

## Electronic Supplementary Information

### Hollow anatase TiO<sub>2</sub> nanoparticles with excellent catalytic activity for dichloromethane combustion

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## Material synthesis and characterization

**TiO<sub>2</sub>-A<sub>1</sub>:** Under vigorous stirring condition, 5.0ml of 15% TiCl<sub>3</sub> solution was added dropwise in 68 ml of ammonium hydroxide, making up the aqueous phase, the aqueous is string at room temperature for 1 h. Then, the mixture was heated at 200 °C for 20 h in the autoclave. The precipitate was collected by centrifugation and washed repeatedly with ethanol and water, and then dried under vacuum at 60 °C for 12 h.

**TiO<sub>2</sub>-A<sub>2</sub>:** Under vigorous stirring condition, 5.0ml of 15% TiCl<sub>3</sub> solution was added dropwise in 10 M hydrochloric acid solution, making up the aqueous phase. After a few minutes, 0.39 g tartaric acid was added into the solution under string. Then, the mixture was heated at 180 °C for 12 h in the autoclave. The precipitate was collected by centrifugation and washed repeatedly with ethanol and water, and then dried under vacuum at 60 °C for 12 h.

**TiO<sub>2</sub>-A<sub>3</sub>:** Under vigorous stirring condition, a certain amount of 25 wt% ammonium hydroxide solution was added dropwise (5 ml / min) in to the TiOSO<sub>4</sub> solution until the value of pH reach 10-11, the aqueous is string at room temperature for 3 h, after 3 h standing, the precipitate was collected by centrifugation and washed repeatedly with water, and then dried at 110 °C for 12 h.

**TiO<sub>2</sub>-B:** 2.6301 g of precursors TiOSO<sub>4</sub>·2H<sub>2</sub>O were dissolved in 50 ml deionized water magnetic stirring at 60 °C. Under vigorous stirring condition, specific amount of urea and sodium hydroxyacetate were added the aqueous phase, stir constantly until forming the yellow clear solution. Then, the mixture was heated at 200 °C for 24 h in the autoclave. The precipitate was collected by centrifugation and washed repeatedly with ethanol and water, and then dried at 80 °C for 12 h.

**TiO<sub>2</sub>-B<sub>1</sub>:** Under vigorous stirring condition, 18.37 g sodium chloride was dissolved in 68 ml of ammonium hydroxide solution, after ten minutes string, 5 ml of 15% TiCl<sub>3</sub> was added dropwise into the mixture solution. Then, the mixture was heated at 200 °C for 24 h in the autoclave after 1 h string. The precipitate was collected by centrifugation and washed repeatedly with water, and then dried under vacuum at 60 °C for 12 h.

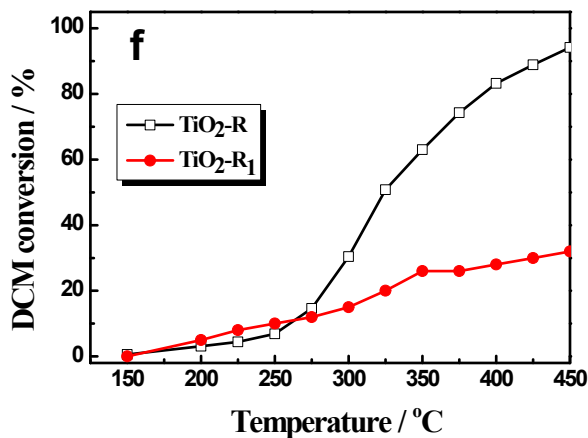
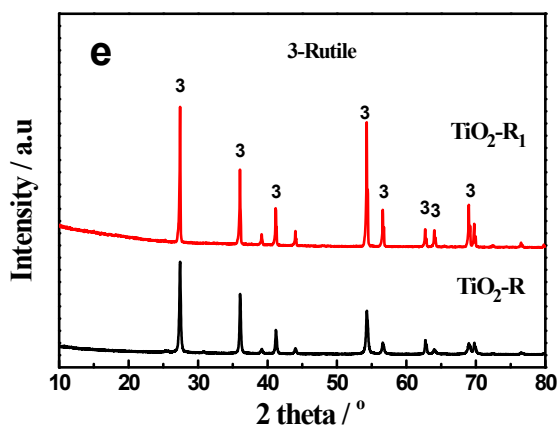
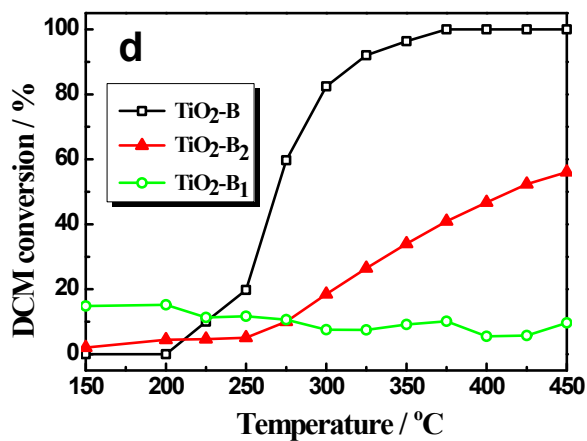
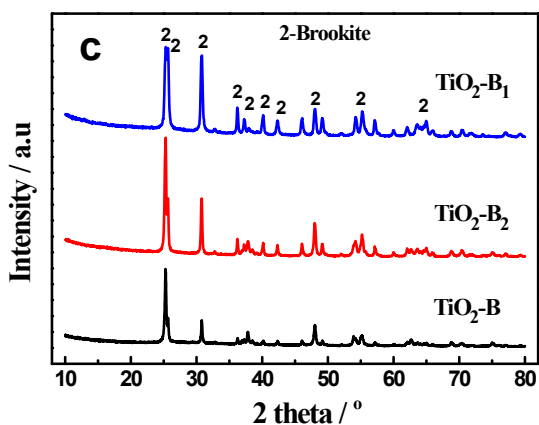
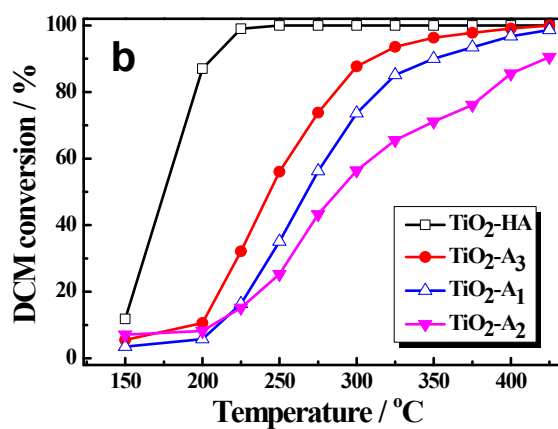
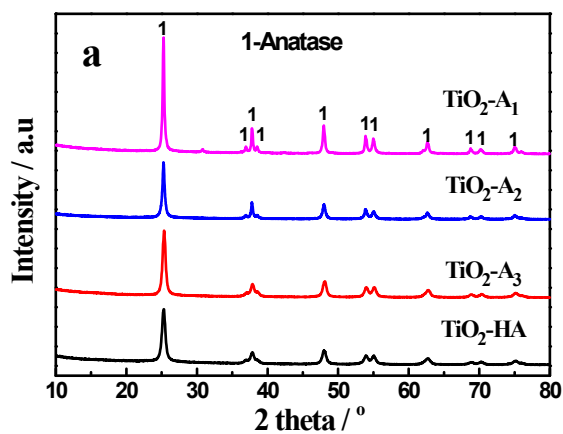
**TiO<sub>2</sub>-B<sub>2</sub>:** Under vigorous stirring condition, 5.0ml of 15% TiCl<sub>3</sub> solution was added dropwise in 30 ml deionized water, then 0.276 g sodium nitrate was added into the mixture solution. Stir constantly until forming the clear colorless solution. 2 M sodium hydroxide solution was added dropwise in to the solution until the value of pH reach 10. Then, the mixture was heated at 200 °C for 20 h in the autoclave. The precipitate was collected by centrifugation and washed repeatedly with water, and then dried under vacuum at 60 °C for 12 h.

**TiO<sub>2</sub>-R:** Under vigorous stirring condition, 5.0ml of 15% TiCl<sub>3</sub> solution was added dropwise in 10 M hydrochloric acid solution, making up the aqueous phase. After ten minutes string, the mixture was heated at 180 °C for 12 h in the autoclave. The precipitate was collected by centrifugation and washed repeatedly with ethanol and water, and then dried under vacuum at 60 °C for 12 h.

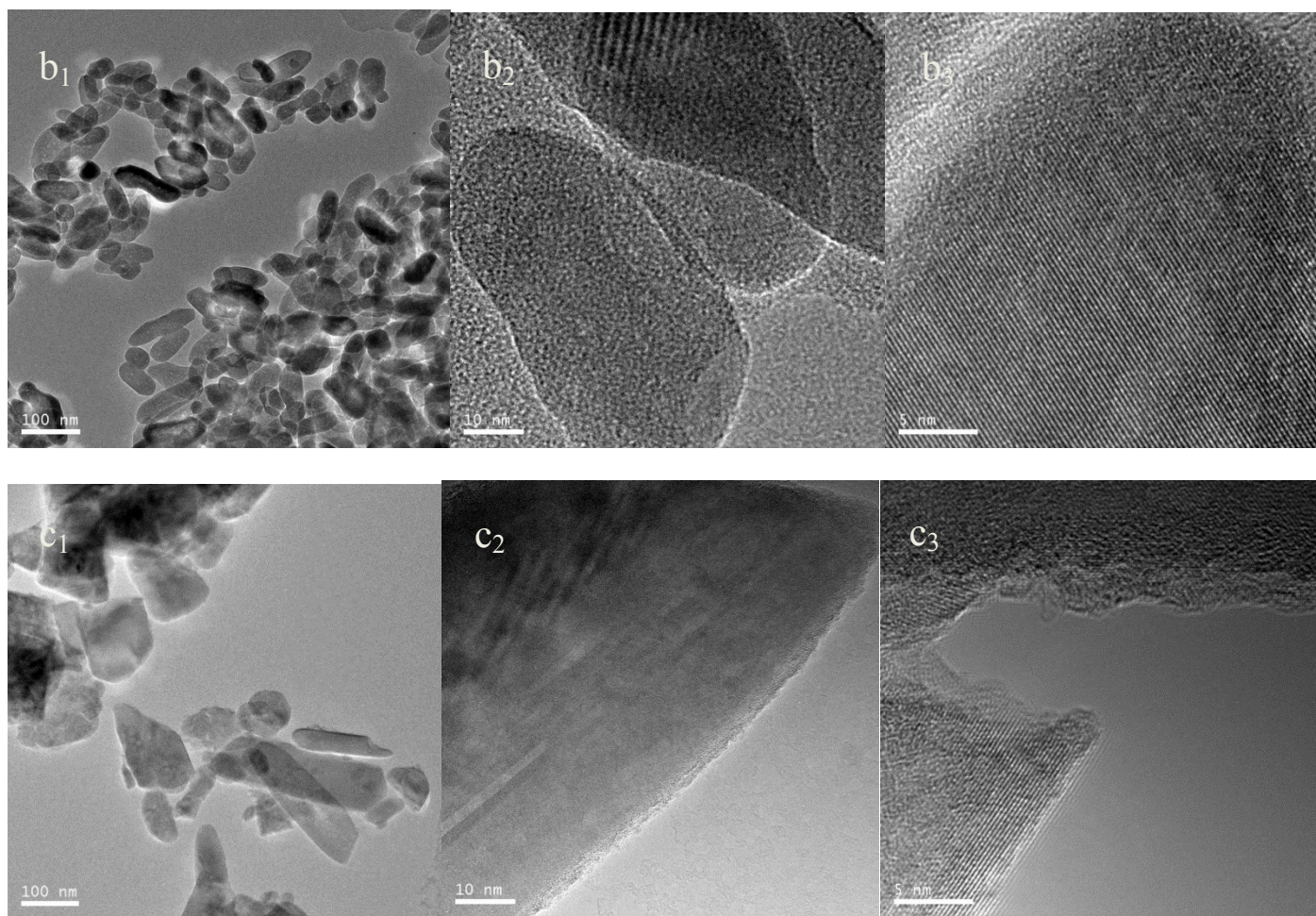
**TiO<sub>2</sub>-R<sub>1</sub>:** The preparation method was as same as the TiO<sub>2</sub>-A except the calcined temperature. All the precursors prepared by different methods mentioned above were calcined in air at 500 °C for 4 h except the TiO<sub>2</sub>-R<sub>1</sub> which was calcined in air at 900 °C.

Powder X-ray diffraction (XRD) patterns of the samples were recorded on an X' Pert Pro powder diffractometer using Cu Ka ( $\lambda = 0.154056$  nm) radiation (40 kV and 30 mA). The diffractograms were recorded within  $2\theta = 10^\circ - 80^\circ$  with a step size of  $0.02^\circ$  and a step time of 10 s. Crystal sizes were calculated using the Scherrer equation. The TEM characterization was carried out on Tecnai G2 F30. The sample was dispersed in absolute alcohol, and then supported on a copper grid before observation. The nitrogen adsorption and desorption isotherms were measured at  $-196^\circ\text{C}$  on a Micromeritics ASAP 2010 in a static mode. All samples were outgassed at  $250^\circ\text{C}$  for 3 h before measurement. The specific surface area was calculated using the BET model. Acidity was characterized by pyridine adsorption followed by FT-IR

(FTIR-pyridine) spectroscopy (Vertex70; scan rate= 32 scans s<sup>-1</sup>; resolution = 2.5 cm<sup>-1</sup>) equipped with a MCT detector. The powders were pressed into self-supporting disks (20mg, 13 mm diameter). The pretreatment temperature was 400 °C for 30 min in order to avoid the reduction of the catalyst at high temperature. After cooling to room temperature, the spectrum of the powder is recorded. Then, the sample is exposed to 5 µL of pyridine for 30 min. Spectra were recorded after evacuation for 30 min at 30, 200 and 400 °C. The amount of Brønsted and Lewis sites is determined by the integration of the area of the peaks at 1537 and 1446 cm<sup>-1</sup>, corresponding respectively to pyridine adsorbed on Brønsted sites and Lewis sites.

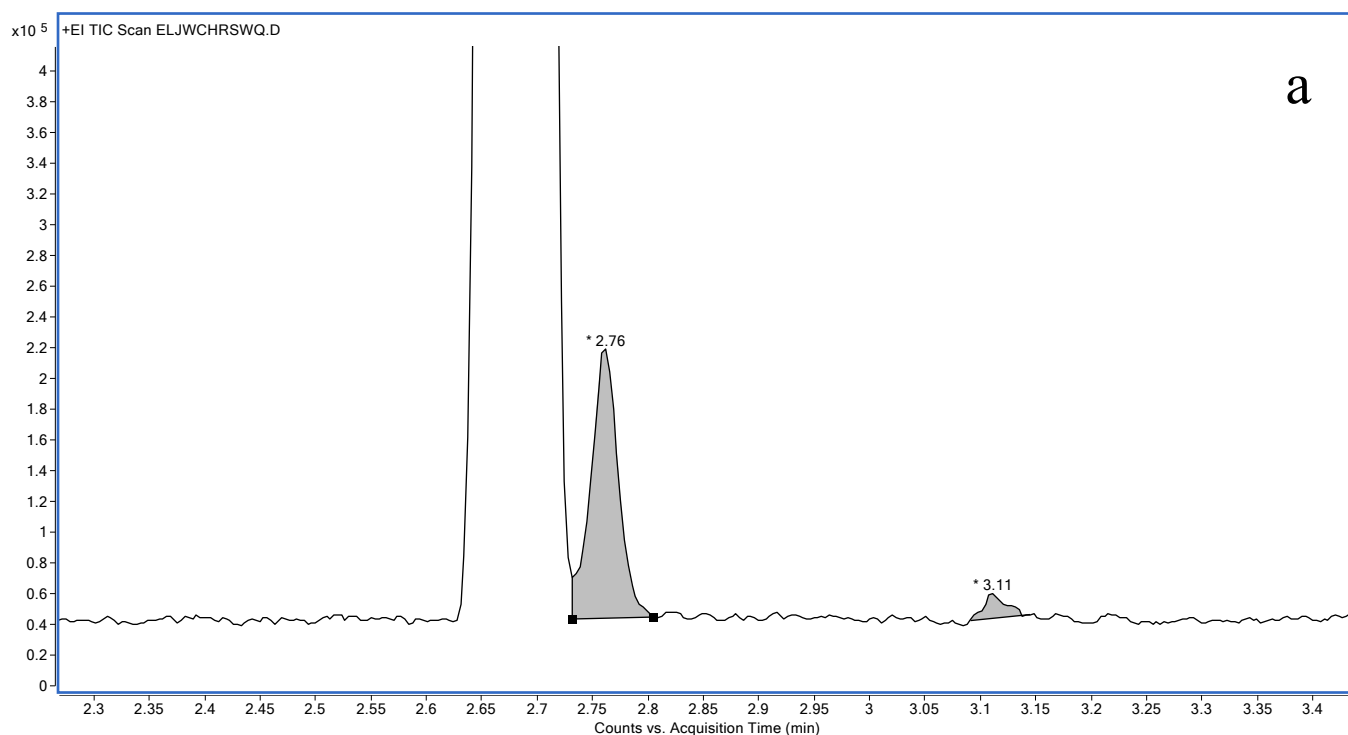


**Fig. S1a (c, e)** XRD patterns of titanium dioxide series catalysts; **b (d, f)** Light-off curves of DCM combustion over titanium dioxide series catalysts; Gas composition: 1000 ppm DCM in air, GHSV = 15000 mL h<sup>-1</sup> (gcat.)<sup>-1</sup>.



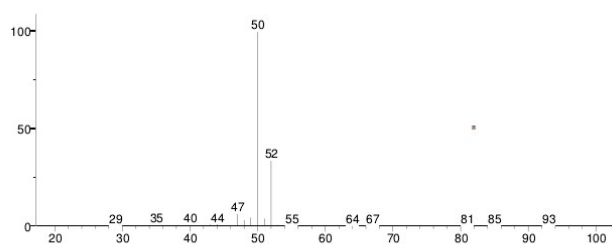
**Fig. S2** TEM and HRTEM images of TiO<sub>2</sub> catalyst. (b) TiO<sub>2</sub>-B; (c) TiO<sub>2</sub>-R.

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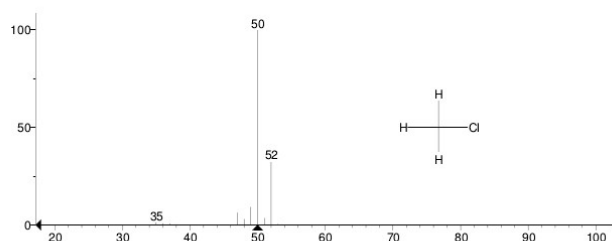


\*\* Search Report Page 1 of 2 \*\*

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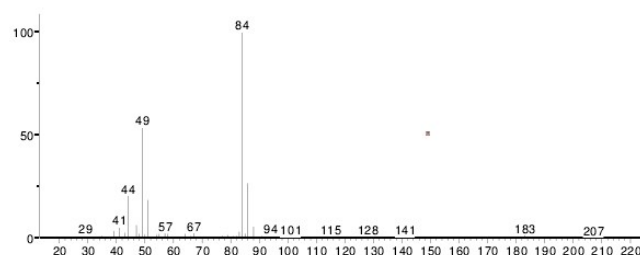
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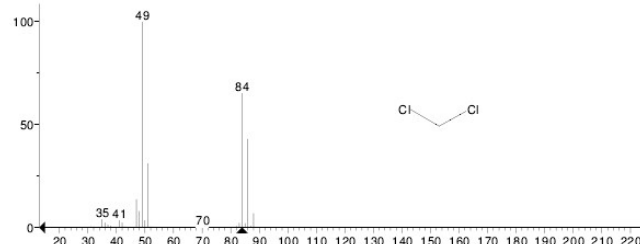
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\*\* Search Report Page 1 of 2 \*\*

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Compound in Library Factor = -115



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CH2Cl2; MF: 793; RMF: 885; Prob 93.7%; CAS: 75-09-2; Lib: mainlib; ID: 16363.



**Fig. S3** GC-MS result of the effluent of the  $\text{TiO}_2$ -HA catalyst for DCM combustion at  $220^\circ\text{C}$ .

It can be seen from Fig.S3 that there is only one organic by-product ( $\text{CH}_3\text{Cl}$ ) in the effluent of the  $\text{TiO}_2$ -HA catalyst for DCM combustion at  $220^\circ\text{C}$ , no other Cl-containing organic compounds are detected.

**Table 1S** The textures and catalytic performances of TiO<sub>2</sub> catalysts

catalysts	BET surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore size(nm)	Particle size(Å)	T <sub>50</sub> / °C	T <sub>90</sub> / °C
TiO <sub>2</sub> -A <sub>1</sub>	31.99	0.24	30.16	508	267	350
TiO <sub>2</sub> -A <sub>2</sub>	17.40	0.10	22.10	257	287	413
TiO <sub>2</sub> -A <sub>3</sub>	33.25	0.09	10.57	232	238	309
TiO <sub>2</sub> -B <sub>1</sub>	137.60	0.16	4.77	408	—	—
TiO <sub>2</sub> -B <sub>2</sub>	18.34	0.22	48.64	390	408	—
TiO <sub>2</sub> -R <sub>1</sub>	5	0.07	23.56	1049	—	—