, AE is equal to the thickness, θ of 68.3° is the interfacial angle between (001) and (101)).

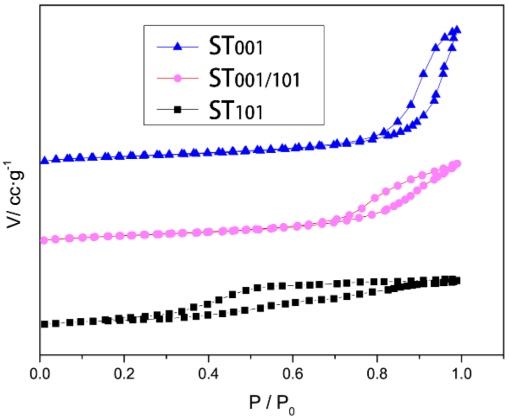

Fig. S4 N_2 adsorption-desorption isotherms for ST_{001}, $ST_{001/101}$ and ST_{101}.

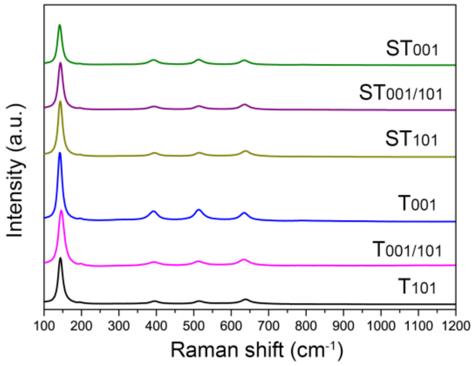

Fig. S5 Raman spectra of ST_{001}, $ST_{001/101}$ and ST_{101} and their TiO_2 parent samples.

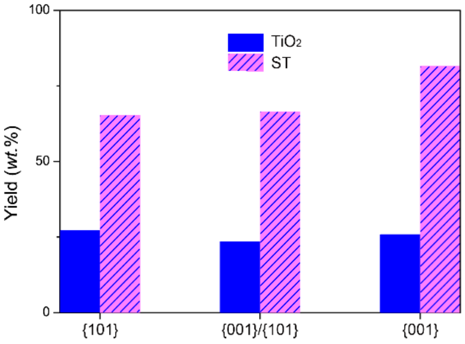

Fig. S6 Comparison of catalytic activities of ST_{001}, $ST_{001/101}$ and ST_{101} and their TiO_2 parent samples. Reaction time is 3 h.

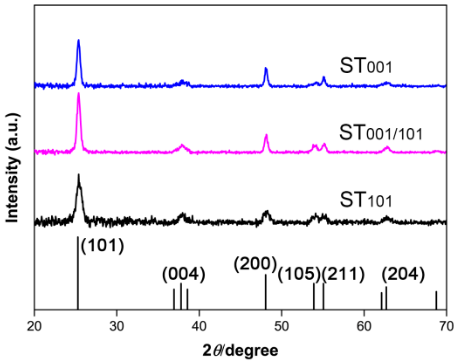

Fig. S7 XRD patterns of ST_{001}, $ST_{001/101}$ and ST_{101} after the Pechmann condensation.

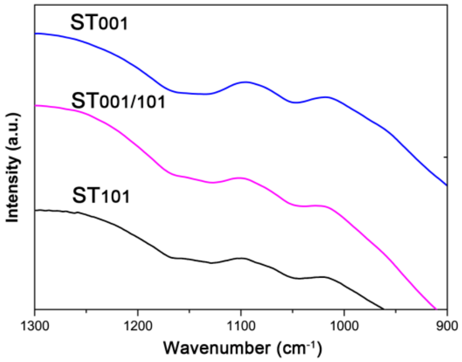

Fig. S8 FT-IR spectra of ST_{001}, $ST_{001/101}$ and ST_{101} after the Pechmann condensation.