

A high-surface-area mesoporous sulfated nano-titania solid superacid with exposed (101) facets for esterification: Facile preparation and catalytic performance

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Supporting Information

Preparation of SO_4^{2-}/AT_{001}

The sulfated anatase TiO_2 with exposed (001) facets is synthesized by the modification of sulfate groups on the surface of anatase TiO_2 with exposed (001) facets. The anatase TiO_2 sample with exposed (001) facets is prepared using the previously reported recipe [1]. The structure of the resulting sample according to the TEM image (Fig. s1) consists of well-defined nanosheets having a rectangular shape with an average side length of ca. 50~80 nm and thickness of ca. 6 nm. The HRTEM image displayed in Fig. s2 indicates that the lattice spacing parallel to the top and bottom facets was ca. 0.235 nm, corresponding to the (001) planes of anatase TiO_2 . Based on the TEM results and on the geometry of TiO_2 crystals [2-4], the percentage of exposed {001} facets is estimated to be about 85 % in average. To obtain sulfated TiO_2 with exposed (001) facets, the resulting TiO_2 sample is annealed in the air atmosphere at 600 °C for 2 h to remove surface fluorine and then modified by surface sulfate groups. Fig. s3 shows the TEM image of the resulting sulfated TiO_2 . It can be seen that the thickness of sulfated TiO_2 increases to about 30~35 nm. However, the side length still keeps unchanged (about 50-80 nm). The HRTEM image in Fig. s4

indicates that the lattice fringes of 0.235 nm are well matched with the {001} planes of anatase TiO₂, confirming that the sulfated TiO₂ sample has exposed {001} facets with percentage of ca. 70 %.

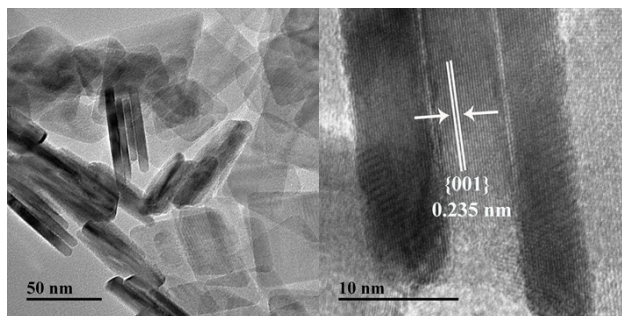


Fig. s1

Fig. s2

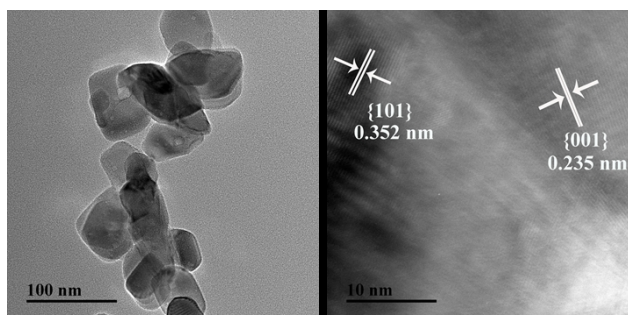


Fig. s3

Fig. s4

References

- [1] Appl. Catal. B: Environ. 2010, 100, 378-385
- [2] Chem. Commun. 2011, 47, 4532-4534
- [3] Phys. Chem. Chem. Phys. 2011, 13, 4853-4861
- [4] J. Am. Chem. Soc. 2010, 132, 11914-11916

Characterization of SO₄²⁻/AT₀₀₁

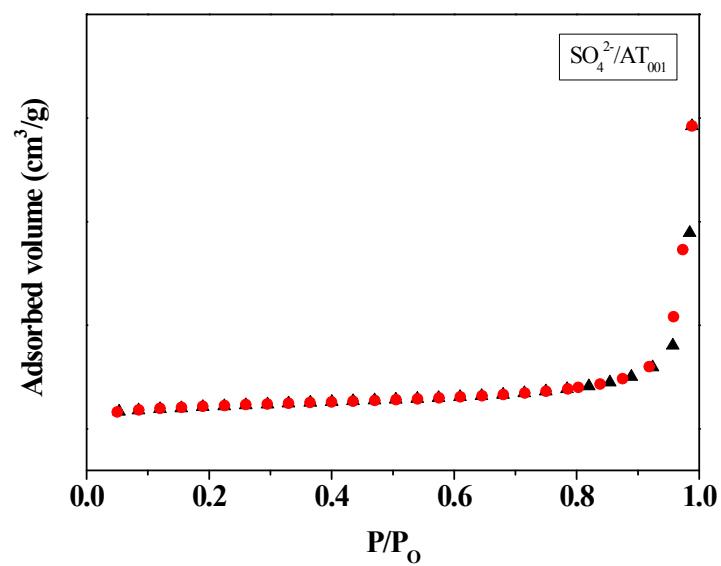


Fig. s5 Nitrogen adsorption-desorption isotherms of SO₄²⁻/AT₀₀₁

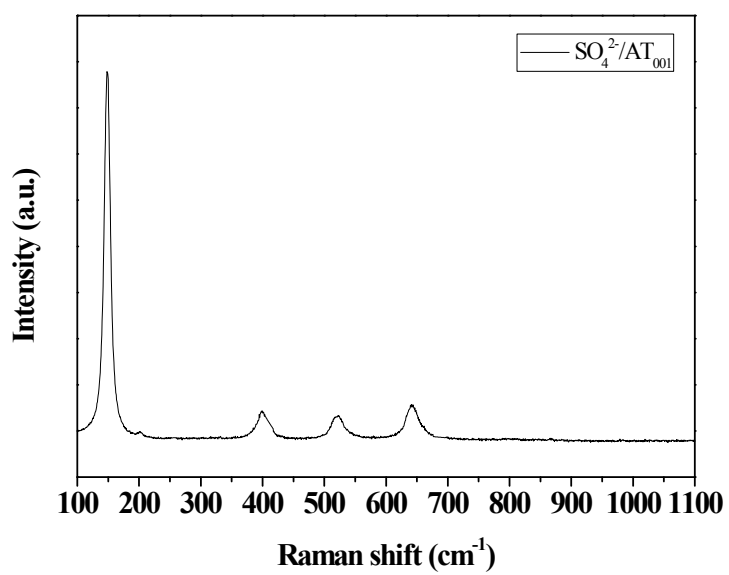


Fig. s6 Raman spectrum of SO₄²⁻/AT₀₀₁

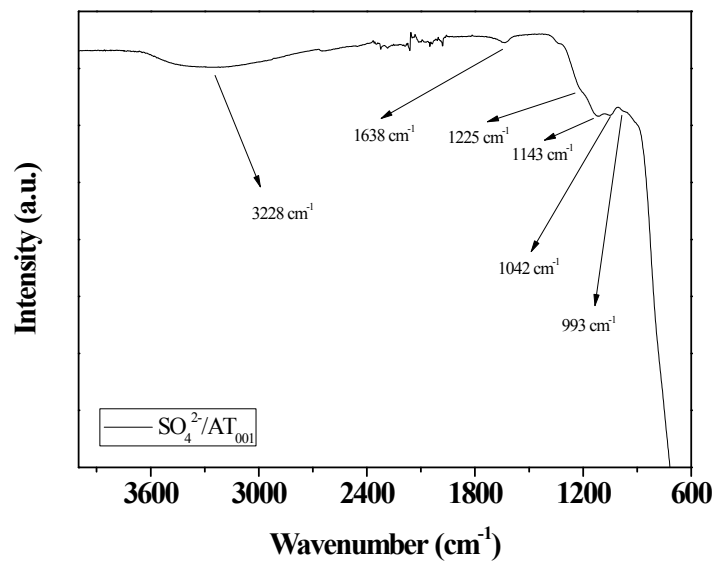
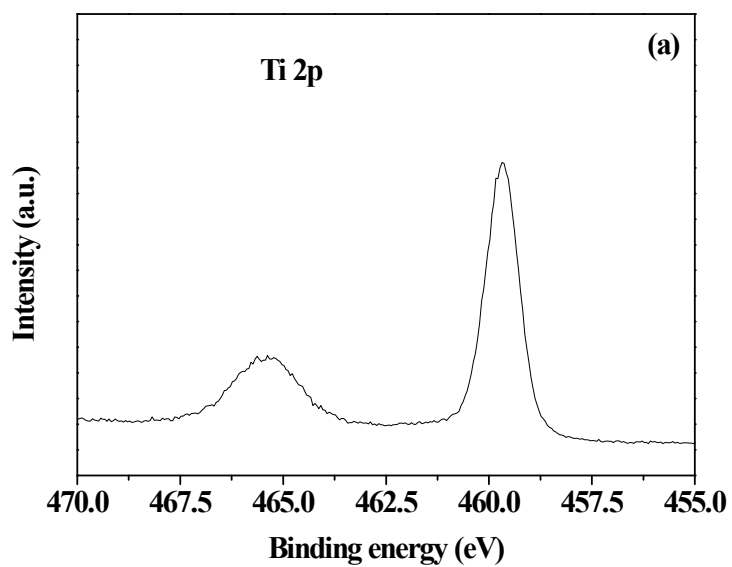


Fig.s7 FTIR spectrum of $\text{SO}_4^{2-}/\text{AT}_{001}$



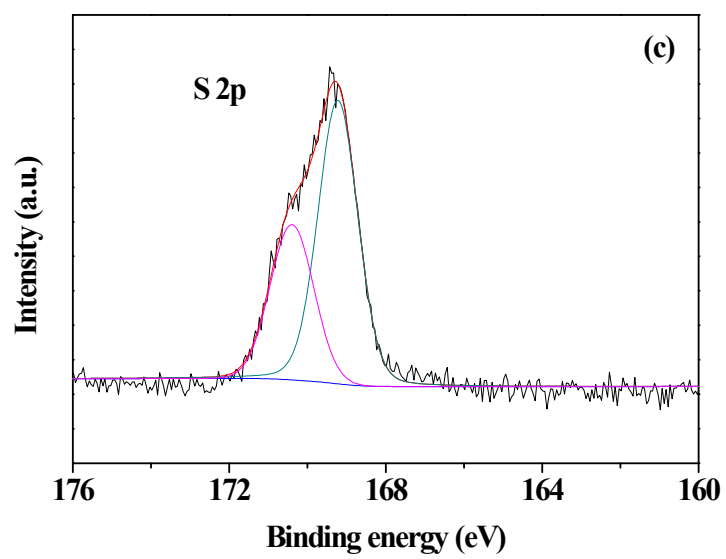
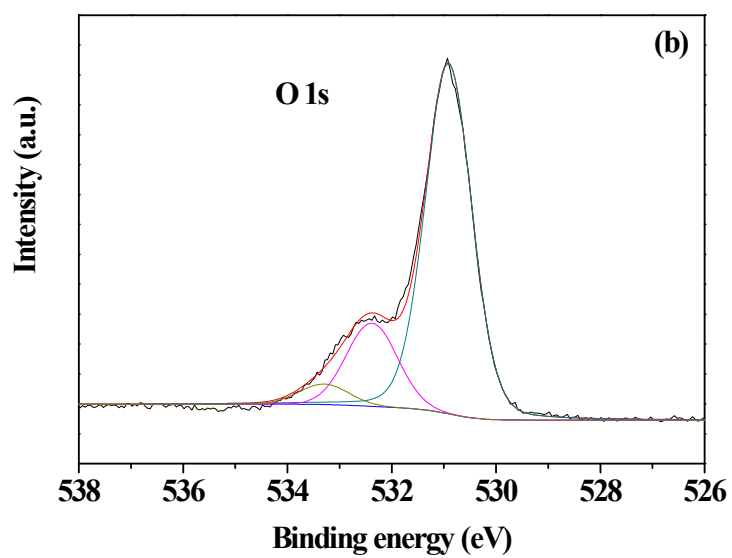


Fig. s8 High-resolution XPS spectra of Ti 2p (a), O 1s (b), S 2p (c) of $\text{SO}_4^{2-}/\text{AT}_{001}$

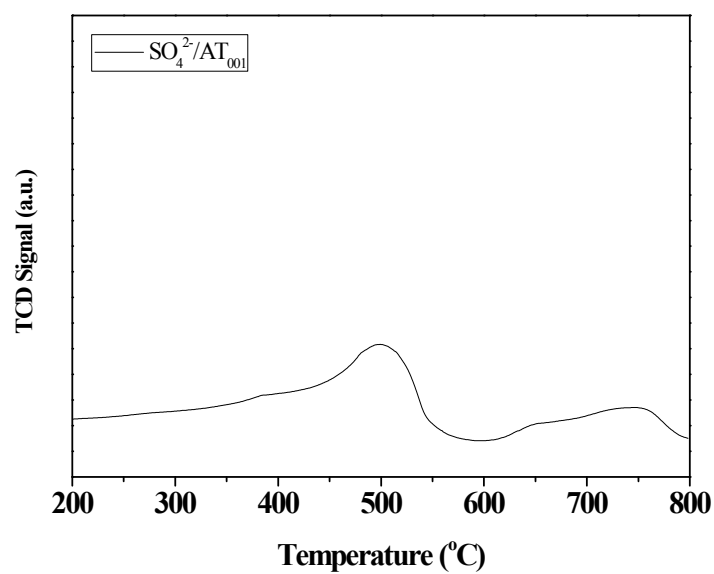


Fig. s9 The profile for temperature-programmed desorption of ammonia on the $\text{SO}_4^{2-}/\text{AT}_{001}$

Table s1 Physicochemical parameters of samples.

Catalyst	$A_{\text{BET}}^{\text{a}}$ (m ² /g)	$V_{\text{tal}}^{\text{b}}$ (cm ³ /g)	$D_{\text{avg}}^{\text{c}}$ (nm)	$G_{\text{sul}}^{\text{d}}$ (μmol/g)	$R_{\text{S/Ti}}^{\text{e}}$ (%)
$\text{SO}_4^{2-}/\text{AT}_{001}$	26	0.11	24.1	469.7	13.8

^a BET surface area. ^b Total pore volume. ^c Average pore diameter. ^d Amount of surface sulfate groups. ^e Surface S/Ti atomic ratio.