

Supporting information

Nature of Crystal Facet Effect of TiO₂ Supported Pd/Pt Catalysts on Selective Hydrogenation of Cinnamaldehyde: Electron Transfer Process Promoted by Interfacial Oxygen Species

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Experiment section

Materials

Chloroplatinic acid (H₂PtCl₆, 37 wt% Pt), sodium borohydride (NaBH₄, 98%), ethanol (EtOH, 99.7%), sodium hydroxide (NaOH, 96%), hydrogen peroxide (H₂O₂, 30%), hydrofluoric acid (HF, 40%), tetrabutyl titanate (C₁₆H₃₆O₄Ti, 98%) were purchased from Sinopharm (China). P25 were provided by Acros organics. Cinnamyl aldehyde (CAL, 98%) were obtained from Aladdin Industrial Corporation. Lithium chloride anhydrous (LiCl, 99%) were purchased from Macklin. All the chemicals were used without further purification

Techniques

The X-ray diffraction (XRD) patterns were required using a Rigaku Ultima Discover X-Ray Diffractometer at a wavelength of Cu K α (1.5405 Å). The TEM images were taken using Hitachi S-4800 microscope and JEOL-JEM-2100 microscope, respectively. FT-IR spectra were recorded by Nicolet Fourier transform infrared spectrometer (NEXUS 670) using the KBr technique. Gas chromatographic mass spectrometry were analyzed and quantified by Agilent HP6890/5973N.

Preparation of TiO₂-101 nanocrystals (bipyramidal TiO₂ nanocrystals)

TiO₂ nanocrystals with different crystal planes exposed are synthesized following Tang et al.'s procedures.¹ The anatase bipyramidal TiO₂ nanocrystals with (101) surface exposed were prepared through two procedures. ²(1) Synthesis of Na-titanates: 1 g P25 was mixed with 40 ml NaOH (10 mol/L). After being stirred for 10 min at ambient conditions, the reaction solution was transferred to a 50 ml Teflon-lined stainless steel autoclave, kept in an electric oven at 120 °C for 24 h and cooled naturally in air. Afterwards, the white products were collected by centrifugation and washed with deionized water (DI) water for several times until the pH was 10.5. Eventually, the Na-titanates

were isolated by centrifugation at 10000 r/min for 10 min. (2) Preparation of bipyramidal TiO₂ nanoparticles: 3 g Na-titanates (wet without drying after centrifugation step), 0.3932 g LiCl and 120 ml deionized water were added into a 200 ml Teflon-lined stainless steel autoclave after being stirred for 15 min. The autoclave was kept at 200 °C for 4 h and afterwards, cooled naturally in air. The precipitates were collected by centrifugation (10000r/min) and then washed with DI water and ethanol for several times, respectively. Finally, the products were dried in vacuum at 60 °C for 12 h.

Preparation of TiO₂-100 nanocrystals (TiO₂ nanorods)

TiO₂ nanocrystals with different crystal planes exposed are synthesized following Tang et al.'s procedures.¹ The Tetragonal faceted-nanorods of anatase TiO₂ with dominant {100} facets have been synthesized by a reported two-step hydrothermal reaction.³ (1) Synthesis of Na-titanates: 1 g P25 was mixed with 40 ml NaOH (10 mol/L). After being stirred for 10 min at ambient conditions, the reaction solution was transferred to a 50 ml Teflon-lined stainless steel autoclave, kept in an electric oven at 120 °C for 24 h and cooled naturally in air. Afterwards, the white products were collected by centrifugation and washed with deionized water (DI) water for several times until the pH was 10.5. Eventually, the Na-titanates were isolated by centrifugation at 10000 r/min for 10 min. (2) Synthesis of anatase nanorods: 4 g Na-titanates (wet without drying after centrifugation step) was added to 152 ml DI water. And then added 8 ml H₂O₂. The mixture was transferred to a 200 ml Teflon-lined stainless steel autoclave after being stirred for 15 min. The autoclave was kept in an oven at 180 °C for 20 h and afterwards, cooled naturally in air. The precipitates were collected by centrifugation (10000r/min) and then washed with DI water and ethanol for several times, respectively. Finally, the products were dried in vacuum at 60 °C for 12 h.

Preparation of TiO₂-001 nanocrystals (TiO₂ nanosheets)

TiO₂ nanocrystals with different crystal planes exposed are synthesized following Tang et al.'s procedures.¹ The anatase TiO₂ nanosheets with (001) surface exposed were synthesized through a published hydrothermal route,⁴ with HF as the capping agent. Firstly, tetrabutyl titanate (10 mL) and hydrofluoric acid (1.8 mL, 40 wt %) were added into a Telfon-lined autoclave (50 mL) after being stirred for 5 min at ambient conditions and then kept at 200 °C for 20 h. After the reaction, we collected the white precipitates by centrifugation and washed it using deionized water, ethanol and NaOH (1 mol/L) for several times. At last, the samples were dried in vacuum at 60 °C for 12 h.

Synthesis of TiO₂-101/100/001-Pt-T (T=300, 500, 700°C) catalysts

H₂PtCl₆·6H₂O aqueous (4 mL, 7.72 mM), 24 mL of ethanol and 0.3 g of TiO₂-(101)/ (100)/ (001) were mixed together and stirred for 12 h at room temperature, and then 24 mg NaBH₄ was introduced. After stirring 30 min, the suspension was filtered and washed with water and ethanol, and drying at 80°C. After impregnation, the sample were calcinated at 300°C, 500°C and 700°C for 2 h in air. The as-obtained samples were denoted as TiO₂-(101)/(100)/(001)-Pt-T (T=300, 500, 700°C). The calculated Pt content was 2 wt%.

Synthesis of TiO₂-101/100/001-Pd-T (T=300, 500, 700°C) catalysts

K₂PdCl₆ aqueous (5.64 mL, 10 mM), 24 mL of ethanol and 0.3 g of TiO₂-(101)/ (100)/ (001)

were mixed together and stirred for 12 h at room temperature, and then 24 mg NaBH₄ was introduced. After stirring 30 min, the suspension was filtered and washed with water and ethanol, and drying at 80°C. After impregnation, the sample were calcinated at 300°C, 500°C and 700°C for 2 h in air. The as-obtained samples were denoted as TiO₂-(101)/(100)/(001)-Pd-T (T=300, 500, 700°C). The calculated Pd content was 2 wt%.

Hydrogenation of cinnamaldehyde (CAL)

CAL hydrogenation reactions were performed on the above catalysts in a stainless-steel autoclave reactor. The reaction was carried out at 60 °C and 2.0 MPa H₂ with a certain amount of catalysts in 4 mL of ethanol, 0.4mL of H₂O, 0.1 mL of CAL and 23 mg catalyst. After the reaction, the reactor was cooled and then slowly depressurized. Finally, the reaction mixture was separated by centrifugation in order to remove the solid catalysts. The reaction products were analyzed and quantified by gas chromatographic mass spectrometry (GC-MS, Agilent HP6890/5973N). The reaction conversion and selectivity were determined by the product analysis.

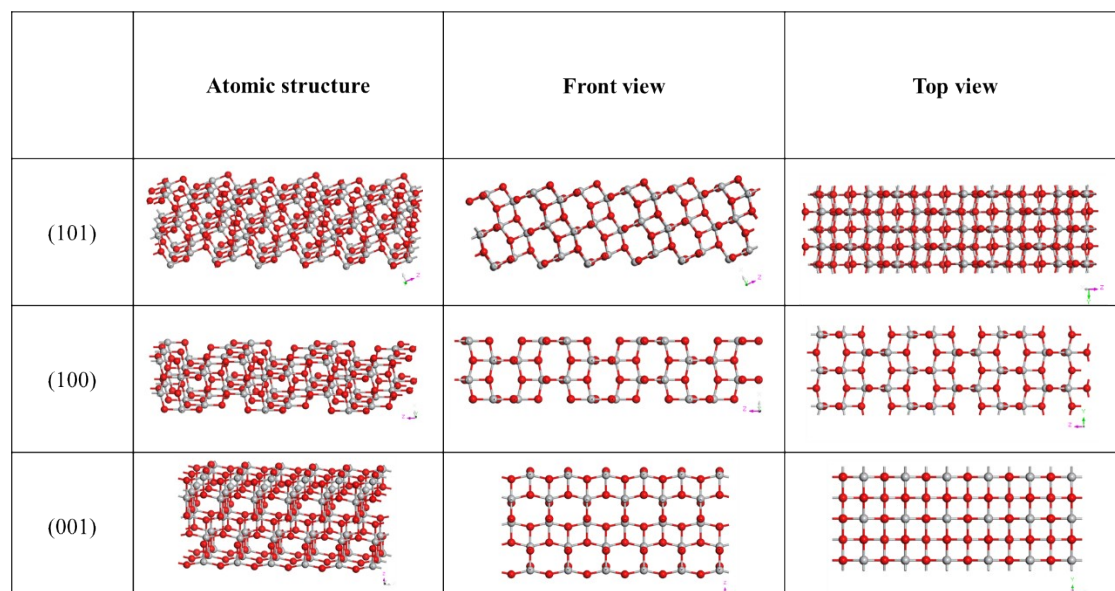


Figure S1. Schematics of atomic structure and front view and top view of of anatase TiO₂ (101), (100), and (001) facets.

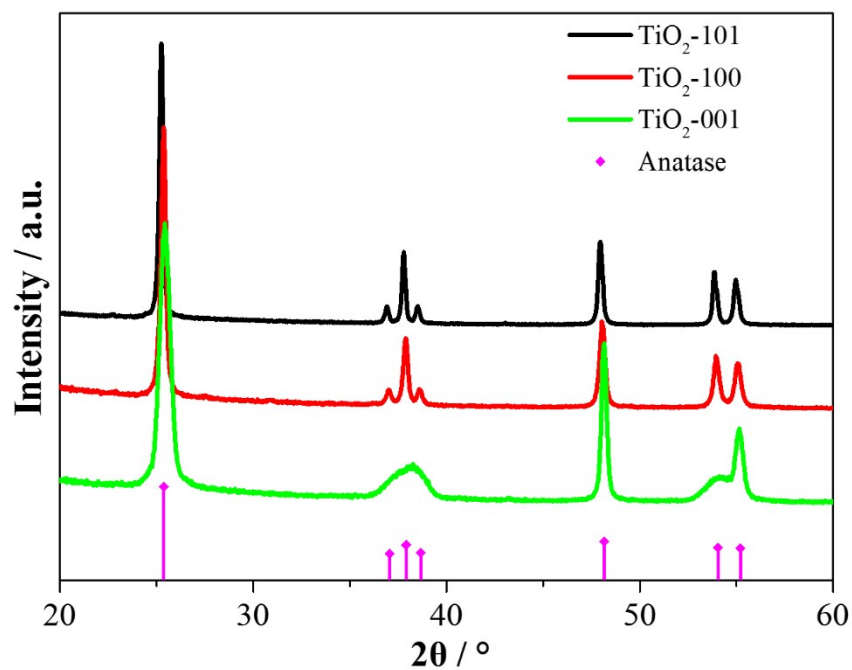


Figure S2. XRD patterns of TiO₂-101 (black), TiO₂-100 (red), TiO₂-001 (green).

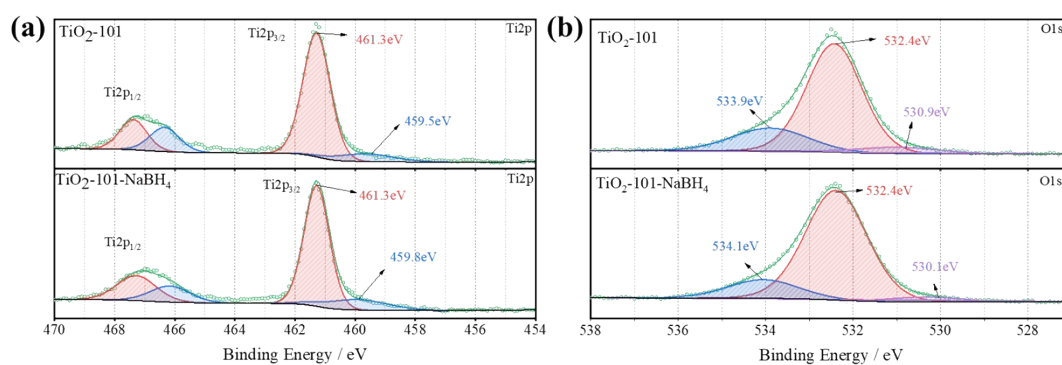


Figure S3. The Ti 2p (a) and O 1s (b) spectra of TiO₂-100 before and after treatment by NaBH₄ reducer.

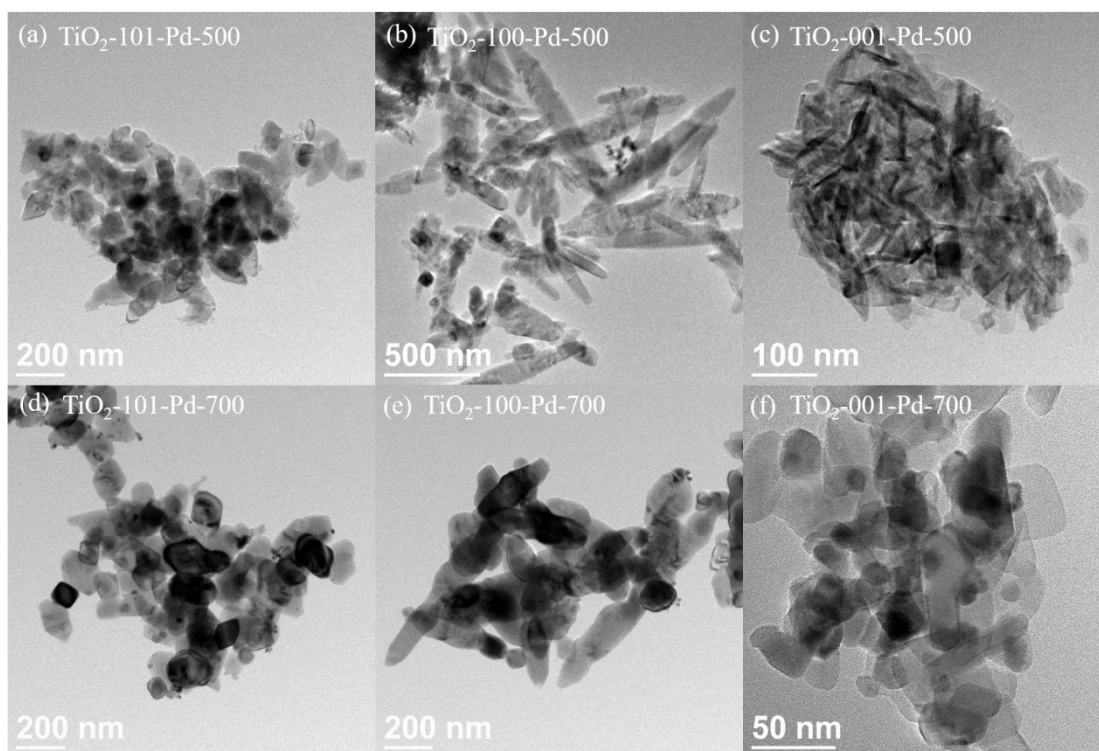


Figure S4. TEM images of TiO₂-101-Pd-500 (a), TiO₂-100-Pd-500 (b), TiO₂-001-Pd-500 (c), TiO₂-101-Pd-700 (d), TiO₂-100-Pd-700 (e) and TiO₂-001-Pd-700.

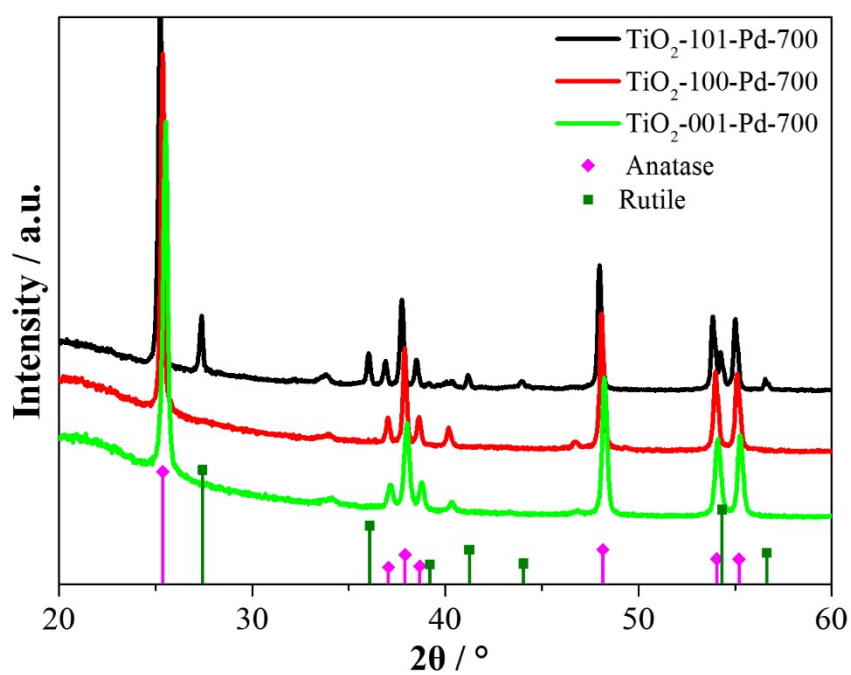


Figure S5. XRD patterns of TiO₂-101-Pd-700-Ar (black), TiO₂-100-Pd-700-Ar (red), TiO₂-001-Pd-700-Ar (green).

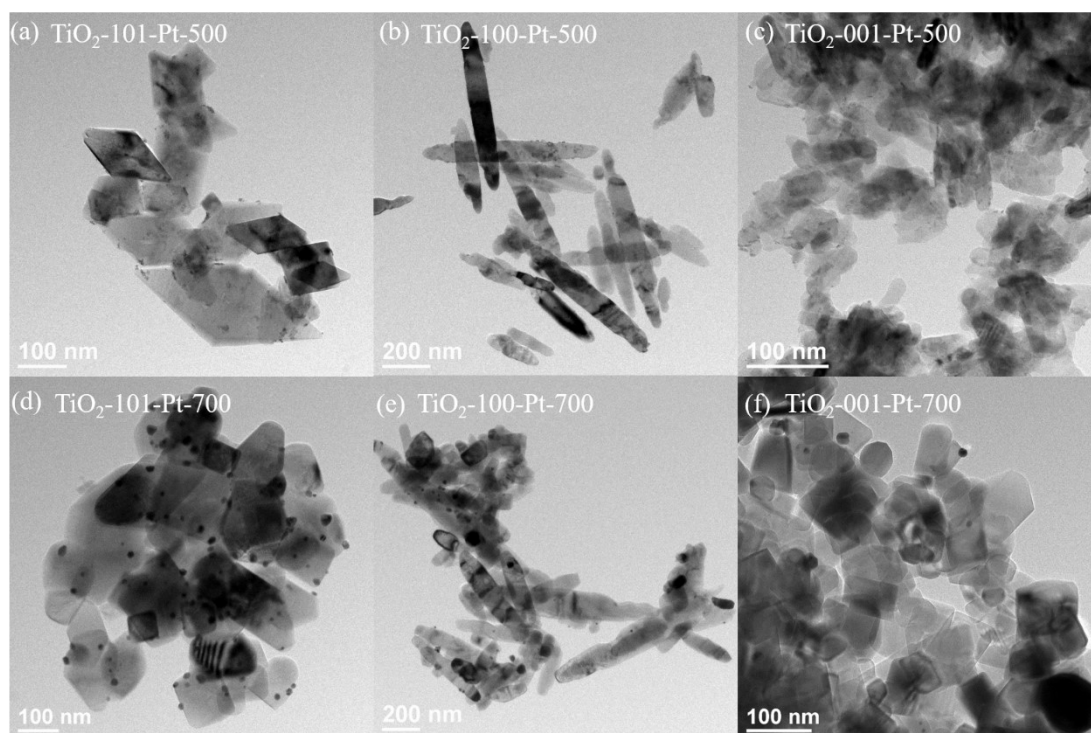


Figure S6. TEM images of TiO₂-101-Pt-500 (a), TiO₂-100-Pt-500 (b), TiO₂-001-Pt-500 (c), TiO₂-101-Pt-700 (d), TiO₂-100-Pt-700 (e) and TiO₂-001-Pt-700.

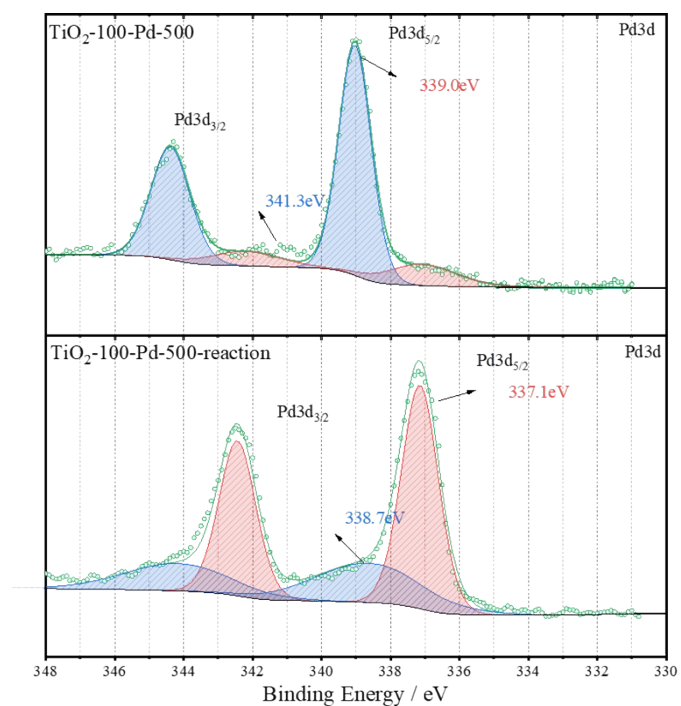


Figure S7. (a) The Pd 3d spectra of TiO₂-100-Pd-500 catalyst before (top) and after hydrogenation reaction (bottom).

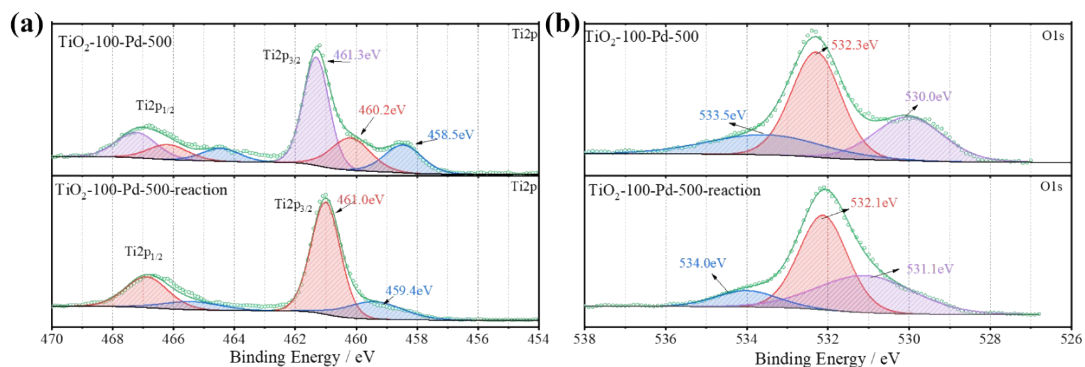


Figure S8. The Ti 2*p* (a) and O 1*s* (b) spectra of TiO₂-100-Pd-500 catalyst before (top) and after hydrogenation reaction (bottom).

Reference

- [1] Tang, M., Li, S., Chen, S., Ou, Y., Hiroaki, M., Yuan, W., Zhu, B., Yang, H., Gao, Y., Zhang, Z., Wang, Y., Facet-Dependent Oxidative Strong Metal-Support Interactions of Palladium-TiO₂ Determined by In Situ Transmission Electron Microscopy. *Angew. Chem. Int. Ed.* **2021**, *60* (41), 22339-22344.
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- [3] Li, J., Xu, D., Tetragonal faceted-nanorods of anatase TiO₂ single crystals with a large percentage of active {100} facets. *Chem. Commun.* **2010**, *46* (13), 2301-3.
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