

## Supporting Information

### **RuO<sub>2</sub>/rutile-TiO<sub>2</sub>: A Superior Catalyst for N<sub>2</sub>O Decomposition**

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† *Electronic Supplementary Information (ESI) available: details of catalyst preparation, reaction measurement, as well as characterization data of XRD, HAADF-STEM, XPS. See DOI: 10.1039/b000000x/*

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## 1. Experimental

### 1.1 Catalyst preparation

#### Synthesis of r-TiO<sub>2</sub> and a-TiO<sub>2</sub> support:

Titanium chloride (99% TiCl<sub>4</sub>, Sinopharm Chemical Reagent Co., Ltd.) was used as the starting materials without any purification. It was dropped slowly into ultra-pure water under an ice water bath to slow down the rapid exothermic reaction. At last the solution was transferred and made up into a volumetric flask and got the transparent aqueous solution with TiCl<sub>4</sub> concentration of 0.91 mol L<sup>-1</sup>.

The TiCl<sub>4</sub> solution (0.91 mol L<sup>-1</sup>) was divided into two parts. One part was diluted 1.5 times and heated at 60 °C for 4 h under stirring, and then aged for 1 h. The other part of the TiCl<sub>4</sub> solution (0.91 mol L<sup>-1</sup>) was tuned by ammonia solution under stirring until the pH of the solution reached 5. Then the solution obtained was also stirred at 60 °C for 4 h and aged for 1 h. Both of the precipitations obtained above were washed using ultra-pure water to remove chloride ions. The precipitations were dried at 120 °C for 12 h and finally calcined in air at 500 °C for 2 h to get the r-TiO<sub>2</sub> and a-TiO<sub>2</sub> supports.

#### Synthesis of RuO<sub>2</sub>/oxide catalysts:

r-TiO<sub>2</sub>, a-TiO<sub>2</sub>, SnO<sub>2</sub>, Alumina and Silica were employed as a support to prepare the RuO<sub>2</sub> catalysts using the impregnation method, respectively. Aqueous solutions (2.55 mL) of RuCl<sub>3</sub> (0.306 mol<sub>Ru</sub> L<sup>-1</sup> in ultra-super water, Sinopharm Chemical Reagent Co., Ltd.), targeted at 5 wt% of Ru loading, were diluted to 25.5 mL and heated at 50 °C under stirring in water bath, then the r-TiO<sub>2</sub> or a-TiO<sub>2</sub> supports (1.500 g) were poured into it and kept stirring until all the solution were evaporated. And then the samples were dried in air at 120 °C for 12 h, and finally calcined in air at 300 °C for 4 h.

### 1.2 Catalytic activity tests

The catalytic performance of the samples for N<sub>2</sub>O decomposition was evaluated in a continuous-flow fixed-bed reactor operating at atmospheric pressure. The catalyst (100 mg, 80~100 mesh) diluted in 500 mg SiO<sub>2</sub> (80~100 mesh) was loaded in a straight quartz reactor, the feed gas containing 30 vol.% N<sub>2</sub>O and balance with Ar was passed through the reactor at a flow rate of 50 ml min<sup>-1</sup> (WHSV: 30,000 ml h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>). The reactor in a furnace was heated from 160 °C to 300 °C at a rate of 4 °C min<sup>-1</sup>. The outlet gas composition was analyzed online three times at each temperature for 30 min with an Agilent 6890N gas chromatograph equipped with Porapak Q and Molecular Sieve 13X columns. The N<sub>2</sub>O conversion was calculated based on the difference between inlet and outlet concentrations.

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### 1.3 Catalyst characterization

Brunauer-Emmett-Teller (BET) surface areas of the catalysts were measured by nitrogen adsorption at -196 °C using a Micromeritics ASAP 2010 apparatus.

X-ray diffraction (XRD) patterns were recorded with a PANalytical X'Pert-Pro powder X-ray diffractometer, using Cu K $\alpha$  monochromatized radiation ( $\lambda = 0.1541$  nm) at a scan speed of 5° min<sup>-1</sup>.

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were obtained on a Tecnai G2 F30 Field Emission Gun Transmission Electron Microscope. High-resolution TEM images were taken on a HITACHI H-9500 transmission electron microscope.

Raman spectra of different materials were collected at room temperature using a in situ Raman reactor (Linkam CCR1000) on a LabRam HR800 confocal microprobe Raman instrument (HORIBA Jobin Yvon, France) with laser excitation at 532 nm or 633 nm (He-Ne laser).

X-ray photoelectron spectra (XPS) were acquired with a VG ESCALAB 210 instrument. Mg K $\alpha$  radiation at an energy scale calibrated versus adventitious carbon (C1s peak at 284.5 eV) was used. Before the measurements, the r-TiO<sub>2</sub> and a-TiO<sub>2</sub> supports were calcined at 500 °C in air for 2 h and the supported RuO<sub>2</sub> catalysts were calcined at 300 °C in air for 4 h.

## 2. Supporting figures

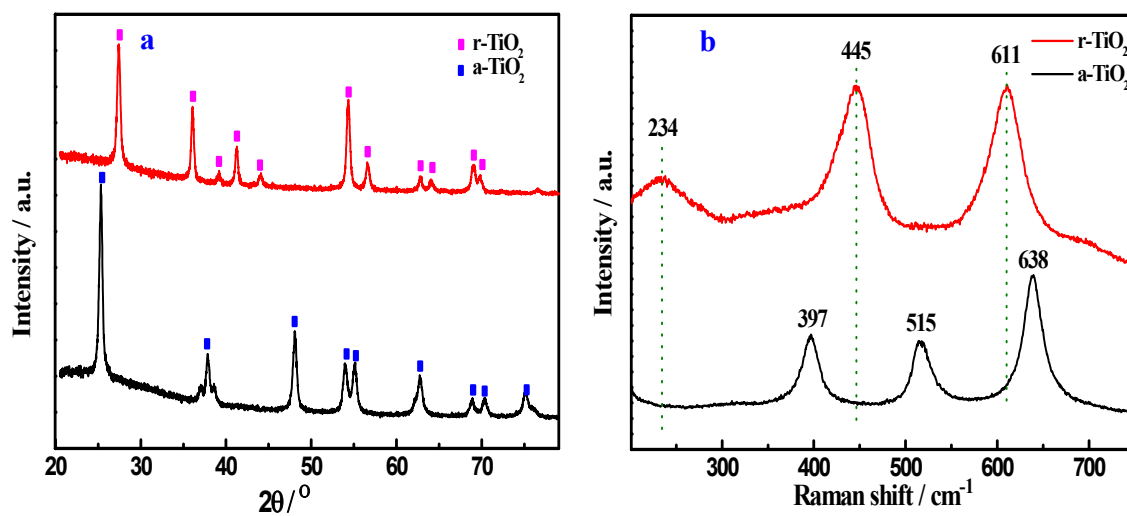


Fig. S1 The XRD patterns (a) of r-TiO<sub>2</sub> and a-TiO<sub>2</sub> supports calcined at 500 °C for 2h and their Raman spectra (b) with excitation lines at 532 nm ( $\lambda_{\max} = 532$  nm)

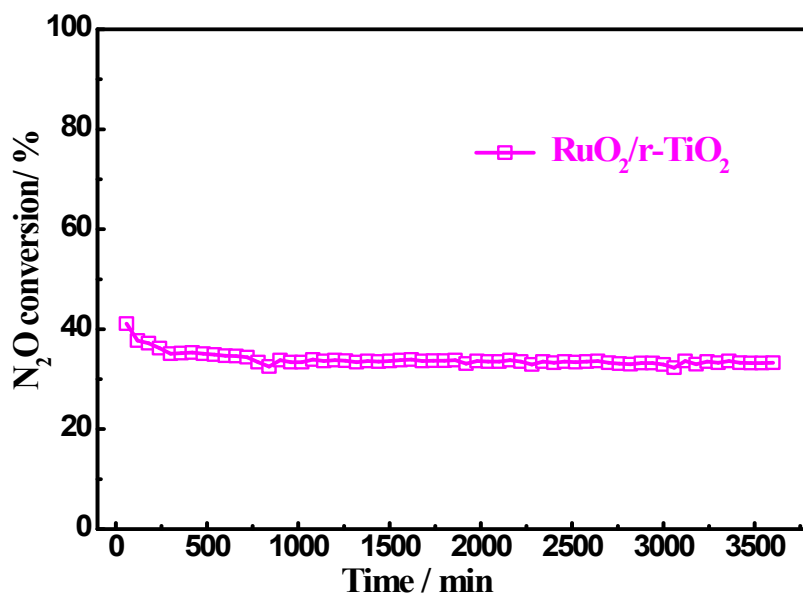


Fig. S2 N<sub>2</sub>O conversion as a function of the reaction time for 5 wt% RuO<sub>2</sub>/r-TiO<sub>2</sub> catalyst at 300 °C  
Reaction conditions: 30 vol% N<sub>2</sub>O balanced with Ar. Weight hourly space velocity (WHSV): 120,000 mL g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>.

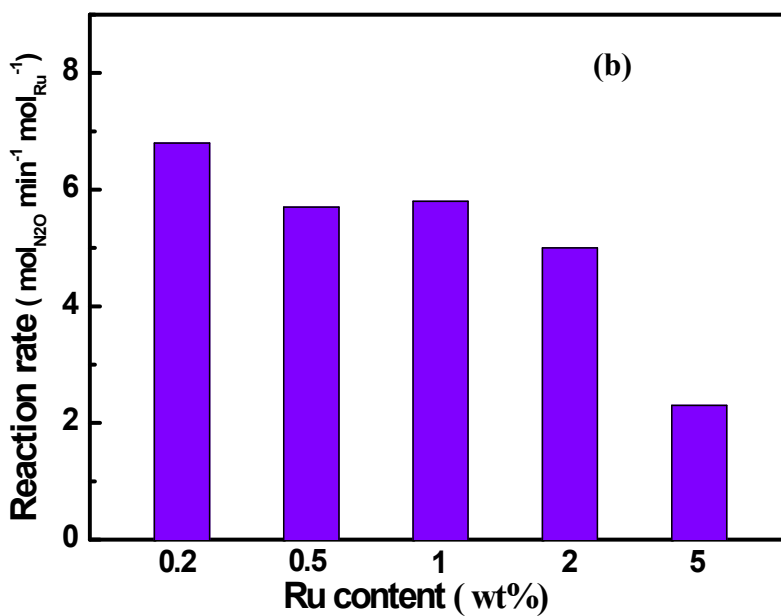
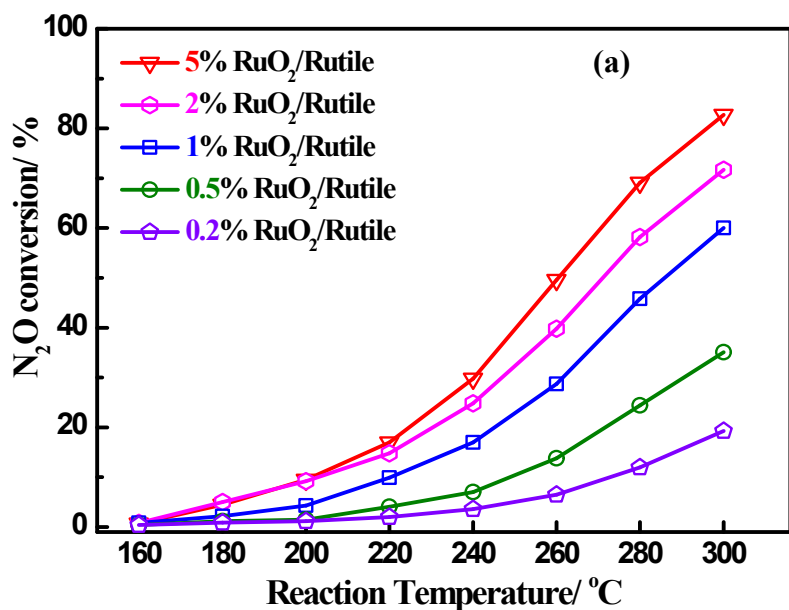
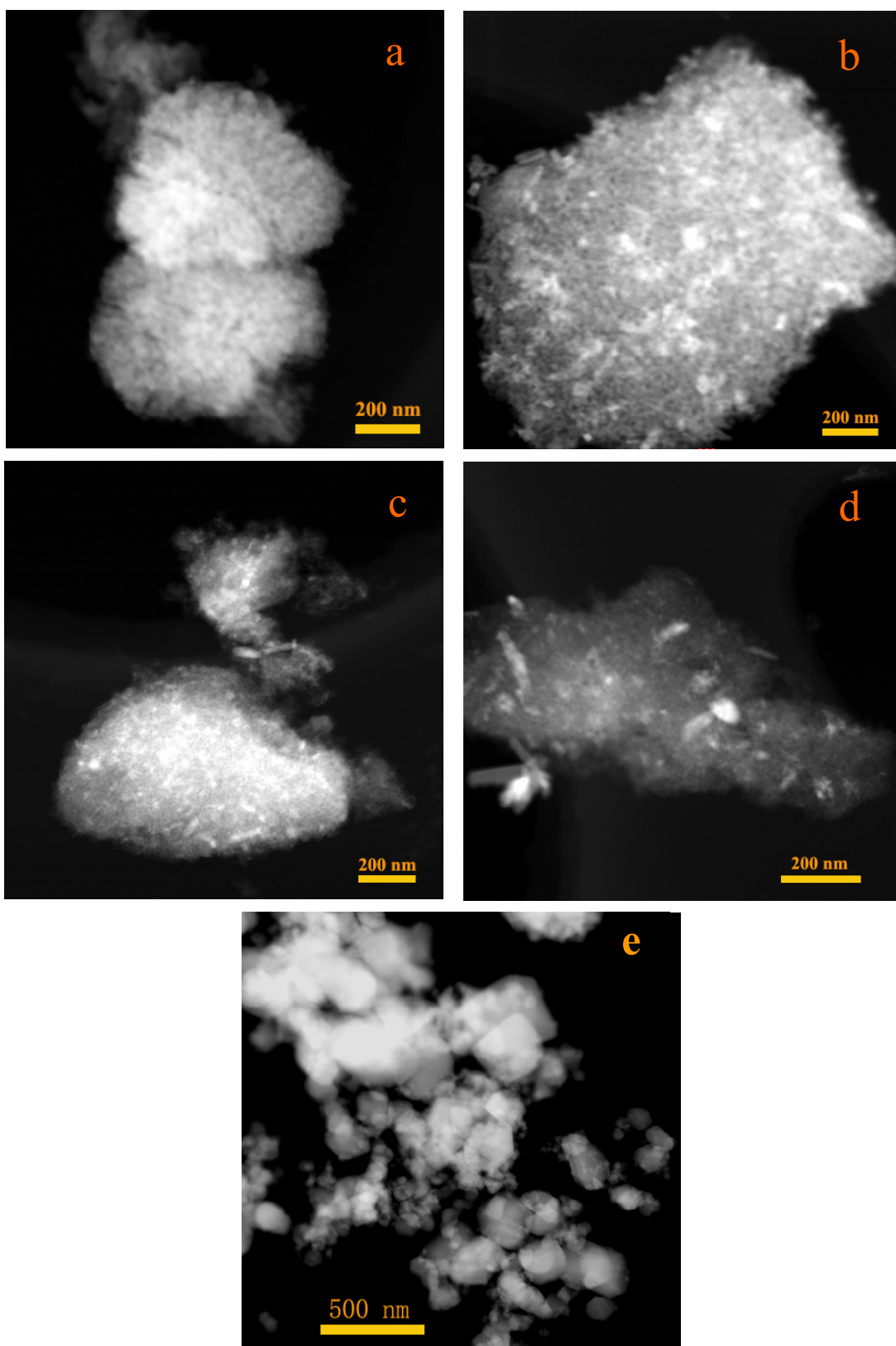
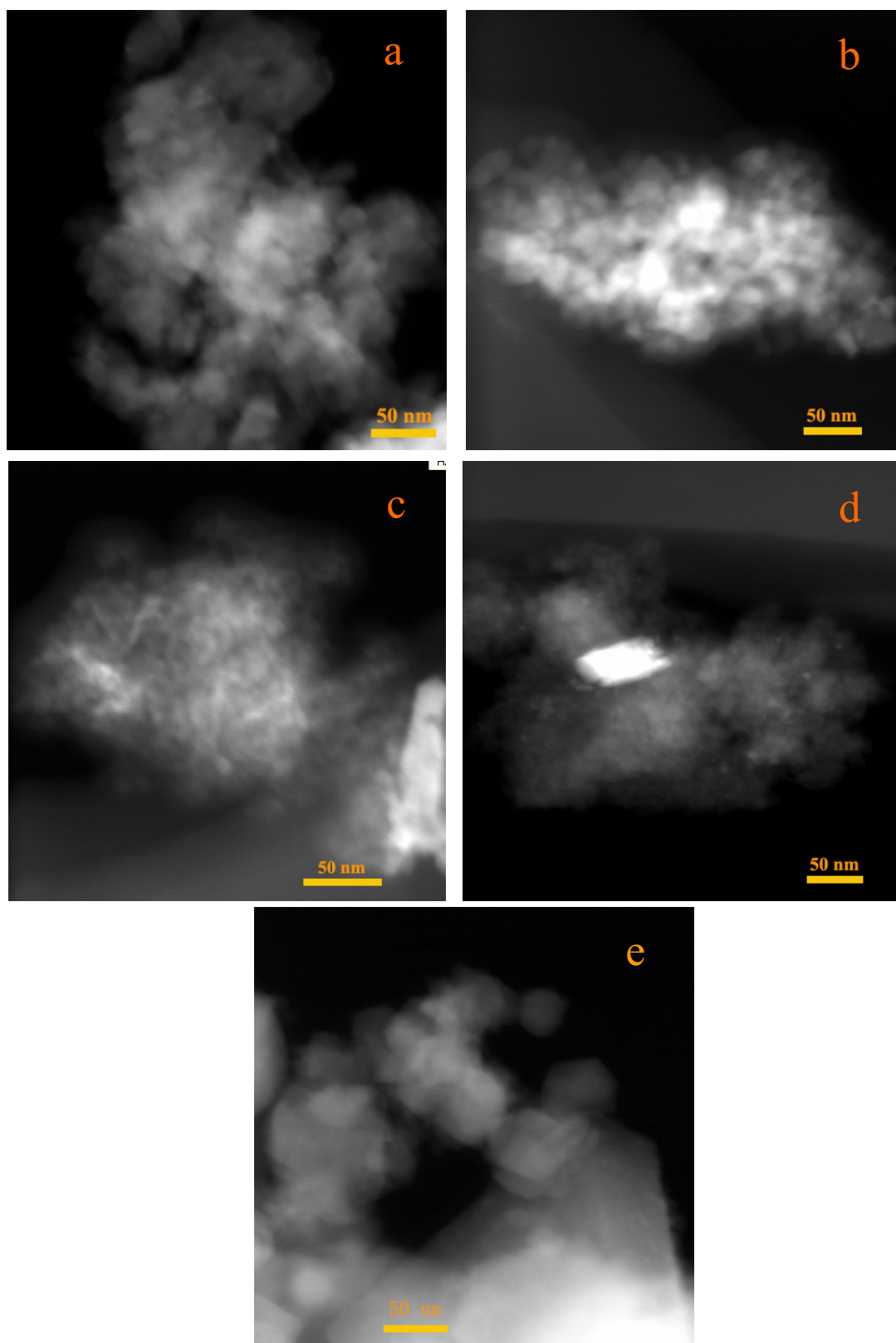


Fig. S3 (a) N<sub>2</sub>O conversions as a function of the reaction temperature and (b) the specific rates calculated at 220 °C for RuO<sub>2</sub>/r-TiO<sub>2</sub> catalysts with different Ru loading  
 Reaction conditions: 30 vol% N<sub>2</sub>O balanced with Ar. Weight hourly space velocity (WHSV): 30,000 mL g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>.



**Fig. S4 HAADF-STEM images of various RuO<sub>2</sub> catalysts with relatively low magnification**

(a), RuO<sub>2</sub>/r-TiO<sub>2</sub>; (b), RuO<sub>2</sub>/a-TiO<sub>2</sub>; (c), RuO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>; (d), RuO<sub>2</sub>/SiO<sub>2</sub>, (e), RuO<sub>2</sub>/SnO<sub>2</sub>.



**Fig. S5 HAADF-STEM images of various RuO<sub>2</sub> catalysts with relatively high magnification**

(a), RuO<sub>2</sub>/r-TiO<sub>2</sub>; (b), RuO<sub>2</sub>/a-TiO<sub>2</sub>; (c), RuO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>; (d), RuO<sub>2</sub>/SiO<sub>2</sub>, (e) , RuO<sub>2</sub>/SnO<sub>2</sub>.



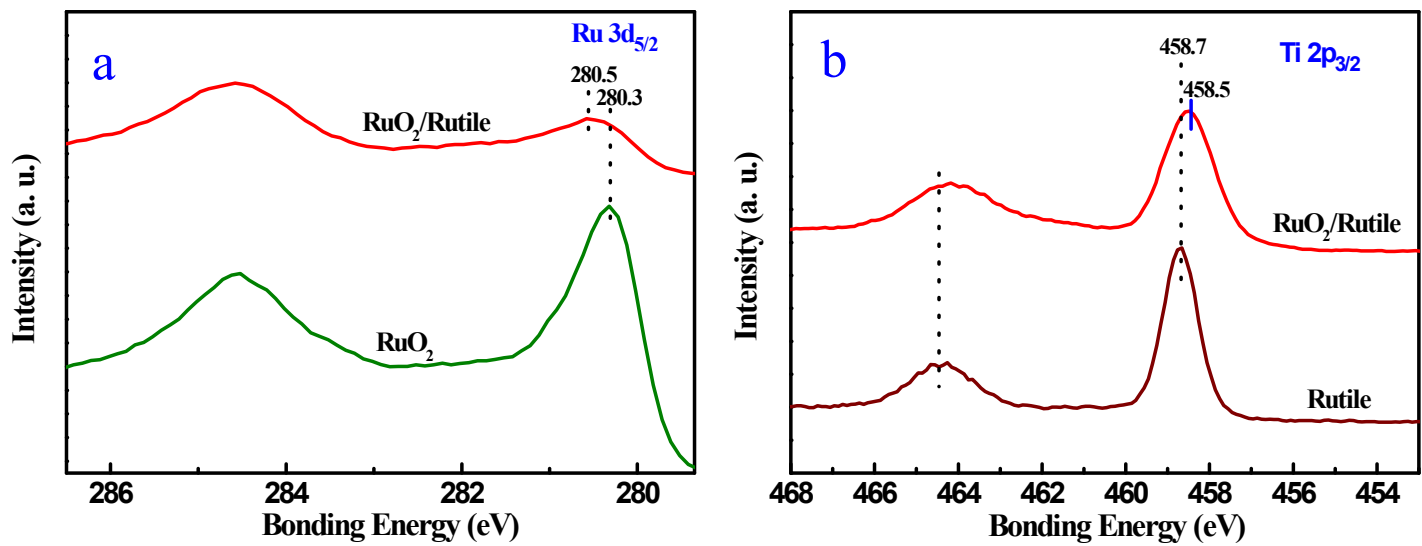


Fig S6 The XPS analysis of RuO<sub>2</sub>/r-TiO<sub>2</sub> catalysts

(a), Ru 3d<sub>5/2</sub>; (b), Ti 2p<sub>3/2</sub>.